Tetrahedron xxx (xxxx) xxx

Contents lists available at ScienceDirect

Tetrahedron

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

P-stereogenic wide bite angle diphosphine ligands

Christine F. Czauderna [a], Alexandra M.Z. Slawin [a], David B. Cordes [a], Jarl Ivar van der Vlugt [b], Paul C.J. Kamer [a, c, *]

[a] EaStCHEM, School of Chemistry, University of St Andrews, Purdie Building, North Haugh, St Andrews KY16 9ST United Kingdom
[b] van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, the Netherlands
[c] Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

ARTICLE INFO

Article history:
Received 24 September 2018
Received in revised form
22 October 2018
Accepted 25 October 2018
Available online xxx

Keywords:
P-stereogenic ligand
Wide bite angle ligand
Ephedrine
Phosphinite borane
Oxazaphospholidine

ABSTRACT

Two modular synthetic approaches for the preparation of novel wide bite angle diphosphine ligands containing stereogenic P-atoms have been developed, leading to compounds (*S*,*S*)-2,2′-bis(methylphenylphosphino)diphenyl ether (**L1**) and (*S*,*S*)-2,2′-bis(ferrocenylphenylphosphino)diphenyl ether (**L2**) in very good diastereomeric ratios. Both protocols involve diphenyl ether as backbone and (2R_P,4S_C,5R_C)-(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine borane (R_P)-**5** as initial auxiliary to induce chirality at phosphorus. The absolute configuration of intermediates (*S*,*S*)-**9**-$(BH_3)_2$ and (*R*,*R*)-**10**-$(BH_3)_2$ as well as the ligands (*S*,*S*)-**L1-BH3** and (*S*,*S*)-**L2** was determined by X-ray crystallographic analysis.

1. Introduction

Chiral diphosphorus ligands are widely used in asymmetric homogeneous catalysis [1]. Many of these ligands feature stereogenic carbon atoms (e.g. Chiraphos, based on a chiral 2,3-dimethylpentane backbone), some form of planar chirality (e.g. Josiphos) or chiral atropisomerism, as present in e.g. binaphthyl-based scaffolds, with BINAP as a well-known example [2]. Diphosphine ligands bearing P-stereogenic centers have also been widely explored [3–6]. It is assumed that the close proximity of the P-stereogenic atom to the catalytically active metal centre offers high potential for asymmetric induction [7]. Several methods for the synthesis of the P-stereogenic phosphine ligands have been developed, including resolution of racemates, synthesis by asymmetric catalysis and also stereoselective synthesis [6,8]. However, the synthesis of P-stereogenic phosphines remains challenging, typically involves multiple steps, generating products that generally display at least some degree of oxidation-sensitivity and also because the free P-stereogenic phosphines are potentially prone to racemisation at phosphorus.

The use of phosphine borane complexes has been explored as versatile precursors for the synthesis of P-stereogenic phosphines [9]. This methodology has provided access to P-stereogenic mono- and diphosphine ligands, but not many *tri*aryl compounds, especially often desired bulky structures, have been accessible with this method to date (Scheme 1) despite the abundance of triarylphosphines used as ligands in homogeneous catalysis [10,11]. Jugé explored a more versatile method based on an enantiomerically pure methyl phosphinite derived from a heterocyclic oxazaphospholidine borane, which has enabled the synthesis of a range of monophosphines and several diphosphine ligands, including triaryl substituted, in high enantiomeric purity [12–14]. Despite recent advances [12b,c], The synthesis is often hampered by steric bulk of the substituents around the phosphorus atom, which makes the synthesis of bulky P-stereogenic diphosphine ligands still very challenging.

Diphosphine ligands with a wide bite angle of 102–110° can enforce excellent regioselectivity in several catalytic reactions, e.g. hydroformylation and allylic substitution [15]. Up to now, few diphosphine ligands are known that combine the concepts of P–stereogenicity and wide bite angle backbone design [16–18] Recently, a breakthrough has been reported by Börner et al. who adapted the well-established Jugé method for Xantphos analogues [19]. Still, it would be very desirable if more general methods for the preparation of the class of wide bite angle P-stereogenic

* Corresponding author. EaStCHEM, School of Chemistry, University of St Andrews, Purdie Building, North Haugh, St Andrews KY16 9ST United Kingdom.
E-mail address: paul.kamer@catalysis.de (P.C.J. Kamer).

https://doi.org/10.1016/j.tet.2018.10.070
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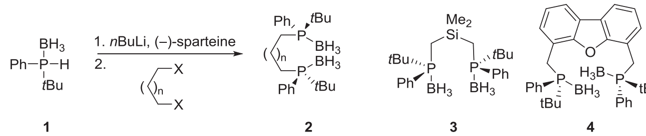
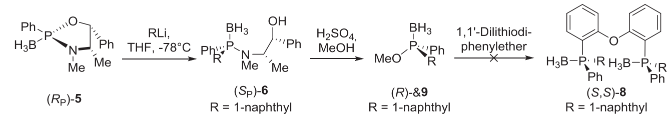
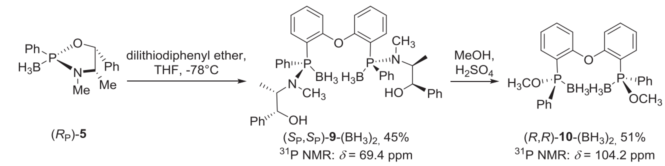


Scheme 1. Synthetic route tp alkyl substituted P-stereogenic diphosphine ligands.



Scheme 2. Unsuccessful route to P-stereogenic DPEPhos.



Scheme 3. Synthetic route to diphosphinite diborane adduct (R,R)-**10**-$(BH_3)_2$.

diphosphorus ligands would become available. Aiming at access to bulky bidentate ligands we expanded on the synthetic methodology using chlorophosphines as more reactive electrophiles compared to methylphosphinites. We herein describe two complementary synthetic procedures to realize wide bite angle P-stereogenic ligands based on diphenyl ether (Fig. 1), thereby providing chiral analogues of the widely employed diphosphine ligand DPEPhos [20–22].

2. Results and discussion

2.1. Synthesis of novel P-stereogenic ligands: small substituents

The anticipated synthesis of P-stereogenic DPEPhos analogues involved the P-stereogenic precursor $(2R_P,4S_C,5R_C)$-(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine borane (R_P)-**5** [12,23]. Unfortunately, methylphosphinite borane (R)-**7**, which is accessible by ring-opening of the oxazaphospholidine borane **5** with 1-lithionaphthalene under retention of configuration to give (S_P)-**6** and subsequent acidic methanolysis with inversion of configuration, [24] proved unreactive toward 2,8-dilithiodiphenyl ether (Scheme 2), likely because of unfavorable steric interference of the diphenyl ether with the bulky borane intermediate [14]. Reactions of related dilithium species such as 1,1′-dilithioferrocene resulted in low enantiomeric excess or the formation of monosubstituted product only [13,25,26]. The low selectivity of these reactions has been attributed to the second nucleophilic attack, which is hampered by the increased steric bulk as well as deactivation of the monosubstituted intermediate formed [25]. We therefore opted to react the diphenyl ether backbone directly with oxazaphospholidine borane (R_P)-**5** to generate intermediate (S_P,S_P)-**9**-$(BH_3)_2$ and after acidic methanolysis the related diphosphinite diborane (R,R)-**10**-$(BH_3)_2$ (Scheme 3) [25].

Single crystals of (S_P,S_P)-**9**-$(BH_3)_2$, obtained by recrystallization from chloroform, were suitable for single crystal X-ray analysis. The resulting molecular structure for (S_P,S_P)-**9**-$(BH_3)_2$, depicted in Fig. 2, confirmed the retention of configuration during the ring-opening reaction of the oxazaphospholidine borane (R_P)-**5** with dilithiodiphenyl ether. The two phenyl rings of the diphenyl ether backbone are not coplanar due to free rotation around the C_{Ph}-O bond. Because both phosphorus atoms are four-coordinated borane adducts, the intramolecular distance between the two phosphorus atoms (6.002(5)Å) is larger than for borane-free wide bite angle diphosphine ligands such as Xantphos (4.080 Å) [21]. The P-B bonds (1.908(13) and 1.897(12) Å) of both phosphorus groups are almost indistinguishable and similar to previous reported phosphine boranes [26,27]. With C-P-X angles (X = B, C, N) between 105.7(5) and 114.3(5) the two phosphorus atoms are close to ideal tetrahedral geometry.

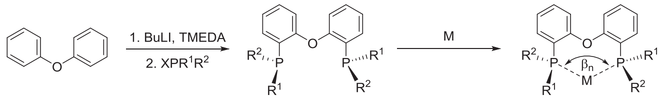


Fig. 1. Proposed strategy to novel P-stereogenic wide bite angle diphosphine ligands.

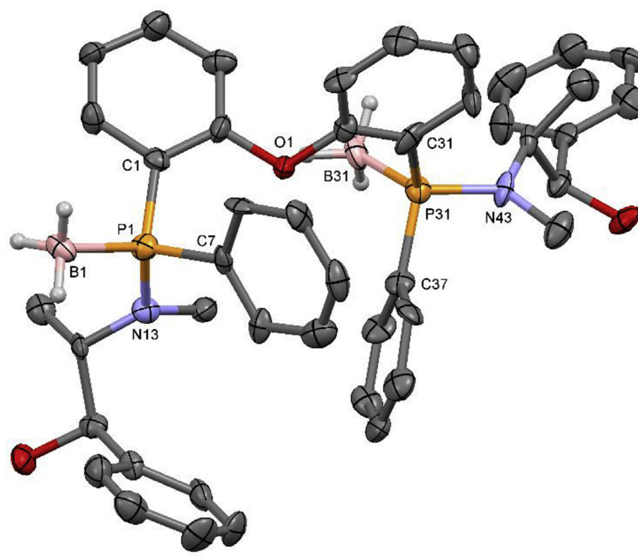


Fig. 2. Thermal ellipsoid plot of compound (S_P,S_P)-**9**-$(BH_3)_2$. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms not bound to boron are omitted for clarity. Selected bond lengths (Å), angles (°) and P···P distances (Å): P1-N13 1.656(9), P1-C7 1.813(11), P1-C1 1.823(10), P1-B1 1.908(13), P31-N43 1.654(9), P31-C37 1.815(11), P31-C31 1.841(12), P31-B31 1.897(12); N13-P1-C7 107.5(5), N13-P1-C1 109.0(5), C7-P1-C1 105.7(5), N13-P1-B1 114.3(5), C7-P1-B1 108.6(5), C1-P1-B1 111.4(5), N43-P31-C37 104.1(5), N43-P31-C31 107.8(5), C37-P31-C31 106.9(5), N43-P31-B31 113.0(5), C37-P31-B31 113.0(6), C31-P31-B31 111.6(6); P1···P31 6.002(5).

The acidic methanolysis of *bis(*aminophosphine) diborane (S_P,S_P)-**9**-$(BH_3)_2$ required three days and subsequently, the BH_3-groups were removed by DABCO at 60 °C. A sharp signal at δ 107.3 was observed in the ^{31}P NMR spectrum and we do not observe the formation of any *meso*-compound. Also the ^{1}H NMR spectrum of (R,R)-**10** does not indicate any *meso*-isomer, hence we propose that no epimerization of the P-centers occurs. Börner and co-workers recently reported P-stereogenic Xantphos and DPEPhos analogues, wherein removal of BH_3 was the key to obtain these compounds [19]. Single crystals of (R,R)-**10**-$(BH_3)_2$ were obtained by recrystallization from slow diffusion of hexane in a concentrated solution in ethyl acetate, The molecular structure of compound (R,R)-**10**-$(BH_3)_2$ (Fig. 3), resulting from an X-ray crystallographic analysis, confirmed that the acidic methanolysis proceeded via an S_N2-type reaction with inversion of the configuration of (S_P,S_P)-**9**-$(BH_3)_2$, similar to the formation of the mono-methylphosphinite borane (S_P)-**7**. The P-$C_{backbone}$ bond lengths (1.813(7) Å and 1.810(7) Å) are similar to the values found for other wide bite angle

Please cite this article as: C.F. Czauderna et al., P-stereogenic wide bite angle diphosphine ligands, Tetrahedron, https://doi.org/10.1016/j.tet.2018.10.070

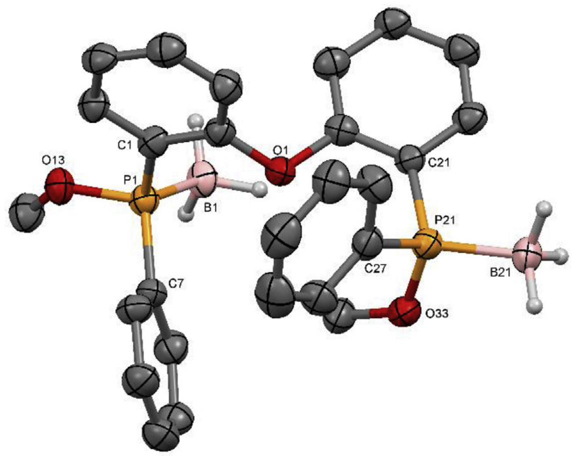
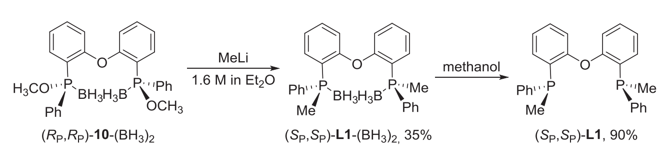


Fig. 3. Thermal ellipsoid plot of compound (R,R)-**10**-$(BH_3)_2$. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms not bound to boron are omitted for clarity. Selected bond lengths (Å), angles (°)and P···P distances (Å): P1-O13 1.604(5), P1-C1 1.813(7), P1-C7 1.823(7), P1-B1 1.892(7), P21-O33 1.599(5), P21-C21 1.810(7), P21-C27 1.819(7), P21-B21 1.915(8); O13-P1-C1 97.5(3), O13-P1-C7 106.3(3), C1-P1-C7 106.1(3), O13-P1-B1 112.6(3), C1-P1-B1 117.7(3), C7-P1-B1 114.8(3), O33-P21-C21 110.4(3), O33-P21-C27 107.6(3), C21-P21-C27 105.9(3), O33-P21-B21 108.0(3), C21-P21-B21 112.2(4), C27-P21-B21 112.7(4); P1···P21 5.796(3).

ligands such as Xantphos [20]. The intramolecular distance between the two phosphorus atoms (5.796(3) Å) is larger than in Xantphos (4.080 Å), which is likely due to the additional BH_3-coordination. The P-B bonds (1.892(7) and 1.915(8) Å) of both phosphorus groups are almost indistinguishable and similar to previous reported phosphine boranes [27]. The tetrahedral geometry is distorted around both phosphorus centers, judging from *e.g.* the B-P-C angles.

Transformation of *bis*methylphosphinite borane (*R*,*R*)-**10**-$(BH_3)_2$ into the desired P-stereogenic diphosphine ligands was dependent on the nature of the nucleophile. Reaction with either phenyllithium or biphenyllithium did not lead to successful introduction of the aryl substituent despite screening several reaction conditions. Furthermore, only small alkyl substituents (Me, ^{n}Bu) were smoothly introduced in the *bis*-methylphosphinite borane (*R*,*R*)-**10**-$(BH_3)_2$ at −78 °C, while *tert*-butyl and *sec*-butyl fragments were inaccessible. Similar limitations for the construction of P-stereogenic phosphinoborane compounds have previously been reported for related bulky diarylmethylphosphinite boranes as starting material [28].

Reaction of bis-methyl phosphinite borane (*R*,*R*)-**10**-$(BH_3)_2$ and methyllithium (Scheme 4) led to a diastereomeric ratio of (*S*,*S*)-**L1**-$(BH_3)_2$/(*R*,*S*)-**L1**-$(BH_3)_2$ (87:12) as determined by ^{1}H and ^{31}P NMR spectroscopy, which was verified by comparing the spectra with an independently synthetized (*rac,meso*)-mixture of **L1**-$(BH_3)_2$ (vide infra). As the amount of *meso*-compound was only 12% it is reasonable to assume that (*R*,*R*)-**L1**-$(BH_3)_2$ has only be formed in small amounts (<5%). Recrystallization of (*S*,*S*)-**L1**-$(BH_3)_2$ by slow diffusion of diethyl ether in a concentrated CH_2Cl_2 solution resulted in single crystals suitable for X-ray crystallography.



Scheme 4. Nucleophilic substitution of methyl phosphinite (S_P,S_P)-**10**-(BH_3) with MeLi and deprotection of the phosphine-borane with MeOH to generate (S,S)-**L1**.

The molecular structure (depicted in Fig. 4) confirmed that the reaction proceeds with inversion of configuration. As for the previous molecular structures, the observed intramolecular distance between the two phosphorus atoms (5.672(11)Å) is larger than for free wide bite angle diphosphine ligands such as Xantphos (4.080 Å). The P-C bond lengths and P-B bonds are similar to the previous cases. With C-P-X angles (X = B, C) between 104.04(11) and 114.94(13)°, the two phosphorus atoms are only slightly distorted from ideal tetrahedral geometry.

The free ligand (*S*,*S*)-**L1** was obtained by deprotection of (*S*,*S*)-**L1**-$(BH_3)_2$ with methanol under reflux, whereafter the trimethyl borate is effectively removed under high vacuum (Scheme 4). This alternative deprotection method was preferred as work-up of this sensitive product was more straightforward. Without further purifications the final ligand (*S*,*S*)-**L1** was obtained in quantitative yield as a sticky, oxygen-sensitive solid with 65% diastereomeric excess (*S*:*S*/*R*:*S* = 87:12). Given the ±12% of *meso*-compound, which was already present, racemisation is negligible, if occurring at all.

2.2. Synthesis of novel P-stereogenic ligands: large substituents

In literature, chlorophosphines are rarely applied in P-stereogenic chemistry because of the limited number of methods available to synthesize enantioenriched P-stereogenic chlorophosphines and their tendency to racemize [29,30]. Chlorophosphine boranes have been synthesized from aminophosphine borane (S_P)-**6** in optically enriched form, although the resulting chlorophosphine boranes are generally sensitize to racemisation, especially in case of small P-atom substituents [31].

Upon replacing the 1-naphthyl substituent in these phosphine species by ferrocene, we discovered that the resulting compound (*R*)-**12** is completely stable towards racemisation. Treatment of oxazaphospholidine borane (R_P)-**5** with lithioferrocene, available via lithiation of 1-bromo-ferrocene, afforded the aminophosphine borane (S_P)-**11** in good yield (Scheme 5). Just as for the previously synthesized aminophosphine boranes (S_P)-**6** (featuring a naphthyl group), ring opening of the oxazaphospholidine borane (R_P)-**5** proceeded with retention of the configuration at phosphorus. Unfortunately, the subsequent reaction of dilithiodiphenyl ether with

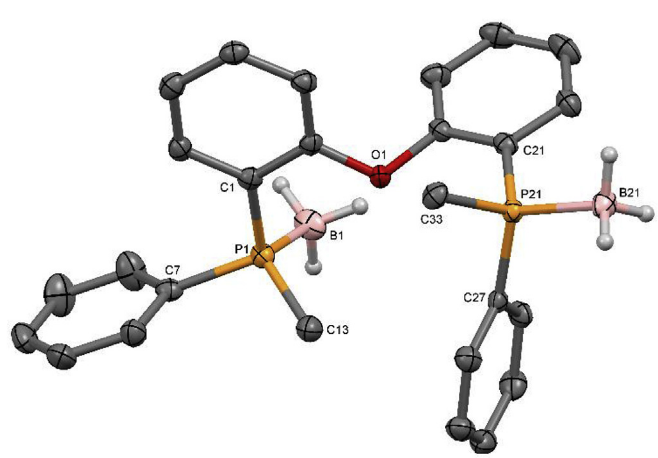
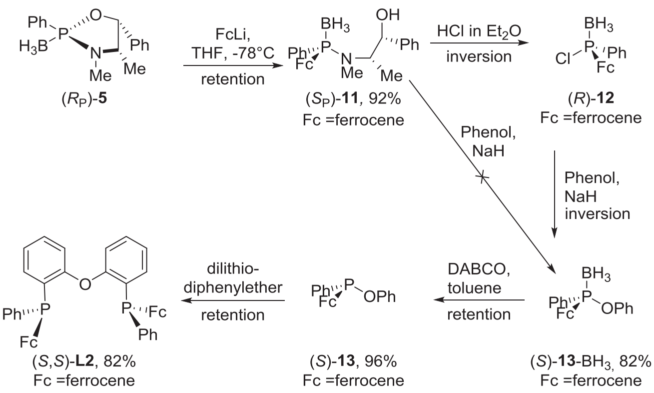


Fig. 4. Thermal ellipsoid plot of compound (S,S)-**L1**-$(BH_3)_2$ Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms not bound to boron are omitted for clarity. Selected bond lengths (Å), angles (°)and P···P distances (Å): P1-C13 1.805(3), P1-C7 1.812(2), P1-C1 1.831(2), P1-B1 1.919(3), P21-C27 1.810(2), P21-C21 1.811(2), P21-C33 1.811(2), P21-B21 1.920(3); C13-P1-C7 105.39(11), C13-P1-C1 107.21(11), C7-P1-C1 104.04(11), C13-P1-B1 114.94(13), C7-P1-B1 112.59(12), C1-P1-B1 111.86(11), C27-P21-C21 105.80(10), C27-P21-C33 106.70(11), C21-P21-C33 107.42(11), C27-P21-B21 113.25(12), C21-P21-B21 113.10(12), C33-P21-B21 110.17(12); P1···P21 5.6472(11).



Scheme 5. Synthetic procedure of (*S,S*)-**L2** via phenylphosphinite borane (*S*)-**13**.

chlorophosphine borane (*R*)-**12** was unsuccessful under various temperatures in different solvents and thus exchanging the leaving group from methoxy (in species (*R,R*)-**10**-$(BH_3)_2$) to a chloride did not enhance the overall reactivity of the P-stereogenic unit. Direct substitution of the ephedrine unit in aminophosphine borane (S_P)-**11** with sodium phenolate was also not successful.

Gratifyingly, this problem could be circumvented by reacting chlorophosphine borane (*R*)-**12** with sodium phenolate (Scheme 5). The ^{31}P NMR spectrum of the reaction mixture showed full conversion after two hours and the product (*S*)-**13**-(BH_3) was easily purified by flash chromatography. The enantiopurity of (*S*)-**13**-(BH_3) was established to be greater than 72% by HPLC. The BH_3 group is easily removed by heating (*S*)-**13**-(BH_3) in toluene in the presence of DABCO at 60 °C overnight with retention of configuration and with high ee (>72%). The free phenylphosphinite compound (*S*)-**13** proved to be relatively stable, *e.g.* it withstands filtration over silica under Ar atmosphere. Treatment of phenyl phosphinite (*S*)-**13** with dilithiodiphenyl ether-TMEDA at −78 °C afforded ligand **L2** as a mixture of three stereoisomers (*rac vs. meso*) in a ratio of 84:16, as established by ^{31}P NMR spectroscopy, which corresponds to a diastereomeric purity of 68% de. We thus established the coupling of an unprotected P-stereogenic compound with a dilithiated co-reagent to afford selective double substitution. The group of Börner recently and independently reported the same approach to furnish xanthene and diphenyl ether-based P-stereogenic (aryl)(aryl′)diphosphines [19].

Fractional crystallization by vapor phase diffusion of diethyl ether into a CH_2Cl_2 solution led to elucidation of the molecular structure of (*S,S*)-**L2** (Fig. 5). As expected the two phenyl rings of the backbone are not co-planar. The P-C bond lengths (between 1.819(5) Å and 1.844(5) Å) are in the same range as the related diphosphine ligand **L1**. The intramolecular distance of the two phosphorus atoms (5.5458(19) Å) is larger than for other wide bite angle diphosphine ligands, but smaller than in the above described (*S,S*)-**L1**-$(BH_3)_2$. The sum of the C-P-C angles (302.9° and 303.0°) is similar to previous reported P-stereogenic diphosphine ligands [13]. Unfortunately, the final ligand (*S,S*)-**L2** slowly racemized during storage.

3. Conclusions

Two modular synthetic approaches to afford the novel wide bite angle diphosphine ligands **L1** and **L2** containing stereogenic P-atoms have been established, starting from the chiral heterocyclic precursor ($2R_P,4S_C,5R_C$)-oxazaphospholidine borane (S_P)-**5**, which is derived from ephedrine. Synthetic pathways involving coupling of methylphosphinite borane (*R*)-**7** or chlorophosphinite borane (*R*)-**12** with dilithiodiphenyl ether were unsuccessful. This problem was overcome by reaction of the ($2R_P,4S_C,5R_C$)-oxazaphospholidine borane (S_P)-**5**, which is more reactive toward nucleophilic substitution, with the dilithiodiphenyl ether. This reaction was followed up by acidic methanolysis and reaction with methyllithium led to the desired ligand **L1**. During the reaction sequence the final ligand **L1** was only obtained with a diastereomeric ratio (*dr*) of 87:12. As an alternative protocol, we explored the use of phenylphosphinite (*S*)-**13** as an intermediate, via the acidolysis of ($2R_P,4S_C,5R_C$)-oxazaphospholidine borane (S_P)-**5**, reaction with sodium phenolate and removal of the BH_3-group. This building block was successfully coupled to the wide bite angle backbone diphenyl ether. Unfortunately, the final ligand **L2** slowly racemized during purification and as a shelved solid. However, the phenyl phosphinite building block (*S*)-**13**, which proved to be stable towards racemisation, provides facile access to a previously undeveloped class of P-stereogenic diphosphine ligands as well as bulky monophosphine ligands.

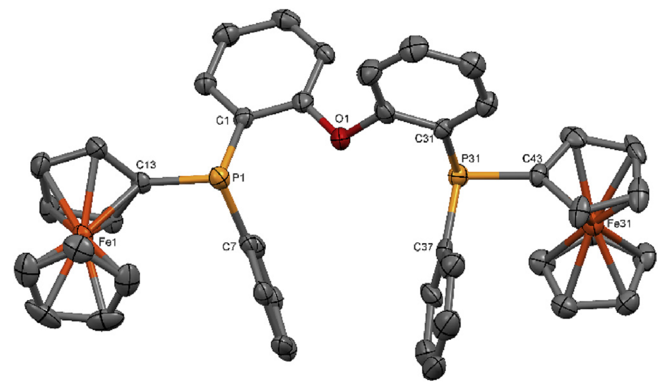


Fig. 5. Thermal ellipsoid plot of compound (S,S)-**L2**. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å), angles (°)and P⋯P distances (Å): P1-C13 1.819(5), P1-C1 1.835(5), P1-C7 1.844(5), P31-C43 1.816(5), P31-C37 1.837(5), P31-C31 1.839(5); C13-P1-C1 100.9(2), C13-P1-C7 100.7(2), C1-P1-C7 101.3(2), C43-P31-C37 100.1(2), C43-P31-C31 100.3(2), C37-P31-C31 102.6(2); P1⋯P31 5.5458(19).

4. Experimental section

All reactions were carried out using standard Schlenk techniques under an atmosphere of purified argon. Toluene was distilled from sodium, THF and Et_2O from Na/benzophenone, hexane from Na/benzophenone/triglyme, methanol and ethanol from Mg and DCM from CaH_2 under argon atmosphere. NMP, stored over molecular sieves, was purchased from Fluka. Chemicals were purchased from Acros Organics, Sigma-Aldrich and Alfa Aesar. Diethylamine and triethylamine were distilled from K_2CO_3. $ClPPh_2$ and PCl_3 were distilled under argon atmosphere before use. Compounds bis(diethylamino)phenylphosphine [32], (R_P)-**5** [12], dilithiodiphenyl ether [33], ($2R_P,4S_C,5R_C$)-(−)-*N*-methyl-*N*-(1-hydroxy)-1-phenyl)prop-2-yl-*P*-(1-naphthyl)-*P*-(phenyl)-phosphinamide borane ((S_P)-**6**) [13], (*S*)-(+)-methyl-(1-naphthyl)-phenylphosphinite borane ((*R*)-**7**) [13], were synthesized according to literature procedures. Washing solutions (water, brine) were degassed by three freeze-pump-thaw cycles and all precursors were dried azeotropically. Silica and aluminium oxide were degassed under vacuum before use. Column chromatography was carried out under argon atmosphere with flame dried glassware. TLC analysis was executed using silica F254 TLC plates from VWR. Silica gel 60 (0.063−0.2 mm; Fluka) was used for flash chromatography. Melting points were determined on a Gallenkamp MF-370 melting point apparatus in open capillaries. ^{1}H, ^{13}C, and ^{31}P

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spectra were measured on a Bruker Advance II 400 (^{1}H: 400.13 MHz; ^{13}C: 100.6 MHz; ^{31}P: 162.0 MHz) or a Bruker Advance 300 NMR spectrometer (^{1}H: 300.13 MHz; ^{13}C: 75.5 MHz; ^{31}P: 121.5 MHz). Chemical shifts (δ) are given in parts per million (ppm). Broad band decoupling was used for ^{13}C and ^{31}P NMR spectra. ^{1}H and ^{13}C spectra were measured relative to the signal of the solvent ($CDCl_3$: 1H: δ, 7.27 ppm, 13C: δ, 77.2 ppm) in which the sample was analysed and are reported relative to Me_4Si. ^{31}P NMR spectra were referenced externally respectively to 85% H_3PO_4. $CDCl_3$ was distilled over CaH_2 and stored over K_2CO_3 under argon. Other deuterated solvents were degassed by three freeze-pump-thaw cycles. Optical rotations were measured in a Perkin-Elmer 341 polarimeter which is regulated by a thermostat at T = 20 °C with l = 10 cm in air at 589 nm (sodium D line) and concentrations (c) are reported in g/100 mL. (*Note*: Highly sensitive compounds are not measured). Mass spectra were collected using a Micromass GC mass spectrometer or a Thermo Scientific DSQ II Single Quadrupole GC/MS spectrometer. FTIR measurements were carried out on a Nicolet 6700 spectrometer (Thermo Fisher Scientific) in transmission mode with a CsI pellet in a N_2-filled glovebox.

4.1. (S_P,S_P)-9-(BH_3)$_2$

A solution of dilithiodiphenyl ether TMEDA-adduct (4.707 g, 11.35 mmol) in a mixture of diethyl ether (25 mL) and tetrahydrofuran (25 mL) was added slowly to a solution of (R_P)-**5** (7.14 g, 24.9 mmol) in tetrahydrofuran (100 mL) at −78 °C. The reaction was allowed to warm slowly to r.t. overnight. The solution was quenched with water and the solvent was evaporated to dryness under high vacuum. The white precipitate was extracted with dichloromethane and purified by a short column (SiO_2, eluent: toluene:ethyl acetate 9:1). (S_P,S_P)-**9**-(BH_3)$_2$ was obtained as white solid (yield: 3.78 g, 5.10 mmol, 45%). ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K) δ (ppm) 7.75-7.67 (m, 2H, PhH), 7.40−7.7.05 (m, 20H, PhH), 6.69-6.57 (m, 6H, PhH), 4.7 (d, 2H, $^3J_{HH}$ = 6.3 Hz), 4.18-4.09 (m, 2H), 3.12 (s, 2H, OH), 1.91 (d, 6H, $^3J_{PH}$ = 8.0 Hz), 1.15, (d, 6H, $^3J_{HH}$ = 6.7 Hz), 1.8-0.2 (m, 6H; BH_3). ^{13}C NMR (100 MHz, CD_2Cl_2, 296 K) δ (ppm) 159.9 (d, J_{PC} = 2.3 Hz, Ph), 143.2, 135.6-121.9 (m, Ph), 78.7 (d, J_{PC} = 6.9 Hz; CH), 58.3 (d, J_{PC} = 10.8 Hz, CH), 30.3 (d, J_{PC} = 4.1 Hz; CH_3), 13.7 (CH_3). ^{31}P NMR (162 MHz, CD_2Cl_2, 296 K) δ (ppm) 69.4 (broad s, P-BH_3). $[\alpha]_D$ (c = 0.261, $CHCl_3$) = +56.3°. m.p. 91−95 °C. Mass (FT-MS + p NSI) m/z calculated for $[C_{44}H_{52}B_2N_2O_3P_2+H]^+$ 739.3765 $(M+H)^+$, obs.: 739.3785 $(M+H)^+$ and $[C_{44}H_{52}B_2N_2O_3P_2-BH_2]^-$ 727.3390 $[M-BH_2^-]^+$, obs.: 727.3387 $[M-BH_2]^-$ (mixture of $[M+H]^+$ and $[M-BH_2^-]^+$ was observed).

4.2. (R,R)-10-(BH_3)$_2$

Methanol (80 mL, degassed, dry) and concentrated H_2SO_4 (0.205 g, 2.09 mmol) were added to a solution of (S_P,S_P)-**9**-(BH_3)$_2$ (0.780 g, 0.99 mmol) in THF (20 mL) whilst cooling the mixture in an ice-bath. After slowly warming to room temperature, the reaction mixture was followed by ^{31}P NMR spectroscopy. After completion, the solvent was evaporated. The product was subjected to column chromatography (SiO_2, eluent: hexane:ethyl acetate 9:1) to give (*R*,*R*)-**10**-(BH_3)$_2$ as white solid (yield: 0.240 g, 0.505 mmol, 51%). $[\alpha]_D^{20}$ (c = 0.252, $CHCl_3$) = −32°. m.p. 118−120 °C. Mass (FT-MS ESI+) m/z calculated for $[C_{26}H_{30}B_2O_3P_2+Na]^+$: m = 497.1754 $(M+Na)^+$, obs.: 497.1760 $(M+Na)^+$. Major product: ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ (ppm) 7.75-7.67 (m, 2H; Ph−H), 7.48−7.15 (m, 20H; Ph−H), 6.07 (ddd, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, $^3J_{PH}$ = 3.8 Hz), 3.69 (d, 6H, $^3J_{PH}$ = 12.3 Hz, OCH_3), 1.3-0.3 (m, 6H, BH_3). ^{13}C NMR (100 MHz, CD_2Cl_2, 296 K) δ (ppm) 159.9 (d, J_{PC} = 2.3 Hz; Ph-C), 143.2, 135.6-121.9 (m, Ph-C), 78.7 (d, J_{PC} = 6.9 Hz; CH-C), 48.3 (d, J_{PC} = 8.8 Hz; CH-C). ^{31}P NMR (162 MHz, CD_2Cl_2, 296 K) δ (ppm) 104.2 (P-BH_3). Minor product: ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ (ppm) 7.7.75 (ddd, 2H, $^3J_{HH}$ = 10.9 Hz, $^4J_{HH}$ = 1.3 Hz, $^3J_{PH}$ = 6.7 Hz), 7.48−7.15 (m, 20H; Ph−H), 6.27 (ddd, 2H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, $^3J_{PH}$ = 3.8 Hz), 3.68 (d, 6H, $^3J_{PH}$ = 12.2 Hz, OCH_3), 1.3-0.3 (m, 6H, BH_3). ^{31}P NMR (162 MHz, CD_2Cl_2, 296 K) δ (ppm) 108.0 (broad, P-BH_3).

4.3. (R,R)-10

A solution of DABCO (11.27 mg, 0.1 mmol, azeotropically dried) was added to a solution of (*R*,*R*)-**10**-(BH_3)$_2$ (9.48 mg, 0.02 mmol) in toluene (5 mL) at r.t. The reaction mixture was heated for 20 h at 60 °C. The volatiles were removed *in vacuo* and the crude reaction mixture was analysed by ^{1}H NMR and ^{31}P NMR spectroscopy without further purification. Yield: 0.240 g (0.50.5 mmol, 51%). ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ (ppm) 7.48-7.43 (m, 6H; Ph−H), 7.26-7.22 (m, 20H; Ph−H), 7.11-7.08 (m, 6H; Ph−H), 3.65 (d, 6H, $^3J_{PH}$ = 14.0 Hz, OCH_3).^{31}P NMR (162 MHz, CD_2Cl_2, 296 K) δ (ppm) 107.3.

4.4. (S,S)-L1-(BH_3)$_2$

MeLi (2.3 mL, 3.4 mmol, 1.5 M in diethylether, freshly titrated) was added to a solution of (*R*,*R*)-**10**-(BH_3)$_2$ (744 mg, 1.55 mmol) in tetrahydrofuran (1 M) at −100 °C. The reaction mixture was slowly warmed up to r.t. overnight. The reaction mixture was quenched with water at room temperature. The product was extracted with dichloromethane and purified by column chromatography (SiO_2, eluent: CH_2Cl_2:hexane 1:1) to give (*S*,*S*)-**L1**-(BH_3)$_2$ as white solid (yield: 0.240 g, 0.54 mmol, 35%). $[\alpha]_D^{20}$ (c = 0.201, $CHCl_3$) = +3.4°. m.p. 159 °C. MS LC-TOF: m/z calculated for $[C_{26}H_{30}B_2OP_2+Na]^+$: m = 465.1856 $(M+Na)^+$, obs.: 465.1859 $(M+Na)^+$. Major product: ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K): δ (ppm) 7.83-7.78 (m, 2H, PhH), 7.35-7.29 (m, 6H), 7.48-7.28 (m, 12H), 7.22-7.12 (m, 4H), 6.04-6.00 (m, 2H), 6.51 (broad dd, 1H, $^3J_{HH}$ = 8.1 Hz, $^3J_{HP}$ = 2.98 Hz), 1.65 (d, 1H, $^2J_{PH}$ = 10.2 Hz), 1.4-0.3 (broad q, BH_3). ^{13}C NMR (100 MHz, CD_2Cl_2, 296 K): δ (ppm) 160.0, 136.2 (d, J_{PC} = 11.8 Hz), 134.8 (d, J_{PC} = 11.0 Hz), 143.7, 134.5, 132.6 (d, J_{PC} = 10.0 Hz), 131.9, 131.6 (d, J_{PC} = 2.1 Hz), 131.4, 129.6 (d, $^1J_{PC}$ = 10.2 Hz), 125.0 (d, $^1J_{PC}$ = 10.4 Hz), 122.5 (d, J_{PC} = 23.4 Hz), 121.4 (d, J_{PC} = 4.2 Hz), 11.8 (d, $^1J_{PC}$ = 40.9 Hz). ^{31}P NMR{^{1}H} (161 MHz, CD_2Cl_2, 296 K): δ (ppm) 7.4 (broad d, $^1J_{PB}$ = 64.1 Hz, P-BH_3). Minor product: ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K): δ (ppm) 7.69-7.64 (m, 4H), 7.35-7.29 (m, 6H), 7.48-7.28 (m, 12H), 7.22-7.12 (m, 2H), 6.68-6.65 (m, 2H), 1.66 (d, 1H, $^2J_{PH}$ = 4.1 Hz), 1.4-0.3 (broad q, BH_3). ^{31}P NMR{^{1}H}(161 MHz, CD_2Cl_2, 296 K): δ (ppm) 7.4 (broad d, $^1J_{PB}$ = 64.1 Hz, P-BH_3).

(*S*,*S*)-**L1.** (*S*,*S*)-**L1**-(BH_3)$_2$ (100 mg, 0.23 mmol) was suspended in methanol and heated at 80 °C overnight. Full deprotection was observed by ^{31}P NMR. All volatiles were removed *in vacuo*. No further purification was necessary and (*S*,*S*)-**L1** was obtained as white sticky solid (yield: 84 mg, 0.202 mmol, 90%). MS LC-TOF: m/z calculated for $[C_{26}H_{24}OP_2+Na]^+$: m = 437.1200 $(M+Na)^+$, obs.: 437.1192 $(M+Na)^+$. Major product: ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K): δ (ppm) 7.43-7.41 (m, 4H), 7.31-7.27 (m, 6H), 7.15-7.11 (m, 4H), 7.02-6.98 (m, 2H), 6.44 (broad dd, 1H, $^3J_{HH}$ = 8.1 Hz, $^2J_{PH}$ = 2.98 Hz), 1.58 (d, 1H, $^2J_{PH}$ = 4.1 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2, 296 K) δ (ppm) 159.7 (d, J_{PC} = 14.6 Hz), 139.9.7 (d, J_{PC} = 12.3 Hz), 133.4 (d, J_{PC} = 19.8 Hz), 132.6 (d, J_{PC} = 3.6 Hz), 130.6, 129.2, 129.1 (d, J_{PC} = 7 Hz),124.3, 118.7, 11.8 (d, J_{PC} = 12.7 Hz). ^{31}P NMR{^{1}H} (161 MHz, CD_2Cl_2, 296 K): δ (ppm) −36.0. Minor product: ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K): δ (ppm) 7.43-7.41 (m, 4H), 7.31-7.27 (m, 6H), 7.15-7.11 (m, 4H), 7.02-6.98 (m, 2H), 6.50 (broad dd, 1H, $^3J_{HH}$ = 8.1 Hz, $^2J_{PH}$ = 2.98 Hz), 1.52 (d, 1H, $^2J_{PH}$ = 4.1 Hz). ^{31}P NMR {^{1}H} (161 MHz, $CDCl_3$, 296 K): δ (ppm) −36.4.

Please cite this article as: C.F. Czauderna et al., P-stereogenic wide bite angle diphosphine ligands, Tetrahedron, https://doi.org/10.1016/j.tet.2018.10.070

4.5. (S_P)-11

tert-Butyllithium (1.6 M in Et_2O; 13.3 mL, 21.25 mmol) was added slowly to a solution of bromoferrocene (2.82 g, 10.62 mmol) in diethyl ether (60 mL) at −78 °C and the solution was stirred for 30 min. The solution was warmed to 0 °C and stirred for an additional 15 min to generate FcLi. Completion of the lithiation was checked by quenching a sample with H_2O and monitoring it by GC/MS. A solution of (*R*)-**5** (3.18 g, 11.16 mmol) in THF (70 mL) was cooled to −78 °C, and the FcLi solution was added via cannula. The solution was allowed to warm to 10 °C and stirred overnight. The reaction mixture was quenched with water (3 mL) and all volatiles were removed *in vacuo*. The crude product was suspended in CH_2Cl_2. The organic layer washed with water and brine, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified via gradient column chromatography (SiO_2,eluent: 100% toluene, gradient increased to toluene:ethyl acetate 9:1) to give diastereomerically pure (S_P)-**11** as orange powder (yield: 4.57 g, 9.7 mmol, 92%). ^1H NMR (500 Mhz, CD_2Cl_2, 296 K) δ (ppm) 7.41-7.28 (m, 10H, PhH), 4.83-4.81 (m, 1H, CH), 4.54 (broad s, 1H, cp), 4.50 (broad s, 1H, cp), 4.46 (broad s, 1H, cp), 4.25 (s, 5H, cp), 4.20 (broad s, 1H, cp), 4.18-4.11 (m, 1H, CH), 2.31 (d, 3H, $^3J_{HH}$ = 8.2 Hz), 1.19 (d, 3H, $^3J_{HH}$ = 6.8 Hz),1.8-0.8 (broad m, 3H; BH_3). ^{13}C NMR (126 MHz, CD_2Cl_2, 296 K) δ (ppm) 143.3, 133.7, 133.1, 131.80 (d, J_{PC} = 10.1 Hz), 130.8 (d, J_{PC} = 1.9 Hz), 128.7, 128.5 (d, J_{PC} = 10.2 Hz), 128.0, 127.1, 79.1 (d, J_{PC} = 5.7 Hz, Cp), 72.9 (d, J_{PC} = 7.3 Hz, Cp), 72.5, 72.4 (d, J_{PC} = 12.8 Hz, Cp), 71.9, 71.6 (d, J_{PC} = 7.8 Hz), 71.5 (d, J_{PC} = 6.7 Hz, Cp), 58.2 (d, J_{PC} = 9.3 Hz), 30.7 (d, J_{PC} = 3.0 Hz), 13.3. ^{31}P NMR{^1H} (162 MHz, CD_2Cl_2, 296 K) δ (ppm) 69.5 (d, J_{PB} = 82.0 Hz, P-BH_3). m.p. 84−88 °C. $[\alpha]_D^{20}$ (c = 0.252, $CHCl_3$) = −106.9°. Mass (TOF-MS ESI^+) *m/z* calculated for $[C_{26}H_{31}BFeNOP+Na]^+$494.1483 $[M+Na]^+$, obs.: 494.1480 $[M+Na]^+$.

4.6. (R)-12

A 2M HCl solution in Et_2O (30.4 mL, 60.74 mmol) was added under stirring at r.t. to a solution of aminophosphine borane (S_P)-**11** (4.77 g, 10.1262 mmol) in toluene (155 mL), After 1.5 h, the reaction mixture turned cloudy and full conversion of the starting material was observed by ^{31}P NMR spectroscopy. The reaction mixture was filtered (Schlenk filter; glass frit P4) and the excess of HCl was removed by several vacuum argon cycles. The crude product (*R*)-**12** was used in solution without evaporation of the solvent. ^{31}P NMR (162 MHz, CD_2Cl_2, 296 K) δ (ppm) 94.9 (broad d, $^1J_{PB}$ = 45.5 Hz, P-BH_3).

4.7. (S)-13-(BH_3)

A solution of phenol (70.87 g, 6.67 mmol) in THF (15 mL) was slowly added to a suspension of NaH (1.7 g, 70.87 mmol) in THF (20 mL) at 0 °C over 20 min. After 20 min at 0 °C, the reaction mixture was allowed to warm to r.t., where after it was stirred for an additional 2 h to generate sodium phenolate. The solution of sodium phenolate (max. 70.87 mml) in THF (35 mL) was slowly added via cannula to a solution of chlorophosphine borane (*R*)-**12** (max. 3.47 g, 10.12 mmol) in toluene (155 mL) at −78 °C and the solution was stirred for 30 min at −78 °C. The solution was warmed to r.t. and stirred overnight. The reaction mixture was quenched with water (3−4 mL) and all volatiles were removed *in vacuo*. The crude product was suspended in CH_2Cl_2, the organic layer washed with water and brine, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by column chromatography (SiO_2,eluent: 100% toluene) to give (*S*)-**13**-(BH_3) as orange solid (yield: 3.33 g, 8,32 mmol, 82%). The enantiomeric excess of (*S*)-**13**-(BH_3) was determined using chiral HPLC measurements and found to be >72% (column: AD-H, eluent: hexane (95%), IPA (5%), flow: 0.5 mL min^{-1}, (*S*)-**13**-(BH_3) = 16.8 min, (*R*)-**13**-(BH_3) = 21.5 min). ^1H NMR (500 MHz, CD_2Cl_2, 296 K) δ (ppm) 8.03-7.99 (m, 2H, PhH), 7.62-7.53 (m, 3H, PhH), 7.23 (t, 2H, $^3J_{HH}$ = 7.3 Hz), 7.09 (t, 1H, $^3J_{HH}$ = 7.4 Hz), 6.99 (d, 2H, $^3J_{HH}$ = 7.8 Hz), 4.7 (broad s, 1H, cp), 4.55 (broad s, 1H, cp), 4.51 (broad s, 1H, cp), 4.39 (broad s, 1H, cp), 4.13 (broad s, 5H, cp), 1.8-0.8 (broad m, 3H; BH_3). ^{13}C NMR (126 MHz, CD_2Cl_2, 296 K) δ (ppm) 153.3(d, J_{PC} = 5.9 Hz), 133.1, 133.0 (d, J_{PC} = 2.1 Hz), 132.6, 132.0 (d, J_{PC} = 11.3 Hz), 130.0, 129.3 (d, J_{PC} = 10.4 Hz), 125.2, 122.1 (d, J_{PC} = 3.9 Hz), 73.4 (d, J_{PC} = 8.2 Hz, CH), 72.2 (d, J_{PC} = 13.3 Hz, Cp), 73.0 (d, J_{PC} = 8.7 Hz, Cp), 72.5 (d, J_{PC} = 10.3 Hz), 71.8 (d, J_{PC} = 77 Hz, Cp), 70.9 (Cp). ^{31}P NMR{^1H} (162 MHz, CD_2Cl_2, 296 K) δ (ppm) 110.3 (q, J_{PB} = 71.5 Hz, P-BH_3). m.p. 38−41 °C. $[\alpha]_D^{20}$ (c = 0.258, $CHCl_3$) = −84.2°. Mass (TOF-MS ESI^+) *m/z* calculated for $[C_{22}H_{22}BFeOP+Na]^+$423.0748 $[M+Na]^+$, obs.: 423.0753 $[M+Na]^+$.

4.8. (S)-13

A solution of DABCO (1.68 g, 14.95 mmol) in toluene (40 mL) was added to a solution of (*S*)-**13**-(BH_3) (1.50 g, 3.73 mmol, azeotropically dried with toluene) in diethylether (100 mL). The reaction mixture was heated for 20 h at 60 °C. After cooling to r.t., toluene was removed *in vacuo*. Purification by filtration over silica (SiO_2; eluent: ethyl acetate) resulted in a light orange solid that was used without further purification (yield: 1.24 g, 3.6 mmol, 96%). ^1H NMR (500 MHz, CD_2Cl_2, 296 K) δ (ppm) 7.77-7.74 (m, 2H, PhH), 7.46−8.42 (m, 3H, PhH), 7.26 (t, 2H, $^3J_{HH}$ = 7.7 Hz), 7.10 (d, 2H, $^3J_{HH}$ = 7.7 Hz), 6.98 (t, 1H, $^3J_{HH}$ = 7.3 Hz), 4.53 (broad s, 1H, cp), 4.45 (broad s, 1H, cp), 4.36 (broad s, 1H, cp), 4.41 (s, 5H, cp), 4.01 (broad s, 1H, cp). ^{13}C NMR (126 MHz, CD_2Cl_2, 296 K) δ (ppm) 156.63(d, J_{PC} = 9.2 Hz), 139.8 (d, J_{PC} = 17.2 Hz), 129.7 (d, J_{PC} = 23.1 Hz), 129.0, 128.6, 127.4 (d, J_{PC} = 7.6 Hz), 121.3, 117.8 (d, J_{PC} = 11.2 Hz), 78.1 (d, J_{PC} = 12.7 Hz, Cp), 71.6 (d, J_{PC} = 22.6 Hz, Cp), 70.9 (d, J_{PC} = 5.6 Hz, Cp), 70.4, 70.3 (d, J_{PC} = 15.5 Hz, Cp), 68.2 (Cp). ^{31}P NMR{^1H} (162 MHz, CD_2Cl_2, 296 K) δ (ppm) 107.02 (s, P-BH_3).

4.9. L2

A suspension of dilithiodiphenyl ether (515 mg, 1.25 mmol) in Et_2O (30 mL) was cooled to −78 °C before THF (15 mL) was added. The suspension was slowly added via cannula to a solution of (*S*)-**13** (1.01 g, 2.6 mmol) in THF (85 mL) at −78 °C. After 1 h at −78 °C, the reaction mixture was allowed to warm to 12 °C and stirred for an additional 14 h at this temperature. The reaction mixture was quenched with methanol (3−4 mL) and all volatiles were removed *in vacuo*. The crude product was suspended in THF and the organic layer washed with water and brine, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by column chromatography (SiO_2, eluent: hexane:CH_2Cl_2 1:1, gradient increased to hexane:CH_2Cl_2 1:2) to give **L2** as orange precipitate (yield: 3.33 g, 8.32 mmol, 82%). Recrystallization by slow diffusion of Et_2O into a solution of **L2** in CH_2Cl_2 yielded single crystals that were suitable for X-ray crystallographic analysis. $[\alpha]_D^{20}$ (c = 0.252, $CHCl_3$) = 163.2°. m.p. 179 °C (decomposition). Mass (TOF-MS ESI^+) *m/z* calculated for $[C_{44}H_{36}Fe_2OP_2+Na]^+$777.0838 $[M+Na]^+$, obs.: 777.0831 $[M+Na]^+$. Major: ^1H NMR (400 MHz, CD_2Cl_2, 296 K) δ (ppm) 7.40-7.23 (m, 10H, PhH), 7.06-6.9 (m, 6H), 6.22 (dd, 2H, $^3J_{HH}$ = 7.6 Hz, $^3J_{PH}$ = 3.5 Hz, PhH), 4.42-4.40 (m, 2H, Cp), 4.36-4.33 (m, 4H, Cp), 4.09 (s, 5H, Cp), 3.89-3.88 (m, 5H, Cp). ^{13}C NMR (100 MHz, CD_2Cl_2, 296 K) δ (ppm) 159.9 (d, J_{PC} = 18.3 Hz), 138.7 (d, J_{PC} = 9.7 Hz), 135.12, 134.9, 134.6 (d, J_{PC} = 10.65 Hz), 132.4 (d, J_{PC} = 16.3 Hz),130.6, 129.2, 129.7-128.7, (m), 123.9, 118.8, 76.2 (d, J_{PC} = 6.7 Hz, Cp), 74.9 (d, J_{PC} = 26.8 Hz, CH), 73.0, 71.9, 71.3, 69.9. ^{31}P NMR (162 MHz, CD_2Cl_2, 296 K) δ (ppm) −29.9 (s). Minor: ^1H NMR

Please cite this article as: C.F. Czauderna et al., P-stereogenic wide bite angle diphosphine ligands, Tetrahedron, https://doi.org/10.1016/j.tet.2018.10.070

(400 MHz, CD_2Cl_2, 296 K) δ (ppm) 7.40-7.23 (m, 10H, PhH), 7.06-6.9 (m, 6H), 6.34 (dd, 2H, $^3J_{HH} = 7.6$ Hz, $^3J_{PH} = 3.5$ Hz, PhH), 4.42-4.40 (m, 2H, Cp), 4.38-4.36 (m, 4H, Cp), 4.05 (s, 5H, Cp), 3.82-3.81 (m, 5H, Cp). ^{31}P NMR (162 MHz, CD_2Cl_2, 296 K) δ (ppm) −28.7 (s).

4.10. L2-$(BH_3)_2$

L2 was azeotropically dried with toluene (3 × 20 mL) and dissolved in THF (100 mL) before adding a 2M $BH_3.SMe_2$ solution in THF (14.12 mL, 28.34 mmol). After 1 h, the reaction mixture was concentrated and the precipitate was azeotropically dried with toluene (3 × 20 mL) to remove excess BH_3SMe_2. The precipitate was suspended in DCM and washed with brine (50 mL) and water (50 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo* to give **L2**-$(BH_3)_2$ as orange solid (yield: 5.43 g, 11.44 mmol, 81%). ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K) δ (ppm) 7.55 (ddd, 2H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.53$ Hz, $^4J_{PH} = 12.8$ Hz, PhH), 7.38-7.32 (m, 4H, PhH), 7.30-7.23 (m, 6H, PhH), 7.19-7.15 (m, 2H, PhH), 7.07-7.04 (m, 2H, PhH), 6.21 (ddd, 2H, $^3J_{HH} = 8.3$ Hz, $^4J_{HH} = 0.7$ Hz, $^3J_{PH} = 3.9$ Hz, PhH), 4.51-4.49 (m, 2H, Cp), 4.43-4.39 (m, 4H, Cp), 4.14-4.13 (m, 2H, Cp), 4.03 (s, 5H, Cp), 1.8-0.8 (broad m, 6H; BH_3). ^{13}C NMR (100 MHz, CD_2Cl_2, 296 K) δ (ppm) 160.7, 135.0 (d, $J_{PC} = 10.4$ Hz), 133.3, 132.8 (d, $J_{PC} = 10.8$ Hz), 131.0, 130.8, 130.4, 128.5 (d, $J_{PC} = 10.8$ Hz), 123.9 (d, $J_{PC} = 10.2$ Hz), 122.6 (d, $J_{PC} = 4.8$ Hz), 122.5, 122.0, 74.0 (d, $J_{PC} = 9.4$ Hz, Cp), 73.5 (d, $J_{PC} = 10.8$ Hz, CH), 72.5 (d, $J_{PC} = 7.9$ Hz, Cp), 71.7 (d, $J_{PC} = 7.8$ Hz, Cp), 70.2 (Cp), 69.2 (d, $J_{PC} = 70.8$ Hz, Cp). ^{31}P NMR (162 MHz, CD_2Cl_2, 296 K) δ (ppm) 12.83 (broad, P-BH_3). m.p. 190–194 °C. $[\alpha]_D^{20}$ (c = 0.252, $CHCl_3$) = 163.2°. Mass (TOF-MS ESI$^+$) *m/z* calculated for $[C_{44}H_{42}B_2Fe_2OP_2+Na]^+$ 805.1494 $[M+Na]^+$, obs.: 805.1486 $[M+Na]^+$.

4.11. Chloro(N,N-diethylamino)phenylphosphine (15)

Chloro(*N,N*-diethylamino)phenylphosphine was synthesized according to literature [34]. To a solution of dichlorophenylphosphine (26.96 g, 150.68 mmol) in diethylether (250 mL) was added a solution of diethylamine (31.2 mL, 22.04 g, 301.4 mmol) in diethylether (50 mL) dropwise at 0 °C. The reaction mixture was stirred overnight. The reaction mixture was filtered over a glass frit to remove ammonium salts and the diethylether was removed by distillation under argon. The residue was distilled under high vacuum to give **15** as clear oil (yield: 28.4 g, 131.4 mmol, 88%). ^{1}H NMR (400 MHz, C_6D_6, 296 K): δ (ppm) 7.83 (broad s, 2H), 7.23-7.18 (m, 3H), 3.04-2.95 (m, 4H, CH_2), 0.94 (broad t, 6H, $^3J_{HH} = 7.1$ Hz, CH_3). ^{13}C NMR (100 MHz, C_6D_6, 296 K): δ (ppm) 140.0 (d, $J_{PC} = 29.4$ Hz), 131.0 (d, $J_{PC} = 20.3$ Hz), 129.8, 128.6 (d, $J_{PC} = 3.9$ Hz), 44.1 (d, $J_{PC} = 12.5$ Hz, CH_2), 14.1 (broad s, CH_3). ^{31}P NMR (161 MHz, C_6D_6, 296 K): δ (ppm) 141.0. b.p. 67–72 °C (0.13 mbar).

4.12. (N,N-diethylamino)(methyl)(phenyl)phosphine (16)

(*N,N*-diethylamino)(methyl)(phenyl)phosphine **16** was synthesized via a modified literature procedure [35]. At −78 °C, MeLi (32.6 mL, 52.1 mmol, 1.6 M in diethylether) was added to a solution of chloro(*N,N*-diethylamino)phenylphosphine (10.21 g, 47.4 mmol) in diethylether (60 mL) at −78 °C. During addition a white precipitate was formed. The reaction mixture was stirred at −78 °C for 1 h before the reaction mixture was placed in an ice/salt bath (−15 °C) and warmed up to r.t. overnight. The reaction mixture was filtered over a P4 frit and the solution was concentrated under high vacuum.

4.13. N,N-diethylamino-1-ferrocenyl-1-phenylphosphine borane (17)

^{t}BuLi (11.6 mL, 18.58 mmol, 1.6 M in pentane) was added to a solution of bromoferrocene (2.459 g, 9.28 mmol) in diethylether (50 mL) via cannula at −78 °C. The reaction mixture was stirred at −78 °C for 1.5 h before it was placed into an ice-bath for 30 min. The reaction mixture was cooled again to −78 °C before being added to a solution of 1-chloro-*N,N*-diethylamino-1-phenylphosphine **15** in diethylether (50 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h before being placed into an ice-salt mixture (−18 °C) and allowed to warm to r.t. overnight. The conversion was monitored by ^{31}P NMR spectroscopy. At r.t. a solution of $BH_3.SMe_2$ (9.28 mL, 18.56 mmol, 2 M in THF) was added to the reaction mixture. After 1 hour, solvent and excess of $BH_3.SMe_2$ were removed under high vacuum. The reaction mixture was suspended in CH_2Cl_2, extracted with water, the organic phase was dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude product was purified by column chromatography (SiO_2, eluent: hexane:ethyl acetate 25:1, gradient increased to hexane:ethyl acetate 25:2). **17** was obtained as orange solid (yield: 3.05 g, 8.04 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ (ppm) 7.72 (broad s, 2H, PhH), 7.45 (s, 3H, PhH), 4.56 (broad s, 1H, cp), 4.52 (broad s, 1H, Cp), 4.48 (broad s, 1H, Cp), 4.39 (broad s, 1H, Cp), 4.31 (broad s, 5H, Cp), 3.16-3.09 (m, 4H, CH_2), 1.04 (broad s, 6H, CH_3) 1.8-0.8 (broad m, 3H; BH_3). ^{13}C NMR (100 MHz, CD_2Cl_2, 296 K) δ (ppm) 134.5, 133.9, 131.5 (d, $J_{PC} = 5.9$ Hz), 130.5, 128.2 (d, $J_{PC} = 5.9$ Hz), 72.8 (d, $J_{CPC} = 70.8$ Hz), 72.7 (d, $J_{PC} = 9.9$ Hz), 71.8 (d, $J_{PC} = 10.4$ Hz), 71.2 (d, $J_{PC} = 7.5$ Hz), 71.0 (d, $J_{PC} = 7.3$ Hz), 70.0. m.p. 54–58 °C. Mass (TOF-MS ESI$^+$) *m/z* calculated for $[C_{20}H_{27}BNFeP+Na]^+$ $[M+Na]^+$ 402.1221, obs.: 402.1215 $[M+Na]^+$.^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ (ppm) 7.35-7.25 (m, 3H), 7.20-7.18 (m, 2H), 2.96-2.91 (m, 4H, CH_2), 1.42 (d, 3H, $^2J_{PH} = 5.72$, CH_3), 1.00 (t, 6H, $^3J_{HH} = 7.1$ Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ (ppm) 144.5 (d, $J_{PC} = 14.6$ Hz), 129.6 (d, $J_{PC} = 15.9$ Hz), 128.0 (d, $J_{PC} = 4.1$ Hz), 127.2, 43.7 (d, $J_{PC} = 14.7$ Hz), 15.3 (d, $J_{PC} = 3.1$ Hz), 14.2 (d, $J_{PC} = 18.4$ Hz). ^{31}P NMR (161 MHz, $CDCl_3$, 296 K): δ (ppm) 83.2 (broad).

4.14. Synthesis of racemic L1

At −78 °C dilithiodiphenyl ether (as the TMEDA-adduct) (0.75 g, 1.085 mmol) was suspended in diethyl ether (30 mL). After another 15 min at −78 °C THF (15 mL) was added. Chloro(methyl)(phenyl) phosphine (0.63 g, 3.9 mmol, 2.2 Eq.) dissolved in THF (50 mL) was added via cannula at −78C. The reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was quenched with degassed water (2 mL) and the solvent was removed under vacuum. After azeotropically drying with toluene (3 × 5 mL) the crude product was purified by filtration over silica (SiO_2, eluent: CH_2Cl_2:hexane 1:1 gradient increased to CH_2Cl_2:hexane 2:1). The product was obtained as white oily solid (yield: m = 0.89 g, 2.145 mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ (ppm) 7.50-7.45 (m, 4H), 7.35-7.29 (m, 6H), 7.20-7.10 (m, 4H), 7.04-7.00((m, 2H), 6.59 (broad dd, 1H, $^3J_{HH} = 8.1$ Hz, $^2J_{PH} = 2.98$ Hz), 6.51(broad dd, 1H, $^3J_{HH} = 8.1$ Hz, $^3J_{HP} = 2.98$ Hz), 1.64 (d, 1H, $^2J_{PH} = 4.1$ Hz), 1.55 (d, 1H, $^2J_{PH} = 4.1$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ (ppm) 158.0 (d, $J_{PC} = 5.5$ Hz), 157.8 (d, $J_{PC} = 4.7$ Hz), 137.8 (d, $J_{PC} = 5.8$ Hz),137.7(d, $J_{PC} = 5.0$ Hz), 131.8, 131.7, 131.6, 131.5, 131.1, 130.8, 130.7, 130.5 (d, $J_{PC} = 16.5$ Hz), 130.3 (d, $J_{PC} = 17.5$ Hz), 128.8, 128.7, 127.5, 127.4, 127.31, 127.27, 127. 127.25, 127.2, 122.4, 122.3, 117.0, 116.97, 10.2 (d, $J_{PC} = 3.5$ Hz), 10.1 (d, $J_{PC} = 4.1$ Hz). ^{31}P NMR (161 MHz, $CDCl_3$, 296 K): δ (ppm) −35.4, −35.6.

Please cite this article as: C.F. Czauderna et al., P-stereogenic wide bite angle diphosphine ligands, Tetrahedron, https://doi.org/10.1016/j.tet.2018.10.070

4.15. L1-$(BH_3)_2$

The product **L1** was dissolved in THF (50 mL) and BH_3SMe_2 (3.97 mmol, 2 M in toluene)was added. After stirring for 16 h, solvent and excess of BH_3SMe_2 were removed in high vacuum. The reaction mixture was solved in CH_2Cl_2, washed with water and dried with $MgSO_4$. After removal of the solvent, the product was obtained as white powder (0.95 g, 2.145 mmol, 100%). No further purification was carried out. ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ (ppm) 8.00 (ddd, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.7$ Hz, $^4J_{PH} = 13.3$ Hz, PhH), 7.84-7.74 (m, 3H), 7.65 (ddd, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.7$ Hz, $^4J_{HP} = 12.8$ Hz, PhH), 7.52-7.05 (m, 34H), 6.67 (ddd, 1H, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 0.9$ Hz, $^3J_{PH} = 3.5$ Hz, PhH), 6.37 (ddd, 1H, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 1.0$ Hz, $^3J_{PH} = 3.0$ Hz, PhH), 6.00 (ddd, 2H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.4$ Hz, $^3J_{PH} = 3.5$ Hz, PhH), 5.67 (ddd, 1H, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.3$ Hz, $^3J_{PH} = 3.4$ Hz, PhH), 1.82 (d, 3H, $^3J_{PH} = 10.2$ Hz, CH_3), 1.64 (d, 6H, $^3J_{PH} = 10.2$ Hz, CH_3), 1.47 (d, 3H, $^3J_{PH} = 10.4$ Hz,CH_3), 1.4-0.3 (broad m, 6H; BH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 296 K): δ (ppm) 160.1, 159.5, 135.8 (d, 6H, $^1J_{CP} = 14.9$ Hz), 135.2 (d, $^3J_{PC} = 12.8$ Hz), 134.2, 134.1, 133.8, 133.7, 132.2, 131.9 (d, $^3J_{PC} = 10.1$ Hz), 131.8, 131.6 (d, $^3J_{PC} = 9.8$ Hz), 131.5, 131.4 (d, $^3J_{PC} = 10.6$ Hz), 131.3, 130.9, 130.8, 130.2, 129.3 (d, $^3J_{PC} = 10.2$ Hz), 129.0 (d, $^3J_{PC} = 10.3$ Hz), 128.7 (d, $^3J_{PC} = 10.3$ Hz), 124.6 (d, $^3J_{PC} = 11.8$ Hz), 124.4 (d, $^3J_{PC} = 11.0$ Hz), 124.3 (d, $^3J_{PC} = 10.8$ Hz), 122.7, 122.1, 121.2, 120.7, 120.65, 120.6, 120.4 (d, $^3J_{PC} = 3.9$ Hz), 120.1 (d, $^3J_{PC} = 3.9$ Hz), 11.1 (d, $^1J_{PC} = 41.4$ Hz, CH_3), 9.6 (d, $^1J_{PC} = 42.1$ Hz, CH_3). ^{31}P NMR{^{1}H}(161 MHz, $CDCl_3$, 296 K): δ (ppm) 9.7 (broad, P-BH_3), 7.4(broad, P-BH_3). m.p. = 144–148 °C. LCTOF: *m/z* calculated for $[C_{26}H_{30}B_2OP_2+Na]^+$: m = 465.1856 $(M+Na)^+$, obs.: 486.1859 $(M+Na)^+$.

4.16. (rac)-13-(BH_3)

HCl (18.49 mL, 37.0 mmol, 2M in Et_2O) was added to a solution of **18**-BH_3 (2.34 g, 6.16 mmol, azeotropically dried with toluene) at 0 °C. The reaction mixture was allowed to warm to r.t. over the course of 30 min. After 1.5 h full conversion was reached, as indicated by ^{31}P NMR spectroscopy. The reaction mixture was filtered over a glass frit (P4) and solvent was removed. The crude product was dissolved in diethyl ether (50 mL) and the precipitate was removed by filtration over a glass frit (P4). (^{31}P NMR (162 MHz, CD_2Cl_2, 296 K) δ (ppm) 94.9 (broad, $^1J_{PB} = 45.5$ Hz, P-BH_3)). A solution of phenol (4.062 g, 4.316 mmol, azeotropically dried with toluene) in tetrahydrofuran (20 mL) was slowly added via cannula to a suspension of NaH (4.062 g, 4.316 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and for 2 h at r.t. The phenolate solution was added to the second (phosphorus-containing) solution in tetrahydrofuran (90 mL) at −78 °C via cannula. The reaction mixture was allowed to warm to r.t. overnight. After quenching the solution with water, the solvent was removed and the product was extracted with water and dichloromethane. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed. The crude product was purified by column chromatography (SiO_2, eluent: 100% toluene) to give (*rac*)-**13**-BH_3 as orange solid (yield: 1.29 g, 3.3 mmol, 75%). ^{1}H NMR (500 MHz, CD_2Cl_2, 296 K) δ (ppm) 8.03-7.99 (m, 2H, PhH), 7.62-7.53 (m, 3H, PhH), 7.23 (t, 2H, $^3J_{HH} = 7.3$ Hz), 7.09 (t, 1H, $^3J_{HH} = 7.4$ Hz), 6.99 (d, 2H, $^3J_{HH} = 7.8$ Hz), 4.7 (broad s, 1H, cp), 4.55 (broad s, 1H, Cp), 4.51 (broad s, 1H, Cp), 4.39 (broad s, 1H, Cp), 4.13 (broad s, 5H, Cp), 1.8-0.8 (broad m, 3H; BH_3). ^{13}C NMR (126 MHz, CD_2Cl_2, 296 K) δ (ppm) 153.3(d, $J_{PC} = 5.9$ Hz), 133.1, 133.0 (d, $J_{PC} = 2.1$ Hz), 132.6, 132.0 (d, $J_{PC} = 11.3$ Hz), 130.0, 129.3 (d, $J_{PC} = 10.4$ Hz), 125.2, 122.1 (d, $J_{PC} = 3.9$ Hz), 73.4 (d, $J_{PC} = 8.2$ Hz, CH), 72.2 (d, $J_{PC} = 13.3$ Hz, Cp), 73.0 (d, $J_{PC} = 8.7$ Hz, Cp), 72.5 (d, $J_{PC} = 10.3$ Hz), 71.8 (d, $J_{PC} = 77$ Hz, Cp), 70.9 (Cp). ^{31}P NMR{^{1}H} (162 MHz, CD_2Cl_2, 296 K δ (ppm) 110.3 (q, $J_{PB} = 71.5$ Hz, P-BH_3). m.p. 44–48 °C. Mass (TOF-MS ESI$^+$) *m/z* calculated for $[C_{22}H_{22}BFeOP+Na]^+$423.0748 $[M+Na]^+$, obs.: 423.0753 $[M+Na]^+$.

4.17. (rac)-13

A solution of DABCO (1.29 g, 11.58 mmol) in toluene (40 mL) was added to a solution of (*rac*)-**13**-BH_3 (1.15 g, 2.88 mmol, azeotropically dried with toluene) in diethyl ether (100 mL). The reaction mixture was heated for 20 h at 60 °C. After cooling down to r.t., toluene was removed *in vacuo*. Purification by filtration over silica (SiO_2, eluent: ethyl acetate) resulted in an orange solid that was used without further purification (yield: 1.04 g, 2.69 mmol, 94%). ^{1}H NMR (500 MHz, CD_2Cl_2, 296 K) δ (ppm) 7.77-7.74 (m, 2H, PhH), 7.46–8.42 (m, 3H, PhH), 7.26 (t, 2H, $^3J_{HH} = 7.7$ Hz), 7.10 (d, 2H, $^3J_{HH} = 7.7$ Hz), 6.98 (t, 1H, $^3J_{HH} = 7.3$ Hz), 4.53 (broad s, 1H, Cp), 4.45 (broad s, 1H, Cp), 4.36 (broad s, 1H, Cp), 4.41 (s, 5H, cp), 4.01 (broad s, 1H, Cp). ^{13}C NMR (126 MHz, CD_2Cl_2, 296 K) δ (ppm) 156.63 (d, $J_{PC} = 9.2$ Hz), 139.8 (d, $J_{PC} = 17.2$ Hz), 129.7 (d, $J_{PC} = 23.1$ Hz), 129.0, 128.6, 127.4 (d, $J_{PC} = 7.6$ Hz), 121.3, 117.8 (d, $J_{PC} = 11.2$ Hz), 78.1 (d, $J_{PC} = 12.7$ Hz, Cp), 71.6 (d, $J_{PC} = 22.6$ Hz, Cp), 70.9 (d, $J_{PC} = 5.6$ Hz, Cp), 70.4, 70.3 (d, $J_{PC} = 15.5$ Hz, Cp), 68.2 (Cp). ^{31}P NMR{^{1}H} (162 MHz, CD_2Cl_2, 296 K) δ (ppm) 107.02 (s, P-BH_3).

4.18. Synthesis of racemic L2

At −78 °C, dilithiodiphenyl ether (as the TMEDA-adduct) (0.409 g, 0.987 mmol) was suspended in diethyl ether (30 mL). After 15 min at −78 °C, THF (15 mL) was added. A solution of (*rac*)-**13** (0.801 g, 2.07 mmol, 2.2 Eq.) in THF (50 mL) was added at −78 °C via cannula. The reaction mixture was slowly warmed to room temperature overnight. The reaction mixture was quenched with degassed water (2 mL) and the solvent was removed under vacuum. The precipitate was suspended in CH_2Cl_2 and washed with water and brine, dried over $MgSO_4$ and the solvent was removed. The crude product was purified by filtration over silica (SiO_2, eluent: CH_2Cl_2:hexane 1:1 gradient increased to CH_2Cl_2:hexane 2:1) to give **L2** as orange solid (yield: 618 mg, 0.81 mmol, 83%). ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K) δ (ppm) 7.40-7.23 (m, 20H, PhH), 7.06-6.9 (m, 12H), 6.34 (dd, 2H, $^3J_{HH} = 7.6$ Hz, $^3J_{PH} = 3.5$ Hz, PhH), 6.20 (dd, 2H, $^3J_{HH} = 7.6$ Hz, $^3J_{PH} = 3.5$ Hz, PhH), 4.42-4.40 (m, 2H, Cp), 4.37-4.32 (m, 4H, Cp), 4.07 (s, 5H, Cp), 4.02 (s, 5H, Cp), 3.87-3.86 (m, 1H, Cp), 3.80-3.79 (m, 1H, Cp). ^{13}C NMR (100 MHz, CD_2Cl_2, 296 K) δ (ppm) 159.8 (d, $J_{PC} = 18.3$ Hz), 159.1 (d, $J_{PC} = 16.9$ Hz), 139.0-138.2 (m), 134.9 (d, $J_{PC} = 7.0$ Hz), 135.1, 134.9, 134.8, 134.6 (d, $J_{PC} = 11.8$ Hz), 134.2, 132.3 (d, $J_{PC} = 16.4$ Hz), 130.6, 130.3, 129.2, 128.7-128.55 (m), 123.8 (d, $J_{PC} = 12.6$ Hz), 118.8, 118.2, 76.1-76.0 (m), 75.4, 75.1 (d, $J_{PC} = 26.7$ Hz, Cp), 76.1 (d, $J_{PC} = 26.8$ Hz, CH), 73.0, 72.8, 72.0-71.9 (m), 71.3, 71.2, 69.9, 69.8. ^{31}P NMR (162 MHz, CD_2Cl_2, 296 K) δ (ppm) −28.8 (s), −29.9 (s). m.p. 178 °C. Mass (TOF-MS ESI$^+$) *m/z* calculated for $[C_{44}H_{36}Fe_2OP_2+Na]^+$ 777.0838 $[M+Na]^+$, obs.: 777.0831$[M+Na]^+$.

4.19. L2-$(BH_3)_2$

BH_3SMe_2 (50 µL, 0.1 mmol, 2 M in THF) was added to a solution of **L2** (15 mg, 0.02 mmol) in THF (5 mL). After stirring for 16 h, solvent and excess of BH_3SMe_2 were removed in high vacuum. (*rac*)-**L2**-$(BH_3)_2$ was only used for NMR spectroscopy and not further purified. (Yield: 15 mg, 0.019 mmol, 100%). ^{31}P NMR (162 MHz, CD_2Cl_2, 296 K) δ (ppm) 15.2 (broad, P-BH_3), 12.6 (broad, P-BH_3).

Please cite this article as: C.F. Czauderna et al., P-stereogenic wide bite angle diphosphine ligands, Tetrahedron, https://doi.org/10.1016/j.tet.2018.10.070

4.20. X-ray crystallography

X-ray diffraction data for all compounds were collected at 93 K by using a Rigaku MM007 High-brilliance RA generator/confocal optics and Mercury CCD system, with Mo Kα radiation (λ = 0.71075 Å). Intensity data were collected using both ω and φ steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects and a multiscan absorption correction was applied by using CrystalClear [36]. Structures were solved by direct (SIR2002 [37] or SIR2004 [38]) or Patterson (PATTY [39]) methods and refined by full-matrix least-squares against F^2 (SHELXL-2013 [40]). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. The positions of boron-bound hydrogens were located from the difference Fourier map, and the riding model applied from these positions. All calculations were performed using the CrystalStructure [41] interface. CCDC 1516737-1516740 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Crystal Data for (R,R)-**10**-BH_3 (M = 859.85 g/mol): orthorhombic, $P2_12_12_1$ (no. 19), a = 9.608(3) Å, b = 18.042(7) Å, c = 25.956(11) Å, V = 4499(3) Å^3, Z = 4, μ = 0.316 mm^{-1}, D_{calc} = 1.269 g/cm^3, 28747 reflections measured, 8176 unique (R_{int} = 0.1593) which were used in all calculations. The final R_1 was 0.0830 ($I > 2\sigma(I)$) and wR_2 was 0.2178 (all data). CCDC 1516737.

Crystal Data for (R,R)-**10**-$(BH_3)_2$ (M = 474.09 g/mol): orthorhombic, $P2_12_12_1$ (no. 19), a = 8.711(4) Å, b = 14.700(5) Å, c = 20.045(8) Å, V = 2566.6(18) Å^3, Z = 4, μ = 0.194 mm^{-1}, D_{calc} = 1.227 g/cm^3, 16296 reflections measured, 4681 unique (R_{int} = 0.0903) which were used in all calculations. The final R_1 was 0.0844 ($I > 2\sigma(I)$) and wR_2 was 0.2315 (all data). CCDC 1516738.

Crystal Data for (S,S)-**L1**-$(BH_3)_2$ (M = 442.09 g/mol): orthorhombic, $P2_12_12_1$ (no. 19), a = 10.781(2) Å, b = 13.320(2) Å, c = 17.524(3) Å, V = 2516.5(7) Å^3, Z = 4, μ = 0.188 mm^{-1}, D_{calc} = 1.167 g/cm^3, 15815 reflections measured, 4565 unique (R_{int} = 0.0274) which were used in all calculations. The final R_1 was 0.0301 ($I > 2\sigma(I)$) and wR_2 was 0.0758 (all data). CCDC 1516739.

Crystal Data for (S,S)-**L2** (M = 754.41 g/mol): orthorhombic, $P2_12_12_1$ (no. 19), a = 9.459(2) Å, b = 14.416(2) Å, c = 25.888(5) Å, V = 3530.1(11) Å^3, Z = 4, μ = 0.947 mm^{-1}, D_{calc} = 1.419 g/cm^3, 22307 reflections measured, 6434 unique (R_{int} = 0.0648) which were used in all calculations. The final R_1 was 0.0426 ($I > 2\sigma(I)$) and wR_2 was 0.675 (all data). CCDC 1516740.

Acknowledgements

This work was supported by an EASTCHEM fellowship. We would like to acknowledge the European Union for additional funding through a Marie Curie Excellence Grant MEXT-2004-014320 and COST action CM0802 PhoSciNet..

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2018.10.070.

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Please cite this article as: C.F. Czauderna et al., P-stereogenic wide bite angle diphosphine ligands, Tetrahedron, https://doi.org/10.1016/j.tet.2018.10.070