Russian Chemical Reviews **73** (7) 671 – 699 (2004) © 2004 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2004v073n07ABEH000838

Chiral phosphites as ligands in asymmetric metal complex catalysis and synthesis of coordination compounds

K N Gavrilov, O G Bondarev, A I Polosukhin

Contents

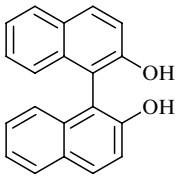
I.	Introduction	671
II.	P-Monodentate phosphites	672
III.	P,N-Bidentate compounds of phosphite nature	679
IV.	P,P-Bidentate phosphites	686
V.	Other groups of chiral phosphite ligands	693
VI.	Conclusion	694

Abstract. The data published during the last five years on the application of chiral derivatives of phosphorous acid in coordination chemistry and enantioselective catalysis are summarised and discussed. The effect of the nature of these ligands on the structure of metal complexes and on the efficiency of catalytic organic syntheses is shown. Hydroformylation, hydrogenation, allylic substitution and conjugate addition catalysed by transition metal complexes with optically active phosphites and hydrophosphoranes are considered. The prospects for the development of this field of research are demonstrated. The bibliography includes 215 references.

I. Introduction

Organic reactions catalysed by chiral transition metal complexes are the basis of modern asymmetric synthesis. This statement was substantiated by the fact that three leading researchers working in this field of chemistry were awarded the Nobel Prize in 2001. The key to obtaining high catalytic results is targeted synthesis of optically active ligands. Among them, of prime importance are phosphorus-containing compounds which are crucial to the progress of such avenues of organic synthesis as asymmetric reduction, isomerisation and formation of carbon – carbon and carbon – heteroatom bonds.[1] These ligands also play an important role in the development of concepts of the geometry and structure of complexes, mutual influence of intra-sphere ligands and the nature of coordination bond.[2] Initially, emphasis was placed on systems with P – C bonds, especially tertiary phosphines. We cannot but agree with Ansell and Wills[3] that this situation is unjust. Indeed, compounds with three P – O and (or) P – N bonds offer a number of considerable advantages.[3–5] First, they are synthetically accessible, because most of them can be synthesised rather simply and in high yield from a variety of optically active precursors. This makes possible a direct one-step phosphorylation of chiral compounds, whereas the synthesis of corresponding phosphine derivatives requires preliminary modification. Second, these compounds exhibit higher oxidative stability because of the absence of the P – C bond in the corresponding structures. This is of great importance in those cases where the oxidation of a phosphorus-containing ligand faces considerable difficulties, *e.g.*, in the synthesis of some types of coordination compounds and catalysis of hydroformylation. Third, these compounds possess a pronounced π-acceptor ability, which allows the coordinated phosphites to stabilise low oxidation states of metals used as complexing agents, thus enhancing their electrophilicity. By and large, replacement of carbon atoms by heteroatoms [oxygen and (or) nitrogen] in the first coordination sphere of phosphorus atom appeared to be a much more efficient tool for control of the chemical stability of ligands and their donor – acceptor properties and steric features compared to traditional introduction of various substituents into benzene rings of the PAr_2 fragment typical of most phosphine systems.

The aforesaid is responsible for an increase, in the last decade, in the number of communications concerned with applications of chiral derivatives of phosphorous acid in the synthesis of coordination compounds and in catalysis. Studies in the field reported before 1998 were summarised in two reviews.[6,7] Most of the P-monodentate ligands considered in these reviews were carbohydrate derivatives but some chiral amino alcohols and diols were also presented. No systematic investigations on their complexation were carried out at that time. The optical yields of catalytic reactions (hydrogenation, hydrosilylation, hydrocyanation) involving these compounds were at most 20% – 30%.[6] However, the first phosphorus-containing derivatives of BINOL (**1**) were synthetically available at that time.



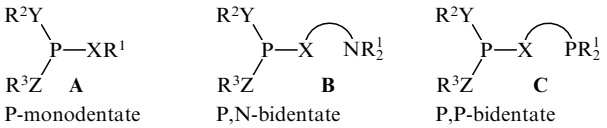
1 (BINOL)

Later on, these BINOL-based compounds were top-ranked among the P-monodentate phosphites (type **A**). The group of P,N-bidentate ligands (type **B**) comprised a few compounds containing sp^3-hybridised peripheral nitrogen atoms, *i.e.*, phosphites and phosphoramidites containing an amino group in the

K N Gavrilov S A Esenin Ryazan State Pedagogical University, ul. Svobody 46, 390000 Ryazan, Russian Federation. Fax (7-0912) 44 43 90. Tel. (7-0912) 77 28 54. E-mail: chem@ttc.ryazan.ru
O G Bondarev, A I Polosukhin A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russian Federation. Fax (7-095) 135 64 71. Tel. (7-095) 135 25 48. E-mail: bond@ineos.ac.ru (O G Bondarev), apol73@yahoo.com (A I Polosukhin)

Received 31 March 2003
Uspekhi Khimii **73** (7) 726 – 756 (2004); translated by A M Raevskiy

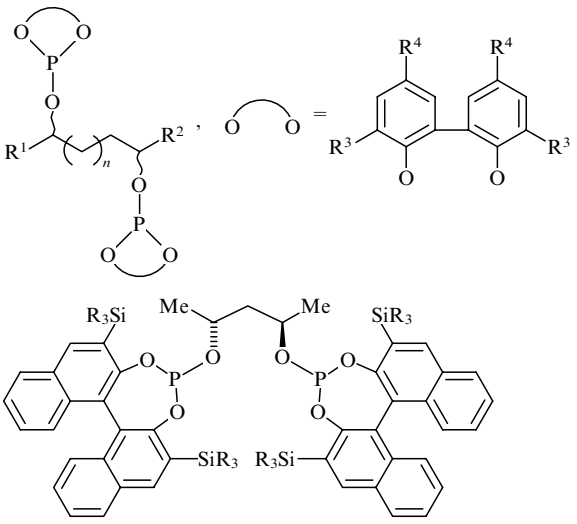
substituent; for simplicity, hereafter we will call them 'aminophosphites' and 'aminophosphoramidites.' No interesting results were obtained when catalytic reactions were performed involving these species.[6] This also holds for the phosphite derivatives of alkaloids.[8] On the contrary, P,P-bidentate ligands (type **C**) have been the subject of numerous studies, which were carried out to gain a better insight into their coordination chemistry and revealed high catalytic efficiency of these compounds.



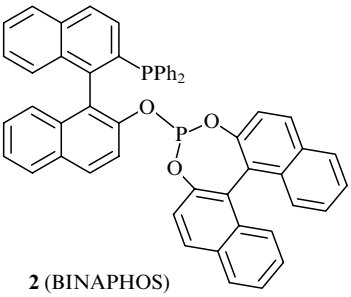
A **B** **C**

X, Y, Z = O or N.

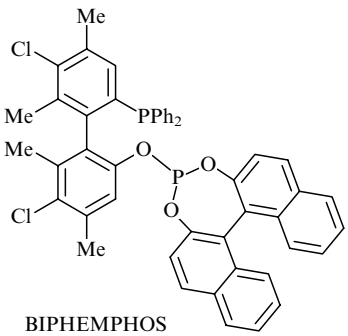
The advances made before 1998 and fully considered in Ref. 7 are as follows: design of two groups of structures providing an enantioselectivity of up to 87% in Rh-catalysed hydroformylation of styrene



by van Leeuwen's group and a series of studies by Takaya *et al.* who first synthesised dissymmetric phosphine-phosphites BINAPHOS (**2**) and BIPHEMPHOS and their simplest derivatives.



2 (BINAPHOS)



BIPHEMPHOS

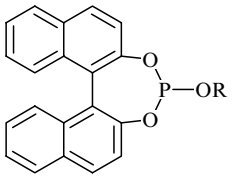
The use of these compounds in Rh-catalysed hydroformylation of a broad spectrum of substrates (vinyl acetate, styrene and its homologues, *N*-vinylphthalimide, cyclic and fluorinated alkenes, 4-vinyl-β-lactam) allowed an *ee* of 87% – 98% to be achieved. They also demonstrated a high enantioselectivity in Pd-catalysed copolymerisation of alkenes and dienes with CO.

Based on analysis of the role played and niche occupied by chiral phosphites in the coordination chemistry and catalytic studies (see above), some predictions were made concerning further use of these compounds.[7] In particular, dissymmetric P,P-bidentate compounds based on amino alcohols, active use of P,N-bidentate systems in asymmetric catalysis and the development of new fields of application of phosphite ligands (hydrosilylation and hydroboronation of C=C bonds) were predicted. These predictions were fully substantiated by further progress in the field, which appeared to be so rapid that recently reported studies[6,7] are now in essence out of date. A large body of new experimental material requires systematisation and discussion. The aim of this review is to consider the data published during the last five years. The data are classified based on the structure (first of all, denticity) of chiral phosphite ligands. This approach seems to be quite logical because it allows the advances of asymmetric catalysis and coordination chemistry to be analysed from a unified standpoint based on the nature of the phosphorus-containing ligand. In addition, in discussing the material we tried to group the studies reported by researchers from the leading scientific schools together and to highlight the most important results concerned with catalytic processes.

II. P-Monodentate phosphites

1. Phosphite derivatives of BINOL

This group of ligands comprises axially chiral compounds (**3a**–**q**) and compounds containing additional C*-stereocentres in the exocyclic substituent (**3r**–**w**).



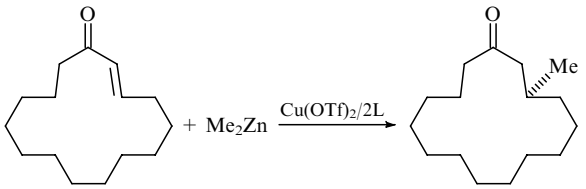
3a–**w** [(S_{ax}) and/or (R_{ax})]

Compound **3**	R	Compound **3**	R
a	Me	**n**	2-BrC_6H_4
b	Pr^i	**o**	2,6-$Me_2C_6H_3$
c	cyclo-C_5H_9	**p**	2,6-$Ph_2C_6H_3$
d	Bu^i	**q**	2-naphthyl
e	CH_2CHEt_2	**r**	(*S*)- or (*R*)-Bu^s
f	neopentyl	**s**	(*S*)- or (*R*)-CH(Ph)Me
g	Bn	**t**	(1*S*,2*R*)- or (1*R*,2*S*)-Ph(cyclo-C_6H_{11})
h	CH_2CH_2OMe	**u**	(1*S*,2*R*)- or (1*R*,2*S*)-(2-naphthyl)cyclohexyl
i	CH_2CH_2Cl	**v**	*O*-methyldianhydro-D-mannityl
j	CH_2CCl_3	**w**	menthyl
k	Ph		
l	4-$MeOC_6H_4$		
m	4-$CF_3C_6H_4$		

They are used in enantioselective processes resulting in the formation of C–C bonds and in hydrogenation of unsaturated esters. For instance, phosphites (S_{ax})-**3k**–**m** provided an *ee* of 32% – 96% in the Ir-catalysed allylic alkylation of esters of cinnamyl alcohol by dimethyl malonate. The highest enantioselectivity at a regioselectivity of 93 : 7 (branched : linear product) was demonstrated by ligand **3k** {$[IrCl(cod)]_2$ was used as precatalyst; cod = cyclooctadiene}.[9]

Asymmetric Cu-catalysed addition of Et_2Zn to acyclic enones $R^1-CH=CH-C(O)-R^2$ (R^1 and/or R^2 = Me, Pr^i, C_5H_{11}, Ph)

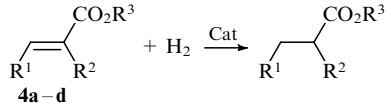
involving phosphites **3t**,**u** was studied.[10,11] It was found that enantioselectivity is governed by the axial chirality, namely, the enantiomeric excess was 56% to 87% for (R_{ax})-**3t**,**u** and at most 33% for (S_{ax})-**3t**,**u**. An odorant (*R*)-(−)-muscone was synthesised following reaction (1) using (R_{ax})-**3t** with a chemical yield of 53% and an optical yield of 79%.



(1)

Tf = CF_3SO_2.

No less important were the results obtained in hydrogenation of prochiral esters **4a**,**b** [reaction (2)].

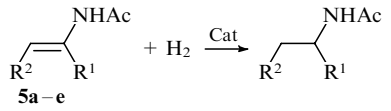


4a–**d** (2)

Compound **4**	R^1	R^2	R^3
a	H	CH_2CO_2Me	Me
b	H	NHAc	Me
c	4-AcO-3-$MeOC_6H_3$	NHAc	H
d	Ph	NHAc	Me

The optical yields of reactions involving (S_{ax})-**3a**,**b**,**k**,**n** were 89%–98% for compound **4a** and 70%–95% for compound **4b** {with $[Rh(cod)_2]^+BF_4^-$ as precatalyst}.[11] Noteworthy is that systems (S_{ax})-**3o**,**p** containing *ortho*-substituted exocyclic phenoxy groups appeared to be of low efficiency, namely, the optical yields in reaction (2) involving substrate **4a** were at most 39%. At the same time ligands bearing additional C*-stereocentres appeared to be excellent stereoselectors: hydrogenation of ester **4a** in the presence of (S_{ax})-**3v** and (R_{ax})-**3v** gave an *ee* of 95% to 98%; the optical yields in hydrogenation of esters **4a**,**b** using phosphites (S_{ax}, S_C)-**3s** and (S_{ax}, R_C)-**3s** were 93% to 99%.[12,13] Similarly, hydrogenation of substrate **4a** and in the presence of epimers (S_{ax})-**3w** and (R_{ax})-**3w** led to an *ee* of 91% to 95%.[14]

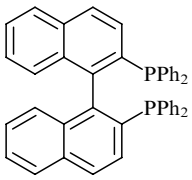
Phosphites **3a**–**j**,**r**,**s** also exhibited a high enantioselectivity (*ee* 75%–97%) in hydrogenation of enamides **5a**–**e** {also with $[Rh(cod)_2]^+BF_4^-$ as precatalyst, reaction (3)}.[15]



5a–**e** (3)

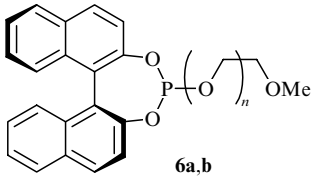
Compound **5**	R^1	R^2	Compound **5**	R^1	R^2
a	Ph	H	**d**	Ph	Me(*Z*)
b	4-ClC_6H_4	H	**e**	Ph	Me(*E*)
c	2-naphthyl	H			

Except for the reaction with ligand **3j** containing a CCl_3 group, which strongly withdraws the electron density and thus increases the π-acceptor ability of the P-centre, a 99%–100% conversion was obtained (*cf.* less than 5% for compound **3j**). Taking into account the above and the low cost of phosphite derivatives of BINOL (about 2% of the cost of the known P,P-bidentate phosphine ligand BINAP),[15] the conclusion about great prospects for industrial applications of these systems seems to be quite substantiated.



BINAP

Probably, this was the reason for the synthesis of phosphites **6a**,**b** with long-chain exocyclic substituents.[16]



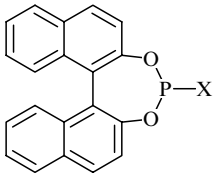
6a,**b**

n = 16 (**a**), 17 (**b**).

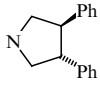
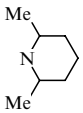
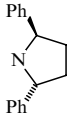
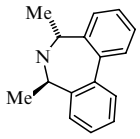
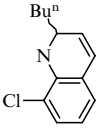
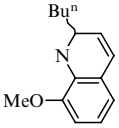
Being used with $[Rh(cod)_2]^+BF_4^-$, ligands **6a**,**b** accelerate hydroformylation of styrene under conditions of phase transfer catalysis. This example demonstrates the possibility of re-use of the catalytic system without loss of efficiency in spite of the low optical yield (17%).

2. Phosphoramidite derivatives of BINOL

Similarly to the phosphite systems, both axially chiral compounds (**7a**–**k**) and compounds containing additional C*-stereocentres (**7l**–**u**) were studied.

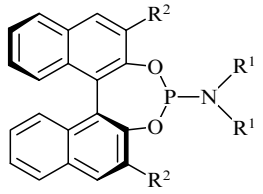


7a–**u** [(S_{ax}) and/or (R_{ax})]

Compound **7**	X	Compound **7**	X
a	NMe_2	**o**	(*R*)-bis(1-naphthylethyl)-amino
b	NEt_2		
c	NPr^i_2		
d	NBn_2	**p**	
e	NMeBn		
f	$N(CH_2)_5$		
g		**q**	
h		**r**	
i			
j	$N(o\text{-}MeOC_6H_4)_2$		
k		**s**	(*S*)- or (*R*)- 
l		**t**	(*S*)- or (*R*)- 

Compound **7**	X	Compound **7**	X
m		**u**	
n	(*S*)- or (*R*)-N(1-PhEt)$_2$		

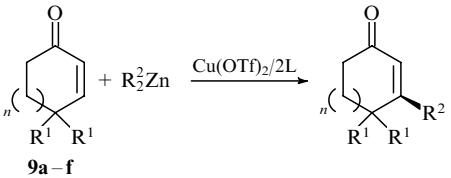
Besides, ligands **8** based on the *ortho*-disubstituted derivatives of BINOL (**1**) were synthesised.



8a–e

Compound **8**	R^1	R^2	Compound **8**	R^1	R^2
a	Me	Me	**d**	Me	Br
b	Pr^i	Me	**e**	Me	Ph
c	$(CH_2CH_2)_2O$	Me			

Undoubtedly, the scientific school headed by Feringa is a leader in the field of synthesis and catalytic applications of ligands **7**. As early as 1994, Feringa reported the synthesis of the first compound in this class, **7a** (MonoPhos).[17] The main field of application of these phosphoramidites is processes involving formation of C–C bonds (first of all, by Cu-catalysed addition of organozinc reactants). For instance, reactions with participation of cyclic α,β-unsaturated ketones **9** [reaction (4)] were studied.



(4)

9a–f

Compound **9**	R^1	*n*	Compound **9**	R^1	*n*
a	H	1	**d**	H	3
b	H	0	**e**	Me	1
c	H	2	**f**	Ph	1

The results of these studies for Et_2Zn are summarised in Table 1. As can be seen, ligand (S_{ax},R_C)-**7n** provides the highest enantioselectivity.[18–20] Its homologue, (S_{ax})-**7o**, bearing bulkier naphthyl substituents is somewhat less efficient, but stereomer (S_{ax},S_C)-**7n** is much less efficient (*ee* 75%).[19] Systems containing no additional C*-stereocentres **7a–j** appeared to be the worst stereoselectors (the maximum optical yield in the reaction with substrate **9a** was 60%, see Table 1).[19]

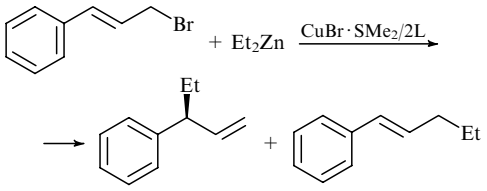
Table 1. Comparative enantioselectivity of a number of P-monodentate chiral phosphoramidites in the Cu-catalysed asymmetric addition of Et_2Zn to cyclic enones [reaction (4)].

Substrate	*ee* (%)	
	ligand (S_{ax})-**7c**	ligand (S_{ax},R_C)-**7n**
9a [a]	60	98
9b	–	10
9c	55	98
9d	–	97
9e	81	98
9f	–	98

[a] The enantioselectivity provided by other ligands involved in the reaction with this substrate was also studied; the results obtained are as follows: 25% for S_{ax}-**7a**, 72% for S_{ax}-**7m** and 94% for S_{ax}-**7o**.

Reactions of other R_2Zn derivatives [R = Me, Pr^i , Bn, C_7H_{15}, $(CH_2)_5OAc$ and $Me_2CH(OEt)_2$] in the presence of compounds **9a** and (S_{ax},R_C)-**7n** were also characterised by high enantioselectivity (*ee* 94%–98%).[20,21] Therefore, it is quite logical that the most efficient ligand, (S_{ax},R_C)-**7n**, also provided excellent results in other related reactions of R_2Zn addition to cyclic aliphatic vinyloxiranes (*ee* up to 96%);[22] α,β-unsaturated nitroacetals (*ee* up to 92%);[23] 4,4-disubstituted cyclohexadienones (*ee* up to 99%);[24] cyclic unsaturated ketones (followed by aldol condensation to give bicyclic enones with an optical yields of up to 98%);[25] and to 4,4,5-trisubstituted cyclohexanones (*ee* up to 97%).[26] Systems R_2Zn/Cu(OTf)$_2$/2L [L = (S_{ax})-**7c**, (S_{ax})-**7l–o**] were employed to achieve enantioselective kinetic resolution of racemic cyclohex-2-enones.[27] Again, ligand (S_{ax},R_C)-**7n** was the best stereoselector and provided a greater than 99% optical purity of the product [*cf*. an *ee* of only 22% for (S_{ax})-**7c**]. A related kinetic resolution of racemic vinyloxiranes with phosphoramidite (S_{ax},R_C)-**7n** was also characterised by *ee* up to 99%.[28] Very high enantioselectivity achieved in the key stage of R_2Zn addition to cyclic enones under the action of Cu(OTf)$_2$/2L [L = (S_{ax},R_C)-**7n**] permitted the development of efficient procedures for the synthesis of optically pure bicyclic alcohols[29] and methyl ester of (–)-prostaglandin E_1.[30]

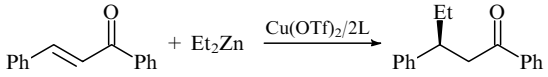
Phosphoramidite (S_{ax},R_C)-**7n** is also used in a promising reaction of synthesis of chiral alkenes. Namely, the optically active product was obtained at 85 : 15 regioselectivity (branched : linear products) and an *ee* of 77% [ligands (S_{ax})-**7c**, (S_{ax})-**7m**, (S_{ax})-**7o** provide an *ee* of at most 31%].[31]



It should be noted that in some cases the best results were obtained using the (R_{ax},S_C)-**7n** enantiomer. A case in point is the addition of Et_2Zn to cyclic enones (*ee* up to 92%)[10] and a variety of nitroolefins (*ee* up to 94%).[32,33]

Recently synthesised[34] ligand (R_{ax})-**7q** can also be considered rather promising. Indeed, the addition of Et_2Zn to enone **9a** catalysed by Cu(OTf)$_2$/2L [reaction (4)] was performed with an optical yield of 93%. Besides, the catalytic synthesis of (*R*)-(–)-muscone involving ligand (R_{ax})-**7q** [reaction (1), see above] is characterised by much higher enantioselectivity (*ee* 95%)[34] compared to the reaction with phosphite (R_{ax})-**3t**.

By and large, phosphoramidites bearing additional C*-stereocentres are much better stereoinductors in reactions of Cu-catalysed addition of organozinc compounds. However, there are also a few exceptions. In particular, the reaction with chalcone showed an *ee* of 90% with ligand (S_{ax})-**7c** and only 75% with (S_{ax},R_C)-**7n**.[18,19]

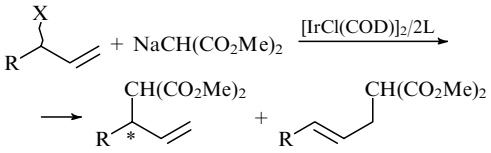


Efforts to obtain *ortho*-disubstituted phosphoramidites **8a–e** lacked support because the enantioselectivity showed by these compounds was no higher than that provided by their unsubstituted analogues **7a–u**.[18,19]

Note that, in spite of quite impressive catalytic results achieved using phosphoramidites **7a–q**, the coordination chem-

istry of these ligands is still poorly studied. Though a general scheme for the catalytic cycle of addition of organozinc reactants to cyclic enones has been reported,[19,20] no data confirming the structure of intermediates are available. The structure of catalytically active complexes is also unknown. Only Feringa and coworkers[18] earlier reported the synthesis and X-ray diffraction study of compound $CuI(L)_3$ [L = (S_{ax})-**7a**], while the course of complexation in the system $Cu(OTf)_2/2L$ is still to be clarified. We believe that one should expect publication of studies aimed at developing polymer-immobilised catalysts for asymmetric conjugate addition reactions. The first step along this line of investigation was reported recently.[35] Cu-Catalysed reaction of Et_2Zn with substrate **9a** [reaction (4)] using various modifications of the (R_{ax})-**7k** ligand covalently bound to hydroxymethylpolystyrene showed optical yields of up to 67%.

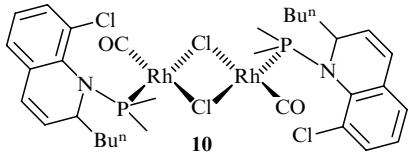
Phosphoramidite derivatives of BINOL (**1**) have also found applications in other reactions of C–C bond formation, in particular, Ir-catalysed allylic substitution.



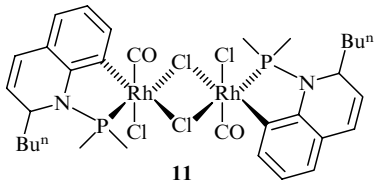
R = Me, CH_2CH_2Ph, Pr^i; X = OAc, Cl, OCO_2Et, $PO(OEt)_2$.

For instance, ligand (R_{ax})-**7a** usually provides a nearly 100% regioselectivity and an optical yield of up to 86% (R = CH_2CH_2Ph and X = OAc).[36,37] Very high chemical yields and regioselectivities are also observed in the presence of ligand (R_{ax},R_C)-**7n** in a related allylic amination reaction of a broad spectrum of substrates R–CH=CH–CH_2OCO_2Me by various amines (with enantioselectivities of 76%–97%).[38]

An interesting group of ligands **7s**,**t** was reported by Faraone *et al.*[39] The first communication was concerned with the synthesis and complexation of epimers **7s**. ^{31}P NMR and IR spectroscopy studies of the system $[RhCl(CO)_2]_2$/L [L = (S_{ax},R_C)-**7s**] revealed the formation of not only a conventional binuclear complex **10** but also its structural isomer **11** with a coordiation number of the Rh atom of 6.



10

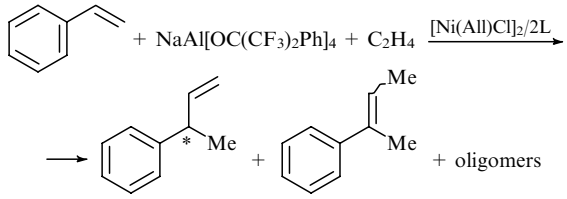


11

The formation of complex **11** involves oxidative addition of the ligand C–Cl bond to rhodium. In the case of epimer (S_{ax},S_C)-**7s** the process is sterically hindered and therefore only complex **10** is formed. The reactions of phosphoramidite (S_{ax},R_C)-**7s** with $[PdCl_2(PhCN)_2]$ or $[PtI_2(cod)]$ (at L : M = 2 mole ratio) resulted in corresponding complexes *cis*-$[MHal_2L_2]$. They were studied by ^{31}P and ^1H NMR, long-wavelength IR spectroscopy and X-ray analysis (complexes $[PtI_2L_2]$).[39]

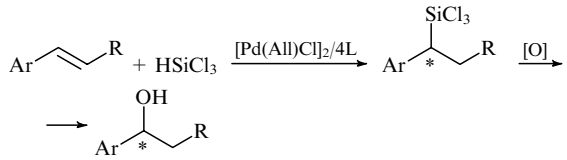
The use of both epimers **7s** in Cu-catalysed addition of Et_2Zn to substrate **9a** [reaction (4)] led to different results. Namely, the optical yield obtained with the ligand (S_{ax},S_C)-**7s** is close to zero, but was 70% for (S_{ax},R_C)-**7s**.[40] This was ascribed to the different orientation of the chloroquinoline fragments in the intermediate copper complexes.

A similar situation was also observed for Ni-catalysed hydrovinylation of styrene.[41,42]



The reaction involving ligand (R_{ax},S_C)-**7s** results nearly exclusively in oligomeric side products, whereas epimer (R_{ax},R_C)-**7s** provides the synthesis of optically active product with nearly 100% regioselectivity and an *ee* of 87%. Related reactions using ligand (R_{ax},R_C)-**7t** and its epimer (R_{ax},S_C)-**7t** showed optical yields of only 8% and 56%, respectively. Nevertheless, the known ligand (R_{ax},S_C)-**7n** is more efficient than phosphites **7s**,**t** in this reaction, because it provides an optical yield of 95%.[41]

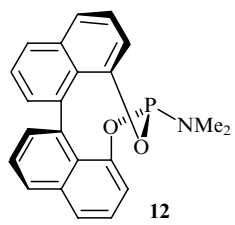
Recently, it was shown that phosphoramidite derivatives of BINOL (**1**) are excellent stereoselectors in not only C–C bond formation reactions but also other catalytic processes. For instance, the best results for hydrosilylation–oxidation of styrene (Ar = Ph, R = H), namely, an *ee* of 99%, were achieved using ligand (S_{ax},R_C)-**7n**.[43]



The optical yields of reactions with other aryl-substituted alkenes are also high (89%–98%). Systems without additional C*-stereocentres demonstrate much lower selectivities, *e.g.*, *ee*'s of 55% and 20% for the ligands (R_{ax})-**7a** and (R_{ax})-**7c**, respectively (with styrene as substrate).

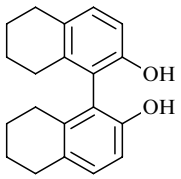
At the same time the structurally simplest phosphoramidites (S_{ax})-**7a**,**b** appeared to be highly efficient ligands in asymmetric reduction. For instance, acetophenone is transformed in α-phenylethanol under the action of complex $BH_3 \cdot THF$ in the presence of catalytic amounts of ligand (S_{ax})-**7b** with an optical yield of up to 99%.[44] Catalytic hydrogenation of prochiral esters **4a** and **4b** following reaction (2) using the catalytic system $[Rh(cod)_2]^+BF_4^-$/2L [L = (S_{ax})-**7a**] is characterised by enantiomeric excesses of 94% and greater than 99%, respectively.[45] Hydrogenation of a large number of enamides [reaction (3)] using the same catalytic system showed optical yields of up to 96% (in particular, 95%, 93% and 89% for substrates **5a**, **5b** and **5d**, respectively).[46,47] The enantioselectivity obtained with derivatives of β-dehydroamino acids is as high as 99% [L = (S_{ax})-**7a**, (S_{ax})-**7e** and (S_{ax},R_C)-**7u**].[48]

Phosphoramidite derivatives of other chiral binaphthyldiols deserve separate consideration. Ligand **12**

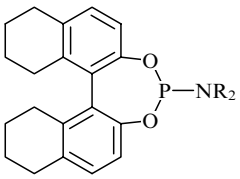


12

was successfully used in the reduction of acetophenone by complex $BH_3 \cdot THF$ (*ee* 96%) and in Cu-catalysed addition of Et_2Zn to enone **9a** [reaction (4), *ee* 83%].[49] For the latter reaction similar results were also shown by phosphoramidite (S_{ax})-**14b** based on H_8-BINOL (**13**), namely, the *ee* was 85% for substrate **9a** and 88% for substrate **9e**.[50]



13 (H_8-BINOL)

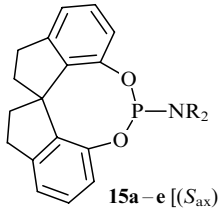


14a, **b** [(S_{ax}) and/or (R_{ax})]

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

The advantage of compound (R_{ax})-**14a** over its analogue **7a** is better solubility in organic solvents and a larger dihedral angle between the tetrahydronaphthalene fragments. It is quite logical that hydrogenation of α-dehydroamino acid esters [reaction (2) with $[Rh(cod)_2]^+BF_4^-$ as precatalyst] in the presence of (R_{ax})-**14a** is more efficient than the process involving ligand **7a**. For all substrates under study, the optical yields exceeded 90% (for compounds **4b**–**d**, it was 99% at nearly 100% conversion).[51,52] It should be noted that ester **4c** is a precursor of the known drug L-DOPA.

Recently,[53] a direct phosphorylation of (*S*)- or (*R*)-1,1′-spiroindan-7,7′-diol to give ligand **15a** was reported. Hydrogenation of substrate **4a** [reaction (2), *ee* 94%] and a number of methyl esters of α-dehydroamino acids in the presence of enantiomer (*S*)-**15a** with $[Rh(cod)_2]^+BF_4^-$ as precatalyst showed *ee* values of up to 99%.[53]



15a–**e** [(S_{ax}) and/or (R_{ax})]

R = Me (**a**), Et (**b**), Pr^i (**c**), cyclo-C_6H_{11} (**d**), CHMePh (**e**).

Ligand (*S*)-**15a** also possesses very high stereoinduction in $[Rh(cod)_2]^+BF_4^-$-catalysed hydrogenation of a series of prochiral enamides [reaction (3)]: the *ee* values obtained were between 91 and greater than 99%.[54] The dependence of enantioselectivity on the ligand structure can be illustrated by the following data:

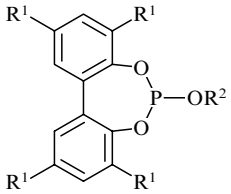
Ligand	(S_{ax})-**7a**	(S_{ax})-**14a**	(S_{ax})-**15a**	(R_{ax})-**15a**	(S_{ax})-**15b**	(S_{ax})-**15c**
ee (%)	95	96	99	96	57	38

Thus, the optical yield dramatically decreases as the substituents at the nitrogen atom (compounds **15a**–**c**) become bulkier. Since the dihedral angle between the aromatic fragments in (S_{ax})-**15a** is larger than in (S_{ax})-**14a**, the enantiomeric excess provided by the former ligand was somewhat higher. Cu-Catalysed addition of Et_2Zn to enone **9a** [reaction (4)] involving ligands **15a**–**e** is also characterised by an *ee* of 98% [the NR_2 fragment of ligand **15e** has the (*R*,*R*)-configuration].[55]

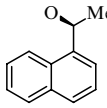
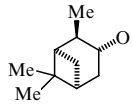
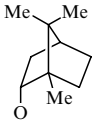
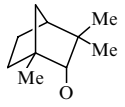
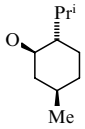
Summarising the material presented in Sections II.1 and II.2, it should be noted that P-monodentate derivatives of BINOL and related binaphthyldiols are highly efficient in various asymmetric catalytic reactions. This first of all concerns Cu-catalysed addition of R_2Zn to unsaturated substrates and Rh-catalysed hydrogenation of C=C bonds. To date, the best results were obtained using phosphoramidite ligands. As applied to the processes mentioned above, phosphoramidite ligands are at least competitive with (and often better than) phosphites in the number of substrates and in stereoinduction achieved, being also active in Ni-catalysed hydrovinylation, Pd-catalysed hydrosilylation–oxidation and reduction of ketones by $BH_3 \cdot THF$ complex. All these reactions are characterised by high and very high optical yields.

3. Phosphites and phosphoramidites based on biphenyldiols

Interest in these systems is based on an attractive idea of replacing axially chiral derivatives of binaphthyldiols by much more accessible and inexpensive biphenyldiols. Though the corresponding ligands (*e.g.*, **16**) undergo atropoisomerisation, bonding to a metal stabilises the configuration of the biphenyl frame.[56]

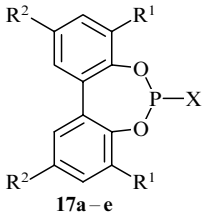


16a–**j**

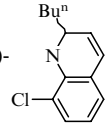
Compound **16**	R^1	OR^2	Compound **16**	R^1	OR^2
a	H		**g**	H	
b	Bu^t		**h**	Bu^t	
c	H		**i**	H	
d	Bu^t		**j**	Bu^t	
e	H				
f	Bu^t				

Complexation and catalysis using the $[Rh(cod)_2]^+BF_4^-$ system involving compounds **16a**–**j** have been studied.[57] ^{31}P NMR studies revealed a nearly 5:1 ratio of atropoisomers in the complexes $[Rh(cod)(L)_2]^+BF_4^-$ (*cf.* an equimolar mixture of unbound ligand atropoisomers). Unsubstituted structures (R^1 = H) provided higher enantioselectivity of hydrogenation of dimethyl itaconate (**4a**) following reaction (2); the enantiomeric excesses were 29% to 75% (the latter value was obtained with ligand **16i**) while at most 19% with $R^1 = Bu^t$.

Phosphoramidites **17a**–**d** were studied in Cu-catalysed addition of Et_2Zn to cyclic α,β-unsaturated ketones [reaction (4)] and nitroolefins.[58–60] Not only were a variety of substrates tested but also the reaction conditions varied [in particular, Cu(I) and Cu(II) salts used in the reactions].

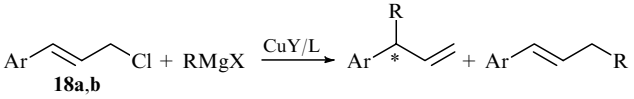


17a–**e**

Compound **17**	R^1	R^2	X
a	H	H	(*S*)- or (*R*)-N(1-PhEt)$_2$
	Me	Me	
c	H	H	(*S*)- or (*R*)-N(1-PhPr)$_2$
	Me	Me	
e	Bu^t	OMe	(*S*)- or (*R*)- 

For instance, substrate **9a** provided an *ee* of 96% to 99% (93%–95% for substrate **9c**), which is comparable with the enantioselectivity of phosphoramidite (S_{ax},R_C)-**7n** (see Table 1). The asymmetric induction achieved with other substrates was strongly affected by the nature of the ligand. In particular, for Ph–CH=CH–NO_2 the ligand (*S*)-**17b** provides an *ee* of 82% [*cf.* only 48% obtained with (R_{ax}, S_C)-**7n**].[60] Unlike derivatives **16a**–**j**, there is no correlation between the stereoinduction achieved and the presence of substituents in the phenyl rings of compounds **17a**–**e**, though by and large systems with $R^1 = R^2 = Me$ appeared to be more efficient.

The asymmetrising potential of ligands **17a**–**d** has found applications in the synthesis of silyl ethers of cyclic enols[61] and in reactions of Grignard reagents with allyl chlorides,[62] which involve conjugate addition of R_2Zn to cyclohexenones.



18a,**b**

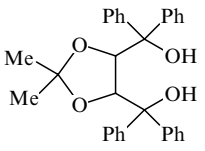
Ar = Ph (**a**), 3-$MeOC_6H_4$ (**b**).

The reaction of EtMgBr with substrate **18a** shows an *ee* of up to 79% involving ligand (*S*)-**17a** and 54% with substituted ligand (*S*)-**17b** [*cf.* at most 49% provided by two BINOL derivatives, (S_{ax})-**7a** and (S_{ax}, S_C)-**7n**]. The best results, that is, an *ee* of 86% at 91 : 9 regioselectivity (branched : linear products) was obtained using ligand (*S*)-**17a** [substrate **18b**, Pr^iMgBr, CuTC (TC is thiophene-2-carboxylate)]. $[IrCl(cod)]_2$/2L-Catalysed allylic amination of Ph–CH=CH–CH_2OCO_2Me by benzylamine was characterised by an optical yield of 87%.[38]

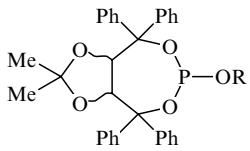
Thus, biphenyldiol-based phosphoramidites **17a**–**d** successfully compete with analogous derivatives of BINOL (**1**). In contrast to ligand **7s**, the reaction of ligand **17e** with $[RhCl(CO)_2]_2$ proceeds selectively and results in a binuclear Rh(III) complex, which is similar to compound **11** and was studied by IR and ^{31}P NMR spectroscopies and by X-ray analysis.[39] The synthesis of compound *cis*-$[PdCl_2(L)_2]$ (L = ligand **17e**) was also reported in that study.[39]

4. TADDOL-based phosphites and phosphoramidites

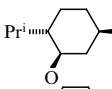
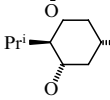
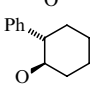
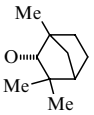
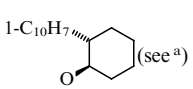
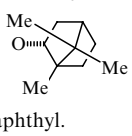
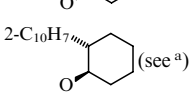
This group comprises the ligands obtained by phosphorylation of (+)- or (−)-α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOL, **19**).



19 (TADDOL)

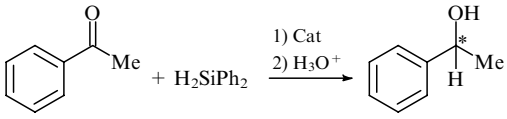


20a–**m** [(*S*) and/or (*R*)]

Compound **20**	OR	Compound **20**	OR
a	OMe	**i**	
b	OBu^t		
c	O-cyclo-C_6H_{11}		
d	OPh	**j**	
e	OH		
f	$OCH_2C{\equiv}C-SiMe_3$		
		k	
g			
		l	 (see [a])
h			
		m	 (see [a])

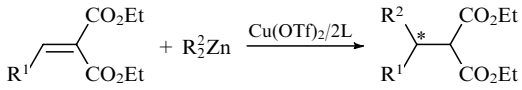
[a] $C_{10}H_7$ is naphthyl.

Initially, phosphites **20a**,**d** were employed in hydrosilylation of acetophenone followed by hydrolysis [reaction (5)].

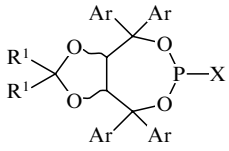


(5)

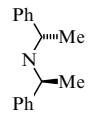
However, the optical yield appeared to be low {less than 25% with $[RhCl(cod)]_2$ as precatalyst}.[63] The enantioselectivity in Cu-catalysed addition of Et_2Zn to enone **9a** [reaction (4)] involving ligands **20a**–**f** was also low (*ee* less than 18%). Among phosphites with fragments of chiral alcohols, the best results in this reaction were provided by compounds (*S*)-**20m** (*ee* 86%) and (*S*)-**20k** (*ee* 96%).[64,65] Thus, in some cases the use of TADDOL-based phosphites leads to worse results compared to the use of, *e.g.*, phosphorus-containing BINOL derivatives. However, the stereoinduction achieved in conjugate addition to alkylidene malonates with L = (*S*)-**20m** can be as high as 73% and only 26% with ligand **7n**.[66]



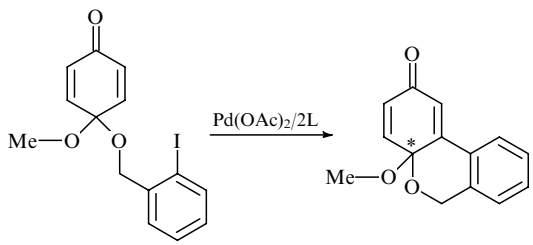
In a model reaction of Et_2Zn with enone **9a** [reaction (4), $Cu(OTf)_2$/2L], ligands **21a**–**h** provide an *ee* of 71%.[65,67]



21a–**h** [(*S*) and/or (*R*)]

Compound **21**	R^1	Ar	X	Compound **21**	R^1	Ar	X
a	Me	Ph	NHMe	**g**	Me	2-MeC_6H_4	NMe_2
b	Me	Ph	NMe_2				
c	Me	Ph	NPr^i_2				
d	Me	Ph	NBn_2	**h**	Me	Ph	
e	Me	Ph	$N(CH_2)_5$				
f	$(CH_2)_4$	Ph	NMe_2				

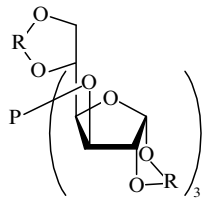
In contrast to the situation for BINOL-based phosphoramidites, in this case the asymmetric induction increases as the substituents at the nitrogen atom become less bulkier. Because of this, the best results are provided by ligand **21b**.[67] It is of considerable importance that the reaction with substrate **9b** (also involving **21b**) shows[67] an *ee* of up to 62% [*cf.* 10% with (S_{ax},R_C)-**7n**, see Table 1]. The enantioselectivities of phosphites (*R*)-**21c** and (S_{ax},S_C)-**7n** in conjugate addition of R_2Zn to alkynylepoxides are comparable (*ee* 36% and 38%, respectively).[68] Recently,[69] ligand (*R*)-**21b** was successfully used in an intramolecular Heck reaction [reaction (6)]; the enantiomeric excess was 96% at 100% conversion.



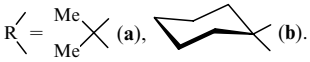
(6)

5. Phosphites and phosphoramidites based on carbohydrates and their derivatives

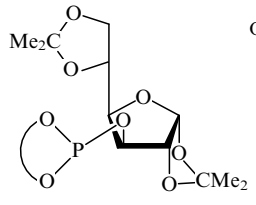
As mentioned above, the pioneering studies in this field were considered earlier.[6] Some examples were also presented in a review [70] concerned with complexes of platinum subgroup metals with carbohydrates. In spite of the fact that phosphorus-containing sugar derivatives are among the long-studied groups of chiral phosphite ligands, they still attract the attention of researchers. For instance, the reaction was reported [71] of compound **22a** with $[CuCl(CO)]_x$ to give a tetranuclear copper(I) complex $[\{CuCl(L)\}_4]$, which was studied by X-ray analysis. The structure of compound **22a** is characterised by a large Tolman cone angle ($\sim 180^\circ$). Because of this, the complex in CD_2Cl_2 solution is in equilibrium with $[\{CuCl(L)_2\}_2]$ dimer (^{31}P NMR data).



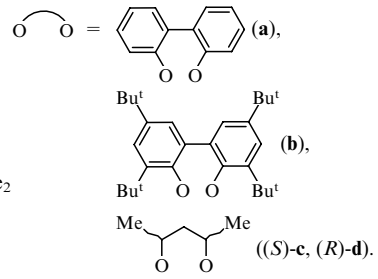
22a,**b**



Ligands **22a**,**b** and **23a**–**d** are used in the synthesis of rhodium(I) complexes and in Rh-catalysed hydrosilylation of acetophenone by diphenylsilane [reaction (5), *ee* less than 58%].[72]

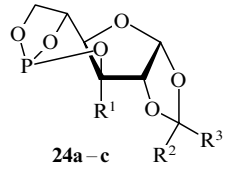


23a–**d**

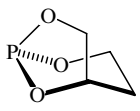


The reactions of compounds **22a**,**b** and **23b** with $[RhCl(cod)]_2$ result in mononuclear complexes [RhCl(cod)(L)]. Further increase in the L : Rh mole ratio (L = **22a**) is not accompanied by the formation of the desired product, $RhCl(L)_3$. Attempts at obtaining $RhCl(L)_3$ starting from $[RhCl(C_2H_4)_2]_2$ also failed. This is also associated with the large cone angle in ligand **22a**. Nevertheless, these two ligands can be in a *cis*-position relative to each other in the coordination sphere of rhodium, which was confirmed by the synthesis of complex $[Rh(acac)L_2]$. It was found that $[RhCl(cod)]_2$ is inefficient as a precatalyst in the hydrosilylation of acetophenone (*ee* at most 11%). The best result, *ee* 58% (see above), was obtained using the $[RhCl(C_2H_4)_2]_2$/6L system (L = compound **22b**).

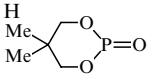
Bicyclophosphites **24a**–**c** and **25** were proposed as efficient ligands for synthesis of coordination compounds. Complexes $[\{CuBr(L)\}_4]$, $[M(CO)_5(L)]$ (M = Cr, Mo) and *cis*-$[PtCl_2(L)_2]$ were synthesised using phosphites **24a**–**c**; and studied by IR spectroscopy, ^{31}P and ^{13}C NMR and by X-ray analysis.[73]



24a–**c**

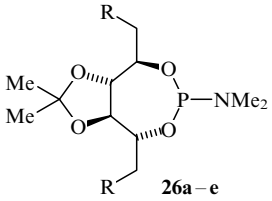


25

Compound **24**	R^1	R^2	R^3
a	H	Me	Me
b	H	H	CCl_3
c		Me	Me

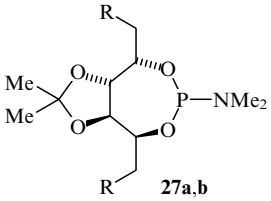
Phosphite **25** derived from (*S*)-1,2,4-butanetriol was employed in the synthesis of complexes with an open and a half-open titanocene.[74]

A novel group of phosphoramidites **26** and **27** [75,76] should be pointed out.



26a–**e**

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



27a,**b**

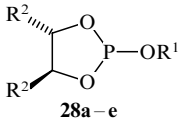
R = H (**a**), Ph (**b**).

They were used to obtain cationic complexes of rhodium(I), $[Rh(cod)(L)_2]^+OTf^-$, and neutral complexes of palladium(II), *cis*-$[PdCl_2(L)_2]$. Two Pd complexes with L = **26a** and **27a** were studied by X-ray analysis. These coordination compounds were also studied by ^1H and ^{31}P NMR spectroscopy and by FAB mass spectrometry. It is unclear why the set of ^{31}P NMR spectral parameters does not include the $^1J(P,Rh)$ spin-spin coupling constants, which are useful for assessing the electron-donor ability of phosphorus-containing ligands.

Complexes $[Rh(cod)L_2]^+OTf^-$ (L = **26**, **27**) were studied as catalysts for the hydrogenation of unsaturated acids, namely, α-(*N*-acetylamino)cinnamic (*ee* up to 89%) and itaconic acid (*ee* up to 94%).[76] In both cases the best results were obtained using phosphoramidite **27b**, whereas its diastereomer **26e** is much less efficient and provides enantiomeric excesses of 36% and 61%, respectively.

6. Other P-monodentate chiral phosphites

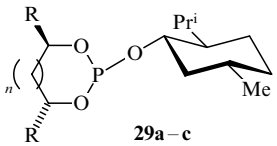
Cyclic phosphites **28a**–**e** based on tartaric acid derivatives are also of interest.



28a–**e**

Compound **28**	R^1	R^2	Compound **28**	R^1	R^2
a	(L)-menthyl	CO_2Et	**d**	(L)-menthyl	CO_2Pr^i
b	(D)-menthyl	CO_2Et	**e**	(L)-menthyl	$CONMe_2$
c	bornyl	CO_2Et			

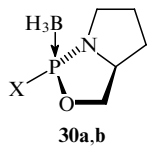
They provided an *ee* of up to 40% in conjugate addition for Et_2Zn to enone **9a** [reaction (4)] and up to 65% in the reaction with benzylidenacetone [with the $Cu(OTf)_2$/2L catalytic system].[77] Though these optical yields cannot be considered high, ligands **28a**–**e** are much better stereoselectors than related phosphites **29a**–**c** whose efficiency in these reactions was characterised by an *ee* of at most 11%.[77]



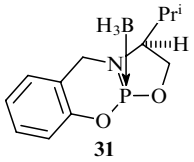
29a–**c**

R = Me: *n* = 1 (**a**), 0 (**b**); R = Ph, *n* = 0 (**c**).

Complexes **30a**,**b** and **31** were used as catalysts of acetophenone reduction by the $BH_3 \cdot THF$ adduct; however, the optical yield was at most 37%.[78]



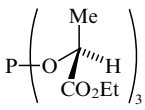
30a,**b**



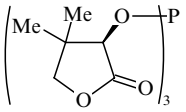
31

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

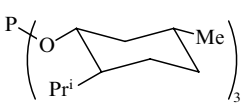
Mention also may be made of phosphites **32**–**34**.



32



33



34

Ligands **32** and **33** were used in complexation with [Fe(chd)$(CO)_3$] (chd = 1,3-cyclohexadiene)[79] and [Ni$(cod)_2$] (see Ref. 80), respectively. Trialkyl phosphite **34** was involved in Cu-catalysed addition of Et_2Zn to enone **9a** [reaction (4), *ee* 36%].[77]

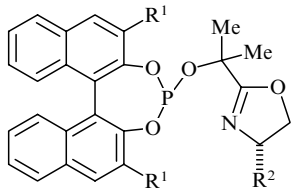
Thus, at present the catalytic potential of compounds **22**–**34** seems to be quite modest as compared to the potential of ligands based on BINOL (**1**) and TADDOL (**19**). However, we believe that it is not completely explored and considerable progress is possible in this field. A good example is provided by the successful use of phosphite **27b** in Rh-catalysed hydrogenation (see above).

III. P,N-Bidentate compounds of phosphite nature

The first synthesis of ligands belonging to this class and their complexation with rhodium(I) was reported in 1993.[81] Since then, methods of synthesis and the coordination chemistry of these compounds have been the subject of some studies;[5,6,8] however, they have been efficiently used in asymmetric catalysis only during the last five years. The introduction of the N-donor centre into the chiral ester or phosphorous acid amidoester molecule makes it possible to extend the field of application of P,N-bidentate compounds of phosphite nature. Therefore, the material presented in this Section is classified with emphasis on the nature of the nitrogen donor centre.

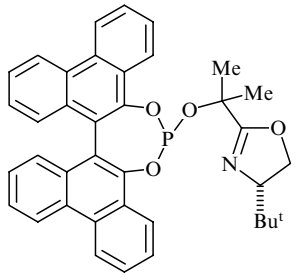
1. Phosphites and phosphoramidites containing an oxazoline fragment

The major contribution to the design of these systems was made by Pfaltz *et al.*[82,83] who proposed a broad spectrum of ligands **35**–**38** based on BINOL (**1**) and related structures.

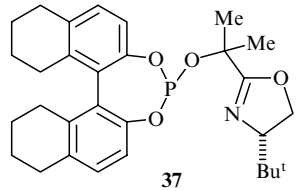


35a–**h** [(S_{ax}) and/or (R_{ax})]

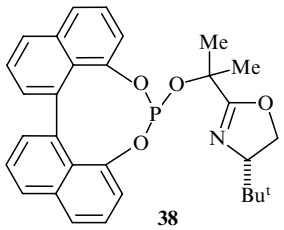
Compound **35**	R^1	R^2	Compound **35**	R^1	R^2
a	H	Pr^i	**e**	Ph	Bu^t
b	H	Ph	**f**	4-PhC_6H_4	Bu^t
c	H	Bu^t	**g**	2,4,6-$Me_3C_6H_2$	Bu^t
d	Me	Bu^t	**h**	3,5-$Bu^t_2C_6H_3$	Bu^t



36 [(S_{ax}) and/or (R_{ax})]

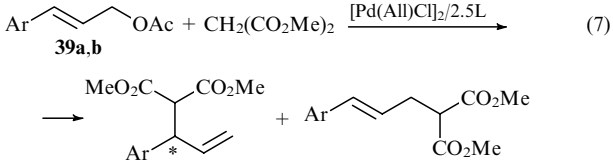


37



38

Pd-Catalysed allylic substitutions involving ligands **35a**–**d** and substrate **39a** [reaction (7)] showed the enantiomeric excesses lying between 7% and 92% and the yields of the branched products in the range 46%–76%.[82,83] The highest enantioselectivity was provided by ligand (S_{ax})-**35d**.[83]



(7)

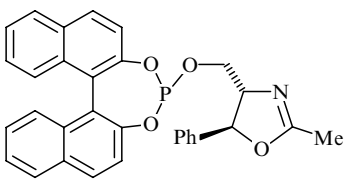
39a,**b**

Ar = Ph (**a**), naphthyl (**b**).

The asymmetric induction depends first of all on the configuration of the oxazoline fragment. Namely, the enantiomeric excess provided by the ligands is 79% for (R_{ax})-**35c** and 90% for (S_{ax})-**35c**, the product configurations in both cases being the same.[83] Substrate **39b** is characterised by greater steric requirements and makes it possible to achieve an *ee* of up to 96% at high regioselectivity and chemical yield [L = (S_{ax})-**35c**].[84] The structure of catalytically active complex {Pd(All)[(S_{ax})-**35c**]}$^+PF_6^-$ was confirmed by X-ray analysis.[82]

Oxazolinophosphites **35c**–**h** and **36**–**38** were studied in the Cu-catalysed addition of Et_2Zn to cyclic enones **9a**–**c** [reaction (4)].[85–87] The enantiomeric excesses obtained for different substrates are as follows: up to 90% for **9a** [L = (R_{ax})-**35d**], up to 94% for **7b** [L = (R_{ax})-**35f**] and up to 94% for **9c** [L = (S_{ax})-**36**]. The high enantioselectivity of the reaction involving enone **9b** should be pointed out, which could not be provided by other phosphites (*cf.* the data listed in Table 1). A study on the dependence of enantioselectivity on the ligand structure revealed no direct correlation between the optical yields and the size of substituents in the *ortho*-positions of the naphthyl rings. However, the presence of these substituents is a necessary condition for high stereoinduction.[85,87]

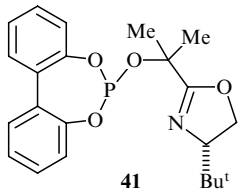
Both epimers of ligand **40** were also described.[88]



40 [(S_{ax}) and (R_{ax})]

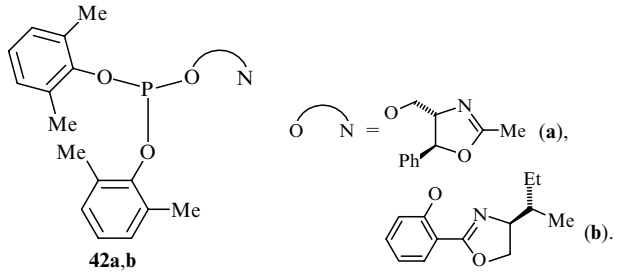
^{31}P NMR spectroscopy, IR spectroscopy and electrospray mass spectrometry data showed that ligand **40** unexpectedly forms dimeric rather than chelate complexes of rhodium(I) with a 'head-to-tail' bridging bonding of the P,N-bidentate ligand and that the structures of the complexes depend on the absolute configuration of BINOL. This remarkable fact should be taken into account in analysis of applications of P,N-bidentate ligands as catalysts, the more so as the stereoinduction involving epimers **40** is also significantly different. Namely, ligands (R_{ax})-**40** and (S_{ax})-**40** provide an *ee* of up to 58% and at most 4%, respectively, in Rh-catalysed hydrosilylation of acetophenone [reaction (5)] .

As mentioned above, the enantioselectivity of oxazolinophosphites **35a**–**d** in Pd-catalysed allylic alkylation is to a great extent governed by the oxazoline fragment. This makes it possible to rule out the axially chiral template BINOL for ligand design purposes. In particular, compound **41** provides an *ee* of 83% in the reaction involving substrate **39a** [reaction (7)].[82]



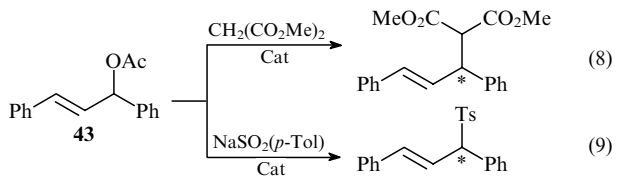
41

Moreover, acyclic ligands **42a**,**b** also appeared to be efficient.



42a,**b**

Pd-Catalysed allylic substitutions of substrate **43** for dimethyl malonate [reaction (8)] and $NaSO_2$(*p*-Tol) [reaction (9)] respectively showed an *ee* of 85% {for $[Pd(All)Cl]_2$/2.5L, L = **42a**}[89] and an *ee* of 92% {for $[Pd(All)(\mathbf{42b})]^+BF_4^-$}.[90]



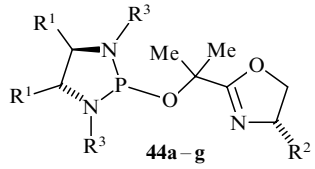
43

(8)

(9)

Chelate mononuclear complexes [RhCl(CO)(L)] with L = **42a**,**b** were synthesised. The complex with phosphite **42a** was studied by X-ray analysis.[89]

Systems based on chiral 1,2-diamines and TADDOL (**19**) and containing oxazoline fragments and phosphite cyclic groups were also synthesised. Oxazolinophosphoramidites **44a**–**g** were found to be highly efficient.



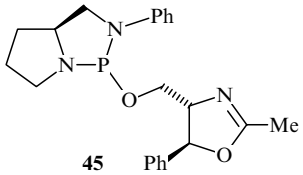
44a–**g**

Compound **44**	R^1	R^2	R^3
a	Ph	Bu^t	Ts
b	$(CH_2)_2$ (see [a])	Bu^t	Ts
c	Ph	Ph	Ts
d	Ph	Bu^t	(1-naphthyl)methyl
e	Ph	Bu^t	4-$MeOC_6H_4$
f	$(CH_2)_2$ (see [a])	Bu^t	4-$MeOC_6H_4$
g	Ph	Bu^t	4-biphenylyl

[a] Here, R^1-R^1.

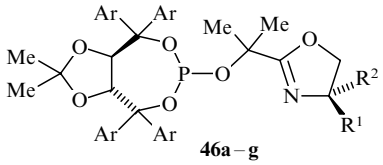
They showed high enantioselectivities in Pd-catalysed substitution of substrates **39a** (*ee* up to 95%), **37b** (*ee* greater than 99%) [reaction (7)] and **43** (*ee* up to 88%) [reaction (8)] for dimethyl malonate. Additionally, Ir-catalysed hydrogenation of various vinylarenes showed an *ee* of greater than 99%.[91,92]

The catalytic system $[Pd_2(dba)_3\cdot CHCl_3]$/2L (L = **45**, dba = dibenzylideneacetone) provides an optical yield of 92% in the reaction of substrate **43** with $NaSO_2$(*p*-Tol) [reaction (9)].[93]



45

Note that in addition to three C*-stereocentres compound **45** also contains a P*-stereocentre in the (*R*)-configuration. In contrast to oxazolinophosphite **42b**, ligand **45** provides a lower stereoinduction in the cationic complex $[Pd(All)(\mathbf{45})]^+BF_4^-$ (*ee* 77%).



46a–**g**

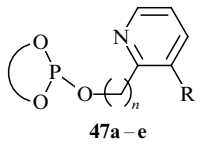
Compound **46**	Ar	R^1	R^2	Compound **46**	Ar	R^1	R^2
a	Ph	H	Ph	**e**	2-naphthyl	Pr^i	H
b	Ph	Ph	H	**f**	Ph	H	Bu^t
c	Ph	H	Pr^i	**g**	2-naphthyl	H	Bu^t
d	Ph	Pr^i	H				

Ligands **46a**–**e** were used[94] in the synthesis of cationic complexes of rhodium(I) $[Rh(cod)(L)]^+BF_4^-$ (complex with L = **46b** was studied by X-ray analysis) and in hydrosilylation of a number of aliphatic and aromatic ketones {with $[RhCl(cod)]_2$ as precatalyst}. The best results were obtained with ligand **46d**, which provided the optical yields of 88% and 95% for the reduction of acetophenone and *tert*-butyl methyl ketone, respectively. Phosphite **46f** provides high optical yields in the Pd-catalysed substitution of substrate **39b** [reaction (7), *ee* 94%] while phosphites **46f**,**g** also behave analogously in Ir-catalysed hydrogenation of 4-$MeOC_6H_4C(Me)=CHMe$ (*ee* 95%).[91,92]

The use of ligand **46c** in Cu-catalysed addition of Et_2Zn to enone **9a** [reaction (4)] and to alkylidene malonates has also been reported; however, the enantioselectivities achieved were low (*ee* at most 22%).[65,66]

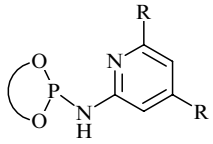
2. Phosphites and phosphoramidites containing pyridine fragments

As in the ligand group considered above, BINOL-based systems **47**–**49** are also known in this group. Phosphites **47a**–**e** and **48a**,**b** were found to be inefficient in the reaction of Pd-catalysed alkylation of substrate **43** by dimethyl malonate [reaction (8)]. They provided optical yields of at most 37%[95] while the use of ligands **47a**,**b** resulted in racemic product.[95,96] Multinuclear NMR studies (including 2D NOESY experiments) showed that this is due to the presence of different configurational isomers of the intermediate palladium complexes.[95,96]



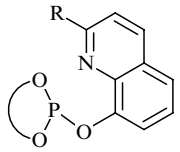
47a–e

n = 0, R = H (**a**);
n = 1: R = H (**b**), Me (**c**), Ph (**d**), Br (**e**).



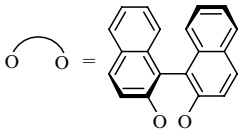
48a,b

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



49a,b

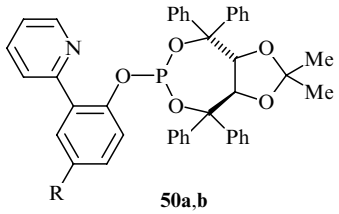
R = H (**a**), Me (**b**).



= S_{ax}-BNaph(O)$_2$.

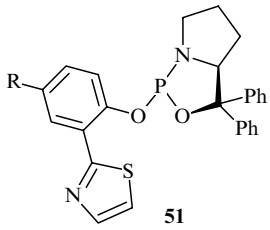
Cu-Catalysed addition of Et_2Zn to enone **9a** [reaction (4)] in the presence of ligands **49a**,**b** also showed a moderate enantioselectivity (*ee* up to 51%).[40] Note that phosphite **49a** is used as a chelate-forming ligand in the synthesis of half-sandwich complexes of ruthenium(II) and rhodium(III), *e.g.*, [RhCl(η^5-C_5Me_5)(S_{ax}-**49a**)]$^+PF_6^-$ (see Ref. 97), which was studied by X-ray analysis. Yet another enantiomer, (R_{ax})-**49a**, was used in the substitution reaction involving substrate **43** and dimethyl malonate {reaction (8), with [Pd(All)Cl]$_2$ as precatalyst, *ee* 31%}.[98]

Quite interesting compounds **50a**,**b** [99, 100]



50a,b

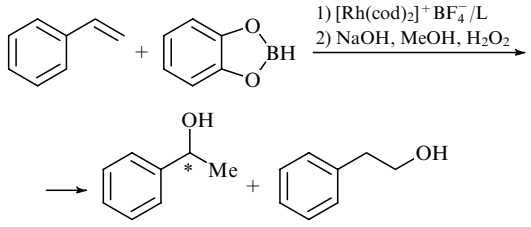
R = H (**a**), OSiBu^{t}Me$_2$ (**b**).



51

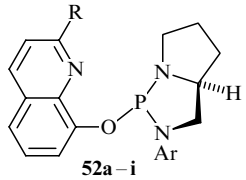
R = OSiBu^{t}Me$_2$.

were studied in the Rh-catalysed hydroboronation–oxidation of styrene.



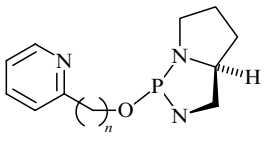
The optical yield was 59% at chemical yields in the range 52%–56% and regioselectivities (branched : linear product ratios) from 77 : 23 to 80 : 20.[100] Similar results were also obtained for compound **51** containing no pyridine fragment.[99, 100]

Shortening of the distance between the chiral fragment and the donor atoms of the ligand is known to favour a significant enhancement of stereoinduction. It is particularly appropriate if these atoms are stereocentres. A number of ligands **52**, **53** containing asymmetric phosphorus atoms were proposed by Buono *et al.*[101–103]



52a–i

Compound **52**	R	Ar	Compound **52**	R	Ar
a	H	Ph	**g**		Ph
b	Me	Ph			
c	Bu^t	Ph	**h**		Ph
d	Ph	Ph			
e	CN	Ph	**i**	H	1-naphthyl
f		Ph			



53a,b

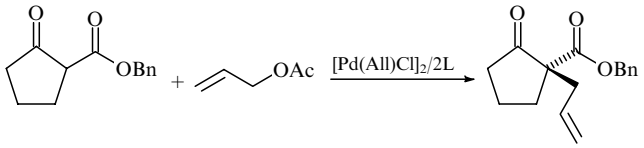
n = 0 (**a**), 1 (**b**).

^{13}C NMR and X-ray diffraction studies of complex [Pd(All)(**52a**)]$^+ClO_4^-$ revealed the (*R*)-configuration of the P*-stereocentre.[101]

The classical allylic substitution in the reaction of substrate **43** with dimethyl malonate {reaction (8), catalytic system [Pd(All)Cl]$_2$/4L, L = **52a–h** or **53a**,**b**} is characterised by an optical yield of up to 87% and by nearly 100% conversion.[98, 102] The highest enantioselectivity was obtained with ligand **52a**, whereas the *ee* provided by its derivatives **52b–h** was at most 55%.[98] A related process, allylic amination of substrate **43** involving benzyl- and veratrylamines as nucleophiles (L = **52a–i** and **53a**,**b**) showed an *ee* of up to 94%.[103] Here, phosphite **52a** was also the most efficient (compound **52b–h** provided the enantiomeric excesses in the range 38%–78%).[98]

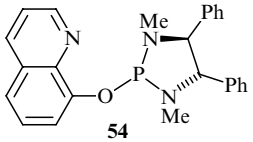
Phosphoramidite **52a** is also used in Pd-catalysed allylic amination of prochiral bicyclic diacetates (*ee* up to 89%),[104] Cu-catalysed Diels–Alder reactions (*ee* greater than 99% at 99% conversion)[105] and conjugate addition of Et_2Zn to cyclohexenone **9a** [reaction (4), *ee* up to 61%].[106]

Yet another example of the potential of ligand **52a** is provided by an elegant reaction to give quaternary C*-stereocentres by allylation of β-ketoesters.[107]

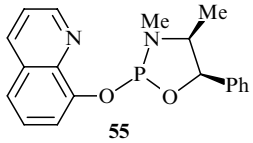


It is characterised by an *ee* of 95%; however, one should keep in mind that the enantioselectivity is quite 'sensitive' to the nature of the substrate and allylating agent. For instance, the optical yield in the reaction involving a homologous keto ester containing a six-membered ring was at most 17%.

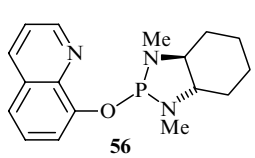
The efficiency of ligand **52a** as stereoselector is most pronounced when comparing it with phosphoramidites **54–57**.



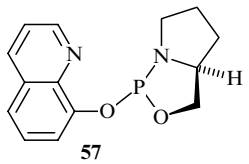
54



55



56



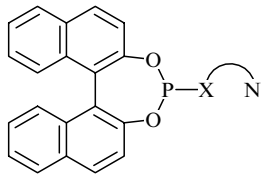
57

Studies of compounds **54**–**57** and (R_{ax})-**49a** in the catalytic processes mentioned above revealed low asymmetrising activities of these species. Namely, the optical yield of Pd-catalysed allylic substitution of substrate **43** for dimethyl malonate [reaction (8)] was at most 31% and 35% in the case of benzylamine; the enantiomeric excess in Cu-catalysed addition of Et_2Zn to enone **9a** [reaction (4)] was only 27%.[98]

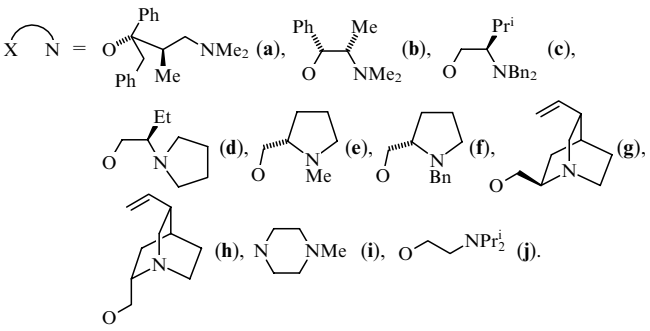
Thus, most ligands containing a pyridine fragment possess low or moderate enantioselectivities. The exceptions are phosphoramidites **52a** and **53**; however, their efficiency may be due to the unique structure of the bicyclic phosphite centre rather than the nitrogen-containing fragment.

3. Aminophosphites and aminophosphoramidites

We begin our discussion of this group of ligands (type **B**) with phosphite derivatives of BINOL **58a**–**j**.

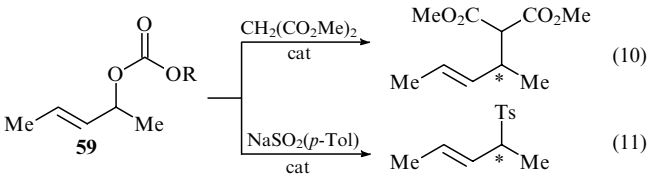


58a–**j** [(S_{ax}) and/or (R_{ax})]



Reactions of compounds **58a**–**g** with $[RhCl(CO)_2]_2$ result in chelate mononuclear complexes [RhCl(CO)(L)]. It was shown that coordination of ligand **58c** proceeds non-selectively due to significant steric hindrances to chelation produced by benzyl substituents at the nitrogen atom. As a result, a *trans*-$[RhCl(CO)(L)_2]$ complex is formed in addition to the metal-containing chelate.[88]

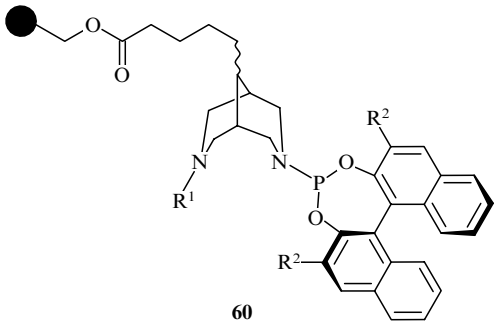
Compounds **58a**,**b** were studied in Pd-catalysed alkylation of substrates **59** by dimethyl malonate {reaction (10), catalytic system $[Pd(All)Cl]_2/2L$}. The optical yield was at most 34%.[88]



(10)

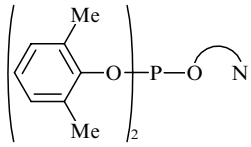
(11)

Similarly to this, phosphite **58h** showed a low enantioselectivity (*ee* 16%) in Rh-catalysed hydroformylation of styrene.[108] Cu-Catalysed addition of Et_2Zn to cyclic enone **9a** in the presence of ligand **58i** [reaction (4)] and Rh-catalysed hydrogenation of enamide **5a** in the presence of ligand **58j** [reaction (3)] result in racemates.[15,19] In this case, the attainment of an *ee* of 67% in the last-mentioned reaction involving a large group of polystyrene-immobilised systems [109] of general structural type **60** seems to be encouraging.

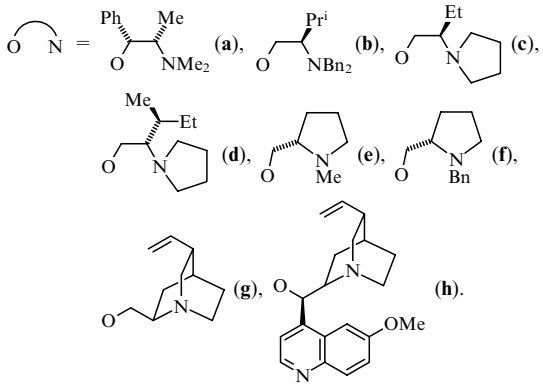


60

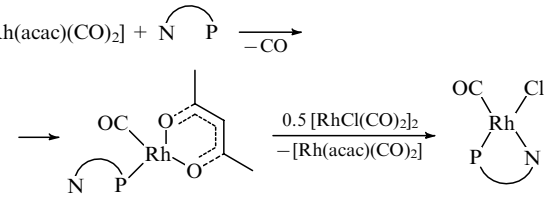
Acyclic aryl phosphites **61** are related to compounds **58**.



61a–**h**

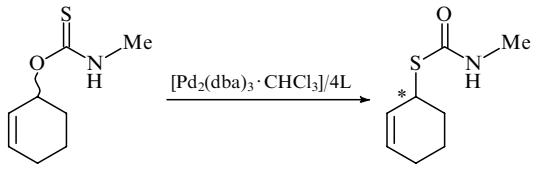


They were used to synthesise chelate complexes [RhCl(CO)(L)]. Similarly to the case of compound **58c**, complexes *trans*-$[RhCl(CO)(L)_2]$ are formed as side reaction products.[110] It is possible to overcome this difficulty and obtain individual metal-containing chelates using an original exchange reaction, which is considered below taking ligand **61b** as an example.



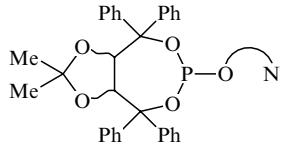
Unfortunately, aryl phosphites **61** are inefficient in Pd-catalysed allylic substitution of substrates **43** [reaction (8)] and **59** [reaction (10)] by dimethyl malonate,[110,111] in sulfonylation of substrate **59** under the action of $NaSO_2$(*p*-Tol) [reaction (11)] and in Rh-catalysed hydrosilylation of acetophenone [reaction (5)].[110] The enantiomeric excess in these reactions was at most 28%.

A quinine-based aryl phosphite **61h** was used in Pd-catalysed enantioselective rearrangement of allyl thiocarbamate, which proceeds at a 100% conversion and an *ee* of 47%.[112]

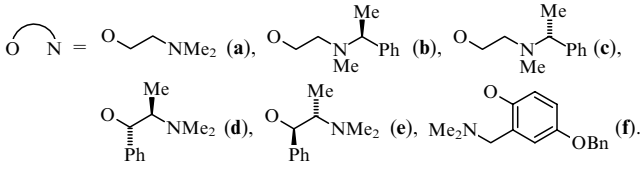


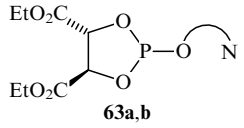
Noteworthy is that ligand **61g** is inefficient in this reaction (*ee* 2%). This is likely due to the large cone angle in structure **61h** ($\Theta = 190^\circ$) and to the presence of additional quinoline donor N atom.

Cu-Catalysed addition of Et_2Zn to cyclic enone **9a** [reaction (4)] in the presence of TADDOL-based phosphites **62** and phosphites **63** based on tartaric acid was also studied. The optical yields were rather low (*ee*s less than 38% for compounds **62a**–**e**[65] and less than 30% for compounds **63a**,**b**). In the latter case, the configuration of the product is controlled by the (*R*,*R*)-diethyl tartrate fragment.[77]

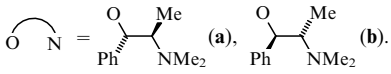


62a–**f** [(*S*) and/or (*R*)]



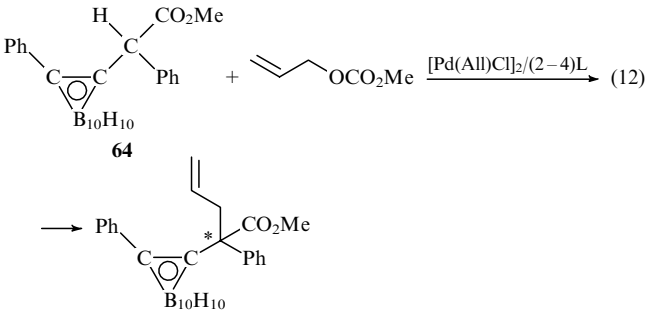


63a,**b**



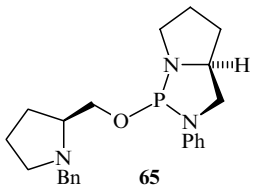
Low optical yield (20%) was also obtained in the methoxycarbonylation of $[Cr(o\text{-}Cl_2C_6H_4)(CO)_3]$ in the presence of complex $[PdCl_2(\mathbf{62f})]$.[113]

Nevertheless, the use of some aminophosphites permitted enhancement of the enantioselectivity. In particular, the first direct Pd-catalysed asymmetric synthesis of carboranes was reported[114] and a number of ligands were studied. The highest optical yield was 48% [reaction (12)].



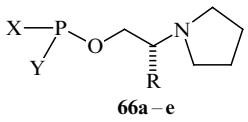
64

^{31}P NMR spectroscopy, IR spectroscopy and mass spectrometry studies of the catalytic system $[Pd(All)Cl]_2$/**65** revealed that phosphoramidite **65** behaves as a P-monodentate ligand, namely, a large amount of complex $[Pd(All)(L)_2]^+Cl^-$ is formed even at an L : Pd = 1 mole ratio (see Ref. 114).

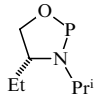


65

Palladium-catalysed allylic substitution reactions involving dimethyl malonate in the presence of phosphite derivatives of (2*R*)-2-pyrrolidin-1-ylbutan-1-ol (**66a**–**e**) were studied.[111]

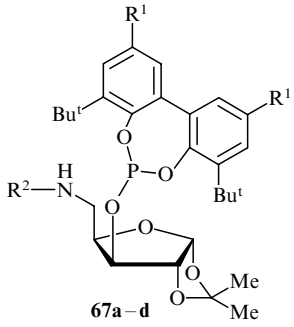


66a–**e**

Compound **66**	X—P / Y	R	Compound **66**	X—P / Y	R
a		Et	**d**		Et
b	$(Pr^iO)_2P$	Et			
c		Et	**e**	$(Pr^iO)_2P$	Pr^i

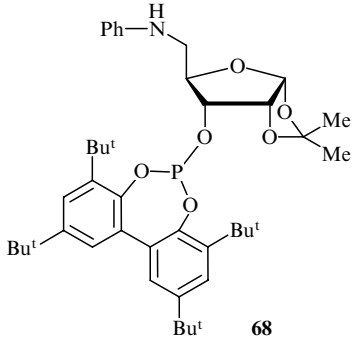
In the case of substrate **43** [reaction (8)] the optical yield was at most 14%, being 61% for allyl acetate **39a** [reaction (7)] {with $[Pd(All)Cl]_2$ as precatalyst, the most efficient ligand was **66b**}.

Cu-Catalysed conjugate addition of Et_2Zn to cyclohexenone **9a** [reaction (4)] in the presence of aminophosphites **67** and **68** based on D-xylose and D-ribose, respectively, is characterised by similar enantioselectivity (*ee* up to 63%).[115]



67a–**d**

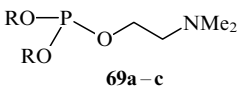
Compound **67**	R^1	R^2
a	Bu^t	Bu^t
b	OMe	Bu^t
c	Bu^t	Pr^i
d	Bu^t	Ph



68

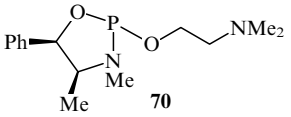
The best stereoselector was found to be ligand **67d**.

A number of chiral aminophosphites, which are used at present only in coordination chemistry of platinum metals, should be pointed out.

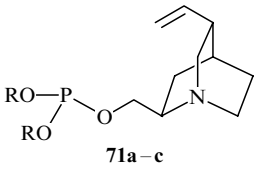


69a–c

R is bornyl (**a**), menthyl (**b**), cholesteryl (**c**).

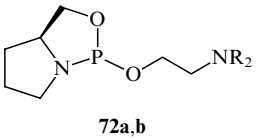


70



71a–c

R–R = $(CH_2)_2$ (**a**);
R = Pr^i (**b**), bornyl (**c**).



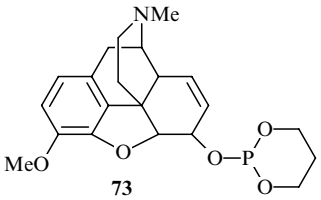
72a,b

NR_2 = NMe_2 (**a**),  (**b**).

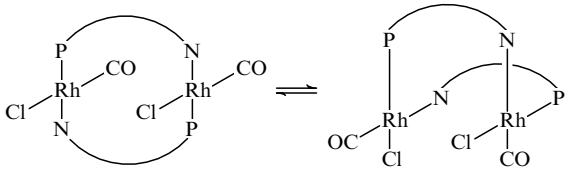
For instance, reactions of compounds **69a–c** with $[PdCl_2(cod)]$ afforded mononuclear chelate complexes $[PdCl_2(L)_2]$, whch were studied by multinuclear NMR spectroscopy, IR spectroscopy, sedimentation analysis and X-ray analysis (for ligand **69a**).[116,117] Aminophosphoramidite **70** also forms an analogous metal-containing chelate in the reaction with $[PdCl_2(cod)]$, whereas the reaction with $[PtCl_2(cod)]$ results in an exclusive product, a compound with P-monodentate bonding of the *cis*-$[PtCl_2(L)_2]$ ligand (according to ^{31}P, ^{13}C and ^{195}Pt NMR spectroscopy and IR spectroscopy).[118]

Similarly to compounds **66a–e** (see above), aminophosphites **71a–c** act as typical chelate-forming agents towards $[RhCl(CO)_2]_2$.[111,119] Ligands **71b,c** behave analogously in the reaction with $[PdCl_2(cod)]$. However, the reaction with phosphite **71a** results not only in chelate $[PdCl_2(L)]$ but also in products of composition $[PdCl_2(L)_2]$, which may be due to the insufficient strength of the metallacycle in the presence of a *spiro*-fragment in the chelate complex.[119]

The reaction of compound **72a** with $[RhCl(CO)_2]_2$ results in a metal-containing chelate [RhCl(CO)L], while ligand **72b** containing a piperidine nitrogen centre also forms a large amount of dimer $[RhCl(CO)L]_2$,[120,121] which has a 'head-to-tail' structure and a *trans*-orientation of the phosphorus and nitrogen atoms at the Rh atom.[121] A codeine-based aminophosphite **73** also forms a structurally similar dimer; in this case, the *trans*-dimer is in equilibrium with *cis*-$[RhCl(CO)(L)]_2$.[122]



73

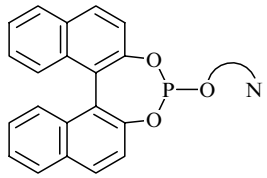


The equilibrium position is governed by the solvent, *viz*., in DMF the complex exists as a *trans*-isomer while a nearly equimolar mixture of the *cis*- and *trans*-isomers is observed in DMSO.

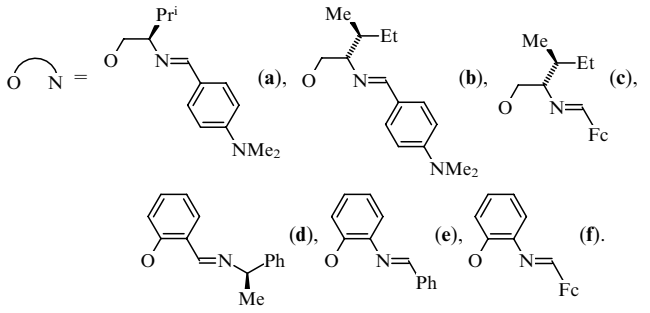
Thus, the coordination behaviour of ligands containing peripheral amino groups is ambiguous. *A priori*, they seem to be typical chelate-forming compounds; however, P-monodentate bonding is often observed. The choice of a particular type of bonding is controlled by the nature of the ligand, the starting metal complex and the solvent. Chelation-preventing factors first of all include the involvement of donor atoms in the five- and six-membered rings (see also Ref. 123) and the presence of bulky substituents at the nitrogen atom. Undoubtedly, these features should be taken into account when predicting and analysing the use of aminophosphites in catalysis. The enantioselectivities obtained to date cannot meet the requirements imposed by modern asymmetric catalysis. Therefore, further investigations and search for new, more efficient ligands are required.

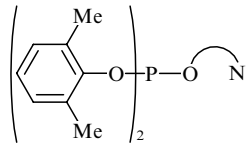
4. Phosphite derivatives of Schiff bases

This is the 'youngest' group of P,N-bidentate derivatives of phosphorous acid, which has been little studied. First of all, aryl phosphite ligands **74** and **75** should be pointed out.

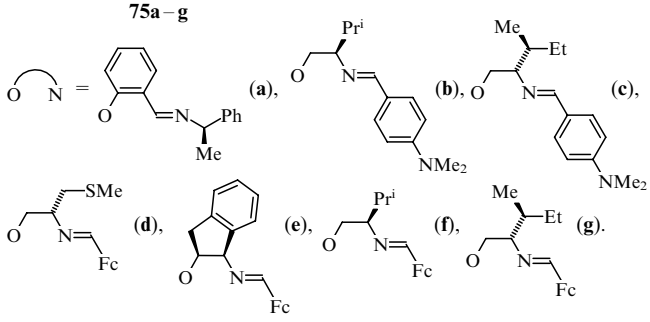


74a–f [(S_{ax}) and/or (R_{ax})]

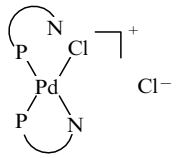




75a–g



Ligands **74a–f** act as typical chelate-forming compounds towards $[RhCl(CO)_2]_2$ and the corresponding reactions result in complexes [RhCl(CO)L].[88] At the same time, particular reaction routes in complexation with Pd(II) are governed by the nature of the starting organometallic compound. For instance, the use of $[PdCl_2(MeCN)_2]$ or $[Pd(All)Cl]_2$ permits high yields of the corresponding metal-containing chelates, *e.g*., $[Pd(All)(L)]^+X^-$ [L = (R_{ax})-**74a**, (R_{ax})-**74c**, (S_{ax})-**74e**; X = Cl, BF_4]. On the contrary, the reaction with $[PdCl_2(cod)]$ proceeds non-selectively [this was shown taking ligands (R_{ax})-**74a** and (R_{ax})-**74f** as examples], resulting in chelates $[PdCl_2(L)]$ and large amounts of side products:



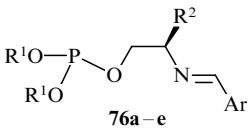
These results must be taken into account when choosing a starting metal complex for Pd-catalysed reactions involving aryl phosphites **74a**–**f**.

Ligands **75a**–**g** containing no cyclic phosphite fragments react with $[RhCl(CO)_2]_2$, $[PdCl_2(cod)]$ or $[Pd(All)Cl]_2$ to give exclusively mononuclear metal-containing chelates, which was also proved by X-ray analysis.[110]

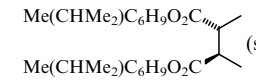
Allylic alkylation of substrate **59** by dimethyl malonate {reaction (10) with $[Pd(All)Cl]_2$ as precatalyst} in the presence of compounds **74a**–**f** proceeds with an optical yield of up to 81% [the most efficient ligand is (R_{ax})-**74c**].[88] However, the presence of the BINOL fragment is not necessary for stereoinduction. Indeed, an *ee* of 82% was also achieved using acyclic aryl phosphite **75g**.[110] Moreover, additional axial chirality even decreases the enantioselectivity in Rh-catalysed hydrosilylation of acetophenone [reaction (5)], namely, ligand **75g** provides an *ee* up to 50%, whereas the epimers (S_{ax})-**74c** and (R_{ax})-**74c** can show at most 20%. Pd-Catalysed reaction of substrate **59** with $NaSO_2(p\text{-Tol})$ [reaction (11)] in the presence of ligand **75g** is also characterised by high enantioselectivity (*ee* 80%).[110]

It should be noted that, according to Ito,[124] substrate **59** is 'uncontrollable' and therefore the optical yields achieved (80%–82%) are in fact very high, thus indicating a great stereodiscriminating potential of phosphites containing Schiff bases. Unfortunately, attempts at realising this potential in other Pd-catalysed allylations have failed as yet. Namely, the enantioselectivity of asymmetric synthesis involving a carborane derivative **64** [reaction (12)] and ligands **74a**,**b** and **75b**,**c**,**f**,**g** was at most 32%.[125]

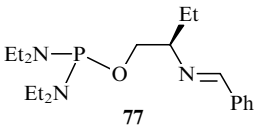
Systems with another structure at the phosphorus centre are also available.



76a–**e**

Compound **76**	R^1	R^2	Ar
a	Pr^i	Et	Ph
b	Pr^i	Pr^i	4-$Me_2NC_6H_4$
c	bornyl	Et	Ph
d	cholesteryl	Pr^i	Ph
e	 (see [a])	Pr^i	4-$Me_2NC_6H_4$

[a] Here, R^1-R^1; menthyl is $Me(CHMe_2)C_6H_9$.



77

Similarly to phosphites **75a**–**g**, compounds **76a**–**e** and **77** behave in reactions with $[RhCl(CO)_2]_2$ and $[PdCl_2(cod)]$ as good chelate-forming compounds[89,126,127] {complexes [RhCl(CO)L] with L = **76a**,**c** were studied by X-ray analysis[126]}. The exception is ligand **76d** containing bulky cholesteryl fragments, which forms a side product $[PdCl_2(L)_2]$ in the reaction with $[PdCl_2(cod)]$.[89] Alkylation of substrate **43** by dimethyl malonate [reaction (8)] in the presence of compounds **76a**–**e** and $[Pd(All)Cl]_2$ is characterised by an *ee* of up to 76%, the best ligand being **76e**.[89,126]

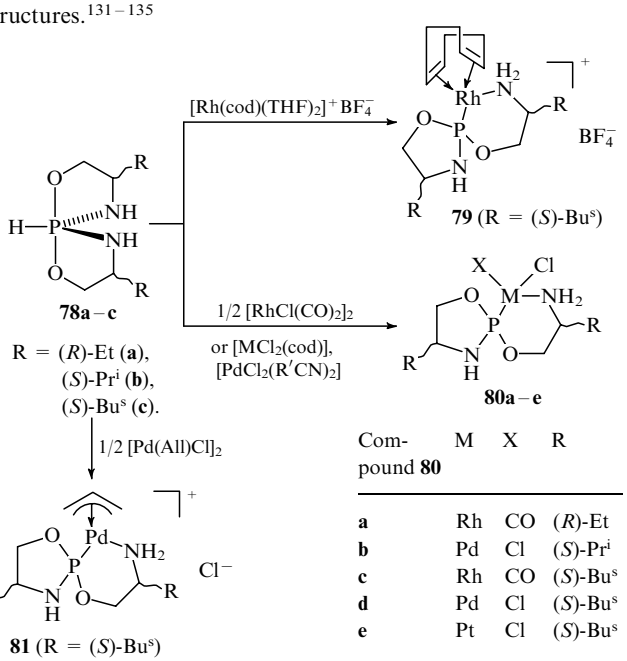
By and large, a small (at the moment) group of phosphites containing Schiff bases appears to be more efficient in asymmetric catalysis than the best aminophosphites known so far. There are grounds for believing that in the future these new compounds will successfully compete with ligands containing oxazoline structural fragments.

It should be emphasised that all P,N-bidentate phosphites possess enhanced π-acceptor abilities (even as compared to the most electron-accepting phosphines containing an amino group in the substituent).[5] This affects the spectral characteristics of chlorocarbonyl rhodium complexes with these ligands. For instance, the spin–spin coupling constants ^1J(P,Rh) of such complexes are, on average, increased by 80–100 Hz and the ν(CO) frequencies are nearly 20–25 cm^{-1} higher. Direct correlations between the optical yields of hydrosilylation of ketones, allylation, hydroboronation–oxidation and the π-acceptor ability of the P,N-bidentate ligand should be pointed out (see Refs 5 and 128 and references cited therein). In some cases one should also take into account the σ-donor ability of nitrogen-containing fragments. In this connection a convenient spectral characteristic was suggested, which permits fast evaluation of the electronic effect of any P,N-bidentate ligand. This is the parameter ν_{Rh}, or the ν(CO) vibrational frequency of [RhCl(CO)L] complexes.[128] The steric characteristics are determined by another parameter, the cone angle at the phosphorus atom, which can be obtained with ease from the semiemirical AM1 calculations.[129]

5. Hydrophosphorane ligands

Hydrophosphoranes (HPs) form a rare and original group of phosphorus-containing ligands. At first glance, their structures contain no potential donor centres because phosphorus atoms have no lone electron pairs while the lone electron pairs of nitrogen or oxygen atoms must be involved in $p_\pi-d_\pi$-conjugation with d orbitals of the phosphorus atom. However, it is these compounds that show a variety of types of bonding to metal ions, namely, the P-, N-, P,N-, P,O- and N,N-coordination. Coordination chemistry of HPs has been analysed in detail in a separate review;[130] however, since then new information on complexation and catalysis involving chiral HPs has been reported. This first of all concerns hydrospirophosphoranes (HSPs) **78** and tricyclic hydrophosphoranes (TCHPs).

Hydrospirophosphoranes are typical chelate-forming compounds, which form metal-containing derivatives of their 'open' structures.[131–135]

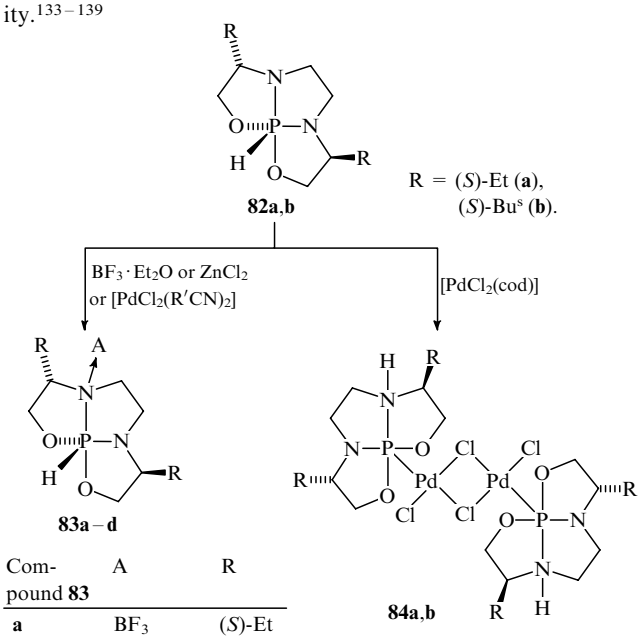


Compound **80**	M	X	R
a	Rh	CO	(*R*)-Et
b	Pd	Cl	(*S*)-Pr^i
c	Rh	CO	(*S*)-Bu^s
d	Pd	Cl	(*S*)-Bu^s
e	Pt	Cl	(*S*)-Bu^s

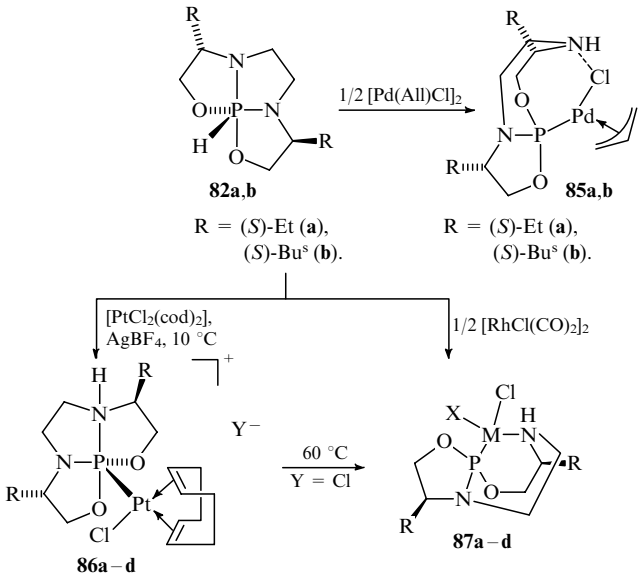
Complexes **79**–**81** are stable compounds. They were thoroughly studied by various methods of physicochemical analysis.[131,133–135] Unfortunately, they usually exist as equimolar mixtures of epimers with respect to the P*-stereocentre, which significantly reduces the scope of their application in asymmetric catalysis.

TCHPs (**82**) provide a source of richer coordination chemistry owing to a larger number of possible complexation routes. However, usually one route (sometimes, two routes) can be realised for a particular ligand; therefore, the corresponding

complexes retain, as a rule, their stereochemical individuality.[133–139]



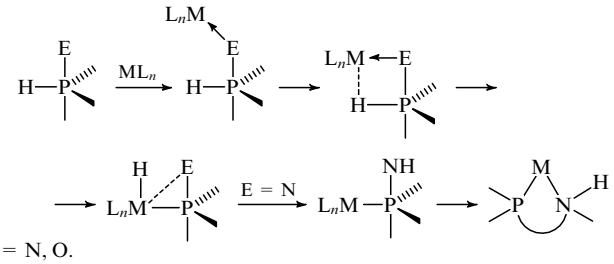
Compound **83**	A	R
a	BF_3	(*S*)-Et
b	$ZnCl_2$	(*S*)-Bu^s
c	PdCl(μ-Cl)	(*S*)-Et
d	PdCl(μ-Cl)	(*S*)-Bu^s



Compound **86**	Y	R
a	Cl	(*S*)-Et
b	BF_4	(*S*)-Et
c	Cl	(*S*)-Bu^s
d	BF_4	(*S*)-Bu^s

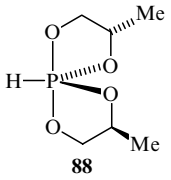
Compound **87**	M	X	R
a	Rh	CO	(*S*)-Et
b	Pt	Cl	(*S*)-Et
c	Rh	CO	(*S*)-Bu^s
d	Pt	Cl	(*S*)-Bu^s

Of considerable interest is to study the complexation mechanism of HPs. Here, two mechanisms are possible, one with and one without involvement of the P(III) tautomers of HPs.[130] In the former case, the role of the transition metal is in essence to shift the tautomeric equilibrium P(V) ⇄ P(III) by bonding to the structure with the tricoordinate phosphorus atom. The latter case is in fact a kind of metal complex catalysis of the opening of the hydrophosphorane structure. The first stage involves complexation at the apical donor atom of HPs (for BF_3 and $ZnCl_2$ this stage is simultaneously the last one, resulting in compounds **83a**,**b**). An important argument in favour of this stage is provided by a direct correlation between the Lewis basicity of HPs and their coordination activity.[133] This stage can be followed by oxidative addition – reductive elimination proceeding *via* agostic and metal hydride intermediates.[133, 135]



From this standpoint compounds **86a**,**c** can be treated as relatively stable intermediates that can be isolated at elevated temperature.[137, 139] Replacement of chloride counterion by non-nucleophilic tetrafluoroborate anion permits the synthesis of rather stable complexes **86b**,**d**, which were studied by various methods including X-ray analysis.[134, 139]

The choice between both complexation mechanisms of HPs and the structures of corresponding products depend first of all on the nature of the phosphorane and the Lewis acid. For instance, coordination of tetraoxohydrospirophosphorane **88** to rhodium(I) and palladium(II) involves a P(III) tautomer.[133]



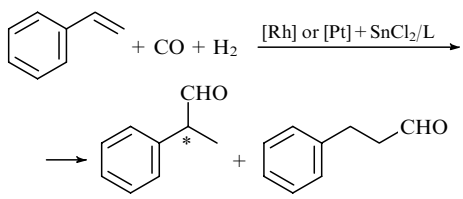
Compared to HSPs, tricyclic hydrophosphoranes are much more prone to retention of the phosphorane frame. At the same time, rhodium(I) and platinum(II) assist the opening of TCHPs more actively than palladium(II).

Hydrophosphoranes **78c** and **82a**,**b** were studied taking Pd-catalysed alkylation of substrate **43** by dimethyl malonate [reaction (8)] as an example.[135] Ligands **78c** and **82a** were found to be inefficient stereoselectors (the enantiomeric excess was 34% and 27%, respectively). A much higher optical yield (up to 74%) was achieved using compound **82b**. At present, this is the best result in asymmetric catalysis involving phosphorane ligands. Noteworthy is that the use of a catalytic system based on $[Pd(All)Cl]_2$ and ligands **82a**,**b** results in the formation of complexes **85a**,**b** with P-monodentate bonding of the 'open' forms of TCHPs. In contrast to this, complexation of $[PdCl_2(R'CN)_2]$ (R′ = Me, Ph) with ligand **82b** affords a mixture of compounds **83d** and **84b** with retention of the phosphorane structure of the ligand. Nevertheless, this system also provides a rather high enantioselectivity (*ee* up to 60%). We believe that these facts point to the great potential of tricyclic hydrophosphoranes as a specific group of chiral phosphorus-containing ligands.

IV. P,P-Bidentate phosphites

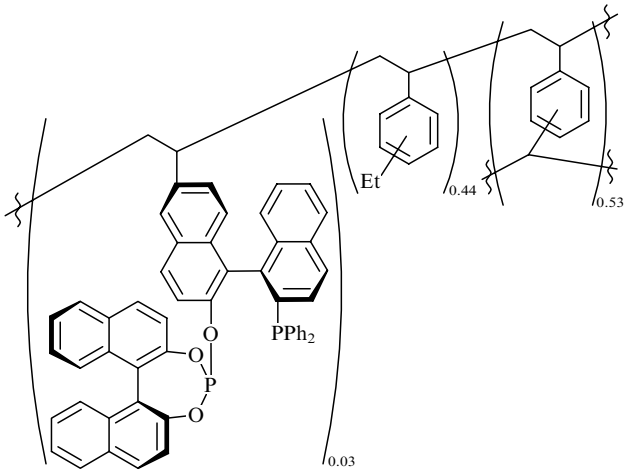
1. Phosphine-phosphites and phosphine-phosphoramidites

We begin this Section with consideration of these systems because the presence of two donor centres of different nature in such molecules makes them similar to the P,N-bidentate ligands considered above. Interest in these compounds is also due to the fact that they combine the two most important classes of chiral phosphorus-containing ligands, *viz*., phosphines and phosphites. First of all, studies aimed at unveiling the potential of the highly efficient ligand BINAPHOS (**2**) are noteworthy. Here, the research avenues are as follows: preparation of polymer-immobilised catalysts, the use of particularly valuable or 'hard-to-access' substrates and operation in supercritical CO_2.



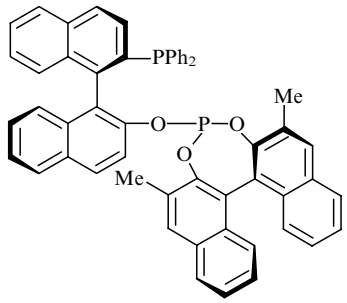
(13)

For instance, polymer-immobilised BINAPHOS provides an *ee* of 89% in Rh-catalysed hydroformylation of styrene [reaction (13)] at high conversion and regioselectivity (the mole fractions of different monomer units are shown in the Scheme).[140, 141]



This polymeric ligand was also successfully used in hydroformylation of (*Z*)-but-2-ene, 3,3,3-trifluoropropene and vinyl acetate with optical yields of 89%–93% including solvent-free processes in the synthesis gas.[142]

BINAPHOS (**2**) has found new fields of application, namely, Rh-catalysed hydroformylation of (i) conjugated dienes, which provides a synthetic route to hard-to-access β,γ-unsaturated aldehydes (*ee* up to 97%),[143] and (ii) allylic alcohols followed by oxidation of intermediate lactols to lactones (*ee* up to 87%).[144] An *ortho*-substituted derivative of BINAPHOS was found to be appropriate for treating heterocyclic olefins (optimisaton of hydroformylation conditions for these substrates faces severe problems).



(*R*,*S*)-3,3′-Me-BINAPHOS

The use of this compound in the reaction shown below provided the enantiomeric excesses in the range 64% to 76%.[145]

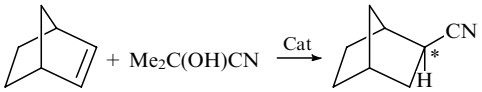


X = O, NBoc, NAc.

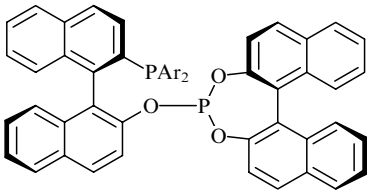
New studies on the mechanism of catalytic hydroformylation involving BINAPHOS,[146] including quantum-chemical calculations[147] have been reported.

Pd-Catalysed copolymerisation of alkenes with CO has been improved;[148] the corresponding metal complex intermediates were studied by spectral methods.[149]

Compounds [M(BINAPHOS)$_2$] [M = Ni(0), Pd(0)] were synthesised and studied by ^{31}P NMR spectroscopy and FAB mass spectrometry.[150] Hydrocyanation of norbornene catalysed by a palladium complex results in an *exo*-nitrile with the highest enantioselectivity achieved so far (48%).



Recently, supercritical CO_2 has became popular as an ecologically safe and non-toxic medium for performing catalytic reactions. However, it has severe limitations due to the poor solubility of many phosphorus-containing ligands in CO_2. To enhance the solubility of BINAPHOS (**2**), a fluorinated derivative, (*R*,*S*)-3-H^{2}F^6-BINAPHOS, was synthesised.[151, 152]

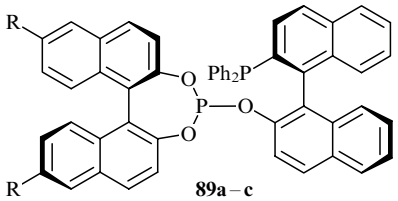


(*R*,*S*)-3-H^{2}F^6-BINAPHOS

Ar = $C_6H_4(CH_2)_2(CF_2)_6$-*m*.

A study on this ligand involved in Rh-catalysed hydroformylation in supercritical CO_2 showed that it demonstrates a high enantioselectivity (*ee* 88%–94%), conversion (>98%) and regioselectivity (branched : linear product ratio from 93 : 7 to 96 : 4) in reactions with different substrates, thus being highly competitive with (*R*,*S*)-BINAPHOS (**2**). Using multinuclear NMR spectroscopy, it was shown that supercritical CO_2 has no effect on the formation of the hydroformylation catalyst, [RhH(CO)$_2$L], and that the catalytic reaction in this medium proceeds by the same mechanism as reactions in organic solvents. (*R*,*S*)-3-H^{2}F^6-BINAPHOS was also found to be highly efficient in hydrogenation processes proceeding in supercritical CO_2 [an *ee* of 97% at 99% conversion was achieved for substrates **4a**,**b** in reaction (2)].

Fluorinated derivatives of BINAPHOS **89a**–**c** were obtained to be used in hydroformylation of styrene [reaction (13)] in supercritical CO_2 or in fluorine-containing solvents.

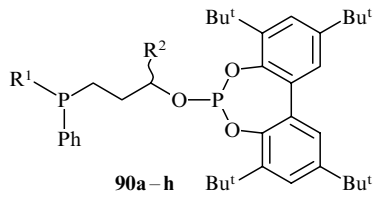


89a–**c**

R = n-$C_4F_9(CH_2)_3$ (**a**), n-$C_6F_{13}(CH_2)_3$ (**b**), n-$C_8F_{17}(CH_2)_3$ (**c**).

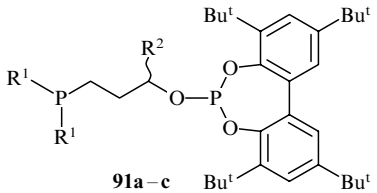
Ligand (*S*,*R*)-**89b** provided an *ee* up to 74% at 90 : 10 regioselectivity (branched : linear product) in supercritical CO_2.[153] Unfortunately, reactions in perfluorinated solvents were characterised by low (at most 11%) conversion of olefins at enantioselectivities of up to 94%.

Another interesting group of phosphine-phosphites comprises a series of ligands **90**–**93** containing both C*- and P*-stereocentres. These compounds were synthesised by van Leeuwen *et al.*[154–157]



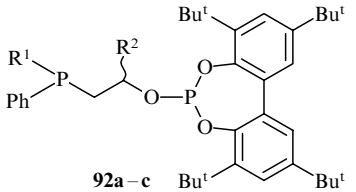
90a–h

Compound **90**	R^1	R^2	Compound **90**	R^1	R^2
(S_P,S_C)-**a**	1-naphthyl	Ph	(R_P,R_C)-**e**	Bu^t	Ph
(S_P,R_C)-**b**	1-naphthyl	Ph	(R_P,S_C)-**f**	Bu^t	Ph
(S_P,S_C)-**c**	2-anisyl	Ph	(R_P,rac_C)-**g**	Bu^t	Ph
(S_P,R_C)-**d**	2-anisyl	Ph	(R_P,R_C)-**h**	Bu^t	Me



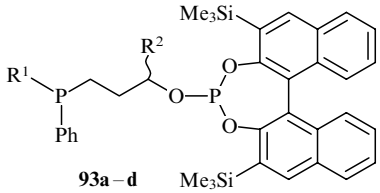
91a–c

Compound **91**	R^1	R^2
(S_C)-**a**	Bu^t	Ph
(S_C)-**b**	Ph	Ph
(S_C)-**c**	Ph	Me



92a–c

Compound **92**	R^1	R^2
(R_P,S_C)-**a**	Bu^t	Ph
(R_P,R_C)-**b**	Bu^t	Ph
(S_C)-**c**	Ph	Me



93a–d

Compound **93**	R^1	R^2
(S_P,S_C,R_{ax})-**a**	1-naphthyl	Ph
(S_P,S_C,S_{ax})-**b**	1-naphthyl	Ph
(R_{ax})-**c**	Ph	H
(S_{ax})-**d**	Ph	H

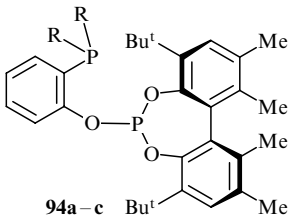
By varying positions and configurations of stereogenic centres it was established how these factors affect the enantioselectivity in catalytic processes.[154–157] Intermediates in the Rh-catalysed hydroformylation of styrene [reaction (13)] were also comprehensively studied by IR spectroscopy and ^{1}H and ^{31}P NMR spectroscopy. It was shown[154] that in trigonal-bipyramidal complexes [RhH(CO)$_2$L] the σ-donor phosphine centre occupies an apical position while the π-acceptor phosphite centre is in an equatorial position. The latter feature as well as manifestation of the so-called co-operative effect (the presence of chiral centres on the phosphine phosphorus atom and on atoms of the bridging group connecting two donor centres) are of great importance for achieving high enantioselectivity. Ligand **90a** used in reaction (13) provided an *ee* of up to 63%.

Cu-Catalysed addition of Et$_2$Zn and Et$_3$Al to cyclic enone **9a** [reaction (4)] in the presence of compounds **90**–**93** was also studied.[155] All reactions showed excellent conversions and regioselectivities at moderate optical yields (22% to 62%).

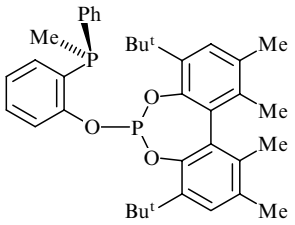
In addition, ligands **90**–**93** were studied in the alkylation of substrate **43** by dimethyl malonate [reaction (8)].[156] The best stereoselector, compound **90b**, provided an *ee* of 83%. The structure of one catalytically active complex, [Pd(All)(**92a**)], was refined by X-ray analysis. It was found that the Pd–C$_{All}$ bond in the *trans*-position relative to the phosphite phosphorus atom is 0.05 Å shorter than the bond in the *trans*-position relative to the phosphine phosphorus atom because of the greater π-acceptor ability of the phosphite centre. In the catalytic cycle, the nucleophile attacks the carbon atom of the allylic ligand in the *trans*-position relative to the phosphine P atom. Thus, a general trend is as follows: intermediates of allylic substitution containing heterobidentate ligands are attacked by nucleophiles at the *trans*-position with respect to the 'softer' (according to Pearson's HSAB principle) donor atom, namely, the phosphine centre in phosphine-phosphites or the phosphorus centre in P,N-bidentate compounds. It was shown that the enantioselectivity provided by compounds **90**–**93** depends on the structural parameters of the phosphite fragment of the ligand including the cone angle.[158]

Phosphine-phosphites **90**–**92** were also used in the asymmetric hydrogenation of substrates **4b**,**d** [reaction (2)] and gave an *ee* of up to 99% at nearly 100% conversion.[157] Similarly to allylic alkylation, the enantioselectivity is controlled by the structural parameters of the phosphite centre and of the C*-stereocentre present in the linker. Catalytically active complexes [Rh(cod)L]$^+$BF$_4^-$ were studied by multinuclear NMR spectroscopy. A double set of signals with similar values of the ^1J(P,Rh) spin–spin coupling constant was explained by either atropoisomerism of the phosphite centre or conformational isomerism of the chelate metallacycle. The joint action of both factors cannot also be ruled out. Note that this presents no obstacles to hydrogenation with excellent optical yields.

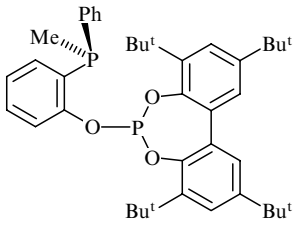
A series of phosphine-phosphite ligands **94** containing chiral phosphite and(or) phosphine fragments was synthesised.[159,160]



94a–c R = Ph (**a**), Me (**b**), Pr^i (**c**).



(S_{ax})-**94e**, (R_{ax})-**94f**

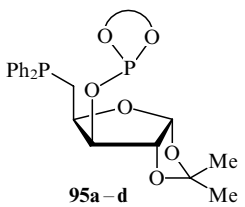


94d

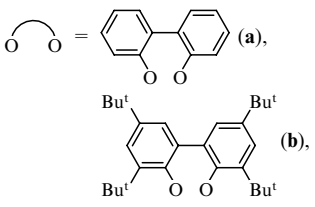
The electronic properties of the donor centres were assessed by analysing the ^1J(P,Se) spin–spin coupling constants of corresponding diselenides. The weaker σ-donor ability of the phosphite moiety compared to the phosphine fragment was confirmed. This is also indicated by the magnitude of the ^1J(P,Rh) spin–spin coupling constant, which for the phosphine centre of complexes [RhCl(CO)L] is 120 Hz lower than for the phosphite centre. X-Ray diffraction studies revealed a *trans*-disposition of the phosphine centre and the carbonyl ligand.

Cationic complexes [Rh(cod)L]$^+$BF$_4^-$ were used in the asymmetric hydrogenation of esters **4a**,**d** [reaction (2)]. It was found that high enantioselectivity requires the presence of an axially chiral phosphite moiety and bulky substituents in the phosphine fragment. For instance, compounds **94a** and **94f** provide an *ee* of 99% (*cf.* at most 49% for ligand **94d**).

A group of phosphine-phosphite derivatives of D-xylose **95a–d** is noteworthy.[161]



95a–d

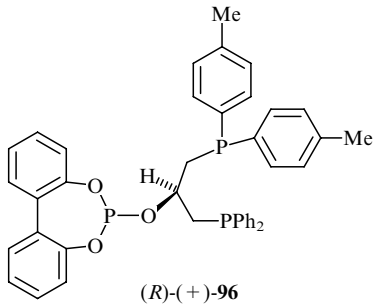


(R_{ax})-BNaph(O)$_2$ (**c**),
(S_{ax})-BNaph(O)$_2$ (**d**).

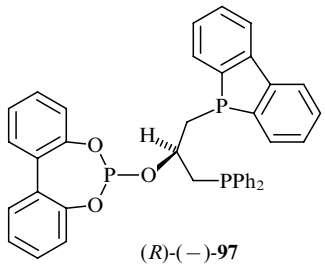
Using these compounds, a Rh-catalysed hydroformylation of styrene [reaction (13)] resulted in a product with a regioselectivity of up to 95 : 5 (branched : linear product) at moderate optical yields (*ee* up to 49%). The best stereoselector was ligand **95b** containing bulky *tert*-butyl substituents. The efficiency of phosphine-phosphites **95** in asymmetric addition of Et_2Zn to enone **9a** [reaction (4)] under the action of copper salts was even lower (the enantioselectivity was at most 19%).[162]

In contrast to this, compounds **95** were successfully used in the Rh-catalysed hydrogenation of substrates **4b**,**d** [reaction (2)] and ligand **95b** provided an *ee* of greater than 99%.[163] Similarly to phosphine-phosphites **90**–**92** (and for the same reasons), spectral analysis of rhodium complexes of compounds **95**, $[Rh(cod)L]^+BF_4^-$, revealed a double set of signals. The stereoinduction was also high.

An original approach is to increase the denticity of phosphine-phosphites by, *e.g.*, incorporating an additional phosphine centre.[164] In this case, Rh-catalysed hydrogenation of esters **4a**,**b** in the presence of ligands **96** and **97** resulted in racemic products. However, one must keep in mind that this is the first step in studies of tridentate phosphine-phosphite ligands.

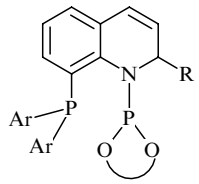


(*R*)-(+)-**96**

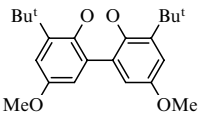


(*R*)-(−)-**97**

Yet another promising research avenue is the synthesis of phosphine-phosphoramidites. In particular, a series of quinoline derivatives **98a**–**d** was proposed.[165]

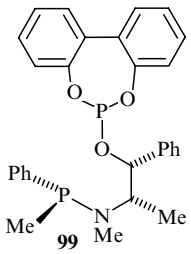


98a–**d** [(R_C) and/or (S_C)]

Compound **98**	Ar	R	
a	Ph	Bu^n	(R_{ax})-BNaph(O)$_2$
b	Ph	Bu^t	(R_{ax})-BNaph(O)$_2$
c	Ph	Bu^n	
d	*m*-$F(CF_2)_6(CH_2)_2C_6H_4$	Bu^n	(R_{ax})-BNaph(O)$_2$

Mixtures of diastereomers were resolved by column chromatography. The first experiments revealed the efficiency of these systems in asymmetric catalysis. Ligand (R_{ax},S_C)-**98a** provided an *ee* of up to 74% at 96 : 4 (branched : linear product) regioselectivity and 79% conversion in hydroformylation of styrene [reaction (13)]. The use of its epimer, (R_{ax},R_C)-**98**, leads to a dramatic decrease in the enantioselectivity down to 5%. In contrast to this, epimer (R_{ax},R_C)-**98a** appeared to be more efficient in hydrogenation of unsaturated acid esters **4a**,**d** [reaction (2)] and provided an *ee* of 98%–99%.

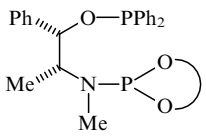
The enantioselectivity of hydroformylation in the presence of aminophosphonite-phosphite **99** was somewhat lower (*ee* 58%).[166]



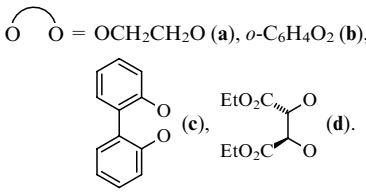
99

NMR and IR spectroscopy studies of catalytically active complexes $[RhH(CO)_2L]$ revealed that the amidophosphonite centre occupies an apical position while the phosphite centre is in an equatorial position. Summing up the results reported in Refs 154, 161 and 166, note that in complexes $[RhH(CO)_2L]$ with dissymmetric P,P-bidentate compounds the equatorial position is occupied by the phosphorus centre, which possesses more pronounced π-acceptor properties. The exception is BINAPHOS (**2**); however, this is due to steric reasons.[7]

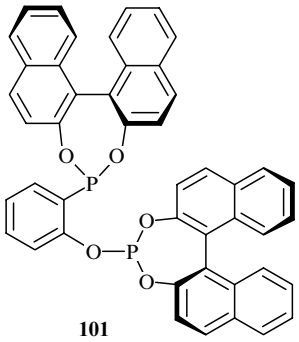
Only one series of aminophosphonite-phosphite ligands **100a**–**d** based on the ephedrine moiety has been reported to date.[167]



100a–**d**



However, the enantioselectivity of Rh-catalysed hydroformylation of styrene [reaction (13)] in the presence of compounds **100a**–**d** was at most 20%. Mention may also be made of phosphonite-phosphite **101** providing an *ee* of up to 80% in Rh-catalysed hydrogenation of ester **4a** [reaction (2)].[168]

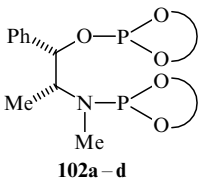


101

2. Phosphite-phosphoramidite and diphosphoramidites

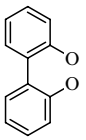
Moving to phosphite-phosphoramidites makes it possible to have two different phosphorus centres in the ligand structure in the

absence of a fragment containing P–C bonds. This approach was realised taking ligands **102a–d** as examples.[167]

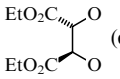


102a–d

O O = OCH_2CH_2O (**a**), *o*-$C_6H_4O_2$ (**b**),



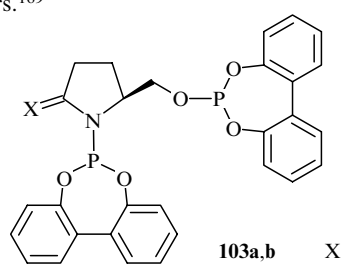
(**c**),



(**d**).

A chelate mononuclear complex $[PtCl_2(L)]$ with phosphite-phosphoramidite **102a** was obtained. However, ligands **102a–d** provided low enantioselectivities in Rh-catalysed hydroformylation of styrene [reaction (13)].

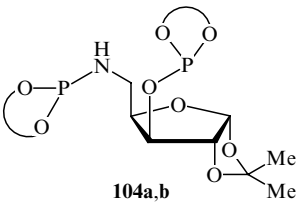
Phosphite derivatives **103** of available (*S*)-prolinol and (*S*)-oxyprolinol appeared to be somewhat better stereoselectors.[169]



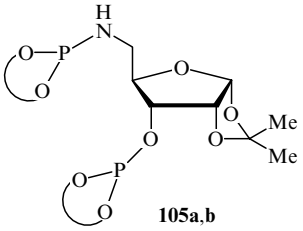
103a,**b** X = 2 H (**a**), O (**b**).

Platinum complexes of these compounds catalyse hydroformylation of styrene [reaction (13)] with an optical yield of up to 44%.

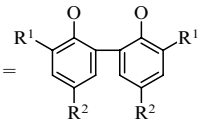
Even higher enantioselectivity (*ee* up to 65%) is provided by rhodium complexes of phosphite-phosphoramidites **104** and **105** based on D-xylose and D-ribose:[170]



104a,**b**

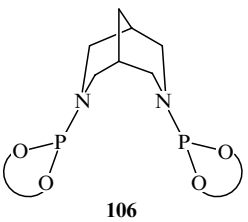


105a,**b**

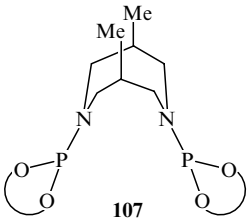
O O =  ; R^1 = Bu^t: R^2 = Bu^t (**a**), OMe (**b**).

Besides, compounds $[Rh(cod)L]^+BF_4^-$ (L = **104** and **104**) were used in asymmetric hydrogenation of substrates **4a**,**b**,**d** [reaction (2)].[171] They provided an *ee* of up to 99% at nearly 100% conversion. Similarly to hydroformylation, the chemical and optical yields depend on the absolute configuration of the C*(3)-stereocentre and on the nature of the *ortho*-substituents in the biphenyl fragment of the ligands.

Symmetrical (C_2) diphosphoramidites **106** and **107** have been reported recently.[172]



106

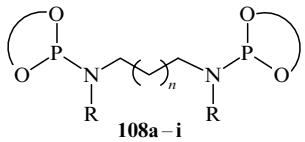


107

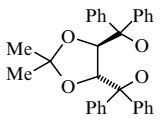
O O = (R_{ax})-BNaph(O)$_2$.

They provided an *ee* of up to 82% in Cu-catalysed addition of Et_2Zn to enones **9a**,**b** [reaction (4)] and up to 90% in Rh-catalysed hydrogenation of esters **4a**,**d** [reaction (2)].

A series of phosphoramidite derivatives of acyclic diamines comprises the following compounds:[173]



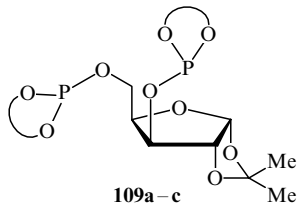
108a–i

Compound **108**	R	*n*	O O
a	Me	0	
b	Me	1	
c	Me	0	(R_{ax})-BNaph(O)$_2$
d	Me	1	
e	Pr^i	1	
f		1	
g		1	
h		0	(S_{ax})-BNaph(O)$_2$
i		1	

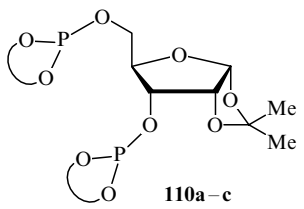
Cu-Catalysed tandem 1,4-addition of Et_2Zn to cyclopentenone **9b** and aldol condensation with benzaldehyde proceed with optical yields of up to 83%. The best ligand is compound **108h**. Conjugate addition of Et_2Zn to enone **9a** [reaction (4)] showed an *ee* of up to 89% with the most efficient diamide ligand **108f** . Ligands **108a**,**b** containing no BINOL moiety are inefficient.

3. Diphosphites based on carbohydrates and their derivatives

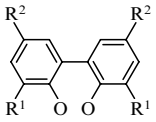
We begin consideration of this type of ligands with diphosphites derived from D-xylofuranose **109** and D-ribofuranose **110**.[174–176]



109a–c

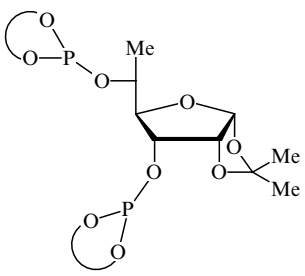


110a–c

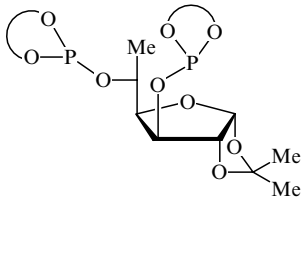
O O =  ; R^1 = R^2 = H (**a**); R^1 = Bu^t: R^2 = OMe (**b**), Bu^t (**c**).

Rh-Catalysed hydrogenation of itaconic acid, hydroformylation of styrene [reaction (13)], Cu-catalysed addition of Et_2Zn to cyclohexenone **9a** [reaction (4)] and Ir-catalysed hydrogenation of imines involving ligands **109** and **110** proceed with optical yields ranging between 50% and 60%. The best results were obtained [177] for allylic substitution of substrate **43** [reaction (8)] for dimethyl malonate (*ee* up to 90%) and benzylamine (*ee* up to 97%); both values were obtained in the presence of diphosphite **109c**). It was established that the stereoinduction is controlled by the configuration of the C*(3)-stereocentre of the furanose ring, while the nucleophile attacks the allylic carbon atom of the intermediate palladium complex, which is in the *trans*-position relative to the phosphite centre at the C(5) atom. Because of this, an increase in the size of substituents at the phosphite centre at the C(5) atom favours enhancement of enantioselectivity.

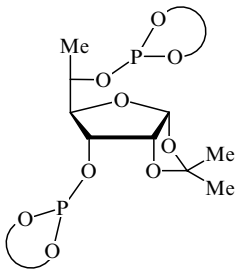
More efficient is a group of phosphite derivatives of 6-deoxy-D-allose, 6-deoxy-D-glucose, 6-deoxy-L-talose and 6-deoxy-L-idose **111**–**114**, which contain an additional C*-stereocentre.[178, 179]



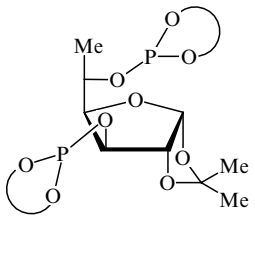
(1*R*,2*R*,3*R*,4*R*,5*R*)-**111a**–**h**



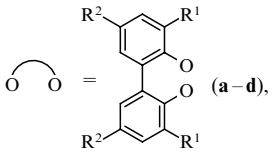
(1*R*,2*R*,3*S*,4*R*,5*R*)-**112a**–**h**



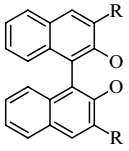
(1*R*,2*R*,3*R*,4*R*,5*S*)-**113a**–**h**



(1*R*,2*R*,3*S*,4*R*,5*S*)-**114a**–**h**



(**a**–**d**),



(**e**–**h**).

Compounds **111**–**114**	R^1	R^2
a	H	H
b	Bu^t	Bu^t
c	Bu^t	OMe
d	$SiMe_3$	H

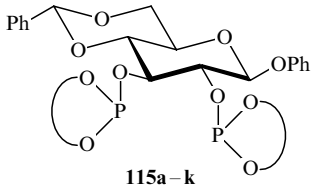
Compounds **111**–**114**	R
(S_{ax})-**e**	H
(R_{ax})-**f**	H
(S_{ax})-**g**	$SiMe_3$
(R_{ax})-**h**	$SiMe_3$

These ligands provided an *ee* of up to 91% in the hydroformylation of styrene [reaction (13)] at amazingly high regioselectivity 99 : 1 (branched : linear products), which is comparable with the efficiency of the BINAPHOS (**2**) ligand. It was shown that the absolute configuration of the product depends on the configuration of the C*(3)-stereocentre while the enantioselectivity is controlled by the co-operative effect of the C*(3)- and C*(5)-stereocentres. NMR and IR spectroscopy studies of intermediates [$RhH(CO)_2L$] revealed that the best stereoselectors are those ligands which occupy two equatorial positions in the coordination sphere of the Rh atom. The dynamic equilibrium between the equatorial and equatorial-axial bonding reduces the enantioselectivity.

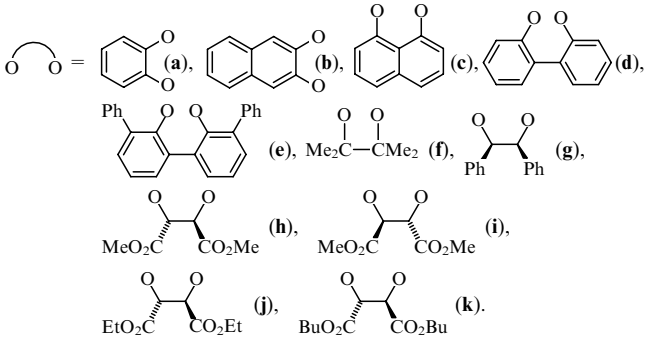
Rh-catalysed hydrogenation of substrates **4a**,**b**,**d** [reaction (2)] in the presence of diphosphite **111d** with bulky trimethylsilyl substituents showed an *ee* of greater than 99% at 100% conversion.[180] Compounds **111**–**113** provide an *ee* of up to 84% in Cu-catalysed addition of Et_2Zn to enone **9a** [reaction (4)].[181] The optical yields in Rh-catalysed hydrosilylation of acetophenone [reaction (5)] involving diphosphites **111**–**114** were lower (*ee* less than 51%).[182] However, trends common to this series of ligands can also be revealed. These are control of the configuration of the product by the stereochemistry of the C*(3) centre and favourable influence of both the co-operative effect of the C*(3) and C*(5) stereocentres and an increase in the size of the *ortho*- and *para*-substituents in the aromatic rings on the enantioselectivity.

The use of ligands **111**–**113** in the Pd-catalysed alkylation of substrate **43** by dimethyl malonate [reaction (8)] should be emphasised. A 100% conversion and an optical yield of 95% were achieved under standard experimental conditions in the presence of diphosphite **112c** and took only 10 min.[183] At present, this is the best result in Pd-catalysed allylic alkylation using P,P-bidentate phosphites.

A series of diphosphite ligands based on phenyl-β-D-glucopyranoside **115a**–**k** and their rhodium and platinum complexes were synthesised.[184] They were studied in hydroformylation of various substrates.

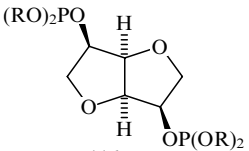


115a–**k**

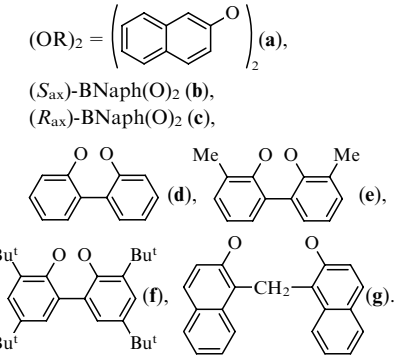


However, the asymmetric induction was low (*ee* 36% with allyl acetate as substrate).

The best stereoselectors in this group of ligands are diphosphite derivatives of dianhydro-D-mannite **116**.[185]



116a–**g**

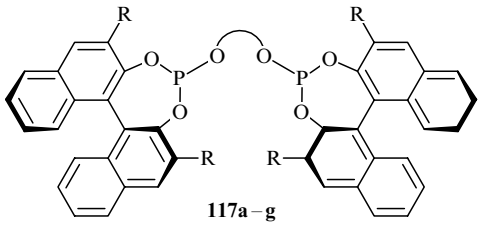


In particular, ligands **116e** and **116c** provide enantiomeric excesses of up to 98% and 96%, respectively, in Rh-catalysed hydrogenation of ester **4a** [reaction (2)]. In both cases the product has the same absolute configuration. A feature of ligands **116a**–**g** is that, in contrast to the general trend, an increase in the size of substituents in the *ortho*- and *para*-positions of the aromatic rings causes a dramatic decrease in enantioselectivity. For instance, the reaction in the presence of a catalyst based on compound **116f** results in a nearly racemic product.

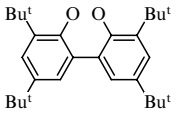
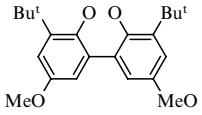
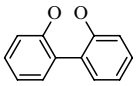
4. Diphosphites based on BINOL and chiral diols

Chan *et al.*[186] proposed a series of aryl phosphite structures based on BINOL (**1**).†

† Ligand **117a** was described earlier (see Ref. 7 and references cited therein).

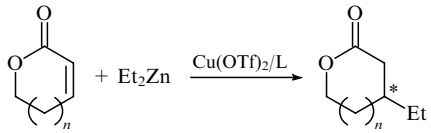


117a–g

Compound **117**	R	O O
a	H	(R_{ax})-BNaph(O)$_2$
b	Me	(R_{ax})-BNaph(O)$_2$
c	H	(R_{ax})-3,3′-Me$_2$-BNaph(O)$_2$
d	H	
e	H	
f	H	*o*-C$_6$H$_4$O$_2$
g	H	

These compounds were studied in the Ni-catalysed hydrocyanation of alkenes. In particular, ligand **117d** provides an *ee* of 65% for styrene and an *ee* of 73% for vinyl acetate.

Cu-Catalysed addition of Et_2Zn to cyclic enone **9a** [reaction (4)] and to enone **9b** proceeds with optical yields of up to 90% and 89%, respectively. Diphosphites **117d**,**f** were found to be the best in both reactions.[187] α,β-Unsaturated lactones **118a**,**b** were also used as substrates.[188] The enantioselectivity of the reaction with lactone **118a** was as high as 92% at 100% conversion. Here, diphosphite **117d** also exhibited the best efficiency. However, passage to the five-membered ring in lactone **118b** was accompanied by a marked decrease in the stereoinduction (*ee* up to 56%). It should be noted that the structure of the catalytically active complex [Cu(MeCN)$_2$(**117d**)]$^+$OTf$^-$ was established by X-ray analysis.[188]

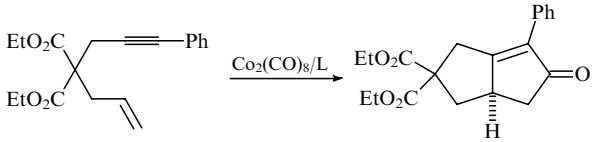


118a,**b**

n = 1 (**a**), 0 (**b**).

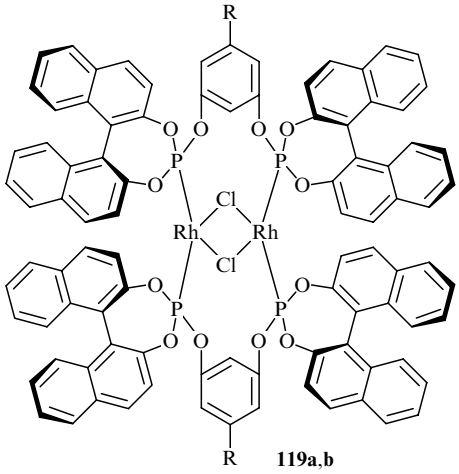
The conversion and enantioselectivity (*ee* up to 28%) provided by a complex [Rh(cod)L]$^+$BF$_4^-$ based on diphosphite **117a** (see Ref. 189) in hydroformylation of styrene [reaction (13)] were similar to those of the catalytic system [Rh(acac)(CO)$_2$]/**117a**. According to IR spectroscopy and ^{31}P and ^{1}H NMR data, this is due to the formation of the same intermediate [RhH(CO)$_2$L] in the catalytic cycle.

Ligand **117a** was also used in the Ir-catalysed hydrogenation of prochiral arylimines (*ee* up to 12%) [190] and in the Co-catalysed intramolecular Pauson–Khand reaction.[191]



The cobalt-phosphite precatalyst and the cobalt-phosphite-alkyl intermediate of the catalytic process were detected by electrospray mass spectrometry and ^{31}P NMR spectroscopy. The best results (*ee* up to 75%) in reactions with various substrates were achieved using aryl-substituted 1,6-alkynes.

Two original dimeric rhodium complexes **119a**,**b** based on the ligands related to diphosphites **117a–g** are noteworthy.[192]

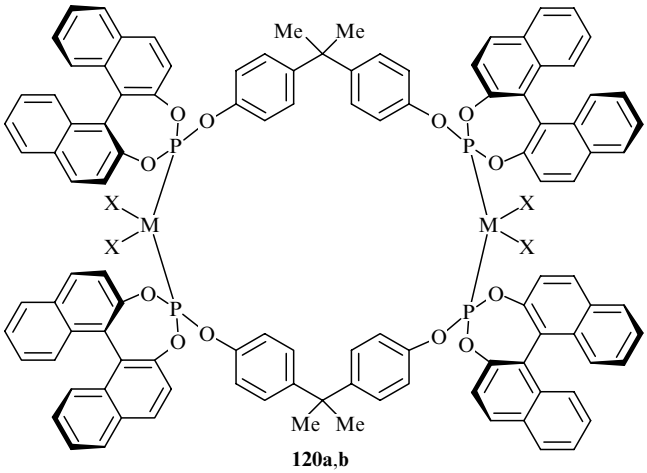


119a,**b**

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

The structure of compound **119a** was established by X-ray analysis. Complexes **119a**,**b** showed low enantioselectivities (*ee* at most 20%) in the hydrosilylation of acetophenone [reaction (5)].

Unusual binuclear metal complexes **120a**,**b** containing twenty-eight-membered macrocycles [193] should also be pointed out.

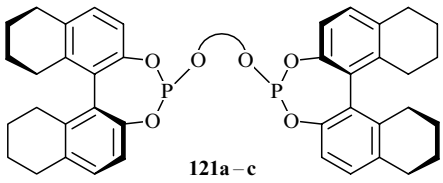


120a,**b**

M = Pd, X = Cl (**a**); M = Pt, X = I (**b**).

The synthesis of such compounds is closely related to the synthesis of chiral supramolecular structures.

Diphosphites **121a–c** based on H$_8$-BINOL (**13**) appeared to be excellent stereoselectors.[194] They provided an *ee* of 97%–99% at 92%–99% conversion in the Cu-catalysed addition of Et_2Zn to enones **9a–c** [reaction (4)].

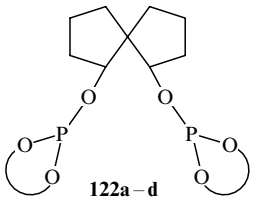


121a–c

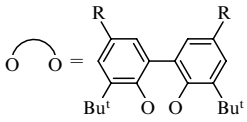
O O = (R_{ax})-BNaph(O)$_2$ (**a**), (R_{ax})-H$_8$-BNaph(O)$_2$ (**b**), (S_{ax})-BNaph(O)$_2$ (**c**).

It was found that the configuration of reaction products and the enantioselectivity remain unchanged as the configuration of the bridging fragment of ligands changes. The optical and chemical yields are rather sensitive to the nature of the solvent. Namely, they increase after replacement of toluene and methylene chloride by diethyl ether possessing more pronounced electron-donor properties. Phosphite **121a** was also used in the addition of Me_2Zn to cyclic enone **9c** [reaction (4)], the optical yield being as high as 99%. This is the best result obtained for this reaction, which is the key stage of the synthesis of anticancer drug clavularin B. Ligand **121a** also exhibited a high efficiency in the reaction of Me_3Al with substrate **9a** (an *ee* of 96% was obtained at high conversion).[195]

The synthesis of diphosphites **122a**–**d** based on *cis*, *trans*-spiro[4.4]nonane-1,6-diol has been reported.[196]



122a–**d**

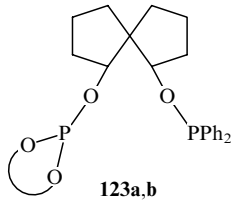


: R = Bu^t (**a**), OMe (**b**),

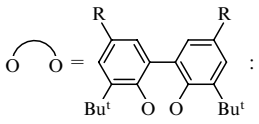
(S_{ax})-BNaph(O)$_2$ (**c**),

(R_{ax})-BNaph(O)$_2$ (**d**).

An attempt at obtaining their diastereomers based on *cis*,*cis*-spiro[4.4]nonane-1,6-diol failed because of steric hindrance (close disposition of bulky substituents). Therefore, only less sterically hindered phosphine-phosphite ligands **123a**,**b** were synthesised. Compounds **122a**–**d** and **123a**,**b** were studied in Rh-catalysed hydroformylation of styrene [reaction (13)] and showed a moderate enantioselectivity (*ee* up to 65%).

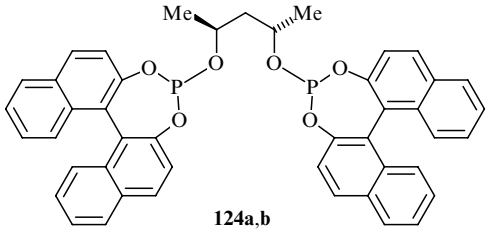


123a,**b**



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

At the same time one of the two ligands based on (2*R*,4*R*)-pentadiol **124a**,**b** provides an *ee* of up to 91% in Pt-catalysed hydroformylation of styrene [reaction (13)].[197]

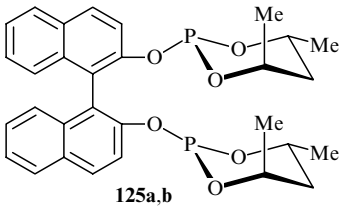


124a,**b**

(2*R*,4*R*)-bis(R_{ax}) (**a**), (2*R*,4*R*)-bis(S_{ax}) (**b**).

Noteworthy is that only diastereomer **124a** is efficient. Here we deal with the co-operative effect of the axial and central chiralities. Catalytically active *cis*-chelate complexes [$PtCl_2$(**124a**)] and [$PtCl(SnCl_3)$(**124a**)] were isolated and studied.

Diphosphites based on BINOL or atropoisomeric diphenyldiols and containing phosphorus centres were considered earlier. However, systems with cyclic phosphite moieties which are based on optically active aliphatic diols are also known. Two examples are provided by ligands **125a**,**b**.[198]

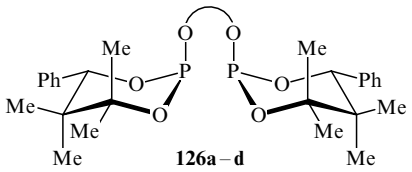


125a,**b**

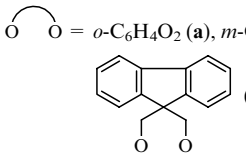
(R_{ax})-bis(4*R*,6*R*) (**a**), (S_{ax})-bis(4*R*,6*R*) (**b**).

The corresponding *cis*-chelate complexes [$PtCl_2$(L)] and [$PtCl(SnCl_3)$L] were obtained and studied by multinuclear NMR spectroscopy and X-ray analysis. Both Pt- and Rh-catalysed hydroformylations of styrene [reaction (13)] in the presence of compounds **125a**,**b** show moderate regioselectivities and optical yields of at most 39%.

Diphosphite derivatives of sterically hindered chiral diols **126**, **127** are noteworthy. They contain, in particular, the dioxaphosphorinane rings in the hindered chair conformation.[199, 200]

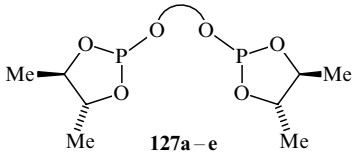


126a–**d**

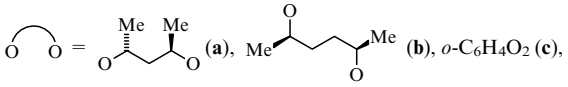


= *o*-$C_6H_4O_2$ (**a**), *m*-$C_6H_4O_2$ (**b**), $OCH_2CMe_2CH_2O$ (**c**),

(**d**).



127a–**e**



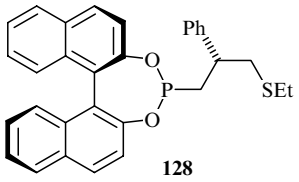
(**a**), (**b**), *o*-$C_6H_4O_2$ (**c**),

(R_{ax})-BNaph(O)$_2$ (**d**), (S_{ax})-BNaph(O)$_2$ (**e**).

The structures of compounds **126a** and **127d** were refined by X-ray analysis. Based on ligands **126a**–**d**, complexes [$Mo(CO)_4$L] and [$(BH_3)_2$L] were synthesised, which can be used in asymmetric catalysis, *e.g.*, hydroformylation and conjugate addition.

V. Other groups of chiral phosphite ligands

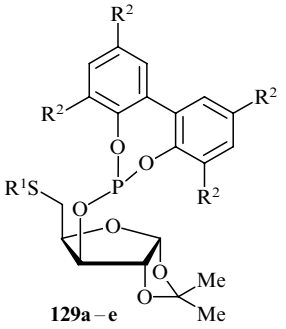
First of all, P,S-bidentate phosphites are of interest. The syntheses of ligand **128** and its complexes of compositions [Pd(alkene)L] (L = fumaronitrile, maleic anhydride, pentadienone)[201] and [Rh(cod)L]$^+$ BF_4^- (see Ref. 202) were reported. These compounds were thoroughly studied by multinuclear NMR spectroscopy, mass spectrometry and X-ray analysis.



128

2D NMR (NOESY) studies revealed that [Pd(alkene)L] exists in solution in the form of two stereoisomers due to the relatively unhindered rotation of the alkene ligands. Phosphite **128** was used in the allylic substitution of unsymmetrical substrate **39a** for dimethyl malonate [reaction (7)] with $[RhCl(cod)]_2$, $[IrCl(cod)]_2$ and $[Pd(1,3\text{-}Ph_2All)Cl]_2$ as precatalysts. The highest stereoinduction was achieved using the rhodium complex (*ee* up to 81%) while the iridium and palladium compounds provided an *ee* of 68% – 70%.

A series of thioether-phosphite ligands **129a – e** based on xylofuranose was applied [162] in the Cu-catalysed conjugate addition of Et_2Zn to enone **9a** [reaction (4)].

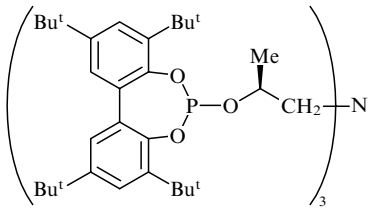


129a – e

Compound **129**	R^1	R^2
a	Me	Bu^i
b	Pr^i	Bu^t
c	Ph	Bu^t
d	Pr^i	H
e	Ph	H

In contrast to the P,P-bidentate systems, the optical yields achieved using ligands **129** appeared to be rather low (at most 41%). Ir-Catalysed hydrogenation of itaconic acid showed an enantioselectivity of up to 51%. Rh-Catalysed hydroformylation of styrene resulted in a racemic product. Probably, the reason is that the ligands are coordinated to the rhodium atom in a monodentate fashion (through the P atom).[203]

A formally P,P,P,N-tetradentate ligand **130** was successfully employed in the Rh-catalysed hydrosilylation of acetophenone [reaction (5) and provided an *ee* of up to 81%].[204]



130

It should be emphasised that phosphite **130** coordinated to $[RhCl(cod)]_2$ behaves as a P,P-bidentate ligand. By and large there are a few phosphites that do not belong to the three major classes considered above.

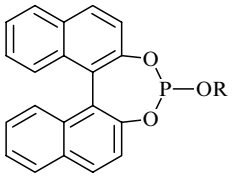
VI. Conclusion

The material presented in this review shows that research on chiral phosphites is progressing rapidly. Over four hundred chiral phosphite compounds are used in asymmetric catalysis, in particular, hydrogenation of C=C and C=N bonds, hydroformylation, hydrosilylation of C=C and C=O bonds, hydroboronation – oxidation, allylic substitution, conjugate addition, hydrovinylation, hydrocyanation and in the Heck, Diels – Alder and Pauson – Khand reactions.

The most important results obtained in enantioselective catalysis using optically active phosphites are summarised in Table 2. As can be seen, considerable advances have been made in hydrogenation, conjugate addition and allylic substitution. On the other hand, the wide use of P-monodentate systems in hydroformylation of ketones and of P,P-bidentate systems in hydrosilylation of ketones seems to be appropriate. Processes in which chiral phosphites are of limited use as yet, namely, hydrosilylation – oxidation and hydroboronation – oxidation of C=C bonds, hydrovinylation and the named reactions mentioned above, deserve much greater attention. Finally, there are also reasons to pay attention to such asymmetric catalytic transformations that were performed up to now exclusively without using chiral phosphite ligands. To start with, examples are proton transfer, cross-coupling and enantioselective rearrangements.

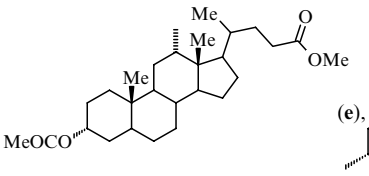
There are a number of unsolved topical problems and potential 'growth points' of the chemistry of chiral phosphite ligands. In particular, studies on the mechanisms of catalytic reactions should be developed more intensively. The results obtained in this field will serve as a basis for recommendations concerned with the choice of experimental conditions and targeted synthesis of the most efficient ligands. Up to now, most of these problems are attacked empirically. Progress towards an understanding of the mechanism of hydroformylation and, to a lesser extent, of allylic substitution in the presence of P,P-bidentate phosphites has been made. Information on other reactions and other ligand groups is scarce. This especially holds for the popular class of P-monodentate phosphites. For instance, there is no theoretical understanding of the reasons for the high asymmetrising activity of these compounds in hydrogenation (earlier, P,P-bidentate chelation was assumed to be a necessary condition). The corresponding studies are in the early stage of development.[206]

At present, P-monodentate chiral phosphites are most widely used. However, different groups of ligands belonging to this class of compounds have been studied in different ways. Emphasis has been placed on compounds derived from BINOL (**1**) and TADDOL (**19**). For instance, the synthesis of a new group of esters and amidoesters of BINOL, **131** and **132**, was reported very recently.

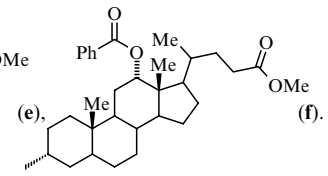


131a – f [(S_{ax}) and/or (R_{ax})]

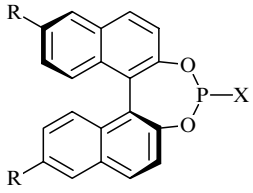
R = Et (**a**), cyclo-C_6H_{11} (**b**), Bu^t (**c**), 9-fluorenyl (**d**),



(**e**),



(**f**).



132a – c

Compound **132**	X	R
a	$N(CH_2)_4$	H
b	NMe(OMe)	H
c	NMe_2	Br

Ligands **131a – d** are used in Rh-catalysed combinatorial hydrogenation [207] while compounds **132a**,**b** are employed in the interesting reaction of conjugate addition of arylboronic acids to α,β-unsaturated substrates {with $[Rh(acac)(C_2H_4)_2]$ as precatalyst}.[208] Comparative studies of these systems and classical diphosphine ligands are in progress. In particular, the advantages of phosphoramidites not only in enantioselectivity but also in the catalytic activity in Rh-catalysed hydrogenation [reaction (2)] are revealed.[209] For instance, a 100% conversion of substrate **4d** in the

Table 2. Relative enantioselectivity of chiral phosphites in the most important catalytic reactions [listed are the maximum *ee* values (%)].

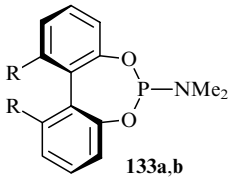
Ligand type	Hydrogenation of C=C bonds	Ref.	Hydroformylation	Ref.	Hydrosilylation of ketones	Ref.	Hydrosilylation or hydroboronation–oxidation of C=C bonds	Ref.	Allylic substitution	Ref.	Conjugate addition of R_2Zn to enones	Ref.
P-Monodentate												
Phosphites based on												
BINOL	99	12, 13	–		–		–		96	9	87	10, 11
biphenyldiols	75	57	–		–		–		–		–	
TADDOL	–		–		25	63	–		–		96	64, 65
carbohydrates	–		–		58	72	–		–		–	
Phosphoramidites based on												
BINOL	>99	45	–		–		99	43, 44	97	38	>99	27
biphenyldiols	–		–		–		–		87	38	99	58–60
TADDOL	–		–		–		–		–		71	67
carbohydrates	94	76	–		–		–		–		–	
P,N-Bidentate												
Oxazoline	>99	91, 92	–		95	94	–		>99	91, 92	94	85–87
Pyridine	–		–		–		59	100	95	107	61	106
Amine	67	109	16	108	94	205	–		61	111	63	115
Imine	–		–		50	110	–		82	110	–	
P,P-Bidentate												
Phosphine-phosphites	>99	163	97	143	–		–		83	156	62	155
Phosphine-phosphoramidites	99	165	74	165	–		–		–		–	
Phosphite-phosphoramidites	99	171	65	170	–		–		–		–	
Diphosphoramidites	90	172	–		–		–		–		89	172, 173
Diphosphites based on												
carbohydrates	>99	180	91	178, 179	51	182	–		97	177	84	181
BINOL and chiral diols	–		91	197	81[a]	204	–		–		99	194
P,S-Bidentate	51	203	0	203	–		–		81	201, 202	41	162

[a] For the formally P,P,P,N-tetradentate ligand **130**.

presense of phosphoramidite **132c** at an optical yield of the product of 94% takes less than 30 min.

The field of application of these ligands is extending continuously. Phosphoramidite (R_{ax},R_C)-**7n** was successfully (enantioselectivity up to 97%) used in a novel Ir-catalysed reaction of allylic etherification of achiral allylic carbonates with alkali metal phenolates.[210] It is of great importance that recent investigations in the field of Cu-catalysed addition of Me_2Zn to acyclic nitroalkenes (*ee* up to 98%)[211] opened novel routes to valuable bioactive compounds (Cyclamenol A, cryptophycins and β-methyl carbopenem antibiotics).

At the same time, increasing the number of phosphite (phosphoramidite) derivatives of BINOL and TADDOL obtained by varying the nature of exocyclic substituents is an extensive approach whose potential has been to a great extent exhausted. For instance, the enantioselectivity achieved in the Cu-catalysed addition of Et_2Zn to acyclic enones in the presence of phosphites **131e**,**f** (see Ref. 212) appeared to be lower (78%) than the enantioselectivity provided by the simpler ligands **3t**,**u**. We believe that it is more useful to extend the range of P-monodentate systems based on substituted diphenyldiols and, probably, on various mononuclear phenols. Here, two examples are provided by phosphoramidites **133a**,**b** based on axially chiral biphenyldiols.[208]



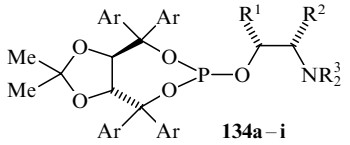
133a,**b** R = OMe (**a**), Ph (**b**).

The use of achiral phenols as, *e.g.*, in the synthesis of ligands **16** and **17** seems to be even more promising. These compounds, provided that BINOL and TADDOL are synthetically accessible ligands, undoubtedly are a step towards the synthesis of much simpler and inexpensive P-monodentate ligands.

A few monodentate systems containing P-stereocentres have been reported to date. However, it was established that ligands containing asymmetric donor atoms are of particular value for asymmetric induction. Therefore, synthesis of such ligands is a quite promising avenue of research in this field of catalysis.

Among P,N-bidentate phosphites, considerable attention should be paid to structures with oxazoline fragments and to phosphite derivatives of Schiff bases. This group of compounds can comprise convenient and efficient systems based on biphenyldiols as well as structures containing stereogenic phosphorus atoms.

We believe that relevant areas of catalytic applications should be found for a variety of aminophosphites. A recent example is provided by the use of ligands **134a–i** in Rh-catalysed hydrosilylation of prochiral ketones.[205]



134a–i

Compound **134**	Ar	R^1	R^2	R^3
a	Ph	Ph	Me	H
b	Ph	Ph	Me	Me
c	Ph	H	H	Me
d	Ph	H	Me	Me
e	Ph	Ph	H	Me
f	Ph	Ph	Me	$(CH_2)_4$ (see [a])
g	Ph	Ph	Me	$(CH_2)_5$ (see [a])
h	Ph	Ph	Ph	Me
i	2-naphthyl	Ph	Me	Me

[a] Here, R^3-R^3.

The best results were obtained using aminophosphite **134b**. The enantiomeric excess was 80% and 94% for the reduction of acetophenone and β-naphthyl methyl ketone, respectively.

As mentioned above, phosphine-phosphites form one of the most efficient groups of P,P-bidentate ligands. Undoubtedly, studies on applications of these compounds in asymmetric catalysis will continue. However, we believe that the synthesis of ligands containing phosphorus centres of different natures and no fragments with P–C bonds is at least equally important. These compounds (phosphite-phosphoramidite, unsymmetrical bisphosphoramidites) can be obtained with ease by phosphorylation of the corresponding amino alcohols and diamines. The data listed in Table 2 point to considerable advances made in applications of these ligands in catalytic reactions.

No planar chiral phosphite ligands have been reported as yet, though this type of chiral phosphines has long been known and comprises a variety of compounds that are excellent stereoselectors.[1,5] Therefore, there are grounds to expect the synthesis of planar chiral phosphites, the more so since the procedure for the synthesis of appropriate starting compounds (*e.g.*, ferrocene series) has already been developed.[213]

In the field of coordination chemistry one can expect a continuation of research into complexation of the most important groups of ligands with catalytically active metals. At present, there are a large number of catalytically efficient phosphites whose complexes with transition metals have not been isolated and studied in detail. This particularly concerns the P-monodentate compounds. Their coordination behaviour was studied much less thoroughly than that of the P,P- and P,N-bidentate systems. The structure of rhodium, palladium and iridium compounds has been studied in more detail, while information on copper complexes is scarce. Obviously, for each group of ligands it is important to combine catalytic experiments and studies on the structure of catalytically active complexes and intermediates of the catalytic cycle.

Is seems appropriate to synthesise a series of related complexes with different ligands for each class of chiral phosphites. Based on their spectral characteristics, the electron-donor properties of ligands will be assessed, which is of great importance for the prediction of catalytic efficiency. Interest in the optically active phosphites continuously increases. This is also indicated by the recently published reviews concerned with the problems of asymmetric synthesis.[214,215] We can with certainty say that application of chiral phosphites has brought coordination chemistry and asymmetric catalysis into a novel epoch.

References

1. I Ojima (Ed.) *Catalytic Asymmetric Synthesis* (New York: Wiley, 2000)
2. Yu N Kukushkin *Reaktsionnaya Sposobnost' Koordinatsionnykh Soedinenii* (Reactivity of Coordination Compounds) (Leningrad: Khimiya, 1987)
3. J Ansell, M Wills *Chem. Soc. Rev.* **31** 259 (2002)
4. D J Wink, T J Kwok, A Yee *Inorg. Chem.* **29** 5006 (1990)
5. K N Gavrilov, A I Polosukhin *Usp. Khim.* **69** 721 (2000) [*Russ. Chem. Rev.* **69** 661 (2000)]
6. K N Gavrilov, I S Mikhel' *Koord. Khim.* **24** 883 (1998) [a]
7. K N Gavrilov, I S Mikhel' *Koord. Khim.* **25** 83 (1999) [a]
8. K N Gavrilov, D V Lechkin *Koord. Khim.* **24** 3 (1998) [a]
9. K Fuji, N Kinoshita, K Tanaka, T Kawabata *Chem. Commun.* 2289 (1999)
10. A Alexakis, C Benhaïm, X Fournioux, A van den Heuvel, J-M Levêque, S March, S Rosset *Synlett* 1811 (1999)
11. A Alexakis, C Benhaim *Eur. J. Org. Chem.* 3221 (2002)
12. M T Reetz, G Mehler *Angew. Chem., Int. Ed.* **39** 3889 (2000)
13. I V Komarov, A Börner *Angew. Chem., Int. Ed.* **40** 1197 (2001)
14. W Chen, J Xiao *Tetrahedron Lett.* **42** 2897 (2001)
15. M T Reetz, G Mehler, A Meiswinkel, T Sell *Tetrahedron Lett.* **43** 7941 (2002)
16. J A J Breuzard, M L Tommasino, M C Bonnet, M Lemaire *J. Organomet. Chem.* **616** 37 (2000)
17. R Hulst, N K de Vries, B L Feringa *Tetrahedron: Asymmetry* **5** 699 (1994)
18. A H M de Vries, A Meetsma, B L Feringa *Angew. Chem., Int. Ed. Engl.* **35** 2374 (1996)
19. L A Arnold, R Imbos, A Mandoli, A H M de Vries, R Naasz, B L Feringa *Tetrahedron* **56** 2865 (2000)
20. B L Feringa *Acc. Chem. Res.* **33** 346 (2000)
21. B L Feringa, M Pineschi, L A Arnold, R Imbos, A H M de Vries *Angew. Chem., Int. Ed. Engl.* **36** 2620 (1997)
22. F Badalassi, P Crotti, F Macchia, M Pineschi, A Arnold, B L Feringa *Tetrahedron Lett.* **39** 7795 (1998)
23. J P G Versleijen, A M van Leusen, B L Feringa *Tetrahedron Lett.* **40** 5803 (1999)
24. R Imbos, M H G Brilman, M Pineschi, B L Feringa *Org. Lett.* **1** 623 (1999)
25. R Naasz, L A Arnold, M Pineschi, E Keller, B L Feringa *J. Am. Chem. Soc.* **121** 1104 (1999)
26. R Imbos, A J Minnaard, B L Feringa *Tetrahedron* **57** 2485 (2001)
27. R Naasz, L A Arnold, A J Minnaard, B L Feringa *Angew. Chem., Int. Ed.* **40** 927 (2001)
28. F Bertozzi, P Crotti, F Macchia, M Pineschi, B L Feringa *Angew. Chem., Int. Ed.* **40** 930 (2001)
29. R Naasz, L A Arnold, A J Minnaard, B L Feringa *Chem. Commun.* 735 (2001)
30. L A Arnold, R Naasz, A J Minnaard, B L Feringa *J. Org. Chem.* **67** 7244 (2002)
31. H Malda, A W van Zijl, L A Arnold, B L Feringa *Org. Lett.* **3** 1169 (2001)
32. N Sewald, V Wendisch *Tetrahedron: Asymmetry* **9** 1341 (1998)
33. A Alexakis, C Benhaim *Org. Lett.* **2** 2579 (2000)
34. Y H Choi, J Y Choi, H Y Yang, Y H Kim *Terahedron: Asymmetry* **13** 801 (2002)
35. O Huttenloch, E Laxman, H Waldmann *Chem. Eur. J.* **8** 4767 (2002)
36. B Bartels, G Helmchen *Chem. Commun.* 741 (1999)
37. B Bartels, C Garcia-Yebra, F Rominger, G Helmchen *Eur. J. Inorg. Chem.* 2569 (2002)
38. T Ohmura, J F Hartwig *J. Am. Chem. Soc.* **124** 15164 (2002)
39. G Franciò, C G Arena, F Faraone, C Graiff, M Lanfranchi, A Tiripicchio *Eur. J. Inorg. Chem.* 1219 (1999)
40. C G Arena, G P Calabrò, G Franciz, F Faraone *Tetrahedron: Asymmetry* **11** 2387 (2000)
41. G Franciò, F Faraone, W Leitner *J. Am. Chem. Soc.* **124** 736 (2002)
42. L J Gooven *Angew. Chem., Int. Ed.* **41** 3775 (2002)

43. J F Jensen, B Y Svendsen, T V la Cour, H L Pedersen, M Johannsen *J. Am. Chem. Soc.* **124** 4558 (2002)
44. M F P Ma, K Li, Z Zhou, C Tang, A S C Chan *Tetrahedron: Asymmetry* **10** 3259 (1999)
45. M van den Berg, A J Minnaard, E P Schudde, J van Esch, A H M de Vries, J G de Vries, B L Feringa *J. Am. Chem. Soc.* **122** 11539 (2000)
46. M van den Berg, R M Haak, A J Minnaard, A H M de Vries, J G de Vries, B L Feringa *Adv. Synth. Catal.* **344** 1003 (2002)
47. X Jia, R Guo, X Li, X Yao, A S C Chan *Tetrahedron Lett.* **43** 5541 (2002)
48. D Peña, A J Minnaard, J G de Vries, B L Feringa *J. Am. Chem. Soc.* **124** 14552 (2002)
49. P Müller, P Nurg, G Bernardinelli *Helv. Chim. Acta* **83** 843 (2000)
50. F-Y Zhang, A S C Chan *Tetrahedron: Asymmetry* **9** 1179 (1998)
51. O Zeng, H Liu, X Cui, A Mi, Y Yiang, X Li, M C K Choi, A S C Chan *Tetrahedron: Asymmetry* **13** 115 (2002)
52. O Zeng, H Liu, X Cui, A Mi, Y Yiang, X Li, M C K Choi, A S C Chan *Tetrahedron* **58** 8799 (2002)
53. Y Fu, J-H Xie, A-G Hu, H Zhou, L-X Wang, Q-L Zhou *Chem. Commun.* 480 (2002)
54. A-G Hu, Y Fu, J-H Xie, H Zhou, L-X Wang, Q-L Zhou *Angew. Chem., Int. Ed.* **41** 2348 (2002)
55. H Zhou, W-H Wang, Y Fu, J-H Xie, W-J Shi, L-X Wang, Q-L Zhou *J. Org. Chem.* **68** 1582 (2003)
56. K Nozaki, N Sakai, T Nanno, T Higashijima, S Mano, T Horiuchi, H Takaya *J. Am. Chem. Soc.* **119** 4413 (1997)
57. W Chen, J Xiao *Tetrahedron Lett.* **42** 8737 (2001)
58. A Alexakis, S Rosset, J Allamand, S March, F Guillen, C Benhaim *Synlett* 1375 (2001)
59. L M Urbaneja, A Alexakis, N Krause *Tetrahedron Lett.* **43** 7887 (2002)
60. A Alexakis, C Benhaim, S Rosset, M Humam *J. Am. Chem. Soc.* **124** 5262 (2002)
61. O Knopff, A Alexakis *Org. Lett.* **4** 3835 (2002)
62. A Alexakis, K Croset *Org. Lett.* **4** 4147 (2002)
63. J-I Sakaki, W B Schweizer, D Seebach *Helv. Chim. Acta* **76** 2654 (1993)
64. A Alexakis, J Vastra, J Burton, C Benhaim, P Mangeney *Tetrahedron Lett.* **39** 7869 (1998)
65. A Alexakis, J Burton, J Vastra, C Benhaim, X Fournioux, A van den Heuvel, J-M Levêque, F Mazé, S Rosset *Eur. J. Org. Chem.* 4011 (2000)
66. A Alexakis, C Benhaim *Tetrahedron: Asymmetry* **12** 1151 (2001)
67. E Keller, J Maurer, R Naasz, T Schader, A Meetsma, B L Feringa *Tetrahedron: Asymmetry* **9** 2409 (1998)
68. F Bertozzi, P Crotti, F Macchia, M Pineschi, A Arnold, B L Feringa *Tetrhedron Lett.* **40** 4893 (1999)
69. R Imbos, A J Minnaard, B L Feringa *J. Am. Chem. Soc.* **124** 184 (2002)
70. D Steinborn, H Junicke *Chem. Rev.* **100** 4283 (2000)
71. M Stolmar, C Floriani, G Gervasio, D Viterbo *J. Chem. Soc., Dalton Trans.* 1119 (1997)
72. A Suarez, A Pizzano, I Fernandez, N Khiar *Tetrahedron: Asymmetry* **12** 633 (2001)
73. E E Nifantyev, M P Koroteev, A M Koroteev, V K Belsky, A I Stash, M Yu Antipin, K A Lyssenko, L Cao *J. Organomet. Chem.* **587** 18 (1999)
74. D Vos, A M Arif, R D Ernst *J. Organomet. Chem.* **553** 277 (1998)
75. A Bayer, U Thewalt, B Rieger *Eur. J. Inorg. Chem.* 199 (2002)
76. A Bayer, D Murszat, U Thewalt, B Rieger *Eur. J. Inorg. Chem.* 2614 (2002)
77. A Alexakis, J Vastra, J Burton, P Mangeney *Tetrahedron: Asymmetry* **8** 3193 (1997)
78. J-M Brunel, O Chiodi, B Faure, F Fotiadu, G Buono *J. Organomet. Chem.* **529** 285 (1997)
79. A Bohac, M Lettrichova, P Hrnciar, M Hutta *J. Organomet. Chem.* **507** 23 (1996)
80. A Tillack, R Selke, Ch Fischer, D Bilda, K Kortus *J. Organomet. Chem.* **518** 79 (1996)
81. K N Gavrilov, E Yu Zhorov *Zh. Neorg. Khim.* **38** 1544 (1993) [b]
82. R Prêtôt, G C Lloyd-Jones, A Pfaltz *Pure Appl. Chem.* **70** 1035 (1998)
83. R Prêtôt, A Pfaltz *Angew. Chem., Int. Ed.* **37** 323 (1998)
84. A Pfaltz *J. Heterocycl. Chem.* **36** 1437 (1999)
85. A K H Knöbel, I H Escher, A Pfaltz *Synlett* 1429 (1997)
86. A Pfaltz *Synlett* 835 (1999)
87. I H Escher, A Pfaltz *Tetrahedron* **56** 2879 (2000)
88. K N Gavrilov, O G Bondarev, R V Lebedev, A I Polosukhin, A A Shyryaev, S E Lyubimov, P V Petrovskii, S K Moiseev, V N Kalinin, N S Ikonnikov, V A Davankov, A V Korostylev *J. Organomet. Chem.* **655** 204 (2002)
89. A I Polosukhin, O G Bondarev, S E Lyubimov, A V Korostylev, K A Lyssenko, V A Davankov, K N Gavrilov *Tetrahedron: Asymmetry* **12** 2197 (2001)
90. O G Bondarev, S E Lyubimov, A A Shiryaev, N E Kadilnikov, V A Davankov, K N Gavrilov *Tetrahedron: Asymmetry* **13** 1587 (2002)
91. R Hilgraf, A Pfaltz *Synlett* 1814 (1999)
92. A Pfaltz, J Blankenstein, R Hilgraf, E Hörmann, S McIntyre, F Menges, M Schönleber, S P Smidt, B Wüstenberg, N Zimmermann *Adv. Synth. Catal.* **345** 33 (2003)
93. K N Gavrilov, O G Bondarev, V N Tsarev, A A Shiryaev, S E Lyubimov, A S Kucherenko, V A Davankov *Izv. Akad. Nauk, Ser. Khim.* 116 (2003) [c]
94. D K Heldmann, D Seebach *Helv. Chim. Acta* **82** 1096 (1999)
95. C G Arena, D Drommi, F Faraone *Tetrahedron: Asymmetry* **11** 4753 (2000)
96. C G Arena, D Drommi, F Faraone *Tetrahedron: Asymmetry* **11** 2765 (2000)
97. D Drommi, F Faraone, G Francalò, D Belletti, C Graiff, A Tiripicchio *Organometallics* **21** 761 (2002)
98. G Delapierre, J M Brunel, T Constantieux, G Buono *Tetrahedron: Asymmetry* **12** 1345 (2001)
99. R Kranich, K Eis, O Geis, S Mühle, J W Bats, H-G Schmalz *Chem. Eur. J.* **6** 2874 (2002)
100. F Blume, S Zemolka, T Fey, R Kranich, H-G Schmalz *Adv. Synth. Catal.* **344** 868 (2002)
101. J M Brunel, T Constantieux, G Buono *J. Org. Chem.* **64** 8940 (1999)
102. J M Brunel, T Constantieux, A Labande, F Lubatti, G Buono *Tetrahedron Lett.* **38** 5971 (1997)
103. T Constantieux, J-M Brunel, A Labande, G Buono. *Synlett* 49 (1998)
104. G Muchow, J M Brunel, M Maffei, O Pardigon, G Buono *Tetrahedron* **54** 10435 (1998)
105. J M Brunel, B Del Campo, G Buono *Tetrahedron Lett.* **39** 9663 (1998)
106. G Delapierre, T Constantieux, J M Brunel, G Buono *Eur. J. Org. Chem.* 2507 (2000)
107. J M Brunel, A Tenaglia, G Buono *Tetrahedron: Asymmetry* **11** 3585 (2000)
108. C Saluzzo, J Breuzard, S Pellet-Rostaing, M Vallet, F LeGuyader, M Lemaire *J. Organomet. Chem.* **643** 98 (2002)
109. O Huttenloch, E Laxman, H Waldmann *Chem. Commun.* 673 (2002)
110. K N Gavrilov, O G Bondarev, R V Lebedev, A A Shiryaev, S E Lyubimov, A I Polosukhin, G V Grintselev-Knyazev, K A Lyssenko, S K Moiseev, N S Ikonnikov, V N Kalinin, V A Davankov, A V Korostylev, H-J Gais *Eur. J. Inorg. Chem.* 1367 (2002)
111. A I Polosukhin, O G Bondarev, A V Korostylev, R Hilgraf, V A Davankov, K N Gavrilov *Inorg. Chim. Acta* **323** 55 (2001)
112. O G Bondarev, K N Gavrilov, V N Tsarev, V A Davankov, G-I Gais *Izv. Akad. Nauk, Ser. Khim.* 1604 (2002) [c]
113. B Gotov, H-G Schmalz *Org. Lett.* **3** 1753 (2001)
114. O G Bondarev, K N Gavrilov, V N Tsarev, V A Davankov, R V Lebedev, S K Moiseev, V N Kalinin *Izv. Akad. Nauk, Ser. Khim.* 484 (2002) [c]
115. M Dieguez, A Ruiz, C Claver *Tetrahedron: Asymmetry* **12** 2861 (2001)
116. K N Gavrilov, I S Mikhel', K A Lysenko, M Yu Antipin, G I Timofeeva, A I Polosukhin, A V Korostylev *Zh. Neorg. Khim.* **42** 593 (1997) [b]
117. K N Gavrilov, A V Korostylev, G I Timofeeva, A I Polosukhin, O G Bondarev, P V Petrovskii *Koord. Khim.* **24** 610 (1998) [a]
118. I S Mikhel', K N Gavrilov, A I Rebrov *Zh. Neorg. Khim.* **44** 1634 (1999) [b]

119. A I Polosukhin, K N Gavrilov, O G Bondarev, A V Korostylev, P V Petrovskii, V A Davankov *J. Organomet. Chem.* **608** 89 (2000)
120. A I Polosukhin, O G Bondarev, S E Lyubimov, A A Shiryaev, K N Gavrilov *Koord. Khim.* **26** 400 (2000) [a]
121. A I Polosukhin, O G Bondarev, S E Lyubimov, A A Shiryaev, P V Petrovskii, K A Lysenko, K N Gavrilov *Koord. Khim.* **27** 630 (2001) [a]
122. K N Gavrilov, A V Korostylev, O G Bondarev, A I Polosukhin, V A Davankov *J. Organomet. Chem.* **585** 290 (1999)
123. A V Korostylev, O G Bondarev, A Yu Kovalevsky, P V Petrovskii, V A Davankov, K N Gavrilov *Inorg. Chim. Acta* **312** 117 (2001)
124. K Ito, R Kashiwagi, K Iwasaki, T Katsuki *Synlett* 1563 (1999)
125. R V Lebedev, S K Moiseev, O G Bondarev, M M Il'in, K N Gavrilov, V N Kalinin *Izv. Akad. Nauk, Ser. Khim.* 476 (2002) [c]
126. K N Gavrilov, A I Polosukhin, O G Bondarev, A V Korostylev, S E Lyubimov, A A Shiryaev, Z A Starikova, V A Davankov *Mendeleev Commun.* 33 (2001)
127. K N Gavrilov, O G Bondarev, A I Polosukhin, S E Lyubimov, V N Tsarev *Koord. Khim.* **28** 152 (2002) [a]
128. K N Gavrilov, A I Polosukhin *Koord. Khim.* **26** 695 (2000) [a]
129. A I Polosukhin, A Yu Kovalevskii, K N Gavrilov *Koord. Khim.* **25** 812 (1999) [a]
130. K N Gavrilov, I S Mikhel' *Usp. Khim.* **65** 242 (1996) [*Russ. Chem. Rev.* **65** 225 (1996)]
131. K N Gavrilov, I S Mikhel', A I Polosukhin, A I Rebrov, G V Cherkaev, G I Timofeeva *Koord. Khim.* **23** 925 (1997) [a]
132. A I Polosukhin, A Yu Kovalevsky, A V Korostylev, V A Davankov, K N Gavrilov *Phosphorus, Sulfur Silicon Relat. Elem.* **159** 69 (2000)
133. K N Gavrilov, A V Korostylev, A I Polosukhin, O G Bondarev, A Yu Kovalevsky, V A Davankov *J. Organomet. Chem.* **613** 148 (2000)
134. O G Bondarev, I S Mikhel', V N Tsarev, P V Petrovskii, V A Davankov, K N Gavrilov *Izv. Akad. Nauk, Ser. Khim.* 110 (2003) [c]
135. K N Gavrilov, A I Polosukhin, O G Bondarev, S E Lyubimov, K A Lyssenko, P V Petrovskii, V A Davankov *J. Mol. Catal. A: Chem.* **196**/**1** – **2** 39 (2003)
136. K N Gavrilov, I S Mikhel', D V Lechkin, A I Rebrov, G V Cherkaev, G I Timofeeva, M G Vinogradov *Zh. Neorg. Khim.* **42** 1676 (1997) [b]
137. I S Mikhel', K N Gavrilov, D V Lechkin, A I Rebrov *Izv. Akad. Nauk, Ser. Khim.* 1416 (1997) [c]
138. K N Gavrilov, A V Korostylev, P V Petrovskiy, A Yu Kovalevsky, V A Davankov *Phosphorus, Sulfur Silicon Relat. Elem.* **155** 15 (1999)
139. I S Mikhel, O G Bondarev, V N Tsarev, G V Grintselev-Knyazev, K A Lyssenko, V A Davankov, K N Gavrilov *Organometallics*, **22,** 925 (2003)
140. K Nozaki, F Shibahara, Y Itoi, E Shirakawa, T Ohta, H Takaya, T Hiyama *Bull. Chem. Soc. Jpn.* **72** 1911 (1999)
141. K Nozaki, Y Itoi, F Shibahara, E Shirakawa, T Ohta, H Takaya, T Hiyama *J. Am. Chem. Soc.* **120** 4051 (1998)
142. K Nozaki, F Shibahara, T Hiyama *Chem. Lett.*, 694 (2000)
143. T Horiuchi, T Ohta, E Shirakawa, K Nozaki, H Takaya *Tetrahedron* **53** 7795 (1997)
144. K Nozaki, W -G Li, T Horiuchi, H Takaya *Tetrahedron Lett.* **38** 4611 (1997)
145. T Horiuchi, T Ohta, E Shirakawa, K Nozaki, H Takaya *J. Org. Chem.* **62** 4285 (1997)
146. T Horiuchi, E Shirakawa, K Nozaki, H Takaya *Organometallics* **16** 2981 (1997)
147. D Gleich, R Schmid, W A Herrmann *Organometallics* **17** 2141 (1998)
148. K Nozaki, Y Kawashima, K Nakamoto, T Hiyama *Macromolecules* **32** 5168 (1999)
149. K Nozaki, T Hiyama *Organometallics* **19** 2031 (2000)
150. T Horiuchi, E Shirakawa, K Nozaki, H Takaya *Tetrahedron: Asymmetry* **8** 57 (1997)
151. G Franciò, K Wittmann, W Leitner *J. Organomet. Chem.* **621** 130 (2001)
152. G Franciò, W Leitner *Chem. Commun.* 1663 (1999)
153. D Bonafoux, Z Hua, B Wang, I Ojima *J. Fluorine Chem.* **112** 101 (2001)
154. S Deerenberg, P C J Kamer, P W N M van Leeuwen *Organometallics* **19** 2065 (2000)
155. M Digguez, S Deerenberg, O Pemies, C Claver, P W N M van Leeuwen, P C J Kamer *Tetrahedron: Asymmetry* **11** 3161 (2000)
156. S Deerenberg, H S Schrekker, G P F van Strijdonck, P C J Kamer, P W N M van Leeuwen, J Fraanje, K Goubitz *J. Org. Chem.* **65** 4810 (2000)
157. S Deerenberg, O Pemies, M Digguez, C Claver, P C J Kamer, P W N M van Leeuwen *J. Org. Chem.* **66** 7626 (2001)
158. C A Tolman *Chem. Rev.* **77** 313 (1977)
159. A Suarez, A Pizzano *Tetrahedron: Asymmetry* **12** 2501 (2001)
160. A Suarez, M A Mendez-Rojas, A Pizzano *Organometallics* **21** 4611 (2002)
161. O Pemies, G Net, A Ruiz, C Claver *Tetrahedron: Asymmetry* **12** 3441 (2001)
162. M Digguez, O Pemies, G Net, A Ruiz, C Claver *J. Mol. Catal. A: Chem.* **185** 11 (2002)
163. O Pemies, M Digguez, G Net, A Ruiz, C Claver *J. Org. Chem.* **66** 8364 (2001)
164. J Scherer, G Huttner, H Heidel *J. Organomet. Chem.* **539** 67 (1997)
165. G Franciz, F Faraone, W Leitner *Angew. Chem., Int. Ed.* **39** 1428 (2000)
166. R Ewalds, E B Eggeling, A C Hewat, P C J Kamer, P W N M van Leeuwen, D Vogt *Chem. Eur. J.* **6** 1496 (2000)
167. O Lot, I Suisse, A Mortreux, F Agbossou, G Nowogrocki *J. Mol. Catal. A: Chem.* **164** 125 (2000)
168. M T Reetz, M Pastd *Tetrahedron Lett.* **41** 3315 (2000)
169. S Naili, I Suisse, A Mortreux, F Agbossou-Niedercorn, G Nowogrocki *J. Organomet. Chem.* **628** 114 (2001)
170. M Digguez, A Ruiz, C Claver *Tetrahedron: Asymmetry* **12** 2827 (2001)
171. M Digguez, A Ruiz, C Claver *Chem. Commun.* 2702 (2001)
172. O Huttenloch, J Spieler, H Waldmann *Chem. Eur. J.* **7** 671 (2001)
173. A Mandoli, L A Arnold, A H M de Vries, P Salvadori, B L Feringa *Tetrahedron: Asymmetry* **12** 1929 (2001)
174. O Pàmies, G Net, A Ruiz, C Claver *Tetrahedron: Asymmetry* **11** 1097 (2000)
175. O Pàmies, G Net, A Ruiz, C Claver *Tetrahedron: Asymmetry* **10** 2007 (1999)
176. E Guiu, B Munoz, S Castillon, C Claver *Adv. Synth. Catal.* **345** 169 (2003)
177. O Pàmies, G P F van Strijdonck, M Diéguez, S Deerenberg, G Net, A Ruiz, C Claver, P C J Kamer, P W N M van Leeuwen *J. Org. Chem.* **66** 8867 (2001)
178. M Diéguez, O Pàmies, A Ruiz, S Castilllon, C Claver *Chem. Eur. J.* **7** 3086 (2001)
179. M Diéguez, O Pàmies, A Ruiz, S Castilllon, C Claver *Chem. Commun.* 1607 (2000)
180. M Diéguez, A Ruiz, C Claver *J. Org. Chem.* **67** 3796 (2002)
181. M Diéguez, A Ruiz, C Claver *Tetrahedron: Asymmetry* **12** 2895 (2001)
182. M Diéguez, O Pàmies, A Ruiz, C Claver *Tetrahedron: Asymmetry* **13** 83 (2002)
183. M Diéguez, S Jansat, M Gomez, A Ruiz, G Muller, C Claver *Chem. Commun.*, 1132 (2001)
184. R Kadyrov, D Heller, R Selke *Tetrahedron: Asymmetry* **9** 329 (1998)
185. M T Reetz, T Neugebauer *Angew. Chem., Int. Ed.* **38** 179 (1999)
186. M Yan, Q-Y Xu, A S C Chan *Tetrahedron: Asymmetry* **11** 845 (2000)
187. M Yan, A S C Chan *Tetrahedron Lett.* **40** 6645 (1999)
188. M Yan, Z-Y Zhou, A S C Chan *Chem. Commun.* 115 (2000)
189. P Uriz, E Fernandez, N Ruiz, C Claver *Inorg. Chem. Commun.* **3** 515 (2000)
190. A Martorell, C Claver, E Fernandez *Inorg. Chem. Commun.* **3** 132 (2000)
191. S J Sturla, S L Buchwald *J. Org. Chem.* **67** 3398 (2002)

192. S Ini, A G Oliver, T D Tilley, R G Bergman *Organometallics* **20** 3839 (2001)
193. C G Arena, D Drommi, F Faraone, C Graiff, A Tiripicchio *Eur. J. Inorg. Chem.* 247 (2001)
194. L Liang, T T L Au-Yeung, A S C Chan *Org. Lett.* **4** 3799 (2002)
195. L Liang, A S C Chan *Tetrahedron: Asymmetry* **13** 1393 (2002)
196. Y Jiang, S Xue, K Yu, Z Li, J Deng, A Mi, A S C Chan *J. Organomet. Chem.* **586** 159 (1999)
197. S Cserépi-Szücs, J Bakos *Chem. Commun.* 635 (1997)
198. S Cserépi-Szücs, G Huttner, L Zsolnai, J Bakos *J. Organomet. Chem.* **586** 70 (1999)
199. A C Dros, A Meetsma, R M Kellogg *Tetrahedron* **55** 3071 (1999)
200. P Kruger, B Wederndorfer, H Werner *Z. Anorg. Allg. Chem.* **626** 2228 (2000)
201. K Selvakumar, M Valentini, P Pregosin *Organometallics* **18** 4591 (1999)
202. M Valentini, K Selvakumar, M Worle, P Pregosin *J. Organomet. Chem.* **587** 244 (1999)
203. O Pàmies, M Diéguez, G Net, A Ruiz, C Claver *Organometallics,* **19** 1488 (2000)
204. S D Pastor, S P Shum *Tetrahedron: Asymmetry* **9** 543 (1998)
205. S Yao, J-C Meng, G Siuzdak, M G Finn *J. Org. Chem.* **68** 2540 (2003)
206. M van den Berg, A J Minnaard, R M Haak, M Leeman, E P Schudde, A Meetsma, B L Feringa, A H M de Vries, C E P Maljaars, C E Willans, D Hyet, J A F Boogers, H J W Henderickx, J G de Vries *Adv. Synth. Catal.* **345** 308 (2003)
207. M T Reetz, T Sell, A Meiswinkel, G Mehler *Angew. Chem., Int. Ed.* **42** 790 (2003)
208. J-G Boiteau, R Imbos, A J Minnaard, B L Feringa *Org. Lett.* **5** 681 (2003)
209. D Pena, A J Minnaard, A H M de Vries, J G de Vries, B L Feringa *Org. Lett.* **5** 475 (2003)
210. F López, T Ohmura, J F Hartwig *J. Am. Chem. Soc.* **125** 3426 (2003)
211. A Duursma, A J Minnaard, B L Feringa *J. Am. Chem. Soc.* **125** 3700 (2003)
212. A Iuliano, P Scafato *Tetrahedron: Asymmetry* **14** 611 (2003)
213. A Togni, T Hayashi *Ferrocenes. Homogenous Catalysis, Organic Synthesis, Material Science* (Weinheim: VCH, 1995)
214. O Molt, T Schrader *Synthesis* 2633 (2002)
215. H-U Blaser, C Malan, B Pugin, F Spindler, H Steiner, M Studer *Adv. Synth. Catal.* **345** 103 (2003)

[a] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[b] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[c] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*