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NOBIN-based chiral phosphite-type ligands and their application in asymmetric catalysis

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Abstract: *P**-monodentate diamidophosphite and diastereomeric *P,N*-containing phosphite ligands have been synthesized from enantiomerically pure *N*-Bn-NOBIN and used as asymmetric inductors in Pd-catalyzed allylic substitution and Cu-catalyzed conjugate addition reactions. The best results (up to 93% *ee*) were obtained for the Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate with 1-cyclohexenylpyrrolidine. The reactions of *P,N*-containing ligands with $Pd(COD)Cl_2$ at molar ratios of L/M = 1 and 2 were studied using ^{1}H, ^{13}C and ^{31}P NMR spectroscopy as well as HRESI mass spectrometry, showing the *trans*-$PdCl_2L_2$ complex was the only product.

Keywords: Asymmetric allylic substitution; Palladium; Asymmetric conjugate addition; Copper; Phosphorus ligands.

Chiral phosphite ligands are extremely attractive for transition-metal-mediated asymmetric catalysis. Indeed they can be simply prepared from readily accessible precursors, are less sensitive to air and other oxidizing agents than typical phosphanes, and are inexpensive. This has allowed the generation of extensive libraries of structurally diverse chiral ligands. In addition, phosphite-type ligands are characterized by a highly modular structure and pronounced

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π-acceptor capacity. See, for example, selected review articles[1-6] and literature reports regarding chiral phosphites,[7-13] phosphoramidites[14-19] and diamidophosphites.[20,21]

The careful selection of a suitable chiral backbone has become crucial in the design of any modern stereoinducer for enantioselective catalysis.[22] Several naturally occuring building blocks, as well as binaphthyl and biphenyl derivatives, have been widely used in the development of phosphite-type chiral ligands.[1-3,8,9,14,22] Conversely, there are only a few examples of phosphite-type ligands $\mathbf{L_{A-C}}$ (Figure 1) based on the NOBIN [(2'-amino-[1,1'-binaphthalen]-2-ol)] chiral synthon[23-29] which is surprising since chiral phosphanes with the NOBIN framework are well-known.[30-37]

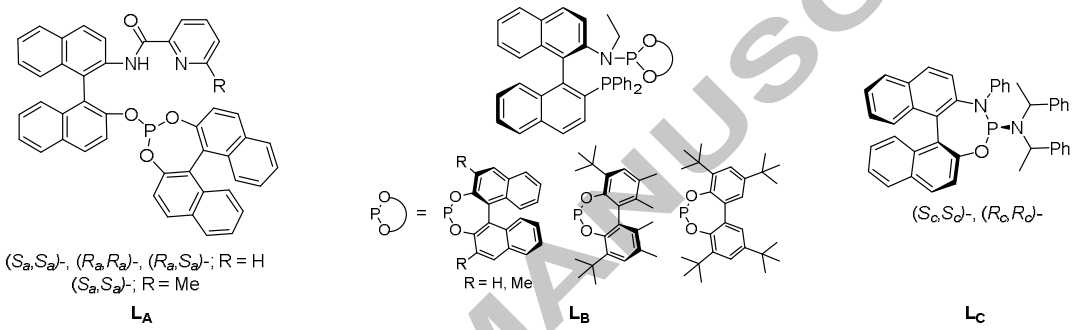
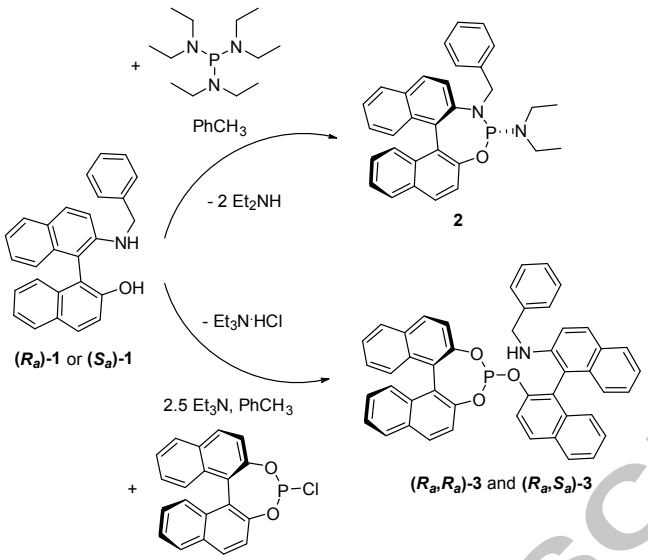


Figure 1. Phosphite-type ligands with the NOBIN backbone.

Herein, we describe the synthesis of new NOBIN-derived *P**-monodentate diamidophosphite and *P,N*-bidentate phosphite ligands as well as their catalytic performance in asymmetric Pd-catalyzed allylic alkylation and Cu-catalyzed conjugate addition reactions. The Pd-catalyzed allylic substitution reaction is a powerful and well-established synthetic tool, which is tolerant of various functional groups and operates with a wide range of nucleophiles. As a consequence this reaction is widely used in the synthesis of enantiomerically pure natural and unnatural compounds.[7,38-47] In particular, the products of alkylation with dimethyl malonate, which proceeds under mild conditions and without involvement of the *C**-stereocenter, can easily be converted to esters and amides of chiral unsaturated carboxylic acids.[46] The Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate with 1-cyclohexenylpyrrolidine has also been used as a key step in the synthesis of a selective antimuscarinic agent.[47,48] Finally, this represents a common benchmark test for initial ligand screening and the enantiomeric excesses obtained are the simplest indexes for the evaluation of new chiral ligands.[7,45,49] Another target, the hydrometallation – Cu-catalyzed 1,4-addition reaction is an operationally simple and convenient process which is tolerant of many functional groups and has been used for the highly enantioselective one-step synthesis of steroid derivatives.[50-53]



Scheme 1. Synthesis of ligands **2**, **(*R*$_a$,*R*$_a$)-3** and **(*R*$_a$,*S*$_a$)-3**.

Starting from (*R*$_a$)- or (*S*$_a$)-BINOL, both enantiomers of *N*-Bn-NOBIN (**(*R*$_a$)-1** and **(*S*$_a$)-1**)) were readily prepared following known methodology.[36,37,54,55] With these enantiomers in hand, *P**-monodentate diamidophosphite **2** as well as *P,N*-containing phosphites **(*R*$_a$,*R*$_a$)-3** and **(*R*$_a$,*S*$_a$)-3** were prepared in a single-step (Scheme 1). Diamidophosphite **2** was synthesized by the direct phosphorylation of **(*R*$_a$)-1** with *N,N,N',N',N'',N''*-hexaethylphosphanetriamine in boiling toluene. This method did not require additional base and the only by-product was volatile $HNEt_2$. Compounds **(*R*$_a$,*R*$_a$)-3** and **(*R*$_a$,*S*$_a$)-3** were obtained by phosphorylation of the corresponding enantiomer of *N*-Bn-NOBIN with (*R*$_a$)-4-chlorodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine[56] in toluene, utilising Et_3N as a HCl scavenger. Compounds **2**, **(*R*$_a$,*R*$_a$)-3** and **(*R*$_a$,*S*$_a$)-3** were obtained as white solids and were found to be sufficiently stable to allow manipulation in the open air and could be stored under dry conditions at room temperature for at least a few months with minimal degradation. Phosphites **(*R*$_a$,*R*$_a$)-3** and **(*R*$_a$,*S*$_a$)-3** readily formed solvates with toluene. Therefore, crystallization from heptane and extended drying under high vacuum were required for the preparation of analytically pure material.

Ligands **2**, **(*R*$_a$,*R*$_a$)-3** and **(*R*$_a$,*S*$_a$)-3** were fully characterized by ^{31}P, ^{1}H and ^{13}C NMR spectroscopy 2D-NMR (COSY, NOESY, HSQC and HMBC), MALDI TOF/TOF mass spectrometry as well as elemental analysis. The data collected was in accordance with the proposed structures. Diamidophosphite **2** with a *P**-stereocenter was formed as single stereoisomer, as indicated by the narrow singlet at δ_P 152.6 observed in the ^{31}P NMR spectrum in $CDCl_3$. It should be emphasized that during the preparation of **(*R*$_a$,*R*$_a$)-3** and **(*R*$_a$,*S*$_a$)-3**, phosphorylation occured exclusively at the hydroxyl group. Note, the presence of signals

characteristic of the protons of the peripheral amino group (δ_H 4.32, d, ^3J = 6.1 Hz, 2H, NCH_2 and δ_H 4.02, t, ^3J = 6.1 Hz, 1H, NH) in the ^{1}H NMR spectrum of solvate **(R_a,R_a)-3** with toluene (see ESI).

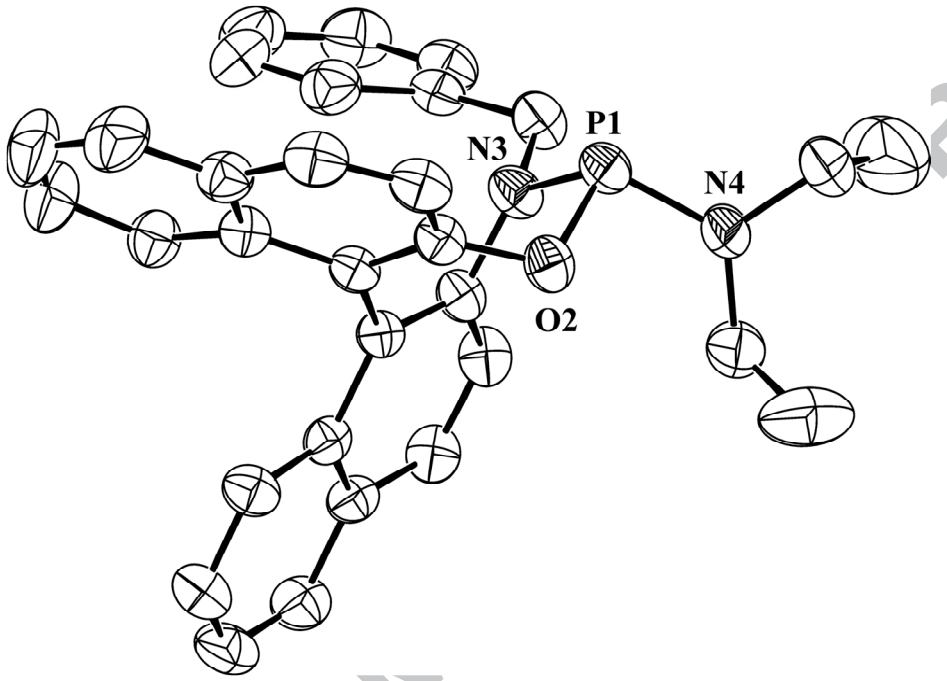
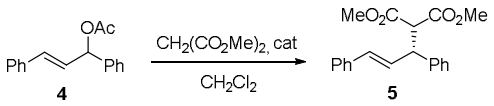


Figure 2. The molecular structure of diamidophosphite **2**, showing the atomic numbering of non-carbon atoms and 40% probability displacement ellipsoids. H atoms have been omitted for clarity.

Single crystals suitable for X-ray crystal structure analysis were obtained for diamidophosphite **2** by crystallisation from toluene at – 20 °C. This analysis showed that ligand **2** crystallizes in the chiral orthorhombic space group $P2_12_12_1$. The *N*-Bn-NOBIN framework corresponded to the (*R*)-enantiomer and the absolute configuration at phosphorus was (*S*) (Figure 2). Note that similar ligands $\mathbf{L_C}$ (Figure 1) containing the (S_a)-*N*-Ph-NOBIN core were found to have *P**-stereocenters with the (*R*)-configuration, irrespective of the absolute configuration of the bis(1-phenylethyl)amine fragment.[29] The mean planes of the two naphthalene cores were inclined to each other at 61.2(2)° and the P1–O2 bond length was 1.665(3) Å. The exocyclic P1–N4 bond (1.649(3) Å) was considerably shorter than the P1–N3 bond (1.730(3) Å) within the 1,3,2-oxazaphosphepine ring, which exhibited a boat conformation. The exocyclic nitrogen atom N4 was planar, whereas the N3 nitrogen was slightly pyramidal (sums of all angles were 360.0(5)° and 354.6(5)°, respectively). The O2–P1–N3 and O2–P1–N4 angles (96.15(14) and 98.52(16)°) showed significant distortions from the tetrahedral arrangements around the *P**-stereocenter meaning the phosphorus lone pair was not hindered by bulky substituents. A search

of the Cambridge Structural Database (CSD, Version 5.35[57] for compounds containing asymmetric phosphorus atoms bonded to the NOBIN fragment has showed no hits.

Table 1. Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate **4** with dimethyl malonate [a]



4 **5**

Entry	*Ligand*	*L/Pd*	*Conversion (%)*	*ee (%)* [b,c]
1	**2**	1	42	4 (*R*)
2	**2**	2	47	55 (*R*)
3	**(*R*$_a$,*R*$_a$)-3**	1	57	78 (*R*)
4	**(*R*$_a$,*R*$_a$)-3**	**2**	**86**	**88 (*R*)**
5	**(*R*$_a$,*S*$_a$)-3**	1	0	-
6	**(*R*$_a$,*S*$_a$)-3**	2	0	-
7	**(*R*$_a$,*R*$_a$)-3**	1	50	57 (*R*) [d]
8	**(*R*$_a$,*R*$_a$)-3**	2	40	13 (*R*) [d]
9	**(*R*$_a$,*S*$_a$)-3**	1	70	50 (*R*) [e]
10	**(*R*$_a$,*S*$_a$)-3**	2	38	31 (*R*) [e]

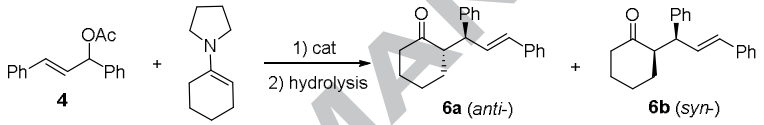
[a] Reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ in CH_2Cl_2 at 18 °C for 48 h, BSA (0.11 mL, 0.44 mmol), KOAc (0.002 g).
[b] Conversion and *ee* were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 99/1, 0.3 mL/min, 254 nm, *t*(*R*) = 28.0 min, *t*(*S*) = 29.3 min).
[c] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[75]
[d] Equimolar mixture of ligand **(*R*$_a$,*R*$_a$)-3** and ZnTPP.
[e] Equimolar mixture of ligand **(*R*$_a$,*S*$_a$)-3** and ZnTPP.

The *N*-Bn-NOBIN-derived ligands **2**, **(*R*$_a$,*R*$_a$)-3** and **(*R*$_a$,*S*$_a$)-3** were evaluated in the Pd-catalyzed asymmetric allylic alkylation reaction of (*E*)-1,3-diphenylallyl acetate **4** with dimethyl malonate using $[Pd(allyl)Cl]_2$ as a palladium source (Table 1). The nucleophile was generated *in situ* using *N,O*–bis(trimethylsilyl) acetamide (BSA) and a catalytic amount of KOAc. *P**-Monodentate ligand **2** showed moderate conversion and enantioselectivity (up to 47% conversion, 55% *ee*, Table 1, entries 1, 2). *P,N*-Bidentate phosphite **(*R*$_a$,*R*$_a$)-3** showed significantly higher conversion and asymmetric induction (up to 86% conversion, 88% *ee*, Table 1, entries 3, 4). In all cases the molar ratio L/Pd = 2 was found to be optimal and the major substitution product had the (*R*)-configuration. Rather surprisingly the diastereomeric ligand **(*R*$_a$,*S*$_a$)-3** generated an inactive catalytic species (Table 1, entries 5, 6).

It is well known that asymmetric catalysts are often very sensitive to small changes in reaction conditions and the addition of suitable achiral compounds which support the chiral catalyst system can be beneficial to the yields and enantioselectivities obtained.[58,59] We observed

that the addition of an equimolar amount of zinc(II) 5,10,15,20-tetraphenylporphyrin (ZnTPP) to ligands **(R_a,R_a)-3** or **(R_a,S_a)-3** prior to addition of $[Pd(allyl)Cl]_2$ had a pronounced influence on both the conversion and asymmetric induction. In particular, **(R_a,R_a)-3** proved to be less efficient in the presence of ZnTPP (up to 50% conversion, 57% *ee* Table 1, entries 7, 8). At the same time, **(R_a,S_a)-3** now afforded product (*R*)-**5** with moderate conversion and enantiomeric purity (up to 70% conversion, 50% *ee*, Table 1, entries 9, 10). It should be noted that N-Zn coordination was not observed by ^1H, ^{13}C and NOESY NMR analyses of equimolar mixtures of **(R_a,R_a)-3** or **(R_a,S_a)-3** with ZnTPP in $CDCl_3$. Therefore, we can speculate that the large aromatic surface of the zinc(II) porphyrin molecule likely plays an important role by creating a pocket that directs the substrate. It is appropriate to assume that π-π interactions between ZnTPP and the aromatic groups of the substrate and (or) ligand can participate here.[60]

Table 2. Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate **4** with 1-cyclohexenylpyrrolidine[a]



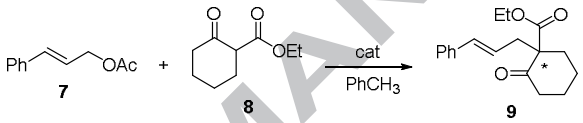
Entry	*Ligand*	*L/Pd*	*T (°C)*	*Conversion (%)* [b]	*anti/syn* [c,d]	*ee (%) **6a/6b***
1	**(R_a,R_a)-3**	1	18	64	79/21	11/85
2	**(R_a,R_a)-3**	2	18	80	71/29	16/44
3	**(R_a,R_a)-3**	1	30	92	73/27	24/84
4	**(R_a,R_a)-3**	2	30	98	54/46	4/9
5	**(R_a,S_a)-3**	1	18	39	56/44	9/78
6	**(R_a,S_a)-3**	**2**	**18**	**52**	**80/20**	**49/93**
7	**(R_a,S_a)-3**	1	30	93	50/50	21/25
8	**(R_a,S_a)-3**	2	30	98	63/37	12/39

[a] Reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ in CH_2Cl_2 for 48 h.
[b] Conversion and *ee* were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*-PrOH = 96/4, 0.5 mL/min, 254 nm, *t*(*S*,*R*)-**6b** = 14.0 min, *t*(*R*,*S*)-**6b** = 15.1 min; *t*(*S*,*S*)-**6a** = 16.9 min, *t*(*R*,*R*)-**6a** = 19.0 min).
[c] Determined by ^1H NMR.
[d] The absolute configuration of the predominant enantiomers of the *anti*- and *syn*-products was assigned by comparison of the HPLC retention times reported in the literature.[62, 63]

Ligands **2**, **(R_a,R_a)-3** and **(R_a,S_a)-3** were also applied to the Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate **4** with 1-cyclohexenylpyrrolidine (Table 2). Enamines can serve as convenient nucleophiles for Pd-catalyzed asymmetric allylic alkylations, avoiding the need to generate unstablilized ketone enolates using strong bases. However, successful examples of Pd-catalyzed enantioselective allylic substitution with enamines are scarce, and this transformation

remains a challenge.[20,47,61-63] Ligand **2** gave no conversion in this reaction, while ligands **(R_a,R_a)-3** and **(R_a,S_a)-3** led to the desired product as a mixture of *anti*- and *syn*- diastereomers **6a** (up to 49% *ee*) and **6b** (up to 93% *ee*), respectively, with low to good conversion and diastereomeric ratios. While the best diastereoselectivity and asymmetric induction were obtained with ligand **(R_a,S_a)-3** (Table 2, entry 6), its diastereoisomer **(R_a,R_a)-3** produced better conversion at room temperature (Table 2, entries 1, 2 and 5, 6). The optimal L/Pd molar ratio was found to be 1 for **(R_a,R_a)-3**, and 2 for **(R_a,S_a)-3**. Excellent conversion was obtained at elevated temperatures, but the degree of diastereoselectivity was reduced in all cases. For the most part, better enantioselectivity was observed at 18 °C. To the best of our knowledge, the reaction with 1-cyclohexenylpyrrolidine is the second example using phosphite-type ligands in the Pd-catalyzed asymmetric allylic alkylation with enamine nucleophiles.[20]

Table 3. Pd-catalyzed allylic alkylation of cinnamyl acetate **7** with ethyl 2-oxocyclohexane-1-carboxylate **8** [a]

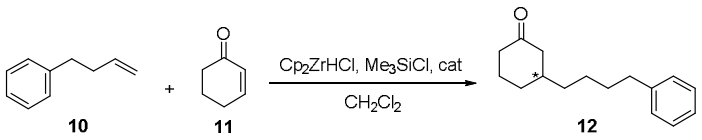


Entry	*Ligand*	*L/Pd*	*Conversion (%)*	*ee (%)* [b,c]
1	**2**	**1**	**44**	**65 (*R*)**
2	**2**	2	0	-
3	**(R_a,S_a)-3**	1	47	62 (*S*)
4	**(R_a,S_a)-3**	2	68	29 (*S*)
5	**(R_a,R_a)-3**	1	0	-
6	**(R_a,R_a)-3**	2	0	-

[a] Reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ in toluene at 20 °C for 48 h, BSA (0.25 mL, 1 mmol), $Zn(OAc)_2$ (0.005 g).
[b] Conversion and *ee* were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*-PrOH = 95/5, 0.4 mL/min, 254 nm, $t(R)$ = 14.3 min, $t(S)$ = 16.4 min).
[c] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[63]

Ligands **2**, **(R_a,R_a)-3** and **(R_a,S_a)-3** were also screened in the allylic alkylation of cinnamyl acetate **7** with ethyl 2-oxocyclohexane-1-carboxylate **8**. It should be noted that the Pd-catalyzed enantioselective synthesis of a quaternary carbon center is still a formidable challenge (Table 3).[38,63,65] Both *P**-monodentate diamidophosphite **2** and phosphite **(R_a,S_a)-3** gave similar results, furnishing quaternary-substituted products (*R*)-**9** and (*S*)-**9** in 44% conversion, 65% *ee* and 47% conversion, 62% *ee*, respectively (Table 3, entries 1, 3). For both ligands L/Pd = 1 was found as the optimal molar ratio. Unfortunately, phosphite **(R_a,R_a)-3** gave no conversion.

Table 4. Hydrometallation of 4-phenyl-1-butene **10** – Cu-catalyzed conjugate addition to cyclohex-2-enone **11** [a]



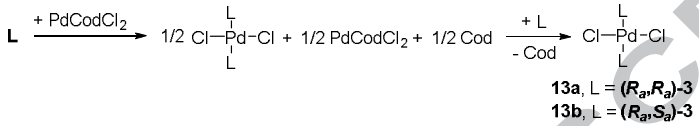
Entry	*Ligand*	*L/Cu*	*Yield (%)*	*ee (%)* [b,c]
1	**2**	**1**	**71**	**44 (*R*)**
2	**2**	2	86	36 (*R*)
3	**(R_a,R_a)-3**	1	0	-
4	**(R_a,R_a)-3**	2	91	18 (*S*)
5	**(R_a,S_a)-3**	1	82	15 (*R*)
6	**(R_a,S_a)-3**	2	44	5 (*R*)

[a] Reactions were carried out with 5 mol% of $(CuOTf)_2 \cdot C_6H_6$ in CH_2Cl_2 at 20 °C for 14 h.
[b] The *ee* was determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*-PrOH = 95/5, 1.0 mL/min, 210 nm, $t(R)$ = 7.6 min, $t(S)$ = 8.1 min).
[c] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[50]

Finally, the Cu-catalyzed conjugate addition of an alkylzirconium reagent (generated *in situ* by hydrometallation of 4-phenyl-1-butene **10** with Schwartz reagent) to cyclohex-2-enone **11** was investigated (Table 4). The reaction of *P**-monodentate ligand **2** in the presence of $(CuOTf)_2 \cdot C_6H_6$ gave product **12** in up to 44% *ee* (Table 4, entries 1, 2). Conversely, phosphites **(R_a,R_a)-3** and **(R_a,S_a)-3** showed variable yields and low enantioselectivity (Table 4, entries 3–6). It should be noted that the asymmetric induction of this reaction is difficult to control. Indeed, subtle differences in the structure of the phosphoramidite ligands have been reported to have a large effect on the enantioselectivity.[50]

The presence of phosphorus and nitrogen donor centers in **(R_a,R_a)-3** and **(R_a,S_a)-3** makes it theoretically possible that *P,N*-bidentate chelate or bridging coordination modes are occurring. In order to shed light on the coordination properties of **(R_a,R_a)-3** and **(R_a,S_a)-3**, we carried out investigations of the palladium complexes obtained from these ligands. As a main precursor to study the coordination behavior of **(R_a,R_a)-3** and **(R_a,S_a)-3**, $Pd(COD)Cl_2$ (COD - cycloocta-1,5-diene) was selected, which is known to give stable complexes with phosphites and phosphoramidites.[66-69] However, the solutions produced by the interaction of **(R_a,R_a)-3** and **(R_a,S_a)-3** with $Pd(COD)Cl_2$ at the molar ratio L/Pd = 1 contained $Pd(COD)Cl_2$, as well as cycloocta-1,5-diene which was liberated during complex formation. This was indicated by the ^1H and ^{13}C spectra of the resulting solutions, which contained resonances of equal intensity for

Pd(COD)Cl_2 δ_H 6.33 (br. s., 4H), 2.93-2.88 (m, 4H), 2.59-2.55 (m, 4H) ppm and δ_C 116.6, 30.9 ppm [70] and COD δ_H 5.62 (br. s., 4H), 2.40 (br. s., 8H) ppm and δ_C 128.1, 28.0 ppm. Addition of a further equivalent of ligand **(R_a,R_a)-3** or **(R_a,S_a)-3** led to the complete disappearance of the Pd(COD)Cl_2 signals. ^{31}P NMR spectra of reaction mixtures each contained one signal at δ_P 107.4 ppm for **13a** and δ_P 101.6 ppm for **13b** whose position was independent of the L/Pd molar ratio used. This provided evidence for the immediate formation of $PdCl_2L_2$ complexes with *P*-monodentate ligand coordination.



Scheme 2. Synthesis of complexes **13a,b**

Therefore, the complex formation of **(R_a,R_a)-3** and **(R_a,S_a)-3** with Pd(COD)Cl_2 can be represented by Scheme 2. The *trans* geometry of **13a,b** was assigned on the basis of the presence of virtual triplets for some of the ^{13}C signals (see ESI). [71-73] HRESI mass spectrometry was used to confirm the elemental composition of both complexes. These results allowed us to conclude that phosphites **(R_a,R_a)-3** and **(R_a,S_a)-3** act as *P*-monodentate ligands, and the nitrogen donor site has no influence on the coordination behavior of the ligands.

To conclude, we have developed phosphite-type chiral ligands bearing the *N*-Bn-NOBIN moiety[74] and applied them to Pd-catalyzed asymmetric allylations and Cu-catalyzed conjugate addition reactions. High enantioselectivities were achieved using (*E*)-1,3-diphenylallyl acetate as a substrate and 1-cyclohexenylpyrrolidine and dimethyl malonate as nucleophiles (*ee* up to 93% and 88%, respectively). The marked influence of small amounts of ZnTPP as an achiral additive on the Pd-catalyzed allylic alkylation was discovered. Additional studies highlighting the potential of these ligands in other asymmetric reactions are currently underway.

Acknowledgements

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74. *Experimental procedures for the preparation of ligands* **2**, **(R_a,R_a)-3** and **(R_a,S_a)-3**: *Procedure for the preparation of ligand* **2**: A solution of $P(NEt_2)_3$ (0.55 mL, 2 mmol) and (R_a)-*N*-Bn-NOBIN (**(R_a)-1**) (0.75 g, 2 mmol) in toluene (6 mL) was stirred at reflux for 90 min. The solution was cooled to 20 °C, filtered through a short plug of Al_2O_3, and the column washed twice with toluene (4 mL). The solvent was evaporated under reduced pressure (40 Torr). The residue was purified by crystallization from heptane at - 20 °C. *(R_a)-5-Benzyl-4-(diethylamino)-4,5-dihydrodinaphtho[2,1-d:1',2'-f][1,3,2]oxazaphosphepine* (**2**): White powder; yield 0.68 g (71%); R_f 0.67 (hexane/ EtOAc, 2/1, silica gel 60 F254); $[\alpha]_D^{25}$ = - 278.4 (*c* 0.5, toluene). $^{31}P\{H\}$ NMR ($CDCl_3$, 162.0 MHz): δ_P = 152.6. ^1H NMR ($CDCl_3$, 600.1 MHz): δ_H = 1.10 (t, $^3J_{H,H}$ = 7.1,

6 H, CH_3); 2.97 (ddq, $^3J_{H,H}$ = 7.1, $^2J_{H,H}$ = 14.1, $^3J_{H,P}$ = 11.1, 2 H, NCH_2); 3.05 (ddq, $^3J_{H,H}$ = 7.1, $^2J_{H,H}$ = 14.1, $^3J_{H,P}$ = 9.7, 2 H, NCH_2); 4.58 (dd, $^2J_{H,H}$ = 15.5, $^3J_{H,P}$ = 3.5, 1 H, NCH_2Ph); 4.72 (dd, $^2J_{H,H}$ = 15.5, $^3J_{H,P}$ = 9.7, 1 H, NCH_2Ph); 6.65-6.62 (m, 4 H, CH_{Ph}); 6.82-6.79 (m, 1 H, CH_{Ph}); 6.92 (d, $^3J_{H,H}$ = 8.6, 1 H, CH_{Ar}); 7.16-7.13 (m, 1 H, CH_{Ar}); 7.24-7.21 (m, 1 H, CH_{Ar}); 7.36 (d, $^3J_{H,H}$ = 8.6, 1 H, CH_{Ar}); 7.40-7.37 (m, 1 H, CH_{Ar}); 7.43-7.40 (m, 1 H, CH_{Ar}); 7.60 (d, $^3J_{H,H}$ = 8.8, 1 H, CH_{Ar}); 7.63 (d, $^3J_{H,H}$ = 8.7, 1 H, CH_{Ar}); 7.83 (d, $^3J_{H,H}$ = 8.5, 1 H, CH_{Ar}); 7.85 (d, $^3J_{H,H}$ = 7.9, 1 H, CH_{Ar}); 7.96 (d, $^3J_{H,H}$ = 8.3, 1 H, CH_{Ar}); 8.03 (d, $^3J_{H,H}$ = 8.7, 1 H, CH_{Ar}). $^{13}C\{H\}$ NMR ($CDCl_3$, 150.9 MHz): δ_C = 15.22 (d, $^3J_{C,P}$ = 2.7, CH_3); 38.94 (d, $^2J_{C,P}$ = 20.9, NCH_2); 51.11 (d, $^2J_{C,P}$ = 43.3, NCH_2Ph); 122.03 (d, $^3J_{C,P}$ = 1.8, CH_{Ar}); 123.26 (s, CH_{Ar}); 124.22 (s, CH_{Ar}); 124.63 (s, CH_{Ar}); 125.63 (s, CH_{Ar}); 125.77 (s, CH_{Ar}); 126.27 (d, $^3J_{C,P}$ = 4.0, C_{Ar}); 126.41 (s, CH_{Ph}); 126.96 (s, CH_{Ar}); 127.47 (d, $^4J_{C,P}$ = 0.6, CH_{Ph}); 127.54 (s, CH_{Ar}); 127.67 (s, CH_{Ph}); 127.88 (s, CH_{Ar}); 128.09 (s, CH_{Ar}); 128.56 (s, CH_{Ar}); 128.64 (s, C_{Ar}); 129.83 (s, CH_{Ar}); 130.98 (s, C_{Ar}); 131.00 (d, $^5J_{C,P}$ = 0.6, C_{Ar}); 132.83 (s, C_{Ar}); 133.16 (d, $^4J_{C,P}$ = 1.8, C_{Ar}); 138.51 (d, $^3J_{C,P}$ = 10.4, $PNCH_2C$); 140.82 (d, $^2J_{C,P}$ = 6.3, PNC); 150.96 (d, $^2J_{C,P}$ = 1.6, POC). MS (MALDI TOF/TOF): *m/z* (%) = 495 (100) $[M + H_2O + H]^+$. $C_{31}H_{29}N_2OP$: calcd: C, 78.13; H, 6.13; N, 5.88; found: C, 78.41; H, 6.18; N, 5.64. *Procedure for the preparation of ligands* **(R_a,R_a)-3** and **(R_a,S_a)-3**: A solution of the appropriate enantiomer of *N*-Bn-NOBIN (**(R_a)-1** or **(S_a)-1**)) (0.75 g, 2 mmol) in toluene (4 mL) was added dropwise to a vigorously stirred solution of (R_a)-4-chlorodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine (0.70 g, 2 mmol) and Et_3N (0.70 mL, 5 mmol) in toluene (6 mL). The mixture that obtained was stirred for 24 h at 20 °C, then heated to 40 °C for 1 h before being cooled to 20 °C. The resulting suspension was filtered through a short plug of Al_2O_3, and the column washed twice with toluene (6 mL). The solvent was evaporated under reduced pressure (40 Torr). The residue was purified by crystallization from heptane. *(R_a)-4-((R_a)-(2'-(Benzylamino)-[1,1'-binaphthalen]-2-yl)oxy)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine* (**(R_a,R_a)-3**): White powder; yield 1.04 g (75%); R_f 0.65 (hexane/ EtOAc, 2/1, silica gel 60 F254); $[\alpha]_D^{24}$ = - 247.5 (*c* 1.0, toluene). $^{31}P\{H\}$ NMR ($CDCl_3$, 162.0 MHz): δ_P = 145.1. ^1H NMR ($CDCl_3$, 400.1 MHz): δ_H = 4.03 (br s, 1 H, NH); 4.32 (s, 2 H, NCH_2); 6.35 (d, $^3J_{H,H}$ = 8.8, 1 H, CH_{Ar}); 7.06 - 7.00 (m, 4 H, CH_{Ar}); 7.13 - 7.08 (m, 2 H, CH_{Ar}); 7.17 (d, $^3J_{H,H}$ = 9.1, 1 H, CH_{Ar}); 7.26 - 7.20 (m, 4 H, CH_{Ar}); 7.32 - 7.28 (m, 3 H, CH_{Ar}); 7.44 - 7.34 (m, 4 H, CH_{Ar}); 7.50 - 7.46 (m, 1 H, CH_{Ar}); 7.57 (d, $^3J_{H,H}$ = 8.8, 1 H, CH_{Ar}); 7.63 (d, $^3J_{H,H}$ = 8.8, 1 H, CH_{Ar}); 7.96 - 7.84 (m, 6 H, CH_{Ar}); 8.01 (d, $^3J_{H,H}$ = 8.8, 1 H, CH_{Ar}). $^{13}C\{H\}$ NMR ($CDCl_3$, 100.6 MHz): δ_C = 47.61 (s, NCH_2); 111.76 (s, C_{Ar}); 113.84 (s, CH_{Ar}); 121.41 (s, CH_{Ar}); 121.49 (s, CH_{Ar}); 121.65 (s, CH_{Ar}); 121.82 (s, CH_{Ar}); 121.93 (s, CH_{Ar}); 122.40 (d, $J_{C,P}$ = 1.7, C_{Ar}); 123.11 (d, $J_{C,P}$ = 3.8, C_{Ar}); 123.99 (s, CH_{Ar}); 124.24 (d, $J_{C,P}$ = 4.5, C_{Ar}); 124.69 (s, CH_{Ar}); 124.98 (s, CH_{Ar}); 125.37 (s, CH_{Ar}); 125.84 (s, CH_{Ar}); 125.87 (s, CH_{Ar}); 126.12 (s, CH_{Ar}); 126.55

(s, CH_{Ar}); 126.61 (s, CH_{Ar}); 126.65 (s, CH_{Ar}); 126.78 (s, CH_{Ar}); 126.93 (s, CH_{Ar}); 127.12 (s, CH_{Ar}); 127.35 (s, C_{Ar}); 127.97 (s, CH_{Ar}); 128.18 (s, CH_{Ar}); 128.20 (s, CH_{Ar}); 128.22 (s, CH_{Ar}); 128.26 (s, CH_{Ar}); 129.44 (s, CH_{Ar}); 129.70 (s, CH_{Ar}); 130.11 (s, CH_{Ar}); 130.16 (s, CH_{Ar}); 131.06 (s, C_{Ar}); 131.41 (s, C_{Ar}); 131.42 (s, C_{Ar}); 132.26 (s, C_{Ar}); 132.67 (s, C_{Ar}); 133.66 (s, C_{Ar}); 134.15 (s, C_{Ar}); 139.48 (s, C_{Ar}); 144.46 (s, C_{Ar}); 147.01 (d, $^{2}J_{C,P}$ = 2.1, POC); 147.48 (d, $^{2}J_{C,P}$ = 4.6, POC); 148.59 (d, $^{2}J_{C,P}$ = 8.0, POC). MS (MALDI TOF/TOF): *m/z* (%) = 690 (100) $[M + H]^{+}$, 599 (22) $[M - Bn + H]^{+}$. $C_{47}H_{32}NO_3P$: calcd: C, 81.84; H, 4.68; N, 2.03; found: C, 82.05; H, 4.82; N, 2.11. *(R_a)-4-((S_a)-(2'-(Benzylamino)-[1,1'-binaphthalen]-2-yl)oxy)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine* (**(R_a,S_a)-3**): White powder; yield 1.24 g (90%); R_f 0.68 (hexane/ EtOAc, 2/1, silica gel 60 F254); $[\alpha]_D^{24}$ = - 597.1 (*c* 1.0, toluene). $^{31}P\{H\}$ NMR ($CDCl_3$, 162.0 MHz): δ_P = 145.6. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ_H = 4.06 (br s, 1 H, NH); 4.39 (s, 2 H, NCH_2); 6.04 (d, $^{3}J_{H,H}$ = 8.8, 1 H, CH_{Ar}); 6.99 (d, $^{3}J_{H,H}$ = 8.8, 1 H, CH_{Ar}); 7.07 - 7.04 (m, 3 H, CH_{Ar}); 7.26 - 7.16 (m, 7 H, CH_{Ar}); 7.51 - 7.29 (m, 9 H, CH_{Ar}); 7.53 (d, $^{3}J_{H,H}$ = 8.8, 1 H, CH_{Ar}); 7.81 (d, $^{3}J_{H,H}$ = 8.0, 1 H, CH_{Ar}); 7.97 - 7.88 (m, 5 H, CH_{Ar}) ; 8.00 (d, $^{3}J_{H,H}$ = 8.8, 1 H, CH_{Ar}). $^{13}C\{H\}$ NMR ($CDCl_3$, 150.9 MHz): δ_C = 47.80 (s, NCH_2); 111.68 (s, C_{Ar}); 114.21 (s, CH_{Ar}); 121.74 (d, $J_{C,P}$ = 1.1, CH_{Ar}); 121.89 (s, CH_{Ar}); 121.98 (s, C_{Ar}); 122.27 (d, $J_{C,P}$ = 4.7, CH_{Ar}); 122.54 (d, $J_{C,P}$ = 2.3, C_{Ar}); 123.75 (d, $J_{C,P}$ = 4.8, C_{Ar}); 124.37 (d, $J_{C,P}$ = 5.1, C_{Ar}); 124.48 (s, CH_{Ar}); 124.74 (s, CH_{Ar}); 125.04 (s, CH_{Ar}); 125.57 (s, CH_{Ar}); 125.89 (s, CH_{Ar}); 126.08 (s, CH_{Ar}); 126.19 (s, CH_{Ar}); 126.74 (s, CH_{Ar}); 126.80 (s, CH_{Ar}); 126.84 (s, CH_{Ar}); 126.86 (s, CH_{Ar}); 127.06 (s, C_{Ar}); 127.21 (s, CH_{Ar}); 127.53 (s, C_{Ar}); 128.09 (s, CH_{Ar}); 128.25 (s, CH_{Ar}); 128.26 (s, CH_{Ar}); 128.29 (s, CH_{Ar}); 128.37 (s, CH_{Ar}); 129.07 (s, CH_{Ar}); 129.36 (s, CH_{Ar}); 130.06 (s, CH_{Ar}); 130.13 (s, CH_{Ar}); 130.30 (s, CH_{Ar}); 131.16 (s, C_{Ar}); 131.51 (s, C_{Ar}); 131.71 (s, C_{Ar}); 132.30 (s, C_{Ar}); 132.78 (d, $J_{C,P}$ = 1.1, C_{Ar}); 133.66 (s, C_{Ar}); 134.51 (d, $J_{C,P}$ = 1.0, C_{Ar}); 139.55 (s, C_{Ar}); 144.75 (s, C_{Ar}); 147.16 (d, $^{2}J_{C,P}$ = 2.6, POC); 147.49 (d, $^{2}J_{C,P}$ = 4.7, POC); 148.75 (d, $^{2}J_{C,P}$ = 8.8, POC). MS (MALDI TOF/TOF): *m/z* (%) = 690 (100) $[M + H]^{+}$, 599 (11) $[M - Bn + H]^{+}$. $C_{47}H_{32}NO_3P$: calcd: C, 81.84; H, 4.68; N, 2.03; found: C, 82.13; H, 4.74; N, 2.18.

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Graphical abstract.