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P-Stereogenic Pinene-Derived Phosphoramidites and Their Use in Copper-Catalyzed Conjugate Additions

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Dedicated to Professor Henning Hopf on the occasion of his 70th birthday

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New P-stereogenic phosphoramidites based on a (–)-pinane framework were synthesized and investigated by NMR spectroscopic methods and single-crystal X-ray structural analysis. The reaction between *cis*-pinandiol **2** and *N*,*N*-dialkylphosphoramidous dichlorides, followed by protection with the BH_3·THF adduct, afforded diastereomeric mixtures of P_S and P_R BH_3–phosphoramidite complexes. After separation by column chromatography, these stereoisomers were obtained in a pure form. The BH_3 group was further cleaved by treatment with Et_2NH at elevated temperature and the obtained free phosphoramidite ligands were used for catalytic enantioselective conjugate addition reactions. As substrates, a series of cyclic and acyclic enones was employed and addition was carried out with Et_2Zn in the presence of catalytic amounts of Cu^I thiophenecarboxylate (CuTC) and a phosphoramidite ligand. The results revealed that the configuration of the phosphorus center controls the configuration of the newly formed stereogenic center of the β-alkylated ketones.

Introduction

The enantioselective Cu-catalyzed conjugate addition of organozinc and organomagnesium reagents to α,β-unsaturated carbonyl compounds has been elaborated into a powerful tool in synthetic organic chemistry.[1] Besides a variety of different P ligands, which have been employed for this reaction, phosphoramidites in particular have received great interest due to their enhanced stability and high enantioselectivity.[2,3] Both the diol moiety and the secondary amine substituent of the phosphoramidite allow the introduction of chirality. Consequently, the stereochemical control, which is provided by different chiral units of a phosphoramidite ligand core, on the steric outcome of conjugate addition reactions can be studied in detail. Furthermore, it has been independently shown by Gavrilov and Gais et al.,[4] and Reetz et al.[5] that the use of unsymmetrical chiral diamines and chiral alcohols or, alternatively, the use of unsymmetrical chiral diols and secondary amines resulted in the diastereoselective formation of phosphoramidites with P-stereogenic centers.[6] However, surprisingly little information is available about the use of P-stereogenic ligands in asymmetric catalysis. Most work has been devoted to hydroformylation,[7] allylic substitution,[4,8a] arylation,[8b] and hydrogenation of ketones and dehydroamino acids.[5,9] To the best of our knowledge, conjugate additions have not been considered so far. In this context, we focused in this contribution on the synthesis of the P-stereogenic phosphoramidite ligands and their application in conjugate addition reactions. For such purpose, we anticipated that (–)-α-pinene **1** might be a suitable scaffold for the synthesis of P-chiral phosphoramidites **6** and **7** (Scheme 1). Previously, we have already shown that (–)-α-pinene **1** could be readily converted into the corresponding bisphosphinites through *cis*-diol **2**.[10,11] In this work we used *cis*-diol **2** as a starting material for preparation of new phosphoramidites **6** and **7**. The synthetic details, the structure of protected new P-chiral phosphoramidites, and preliminary results, with regard to the application of the new ligands in conjugate addition reactions, are reported below.

Results and Discussion

Synthesis and Structure of P-Chiral Phosphoramidites

As shown in Scheme 1, (–)-α-pinene **1** was submitted to dihydroxylation according to our previously published method[10] to give diol **2** with *cis* orientation of the neighbor hydroxy groups. The phosphoramino function was introduced into the *cis*-pinandiol framework through two different synthetic pathways. In the first approach, compound

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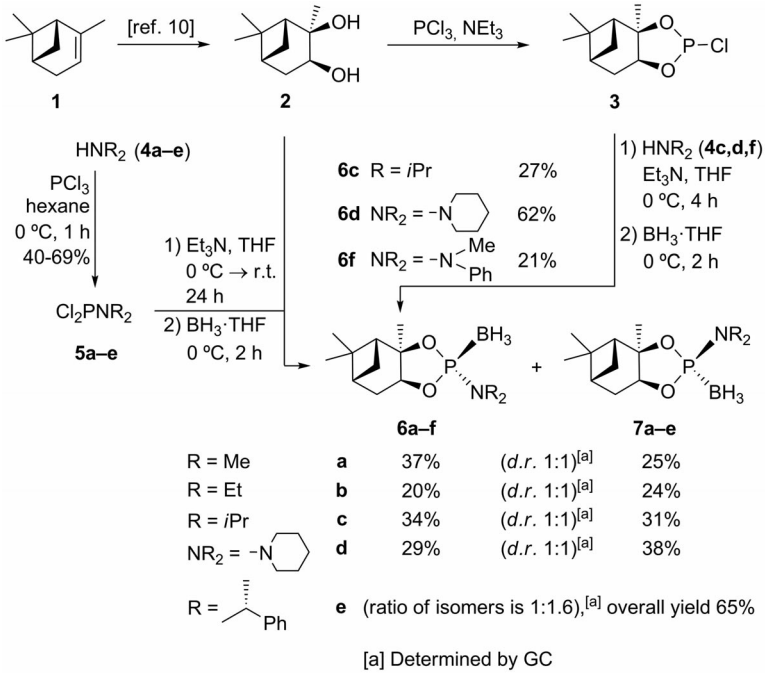


Scheme 1.

2 was treated with PCl_3 in the presence of Et_3N,[12] which led to the formation of chlorophosphite **3**. This product was used without further isolation and treated at low temperature in THF with a series of dialkylamines **4c**,**d**,**f** in the presence of Et_3N. After subsequent reaction with BH_3·THF, the raw products were subjected to chromatography on silica gel, selectively giving the P_S-configured phosphoramidite–borane complexes **6c**,**d**,**f** (see the Supporting Information). However, the overall yields obtained by this route were quite low. Possibly, due to the presence of the bulky (–)-pinane moiety, the phosphorus center in **3** is barely accessible for nucleophilic substitution reactions. To increase the productivity and get access to P_R-stereoisomers **7**, we looked for another synthetic procedure. Alternatively, a series of (dialkylamino)phosphorus dichlorides **5a**–**e** was prepared by the reaction between an excess amount of dialkylamines **4a**–**e** and phosphorus trichloride, following a procedure by van Leeuwen and co-workers.[13] The treatment of *cis*-diol **2** with *N*,*N*-dialkylphosphoramidous dichlorides **5a**–**e** in THF at temperatures between 0 and 25 °C and subsequent protection with BH_3·THF led to the new phosphoramidite–borane products as mixtures of diastereomers **6** and **7** (with a ratio of 1:1, Scheme 1). A preparative separation of diastereomers **6** and **7** was achieved by means of column chromatography on silica gel, and compounds **6a**–**d** and **7a**–**d** were isolated in a pure state as colorless crystalline solids. The only exceptions were the (*S*,*S*)-bis(α-methylbenzyl)amine-derived ligands **6e** and **7e**. For the synthesis of **6e** and **7e**, *cis*-diol **2** was deprotonated with an excess amount of *n*BuLi. Subsequent reaction with **5e**, followed by protection with BH_3·THF, gave a diastereomeric mixture of **6e** and **7e** (ratio of isomers 1:1.6, isolated yield 65%). Unfortunately, phosphoramidites **6e** and **7e** always showed very close R_f values and could not be separated from each other by preparative chromatography methods.

X-ray crystal-structure analysis of single crystals obtained from the products **6b** and **7d** allowed the determination of the absolute configuration around the P-stereogenic center in **6** and **7** (Figures 1 and 2).[14]

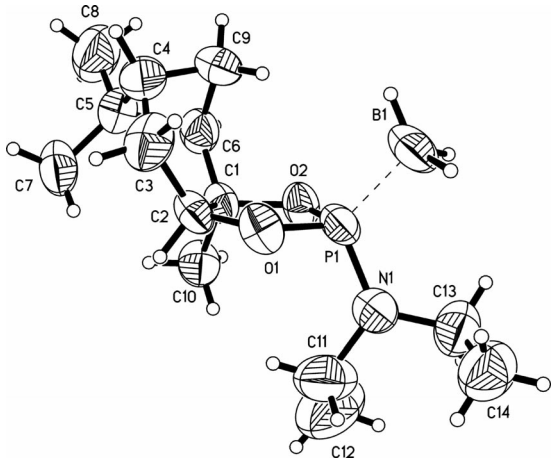


Figure 1. Structure of compound **6b** in the solid state. View along the five-membered ring system, flat conformation [for a better overview, anisotropic displacement parameters with 35% probability and without disordered ethyl function (C13, C14)].

The BH_3–phosphoramidite complex **6b** features a 1,2-dioxo-substituted (–)-pinane framework with the oxygen atoms occupying positions *cis* to each other (Figure 1). The oxygen atoms are connected with the (–)-pinane framework [C1–O2: 1.519(6) Å, C2–O1: 1.529(6) Å]. In addition, they are bonded with the same phosphorus center in a chelate

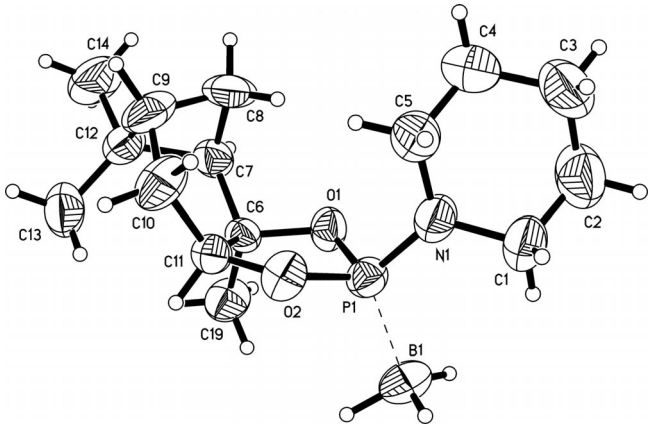


Figure 2. Structure of phosphoramidite **7d** in the solid state. View along the five-membered ring system, envelope conformation, O1 out-of-plane.

fashion [O1–P1: 1.597(3) Å, O2–P1: 1.595(3) Å]. The phosphorus atom, both oxygen atoms, and the C1 and C2 carbon atoms create the five-membered chelate [C_2O_2P] ring anellated with the (–)-pinane core through the C1 and C2 positions. The [C_2O_2P] ring has an *exo* orientation, whereas the methyl substituent at C1 atom is directed *endo* relative to the (–)-pinane core [C1–C10: 1.515(5) Å]. In addition to the two oxygen atoms, the phosphorus center is connected with a secondary diethylamino group [P1–N1: 1.633(5) Å] and with a BH_3 moiety by a strong dative donor–acceptor bond [P1–B1: 1.892(6) Å]. The phosphorus center in **6b** is tetracoordinated (trigonal pyramidal) and has an *S* configuration with BH_3– and –NEt_2 substituents oriented *exo* and *endo* relative to the (–)-pinanephosphite core [enantiopol parameter is 0.0(2)]. In this *S* configuration the steric repulsive interactions between the bulky (–)-pinane and the Et_2N– units are minimized, as these moieties are placed far from each other with a closest calculated H(Et_2N)···H[(–)-pinane] distance of 2.29 Å. The [C_2O_2P] ring is almost flat. The puckering angle between two planes, defined by O2–P1–O1 atoms and O2–C1–C2–O1 atoms, respectively, is 1.56°. The C1–O2–P1 and the C2–O1–P1 angles are 115.7(2) and 115.6(2)°, respectively. Based on these observations, sp^2 hybridization of oxygen atoms could be proposed, with one of the free electron pairs occupying a nonhybridized p orbital, which is oriented perpendicular to the [C_2O_2P] cycle. Electron density from this p orbital could easily be donated through π–π interactions to empty d orbitals of the same symmetry on the phosphorus center (according to the "backdonation" concept), thus stabilizing the structure of complex **6b**.

The structural features of the piperidino-substituted BH_3–phosphoramidite complex **7d** are rather similar to those of the related compound **6b** (Table 1). Compound **7d** features the (–)-pinane core with the [C_2O_2P] ring anellated in an *exo* position. In contrast to analogue **6b**, the phosphorus center in **7d** has the *R* configuration with the *exo*-positioned piperidine substituent [observed enantiopol parameter –0.07(16)] (Figure 2). The *exo*-oriented large piperidine group appeared to be in a close vicinity of the bulky (–)-pinane core. The closest calculated H(piperidino)···H[(–)-pinane] distance is 2.03 Å, which is much shorter than that found for derivative **6b** (see above). The strong steric repulsion between these large groups leads to a considerable puckering of the [C_2O_2P] ring in **7c**. The puckering angle, defined as above for **6b** isomer, is 19.28°. The [C_2O_2P] ring adopts an envelope-like conformation. The C6–O1–P1 and the C11–O2–P1 angles are 112.89(16) and 113.69(18)°, respectively. The P1–N1 bond and the B1–P1 connection have typical values of 1.620(3) and 1.898(4) Å, respectively. The piperidine unit, connected to the phosphorus center, has a chair conformation with diastereotopic hydrogen atoms placed in axial and equatorial positions of the piperidine ring.

Table 1. Selected structural parameters of BH_3–phosphoramidite complexes **6b** and **7d**.[a]

	6b	**7d**		**6b**	**7d**
C1–O2	1.465(4)	1.466(3)	C1–C2–O1	107.3(3)	107.4(2)
C2–O1	1.434(5)	1.450(4)	C2–C1–O2	104.9(3)	104.5(2)
P1–O1	1.597(3)	1.612(2)	C1–O2–P1	115.7(2)	112.89(16)
P1–O2	1.595(3)	1.606(2)	C2–O1–P1	115.6(2)	113.69(18)
P1–B1	1.892(6)	1.898(4)	O1–P1–O2	95.92(15)	95.82(11)
P1–N1	1.633(5)	1.620(3)	B1–P1–N1	113.3(3)	114.53(19)
C1–C10	1.515(5)	1.519(4)	N1–P1–O1	106.8(2)	105.33(16)

[a] Bond lengths given in Å and angles in °. Atom numbering according to **6b**.

The P_S-configured complex **6b** features a typical ^{1}H NMR spectroscopic A_3B_2 spin system for the –NEt_2 group at δ_H = 1.12 and 3.15 ppm; three singlets for (–)-pinane methyl substituents at δ_H = 0.87, 1.30, and 1.56 ppm; multiple signals for CH and CH_2 protons of the (–)-pinane core at δ_H = 1.94, 1.98, 2.10, 2.17, 2.24, 2.40, and 4.58 ppm (total 7H of relative intensity). The ^{31}P NMR spectroscopic signal of **6b** appeared at low field at δ_P = 144.8 ppm. In the ^{13}C NMR spectra, all possible $^{2,3}J_{P,C}$ couplings between carbon atoms of the (–)-pinane core, the –NEt_2 group, and the phosphorus center have been detected (see the Exp. Section and Supporting Information). In this row, the $^2J_{P,C}$ couplings between carbon atoms of the [C_2O_2P] ring and the phosphorus center appeared to be essential to recognize the absolute configuration at the P-stereogenic center in compounds **6** and **7** (see below). For complex **6b**, they are 4.5 and 7.2 Hz, respectively. Whereas the P_R-configured isomer **7b** shows an ^{1}H NMR spectrum analogous to **6b** (see the Supporting Information), the ^{31}P NMR spectroscopic signal of **7b** is noticeably shifted upfield to δ_P = 142.8 ppm. Moreover, in isomer **7b**, the absence of the characteristic $^2J_{P,C}$ couplings within the [C_2O_2P] ring has been detected. Based on these observations, it could in general be concluded that BH_3–phosphoramidite complexes, which display a ^{31}P NMR spectroscopic signal at low field and distinct $^2J_{P,C}$ couplings in the ^{13}C NMR spectra between the carbon atoms of the (–)-pinane core and the phosphorus center, are the P_S stereoisomers **6** (Figure 3). Conversely, for the P_R analogues **7**, upfield-shifted ^{31}P NMR spectroscopic resonances together with absence of detectable $^2J_{P,C}$ couplings (except those between the amine unit and P-

stereogenic center) in the ^{13}C NMR spectra could be expected (Figure 3).[15] To verify this statement, we carefully analyzed the pair of isomers **6d** and **7d**, for which compound **7d** had the assigned P_R configuration, determined from single-crystal X-ray structural studies (see above). Both compounds behaved as expected. They showed very similar ^1H NMR spectroscopic features (see the Supporting Information). The ^{31}P NMR spectroscopic signal of P_R-configured complex **7d** was shifted upfield relative to that of the P_S-configured analogue **6d** (δ_P = 142.3 ppm for **7d** vs. δ_P = 146.0 ppm for **6d**). Whereas $^2J_{P,C}$ couplings between the carbon atoms of the (–)-pinane core and the phosphorus center were observed for complex **6d** (4.6 and 7.5 Hz, respectively), these $^2J_{P,C}$ couplings were not detected for P_R-configured isomer **7d**. Having a clear assignment for the P_S-configured diastereomer **6b** and the P_R-configured diastereomer **7d**, the absolute configuration of the P-stereogenic center for the series of complexes **6a**–**e** and **7a**–**d** was determined on the basis of the ^{13}C and ^{31}P NMR spectroscopic data.

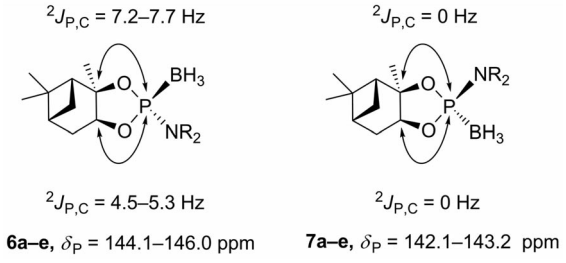
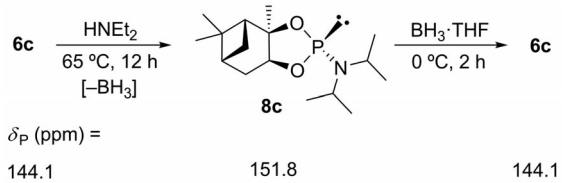


Figure 3. ^{13}C and ^{31}P NMR spectroscopic features of P_S-stereoisomers **6** and P_R-stereoisomers **7**.

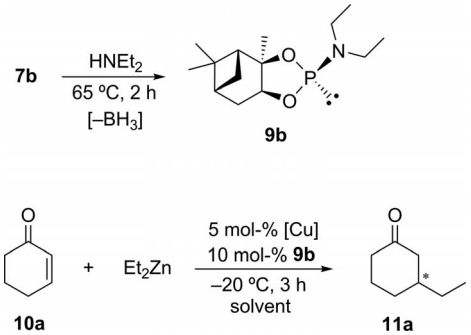
The BH_3–phosphoramidite complexes were relatively stable and could easily be handled. However, for catalytic purposes they had to be deprotected prior to use. In a typical procedure, a BH_3–phosphoramidite complex was deprotected by heating in Et_2NH, followed by removal of all volatiles under high vacuum.[16] As a free phosphoramidite ligand is released during this process, there is potentially the possibility of inversion or even racemization of the P-stereogenic center under conditions of prolonged heating. To examine the result of the deprotection, we carried out a series of experiments. The P_S-configured BH_3–phosphoramidite complex **6c** (δ_P = 144.1 ppm) was heated in Et_2NH at 65 °C for 12 h. An excess amount of Et_2NH and volatile byproducts were removed under high vacuum. The residue, which consisted of the free ligand **8c**, was investigated by means of ^{31}P NMR spectroscopy. The compound **8c** featured a ^{31}P NMR spectroscopic singlet at δ_P = 151.8 ppm. The same compound **8c** was then treated with the BH_3·THF complex under typical conditions (THF, 0 °C, 2 h). After workup, the product of the reaction displayed a ^1H NMR spectrum and optical rotation angle identical to those recorded independently for P_S-configured BH_3–phosphoramidite complex **6c**. The observed ^{31}P NMR spectroscopic shifts of the product and the starting complex **6c** were the same (see Scheme 2). This means that during the deprotection–protection sequence the configuration of the P-stereogenic center remained unchanged.



Scheme 2.

Enantioselective Conjugate Addition Reactions

It has been previously shown that phosphoramidite ligands provide high activity and stereoselectivity in conjugate addition reactions.[2] The influence of both the structure of the ligand core and nature of the amino function on the steric outcome of the reaction has been investigated in detail.[3] The first phosphoramidite ligands employed for catalytic conjugate addition were based on a chiral binaphthol core with attached achiral dialkylamino substituent.[2l] They showed high conversion (more than 80%) and moderate up to high enantioselectivity in 1,4-addition of Et_2Zn to cyclohexenone (up to 60% *ee*) and chalcone (up to 81% *ee*) substrates.[12] The modification with a chiral bis(α-methylbenzyl)amino substituent was highly active and selective in 1,4-addition reactions of Et_2Zn to cyclohexenone, but selectivity decreased in the case of cycloheptenone (53% *ee*).[17] Lately, new flexible biphenol-derived ligands have been designed and used for Cu-mediated conjugate addition of Et_2Zn to a number of cyclic and acyclic activated unsaturated substrates with very good yields and selectivities.[18] In our preliminary experiments, we mainly focused on studying the influence of stereochemical configuration around the P-stereogenic center of the phosphoramidite ligand on the selectivity of the conjugate addition. To find optimum conditions for the catalytic reactions, cyclohexenone **10a** was treated with diethylzinc in the presence of ligand **9b** (10 mol-%) and various copper precursors (5 mol-%) in different solvents (Scheme 3).[19]



Scheme 3.

The obtained enantioselectivities were strongly dependent on the copper source and to a lesser extent on the solvent (for details, see the Supporting Information). Whereas $Cu(OTf)_2$ worked best in toluene (17% *ee*) relative to Et_2O

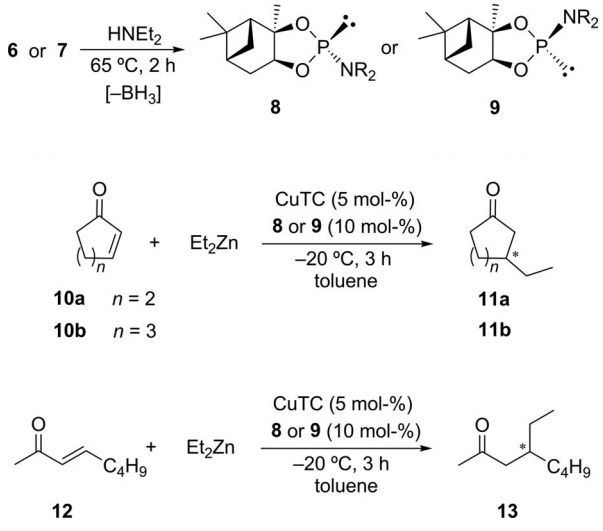
Table 2. Conjugate addition of Et_2Zn to enones **10** and **12** in the presence of ligands **8**, **9**, and CuTC.[a]

Entry	Enone	Ligand	R	Configuration at P center	Product	Conversion [%][b]	*ee* [%][c]	Configuration of product[d]
1	**10a**	**8b**	Et	(*S*)	**11a**	100	3	(*R*)
2	**10a**	**9b**	Et	(*R*)	**11a**	100	36	(*S*)
3	**10a**	**8c**	*i*Pr	(*S*)	**11a**	100	12	(*R*)
4	**10a**	**9c**	*i*Pr	(*R*)	**11a**	100	21	(*S*)
5	**10b**	**8b**	Et	(*S*)	**11b**	100	26	(*R*)
6	**10b**	**9b**	Et	(*R*)	**11b**	100	23	(*S*)
7	**10b**	**8c**	*i*Pr	(*S*)	**11b**	85	33	(*R*)
8	**10b**	**9c**	*i*Pr	(*R*)	**11b**	88	33	(*S*)
9	**12**	**8b**	Et	(*S*)	**13**	43	2	(–)
10	**12**	**9b**	Et	(*R*)	**13**	96	27	(–)
11	**12**	**8c**	*i*Pr	(*S*)	**13**	90	11	(–)
12	**12**	**9c**	*i*Pr	(*R*)	**13**	83	50	(–)

[a] Reaction conditions: substrate (1 equiv.), Et_2Zn (1.5 equiv.), CuTC (5 mol-%), **8** or **9** (10 mol-%), toluene, –20 °C, 3 h. [b] Determined by GC (undecane as an internal standard). [c] Determined by GC or HPLC on a chiral phase (see details in the Supporting Information). [d] Determined by a comparison of observed optical rotation data with literature.

(8% *ee*) and CH_2Cl_2 (7% *ee*), $Cu(OAc)_2$ yielded moderate enantioselectivity (21% *ee*) only in Et_2O. By using copper(I) thiophenecarboxylate (CuTC), the selectivity could be increased in all solvents. The most pronounced effect was observed in toluene, in which higher *ee* values (34% *ee*), relative to Et_2O (18% *ee*) or CH_2Cl_2 (17% *ee*), were obtained. Thus, copper(I) thiophenecarboxylate and toluene were chosen for the following catalytic reactions.

Prior to the catalytic reaction, BH_3–phosphoramidite complexes **6a**–**d** and **7a**–**d** were deprotected in a manner already used for the generation of ligand **8c** (heating in Et_2NH at 65 °C for 12 h; see above and Scheme 4).[16] In this way, a series of P_S- and P_R-configured ligands **8a**–**d** and **9a**–**d**, respectively, have been obtained and immediately employed for further catalytic experiments. In a general reaction setup, we used CuTC (5 mol-%), ligand **8** or **9** (10 mol-%), enone substrate (1 equiv.), and $ZnEt_2$ (1.5 equiv.) alkylation reagent. The reaction was carried out at –20 °C for 3 h. Selected obtained results are summarized in Table 2 and Scheme 4. Regardless of the enone substrate, the ligands **8d** and **9d**, which bore bulky piperidine groups, did not show high enantioselectivity in conjugate addition of $ZnEt_2$, albeit in most of the runs high yields of alkylated products were obtained. The same behavior was observed for NMe_2-substituted ligand **9a**. Possibly, these ligands were too labile under the applied reaction conditions. The phosphoramidites **8b** and **9b**, **8c** and **9c**, which have Et_2N– and iPr_2N– functionalities, respectively, showed different results. In the conjugate addition of Et_2Zn to the cyclic enone **10a** as well as to the acyclic substrate **12**, P_S-configured ligands **8b**,**c** displayed poor enantioselectivities up to 12% *ee* (Table 2, entries 1, 3, 9, and 11). At the same time, P_R-configured analogues **9b**,**c** gave alkylated ketones with pronounced moderate enantioselectivity in the range of 21–50% *ee*. Clearly, an *R* configuration of the P-stereogenic center leads to enhanced enantioselectivity of the conjugate addition. It has been shown above that, due to steric factors, the P_S- and P_R-configured BH_3–phosphoramidite complexes **6b** and **7d** have slightly different molecular structures (Figure 1 and Figure 2). The structural difference could be an important factor, thereby distinguishing the enantioselectivity of conjugate addition within a series of P_S- and P_R-configured phosphoramidite ligands **8b**,**c** and **9b**,**c**. When more flexible cycloheptenone substrate **10b** was employed, both series of phosphoramidites **8b**,**c** and **9b**,**c** gave very similar moderate enantioselectivity values, regardless of the configuration around the P-stereogenic center (around 23–26% *ee* for the **8b/9b** pair and 33% *ee* for the **8c/9c** pair). In conjugate addition of Et_2Zn to cyclic enones **10a**,**b**, P_S-configured ligands **8a**–**c** gave mixtures with a predominant content of *R*-alkylated ketone, whereas the *S*-alkylated ketone was the major enantiomer provided by P_R-configured ligands **9a**–**c** (see Table 2).



Scheme 4.

Conclusion

New P-stereogenic phosphoramidites were synthesized and investigated by NMR spectroscopic methods and single-crystal X-ray structural analysis. P_S and P_R diastereomers can be simply separated by column chromatography and distinguished by using NMR spectroscopy. It appeared that the configuration of the P-stereogenic center in

a free ligand, generated from its BH_3 complex, is rather stable even at elevated temperatures, though this could be dependent on the amine functionality. Preliminary experiments showed that the configuration of the P-chiral center in a phosphoramidite ligand has a distinct influence on the enantioselectivity of a conjugate addition reaction. The P_S ligand favors the formation of an *R*-alkylated product, and vice versa for the P_R ligand. In addition, P_S- and P_R-configured (–)-pinane-based phosphoramidites displayed slight structural differences in the conformation of a phosphoramidite cycle. Such structural divergence between P_S and P_R isomers could be the reason that enantioselectivity in conjugated addition of Et_2Zn to cyclohexenone and octenone was low when P_S-configured phosphoramidite ligands were employed. At the same time, P_R-phosphoramidites showed enhanced enantioselectivity up to 50% *ee*. Further studies to improve overall enantioselectivity of conjugate addition reactions are currently in progress.

Experimental Section

General Information: All reactions were carried out under a nitrogen atmosphere with Schlenk-type glassware. Solvents were dried and distilled under nitrogen prior to use. Reaction progress and purity were monitored by GC with a Hewlett–Packard HP 6890 equipped with a HP-5MS column (30 m × 0.32 mm) or with a Thermo-Finnigan Trace GC Ultra equipped with a Optima-5MS column (30 m × 0.25 mm) using different temperature programs. Hydrogen was used as a carrier gas. Enantioselectivities were determined by GC on chiral stationary phases with a Fisons HRGC MEGA 8560 or a Thermo-Finnigan Trace GC Ultra instrument. The enantiomers are stated as major and minor with their exact retention times. Flash chromatography was performed on silica gel, grain size 40–63 μm (Macherey–Nagel).

The following instruments were used for physical characterization of the compounds. Elemental analyses: Carlo–Erba Strumentazione Elemental Analyzer, Modell 1106. NMR spectroscopy: Bruker AC 250 F (^{1}H, 250 MHz; ^{13}C, 63 MHz), Bruker ARX-500 (^{1}H, 500 MHz; ^{13}C, 126 MHz), Bruker ARX-300 (^{31}P, 121 MHz). Assignments of the resonances are supported by 2D experiments and chemical-shift calculations. ^{1}H and ^{13}C NMR spectra were referenced to an internal Me_4Si standard, ^{31}P NMR spectra were referenced to an external $P(OEt)_3$ sample in C_6D_6 (^{31}P: δ = 138.0 ppm). IR: Bruker 22 FTIR Spectrometer with an golden-gate single-reflection Diamant ATR system. MS: Finnigan MAT 95 Spectrometer (CI) with methane as a carrier gas, Varian MAT711 (EI, 70 eV). Optical rotation: Perkin–Elmer 241LC Polarimeter (20 °C, 589 nm).

X-ray Diffraction: Data sets were collected with a Nicolet P3F diffractometer. Programs used for data collection: Siemens P3/PC Data Collection System; for data reduction: SHELXTL-plus, XDISK; structure solution: SHELXS-97; for structure refinement: SHELXS-97; graphics: SHELXTL-plus, XP.[14]

General Procedure for Preparation of Complexes 6a–d and 7a–d: Et_3N (607 mg, 6.00 mmol) was added at room temperature to a stirred solution of *cis*-pinandiol **2** (510 mg, 3.00 mmol) in THF (10 mL). The reaction was stirred at room temperature for 15 min and then cooled to 0 °C. *N*,*N*-Dialkylaminophosphorus dichlorides **5a**–**d** (3.00 mmol) was added dropwise to this cooled mixture at 0 °C, and the resulting suspension was stirred at 0 °C for 45 min and then at room temperature for 24 h. After filtration, all volatiles were removed in vacuo. The residue was mixed at 0 °C with BH_3·THF complex (1 M solution in THF, 3.00 mL, 3.00 mmol) and stirred at 0 °C for 2 h. After evaporation under reduced pressure, the stereoisomeric products (ratio of stereoisomers was always 1:1 according to GC) were separated and purified by means of flash chromatography on silica gel.

(1*R*,2*S*,4*R*,6*S*,8*R*)-*N*,*N*-Dimethyl(4-boronato-2,9,9-trimethyl-3,5-dioxa-4-phosphatricyclo[6.1.1.0^{2,6}]dec-4-yl)amine (6a) and (1*R*,2*R*,4*R*,6*S*,8*R*)-*N*,*N*-Dimethyl(4-boronato-2,9,9-trimethyl-3,5-dioxa-4-phosphatricyclo[6.1.1.0^{2,6}]dec-4-yl)amine (7a): According to the general procedure, treatment of **5a** (1.17 g, 8.00 mmol) with *cis*-pinandiol **2** (1.36 g, 8.00 mmol), Et_3N (2.24 mL, 16 mmol), and BH_3·THF complex (1 M solution in THF, 8.00 mL, 8.00 mmol) in THF (20 mL) gave after flash chromatography separation [eluent: EtOAc/PE, 1:10, silica gel; R_f (**6a**) = 0.28, R_f (**7a**) = 0.38] complexes **6a** (766 mg, 37%) and **7a** (504 mg, 25%).

Complex **6a**: M.p. 90 °C. $C_{12}H_{25}BNO_2P$ (257.12): calcd. C 56.06, H 9.80, N 5.45; found C 56.74, H 9.90, N 5.49. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ = 0.69 (1:1:1:1 br. qd, $^1J_{B,H}$ = 92 Hz, $^2J_{PH,}$ = 15 Hz, 3 H, BH_3), 0.87 (s, 3 H, 12-H), 1.30, 1.57 (each s, each 3 H, 11 and 11′-H), 1.88 (d, $^2J_{H,H}$ = 11.0 Hz, 10-H^{ax}), 1.94 (m, 1 H, 8-H), 2.12 (m, 1 H, 7-H^{ax}), 2.17 (t, $^3J_{H,H}$ = 5.7 Hz, 1 H, 1-H), 2.25 (dtd, $^2J_{H,H}$ = 11.0 Hz, $^3J_{H,H}$ = 5.7 Hz, $^3J_{H,H}$ = 2.2 Hz, 1 H, 10-H^{eq}), 2.41 (AB type ddt, $^2J_{H,H}$ = 14.9 Hz, $^3J_{H,H\text{-}trans}$ = 8.8 Hz, $^3J_{H,H}$ = 2.5 Hz, 1 H, 7-H^{eq}), 2.76 (d, $^3J_{P,H}$ = 9.8 Hz, 6 H, NMe_2), 4.59 (ddd, $^3J_{P,H}$ = 9.3 Hz, $^3J_{H,H\text{-}trans}$ = 8.8 Hz, $^3J_{H,H\text{-}cis}$ = 2.8 Hz, 1 H, 6-H) ppm. ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 298 K): δ = 24.3 (C-12), 26.3 (C-10), 27.1, 28.4 (C-11 and C-11′), 35.0 (d, $^3J_{P,C}$ = 3.8 Hz, C-7), 36.2 ($^2J_{P,C}$ = 5.3 Hz, NMe_2), 38.8 (C-9), 39.3 (C-8), 52.2 (d, $^3J_{P,C}$ = 5.5 Hz, C-1), 79.5 (d, $^2J_{P,C}$ = 4.8 Hz, C-6), 88.9 (d, $^2J_{P,C}$ = 7.2 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K) δ = 144.9 ppm. IR (film): $\tilde{\nu}$ = 3312, 2978, 2938 (s), 2873, 2821, 2391 (br), 2362 (br), 2270, 2135, 1481, 1450, 1388, 1379, 1355, 1302, 1265, 1245, 1190, 1138, 1124, 1075, 1056, 1026 (s), 1008 (s), 940, 921, 897, 872, 855, 837, 808, 765, 739, 705, 648 cm^{-1}. MS (EI): *m*/*z* (%) = 257 (1) [M$^+$], 244 (6), 243 (60), 228 (1), 214 (1), 200 (3), 152 (2), 137 (3), 136 (16), 135 (23), 119 (16), 108 (29), 94 (10), 93 (100), 80 (7), 77 (14), 55 (10), 44 (17), 41 (23), 29 (7). $[\alpha]_D^{20}$ = +15.6 (*c* = 1, CH_2Cl_2).

Complex **7a**: M.p. 92 °C. $C_{12}H_{25}BNO_2P$ (257.12): calcd. C 56.06, H 9.80, N 5.45; found C 56.20, H 9.69, N 5.41. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ = 0.66 (1:1:1:1 br. qd, $^1J_{B,H}$ = 92 Hz, $^2J_{P,H}$ = 15 Hz, 3 H, BH_3), 0.88 (s, 3 H, 12-H), 1.32, 1.65 (each s, each 3 H, 11 and 11′-H), 1.67 (d, $^2J_{H,H}$ = 10.4 Hz, 10-H^{ax}, tentative assignment), 1.98 (m, 1 H, 8-H), 2.03 (dm, $^2J_{H,H}$ = 14.1 Hz, 1 H, 7-H^{ax}), 2.18 (t, $^3J_{H,H}$ = 5.4 Hz, 1 H, 1-H), 2.24 (dtd, $^2J_{H,H}$ = 10.4 Hz, $^3J_{H,H}$ = 5.4 Hz, $^3J_{H,H}$ = 2.2 Hz, 1 H, 10-H^{eq}), 2.45 (dm, $^2J_{H,H}$ = 14.1 Hz, 1 H, 7-H^{eq}), 2.82 (d, $^3J_{P,H}$ = 9.8 Hz, 6 H, NMe_2), 4.49 (ddd, $^3J_{P,H}$ = 9.0 Hz, $^3J_{H,H\text{-}trans}$ = 8.7 Hz, $^3J_{H,H\text{-}cis}$ = 2.5 Hz, 1 H, 6-H) ppm. ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 298 K): δ = 24.4 (C-12), 25.6 (C-10), 27.1, 28.5 (C-11 and C-11′), 34.3 (d, $^3J_{P,C}$ = 3.0 Hz, C-7), 36.4 ($^2J_{P,C}$ = 6.4 Hz, NMe_2), 39.1 (C-9), 40.0 (C-8), 52.1 (d, $^3J_{P,C}$ = 4.3 Hz, C-1), 76.7 (C-6), 86.2 (C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = 142.1 ppm. IR (film): $\tilde{\nu}$ = 3017, 2984, 2943, 2922, 2852, 2852, 2822, 2799, 2382 (s), 2351, 1737, 1476, 1452, 1387, 1370, 1353, 1307, 1279, 1266, 1248, 1229, 1186, 1159, 1134, 1117, 1076, 1065, 1013, 998, 983, 953, 931, 914, 890, 869, 849 cm^{-1}. MS (EI): *m*/*z* (%) = 258 (1) [M$^+$], 245 (1), 244 (2), 243 (67), 228 (2), 214 (1), 200 (4), 173 (3), 137 (3), 136 (17), 135 (25), 121 (10), 108 (18), 95 (3), 94 (10), 93 (100), 80 (6), 77 (11), 55 (8), 45 (8), 44 (14), 41 (17), 29 (5), 28 (17). $[\alpha]_D^{20}$ = –60.5 (*c* = 1, $CHCl_3$).

(1*R*,2*R*,4*S*,6*S*,8*R*)-*N*,*N*-Diethyl(4-boronato-2,9,9-trimethyl-3,5-dioxa-4-phosphatricyclo[6.1.1.0^{2,6}]dec-4-yl)amine (6b) and (1*R*,2*R*,4*R*,6*S*,8*R*)-*N*,*N*-Diethyl(4-boronato-2,9,9-trimethyl-3,5-dioxa-4-phosphatricyclo[6.1.1.0^{2,6}]dec-4-yl)amine (7b): According to the general procedure, treatment of **5b** (522 mg, 3.00 mmol) with *cis*-pinandiol **2** (510 mg, 3.00 mmol) gave after flash chromatography separation [eluent: EtOAc/PE, 1:10, silica gel; R_f (**6b**) = 0.29, R_f (**7b**) = 0.42] complexes **6b** (167 mg, 20%) and **7b** (205 mg, 24%).

Complex **6b**: M.p. 85 °C. $C_{14}H_{29}BNO_2P$ (285.17): calcd. C 58.97, H 10.25, N 4.91; found C 59.29, H 10.15, N 4.57. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ = 0.69 (1:1:1:1 br. q, $^1J_{B,H}$ = 90 Hz, 3 H, BH_3), 0.87 (s, 3 H, 12-H), 1.12 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3^{Et}), 1.30, 1.56 (each s, each 3 H, 11 and 11′-H), 1.94 (m, 1 H, 8-H), 1.98 (d, $^2J_{H,H}$ = 10.8 Hz, 10-H^{ax}), 2.13 (m, 1 H, 7-H^{ax}), 2.17 (t, $^3J_{H,H}$ = 5.5 Hz, 1 H, 1-H), 2.24 (dtd, $^2J_{H,H}$ = 10.8 Hz, $^3J_{H,H}$ = 5.5 Hz, $^3J_{H,H}$ = 2.2 Hz, 1 H, 10-H^{eq}), 2.41 (AB type ddt, $^2J_{H,H}$ = 14.9 Hz, $^3J_{H,H\text{-}trans}$ = 8.9 Hz, $^3J_{H,H}$ = 2.4 Hz, 1 H, 7-H^{eq}), 3.15 (m, 4 H, CH_2^{Et}), 4.58 (ddd, $^3J_{P,H}$ = 9.7 Hz, $^3J_{H,H\text{-}trans}$ = 8.9 Hz, $^3J_{H,H\text{-}cis}$ = 2.8 Hz, 1 H, 6-H) ppm. ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 298 K): δ = 14.1 (d, $^3J_{P,C}$ = 2.0 Hz, CH_3^{Et}), 24.4 (C-12), 26.3 (C-10), 27.1, 28.4 (C-11 and C-11′), 35.0 (d, $^3J_{P,C}$ = 3.7 Hz, C-7), 38.7 (d, $^2J_{P,C}$ = 5.6 Hz, CH_2^{Et}), 38.8 (C-9), 39.4 (C-8), 52.2 (d, $^3J_{P,C}$ = 5.6 Hz, C-1), 79.2 (d, $^2J_{P,C}$ = 4.5 Hz, C-6), 89.0 (d, $^2J_{P,C}$ = 7.2 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K) δ = 144.8 ppm. IR (film): $\tilde{\nu}$ = 2976, 2931, 2874, 2387, 2255, 2145, 1741, 1466, 1449, 1382, 1264, 1210, 1173, 1134, 1077, 1027, 1007, 990, 953, 338, 898, 870, 806, 789, 693, 643 cm^{-1}. MS (EI): *m*/*z* (%) = 285 (3) [M$^+$], 272 (8), 271 (69) [M$^+$ – BH_3], 256 (7), 242 (1), 228 (2), 199 (3), 165 (3), 164 (40), 148 (2), 138 (9), 135 (23), 120 (23), 94 (13), 93 (100), 79 (8), 72 (24), 58 (8), 44 (3), 43 (12), 28 (19). $[\alpha]_D^{20}$ = ± 0 (*c* = 1, $CHCl_3$).

Complex **7b**: M.p. 51 °C. $C_{14}H_{29}BNO_2P$ (285.17): calcd. C 58.97, H 10.25, N 4.91; found C 59.08, H 10.14, N 4.85. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ = 0.66 (1:1:1:1 br. q, $^1J_{B,H}$ = 88 Hz, 3 H, BH_3), 0.88 (s, 3 H, 12-H), 1.13 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, CH_3^{Et}), 1.32, 1.66 (each s, each 3 H, 11 and 11′-H), 1.58 (d, $^2J_{H,H}$ = 10.3 Hz, 10-H^{ax}), 1.98 (m, 1 H, 8-H), 2.02 (dm, $^2J_{H,H}$ = 14.0 Hz, 1 H, 7-H^{ax}), 2.18 (t, $^3J_{H,H}$ = 5.6 Hz, 1 H, 1-H), 2.25 (dtd, $^2J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 5.6 Hz, $^3J_{H,H}$ = 1.8 Hz, 1 H, 10-H^{eq}), 2.43 (dm, $^2J_{H,H}$ = 14.0 Hz, 1 H, 7-H^{eq}), 3.25 (m, 4 H, CH_2^{Et}), 4.47 (ddd, $^3J_{P,H}$ = 9.0 Hz, $^3J_{H,H\text{-}trans}$ = 6.7 Hz, $^3J_{H,H\text{-}cis}$ = 2.4 Hz, 1 H, 6-H) ppm. ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 298 K): δ = 14.4 (d, $^3J_{P,C}$ = 1.6 Hz, CH_3^{Et}), 24.3 (C-12), 25.5 (C-10), 27.1, 28.5 (C-11 and C-11′), 34.4 (d, $^3J_{P,C}$ = 3.5 Hz, C-7), 39.0 (d, $^2J_{P,C}$ = 6.3 Hz, CH_2^{Et}), 39.1 (C-9), 39.8 (C-8), 52.0 (d, $^3J_{P,C}$ = 4.4 Hz, C-1), 76.4 (C-6), 85.7 (C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = 142.8 ppm. IR (film): $\tilde{\nu}$ = 2980, 2936 (s), 2871, 2382 (s), 2351, 2247, 2117, 2009, 1722, 1453, 1382, 1292, 1248, 1208, 1173, 1130, 1078, 1029, 1008, 989, 960, 936, 915, 889, 870, 837, 800, 790, 733, 691, 631 cm^{-1}. MS (EI): *m*/*z* (%) = 285 (1) [M$^+$], 273 (1), 272 (12), 271 (72) [M$^+$ – BH_3], 256 (9), 242 (1), 228 (3), 199 (3), 165 (1), 164 (8), 148 (1), 138 (15), 135 (26), 120 (22), 94 (10), 93 (100), 79 (7), 72 (25), 58 (9), 44 (3), 43 (12), 29 (3), 28 (14). $[\alpha]_D^{20}$ = –49.4 (*c* = 1, $CHCl_3$).

X-ray Crystal Structure Analysis of Complex 6b: Formula $C_{14}H_{29}BNO_2P$; colorless crystal 0.9 × 0.6 × 0.5 mm; M_r = 285.16; *a* = 7.548(3) Å, *b* = 10.880(4) Å, *c* = 21.343 (7) Å; *V* = 1752.8(11) Å^3; $\rho_{calcd.}$ = 1.081 g cm^{-3}; μ = 0.1550 mm^{-1}; *Z* = 4; orthorhombic, space group $P2_12_12_1$ (no. 19); λ = 0.71073 Å; *T* = 293(2) K; Wyckoff scan, 3140 reflections collected ($-1 \le h \le 9$, $-1 \le k \le 14$, $-1 \le l \le 28$), [(sin θ)/λ] = 0.66 Å^{-1}; 2966 independent (R_{int} = 0.0605) and 1886 observed reflections [$I \ge 2\sigma(I)$]; 192 refined parameters, 28 restraints (disorder of one ethyl function of the diethylamino moiety); R_1 = 0.0643, wR_2 = 0.1641 {[$I \ge 2\sigma(I)$]}; max. (min.) residual electron density 0.270 (–0.225) e Å^{-3}; Flack parameter 0.0(2), data collection with a Nicolet P3F diffractometer.

(1*R*,2*R*,4*S*,6*S*,8*R*)-*N*,*N*-Diisopropyl-(4-boronato-2,9,9-trimethyl-3,5-dioxa-4-phosphatricyclo[6.1.1.0^{2,6}]dec-4-yl)amine (6c) and (1*R*,2*R*,4*R*,6*S*,8*R*)-*N*,*N*-Diisopropyl-(4-boronato-2,9,9-trimethyl-3,5-dioxa-4-phosphatricyclo[6.1.1.0^{2,6}]dec-4-yl)amine (7c): According to the general procedure, treatment of **5c** (1.61 g, 8.00 mmol) with *cis*-pinandiol **2** (1.36 g, 8.00 mmol), Et_3N (2.24 mL, 16 mmol), and BH_3·THF complex (1 M solution in THF, 8.00 mL, 8.00 mmol) in THF (20 mL) gave after flash chromatography separation [eluent: EtOAc/PE, 1:10, silica gel; R_f (**6c**) = 0.31, R_f (**7c**) = 0.47] complexes **6c** (851 mg, 34%) and **7c** (778 mg, 31%).

Complex **6c**: M.p. 130–131 °C. $C_{16}H_{33}BNO_2P$ (313.23): calcd. C 61.35, H 10.62, N 4.47; found C 61.47, H 10.51, N 4.47. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ = 0.83 (1:1:1:1 br. q, $^1J_{B,H}$ = 87 Hz, 3 H, BH_3), 0.87 (s, 3 H, 12-H), 1.29, 1.32 [each d, $^3J_{H,H}$ = 7.0 Hz, each 6 H, $CH_3^{iPr(A)}$ and $CH_3^{iPr(B)}$], 1.30, 1.57 (each s, each 3 H, 11 and 11′-H), 1.93 (m, 1 H, 8-H), 2.02 (d, $^2J_{H,H}$ = 10.5 Hz, 10-H^{ax}), 2.16 (m, 1 H, 7-H^{ax}), 2.17 (t, $^3J_{H,H}$ = 5.3 Hz, 1 H, 1-H), 2.22 (m, 1 H, 10-H^{eq}), 2.42 (AB type ddt, $^2J_{H,H}$ = 14.8 Hz, $^3J_{H,H\text{-}trans}$ = 8.8 Hz, $^3J_{H,H}$ = 2.4 Hz, 1 H, 7-H^{eq}), 3.71 (d of septet, $^3J_{P,H}$ = 15.1 Hz, $^3J_{H,H}$ = 7.0 Hz, 2 H, CH^{iPr}), 4.60 (ddd, $^3J_{P,H}$ = 9.3 Hz, $^3J_{H,H\text{-}trans}$ = 8.8 Hz, $^3J_{H,H\text{-}cis}$ = 2.7 Hz, 1 H, 6-H) ppm. ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 298 K): δ = 22.7, 23.5 [two d, $^3J_{P,C}$ = 2.0/2.3 Hz, $CH_3^{iPr(A)}$ and $CH_3^{iPr(B)}$], 24.4 (C-12), 26.1 (C-10), 27.1, 28.6 (C-11 and C-11′), 35.0 (d, $^3J_{P,C}$ = 4.0 Hz, C-7), 38.8 (C-9), 39.5 (C-8), 46.1 (d, $^2J_{P,C}$ = 6.2 Hz, CH^{iPr}), 52.5 (d, $^3J_{P,C}$ = 5.9 Hz, C-1), 79.5 (d, $^2J_{P,C}$ = 5.3 Hz, C-6), 89.6 (d, $^2J_{P,C}$ = 7.7 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ = 145.1 ppm. IR (film): $\tilde{\nu}$ = 2976, 2933 (s), 2875, 2397 (s), 2269, 2160, 1634, 1474, 1449, 1411, 1387, 1369, 1313, 1282, 1264, 1243, 1205, 1182, 1157, 1122, 1077, 1057, 1010, 985 (s), 838, 918, 894, 871, 852 cm^{-1}. MS (EI): *m*/*z* (%) = 313 (3) [M$^+$], 300 (13), 299 (70) [M$^+$ – BH_3], 284 (16), 257 (3), 256 (15), 217 (1), 200 (1), 199 (4), 192 (10), 176 (1), 166 (5), 150 (10), 136 (23), 135 (35), 94 (6), 93 (100), 79 (6), 55 (7), 43 (23), 27 (5). $[\alpha]_D^{20}$ = +6.5 (*c* = 1, CH_2Cl_2). Ligand **6c** was deprotected by heating at 65 °C for 12 h with an excess amount of Et_2NH. ^{31}P{^{1}H} NMR spectrum of free ligand **8c** (121 MHz, C_6D_6, 298 K): δ = 151.8 ppm. The free ligand was treated with BH_3·THF complex at 0 °C for 2 h to give back complex **6c** [^{31}P(^{1}H) NMR (121 MHz, C_6D_6, 298 K): δ = 145.1 ppm].

Complex 7c: M.p. 82 °C. $C_{16}H_{33}BNO_2P$ (313.23): calcd. C 61.35, H 10.62, N 4.47; found C 61.10, H 10.56, N 4.19. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ = 0.77 (1:1:1:1 br. q, $^1J_{B,H}$ = 87 Hz, 3 H, BH_3), 0.88 (s, 3 H, 12-H), 1.31, 1.32 [each d, $^3J_{H,H}$ = 7.0 Hz, each 6 H, $CH_3^{iPr(A)}$ and $CH_3^{iPr(B)}$], 1.31, 1.70 (each s, each 3 H, 11 and 11′-H), 1.59 (d, $^2J_{H,H}$ = 10.2 Hz, 10-H^{ax}), 1.96 (m, 1 H, 8-H), 2.01 (dm, $^2J_{H,H}$ = 14.6 Hz, 1 H, 7-H^{ax}), 2.18 (t, $^3J_{H,H}$ = 5.4 Hz, 1 H, 1-H), 2.21 (dtd, $^2J_{H,H}$ = 10.2 Hz, $^3J_{H,H}$ = 5.4 Hz, $^3J_{H,H}$ = 2.2 Hz, 1 H, 10-H^{eq}), 2.43 (AB type ddm, $^2J_{H,H}$ = 14.6 Hz, $^3J_{H,H\text{-}trans}$ = 8.8 Hz, 1 H, 7-H^{eq}), 3.97 (d of septet, $^3J_{P,H}$ = 15.5 Hz, $^3J_{H,H}$ = 7.0 Hz, 2 H, CH^{iPr}), 4.50 (ddd, $^3J_{H,H\text{-}trans}$ = 8.8 Hz, $^3J_{P,H}$ = 6.0, $^3J_{H,H\text{-}cis}$ = 2.1 Hz, 1 H, 6-H) ppm. ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 298 K): δ = 23.1, 23.2 [two d, $^3J_{P,C}$ = 2.1/2.6 Hz, $CH_3^{iPr(A)}$ and $CH_3^{iPr(B)}$], 24.4 (C-12), 25.3 (C-10), 27.1, 28.8 (C-11 and C-11′), 34.2 (d, $^3J_{P,C}$ = 3.6 Hz, C-7), 39.2 (C-9), 39.8 (C-8), 46.2 (d, $^2J_{P,C}$ = 6.1 Hz, CH^{iPr}), 52.3 (d, $^3J_{P,C}$ = 3.9 Hz, C-1), 76.1 (C-6), 85.7 (C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = 143.2 ppm. IR (neat): $\tilde{\nu}$ = 3580, 2985, 2915, 2874, 2397 (s), 2354, 2276, 2177, 2148, 2018, 1967, 1648, 1472, 1451, 1409, 1387, 1370,

1280, 1244, 1205, 1157, 1127, 1078, 1058, 1014, 984, 951, 935, 913, 890, 869 cm^{-1}. MS (EI): *m*/*z* (%) = 301 (1), 300 (11), 299 (60) [M$^+$ – BH_3], 284 (11), 257 (3), 256 (17), 217 (1), 199 (3), 166 (7), 150 (13), 136 (27), 135 (30), 94 (13), 93 (100), 44 (8), 43 (25), 27 (5). $[\alpha]_D^{20}$ = –43.9 (*c* = 1, CH_2Cl_2).

(1*R*,2*R*,4*S*,6*S*,8*R*)-1-(4-Boronato-2,9,9-trimethyl-3,5-dioxa-4-phosphatricyclo[6.1.1.0^{2,6}]dec-4-yl)piperidine (6d) and (1*R*,2*R*,4*R*,6*S*,8*R*)-1-(4-Boronato-2,9,9-trimethyl-3,5-dioxa-4-phosphatricyclo[6.1.1.0^{2,6}]dec-4-yl)piperidine (7d): According to the general procedure, treatment of **5d** (1.49 g, 8.00 mmol) with *cis*-pinandiol **2** (1.36 g, 8.00 mmol), Et_3N (2.24 mL, 16 mmol), and BH_3·THF complex (1 M solution in THF, 8.00 mL, 8.00 mmol) in THF (30 mL) gave after flash chromatography separation [eluent: EtOAc/PE, 1:10, silica gel; R_f (**6d**) = 0.40, R_f (**7d**) = 0.47] complexes **6d** (691 mg, 29%) and **7d** (911 mg, 38%).

Complex **6d**: M.p. 69–70 °C. $C_{15}H_{29}BNO_2P$ (297.19): calcd. C 60.62, H 9.84, N 4.71; found C 60.77, H 9.82, N 4.60. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ = 0.68 (1:1:1:1 br. q, $^1J_{B,H}$ = 90 Hz, 3 H, BH_3), 0.87 (s, 3 H, 12-H), 1.30, 1.55 (each s, each 3 H, 11 and 11′-H), 1.52 (m, 2 H, 15-H), 1.59 (m, 4 H, 14-H), 1.90 (d, $^2J_{H,H}$ = 10.9 Hz, 10-H^{ax}), 1.93 (m, 1 H, 8-H), 2.12 (m, 1 H, 7-H^{ax}), 2.16 (t, $^3J_{H,H}$ = 5.6 Hz, 1 H, 1-H), 2.23 (dtd, $^2J_{H,H}$ = 10.9 Hz, $^3J_{H,H}$ = 5.6 Hz, $^3J_{H,H}$ = 2.2 Hz, 1 H, 10-H^{eq}), 2.41 (AB type ddt, $^2J_{H,H}$ = 14.7 Hz, $^3J_{H,H\text{-}trans}$ = 9.1 Hz, $^3J_{H,H}$ = 2.4 Hz, 1 H, 7-H^{eq}), 3.16 (m, 4 H, 13-H), 4.58 (ddd, $^3J_{P,H}$ = 9.5 Hz, $^3J_{H,H\text{-}trans}$ = 9.1 Hz, $^3J_{H,H\text{-}cis}$ = 2.8 Hz, 1 H, 6-H) ppm. ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 298 K): δ = 24.3, 24.4 (C-12 and C-15), 26.3 (C-10), 26.3 (d, $^3J_{P,C}$ = 2.9 Hz, C-14), 27.1, 28.4 (C-11 and C-11′), 35.1 (d, $^3J_{P,C}$ = 2.9 Hz, C-7), 38.7 (C-9), 39.4 (C-8), 45.1 (d, $^2J_{P,C}$ = 3.8 Hz, C-13), 52.3 (d, $^3J_{P,C}$ = 5.4 Hz, C-1), 79.3 (d, $^2J_{P,C}$ = 4.6 Hz, C-6), 88.8 (d, $^2J_{P,C}$ = 7.5 Hz, C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K) δ = 146.0 ppm. IR (neat): $\tilde{\nu}$ = 3160, 2967, 2924 (s), 2866, 2849, 295 (s), 2359, 2187, 1964, 1468, 1443, 1389, 1373, 1360, 1338, 1277, 1259, 1208, 1169, 1139, 1112, 1057, 1025, 1012, 992, 954, 918, 898, 870, 853 cm^{-1}. MS (EI): *m*/*z* (%) = 298 (1), 297 (5) [M$^+$], 284 (12), 283 (67) [M$^+$ – BH_3], 268 (1), 240 (2), 199 (3), 177 (3), 176 (25), 152 (2), 149 (9), 132 (23), 108 (25), 94 (10), 93 (100), 56 (3), 55 (13), 41 (18), 29 (5), 28 (18). $[\alpha]_D^{20}$ = +1.2 (*c* = 1, $CHCl_3$).

Complex **7d**: M.p. 112 °C. $C_{15}H_{29}BNO_2P$ (297.19): calcd. C 60.62, H 9.84, N 4.71; found C 60.82, H 9.94, N 4.67. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ = 0.67 (1:1:1:1 br. q, $^1J_{B,H}$ = 90 Hz, 3 H, BH_3), 0.88 (s, 3 H, 12-H), 1.32, 1.65 (each s, each 3 H, 11 and 11′-H), 1.53 (m, 2 H, 15-H), 1.59 (m, 4 H, 14-H), 1.60 (d, $^2J_{H,H}$ = 10.5 Hz, 10-H^{ax}), 1.98 (m, 1 H, 8-H), 2.02 (dm, $^2J_{H,H}$ = 13.9 Hz, 1 H, 7-H^{ax}), 2.18 (t, $^3J_{H,H}$ = 5.5 Hz, 1 H, 1-H), 2.22 (dtd, $^2J_{H,H}$ = 10.5, $^3J_{H,H}$ = 5.5, $^3J_{H,H}$ = 2.2 Hz, 1 H, 10-H^{eq}), 2.44 (dm, $^2J_{H,H}$ = 13.9 Hz, 1 H, 7-H^{eq}), 3.28 (m, 4 H, 13-H), 4.48 (ddd, $^3J_{P,H}$ = 9.2 Hz, $^3J_{H,H\text{-}trans}$ = 7.9 Hz, $^3J_{H,H\text{-}cis}$ = 2.3 Hz, 1 H, 6-H) ppm. ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 298 K): δ = 24.3, 24.4 (C-12 and C-15), 25.6 (C-10), 26.3 (d, $^3J_{P,C}$ = 2.9 Hz, C-14), 27.1, 28.5 (C-11 and C-11′), 34.4 (d, $^3J_{P,C}$ = 2.9 Hz, C-7), 39.1 (C-9), 40.0 (C-8), 45.3 (d, $^2J_{P,C}$ = 4.7 Hz, C-13), 52.2 (d, $^3J_{P,C}$ = 4.5 Hz, C-1), n.o. (C-6), 86.1 (C-2) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = 142.3 ppm. IR (neat): $\tilde{\nu}$ = 3522, 2986, 2939 (s), 2850, 2386 (s), 1718, 1519, 1455, 1373, 1339, 1277, 1247, 1207, 1162, 1118, 1062, 1009, 992, 690, 914, 885, 867, 847, 801, 756, 731, 696, 635, 594, 561 cm^{-1}. MS (EI): *m*/*z* (%) = 297 (1) [M$^+$], 283 (84) [M$^+$ – BH_3], 268 (2), 240 (2), 213 (3), 201 (3), 176 (3), 161 (2), 150 (19), 136 (24), 132 (28), 119 (12), 108 (13), 93 (100), 84 (29), 77 (12), 67 (7), 55 (16), 41 (21), 39 (5). $[\alpha]_D^{20}$ = –29.3 (*c* = 1, $CHCl_3$).

X-ray Crystal Structure Analysis of Complex 7d: Formula $C_{15}H_{29}BNO_2P$; colorless crystal 0.9 × 0.7 × 0.5 mm; M_r = 297.17; *a* = 7.9654(16) Å, *b* = 10.539(2) Å, *c* = 10.4857(15) Å; β = 101.312(13)°; *V* = 863.2(3) Å^3; $\rho_{calcd.}$ = 1.143 g cm^{-3}; μ = 0.160 mm^{-1}; *Z* = 2; monoclinic, space group $P2_1$ (no. 4); λ = 0.71073 Å; *T* = 293(2) K; Wyckoff-Scan, 4171 reflections collected ($0 \le h \le 12$, $0 \le k \le 17$, $-16 \le l \le 16$), [(sin θ)/λ] = 0.81 Å^{-1}; 3951 independent (R_{int} = 0.0320) and 2941 observed reflections [$I \ge 2\sigma(I)$], 194 refined parameters; R_1 = 0.0672, wR_2 = 0.1620 ([$I \ge 2\sigma(I)$]); max. (min.) residual electron density 0.342 (–0.218) e Å^{-3}; Flack parameter –0.07(16), data collection with a Nicolet P3F diffractometer.

General Procedure for Enantioselective 1,4-Conjugate Addition of Et_2Zn to α,β-Unsaturated Substrates with Phosphoramidite Pinane-Based Complexes 6a–d and 7a–d: Prior to the addition reaction, complexes **6a**–**d** and **7b**–**d** were deprotected by heating in Et_2NH (3 mL) at 65 °C for 12 h. After removal of all volatiles and drying for 2 h under vacuum, the residue (the deprotected ligand) was dissolved in toluene, and the aliquot of this stock solution (1 mL, 0.10 mmol of ligand) was added to a suspension of Cu^I thiophenecarboxylate (9.5 mg, 0.05 mmol) in toluene (2 mL). Subsequently, Et_2Zn (1 M solution in hexane, 1.5 mL, 1.5 mmol) and then substrate (1.00 mmol) were added at –20 °C. The resulting mixture was stirred at –20 °C for 3 h. The reaction was quenched with HCl (1 N, 20 mL). After extraction with Et_2O (3 × 15 mL), the combined organic phases were washed with water (5 mL) and dried with $MgSO_4$. Solvents were evaporated under reduced pressure, and the residue was directly investigated by GC or HPLC on chiral phase to determine the enantiomeric selectivity of the addition reaction. (For the results of enantioselective addition, see Table 2 and the Supporting Information).

Supporting Information (see also the footnote on the first page of this article): Text, tables, and figures that give further experimental and spectroscopic details.

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