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Novel *P,N*-Bidentate Phosphite Ligands in Asymmetric Catalysis

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ABSTRACT Results achieved by the authors in the synthesis of chiral *P,N*-phosphite ligands are summarized. Three groups of new chiral *P,N*-phosphites are discussed, namely, ligands derived from 1,1′-bi-2-naphthol, ligands possessing an acyclic phosphorus center, and *P**-chiral ligands derived from (*S*)-2-anilinomethylpyrrolidine. An overview of complexation of the ligands with Rh(I) and Pd(II) precursors is given. Accessibility and stability of chiral phosphite ligands possessing acyclic phosphorus was analyzed for the first time along with their efficiency in terms of stereoselectivity. The title ligands are shown to be highly efficient in the Pd-catalyzed allylic alkylation (up to 85% ee) and, especially, allylic sulfonylation (up to 97% ee) reactions in certain cases outperformed all known catalytic systems. *Chirality 15:S97–S103, 2003.* © 2003 Wiley-Liss, Inc.

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During the last few years Pd-catalyzed allylic substitution has become one of the most versatile methods for the enantioselective formation of C-C and C-heteroatom bonds. A wide variety of applied substrates and nucleophiles together with high chemical and optical yields make this method attractive for application in the synthesis of complex organic compounds.[1] Despite this impressive progress, many challenges, notably with regard to extension of substrate scope, selectivity, and activity, make the design of new chiral ligands a vital task. One of the leading ligand groups for allylic substitution reactions are *P,N*-hybrid ligands, which deliver excellent results with a wide range of substrates and nucleophiles.[1,2] Traditionally, the vast majority of research has focused on the development of *phosphine* ligands, usually possessing a -PPh_2 group. Therefore, opportunities for the tuning of ligand structures were restricted to their nonphosphorus-containing part. But recently several examples of highly efficient *P,N*-bidentate *phosphites* and *phosphoramidites* were reported.[3–9] These types of ligands notably benefit from simplicity of preparation, high π-acidity of the phosphorus atom, and resistance to oxidative destruction. Additionally, in contrast to traditional phosphines, an environment around the phosphorus atom in phosphites is widely variable, providing additional opportunities for the fine-tuning of ligand structures.[10–14] A large range of ligands can be prepared from inexpensive starting materials, including those with chirality at phosphorus arising from the use of homochiral diols or aminoalcohols.

Our group is interested in the development of new chiral phosphorus ligands. This article represents an overview of our recent results achieved in the synthesis of chiral *P,N*-bidentate phosphites and their application in the Pd-catalyzed allylic substitution reactions. The ligands described in this article can be conveniently classified into three categories according to the structure of their phosphorus-containing fragment: 1) BINOL based ligands; 2) ligands with acyclic phosphorus center; and 3) *P**-chiral ligands derived from (*S*)-2-anilinomethylpyrrolidine.

LIGANDS DERIVED FROM 1,1′-BI-2-NAPHTHOL (BINOL)

In the last 10 years (*R*)- and (*S*)-1,1′-bi-2-naphthol (BINOL) proved to be useful building blocks in the synthesis of chiral phosphite ligands. *P*-mono-, *P,P*-bidentate phosphites and *P,P*-phosphinophosphites derived from BINOL delivered excellent results in asymmetric allylic substitution transformations,[6,15] but only two examples of *P,N*-ligand applications have been reported. Thus, chiral phosphite-oxazolines performed efficiently in the Pd-

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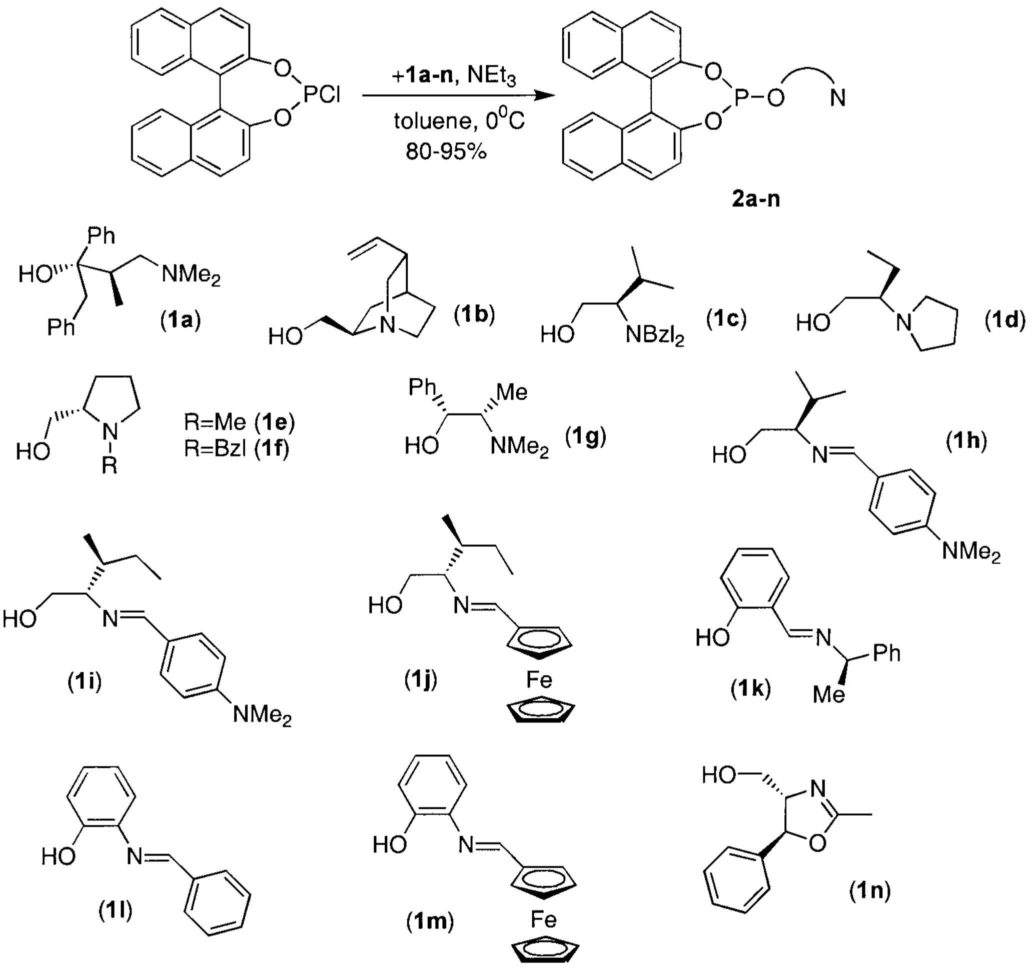


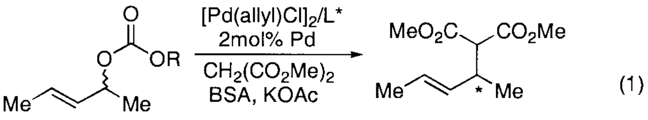
Scheme 1. Synthesis of ligands **2a–n.**

catalyzed alkylation of monosubstituted allyl acetates (up to 96% ee),[3] while phosphite-pyridine ligands afforded only up to 37% ee in the allylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate.[5]

We have applied a large set of easily accessible amino- and imino-alcohols to obtain a series of new *P,N*-bidentate phosphite ligands **2a–n** (Scheme 1).[16] These ligands possess an identical phosphorus-containing BINOL fragment, while the amino alcohol component differs in the amino group structure, length of the carbon bridge, and in number and position of C*-chiral centers. This gave us an opportunity to investigate how changes in the ligands structure affect their complexation and catalytic performance.

When reacted with transition metal precursors, **2a–n** act generally as typical chelating ligands. Thus, their reaction with $[Rh(CO)_2Cl]_2$ results in [Rh(CO)Cl(L)] chelate products. The only exception is **2n,** which unexpectedly gives dimeric complexes $[Rh(CO)Cl(L)]_2$ where ligand molecules act as bridges between two rhodium atoms. The dimers are probably formed due to the presence of a cyclic oxazoline fragment, because it is known that insertion of the phosphorus or nitrogen atoms of *P,N*-bidentate ligands into cycles can prevent the ligands from chelation.[17] Of special interest and practical importance is the reaction of the novel ligands with Pd(II) complexes, which are often used as the catalytic precursors in the allylic substitution reactions.[2] Interestingly, complexation of amino phosphite **2g** and imino phosphites **2h-j,l,m** with $[PdCl_2(COD)]$ produces mixtures of various neutral and cationic complexes, while the use of $[PdCl_2(CH_3CN)_2]$ and $[Pd(allyl)Cl]_2$ gives rise to selective formation of the neutral $[PdCl_2(L)]$ and cationic [Pd(allyl)(L)]Cl palladium chelates, correspondingly. This remarkable influence of the starting Pd complex on the structure of complexation products should be taken into account when choosing metal precursors for catalytic reactions.

Several of the newly obtained ligands were tested in the Pd-catalyzed allylic alkylation of 3-penten-2-yl carbonate with dimethyl malonate (Scheme 2, Table 1). C*-Stereocenters in the amino alcohol fragment appear to be crucial for high enantioselectivity, since (S^{ax})-**2l,** which does not have one, gave only 7% ee (Table 1, entry 29). For **2h, 2i,** and **2j,** which were employed in both diastereomeric forms, no clear matched/mismatched cases can be recognized, as the optical yields vary widely depending on the temperature and solvent. The best results were achieved with the ligands bearing imino groups—(S^{ax})-**2h** and (R^{ax})-**2j** (up to 81% ee). It is notable that (S^{ax})-**2j** and (R^{ax})-



Scheme 2. Pd-catalyzed alkylation of 3-penten-2-yl ethyl carbonate with dimethyl malonate.

2j showed generally better stereoselectivity than structurally related (S^{ax})-**2i** and (R^{ax})-**2i.** As the electronic properties of ligands **2i** and **2j** are almost identical, the difference is caused by their steric features. Compounds **2i** and **2j** are of similar structures and differ only in the –N=CHR fragment. To estimate the bulkiness of the R substituents, the cone angles[18] θ_R for the $p\mathrm{C_6H_4NMe_2}$ and $\mathrm{Cp_2Fe}$ fragments were calculated and the cone angle of the $\mathrm{Cp_2Fe}$ fragment (θ_R = 159) was found to be significantly larger than that of the $p\mathrm{C_6H_4NMe_2}$ fragment (θ_R = 133).[16] Therefore, bulky substituents attached to the imine group in *P,N*-iminophosphite ligands are likely to lead to higher optical yields in the catalytic process.

The enantioselectivity achieved with ligand (R^{ax})-**2j** (81% ee) can be considered comparatively high. It is notable that 1,3-dimethyl-substituted allyl substrates are reputed to be "unmanageable"[19] and it is difficult to reach high stereoselectivity in such cases. To the best of our knowledge, only two *P,N*-ligands demonstrated, after thorough optimization of the reaction conditions, enantioselectivity higher than 80%: one of the new generation phosphinooxazolines (70–90% ee)[20] and a 2-(phosphinoaryl)pyridine derived ligand (Scheme 2, R = Me, *i*Pr, Ph, 78–93% ee).[19] Hence, imino phosphite (R^{ax})-**2j** holds a noteworthy position, surpassing most of the known *P,N*-bidentate ligands.[21–23]

TABLE 1. Enantioselective allylic alkylation according to Scheme 2 (R = Et, L*/Pd = 2)

Entry	L*	Solvent	T, °C	Yield, %[a]	Ee, %
1	(R^{ax})-**2a**	THF	rt	30	2 (*S*)
2	(R^{ax})-**2a**	THF	–18	3	34 (*S*)
3	(R^{ax})-**2g**	THF	rt	50	26 (*R*)
4	(R^{ax})-**2g**	THF	5	45	21 (*R*)
5	(R^{ax})-**2g**	THF	–18	30	18 (*R*)
6	(S^{ax})-**2h**	THF	65	60	2 (*S*)
7	(S^{ax})-**2h**[b]	THF	rt	80	46 (*S*)
8	(S^{ax})-**2h**[c]	THF	rt	30	9 (*S*)
9	(S^{ax})-**2h**	THF	rt	90	58 (*S*)
10	(S^{ax})-**2h**	THF	5	70	43 (*S*)
11	(S^{ax})-**2h**	THF	–20	70	35 (*S*)
12	(S^{ax})-**2h**	CH_2Cl_2	rt	85	4 (*S*)
13	(S^{ax})-**2h**	Toluene	rt	0	—
14	(S^{ax})-**2h**	CH_3CN	rt	0	—
15	(R^{ax})-**2h**	THF	rt	95	5 (*S*)
16	(R^{ax})-**2h**	THF	5	65	11 (*S*)
17	(R^{ax})-**2h**	THF	–20	65	3 (*S*)
18	(R^{ax})-**2h**	CH_2Cl_2	rt	0	—
19	(S^{ax})-**2i**	THF	rt	90	41 (*R*)
20	(S^{ax})-**2i**	THF	–18	55	39 (*R*)
21	(R^{ax})-**2i**	THF	rt	95	48 (*R*)
22	(S^{ax})-**2j**	THF	rt	65	50 (*R*)
23	(S^{ax})-**2j**	CH_2Cl_2	rt	98	49 (*R*)
24	(R^{ax})-**2j**	THF	rt	25	74 (*R*)
25	(R^{ax})-**2j**[b]	THF	rt	55	76 (*R*)
26	(R^{ax})-**2j**	THF	5	86	81 (*R*)
27	(R^{ax})-**2j**	CH_2Cl_2	rt	93	19 (*R*)
28	(R^{ax})-**2j**	Toluene	rt	80	81 (*R*)
29	(S^{ax})-**2l**	THF	rt	20	7 (*S*)
30	(R^{ax})-**2n**	THF	rt	40	28 (*R*)

[a] Isolated yield.
[b] L*/Pd = 1.
[c] L*/Pd = 4.

LIGANDS POSSESSING ACYCLIC PHOSPHORUS CENTER

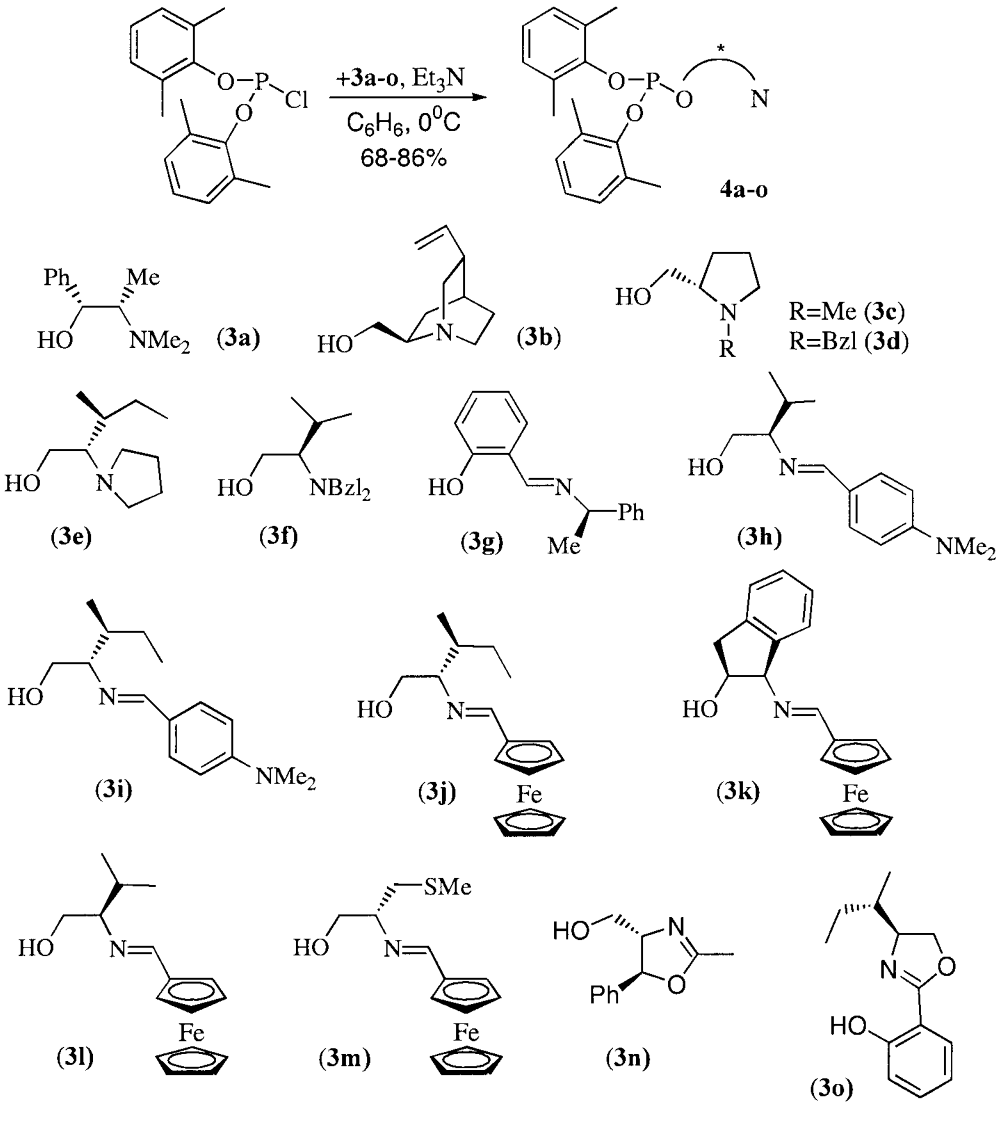
In practice, the vast majority of phosphite *P,N*-ligands contain a cyclic structure in which the phosphorus atom is a component of a heterocyclic ring. This feature is commonly believed to be responsible for an increase in ligand stability relative to acyclic systems.[15] But recently reported examples of acyclic chiral *P,N*-phosphites demonstrated high stability and synthetic accessibility combined with promising catalytic results,[8,9] which prompted us to develop new representatives of these literally unexplored ligands.

As a starting material for constructing the phosphorus atom environment bulky 2,6-dimethylphenol was employed, as sterically congested phosphorus is often favorable for high enantioselectivity.[24] Ligands **4a–o** were synthesized by one-step phosphorylation of the corresponding amino- and imino-alcohols using bis(2,6-dimethylphenyl) chlorophosphite (Scheme 3).[9] They were found to be soluble in conventional organic solvents and stable in dry conditions for several months.[25–27]

On treatment with $[Rh(CO)_2Cl]_2$, their chelate [Rh(CO)-Cl(L)] complexes were obtained. Notably, the ligands bearing cyclic **(4b–e)** or sterically hindered acyclic **(4f)** *sp*^{3}-nitrogen donor centers produced some amount of *trans*-$[Rh(CO)Cl(\eta^1\text{-}L)_2]$ complexes, in which the compounds function as *P*-monodentate ligands. Imino phosphites **4g–m** and phosphite-oxazolines **4n,o** proved to be more typical chelate ligands than amino phosphites, as the former gave chelate products only. Reaction of the imino phosphites and phosphite-oxazolines with Pd(II) metal precursors also produced chelates exclusively. Thus, ligands **4i,l,n** in the reaction with $[Pd(COD)Cl_2]$ delivered neutral $[PdCl_2(L)]$ complexes, while **4j** and **4o** gave [Pd(allyl)(L)]Cl cationic products in the reaction with $[Pd(allyl)Cl]_2$. All the metal complexes were fully characterized, including X-ray analysis of [Rh(CO)Cl**(4i)**], $[PdCl_2$**(4i)**] and $[PdCl_2$**(4l)**].[25]

The results achieved with the new *P,N*-(aryl phosphites) **4a–o** in the Pd-catalyzed allylic alkylation reaction (1) (Scheme 2) are summarized in Table 2.

Analogously to the BINOL-based ligands (see above), systems with *sp*^{2}-hybridized nitrogen atoms (up to 82% ee) are more effective than those with *sp*^{3}-nitrogen (<11% ee). Optical yields greatly depend on the substituent at the chiral center. More bulky substituent leads to higher enantioselectivity, as clearly demonstrated by the homologous ligands **4h** (24% ee) and **4i** (58% ee), as well as **4l** (38% ee)



Scheme 3. Synthesis of ligands **4a–o.**

and **4j** (82% ee). The same effect had the substituents attached to the imine group, as ligand **4j** possessing a bulky Cp_2Fe fragment delivered better results than structurally related **4i** bearing a smaller *p*$C_5H_4NMe_2$ building block.[25] This situation has strong analogies with the previously discussed BINOL-derived ligands **2i** and **2j.** In general, ligand **4j** demonstrated almost the same enantioselectivity as the best of the BINOL-derived ligand **2j,** which should be considered a good result for a simple acyclic *P,N*-phosphite, especially remembering the "unmanageability" of the used substrate.

When a sulfur nucleophile *p*$TolSO_2Na$ was employed (Scheme 4, Table 3), the main tendencies were similar to those in the reaction (1). In particular, the highest enantioselectivities were demonstrated by the ligands with distant imino groups. It is important to note that the optical yield produced by iminophosphite **4j** (80% ee) is the best so far achieved in this reaction using *P,N*-ligands. Phosphinooxazolines, the most effective previously described *P,N*-ligands, gave up to 59% ee.[28] Moreover, unlike phosphinooxazolines, our ligands did not give rise to the formation of a sulfinic acid ester as a side product. To the best of our knowledge, the only ligand giving higher results in the reaction (99% ee, with $Pd_2(dba)_3$ as a precatalyst) is one of Trost's *P,P*-bidentate ligands,[29] which form 13-membered chelate palladium complexes.[2]

In a very common testing reaction featured in Scheme 5, only oxazoline-phosphite **4n** was applied (Table 4). The reaction temperature and solvent can be varied without any loss of ee, but at a low temperature the reaction proceeds much slower. The demonstrated enantioselectivity is moderate, but nevertheless one of the highest achieved so far with *P,N*-phosphite ligands.[4,5,28]

Another phosphite-oxazoline, namely **4o,** was employed to good effect in Pd-catalyzed allylic sulfonylation (Scheme 6, Table 5). The preformed chelate palladium complex ap pears to be a superior catalyst in this case, affording 92% ee. This result is as high as that achieved with phosphino-

TABLE 2. Enantioselective allylic alkylation according to Scheme 2 (R = Et, L*/Pd = 2)

Entry	L*	Solvent	T, °C	Yield, %[a]	Ee, %
1	**4b**	THF	rt	90	11 (*S*)
2	**4d**	THF	rt	35	2 (*R*)
3	**4f**	THF	rt	30	4 (*S*)
4	**4h**	THF	rt	60	24 (*S*)
5	**4i**	THF	rt	50	58 (*S*)
6	**4i**	CH_2Cl_2	rt	85	57 (*R*)
7	**4j**	THF	65	65	49 (*R*)
8	**4j**	THF	rt	65	69 (*R*)
9	**4j**	THF	5	70	77 (*R*)
10	**4j**	THF	–18	25	52 (*R*)
11	**4j**	CH_3CN	rt	55	54 (*R*)
12	**4j**	DMF	rt	70	45 (*R*)
13	**4j**	$(CH_2OMe)_2$	rt	60	53 (*R*)
14	**4j**	Toluene	rt	60	61 (*R*)
15	**4j**	CH_2Cl_2	rt	80	80 (*R*)
16	**4j**	CH_2Cl_2	5	75	81 (*R*)
17	**4j**	CH_2Cl_2	–18	30	76 (*R*)
18	**4j**[b]	CH_2Cl_2	rt	80	82 (*R*)
19	**4k**	THF	rt	65	52 (*S*)
20	**4l**	THF	rt	75	38 (*S*)
21	**4l**	THF	–18	40	21 (*S*)
22	**4m**	CH_2Cl_2	rt	90	13 (*R*)

[a] Isolated yield.
[b] L*/Pd = 1.

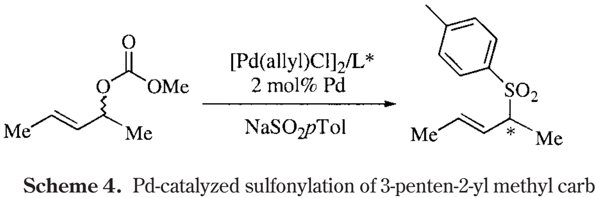
oxazolines, which are the most effective ligands described thus far for the reaction (up to 93% ee).[28]

In conclusion, the acyclic *P,N*-phosphite ligands **4a–o** have demonstrated their stability, synthetic accessibility, and promising results in a number of catalytic applications. This makes it possible to consider the discussed compounds as highly competitive chiral ligands deserving further investigation and development.

*P**-CHIRAL LIGANDS DERIVED FROM (S)-2-ANILINOMETHYLPYRROLIDINE

During the last few years, easily accessible (*S*)-2-anilinomethylpyrrolidine **(5)** has been actively used for the synthesis of ligands bearing chirality at the phosphorus atom. Thus, a highly diastereoselective reaction between **5** and $P(NMe_2)_3$ followed by addition of various alcohols gave rise to a series of *P*-chiral pyridine-phosphines.[7,31,32] These compounds were applied to good effect in asymmetric allylic alkylation and amination, which prompted us to broaden the range of these promising ligands, as well as their catalytic applications.

The synthesis of new *P,N*-ligands **8a–c** is featured in Scheme 7. For the first time, we found that the reaction of



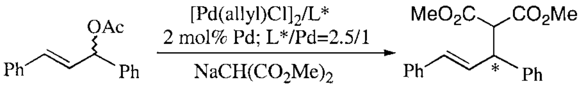
(2)

Scheme 4. Pd-catalyzed sulfonylation of 3-penten-2-yl methyl carbonate with sodium *p*-toluenesulfinate.

TABLE 3. Enantioselective allylic sulfonylation according to Scheme 4

Entry	L*	L*/Pd ratio	Solvent	T, °C	Yield, %[a]	ee, %
1	**4b**	2/1	THF	rt	47	12 (*S*)
2	**4c**	2/1	THF	rt	22	10 (*S*)
3	**4i**	2/1	THF	rt	63	44 (*R*)
4	**4i**	2/1[b]	THF	rt	53	46 (*R*)
5	**4i**	2/1	THF	0	48	56 (*R*)
6	**4i**	1/1	THF	rt	65	50 (*R*)
7	**4i**	1/1	DCM	rt	59	50 (*R*)
8	**4j**	2/1	THF	rt	74	63 (*R*)
9	**4j**	2/1	THF	0	51	78 (*R*)
10	**4j**	2/1[b]	THF	0	38	76 (*R*)
11	**4j**	1/1	DCM	rt	45	76 (*R*)
12	**4j**	1/1	DCM	0	21	80 (*R*)
13	**4k**	2/1	THF	rt	69	45 (*S*)
14	**4k**	2/1	THF	0	42	54 (*S*)
15	**4k**	1/1	THF	–20	20	50 (*S*)

[a] Isolated yield.
[b] $Pd_2(dba)_3$ × $CHCl_3$.



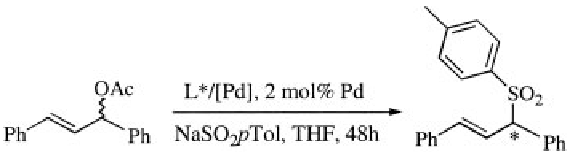
(3)

Scheme 5. Pd-catalyzed alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate sodium salt using ligand **4n.**

TABLE 4. Enantioselective allylic alkylation according to Scheme 5

Entry	Solvent	T, °C	Time (h)	Yield, %[a]	Ee, %
1	THF	rt	3	75	85 (*R*)
2	CH_2Cl_2	rt	3	83	85 (*R*)
3	THF	0°C	48	21	85 (*R*)

[a] Isolated yield.



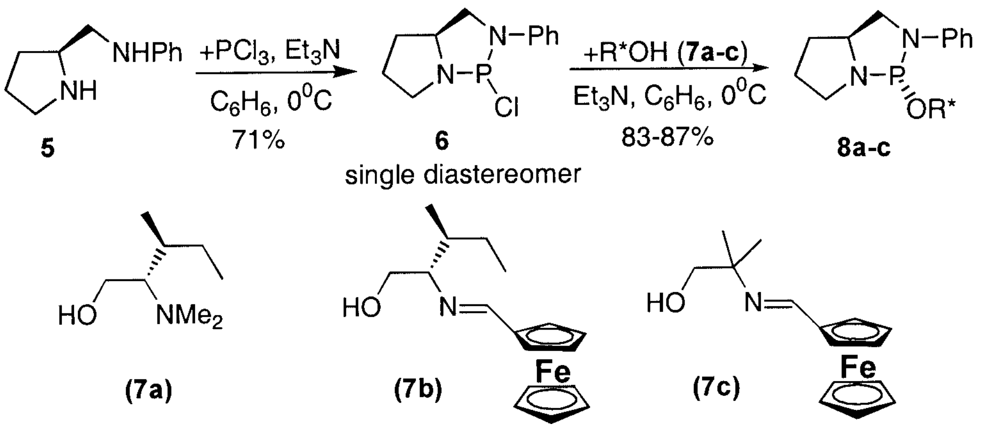
(4)

Scheme 6. Pd-catalyzed sulfonylation of 1,3-diphenyl-2-propenyl acetate with sodium *p*-toluenesulfinate.

TABLE 5. Enantioselective allylic sulfonylation according to Scheme 6 using ligand 4o

No.	Catalyst	Yield, %[a]	ee, %
1	$[Pd(allyl)Cl]_2/2L^*$	45	84 (*S*)
2	$[Pd(allyl)Cl]_2/4L^*$	48	88 (*S*)
3	$[Pd(allyl)(L)]BF_4$	57	92 (*S*)
4	$Pd_2(dba)_3$ × $CHCl_3/2L^*$	50	80 (*S*)

[a] Isolated yield.



Scheme 7. Synthesis of ligands **8a–c.**

5 with PCl_3 produces the chloro derivative **6** as a single diastereomer. Therefore, in contrast to known procedures, it became possible to perform the second step in mild conditions avoiding prolonged refluxing in toluene.[7,31–34] All three compounds **8a–c** were obtained in diastereomerically pure form, and the configuration of the phosphorus atom was determined as *R*. Reaction of **8a–c** with $[Rh(CO)_2Cl]_2$ produced rhodium chelates [Rh(CO)Cl(L)] selectively and in nearly quantitative yield. Complexation of **8a–c** with $[Pd(allyl)Cl]_2$ also proceeded cleanly, affording chelate products [Pd(allyl)(L*)]Cl, which can be easily transformed into complexes with other counterions by interaction with the corresponding silver salts.

The new chiral ligands were tested in the allylic sulfonylation reaction (4) (Scheme 6, Table 6). Again, the ligand bearing sp^3-hybride nitrogen **(8a)** showed generally lower activity and stereoselectivity than **8b** and **8c,** which possess sp^2-hybride nitrogen. Increasing the L*/Pd ratio was found to slightly improve the enantioselectivity. The highest enantioselectivity level was achieved with preformed chelates [Pd(allyl)(L*)]X, especially when $X = BF_4^-$ (Table 6, entries 8 and 10). It is remarkable that the enantioselectivities shown by ligands **8b** (96% ee) and **8c** (97% ee) are the best so far achieved in the reaction, surpassing the 93% ee optical yield previously obtained with chiral phosphinooxazolines.[28]

TABLE 6. Enantioselective allylic sulfonylation according to Scheme 6 using ligands 8a–c

Entry	Ligand	Catalyst	Yield, %[a]	Ee, %
1	**8a**	$[Pd_2(dba)_3 \times CHCl_3]/2L^*$	16	20 (*S*)
2	**8a**	$[Pd(allyl)Cl]_2/2L^*$	29	87 (*S*)
3	**8a**	$[Pd(allyl)Cl]_2/4L^*$	20	90 (*S*)
4	**8a**	$[Pd(allyl)(L^*)]BF_4$	29	83 (*S*)
5	**8b**	$[Pd_2(dba)_3 \times CHCl_3]/2L^*$	29	88 (*S*)
6	**8b**	$[Pd(allyl)Cl]_2/4L^*$	78	84 (*S*)
7	**8b**	[Pd(allyl)(L*)]Cl	94	80 (*S*)
8	**8b**	$[Pd(allyl)(L^*)]BF_4$	99	96 (*S*)
9	**8c**	$[Pd(allyl)Cl]_2/2L^*$	26	94 (*S*)
10	**8c**	$[Pd(allyl)(L^*)]BF_4$	85	97 (*S*)

[a] Isolated yield.

CONCLUSION

We have developed three groups of chiral *P,N*-hybrid phosphites and phosphoramidites, which generally behave as typical chelating ligands. The investigated ligands have demonstrated moderate to excellent enantioselectivities in the Pd-catalyzed allylic alkylation (81–85% ee) and, especially, allylic sulfonylation reactions (80–97% ee). Remarkably, in the reaction (4) (Scheme 6) ligands **8b** and **8c** have outperformed all previously tested catalytic systems, affording optical yields of up to 97% ee. In general, the ligands possessing sp^2-nitrogen were more effective than those bearing sp^3-nitrogen. For imino phosphites, the ligands with bulky substituents at the C*-chiral centers, as well as at the imino groups, have been found to be superior. It has been shown for the first time that phosphite ligands possessing acyclic phosphorus can be easily accessible, stable, and efficient in terms of stereoselectivity.

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LITERATURE CITED

1. Pfaltz A, Lautens M. Allylic substitution reactions. In: Jacobsen EN, Pfaltz A, Yamamoto H, editors. Comprehensive asymmetric catalysis. Berlin: Springer; 1999. Vol. 2. p 881.
2. Trost BM, Lee C. Asymmetric allylic alkylation reactions. In: Ojima I, editor. Catalytic asymmetric synthesis, 2nd ed. New York: Wiley-VCH; 2000. p 593–649.
3. Pretot R, Pfaltz A. New ligands for regio- and enantiocontrol in Pd-catalyzed allylic alkylation. Angew Chem Int Ed 1998;37:323–325.
4. Hilgraf R, Pfaltz A. Chiral bis(N-tosylamino)phosphite- and TADDOL-phosphiteoxazolines as ligands in asymmetric catalysis. Synlett 1999: 1814–1816.
5. Arena CG, Drommi D, Faraone F. Steric and chelate ring size effects on the enantioselectivity in palladium catalyzed allylic alkylation with new chiral *P,N*-ligands. Tetrahedron: Asymmetry 2000;11:4753–4759.
6. Mccarty M, Guiry PJ. Axially chiral bidentate ligands in asymmetric catalysis. Tetrahedron 2001;57:3809–3844.
7. Delapierre G, Brunel JM, Constantieux T, Buono G. Design of a new class of chiral quinoline-phosphine ligands. Synthesis and application in asymmetric catalysis. Tetrahedron: Asymmetry 2001;12:1345–1352.
8. Gavrilov KN, Polosukhin AI, Bondarev OG, Korostylev AV, Lyubimov

SE, Shiryaev AA, Starikova ZA, Davankov VA. Iminophosphites as new chiral *P,N*-bidentate ligands. Mendeleev Commun 2001:33–35.

9. Polosukhin AI, Bondarev OG, Korostylev AV, Hilgraf R, Davankov VA, Gavrilov KN. Phosphite derivatives of (2*R*)-2-N-pyrrolidin-1-yl-butan-1-ol: synthesis, chelation with Rh(I) and testing in the Pd-catalysed allylic alkylation. Inorg Chim Acta 2001;323:55–61.
10. Escher IH, Pfaltz A. New chiral oxazoline-phosphite ligands for the enantioselective copper-catalyzed 1,4-addition of organozinc reagents to enones. Tetrahedron 2000;56:2879–2888.
11. Knöbel AKH, Escher IH, Pfaltz A. Enantioselective copper-catalyzed 1,4-addition of organozinc reagents to enones using chiral oxazoline-phosphite ligands. Synlett 1997:1429–1431.
12. Hu X, Chen H, Zhang X. Development of new chiral P,N ligands and their application in the Cu-catalyzed enantioselective conjugate addition of diethylzinc to enones. Angew Chem Int Ed 1999;38:3518–3521.
13. Alexakis A, Benhaim C. Enantioselective copper-catalysed conjugate addition. Eur J Org Chem 2002;19:3221–3226.
14. Molt O, Scrader T. Asymmetric synthesis with chiral cyclic phosphorus auxiliaries. Synthesis 2002:2633–2670.
15. Ansell J, Wills M. Enantioselective catalysis using phosphorus-donor ligands containing two or three P-N or P-O bonds. Chem Soc Rev 2002;31:259–268.
16. Gavrilov KN, Bondarev OG, Lebedev RV, Polosukhin AI, Shyryaev AA, Lyubimov SE, Petrovskii PV, Moiseev SK, Kalinin VN, Ikonnikov NS, Davankov VA, Korostylev AV. New amino-, imino- and oxazolinophosphites based on 1,1′-bi-2-naphtol: coordination and catalytic properties. J Organomet Chem 2002;655:204–217.
17. Korostylev AV, Bondarev OG, Kovalevsky AY, Petrovskii PV, Davankov VA, Gavrilov KN. Complexation properties of aminophosphites bearing phosphorus and nitrogen atoms included in six-membered cycles. Inorg Chim Acta 2001;312:117–124.
18. Datta D, Majumdar D. Steric effects of alkyl groups: a cone angle approach. J Phys Org Chem 1991;4:611–617.
19. Ito K, Kashiwagi R, Iwasaki T, Katsuki T. Asymmetric allylic alkylation using a palladium complex of chiral 2-(phosphinoaryl)pyridine ligands. Synlett 1999:1563–1566.
20. Weise B, Helmchen G. Chiral phosphinooxazolines with a bi- or tricyclic oxazoline moiety—applications in Pd-catalyzed allylic alkylations. Tetrahedron Lett 1998;39:5727–5730.
21. Saitoh A, Achiwa K, Tanaka K, Morimoto T. Versatile chiral bidentate ligands derived from amino acids: synthetic applications and mechanistic considerations in the palladium-mediated asymmetric allylic substitutions. J Org Chem 2000;65:4227–4240.
22. Liu S, Müller JFK, Neuburger M, Schaffner S, Zehnder M. Synthesis, X-ray crystal-structure analysis, and NMR studies of (3-allyl)palladium(II) complexes containing a novel dihydro(phosphinoaryl)oxazine ligand: application in palladium-catalyzed asymmetric synthesis. Helv Chim Acta 2000;83:1256–1267.
23. Vyskocil S, Smrcina M, Hanus V, Polasek M, Kocovsky P. Derivatives of 2-amino-2′-diphenylphosphino-1,1′-binaphthyl (MAP) and their application in asymmetric palladium(0)-catalyzed allylic substitution. J Org Chem 1998;63:7738–7748.
24. Buisman GJH. Asymmetric hydroformylation with chiral diphosphite ligands. University of Amsterdam; 1995.
25. Gavrilov KN, Bondarev OG, Lebedev RV, Shiryaev AA, Lyubimov SE, Polosukhin AI, Grintselev-Knyazev GV, Lyssenko KA, Moiseev SK, Ikonnikov NS, Kalinin VN, Davankov VA, Korostylev AV, Gais HJ. Easily accessible chiral *P,N*-bidentate arylphosphites, their complexation and application in enantioselective allylic alkylation, sulfonylation and hydrosilylation. Eur J Inorg Chem 2002;5:1367–1376.
26. Polosukhin AI, Bondarev OG, Lyubimov SE, Korostylev AV, Lyssenko KA, Davankov VA, Gavrilov KN. New chiral phosphite ligands bearing *sp*^{2}-nitrogen: complexation properties and palladium(II)-catalysed enantioselective allylic alkylation. Tetrahedron: Asymmetry 2001;12:2197–2204.
27. Bondarev OG, Lyubimov SE, Shiryaev AA, Kadilnikov NE, Davankov VA, Gavrilov KN. New highly efficient chiral phosphitooxazoline ligand for Pd-catalyzed asymmetric allylic sulfonylation. Tetrahedron: Asymmetry 2002;13:1587–1588.
28. Eichelmann H, Gais HJ. Palladium-catalyzed asymmetric allylic sulfonylation. Tetrahedron: Asymmetry 1995;6:643–646.
29. Trost B, Radinov R. On the effect of a cation binding site in an asymmetric ligand for a catalyzed nucleophilic substitution reaction. J Am Chem Soc 1997;119:5962–5963.
30. Brunel JM, Constantieux T, Buono G. A practical method for the large-scale synthesis of diastereomerically pure (2R,5S)-3-phenyl-2-(8-quinolinoxy)-1,3-diaza-2-phosphabicyclo-[3.3.0]-octane ligand (QUIPHOS). Synthesis and X-ray structure of its corresponding chiral π-allyl palladium complex. J Org Chem 1999;64:8940–8942.
31. Brunel JM, Constantieux T, Labande A, Lubatti F, Buono G. Enantioselective palladium catalyzed allylic substitution with new chiral pyridine-phosphine ligands. Tetrahedron Lett 1997;38:5971–5974.
32. Constantieux T, Brunel JM, Labande A, Buono G. Enantioselective palladium catalyzed allylic amination using new chiral pyridine-phosphine ligands. Synlett 1998:49–50.
33. Breeden SW, Wills M. ESPHOS and SEMI-ESPHOS: a new family of mono- and bidentate diazaphospholidine ligands for asymmetric catalysis. J Org Chem 1999;64:9735–9738.
34. Bondarev OG, Gavrilov KN, Tsarev VN, Davankov VA, Lebedev RV, Moiseev SK, Kalinin VN. Pd-catalysed asymmetric allylation and complexation using P,N-bidentate derivatives of (S)-2-anilinemethylpirrolidine. Russ Chem Bull 2002;51:521–525.