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*P**,*P**-Bidentate diastereoisomeric bisdiamidophosphites based on *N*-benzyltartarimide and their applications in asymmetric catalytic processes

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ABSTRACT

Two novel *P**-stereogenic bisdiamidophosphites derived from (3*R*,4*R*)-*N*-benzyltartarimide as a chiral 1,2-diol have been prepared from readily available starting materials. Palladium and rhodium catalytic systems containing these new *P**,*P**-bidentate ligands afforded 96%, 83% and 65% ee in asymmetric allylic substitution, hydrogenation and addition processes, respectively. These diastereomeric diamidophosphites were found to be complementary stereoselectors.

1. Introduction

Transition-metal asymmetric catalysis has found wide-spread application and is the subject of intensive research both in industry and academia.[1] Phosphite-type chiral compounds have become one of the most successful, versatile, and commonly used classes of organophosphorus ligands for asymmetric catalysis due to their ready accessibility, modular nature and applicability in a wide range of metal-catalysed transformations. The most important advantages of phosphite-type ligands include their pronounced π-acidity, oxidation stability, as well as their synthetic availability and low cost.[2,3] In contrast to monodentate phosphites, libraries of chiral bidentate phosphite-type ligands are scarce, despite the importance of bidentate phosphorus ligands in asymmetric transition-metal-catalysed reactions.[1] This is attributed to the intrinsically more complicated synthesis of bidentate ligands compared to that of monodentate ligands. This is especially true for bidentate ligands with the chirogenic phosphorus donor atoms. In their complexes, the asymmetric phosphorus atoms bind directly to the metal atom. This factor eliminates potentially inefficient secondary transfer of chirality from the ligand backbone and, thus, provides a more efficient chiral environment at the site where the enantioselection originates.[4] Nevertheless, there are only a few examples of very promising *P,P*-bidentate phosphite-type ligands with stereogenic phosphorus atoms in the literature.[3h,5]

The sterically rigid fragment is also a desirable element of structure of the successful stereoinductors. For example, ligands $\mathbf{L_A}$ and $\mathbf{L_B}$ with a pyrrolidine-2,5-dione backbone afford high enantioselectivities for the Rh-catalysed hydrogenation of enamides and Pd-catalysed allylic alkylation (Fig. 1).[6] Motivated by our continuing efforts in the design and synthesis of novel *P**-chiral ligands for use in asymmetric catalysis,[7] we have prepared *P**,*P**-bidentate bisdiamidophosphites (S_C,R_P)-**3** and (R_C,S_P)-**3** as diastereomeric stereoselectors. It should be noted that (S_C,R_P)-**3** and (R_C,S_P)-**3** have a rigid pyrrolidine-2,5-dione fragment and diazaphospholidine cycles. Notably, diazaphospholidines have several important advantages. In general, they are good π-acceptor ligands, thanks to the availability of low-lying π^*_{PN} orbitals, and good σ-donor ligands. Incorporation of the phosphorus atom in a cyclic structure, in particular a five-membered ring, is a key feature, as it increases stability towards air and moisture.[8]

2. Results and discussion

2.1. Synthesis of the ligands

(3*R*,4*R*)-*N*-Benzyltartarimide **2** was chosen as a suitable building block for the synthesis of novel *P**,*P**-bidentate ligands (Scheme 1). This diol is readily prepared by the direct condensation of tartaric acid with benzylamine.[9] Then, bisdiamidophosphites (S_C,R_P)-**3** and (R_C,S_P)-**3**, based on rigid pyrrolidine-2,5-dione backbone, were synthesised stereospecifically in two steps from

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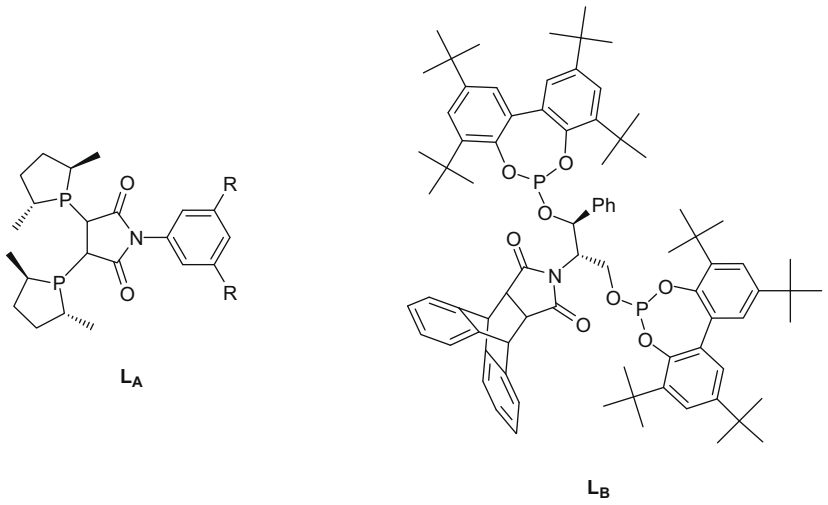
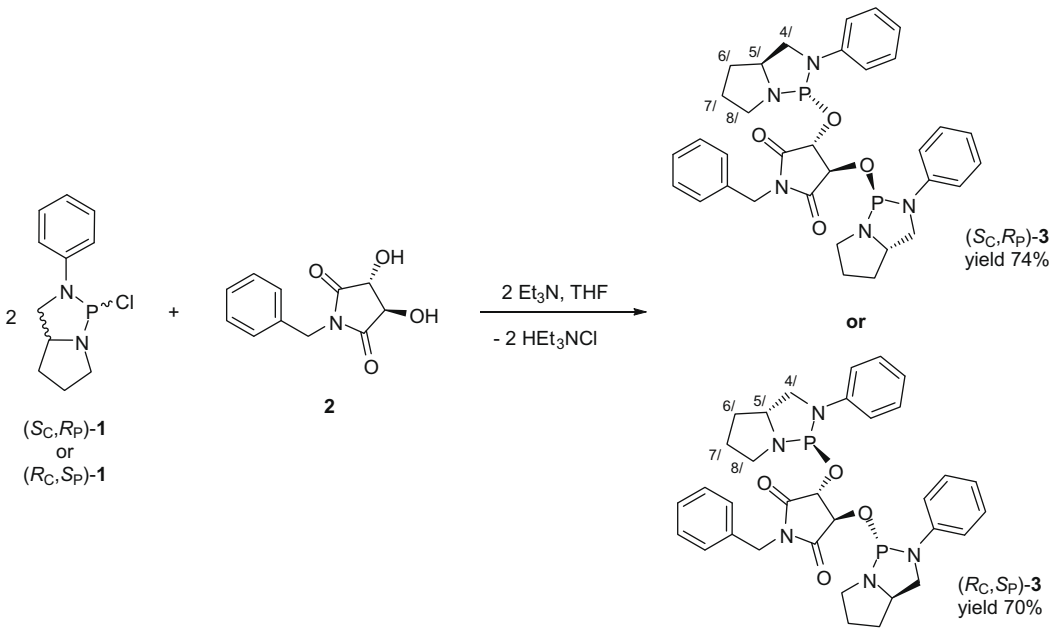


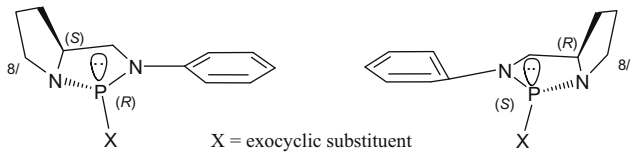
Figure 1. Bidentate organophosphorus ligands with a pyrrolidine-2,5-dione backbone.



Scheme 1. Synthesis of the diastereomeric bisdiamidophosphites (S_C,R_P)-**3** and (R_C,S_P)-**3**.

(*S*)-2-(anilinomethyl)pyrrolidine or (*R*)-2-(anilinomethyl)pyrrolidine. In turn, these enantiomeric diamines are easily accessible in two steps from (*S*)- or (*R*)-glutamic acid, respectively.[10] These compounds react with PCl_3 in benzene to yield phosphorylating reagents (S_C,R_P)-**1** and (R_C,S_P)-**1**.[7a] Subsequent treatment of suitable chlorodiamidophosphites (S_C,R_P)-**1** or (R_C,S_P)-**1** with diol **2** in THF affords the desired compounds. The reaction requires the presence of Et_3N as an HCl scavenger. Flash chromatography of the crude products affords pure ligands (S_C,R_P)-**3** and (R_C,S_P)-**3** as yellow powders in 74% and 70% yields, respectively. It is noteworthy that owing to the ease of each step, as well as the easy-to-handle nature of all the related intermediates, (S_C,R_P)-**3** and (R_C,S_P)-**3** can be prepared on a multigram scale. These bisdiamidophosphites were found to be stable enough to allow manipulation in open air and can be stored under a dry atmosphere for several months at room temperature without any degradation. Besides, they are rather stable in solutions in common organic solvents.

During the phosphorylation process, the exclusive formation of stereospecific bisdiamidophosphites (S_C,R_P)-**3** and (R_C,S_P)-**3** takes place. The ^{31}P NMR spectra of their solutions in $CDCl_3$ exhibited narrow singlets at δ_P 130.8 and 128.6, respectively. According to the literature data, both natural (S_C,R_P)-**3** and unnatural (R_C,S_P)-**3** diastereomers [based on natural (*S*)- and unnatural (*R*)-glutamic acid, respectively] have the pseudoequatorial orientation of the exocyclic substituent at the phosphorus atom and *anti*-orientations between this substituent and the $-(CH_2)_3-$ part of the pyrrolidine fragment of phosphabicyclic skeleton and, as consequence, *cis*-orientations of the phosphorus atom lone pair and C(8′).[7a,10b,11] This was concluded from the large ^2J(C(8′),P) value (35.0 Hz) in their ^{13}C NMR spectra (see Section 4).[7a,10b,12] In the case of the ligand (S_C,R_P)-**3** based on natural (*S*)-glutamic acid, this corresponds to the (*R*)-configuration at the P^*-stereocentres. Correspondingly, the unnatural ligand (R_C,S_P)-**3** with a (*R*)-C^*(5′) stereocentre in the phosphabicyclic skeleton is characterised by an (*S*)-configuration of the asymmetric phosphorus atoms (Fig. 2).[7c,10b,11e]



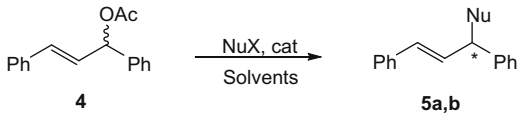
natural (S_C,R_P)-diastereomer unnatural (R_C,S_P)-diastereomer

Figure 2. Stereochemistry of the phosphabicyclic part in ligands (S_C,R_P)-**3** and (R_C,S_P)-**3**.

2.2. Pd-catalysed asymmetric allylic substitution

The enantioselective Pd-catalysed allylic substitution has emerged as a powerful synthetic tool. In addition to a high level of asymmetric induction, the advantages of this method include its tolerance of a wide range of functional groups and great flexibility in the type of bonds that can be formed.[13] It should be noted that many ligands have been designed for the benchmark allylic substitution with (*E*)-1,3-diphenylallyl acetate and led to excellent enantioselectivity. Nevertheless, the availability of new diverse chiral ligands and a necessity to estimate their efficiency are strong motivators for further investigations.[1,2,13] With novel P^*,P^*-bidentate ligands in hand, we set out to study their application in the Pd-catalysed asymmetric allylic sulfonylation and alkylation of (*E*)-1,3-diphenylallyl acetate **4** with sodium *para*-toluene sulfinate and dimethyl malonate (Table 1). Both reactions are common benchmark tests for novel groups of stereoselectors, and powerful tools in the total synthesis of natural products.[13b]

Table 1
Pd-catalysed allylic sulfonylation and alkylation of (*E*)-1,3-diphenylallyl acetate **4**[a]



4 **5a,b**

Nu = SO_2pTol, X = Na, **5a**
Nu = $CH(CO_2Me)_2$ X = H, **5b**

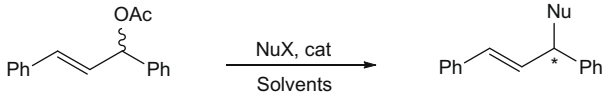
Entry	Ligand	L/Pd	Solvent	Conv.[b] (%)	ee (%)
Allylic sulfonylation with sodium para-toluene sulfinate[c]					
1	(S_C,R_P)-**3**	1/1	THF	83	58 (*R*)
2	(S_C,R_P)-**3**	2/1	THF	90	92 (*R*)
3	(R_C,S_P)-**3**	1/1	THF	86	55 (*S*)
4	(R_C,S_P)-**3**	2/1	THF	89	46 (*S*)
Allylic alkylation with dimethyl malonate (BSA, KOAc)[d]					
5	(S_C,R_P)-**3**	1/1	CH_2Cl_2	100	89 (*S*)
6	(S_C,R_P)-**3**	2/1	CH_2Cl_2	63	70 (*S*)
7	(S_C,R_P)-**3**	1/1	THF	90	85 (*S*)
8	(S_C,R_P)-**3**	2/1	THF	34	40 (*S*)
9	(R_C,S_P)-**3**	1/1	CH_2Cl_2	98 (92)[e]	96 (*R*)
10	(R_C,S_P)-**3**	2/1	CH_2Cl_2	97	84 (*R*)
11	(R_C,S_P)-**3**	1/1	THF	0	—
12	(R_C,S_P)-**3**	2/1	THF	0	—

[a] All reactions were carried out with 2 mol % of $[Pd(allyl)Cl]_2$ at room temperature for 48 h.
[b] Isolated yield of **5a** in allylic sulfonylation.
[c] Enantiomeric excess of **5a** was determined by HPLC (Daicel Chiralcel OD, C_6H_{14}/*i*-PrOH = 4/1, 0,5 ml/min, 254 nm).
[d] The conversion of substrate **4** and enantiomeric excess of **5b** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 99/1, 0.6 ml/min, 254 nm).
[e] Isolated yield of **5b** is given in brackets.

The test reactions were evaluated using catalysts generated in situ by interaction of $[Pd(allyl)Cl]_2$ and an appropriate bis-diamidophosphite. In particular, these new catalytic systems led to the expected sulfonylated product **5a** with very good conversion (83–90%) and enantioselectivity (up to 92%, Table 1, entries 1–4). Natural diastereomer (S_C,R_P)-**3** provides much higher asymmetric induction than unnatural (R_C,S_P)-**3**. In the case of allylic alkylation with (S_C,R_P)-**3**, reactions in CH_2Cl_2 gave higher conversion and enantioselectivities than those in THF. The molar ratio L/Pd = 1 is optimal. In contrast to allylic sulfonylation, unnatural ligand (R_C,S_P)-**3** is slightly more stereoselective (Table 1, entries 5 and 9) demonstrating excellent enantioselectivity (up to 96%). Surprisingly, palladium complexes with (R_C,S_P)-**3** did not show any activity in THF solutions (Table 1, entries 11 and 12).

Further studies focused on the asymmetric allylic amination of (*E*)-1,3-diphenylallyl acetate **4** (Table 2). Firstly, the new ligands were tested in the Pd-catalysed allylic amination of **4** with dipropylamine as an *N*-nucleophile, under standard conditions.

Table 2
Pd-catalysed allylic amination of (*E*)-1,3-diphenylallyl acetate **4**[a]



4 **5c,d**

Nu = $N(Pr)_2$, X = H, **5c**
Nu = $N(CH_2)_4$, X = H, **5d**

Entry	Ligand	L/Pd	Solvent	Conv. (%)	ee (%)
Allylic amination with dipropylamine[b]					
1	(S_C,R_P)-**3**	1/1	CH_2Cl_2	70	51 (+)
2	(S_C,R_P)-**3**	2/1	CH_2Cl_2	50	50 (+)
3	(S_C,R_P)-**3**	1/1	THF	18	20 (+)
4	(S_C,R_P)-**3**	2/1	THF	20	53 (+)
5	(R_C,S_P)-**3**	1/1	CH_2Cl_2	73 (66)[c]	73 (−)
6	(R_C,S_P)-**3**	2/1	CH_2Cl_2	100	60 (−)
7	(R_C,S_P)-**3**	1/1	THF	75	70 (−)
8	(R_C,S_P)-**3**	2/1	THF	98	45 (−)
Allylic amination with pyrrolidine[d]					
9	(S_C,R_P)-**3**	1/1	CH_2Cl_2	100	46 (*R*)
10	(S_C,R_P)-**3**	2/1	CH_2Cl_2	100	60 (*R*)
11	(S_C,R_P)-**3**	1/1	THF	42	30 (*R*)
12	(S_C,R_P)-**3**	2/1	THF	26	10 (*R*)
13	(R_C,S_P)-**3**	1/1	CH_2Cl_2	95 (85)[e]	73 (*S*)
14	(R_C,S_P)-**3**	2/1	CH_2Cl_2	98	71 (*S*)
15	(R_C,S_P)-**3**	1/1	THF	97	57 (*S*)
16	(R_C,S_P)-**3**	2/1	THF	99	67 (*S*)

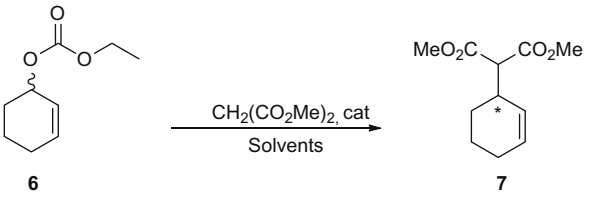
[a] All reactions were carried out with 2 mol % of $[Pd(allyl)Cl]_2$ at room temperature for 48 h.
[b] The conversion of the substrate **4** and enantiomeric excess of **5c** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH/$HN(Et)_2$ = 1000/1/1, 0.4 ml/min, 254 nm, $t(+)$ = 8.2 min, $t(-)$ = 9.1 min).
[c] Isolated yield of **5c** is given in brackets.
[d] The conversion of the substrate **4** and enantiomeric excess of **5d** were determined by HPLC (Daicel Chiralcel OD-H, OD-H, C_6H_{14}/*i*-PrOH/$HN(Et)_2$ = 200/1/0,1 0.9 ml/min, 254 nm).
[e] Isolated yield of **5d** is given in brackets.

Both enantiomers of the product **5c** can be obtained with moderate to good enantioselectivity. The influence of the stereochemistry of the diastereoisomeric ligands, solvent, and L/Pd molar ratio on the catalytic activity and enantioselectivity was investigated. Listed factors strongly affect activity and enantioselectivity of the allylic amination. As a rule, CH_2Cl_2 is the solvent of choice and a molar ratio L/Pd = 1 is optimal. The best result (up to 73% ee) was obtained with unnatural ligand (R_C,S_P)-**3** (Table 2, entry 5). Pyrrolidine was also employed as an *N*-nucleophile in the allylic amination of **4**. Analogously to the reaction with dipropylamine, CH_2Cl_2 is the solvent of choice, and unnatural diastereomer (R_C,S_P)-**3** is a good stereoinductor providing up to 73% ee (Table 2, entry 13).

To investigate further the potential of the new readily available ligands, they were tested in the Pd-catalysed allylic alkylation of a cyclic substrate, namely cyclohex-2-enyl ethyl carbonate **6**, with dimethyl malonate (Table 3). The enantioselectivity for the cyclic substrate **6** is usually more difficult to control than for the hindered substrate **4**. For high ees to be achieved it is crucial that ligands create a small chiral pocket around the metal centre, mainly because of the presence of less sterically demanding *syn* substituents.[14]

It is clear that (R_C,S_P)-**3** demonstrates a higher catalytic activity and enantioselectivity than (S_C,R_P)-**3** (Table 3, entries 1–4 and 5–8). As in the aforementioned catalytic reactions, the process is rather sensitive to the solvent used; best ee-values were observed in CH_2Cl_2. In general, unnatural bisdiamidophosphite (R_C,S_P)-**3** showed enantioselectivity of up to 65% in the asymmetric synthesis of **7**, which is appreciable for the sterically undemanding substrate **6** (see Ref. 14 and references cited therein).

Table 3
Pd-catalysed allylic alkylation of cyclohex-2-enyl ethyl carbonate **6** with dimethyl malonate[a]



6 **7**

Entry	Ligand	L/Pd	Solvent	Conv.[b] (%)	ee (%)
1	(S_C,R_P)-**3**	1/1	CH_2Cl_2	100	20 (*R*)
2	(S_C,R_P)-**3**	2/1	CH_2Cl_2	47	30 (*R*)
3	(S_C,R_P)-**3**	1/1	THF	63	19 (*R*)
4	(S_C,R_P)-**3**	2/1	THF	30	26 (*R*)
5	(R_C,S_P)-**3**	1/1	CH_2Cl_2	99	39 (*S*)
6	(R_C,S_P)-**3**	2/1	CH_2Cl_2	84 (77)[c]	65 (*S*)
7	(R_C,S_P)-**3**	1/1	THF	65	27 (*S*)
8	(R_C,S_P)-**3**	2/1	THF	43	35 (*S*)

[a] All reactions were carried out with 2 mol % of $[Pd(allyl)Cl]_2$ at room temperature for 48 h (BSA, KOAc).
[b] The conversion of the substrate **6** and enantiomeric excess of **7** were determined by HPLC (Daicel Chiralcel AD, C_6H_{14}/*i*-PrOH = 200/1, 1 ml/min, 219 nm, *t*(*R*) = 11.3 min, *t*(*S*) = 12.1 min).
[c] Isolated yield of **7** is given in brackets.

2.3. Rh-catalysed asymmetric hydrogenation and addition of phenylboronic acid

Catalytic systems containing bisdiamidophosphites (S_C,R_P)-**3** and (R_C,S_P)-**3** were used in the Rh-catalysed asymmetric hydrogenation of certain α-dehydrocarboxylic acid esters. It is necessary to note that the asymmetric catalytic hydrogenation of unsaturated bonds, which employs dihydrogen and small amounts of transition-metal complexes intrinsically modified by chiral ligands, is now recognised as being the most promising strategy for the synthesis of large amounts of enantiomerically pure products.[4] In this regard, the results of the Rh-catalysed hydrogenation of benchmark substrates **8a–c** (Table 4) are presented. One can thus directly compare the efficacy of different ligand systems. Hydrogenation experiments were performed in propylene carbonate or CH_2Cl_2 at room temperature (with $[Rh(cod)_2]BF_4$ as a catalyst precursor, L/Rh = 1).

In all cases, unnatural bisdiamidophosphite (R_C,S_P)-**3** was found to be a superior sereoselector. In the transformation of **8a**,**b** to **9a**,**b**, ligand (R_C,S_P)-**3** showed good enantioselectivity (83% ee, Table 4, entries 3 and 6). Moderate enantioselectivity (66% ee, Table 4, entry 8) was observed in the Rh-catalysed hydrogenation of substrate **8c**. Notably, in propylene carbonate, products **9a** and **9b** were formed with lower enantioselectivity than in CH_2Cl_2. It is important to note that rhodium catalysts, which are formed in situ by the interaction of $[Rh(cod)_2]BF_4$ with one equivalent of the appropriate bisdiamidophosphite in CH_2Cl_2, are cationic metal chelates $[Rh(cod)(L)]BF_4$. For (S_C,R_P)-**3** and (R_C,S_P)-**3**, only doublets of the desired complexes were observed in the ^{31}P NMR spectra of the reaction solutions (δ_P 121.1, ^1J(P,Rh) = 214.3 Hz; δ_P 121.8, ^1J(P,Rh) = 210.4 Hz, respectively). MALDI TOF/TOF mass spectral examination of the resulting solutions revealed the mononuclear nature of the complexes (*m*/*z* (*I*, %)): 841 (19) $[M-BF_4]^+$, 733 (100) $[M-BF_4-cod]^+$.

Table 4
Rh-catalysed hydrogenation of α-dehydrocarboxylic acid esters[a]

8a-c **9a-c**

R^1 = H, R^2 = CH_2CO_2Me, R^3 = Me, **8a** and **9a**
R^1 = Ph, R^2 = NHAc, R^3 = Me, **8b** and **9b**
R^1 = H, R^2 = NHAc, R^3 = Me, **8c** and **9c**

Entry	Substrate	Ligand	Solvent	Time (min)	Conv.[b,c,d] (%)	ee (%)
1	**8a**	(S_C,R_P)-**3**	CH_2Cl_2	1440	100	16 (*S*)
2	**8a**	(R_C,S_P)-**3**	PC[e]	1200	16	59 (*R*)
3	**8a**	(R_C,S_P)-**3**	CH_2Cl_2	1200	94	83 (*R*)
4	**8b**	(S_C,R_P)-**3**	CH_2Cl_2	1440	100	26 (*R*)
5	**8b**	(R_C,S_P)-**3**	PC	960	85	73 (*S*)
6	**8b**	(R_C,S_P)-**3**	CH_2Cl_2	1200	93	83 (*S*)
7	**8c**	(S_C,R_P)-**3**	CH_2Cl_2	1440	100	30 (*R*)
8	**8c**	(R_C,S_P)-**3**	CH_2Cl_2	1440	100	66 (*S*)

[a] All reactions were carried out with 1 mol % of $[Rh(cod)_2]BF_4$ at 25 °C and 1 bar H_2.
[b] The conversion of substrate **8a** and enantiomeric excess of **9a** were determined by GC (Lipodex E, 25 m × 0.25 mm, 80 °C, 1 ml/min) or HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 98/2, 0.8 ml/min, 220 nm, *t*(*R*) = 9.1 min, *t*(*S*) = 16.1 min).
[c] The conversion of the substrate **8b** and enantiomeric excess of **9b** were determined by GC (Lipodex E, 25 m × 0.25 mm, 145 °C, 1 ml/min).
[d] The conversion of substrate **8c** and enantiomeric excess of **9c** were determined by GC (XE-valin(*tert*-butylamide) 4 × 0.25 mm, 85 °C, 1 ml/min).
[e] Propylene carbonate.

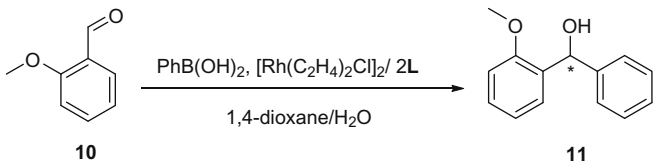
Finally, novel P^*,P^*-bidentate ligands were applied as stereoselectors in the Rh-catalysed addition of phenylboronic acid to 2-methoxybenzaldehyde **10** (Table 5). The reaction was carried out in 1,4-dioxane/H_2O (1:1) in the presence of $[Rh(C_2H_4)_2Cl]_2$, L/Rh = 1.

Unnatural bisdiamidophosphite (R_C,S_P)-**3** exhibited quantitative conversion, but asymmetric induction was very low. In contrast, natural diastereomer (S_C,R_P)-**3** provided a satisfactory conversion and enantioselectivity (65%, Table 5, entry 1). The result achieved with (S_C,R_P)-**3** is rather remarkable, since the well-known bisphosphine (*R*,*R*)-*i*-Pr-DuPHOS and (*S*)-BINOL-based bisphosphoramidite gave only up to 50% ee.[15]

3. Conclusion

In conclusion, new diastereomeric P^*,P^*-bidentate bisdiamidophosphites with a 3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane skeleton and pyrrolidine-2,5-dione backbone were synthesised and evaluated in the Pd-catalysed asymmetric allylic substitution and Rh-catalysed asymmetric hydrogenation and addition reactions. It was shown that the novel stereoinductors are comple-

Table 5
Rh-catalysed addition of phenylboronic acid to 2-methoxybenzaldehyde[a]



10 11

Entry	Ligand	Conv.[b] (%)	ee (%)
1	(S_C,R_P)-**3**	72 (63)[c]	65 (*S*)
2	(R_C,S_P)-**3**	100	3 (*R*)

[a] All reactions were carried out with 1 mol % of $[Rh(C_2H_4)_2Cl]_2$ at room temperature for 48 h ($KF{\cdot}2H_2O$).
[b] The conversion of the substrate **10** and enantiomeric excess of **11** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 9/1, 1 ml/min, 230 nm, *t*(*S*) = 14 min, *t*(R) = 14.3 min).
[c] Isolated yield of **11** is given in brackets.

mentary to each other in enantioselective catalysis. Inversion of the absolute configuration at the $C^*(5')$ stereocentre and, as a result, at the $P^*(2')$ stereocentre in the phosphabicyclic frameworks of the novel ligands allows us to control the degree and direction of asymmetric induction. Thus, in each of the tested catalytic reactions, diastereoisomeric ligands afforded products with opposite absolute configurations. Furthermore, in the Pd-catalysed allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate and in the Rh-catalysed addition of phenylboronic acid to 2-methoxybenzaldehyde, natural diastereomer (S_C,R_P)-**3** is a more efficient stereoselector; however, in the Pd-catalysed allylic alkylation of (*E*)-1,3-diphenylallyl acetate and cyclohex-2-enyl ethyl carbonate, allylic amination of (*E*)-1,3-diphenylallyl acetate and in the Rh-catalysed hydrogenation of α-dehydrocarboxylic acid esters, unnatural diastereomer (R_C,S_P)-**3** is superior. Further modifications of the new ligands and their applications to other asymmetric reactions are currently in progress in our laboratories.

4. Experimental

4.1. General methods

IR spectra were recorded on Specord M-80 spectrophotometer in $CHCl_3$ (NaCl cuvette). ^{31}P, ^{13}C and ^1H NMR spectra were recorded with a Bruker AMX 400 instrument (162.0 MHz for ^{31}P, 100.6 MHz for ^{13}C and 400.13 MHz for ^1H). Complete assignment of all the resonances in ^{13}C NMR spectra was achieved by the use of DEPT techniques. Chemical shifts (ppm) are given relative to Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P NMR). Mass spectra were recorded with a Bruker Daltonics Ultraflex spectrometer (MALDI TOF/TOF). Optical rotations were measured on a Perkin–Elmer 341 polarimeter. Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

All reactions were carried out under a dry argon atmosphere in flame-dried glassware and in freshly dried and distilled solvents; triethylamine, pyrrolidine and dipropylamine were distilled over KOH and then over a small amount of $LiAlH_4$ before use. Phosphorylating reagents—(2*R*,5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (S_C,R_P)-**1** and (2*S*,5*R*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (R_C,S_P)-**1** were prepared analogously to the known procedure.[7a] $Pd(allyl)Cl]_2$[16] and $[Rh(cod)_2]BF_4$[17] were prepared as described earlier. Pd-catalysed allylic substitution: sulfonylation of substrate **4** with sodium *para*-toluene sulfinate, alkylation with dimethyl malonate, amination with dipropylamine and pyrrolidine; and alkylation of substrate **6** with dimethyl malonate were performed according to the appropriate procedures.[7a,18–21] The Rh-catalysed hydrogenation of α-dehydrocarboxylic acid esters **8a–c** was performed as published.[22,23] The Rh-catalysed addition of phenylboronic acid to 2-methoxybenzaldehyde **10** was performed according to the known procedure.[24] Conversion of substrate **10** and ee of product **11** were determined using HPLC (Daicel Chiralcel OD-H column) according to the literature.[15b,24] Starting substrates **4**, **6** and **8b** were synthesised as published.[16,25,26] Dimethyl malonate, BSA (*N*,*O*–bis(trimethylsilyl) acetamide), sodium *para*-toluene sulfinate, dimethyl itaconate, methyl 2-acetamidoacrylate, 2-methoxybenzaldehyde, phenylboronic acid and $[Rh(C_2H_4)_2Cl]_2$ were purchased from Aldrich and Acros Organics and used without further purification.

4.2. General procedure for the synthesis of ligands (S_C,R_P)-3 and (R_C,S_P)-3

A solution of compound **2** (1.11 g, 5 mmol) in THF (15 ml) was added dropwise at 20 °C over 20 min to a vigorously stirred solution of (S_C,R_P)-**1** or (R_C,S_P)-**1** (2.41 g, 10 mmol) and Et_3N (1.45 ml, 10.4 mmol) in THF (30 ml). The mixture was then heated to the boiling point, stirred for 1.5 h, cooled to 20 °C and filtered. The filtrate was concentrated in vacuo (40 Torr). The residue was purified by flash chromatography on silica gel (hexane/AcOEt 1:2).

4.2.1. 3,4-Bis[(2′*R*,5′*S*)-3′-phenyl-1′,3′-diaza-2′-phosphabicyclo[3.3.0]octyloxy]-(3*R*,4*R*)-1- benzylpyrrolidine-2,5-dione (S_C,R_P)-3

(Hexane/AcOEt 1:2 R_f = 0.80) (2.33 g, yield 74% as yellow powder). $[\alpha]_D^{20} = -288.9$ (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): ν(C=O) = 1708 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.83 (dq, 2H, *J* = 10.7 Hz), 1.9 (m, 4H), 2.1 (dq, 2H, *J* = 10.9 Hz), 2.4 (ddd, 2H, *J* = 8.3, 6.9, 5.7 Hz), 3.1 (m, 4H), 3.6 (m, 4H), 4.68 (m, 4H), 6.65 (d, 4H, *J* = 7.7 Hz), 7.09 (t, 4H, *J* = 7.6 Hz), 7.2 (m, 3H), 7.36 (d, 2H, *J* = 7.7, 7.3 Hz), 7.74 (d, 2H, *J* = 8.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 26.4 [d, ^3J = 4.4 Hz, C(7′)], 31.9 [s, C(6′)], 42.4 (s, CH_2N), 48.1 [d, ^2J = 35.0 Hz, C(8′)], 53.8 [d, ^2J = 7.3 Hz, C(4′)], 62.9 [d, ^2J = 8.0 Hz, C(5′)], 74.7 (s, CHO), 115.5 (d, ^3J = 13.1 Hz, CH_{Ar}), 119.6 (s, CH_{Ar}), 128.0 (s, CH_{Ar}, Bn), 128.7 (s, CH_{Ar}, Bn), 128.9 (s, CH_{Ar}, Bn), 129.2 (s, CH_{Ar}), 135.3 (s, C_{Ar}, Bn), 145.2 (d, ^2J = 16.0 Hz, C_{Ar}), 172.4 (s, C=O). MS (MALDI TOF/TOF), *m*/*z* (*I*, %): 669 (61) $[M+K]^+$, 653 (100) $[M+Na]^+$, 631 (11) $[M+H]^+$, 408 (76) $[M-C_{11}H_{15}N_2OP]^+$. Anal. Calcd for $C_{33}H_{37}N_5O_4P_2$: C, 62.95; H, 5.92; N, 11.12. Found: C, 63.20; H, 5.79; N, 11.22.

4.2.2. 3,4-Bis[(2′*S*,5′*R*)-3′-phenyl-1′,3′-diaza-2′-phosphabicyclo-[3.3.0]octyloxy]-(3*R*,4*R*)-1- benzylpyrrolidine-2,5-dione (R_C,S_P)-3

(Hexane/AcOEt 1:2 R_f = 0.90) (2.2 g, yield 70% as yellow powder). $[\alpha]_D^{20} = +252.4$ (*c* 1.0, $CHCl_3$). IR ($CHCl_3$): ν(C=O) = 1704 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.86 (dq, 2H, *J* = 10.3 Hz), 2.1 (m, 4H), 2.2 (dq, 2H, *J* = 11.1 Hz), 2.4 (ddd, 2H, *J* = 8.1, 7.0, 5.9 Hz), 3.0 (m, 4H), 3.7 (m, 4H), 4.72 (m, 4H), 6.66 (d, 4H, *J* = 7.5 Hz), 7.19 (t, 4H, *J* = 7.6 Hz), 7.3 (m, 3H), 7.41 (d, 2H, *J* = 7.7, 7.2 Hz), 7.8 (d, 2H, *J* = 8.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 26.6 [d, ^3J = 4.4 Hz, C(7′)], 31.5 [s, C(6′)], 42.4 (s, CH_2N), 48.0 [d, ^2J = 35.0 Hz, C(8′)], 53.7 [d, ^2J = 6.6 Hz, C(4′)], 62.8 [d, ^2J = 8.0 Hz, C(5′)], 73.7 (s, CHO), 115.3 (d, ^3J = 12.4 Hz, CH_{Ar}), 119.5 (s, CH_{Ar}), 128.0 (s, CH_{Ar}, Bn), 128.7 (s, CH_{Ar}, Bn), 128.8 (s, CH_{Ar}, Bn), 129.2 (s, CH_{Ar}), 135.4 (s, C_{Ar}, Bn), 145.3 (d, ^2J = 17.5 Hz, C_{Ar}), 172.9 (s, C=O). MS (MALDI TOF/TOF), *m*/*z* (*I*, %): 669 (100) $[M+K]^+$, 653 (89) $[M+Na]^+$, 631 (17) $[M+H]^+$, 408 (55) $[M-C_{11}H_{15}N_2OP]^+$. Anal. Calcd for $C_{33}H_{37}N_5O_4P_2$: C, 62.95; H, 5.92; N, 11.12. Found: C, 63.15; H, 6.0; N, 11.0.

4.3. General procedure for the synthesis of the rhodium complexes with ligands (S_C,R_P)-3 and (R_C,S_P)-3 for the ^{31}P NMR and MALDI TOF/TOF experiments

Cationic rhodium complexes with diamidophosphites (S_C,R_P)-**3** and (R_C,S_P)-**3** were synthesised for the instrumental investigations as follows: a solution of the appropriate ligand (0.031 g, 0.05 mmol) in CH_2Cl_2 (1 ml) was added dropwise to a stirred solution of $[Rh(cod)_2]BF_4$ (0.02 g, 0.05 mmol) in the same solvent (1 ml). A sample of the resulting solution (1 ml) was then transferred to an NMR tube and spectroscopic experiments were carried out. In the case of MALDI TOF/TOF, a sample of the resulting solution (0.1 ml) was diluted with CH_2Cl_2 (10 ml) before spectroscopic experiments.

4.4. General experimental procedures for asymmetric catalytic reactions

4.4.1. General procedure for the Pd-catalysed allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate 4 with sodium *para*-toluene sulfinate

A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and the appropriate ligand (0.013 g or 0.026 g, 0.02 mmol or 0.04 mmol) in THF (2 ml) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (0.1 ml, 0.5 mmol) was added and the solution stirred for 15 min, then sodium *para*-toluene sulfinate (0.178 g, 1 mmol) was added and the reaction mixture stirred for a further 48 h, quenched with brine (5 ml) and extracted with THF (3 × 3 ml). The organic layer was washed with brine (2 × 3 ml) and dried over $MgSO_4$. The solvent was evaporated at reduced pressure (40 Torr). Crystallisation of the residue from EtOH, followed by desiccation in vacuo (10 Torr, 12 h), gave (*E*)-1,3-diphenyl-3-tosylprop-1-ene **5a** as white crystals. The enantiomeric excess of **5a** was determined by HPLC.

4.4.2. General procedure for Pd-catalysed allylic alkylation of (*E*)-1,3-diphenylallyl acetate 4 or cyclohex-2-enyl ethyl carbonate 6 with dimethyl malonate

A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and the appropriate ligand (0.013 g or 0.026 g, 0.02 mmol or 0.04 mmol) in the appropriate solvent (2 ml) was stirred for 40 min. Then, (*E*)-1,3-diphenylallyl acetate or cyclohex-2-enyl ethyl carbonate (0.5 mmol) was added and the solution stirred for 15 min. Dimethyl malonate (0.10 ml, 0.87 mmol), BSA (0.22 ml, 0.87 mmol) and potassium acetate (0.002 g) were added. The reaction mixture was stirred for 48 h, diluted with CH_2Cl_2 or THF (2 ml) and filtered through Celite. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuo (10 Torr, 12 h) to afford a residue containing dimethyl 2-((*E*)-1,3-diphenylallyl)malonate **5b** or dimethyl 2-(cyclohex-2-enyl)malonate **7**. In order to evaluate the ee and conversion, the obtained residue was dissolved in appropriate eluent mixture (8 ml) and a sample was taken for HPLC analysis.

4.4.3. General procedure for the Pd-catalysed allylic amination of (*E*)-1,3-diphenylallyl acetate 4 with dipropylamine or pyrrolidine

A solution of $[Pd(allyl)Cl]_2$ (0.0037 g, 0.01 mmol) and the appropriate ligand (0.013 g or 0.026 g, 0.02 mmol or 0.04 mmol) in the appropriate solvent (2 ml) was stirred for 40 min. Then (*E*)-1,3-diphenylallyl acetate (0.1 ml, 0.5 mmol) was added and the solution stirred for 15 min, then freshly distilled dipropylamine or pyrrolidine (1.5 mmol) was added and the reaction mixture was stirred for further 48 h. The resulting solution was filtered through Celite. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuo (10 Torr, 12 h) affording a residue containing (*E*)-1,3-diphenyl-*N*,*N*-dipropylprop-2-en-1-amine **5c** or 1-((*E*)-1,3-diphenylallyl)pyrrolidine **5d**. In order to evaluate the ee and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 ml) and a sample was taken for HPLC analysis.

4.4.4. General procedure for the Rh-catalysed hydrogenation of α-dehydrocarboxylic acid esters 8a–c

A solution of $[Rh(cod)_2]BF_4$ (0.002 g, 0.005 mmol) and the appropriate ligand (0.003 g, 0.005 mmol) in 8 ml of the appropriate solvent was stirred for 40 min. Then, the resulting solution and the prochiral olefin (0.5 mmol) were transferred into the hydrogenation device (a standard device for hydrogenation under 1 bar hydrogen pressure) under a hydrogen atmosphere. The hydrogenation was followed by measurement of the gas-consumption under isothermic (25 °C) and isobaric (1 bar) conditions with an automatically registering gas measuring device. When no further gas consumption occurred the reaction was finished. The conversions were determined by GC/HPLC simultaneously with determination of the ee values. In some cases, conversions were also determined by ^{1}H NMR.

4.4.5. General procedure for Rh-catalysed addition of phenylboronic acid to 2-methoxybenzaldehyde 10

A solution of $[Rh(C_2H_4)_2Cl]_2$ (0.004 g, 0.0104 mmol) and the appropriate ligand (0.013 g, 0.0208 mmol) in 1,4-dioxane (1.5 ml) was stirred for 40 min. Then, $PhB(OH)_2$ (0.25 g, 2.1 mmol), $KF \times 2H_2O$ (0.2 g, 2.1 mmol), water (1.5 ml) and 2-methoxybenzaldehyde (0.14 g, 1.04 mmol) were added sequentially and the reaction mixture was stirred for further 48 h at room temperature. The resulting mixture was extracted with CH_2Cl_2 (3 × 3 ml) and the organic layer was dried over $MgSO_4$. The solvent was evaporated at reduced pressure (40 Torr). The resulting (2-methoxyphenyl)(phenyl)methanol **11** was purified by column chromatography on silica gel (hexane/AcOEt 9:1) and subjected to enantiomeric excess analysis by chiral HPLC.

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