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Designing P-Chirogenic 1,2-Diphosphinobenzenes at Both P-Centers Using P(III)-Phosphinites

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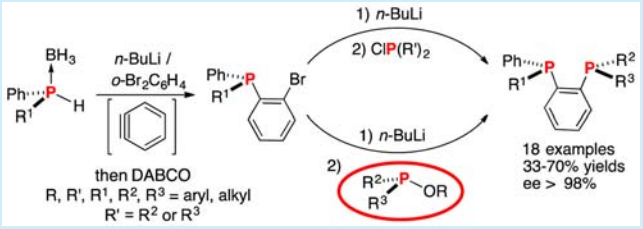
Supporting Information

ABSTRACT: A new enantiodivergent synthesis of P-chirogenic 1,2-diphosphinobenzenes (DP*B) bearing the chirality on one or both phosphorus centers is reported using aryne chemistry. The principle is based on successive reactions of 1,2-dibromobenzene with *sec*-phosphide boranes, then DABCO to remove the borane, and finally with chlorophosphines or P(III)-chirogenic phosphinites. The efficiency of this synthesis was demonstrated by the stereoselective preparation of (*S*,*S*)-1,2-bis(*o*-anisylphenylphosphino)benzene. A comparison of DIPAMP and homochiral DP*B ligands in asymmetric Rh- or Pd-catalyzed reactions was reported.



Chiral phosphines are currently used in coordination chemistry and in asymmetric catalysis by chiral transition metal complexes.[1] However, this chemical class also concerns organocatalysis,[2] molecular materials,[3] polymers of coordination,[4] stereoselective reagents,[5] and compounds of therapeutic value.[6] Among the chiral phosphine classes,[1] the C_1- and C_2-symmetric 1,2-diphosphinobenzenes receive particular attention because the phenylene bridge between the two P atoms gives characteristic steric and electronic properties to the complex formed with the phosphine moieties. Since Burk's pioneering work on the development of the DuPHOS ligands **1** in Rh-catalyzed asymmetric hydrogenation,[7] many diphosphines such as **2**−**6** with aromatic or heteroaromatic rings as bridges have been developed in asymmetric catalysis.[8] Most of these ligands are chiral by virtue of the carbon backbone, whereas few examples are described with P-chirogenic centers such as **2**−**5** (Figure 1).[9] In the case of diphosphine **5**, it was noted that the chirality is provided by carbon and phosphorus centers (Figure 1).

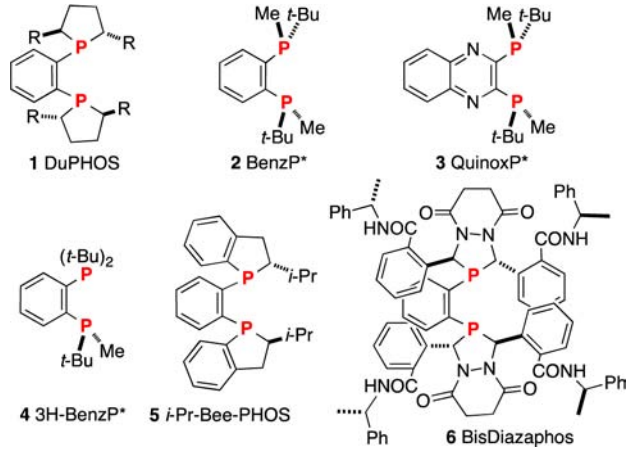


Figure 1. Representative chiral 1,2-diphosphino aromatic-bridged ligands.

Chiral 1,2-diphosphinobenzene ligands **1**, **5**, and **6** are usually synthesized according to nonversatile methods which require multistep procedures. In the case of the P-chirogenic diphosphinobenzenes (DP*B) **2**, **3**, or **4**, their syntheses were performed using the *tert*-butylmethylphosphine borane **8** as a building block (Scheme 1a).[9] However, this method is mainly restricted to phosphines carrying a *tert*-butyl and a methyl substituent, which are required for the preparation of **8** by kinetic resolution of *tert*-butyldimethylphosphine borane **7** in the presence of sparteine (Scheme 1a).[9]

Stereoselective synthesis of ligand **12** was reported using the (+)-ephedrine method (Scheme 1b).[10] This synthesis is based on the diastereoselective ring opening of the oxazaphospholidine−borane complex (−)-**9** by the organolithium reagent prepared by metal-halide exchange from 2-bromophenyl(diphenyl)-phosphine **10a**. Methanolysis of the ring-opened compound **11**, followed by reaction with an organolithium reagent (RLi) and BH_3 removal, led to the P-chirogenic **12** bearing the chirality on one P-center (Scheme 1b).[10]

We described an efficient stereoselective synthesis of P-chirogenic *o*-halogenophenylphosphines **10** from secondary phosphine boranes **13** using aryne chemistry (Scheme 2).[11] Compounds **10** have been applied to the synthesis of *o*-hydroxyalkyl- and *o*-boronatophenyl P-chirogenic phosphines.[12] In continuation of this work, we now report the enantiodivergent synthesis of C_1- and C_2-symmetric P-chirogenic 1,2-diphosphinobenzenes **12**.[11a]

The principle of the synthesis is based on the phosphination of the *o*-bromophenylphosphines **10** in the ortho position using

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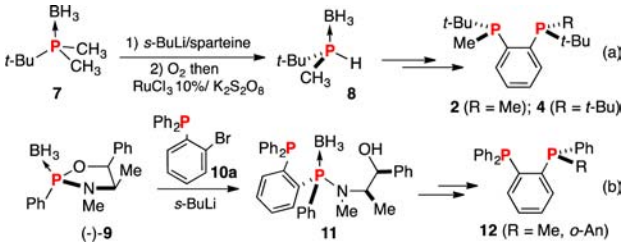
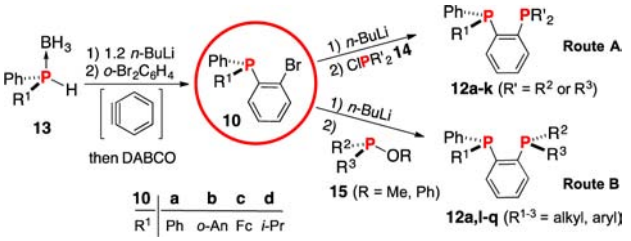
Scheme 1. Stereoselective Synthesis of 1,2-Diphosphinobenzene-Type Ligands



Scheme 2. Stereoselective Synthesis of P-Chirogenic DP*B 12

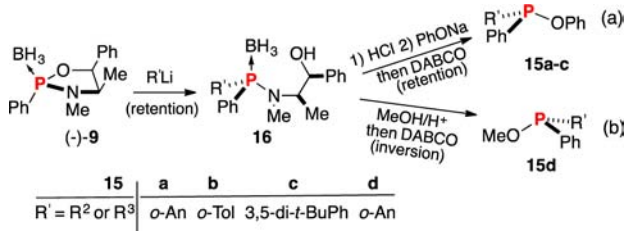


either chlorophosphines **14** or phosphinites **15** (Scheme 2, route A or B). Synthesized P-chirogenic 1,2-diphosphinobenzenes are summarized in Table 1.

o-Bromophenylphosphine boranes **10** were previously prepared in yields up to 75% by reaction of P-chirogenic *sec*-phosphine boranes **13** with *n*-butyllithium (1.2 equiv) and 1,2-dibromobenzene, followed by decomplexation with DABCO, according to the procedure described in the literature.[11,12] Addition of *n*-butyllithium to **10** at −78 °C led, by metal−halogen exchange, to the corresponding carbanions in the ortho position, which react with the chlorophosphines **14** to afford the free P-chirogenic diphosphines **12a−k** stereoselectively in 37−70% isolated yields (Scheme 1, route A; Table 1, entries 1−11). On the other hand, when *o*-carbanions derived from **10** reacted with the P(III)-phosphinites **15**, diphosphines **12l−q** were obtained in 33−67% yields with 99% ee (Scheme 1, route B; Table 1, entries 12−19). Very interestingly, no racemization was detected by reaction with the P(III)-chirogenic phosphinites **15**, and this method allowed us to synthesize diphosphines such as **12o−q** with two P-chirogenic centers (entries 17−19).

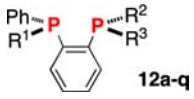
Free P(III)-chirogenic phosphinites **15** were prepared using the (+)-ephedrine method starting from (−)-**9**.[13] Thus, reaction of complex **9** with organolithium reagents R′Li led to the ring-opened products **16**, which successively reacted with either HCl in toluene and then sodium phenolate or methanol in acidic conditions to afford P-chirogenic phosphinites **15a−d** stereoselectively in 67−74% overall yields after decomplexation with DABCO (Scheme 3). Note that as the stereochemistry of routes

Scheme 3. Synthesis of P(III)-Chirogenic Phosphinites 15



A and B proceeded with retention and inversion, respectively, the phenyl and methyl P(III)-chirogenic phosphinites **15a−c** and **15d** were obtained with opposite absolute configurations at the P-

Table 1. Structure of P-Chirogenic DP*B 12[a,b]



entry	R^1	R^2	R^3	diphosphines **12**	yield[c] (%)
1	*o*-An	Ph	Ph	(*S*)-**12a**	70
2	*o*-An	1-Np	1-Np	(*S*)-**12b**	44
3	*o*-An	*o*-Tol	*o*-Tol	(*S*)-**12c**	37
4	*o*-An	*p*-Tol	*p*-Tol	(*S*)-**12d**	52
5	*o*-An	*p*-$CF_3C_6H_4$	*p*-$CF_3C_6H_4$	(*S*)-**12e**	58
6	*o*-An	*m*-Xyl	*m*-Xyl	(*S*)-**12f**	61
7	*o*-An	3,5-$(CF_3)_2C_6H_3$	3,5-$(CF_3)_2C_6H_3$	(*S*)-**12g**	44
8	*o*-An	*c*-Hex	*c*-Hex	(*S*)-**12h**	47
9	*o*-An	*i*-Pr	*i*-Pr	(*S*)-**12i**	43
10	Fc	Ph	Ph	(*R*)-**12j**	56
11	*i*-Pr	Ph	Ph	(*R*)-**12k**	45
12[d]	Ph	*o*-Tol	Ph	(*S*)-**12l**	54
13[e]	Ph	3,5-(*t*-Bu)$_2$C$_6$H$_3$	Ph	(*S*)-**12m**	45
14[f]	Ph	*o*-An	Ph	(*S*)-**12a**	67
15[g]	Ph	Ph	*o*-An	(*R*)-**12a**	55
16[h]	Ph	*o*-biPh	Ph	(*S*)-**12n**	33
17[h]	*o*-An	*o*-biPh	Ph	(*S,S*)-**12o**	35
18[f]	*o*-An	*o*-An	Ph	(*S,S*)-**12p**	52
19[f]	*i*-Pr	*o*-An	Ph	(*R,S*)-**12q**	56

[a]Diphosphines **12a−k** (R^2 = R^3 = R′) were synthesized according to route A (entries 1−11); diphosphines **12a,l−q** were synthesized according to route B (entries 12−19). [b]Diphosphines have 99% ee, determined by HPLC on a chiral column (except (*R*)-**12k**, 98% ee, entry 11). [c]Isolated yields. [d]From **15b**. [e]From **15c**. [f]From **15a**. [g]From **15d**. [h]From **15e**.

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center, which allowed us to use them in enantiodivergent synthesis (Scheme 3).[14] In addition, methyl (*R*)-(*o*-biphenyl)-phenylphosphinite **15e** was also prepared as described above but starting from complex (+)-**9** derived from (−)-ephedrine (see Supporting Information).

Both enantiomers of the P-chirogenic 1,2-diphosphinobenzene **12a** were prepared according to route B by reaction of the carbanions derived from 2-bromophenyl(diphenyl)phosphine **10a**, with phenyl or methyl *o*-anisylphenylphosphinites **15a** (or **15d**), respectively (Scheme 2; Table 1, entries 14 and 15). On the other hand, diphosphinobenzene (*S*)-**12a** was also obtained using (*S*)-*o*-anisyl(bromophenyl)phenyl phosphine **10b** and chlorodiphenylphosphine **14a** (R = Ph) (Scheme 2, route A; Table 1, entry 1).

All P-chirogenic 1,2-diphosphinobenzenes (DP*B) **12** prepared by methods A and B were analyzed by HPLC on a chiral column (>98% ee) and were fully characterized (see Supporting Information).

Crystallization of DP*B (*S*)-**12a** and (*R*)-**12j** provided crystals suitable for X-ray diffraction analyses, and their OLEX2 views are shown in Supporting Information. Interestingly, this method offers the possibility to synthesize C_1- and C_2-symmetric P-chirogenic 1,2-diphosphinobenzenes bearing the chirality on both P-centers. Thus, DP*B **12o−q** were synthesized in yields up to 56% by successive reactions of the *o*-bromophenyl phosphines (*S*)-**10b** (or (*R*)-**10d**) with *n*-BuLi to perform the metal-halide exchange and then with the P-chirogenic phosphinites **15e** (or **15a**), respectively (Scheme 2, route B). Note that the reactions leading to C_2-symmetric DP*B were diastereoselective because no epimers (or meso) could be detected. This demonstrated that the substitution of the P(III)-chirogenic phosphinites **15a** or **15e** was highly stereospecific.

Compound DP*B **12p** was recrystallized in a dichloromethane/methanol mixture, providing crystals suitable for X-ray diffraction analyses. The OLEX2 view is shown in Figure 2.

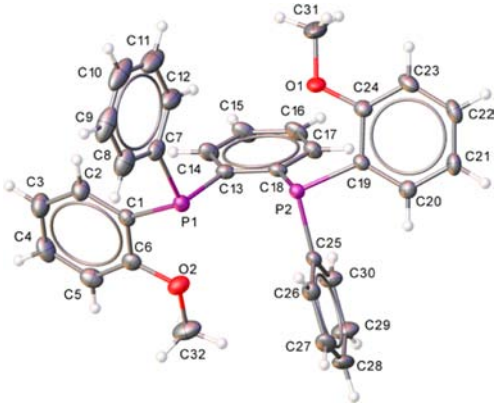
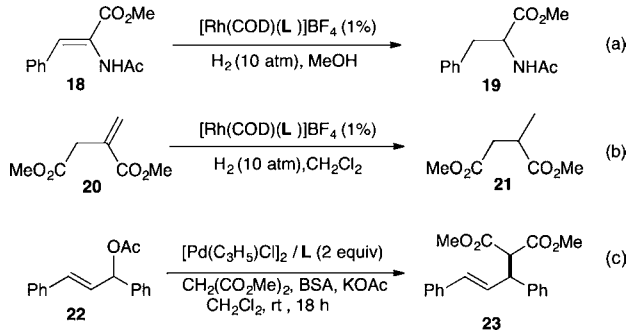


Figure 2. OLEX2 view of P-chirogenic diphosphine (*S*,*S*)-**12p**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): C13−P1 = 1.838(4), C18−P2 = 1.835(3); C7−P1−C1 = 102.21(13), C25−P2−C19 = 100.77(14); C14−C13−P1−C1 = 17.1(3)°, C17−C18−P2−C19 = 14.9(3)°.

Compound **12p** crystallizes in the noncentrosymmetric C_2 space group, and the *S* absolute configuration at the P atoms is supported by refinement of the Flack parameter. The structure shows that the *o*-anisylphenylphosphino moieties do not significantly alter the planarity of the P-*o*-An bonds with the phenylene bridge, as proven by the dihedral angles C14−C13−P1−C1 and C17−C18−P2−C19 of 17.1(3) and 14.9(3)°, respectively. The aromatic substituents of the phosphine moieties are perpendicular to each other, with mean angles of 95.39(12)° (see Supporting Information).

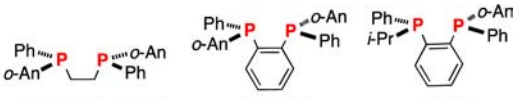
Homochiral 1,2-bis(*o*-anisylphenylphosphino)benzene (*S*,*S*)-**12p** and DIPAMP (*S*,*S*)-**17** ligands were used in asymmetric Rh- and Pd-catalyzed reactions, and their efficiencies were compared (Scheme 4). Modified DP*B ligand (*R*,*S*)-**12q**, obtained by substituting one *o*-anisyl substituent of **12p** for *i*-propyl, was also tested in these conditions.

Scheme 4. Asymmetric Transition-Metal-Catalyzed Reactions Studied Using P-Chirogenic Ligands 17, 12p, and 12q



Cationic rhodium complexes [Rh(COD)L]BF_4 were previously prepared in yields up to 70% by mixing [Rh(COD)$_2$]BF_4 with the ligands L= **17**, **12p**, and **12q**. Whereas the phenylalanine derivative (*R*)-**19** was obtained with 92% ee using DIPAMP (*S*,*S*)-**17**, 19 and 22% ee values were obtained with homochiral (*S*,*S*)-**12p** and modified DP*B **12q** ligands, respectively (Table 2,

Table 2. Comparative Asymmetric Catalysis with P-Chirogenic Ligands 17 (DIPAMP), 12p, and 12q



DIPAMP (*S*,*S*)-**17** (*S*,*S*)-**12p** (*R*,*S*)-**12q**

entry	product[a]	(abs.conf. of product) ee %[b] (*S*,*S*)-**17**	(*S*,*S*)-**12p**	(*R*,*S*)-**12q**
1	**19**	(*R*)-92%	(*R*)-19%	(*S*)-22%
2	**21**	(*S*)-48%	(*R*)-46%	(*R*)-76%
3	**23**	(*S*)-33%	(*S*)-53%	(*S*)-15%

[a]Products **19**, **21**, and **23** were obtained in almost quantitative yields according to the conditions mentioned on Scheme 4. [b]The ee was determined by HPLC on a chiral column.

entry 1). On the other hand, when dimethyl itaconate **20** was hydrogenated in dichloromethane with the Rh complexes prepared as above, the configuration (*S* or *R*) of the resulting diester **21** surprisingly depended on the nature of the DIPAMP (*S*,*S*)-**17**, DP*B (*S*,*S*)-**12p**, and **12q** (entry 2). In these conditions, the best result was obtained with DP*B **12q**, which led to the methyl (*R*)-methylsuccinate **21** with 76% ee (entry 2). Finally, when the P-chirogenic ligands were tested in Pd-catalyzed allylation of methyl malonate, allylated product (*S*)-**23** was obtained with up to 53% ee (entry 3). In this case, asymmetric induction was slightly higher using DP*B (*S*,*S*)-**12p** than using homochiral DIPAMP (*S*,*S*)-**17** ligand.

In conclusion, a new and efficient stereoselective synthesis of P-chirogenic diphosphinobenzene ligands was reported. This

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method allowed us to synthesize C_1- or C_2-symmetric DP*B ligands bearing the chirality on one or both phosphorus centers, by phosphination of 2-bromophenylphosphines, previously prepared due to the aryne chemistry, with chlorophosphines or P(III)-chirogenic phosphinites. Interestingly, according to the use of either phenyl or methyl P(III)-chirogenic phosphinite, prepared from the same aminophosphine borane precursor, both DP*B enantiomers were independently obtained. A brief comparison of the homochiral DP*B and DIPAMP ligands in asymmetric metal-based catalysis has shown that the former gave better results in Pd-catalyzed allylation, while DIPAMP affords the best asymmetric induction in the hydrogenation of methyl α-acetamido cinnamate. This new enantiodivergent synthesis, based in part on the use of P(III)-chirogenic phosphinite, is a powerful method for the design and development of the DP*B ligands bearing one or two P-chirogenic centers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01275.

Experimental data, selected spectral data for all new compounds, and X-ray data for (*S*)-**12a**, (*R*)-**12j**, and (*S*,*S*)-**12p** (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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(14) It should be noted that little or no reaction was obtained by reaction with the borane complex of the phosphinite **15**.

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