Tetrahedron Letters 52 (2011) 5706–5710

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Phosphoramidites based on phenyl-substituted 1,2-diols as ligands in palladium-catalyzed asymmetric allylations: the contribution of steric demand and chiral centers to the enantioselectivity

Konstantin N. Gavrilov [a,*], Sergey V. Zheglov [a], Mariya N. Gavrilova [a], Ilya V. Chuchelkin [a], Nikolay N. Groshkin [a], Eugenie A. Rastorguev [b], Vadim A. Davankov [b]

[a] Department of Chemistry, Ryazan State University, 46 Svoboda Street, 390000 Ryazan, Russian Federation
[b] Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street, 119991 Moscow, Russian Federation

ARTICLE INFO

Article history:
Received 23 June 2011
Revised 11 August 2011
Accepted 22 August 2011
Available online 28 August 2011

Keywords:
Asymmetric allylic substitution
Palladium
Phosphorus ligands
Phosphoramidites

ABSTRACT

A small family of readily available phosphoramidite ligands, including compounds with *P**-stereocenters, has been prepared from phenyl-substituted 1,2-diols as simple and cheap starting materials. Using these ligands, up to 84% ee was achieved in Pd-catalyzed asymmetric allylic substitution. The influence of structural modules such as asymmetric atoms and steric demand on the enantioselectivity is discussed.

The syntheses of drugs, chemical agents for plant protection, food additives, flavors, liquid crystals, and enantiopure polymers are based on modern approaches to optically pure compounds. One of the leading approaches is asymmetric metal complex catalysis.[1] In turn, the activity and stereoselectivity of metal complex catalysts depend largely on the successful design and synthesis of appropriate chiral ligands, among which phosphorus-containing compounds are noteworthy. Accordingly, one of the core research activities in the field of asymmetric catalysis is the ongoing development of new phosphorus ligands aimed at higher levels of efficiency and selectivity to meet the increasing demands of both academic and industrial sectors. Although the use of numerous chiral phosphorus ligands has been reported, the tuning of existing ligands and/or the development of novel chiral ligands with improved performance continue to attract the interest of synthetic chemists.[1b,2]

Optically active phosphite-type compounds play important roles, because of their intrinsic electronic properties and steric variability. Indeed, various P–O and/or P–N bond containing phosphorus ligands can be constructed in large quantities through the use of relatively simple condensation processes, and from inexpensive starting materials. Another advantage of phosphite-type ligands is that they are less sensitive to air and other oxidizing agents than phosphines. Hence, this makes it possible to develop a protocol for the ligand synthesis that does not necessitate the use of a glove box. Furthermore, they are amenable to parallel synthesis, even in solid phase synthesis. Such key advantages allow the preparation and screening of extensive libraries of chiral ligands aiming at high activities and selectivities for each particular reaction. In addition, phosphite-type ligands are characterized by pronounced π-acidity and low cost.[3,4]

Phosphoramidites represent a highly versatile and readily accessible class of chiral phosphite-type ligands. Their modular structure enables the formation of a series of ligands and simple fine-tuning for a specific catalytic reaction. Phosphoramidites frequently show exceptional levels of stereocontrol, and their monodentate nature is essential in combinatorial catalysis, where a ligand-mixture approach is used. Phosphoramidites with a BINOL-backbone are considered as so-called 'privileged ligands'.[4l,5] Biphenol-, SPINOL-, TADDOL-, BIFOL-, diphenylprolinol-based phosphoramidites, as well as phosphoramidites DpenPhos and CydamPhos, also have demonstrated high enantioselectivities in transition metal catalyzed asymmetric transformations.[6]

Herein we report the synthesis and application of some phosphoramidites containing 1,3,2-dioxaphospholane rings based on phenyl-substituted 1,2-diols, including the compounds possessing a *P**-stereocenter in Pd-catalyzed asymmetric allylic substitution. Enantioselective Pd-catalyzed allylic substitution has emerged as a powerful synthetic tool which is tolerant of various functional

* Corresponding author. Tel.: +7 4912 280580; fax +7 4912 281435.
E-mail address: k.gavrilov@rsu.edu.ru (K.N. Gavrilov).

0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.08.122

groups in the substrate and operates with a wide range of C-, N-, O-, S- and P-nucleophiles. On the one hand, this is a common benchmark test for evaluating new chiral ligands. On the other, Pd-catalyzed allylic substitution is a novel and highly efficient strategy in the total synthesis of enantiopure natural and unnatural products.[1c,7]

A well-conceived ligand should possess one or more structural features (modules) that may be varied readily in a systematic fashion, in order to optimize the design for the given purpose. The design is informative to the extent that variations in the ligand modules can be correlated to changes in the reactivity or selectivity of the catalyst. A set of such powerful modules includes asymmetric atoms and steric demands.[1b,2c,d] Phosphoramidites **5–7** with a 1,2-diol-backbone illustrate successfully this concept.

The monodentate phosphoramidites **5–7** were synthesized via one-step phosphorylation of the corresponding phenyl-substituted 1,2-diols **2–4** with hexaethylphosphorous triamide (**1**) (Scheme 1) in toluene (in the case of **5** and **7**) or under solvent-free conditions (in the case of **6**). This convenient method does not require an additional base and the only by-product is volatile $HNEt_2$. The starting optically active diols **2** and **3** are commercially available; diol **4** was synthesized in two steps from (*S*)-mandelic acid.[8] It should be noted that (*S,S*)-hydrobenzoin (**3**) and (*S*)-1,1,2-triphenylethane-1,2-diol (**4**) are important chiral auxiliaries and synthetic building blocks.[9] Since all the precursors are inexpensive and readily available, the ligands **5–7** can be prepared on multigram scale. The 1,2-diol-based phosphoramidites **5–7** are colorless liquids or white solids, which are readily soluble in common organic solvents. They were fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, EI and/or MALDI TOF/TOF mass spectrometry as well as by elemental analysis. Compounds **5–7** and their solutions must be kept under anhydrous conditions due to their sensitivity toward moisture.

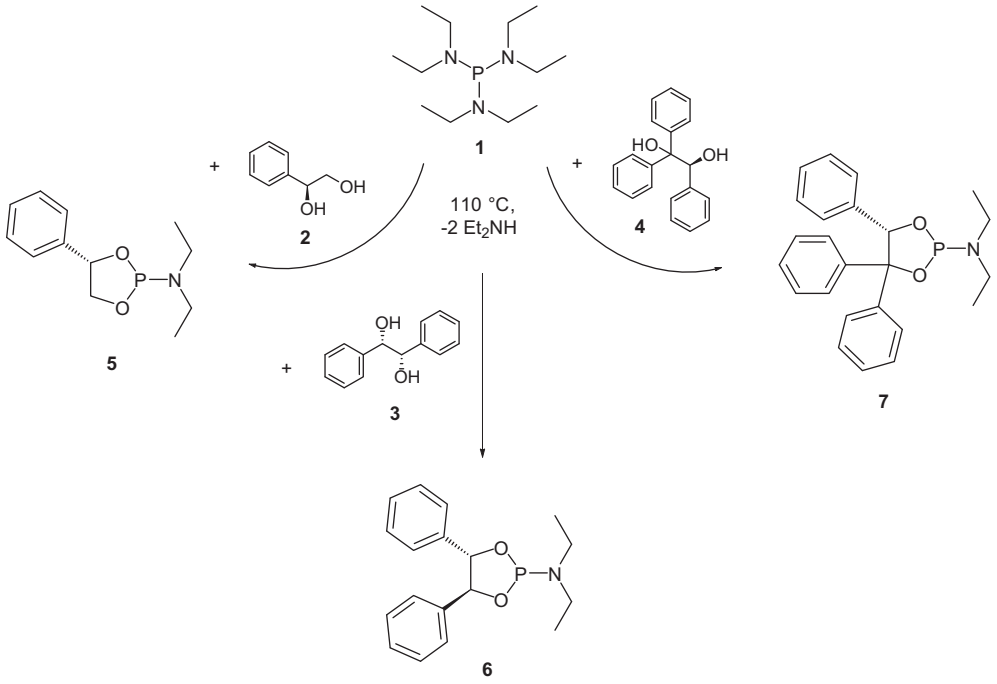
The phosphoramidites **5–7** possess: (i) a 1,3,2-dioxaphospholane ring with one to three phenyl substituents and an NEt_2 substituent on the phosphorus atom, (ii) one or two *C**-stereocenters, (iii) chirogenic phosphorus donor atoms in the case of **5** and **7**. The ^{31}P NMR spectroscopic data for compounds **5–7** are summarized in Table 1. Compound **5** was a mixture of epimers with respect to the phosphorus stereocenter and contained 71% of the major *P**-epimer, while ligand **7** was formed as a single stereoisomer (Table 1). We did not establish the absolute configuration of the *P**-stereocenter in the structure of ligand **7**. Nevertheless, considering the data presented in an article on the related compound, (2*R*,5*S*)-2-chloro-4,4,5-triphenyl-1,3,2-dioxaphospholan,[10] it can be assumed that we obtained the (2*R*,5*S*)-epimer of **7**. The ^{13}C NMR spectra of these ligands are characterized by similar spin-spin coupling constants $^2J_{C(4),P}$ and $^2J_{C(5),P}$ (7.1 and 7.0 Hz for (2*R*,5*S*)-2-chloro-4,4,5-triphenyl-1,3,2-dioxaphospholan, 9.0 and 8.9 Hz for **7**, respectively), which indicate that their asymmetric phosphorus atoms have the same absolute configurations.[11] It should be added that the (*R*)-configuration of the *P**-stereocenter in (2*R*,5*S*)-2-chloro-4,4,5-triphenyl-1,3,2-dioxaphospholan has been proved by single crystal X-ray diffraction.[10] To estimate the steric demands of phosphoramidites **5–7**, we calculated their Tolman cone angles using the reported semi-empirical quantum-mechanical AM1 method with full optimization of geometrical parameters.[12] The results obtained showed that the steric parameters (θ) of ligands **5–7** gradually increased within the intervals of 117°–138°, peaking at compound **7** bearing three phenyl substituents (Table 1).

In order to examine the influence of the asymmetric atoms and steric demand, phosphoramidites **5–7** were tested in the asymmetric Pd-catalyzed allylic substitution of (*E*)-1,3-diphenylallyl acetate (**10**) as a benchmark catalytic process (Tables 2 and 3). The reactions were run in THF or CH_2Cl_2. The results obtained showed that

Table 1
^{31}P NMR chemical shifts (162.0 MHz, $CDCl_3$, 25 °C) and cone angles θ (°) of ligands **5–7**.

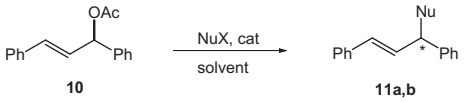
Ligand		δ_P	θ
5	(29%)[a]	149.7	117
	(71%)[a]	146.5	
6		149.4	126
7		142.9	138

[a] Percentage of *P**-epimers.



Scheme 1. Synthesis of phosphoramidites **5–7**.

Table 2
Pd-catalyzed allylic sulfonylation and alkylation of (*E*)-1,3-diphenylallyl acetate (**10**)[a]



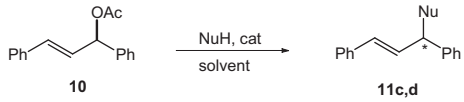
10 **11a,b**

N u= SO_2pTol, X = Na, **11a**
Nu = $CH(CO_2Me)_2$ X = H, **11b**

Entry	Ligand	L/Pd	Solvent	Conversion (%)	ee (%)
Allylic sulfonylation with sodium p-toluenesulfinate [b]					
1	**5**	1	THF	94[c]	40 (R)
2	**5**	2	THF	95[c]	50 (R)
3	**6**	1	THF	97[c]	30 (R)
4	**6**	2	THF	80[c]	65 (R)
5	**6**	**2**	**THF**	**90[c]**	**80 (R)** [d]
6	**7**	1	THF	83 [c]	35 (R)
7	**7**	2	THF	96[c]	50 (R)
8	**7**	2	THF	81[c]	62 (R) [e]
Allylic alkylation with dimethyl malonate (BSA, KOAc) [f]					
9	**5**	1	CH_2Cl_2	100	5 (R)
10	**5**	2	CH_2Cl_2	100	8 (R)
11	**5**	1	THF	—	—
12	**5**	2	THF	10	2 (R)
13	**6**	1	CH_2Cl_2	100	30 (R)
14	**6**	2	CH_2Cl_2	100	80 (R)
15	**6**	1	THF	16	20 (R)
16	**6**	2	THF	30	40 (R)
17	**6**	**2**	**CH_2Cl_2**	**100**	**84 (R)**[d]
18	**6**	2	THF	98	38 (R)[d]
19	**7**	1	CH_2Cl_2	100	70 (S)
20	**7**	2	CH_2Cl_2	100	37 (S)
21	**7**	1	THF	94	40 (S)
22	**7**	2	THF	100	32 (S)
23	**7**	2	CH_2Cl_2	100	26 (S)[e]
24	**7**	2	THF	90	25 (S)[e]

[a] All reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ at room temperature for 48 h.
[b] Enantiomeric excess of **11a** was determined by HPLC (Daicel Chiralcel OJ, C_6H_{14}/*i*-PrOH = 4:1, 0.5 ml/min, 254 nm).
[c] Isolated yield of **11a**.
[d] With complex **8** as the catalyst.
[e] With complex **9** as the catalyst.
[f] The conversion of substrate **10** and enantiomeric excess of **11b** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 99:1, 0.6 ml/min, 254 nm).

Table 3
Pd-catalyzed allylic amination of (*E*)-1,3-diphenylallyl acetate (**10**)[a]

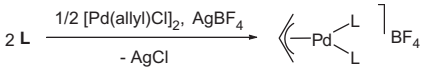


10 **11c,d**

Nu = $N(Pr)_2$, **11c**
Nu = $N(CH_2)_4$, **11d**

Entry	Ligand	L/Pd	Solvent	Conversion (%)	ee (%)
Allylic amination with dipropylamine[b]					
1	**5**	1	CH_2Cl_2	100	5 (−)
2	**5**	2	CH_2Cl_2	100	2 (−)
3	**5**	1	THF	100	9 (−)
4	**5**	2	THF	100	15 (−)
5	**6**	1	CH_2Cl_2	100	35 (−)
6	**6**	2	CH_2Cl_2	100	39 (−)
7	**6**	**1**	**THF**	**14**	**74 (−)**
8	**6**	2	THF	16	71 (−)
9	**6**	2	CH_2Cl_2	100	39 (−)[c]
10	**6**	2	THF	100	47 (−)[c]
11	**7**	1	CH_2Cl_2	100	15 (+)
12	**7**	2	CH_2Cl_2	100	13 (+)
13	**7**	1	THF	24	11 (+)
14	**7**	2	THF	44	11 (+)
15	**7**	2	CH_2Cl_2	100	10 (+)[d]
Allylic amination with pyrrolidine [e]					
16	**5**	1	CH_2Cl_2	100	5 (*S*)
17	**5**	2	CH_2Cl_2	100	3 (*S*)
18	**5**	1	THF	100	29 (*S*)
19	**5**	2	THF	100	19 (*S*)
20	**6**	1	CH_2Cl_2	100	49 (*S*)
21	**6**	2	CH_2Cl_2	100	57 (*S*)
22	**6**	1	THF	72	60 (*S*)
23	**6**	**2**	**THF**	**57**	**65 (*S*)**
24	**6**	2	CH_2Cl_2	100	60 (*S*)[c]
25	**6**	2	THF	100	54 (*S*)[c]
26	**7**	1	CH_2Cl_2	100	63 (*R*)
27	**7**	2	CH_2Cl_2	100	57 (*R*)
28	**7**	1	THF	100	60 (*R*)
29	**7**	2	THF	100	54 (*R*)
30	**7**	2	CH_2Cl_2	100	49 (*R*)[d]

[a] All reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ at room temperature for 48 h.
[b] The conversion of substrate **10** and enantiomeric excess of **11c** 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] With complex **8** as the catalyst.
[d] With complex **9** as the catalyst.
[e] The conversion of substrate **10** and enantiomeric excess of **11d** 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).



8 (L = **6**)
9 (L = **7**)

Scheme 2. Synthesis of cationic palladium complexes **8** and **9**.

the efficiency of these ligands differs dramatically. In most cases ligand **5** demonstrated an excellent conversion, but its enantioselectivity was poor (in allylic alkylation and amination, no more than 29% ee) or mediocre (in allylic sulfonylation, up to 50% ee, Table 2, entries 1 and 2). Presumably, this is caused by the rather low steric demand (θ = 117°) of phosphacyclane **5**, and by the low ratio of its *P**-epimers (Table 1).

At the same time, the use of phosphoramidites **6** and **7** resulted in moderate to good enantioselectivities in most cases (Tables 2 and 3). Hence, with these ligands cationic palladium catalysts **8** and **9** were prepared (Scheme 2). Compounds **6** and **7** readily react with $[Pd(allyl)Cl]_2$ (CH_2Cl_2/THF, $AgBF_4$ as chloride scavenger, room temperature, 3 h) to give cationic complexes of the type $[Pd(allyl)(L)_2]BF_4$ bearing two molecules of the monodentate phosphorous ligand. The ^{31}P NMR spectra of isolated complexes (in $CDCl_3$) exhibited a singlet at δ_P 146.2 for **8** and an AB system (δ_P 140.9, d and δ_P 140.0, d, $^2J_{P,P'}$ 102.1 Hz) for **9** either due to the fast interconversion of the *exo*- and *endo*-isomers or to the absence of one of them.[13] The AB system in the ^{31}P NMR spectrum of complex **9** indicates the nonequivalence of the two *P**-monodentate ligands **7** in the coordination sphere of palladium.[14] The MS spectroscopic and elemental analysis data (see Supplementary data) were also in good agreement with the proposed structures of **8** and **9**.

In the allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate, product (*R*)-**11a** was obtained in 90% yield and 80% ee when complex **8** was employed as the chiral auxiliary (Table 2, entry 5). When the reaction was carried out with $[Pd(allyl)Cl]_2$ as the precatalyst, ligand **6** afforded (*R*)-**11a** having a moderate enantiomeric purity (up to 65% ee). On the whole, the palladium catalysts with ligand **7** provided no more than 62% ee (Table 2, entries 6–8).

In the Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate with dimethyl malonate, the best result (quantitative conversion and 84% ee) was obtained again with cationic complex **8** (Table 2, entry 17). It is clear that CH_2Cl_2 is the solvent of choice (Table 2, entries 13–24). In all cases, the catalytic systems based on phosphoramidite **6** led to the product **11b** with (*R*)-configura

tion, and the optimal molar ratio was L/Pd = 2. *P**-chiral ligand **7** showed lower enantioselectivities (up to 70% ee, Table 2, entry 19). Unlike the allylic alkylation with ligand **6**, in the case of ligand **7** the product **11b** had (*S*)-configuration, and the best asymmetric induction was achieved with L/Pd = 1 (Table 2, entries 19–24). In particular, the cationic complex **9** bearing two ligands **7** in a coordination sphere of palladium provided low enantioselectivity (no more than 26% ee, Table 2, entries 23 and 24).

Allylic amination of compound **10** with dipropylamine in the presence of ligand **6** gave product (−)-**11c** with up to 74% ee. The reaction in THF was more enantioselective, while a higher conversion was achieved in CH_2Cl_2. The L/Pd molar ratio had virtually no effect on the enantioselectivity (see Table 3, entries 5–10). At the same time, ligand **7** demonstrated low enantioselectivity almost irrespective of both the L/Pd molar ratio and the solvent (10–15% ee, Table 3, entries 11–15). Interestingly, in this reaction, as in the case of the above discussed allylic alkylation of (*E*)-1,3-diphenylallyl acetate, phosphoramidites **6** and **7** favored the formation of the opposite enantiomers of product **11c**.

We also investigated the allylic amination of (*E*)-1,3-diphenylallyl acetate with pyrrolidine as an *N*-nucleophile. In this reaction, phosphoramidites **6** and **7** were moderate stereoinductors providing up to 65% and 63% ee, respectively (Table 2, entries 23 and 26). As a rule, the conversion was quantitative. The enantiomeric excess does not depend (or poorly depends) on the solvent and the molar ratio L/Pd. As in the reactions with dimethyl malonate and dipropylamine, compounds **6** and **7** afforded different enantiomers of amine **11d**. Accordingly, ligand **6** led to the (*S*)-enantiomer of **11d**, and ligand **7** the (*R*)-enantiomer.

In conclusion, three monodentate phosphoramidites **5–7** based on (*S*)-1-phenylethane-1,2-diol, (*S,S*)-hydrobenzoin and (*S*)-1,1,2-triphenylethane-1,2-diol were obtained via a simple synthesis. Some conclusions can be drawn from the results obtained with these ligands in the Pd-catalyzed asymmetric allylation. As stated above, ligand **5** gave poor or mediocre enantioselectivity due to its low steric demand and low epimeric ratio. Among the phosphoramidites **6** and **7** the former was more efficient. It should be noted that phosphacyclane **7** is more sterically demanding than **6** and has a *P**-stereocenter. Presumably, the low enantioselectivity in the Pd-catalyzed allylic alkylation at a molar ratio L/Pd = 2 was caused by steric hindrance in the $[Pd(1,3\text{-}Ph_2\text{-}allyl)(\mathbf{7})_2]^+$ intermediate.[15] In certain processes with participation of **7**, for example, in the allylic amination with dipropylamine, a mismatched combination of *P**- and *C**-stereocenters takes place. At the same time, the choice between **6** and **7** makes it possible to control the sign of asymmetric induction in most cases. To sum up, the results obtained with phosphoramidites **6** and **7** show the considerable potential of such ligands in enantioselective catalysis. Indeed, in the Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate with dimethyl malonate they are more efficient than a series of BINOL-based phosphoramidites and comparable with TADDOL-based phosphoramidites.[16] Enantioselectivity can be further improved by introduction of bulky N-containing exocyclic substituents at the phosphorus atom instead of the NEt_2 group, including substituents with additional *C**-stereocenters. Such experiments are in progress in our laboratory.

Experimental procedures for the preparation of ligands **5**–**7**: Procedure for the preparation of ligand **5**. A solution of $P(NEt_2)_3$ (**1**) (2.74 ml, 10 mmol) and (*S*)-1-phenylethan-1,2-diol (**2**) (1.38 g, 10 mmol) in toluene (25 ml) was stirred under reflux for 1 h. All volatiles were removed under vacuum and the crude product was purified by flash chromatography on silica gel (EtOAc/hexane, 1:3) and then by bulb-to-bulb distillation under vacuum (T_{bath} = 125–134 °C, 1 Torr).

(4S)-2-Diethylamino-4-phenyl-1,3,2-dioxaphospholan (**5**): Colorless liquid; yield 1.77 g (74%); R_f 0.9 (EtOAc/hexane, 1:1, Silica Gel 60 F254). ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ = 1.11 (t, J = 8.1 Hz, 6H, CH_3); 3.12 (m, 4H, NCH_2); 3.68 (m, 1H, OCH_2); 4.51 (m, 1H, OCH_2); 5.27 (br t, J = 6.1 Hz, 1H, OCH); 7.31 (m, 2H, CH_{Ar}); 7.39 (m, 3H, CH_{Ar}), major epimer; 1.10 (t, J = 7.9 Hz, 6H, CH_3); 3.15 (m, 4H, NCH_2); 3.71 (m, 1H, OCH_2); 4.21 (m, 1H, OCH_2); 5.11 (dd, J = 9.9 Hz, J = 6.1 Hz, 1 H, OCH); 7.29 (m, 2H, CH_{Ar}); 7.38 (m, 3H, CHAr), minor epimer. ^{13}C{H} NMR (100.6 MHz, $CDCl_3$, 25 °C): δ_C = 15.0 (d, ^3J = 3.0 Hz, CH_3); 37.9 (d, ^2J = 21.1 Hz, NCH_2); 70.9 (d, ^2J = 7.9 Hz, OCH_2); 76.5 (d, ^2J = 9.0 Hz, OCH); 125.6 (s, CH_{Ar}); 127.8 (s, CH_{Ar}); 128.3 (s, CH_{Ar}); 139.7 (d, ^3J = 5.0 Hz, C_{Ar}), major epimer; δ_C = 14.9 (d, ^3J = 3.1 Hz, CH_3); 37.8 (d, ^2J = 21.0 Hz, NCH_2); 68.7 (d, ^2J = 6.0 Hz, OCH_2); 77.2 (d, ^2J = 5.9 Hz, OCH); 125.3 (s, CH_{Ar}); 127.9 (s, CH_{Ar}); 128.4 (s, CH_{Ar}); 137.6 (d, ^3J = 4.0 Hz, C_{Ar}), minor epimer. MS (EI, 70 eV): *m/z* (%) = 239 (100) $[M]^+$. Anal. Calcd for $C_{12}H_{18}NO_2P$: C, 60.24; H, 7.58; N, 5.85. Found: C, 60.48; H, 7.62; N, 5.64.

Procedure for the preparation of ligand **6**: A mixture of $P(NEt_2)_3$ (**1**) (2.74 ml, 10 mmol) and (*S,S*)-hydrobenzoin (**3**) (2.14 g, 10 mmol) was stirred at 110 °C for 45 min. Next the mixture was stirred under vacuum (10 Torr, 90 °C) for 30 min to remove $HNEt_2$ and cooled to 20 °C. The residue was purified by bulb-to-bulb distillation in vacuum (T_{bath} = 171–182 °C, 1 Torr) and then by flash chromatography on aluminum oxide (toluene).

(4S,5S)-2-Diethylamino-4,5-diphenyl-1,3,2-dioxaphospholan (**6**): White waxy solid; yield 2.18 g (69%); R_f 0.7 (EtOAc/hexane, 1:1, Alugram Alox N/UV_{254}). ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ = 1.19 (t, J = 8.0 Hz, 6H, CH_3); 3.27 (m, 4H, NCH_2); 4.84 (br s, 2H, OCH); 7.19–7.35 (m, 10H, CH_{Ar}). ^{13}C{H} NMR (100.6 MHz, $CDCl_3$, 25 °C): δ_C = 15.4 (d, ^3J = 4.0 Hz, CH_3); 38.4 (d, ^2J = 28.2 Hz, NCH_2); 82.6 (d, ^2J = 9.1 Hz, OCH); 84.7 (d, ^2J = 8.1 Hz, OCH); 126.4 (s, CH_{Ar}); 127.2 (s, CH_{Ar}); 128.2 (s, CH_{Ar}); 128.3 (s, CH_{Ar}); 128.4 (s, CH_{Ar}); 128.5 (s, CH_{Ar}); 136.7 (d, ^3J = 6.0 Hz, C_{Ar}); 138.1 (d, ^3J = 10.1 Hz, C_{Ar}). MS (EI, 70 eV): *m/z* (%) = 315 (8) $[M]^+$, 181 (100) $[PhCH_2CHPh]^+$. Anal. Calcd for $C_{18}H_{22}NO_2P$: C, 68.56; H, 7.03; N, 4.44. Found: C, 68.71; H, 7.16; N, 4.54.

Procedure for the preparation of ligand **7**: A solution of $P(NEt_2)_3$ (**1**) (2.74 ml, 10 mmol) and (*S*)-1,1,2-triphenylethan-1,2-diol (**4**) (2.90 g, 10 mmol) in toluene (30 ml) was stirred under reflux for 2 h. Next the solution was cooled to 20 °C and filtered through a short aluminum oxide plug. The filtrate was concentrated in vacuum (40 Torr) and the crude product was purified by flash chromatography on silica gel (CH_2Cl_2) and then by careful trituration with EtOAc/hexane (1:25). The precipitated white solid was separated by centrifugation and dried in vacuum (1 Torr) for 1 h.

(5S)-2-Diethylamino-4,4,5-triphenyl-1,3,2-dioxaphospholan (**7**): White powder; yield 2.54 g (65%); R_f 0.85 (EtOAc/hexane, 1:5, silica gel 60 F254). ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ = 1.04 (t, J = 7.5, 6H, CH_3), 3.04 (m, 4H, NCH_2), 5.93 (s, 1 H, OCH), 6.92–7.14 (m, 10H, CH_{Ar}), 7.31 (d, J = 8.0, 1H, CH_{Ar}), 7.38 (t, J = 7.9, 2H, CH_{Ar}), 7.69 (d, J = 7.9, 2H, CH_{Ar}). ^{13}C{H} NMR (100.6 MHz, $CDCl_3$, 25 °C): δ_C = 15.0 (d, ^3J = 3.0, CH_3), 38.3 (d, ^2J = 21.1, NCH_2), 84.4 (d, ^2J = 8.9, OCH), 90.6 (d, ^2J = 9.0, OC), 126.7 (s, CH_{Ar}), 126.9 (s, CH_{Ar}), 127.0 (s, CH_{Ar}), 127.4 (s, CH_{Ar}), 127.5 (s, CH_{Ar}), 127.7 (s, CH_{Ar}), 127.8 (s, CH_{Ar}), 128.1 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 137.5 (d, ^3J = 7.0, C_{Ar}), 141.1 (d, ^3J = 3.1, C_{Ar}), 143.6 (s, C_{Ar}). MS (EI, 70 eV): *m/z* (%) = 391 (1) $[M]^+$, 257 (100) $[Ph_2CHCHPh]^+$. MS (MALDI TOF/TOF): *m/z* (%) = 430 (100) $[M+K]^+$, 273 (39) $[Ph_2CHC(OH)Ph]^+$, 257 (66) $[Ph_2CHCHPh]^+$. Anal. Calcd for $C_{24}H_{26}NO_2P$: C, 73.64; H, 6.69; N, 3.58. Found: C, 73.87; H, 6.59; N, 3.46.

Acknowledgments

We acknowledge the financial support from the Russian Foundation for Basic Research (Grant No. 11-03-00347-a) and a grant from the President of the Russian Federation for Young Candidates of Sciences (No. MK-3889.2010.3).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.08.122.

References and notes

1. (a) Brown, J. M. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. I, pp 121–182; (b) Ohkuma, T.; Kitamura, M.; Noyori, R. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, 2000; pp 1–110; (c) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921; (d) Blaser, H.-U.; Schmidt, E. *Asymmetric Catalysis on Industrial Scale*; Wiley-VCH: Weinheim, 2004; (e) Burk, M. J. *Acc. Chem. Res.* **2000**, *33*, 363.
2. (a) Falciola, C. A.; Alexakis, A. *Eur. J. Org. Chem.* **2008**, 3765; (b) Hargaden, G. C.; Guiry, P. J. *Chem. Rev.* **2009**, *109*, 2505; (c) Au-Yeung, T. T.-L.; Chan, S.-S.; Chan, A. S. C. *Adv. Synth. Catal.* **2003**, *345*, 537; (d) Caldentey, X.; Pericas, M. A. *J. Org. Chem.* **2010**, *75*, 2628.
3. Claver, C.; Pamies, O.; Dieguez, M. In Börner, A., Ed.; Phosphorus Ligands in Asymmetric Catalysis; Wiley-VCH: Weinheim, 2008; Vol. II, pp 507–528.
4. (a) Ansel, J.; Wills, M. *Chem. Soc. Rev.* **2002**, *31*, 259; (b) Alexakis, A.; Benhaim, C. *Eur. J. Org. Chem.* **2002**, *19*, 3221; (c) Molt, O.; Schrader, T. *Synthesis* **2002**, 2633; (d) Reetz, M. T.; Mehler, G.; Meiswinkel, A.; Sell, T. *Tetrahedron Lett.* **2002**, *43*, 7941; (e) Dieguez, M.; Pamies, O.; Claver, C. *Tetrahedron:Asymmetry* **2004**, *15*, 2113; (f) Gavrilov, K. N.; Bondarev, O. G.; Polosukhin, A. I. *Russ. Chem. Rev.* **2004**, *73*, 671; (g) Jerphagnon, T.; Renaud, J.-L.; Bruneau, C. *Tetrahedron: Asymmetry* **2004**, *15*, 2101; (h) Reetz, M. T.; Mehler, G.; Bondarev, O. *Chem. Commun.* **2006**, 2292; (i) de Vries, J. G.; Lefort, L. *Chem. Eur. J.* **2006**, *12*, 4722; (j) Jagt, R. B. C.; Toullec, P. Y.; Geerdink, D.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 2789; (k) Swennenhuis, B. H. G.; Chen, R.; van Leeuwen, P. W. N. M.; de Vries, J. G.; Kamer, P. C. J. *Org. Lett.* **2008**, *10*, 989; (l) Teichert, J. F.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2010**, *49*, 2486; (m) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Claver, C.; Pamies, O.; Dieguez, M. *Chem. Rev.* **2011**, *111*, 2077.
5. Krausová, Z.; Sehnal, P.; Bondzic, B. P.; Chercheja, S.; Eilbracht, P.; Stará, I. G.; Saman, D.; Starý, I. *Eur. J. Org. Chem.* **2011**, 3849.
6. (a) Chapsal, B. D.; Hua, Z.; Ojima, I. *Tetrahedron: Asymmetry* **2006**, *17*, 642; (b) Vuagnoux-d'Augustin, M.; Kehrli, S.; Alexakis, A. *Synlett* **2007**, 2057; (c) Qiao, X.-C.; Zhu, S.-F.; Zhou, Q.-L. *Tetrahedron:Asymmetry* **2009**, *20*, 1254; (d) Pellissier, H. *Tetrahedron* **2008**, *64*, 10279; (e) Kop-Weiershausen, T.; Lex, J.; Neudörfl, J.-M.; Goldfuss, B. *Beilstein J. Org. Chem.* **2005**, 1; (f) Bondarev, O. G.; Goddard, R. *Tetrahedron Lett.* **2006**, *47*, 9013; (g) Liu, Y.; Ding, K. *J. Am. Chem. Soc.* **2005**, *127*, 10488; (h) Zhao, B.; Wang, Z.; Ding, K. *Adv. Synth. Catal.* **2006**, *348*, 1049.
7. (a) McCarthy, M.; Guiry, P. J. *Tetrahedron* **2001**, *57*, 3809; (b) Crepy, K. V. L.; Imamoto, T. *Adv. Synth. Catal.* **2003**, *345*, 79; (c) Graening, T.; Schmalz, H. G. *Angew. Chem., Int. Ed.* **2003**, *42*, 2580; (d) Chapsal, B. D.; Ojima, I. *Org. Lett.* **2006**, *8*, 1395; (e) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258; (f) Dieguez, M.; Pamies, O. *Acc. Chem. Res.* **2010**, *43*, 312; (g) Lam, F. L.; Kwong, F. Y.; Chan, A. S. C. *Chem. Commun.* **2010**, *46*, 4649; (h) Fernandez-Perez, H.; Etayo, P.; Panossian, A.; Vidal-Ferran, A. *Chem. Rev.* **2011**, *111*, 2119; (i) Lafrance, D.; Bowles, P.; Leeman, K.; Rafka, R. *Org. Lett.* **2011**, *13*, 2322.
8. Braun, M.; Gräf, S.; Herzog, S. *Org. Synth. Coll.* **1998**, *9*, 507.
9. (a) Okano, K. *Tetrahedron* **2011**, *67*, 2483; (b) Braun, M.; Sacha, H.; Galle, D.; Baskaran, S. *Pure Appl. Chem.* **1996**, *68*, 561; (c) Ridder, D.; Wunderlichb, H.; Braun, M. *Eur. J. Org. Chem.* **1998**, 1071.
10. Meier, T.; Braun, M.; Frank, W. *Phosphorus, Sulfur, Silicon, Relat. Elem.* **2009**, *184*, 2536.
11. Arzoumanian, H.; Buono, G.; Choukrad, M.; Petrignani, J.-F. *Organometallics* **1988**, *7*, 59.
12. (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313; (b) Polosukhin, A. I.; Kovalevskii, A. I.; Gavrilov, K. N. *Russ. J. Coord. Chem.* **1999**, *25*, 758.
13. Tsarev, V. N.; Lyubimov, S. E.; Shiryaev, A. A.; Zheglov, S. V.; Bondarev, O. G.; Davankov, V. A.; Kabro, A. A.; Moiseev, S. K.; Kalinin, V. N.; Gavrilov, K. N. *Eur. J. Org. Chem.* **2004**, 2214. and references cited therein.
14. Gavrilov, K. N.; Lyubimov, S. E.; Zheglov, S. V.; Benetsky, E. B.; Davankov, V. A. *J. Mol. Catal. A: Chem.* **2005**, *231*, 255.
15. Trost, B. M.; Lee, C. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, 2000; pp 593–649.
16. (a) Mikhel, I. S.; Bernardinelli, G.; Alexakis, A. *Inorg. Chim. Acta* **2006**, *359*, 1826; (b) Boele, M. D. K.; Kamer, P. C. J.; Lutz, M.; Spek, A. L.; de Vries, J. G.; van Leeuwen, P. W. N. M.; van Strijdonck, G. P. F. *Chem. Eur. J.* **2004**, *10*, 6232.