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Study of the Reaction of Bulky Aryllithium Reagents with 3,4-Dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane Derived from Ephedrine†

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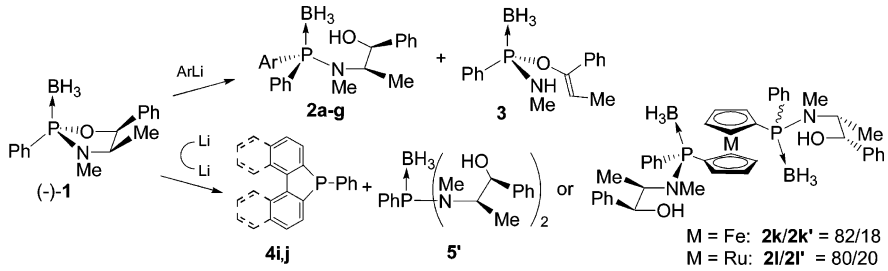

The ring opening of enantiomerically pure 3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane (**1**) with a variety of bulky aryllithium reagents was studied. Our results are not in total agreement with those obtained by others. In fact, several 2,6-disubstituted aryl groups were successfully appended to the phosphorus atom, furnishing the corresponding (*N*-ephedrino)phosphine boranes **2a**−**g** with dr >99:1. However, when the attack on the phosphorus atom is hindered, deprotonation on the benzylic position occurs, leading to the formation of enantiomerically pure *trans*-(*N*-methylamino)(phenyl)(1-phenyl-1-propenyloxy)phosphine-*P*-borane (**3**). While the attack of 2,2′-dilithio-1,1′-biarenes leads to the corresponding (*P*-phenyl)phosphole derivatives (**4i**,**j**) and to [bis(*N*-ephedrino)](phenyl)phosphine-*P*-borane (**5**), the attack of 1,1′-dilithiometallocenes (M = Fe, Ru) leads to a separable diastereomeric mixture of 1,1′-bis[(*N*-ephedrino)(phenyl)phosphino-*P*-borane]metallocenes (**2k**,**l**/**2k**′,**l**′) with dr ∼80:20.

Introduction

Highly sought by the chemical industry in the asymmetric transition-metal-catalyzed processes, enantiomerically pure phosphine ligands constitute a key component of the catalysts conveying the chiral information to the end product.[1] Soon after the discovery of the chelating DIOP ligand by Kagan et al.,[2] Knowles et al. devised the chelating *P*-stereogenic diphosphine DiPAMP ligand and applied it in the rhodium-catalyzed asymmetric hydrogenation-based L-DOPA process.[3] The close proximity of a stereogenic element to the metal center of catalysis is assumed to have a pronounced impact on the asymmetric induction.[4] Since then, various types of phosphines were synthesized especially those possessing a stereogenic backbone. At a fast pace, their use became widespread in asymmetric catalysis as was the case with the atropisomeric BINAP ligand and related type ligands (e.g., BIPHEMP, MeO-BIPHEP), the ferrocene-based ligands (e.g., Josiphos and Mandyphos families) and the DuPhos-type ligands.[1c]

In our ongoing research program in metal-mediated asymmetric transformations, we were interested to prepare a series of "tailor-made" and structurally diverse C_2-symmetrical *P*-

† This paper is dedicated to the memory of Professor Hidemasa Takaya, deceased on October 4, 1995.

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(1) (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley & Sons: New York, 1994. (b) *Comprehensive Asymmetric Catalysis I*−*III*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999. (c) *Asymmetric Catalysis on Industrial Scale*; Blaser, H. U., Schmidt, E., Eds.; Wiley-VCH: Weinheim, Germany, 2004.

(2) Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc*. **1972**, *94*, 6429−6433.

(3) (a) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc*. **1977**, *99*, 5946−5952. (b) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. U.S. Patent 1977/4005127. (c) Knowles, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 1998−2007.

(4) Halpern, J. *Science* **1982**, *217*, 401−407.

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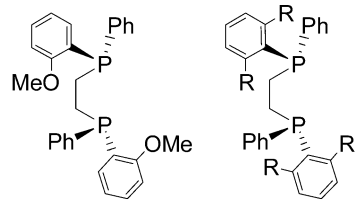
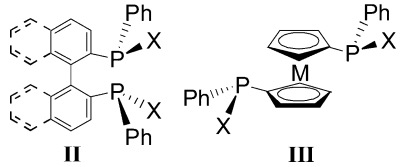
stereogenic diphosphine ligands and their precursors. One structure of ligands would consist of a bulky aryl group on the phosphorus atom with an ethane bridge (**I**) (DiPAMP-like structure), and other families would have either a biaryl bridge (**II**) or a metallocene bridge (**III**).

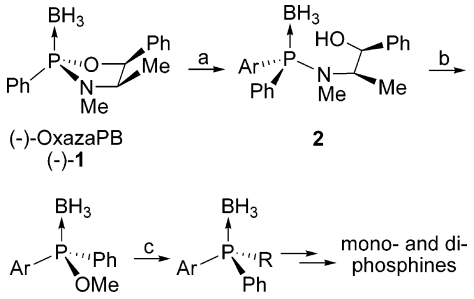




We envisaged the synthesis of the targeted *P*-stereogenic phosphines and their precursors via the Jugé−Stephan asymmetric route, relying upon the enantiomerically pure 1,3,2-oxazaphospholidine-2-borane complex (oxazaPB) (**1**) derived from ephedrine.[5] The synthon **1** has proven to be very useful to access a wide array of borane-complexed *P*-stereogenic organophosphorus compounds: amino-, alkoxy-, chloro-, mono-, diphosphines, etc. The liberation of the phosphine occurs with full retention of configuration under mild conditions.[6a] Other approaches to *P*-stereogenic phosphines are known, as well; however, they possess limited synthetic flexibility.[6] The Jugé−Stephan synthetic strategy is based on the sequential displacement of the ephedrine auxiliary from **1**; this involves first the P−O bond fission by organolithium reagents and second the acid-catalyzed P−N bond methanolysis to a P−OMe bond followed by the displacement of the MeO group by another organolithium (Scheme 1). Both configurations at the phosphorus atom can be prepared starting either from (+)- or (−)-ephedrine or by a reverse order of introduction of the desired groups. The exemplification of the interesting features of **1** was its first use toward a practical synthesis of DiPAMP ligand.[5] Moreover, it was shown that *P*-stereogenic (*N*-ephedrino)-phosphines derived from **1** could serve as ligands in asymmetric hydrogenation and hydroformylation.[7]

Several research groups worldwide have adopted this methodology to prepare a variety of enantiomerically pure *P*-stereogenic organophosphorus compounds.[8] However, the introduction of the substituents is constrained by the steric requirements of the carbanionic reagent, and reverting to forcing conditions compromises the stereoselectivity. In some cases, delaying the introduction of the most spatially demanding group until the final stage (step c) led to an increased yield and a high degree of stereocontrol. For example, Brown et al. have studied the introduction of sterically encumbered groups, such as 1-adamantyl, *tert*-butyl, and ferrocenyl, by displacement of the MeO group.[8b] Nevertheless, several failed attempts are reported in the literature by prominent research groups to append interesting bulky aryl groups on the phosphorus atom, for example, 2-mesityl, 2,4,6-trimethoxyphenyl, or 9-anthryl, either at the oxazaPB (**1**) ring-opening step (step a) or at the displacement of the MeO group (step c).[9a] This was ascribed to the inherent steric bulk of the aryl groups to be introduced with no other details. Furthermore, it was reported in the literature that the attack of 1,1′-dilithioferrocene·2 TMEDA adduct on **1** led to an inseparable diastereomeric mixture of 1,1′-bis[(*N*-ephedrino)(phenyl)phosphino-*P*-borane]ferrocenes.[9b,c]

SCHEME 1[a]



[a] Reagents: (a) ArLi/THF, −20 °C to rt; (b) MeOH/H^+, rt; (c) RLi/THF, −20 °C to rt.

Though much effort has been devoted to the preparation of some of the above-mentioned intermediates, we still decided to reinvestigate the action of a selection of bulky aryllithium reagents on **1**. Due to the strong distortion of the five-membered ring of **1**,[10] this precursor is more reactive toward the attack of organolithium reagents than the methyl phosphinite borane intermediate,[11] and the resulting (*N*-ephedrino)phosphine borane **2** would allow further transformations.

(5) (a) Jugé, S.; Stephan, M.; Laffitte, J. A.; Genêt, J. P. *Tetrahedron Lett.* **1990**, *31*, 6357−6360. (b) Jugé S.; Genêt J. P. WO 9100286, 1991.

(6) (a) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244−5252. (b) Corey, E. J.; Zhuoliang, C.; Tanoury, G. J. *J. Am. Chem. Soc.* **1993**, *115*, 11000−11001. (c) Muci, A. R.; Campos, K. R.; Evans, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9075−9076. (d) Ohashi, A.; Kikuchi, S.; Yasutake, M.; Imamoto, T. *Eur. J. Org. Chem.* **2002**, *15*, 2535−2546.

(7) (a) Moulin, D.; Darcel, C.; Jugé, S. *Tetrahedron: Asymmetry* **1999**, *10*, 4729−4743. (b) Ewalds, R.; Eggeling, E. B.; Hewat, A. C.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Vogt, D. *Chem.−Eur. J.* **2000**, *6*, 1496−1504. (c) Darcel, C.; Kaloun, E. B.; Merdès, R.; Moulin, D.; Riegel, N.; Thorimbert, S.; Genêt, J. P.; Jugé, S. *J. Organomet. Chem.* **2001**, *624*, 333−343. (d) In *OMCOS 13*, Geneva, 2005; Darcel, C.; Richard, P.; Jugé, S. P−421.

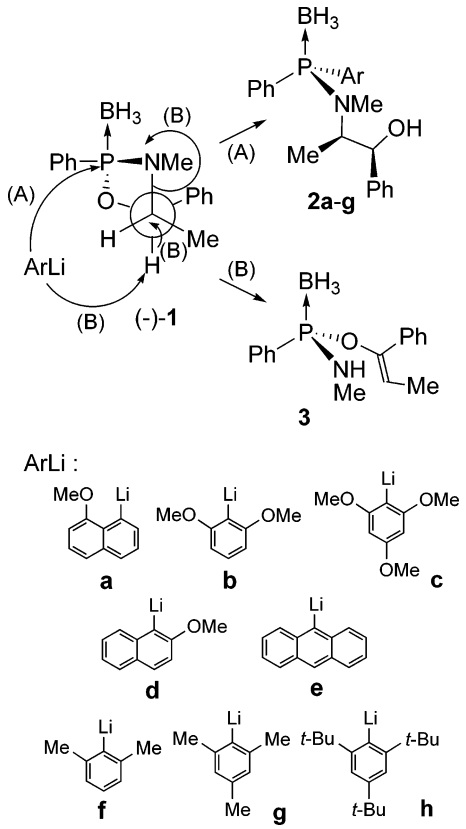
(8) (a) Tollefson, M. B.; Li, J. J.; Beak, P. *J. Am. Chem. Soc.* **1996**, *118*, 9052−9061. (b) Brown, J. M.; Laing, J. C. P. *J. Organomet. Chem.* **1997**, *529*, 435−444. (c) Yang, H.; Alvarez-Gressier, M.; Lugan, N.; Mathieu, R. *Organometallics* **1997**, *16*, 1401−1409. (d) Zhang, X. WO 9713763, 1997. (e) Maienza, F.; Wörle, M.; Steffanut, P.; Mezzetti, A.; Spindler, F. *Organometallics* **1999**, *18*, 1041−1049. (f) Schuman, M.; Trevitt, M.; Redd, A.; Gouverneur, V. *Angew. Chem., Int. Ed.* **2000**, *39*, 2491−2493. (g) Nettekoven, U.; Kamer, P. C. J.; Widhalm, M.; van Leeuwen, P. W. N. M. *Organometallics* **2000**, *19*, 4596−4607. (h) Nettekoven, U.; Widhalm, M.; Kalchhauser, H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Lutz, M.; Spek, A. L. *J. Org. Chem.* **2001**, *66*, 759−770. (i) Colby, E. A.; Jamison, T. F. *J. Org. Chem.* **2003**, *68*, 156−166. (j) Bauduin, C.; Moulin, D.; Kaloun, E. B.; Darcel, C.; Juge, S. *J. Org. Chem.* **2003**, *68*, 4293−4301. (k) Rippert, A. J.; Linden, A.; Hansen, H.-J. *Helv. Chim. Acta* **2000**, *83*, 311−321.

(9) (a) Maienza, F.; Spindler, F.; Thommen, M.; Pugin, B.; Malan, C.; Mezzetti, A. *J. Org. Chem.* **2002**, *67*, 5239−5249. (b) Kaloun, E. B.; Merdès, R.; Genêt, J. P; Uziel, J.; Jugé, S. *J. Organomet. Chem.* **1997**, *529*, 455−463; according to this publication, three diastereomers of 1,1′-bis{[(1*S*,2*R*)-(*N*-ephedrino)](phenyl)phosphino-*P*-borane}ferrocene were formed in 10% yield. (c) Nettekoven, U.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Widhalm, M.; Spek, A. L.; Lutz, M. *J. Org. Chem.* **1999**, *64*, 3996−4004; according to this publication, attack of 1,1′-dilithioferrocene (**k**)·2 TMEDA on (−)-**1** led to (R_P,R_P)/(R_P,S_P) = 65:35; no yield is mentioned.

(10) Jugé, S.; Stephan, M.; Genêt, J. P.; Halut-Desportes, S.; Jeannin, S. *Acta Crystallogr.* **1990**, *C46*, 1869−1872.

(11) This fact is in sharp contrast with a claim in ref 9c saying that the reactivity of phosphinite boranes surpasses the oxazaPB one.

SCHEME 2



Results and Discussion

Investigation of OxazaPB (1) Ring Opening with ArLi (a−h). Bulky aryllithium reagents **a**−**h** prepared in an appropriate solvent (hexane or Et_2O) were allowed to react with (−)-(2*S*,4*R*,5*S*)-**1** derived from (+)-ephedrine in THF from −20 °C to rt, and the evolution of the reaction was followed by TLC and ^{31}P NMR (Scheme 2). After reaction workup and to our delight, ^1H and ^{31}P NMR revealed the formation of the corresponding (*N*-ephedrino)phosphine boranes **2a**−**g**; they were isolated after column chromatography in 4−65% yield.[12] The highest yield of **2** was attained with **a**, **f**, and **g**. With **e**, the compound **2e** was formed only when **1** was added at rt (addition at −20 °C led solely to **3**). However, with supermesityllithium **h** (Mes*Li formed from Mes*Br[13]), no reaction occurred, and after hydrolysis, Mes*H was obtained. In the case of **2a**, ^1H NMR of the crude revealed the formation of a mixture of 8- and 2-*P*-substituted 1-methoxynaphthalene (90:10 ratio).[14] For **2e**, ^1H NMR of the crude showed the formation of the (S_P)-diastereomer in up to 3%, while for all the rest, <1% of the other diastereomer was formed if observed at all.

X-ray diffraction analysis of product **2b** revealed the expected (R_P) absolute configuration resulting from retention of configuration (Figure 1). Despite the bulkiness of the 2,6-dimethoxyphenyl group, the stereogeometry (bond lengths and angles) around the phosphorus atom is comparable to the one observed in the compound possessing an *o*-anisyl group in place of the 2,6-dimethoxyphenyl group.[15] However, by contrast to the *o*-anisyl analogue, one MeO group in **2b** is engaged in a rather short intramolecular interaction with the BH_3 group [O(1)···B = 3.005(3) Å].

The formation of (R_P)-(*N*-ephedrino)phosphine boranes **2b**−**g** was accompanied by the formation of *trans*-(S_P)-(*N*-methylamino)(phenyl)(1-phenyl-1-propenyloxy)phosphine-*P*-borane (**3**) as revealed by X-ray diffraction analysis (Figure 2). According to ^1H, ^{13}C, and ^{31}P NMR analyses, a single geometrical isomer was formed. To the best of our knowledge, this is the first isolated enantiomerically pure compound with a structure possessing a stereogenic phosphorus atom linked to the oxygen of an enol.[16] Interestingly, the C(11)−P−O angle [97.98(8)°] is rather small and the phenyl group is positioned almost above the oxygen atom. Also, with a O−P−C(11)−C(16) = −15.8-(2)°, the C(16) has a close interaction with the oxygen atom [C(16)···O = 2.858(3) Å].

The formation of compound **3** is attributed to the ArLi attack on the benzylic proton[17] of the ephedrine moiety (Scheme 2, pathway B) accompanied by an *anti*-elimination of the [*N*-(methylamino)](phenyl)phosphino-*P*-borane group and resulting in a net *trans* geometry. The formation of **3** is slower with respect to the privileged organolithium reagent attack on the phosphorus atom (pathway A). However, if this attack is hindered, then the attack on the benzylic proton becomes the predominant reaction. Thus, the ratios of products **2** against product **3** for **2b**, **2c**, **2d**, **2e**, **2f**, and **2g** were 40:60, 38:62, 52:48, 5:95 (at rt; 0:100 at −20 °C), 50:50, and 68:32, respectively.

Investigation of OxazaPB (1) Ring Opening with 2,2′-Dilithio-1,1′-biarenes (i,j). This synthetic strategy would lead to hybrid ligands **II** possessing two stereogenic elements: on the phosphorus atom and on the side chain (Scheme 3).

According to the standard reaction conditions, the reaction of 2,2′-dilithio-1,1′-biphenyl (**i**) or 2,2′-dilithio-1,1′-binaphthalene (**j**) with (+)-**1** did not afford in our hands either the desired 2,2′-bis[(*N*-ephedrino)(phenyl)phosphino-*P*-borane]-1,1′-biphenyl or the 2,2′-bis[(*N*-ephedrino)(phenyl)phosphino-*P*-borane]-1,1′-binaphthalene, respectively.[12,18] Instead, a complex

(12) Reaction crude was systematically analyzed by ^1H and ^{31}P NMR to verify the exclusion of (C_4H_9)(*N*-ephedrino)(phenyl)phosphine-*P*-borane wherein C_4H_9 = *n*-Bu,[5a] *s*-Bu (**2n**), or *t*-Bu.[8k] (R_P)-(*s*-Butyl)[(1*S*,2*R*)-(*N*-ephedrino)](phenyl)phosphine-*P*-borane (**2n**) was prepared according to the Jugé−Stephan route (see Supporting Information).

(13) To a cold (−50 °C) solution of Mes*Br in THF was added *s*-BuLi (1 equiv), and the reaction was left to stir for 30 min and then brought up to 0 °C for 15 min. For the synthesis of Mes*Br, see: Knorr, R.; Pires, C.; Behringer, C.; Menke, T.; Freudenreich, J.; Rossmann, E. C.; Böhrer, P. *J. Am. Chem. Soc.* **2006**, *128*, 14845−14853.

(14) (a) Shirley, D. A.; Cheng, C. F. *J. Organomet. Chem.* **1969**, *20*, 251−252. (b) (R_P)-[(1*S*,2*R*)-(*N*-Ephedrino)](1-methoxynaphth-2-yl)(phenyl)-phosphine-*P*-borane was prepared regioselectively from 2-bromo-1-methoxynaphthalene and (−)-**1** according to the Jugé−Stephan route, and this will be published in due course.

(15) Jugé, S.; Stephan, M.; Merdès, R.; Genêt, J. P.; Halut-Desportes, S. *J. Chem. Soc., Chem. Commun.* **1993**, 531−533.

(16) A diastereomeric mixture of vinylphosphonamides was obtained from 2-phenyl-1,3,2-oxazaphospholidine derived from (*S*)-prolinol via the Perkow reaction. For this, see: Faure, B.; Pardigon, O.; Buono, G. *Tetrahedron* **1997**, *53*, 11577−11594.

(17) A deprotonation−reprotonation sequence of (2*S*,4*S*,5*R*)-3,4-dimethyl-2-adamantyl-5-phenyl-1,3,2-oxazaphospholidine-2-oxide to (2*S*,4*S*,5*S*)-3,4-dimethyl-2-adamantyl-5-phenyl-1,3,2-oxazaphospholidine-2-oxide was observed.[8b]

(18) A quantity of 2.1 equiv of *n*- or *s*-BuLi was used to convert the 2,2′-dibromo-1,1′-biarene (at −20 to 0 °C in Et_2O or THF) into 2,2′-dilithio-1,1′-biarene (**i**,**j**) to ensure complete transmetalation. ^1H and ^{31}P NMR analyses of the crude materials showed mainly the formation of the corresponding (*P*-phenyl)phosphole derivative (**4i**,**j**) and a complex mixture of (*N*-ephedrino)phosphine-*P*-boranes present in a small amount (δ_P around +70). Use of 2,2′-dilithio-1,1′-biphenyl (**i**)·2 TMEDA adduct generated in hexane or cyclohexane from biphenyl, *n*-BuLi (2 equiv), and TMEDA (2 equiv) at rt within 16 h led to similar results. For the preparation of 2,2′-dilithio-1,1′-biphenyl (**i**)·2 TMEDA adduct, see: (a) Neugebauer, W.; Kos, A. J.; von Ragué Schleyer, P. *J. Organomet. Chem.* **1982**, *228*, 107−118. (b) Schaub, T.; Radius, U. *Tetrahedron Lett.* **2005**, *46*, 8195−8197.

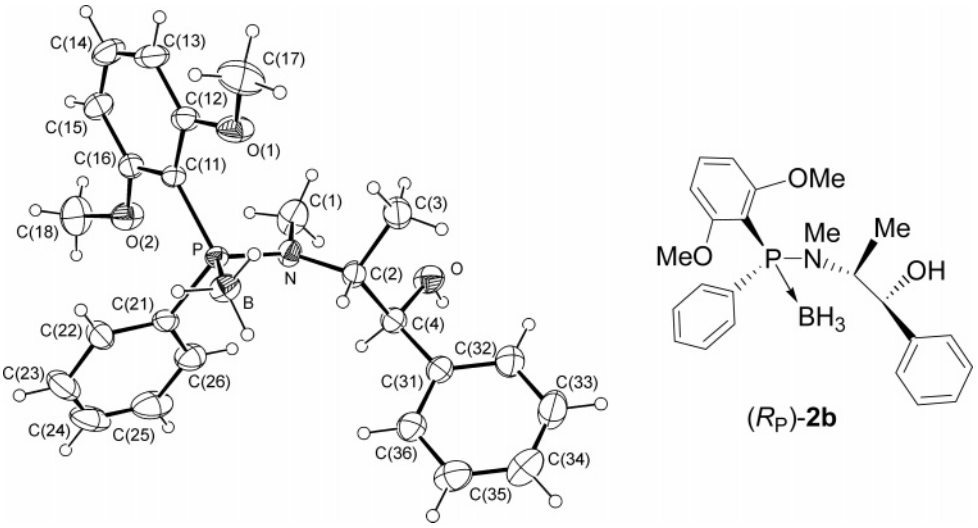


FIGURE 1. ORTEP drawing of (R_P)-**2b** at the 30% probability level. Selected bond lengths (Å) and angles (°): P−B 1.924(2); P−N 1.654(2); P−C(21) 1.812(2); P−C(11) 1.822(2); C(11)−P−B 116.5(1); C(11)−P−N 106.97(8); C(11)−P−C(21) 106.09(8); C(21)−P−B 104.9(1); C(21)−P−N 108.43(9); B−P−N 113.45(9).

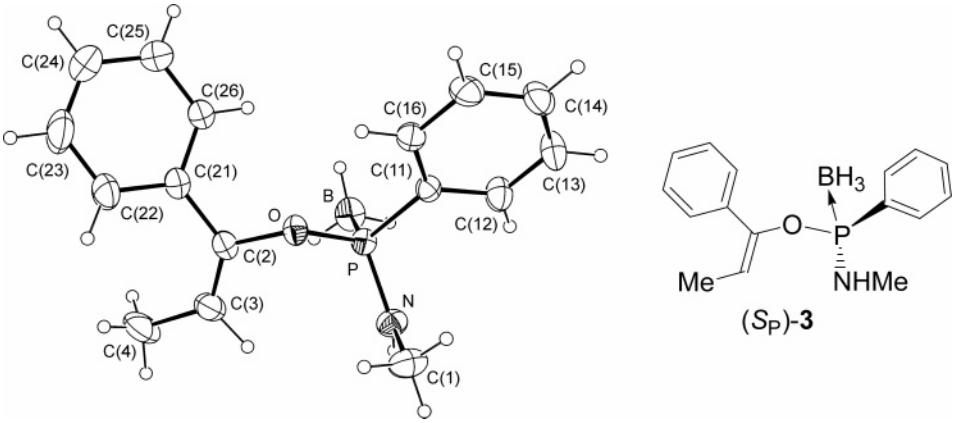


FIGURE 2. ORTEP drawing of (S_P)-**3** at the 30% probability level. Selected bond lengths (Å) and angles (°): P−B 1.885(3); P−N 1.633(2); P−O 1.621(1); P−C(11) 1.803(2); C(2)−C(3) 1.322(3); C(11)−P−B 114.7(1); C(11)−P−N 105.71(9); C(11)−P−O 97.98(8); O−P−B 115.0(1); O−P−N 110.18(9); B−P−N 112.1(1).

mixture was obtained from which the corresponding *P*-phenyl-5*H*-dibenzophosphole (**4i**) and *P*-phenyl-7*H*-dinaphtho[2,1-*b*:1′,2′-*d*]phosphole (**4j**) were isolated in up to 25% yield. ^{1}H NMR analysis of the crude showed no formation of compound **3** but the formation of bis[(1*R*,2*S*)-(*N*-ephedrino)](phenyl)phosphine-*P*-borane (**5**) which was isolated in 15% yield. X-ray diffraction analysis of its dimethyl ether derivative **5a** ascertained its structure. The formation of compound **5** arises from the ring opening of (+)-**1** with the displaced (1*R*,2*S*)-*N*,*O*-dilithioephedrine by attack of the amide part. Product **5** was independently prepared in 81% yield by reacting preformed (1*R*,2*S*)-*N*,*O*-dilithioephedrine with (+)-**1** in THF.

According to the literature, the attack of 2,2′-dilithio-1,1′-biphenyl (**i**) on dichlorophenylphosphine, chlorodiphenylphosphine, and the like gives rise to the (*P*-phenyl)phosphole derivative **4i**.[19a−c] However, the attack of 2,2′-dilithio-1,1′-binaphthalene (**j**) on dichlorophenylphosphine yields the (*P*-phenyl)phosphole derivative **4j**, but furnishes BINAP using chlorodiphenylphosphine.[19d,e]

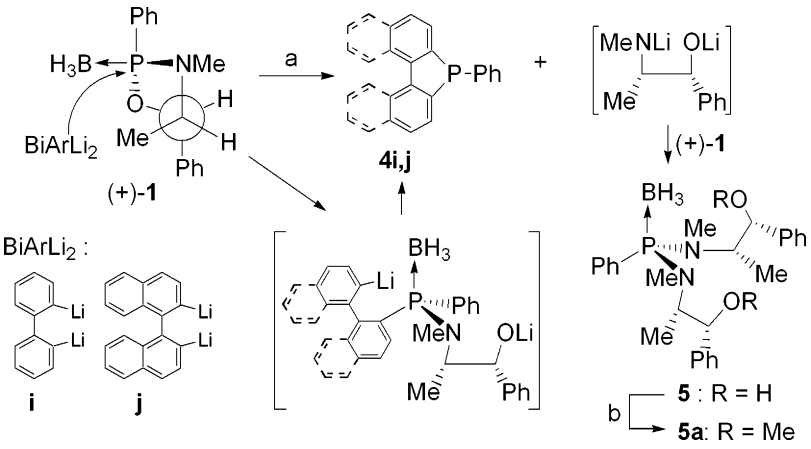
The P−N bond of the (*N*-ephedrino)phosphine boranes is always preserved under the organolithium attack even in presence of a 30% excess of the reagent. In this case, after the attack of the first aryl anion on the phosphorus atom, the ring closure with a concomitant displacement of the ephedrine moiety is favored by the proximity of the second aryl anion and its slow attack on another molecule of **1**. Consequently, such a flattened cyclic arylphosphine structure readily loses the BH_3 protecting group either during the reaction or upon workup. ^{31}P NMR analysis of the reaction mixture showed the presence of a small amount of the BH_3 adduct (δ_P +25; in comparison with an authentic sample).

Thus, we were unable to prepare via this strategy either the desired 2,2′-bis[(*N*-ephedrino)(phenyl)phosphino-*P*-borane]-1,1′-biphenyl or the 2,2′-bis[(*N*-ephedrino)(phenyl)phosphino-*P*-borane]-1,1′-binaphthalene.

(19) (a) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1955**, *77*, 6380−6381. (b) Brunner, H; Janura, M. J. *Synthesis* **1998**, 45−55. (c) Desponds, O.; Schlosser, M. *J. Organomet. Chem.* **1996**, *507*, 257−261. (d) Brown, K. J.; Berry, M. S.; Waterman, K. C.; Lingenfelter, D.; Murdoch, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 4717−4723. (e) Gladiali, S.; Dore, A.; Fabbri, D., De Lucchi, O.; Valle, G. *J. Org. Chem.* **1994**, *59*, 6363−6371.

(20) Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241−249.

SCHEME 3[a]



[a] Reagents: (a) 2,2′-dilithio-1,1′-biarene (0.4 molar equiv)/THF, −20 °C to rt; (b) MeI/NaH/THF, rt.

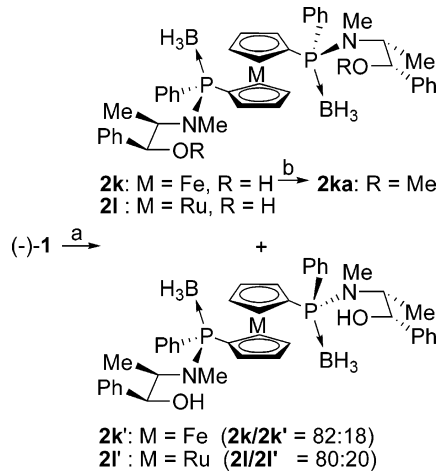
Investigation of OxazaPB (1) Ring Opening with 1,1′-Dilithioferrocene (k) and -ruthenocene (l). Following milder reaction conditions than those adopted by others,[9b] the reaction of 1,1′-dilithioferrocene (**k**)·2 TMEDA[20] adduct at −20 °C to rt with (−)-**1** furnished the desired (R_P,R_P)-1,1′-bis{[(1*S*,2*R*)-(*N*-ephedrino)](phenyl)phosphino-*P*-borane}ferrocene (**2k**) accompanied by the (R_P,S_P)-diastereomer **2k′** and [(1*S*,2*R*)-(*N*-ephedrino)](ferrocenyl)(phenyl)phosphine-*P*-borane[21] (disubstitution/monosubstitution ratio 95:5).[12] ^{1}H NMR of the crude showed that compound **3** was not formed. Furnishing identical diastereomeric ratio, 1,1′-dilithioferrocene (**k**) prepared from transmetalation of 1,1′-dibromoferrocene with *n*-BuLi (2.1 equiv) led, however, to a better yield than using the adduct prepared from ferrocene/*n*-BuLi/TMEDA (Scheme 4).

The diastereomers **2k** and **2k′** formed in 82:18 dr were separated by column chromatography; the major diastereomer **2k** was isolated in 64% yield, and the minor **2k′** in 10% yield.[9c,22] The absolute configuration of **2k** was confirmed by X-ray diffraction analysis of its dimethyl ether derivative **2ka**.

As the opening of **1** with ferrocenyllithium occurs with a high diastereoselectivity (de >98%), we can ascertain that after the first nucleophilic attack the increased steric bulkiness affects the second nucleophilic attack accounting for the obtained result (dr = 82:18). The lower selectivity obtained thus derives from the second nucleophilic attack.

By analogy to ferrocene-bridged *P*-stereogenic diphosphine ligands and their precursors, we aimed for the synthesis of their yet unknown ruthenocene analogues. Thus, the reaction of 1,1′-dilithioruthenocene (**l**)·2 TMEDA[23] adduct at 0 °C to rt with (−)-**1** furnished (R_P,R_P)-1,1′-bis{[(1*S*,2*R*)-(*N*-ephedrino)](phenyl)phosphino-*P*-borane}ruthenocene (**2l**) accompanied by the (R_P,S_P)-diastereomer **2l′**, (R_P)-[(1*S*,2*R*)-(*N*-ephedrino)](ruthenocenyl)(phenyl)phosphine-*P*-borane (**2m**), and a ruthenocene three-times substituted with (*N*-ephedrino)(phenyl)phosphino-*P*-borane group (monosubstitution/disubstitution/trisubstitution ratio 19:72:9 of isolated products). The diastereomers **2l** and **2l′** were formed in dr = 80:20 (by ^{1}H NMR), and the major diastereomer **2l** was isolated in 34% yield after column chromatography. The absolute configuration of **2l** (as well as of the monosubstituted ruthenocene **2m**) is assumed to be identical to **2k**. Independently, we have prepared (R_P)-[(1*S*,2*R*)-(*N*-ephedrino)](ruthenocenyl)(phenyl)phosphine-*P*-borane (**2m**) from (−)-**1** in 27% yield, and ^{1}H NMR analysis revealed a dr of 96:4.

SCHEME 4[a]



[a] Reagents: (a) 1,1′-dilithiometallocene (**i**,**j**) (M = Fe: with or without TMEDA; M = Ru: with TMEDA)/THF, −20 °C to rt; (b) MeI/NaH/THF, rt.

The (R_P,R_P)-1,1′-bis{[(1*S*,2*R*)-(*N*-ephedrino)](phenyl)phosphino-*P*-borane}metallocenes (**2k**,**l**) constitute the precursors to *P*-stereogenic metallocene-bridged diphosphine ligands according to the general synthetic strategy.[5,9b]

Conclusion

We have succeeded to introduce with high stereoselectivity bulky aryl groups on the *P*-stereogenic phosphorus atom by ring

(21) Independently, we have prepared (R_P)-[(1*S*,2*R*)-(*N*-ephedrino)]-(ferrocenyl)(phenyl)phosphine-*P*-borane from (−)-**1** according to Nettekoven et al.[8h] The authors have reported that (S_P)/(R_P) = 81:9 (~90% yield). However, we found a dr >98:2 with monosubstitution/disubstitution = 95:5. Previously, Brown et al.[8b] have reported that the ferrocenyllithium attack on (S_P)-methyl (*o*-anisyl)(phenyl)phosphinite-*P*-borane led to 92% ee and isolated yields of monosubstitution/disubstitution = 67:3. Ferrocenyllithium was prepared from ferrocene and *t*-BuLi according to: (a) Rebière, F.; Samuel, O.; Kagan, H. B. *Tetrahedron Lett.* **1990**, *31*, 3121−3124. (b) Herberhold, M.; Ayazi, A.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **2002**, *656*, 71−80.

(22) The attack of 1,1′-dilithioferrocene (**k**)·2 TMEDA complex on (R_P)-methyl (*o*-anisyl)(phenyl)phosphinite-*P*-borane led to 1,1′-bis[(*o*-anisyl)-(phenyl)phosphino-*P*-borane]ferrocene with (S_P,S_P)/(S_P:R_P) = 3.5:1 (93% yield).[8e]

(23) Bednarik, L.; Neuse, E. *J. Organomet. Chem.* **1979**, *168*, C8−C12.

opening of enantiomerically pure 3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane (**1**) using organolithium reagents. We have prepared in 4−65% yield (Ar)(*N*-ephedrino)(phenyl)phosphine-*P*-boranes **2** with Ar = 8-methoxynaphth-1-yl, 2-methoxynaphth-1-yl, 2,6-dimethoxyphenyl, 2,4,6-trimethoxyphenyl, 9-anthryl, 2,6-dimethylphenyl, and 2-mesityl. However, when the attack on the phosphorus atom is hindered, the deprotonation of the benzylic proton occurs, yielding the *trans*-(*N*-methylamino)(phenyl)(1-phenyl-1-propenyloxy)phosphine-*P*-borane (**3**).

While the attack of 2,2′-dilithio-1,1′-biarenes led to the corresponding (*P*-phenyl)phosphole derivatives **4i**,**j** and to [bis-(*N*-ephedrino)](phenyl)phosphine-*P*-borane (**5**), the attack of 1,1′-dilithiometallocene (M = Fe, Ru) led to a separable diastereomeric mixture of 1,1′-bis[(*N*-ephedrino)(phenyl)phosphino-*P*-borane]metallocenes (**2k**,**l**/**2k**′,**l**′). The obtained diastereoselectivity (dr ∼80:20) derives from the lower selectivity occurring at the second nucleophilic attack. Thus, ruthenocenes bearing a *P*-stereogenic atom were synthesized for the first time.

The application of the novel (Ar)(*N*-ephedrino)(phenyl)-phosphine-*P*-boranes **2a**−**g**,**k**,**l**, *trans*-(S_P)-(*N*-methylamino)-(phenyl)(1-phenyl-1-propenyloxy)phosphine-*P*-borane (**3**), bis-[(1*R*,2*S*)-(*N*-ephedrino)](phenyl)phosphine-*P*-borane (**5**), and their derivatives in organophosphorus and in asymmetric syntheses is in progress and will be communicated in due course.

Experimental Section

General. All reactions were carried out under a nitrogen atmosphere using anhydrous and degassed solvents. The starting (−)-(2*S*,4*R*,5*S*)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane ((−)-oxazaPB, (−)-**1**) and its enantiomer were prepared according to published procedure.[5] Organolithium reagents were prepared from the appropriate arene or bromoarene according to known literature procedures.

OxazaPB (1) Ring Opening with ArLi (a−g): (R_P)-[(1*S*,2*R*)-(*N*-Ephedrino)](8-methoxynaphth-1-yl)(phenyl)phosphine-*P*-borane (2a). To a cyclohexane (20 mL) solution of 1-methoxynaphthalene (1.58 g, 10.0 mmol) was added *t*-BuLi (10 mmol).[14a] The mixture was left to stir at rt for 3−4 days until the reddish color disappeared, then the supernatant was decanted off and the solid was rinsed with cyclohexane (2 × 20 mL). To the cooled (0 °C) solid was added a solution of (−)-**1** (1.43 g, 5.0 mmol) in THF (15 mL). After stirring at rt for 18 h, the reaction was quenched with H_2O. Following concentration, the residue was partitioned between CH_2Cl_2 (30 mL) and H_2O (15 mL), and the organic layer was dried over Na_2SO_4 then concentrated. ^{1}H NMR of the crude showed a mixture consisting of 8- and 2-*P*-substituted 1-methoxynaphthalene (90:10 ratio). Purification on silica gel eluting with toluene (R_f 0.1) yielded **2a** (1.44 g, 65%) as a white powder: mp 130−133 °C (hexane); $[\alpha]^{25}_D$ −146.3 (*c* 0.4, $CHCl_3$); δ_H (300 MHz, $CDCl_3$, TMS) 0.50−1.85 (br m, 3H), 1.28 (d, *J* = 6.7 Hz, 3H), 2.01 (br s, 1H), 2.36 (d, *J* = 7.0 Hz, 3H), 3.01 (s, 3H), 4.60 (br s, 1H), 5.00 (d, *J* = 4.1 Hz, 1H), 6.54 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.10−7.57 (m, 13 H), 7.77−7.91 (m, 2H); δ_C (75 MHz, $CDCl_3$) 12.0 (d, J_{C-P} = 2.5 Hz), 31.3 (d, J_{C-P} = 3.3 Hz), 51.9, 57.9 (d, J_{C-P} = 8.1 Hz), 78.7 (d, J_{C-P} = 3.4 Hz), 105.5, 120.7, 125.1 (d, J_{C-P} = 50.6 Hz), 125.3 (d, J_{C-P} = 10.5 Hz), 126.1, 126.5, 126.6 (d, J_{C-P} = 7.0 Hz), 127.1, 127.6 (d, J_{C-P} = 10.8 Hz), 128.1, 129.0 (d, J_{C-P} = 2.5 Hz), 129.5 (d, J_{C-P} = 10.4 Hz), 131.4 (d, J_{C-P} = 2.6 Hz), 132.6 (d, J_{C-P} = 7.2 Hz), 134.8 (d, J_{C-P} = 74.4 Hz), 135.7 (d, J_{C-P} = 6.9 Hz), 142.9, 154.1; δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +77.9 (br s); HRMS (ESI) *m*/*z* calcd for $C_{27}H_{32}BNO_2P$ [M^+ + H] 444.226, found 444.227. Anal. Calcd for $C_{27}H_{31}BNO_2P$: C, 73.15; H, 7.05; N, 3.16. Found: C, 73.31; H, 7.18; N, 3.02.

(R_P)-[(1*S*,2*R*)-(*N*-Ephedrino)](2,6-dimethoxyphenyl)(phenyl)-phosphine-*P*-borane (2b). To a THF (50 mL) solution of 1,3-dimethoxybenzene (6.22 g, 45 mmol) was added *n*-BuLi (45 mmol) at 0 °C.[24] The mixture was left to stir for 4 h at rt, and (−)-**1** (9.10 g, 31.9 mmol) in THF (30 mL) was added at −20 °C. After stirring at rt for 24 h, the reaction was quenched with H_2O. The concentrated residue was partitioned between CH_2Cl_2 (250 mL) and H_2O (100 mL), and the organic layer was dried over Na_2SO_4 then concentrated. ^{1}H and ^{31}P NMR revealed **2b**/**3** ratio of 40:60. The crude was purified on silica gel eluting with toluene, then toluene/EtOAc 8:2 (R_f 0.25 in toluene/EtOAc 9:1) and recrystallized from hexane to yield **2b** as colorless crystals (4.75 g, 35%): mp 147−150 °C; $[\alpha]^{25}_D$ −23.3 (*c* 1.0, $CHCl_3$); δ_H (300 MHz, $CDCl_3$, TMS) 0.47−1.70 (br m, 3H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.97 (br d, *J* = 4.0 Hz, 1H), 2.58 (d, *J* = 8.3 Hz, 3H), 3.48 (s, 6H), 4.40 (hept, *J* = 6.1 Hz, 1H), 4.86 (m, 1H), 6.51 (dd, *J* = 3.5, 8.4 Hz, 2H), 7.11−7.45 (m, 11H); δ_C (75 MHz, $CDCl_3$) 12.0 (d, J_{C-P} = 2.2 Hz), 30.9 (d, J_{C-P} = 3.6 Hz), 55.2, 58.5 (d, J_{C-P} = 10.5 Hz), 79.1 (d, J_{C-P} = 6.0 Hz), 104.6 (d, J_{C-P} = 4.4 Hz), 106.8 (d, J_{C-P} = 54.9 Hz), 126.5, 127.4 (d, J_{C-P} = 1.6 Hz), 127.5, 128.3, 128.5 (d, J_{C-P} = 2.2 Hz), 129.0 (d, J_{C-P} = 10.4 Hz), 133.6, 137.0 (d, J_{C-P} = 74.2 Hz), 142.6, 162.9 (d, J_{C-P} = 2.2 Hz); δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +63.2 (br m). Anal. Calcd for $C_{24}H_{31}BNO_3P$: C, 68.10; H, 7.38; N, 3.31. Found: C, 68.43; H, 7.61; N, 2.98.

(R_P)-[(1*S*,2*R*)-(*N*-Ephedrino)](2,4,6-trimethoxyphenyl)(phenyl)-phosphine-*P*-borane (2c). To a THF (2 mL) solution of 1,3,5-trimethoxybenzene (218 mg, 1.3 mmol) was added *n*-BuLi (1.3 mmol) at 0 °C.[24] The mixture was left to stir for 1.5 h at rt, and (−)-**1** (285 mg, 1.0 mmol) was added at 0 °C. After stirring at rt for 72 h, the reaction was quenched with H_2O. The concentrated residue was partitioned between CH_2Cl_2 (10 mL) and H_2O (5 mL), and the organic layer was dried over Na_2SO_4 then concentrated. ^{1}H and ^{31}P NMR revealed **2c**/**3** ratio of 38:62. The crude was purified on silica gel eluting with toluene/EtOAc 9:1 (R_f 0.3) to yield **2c** as colorless viscous oil (110 mg, 24%, ∼95% purity according to ^{1}H NMR): δ_H (300 MHz, $CDCl_3$, TMS) 0.35−1.70 (br m, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.95 (br d, *J* = 4.3 Hz, 1H), 2.57 (d, *J* = 8.4 Hz, 3H), 3.47 (s, 6H), 3.82 (s, 3H), 4.39 (m, 1H), 4.86 (m, 1H), 6.05 (d, *J* = 3.1 Hz, 2H), 7.06−7.35 (m, 8H), 7.43 (m, 2H); δ_C (75 MHz, $CDCl_3$) 12.2 (d, J_{C-P} = 1.8 Hz), 30.6 (d, J_{C-P} = 3.8 Hz), 55.1, 55.3, 58.4 (d, J_{C-P} = 10.6 Hz), 79.0 (d, J_{C-P} = 6.0 Hz), 91.2 (d, J_{C-P} = 4.9 Hz), 98.8 (d, J_{C-P} = 60.5 Hz), 126.6, 127.3, 127.4 (d, J_{C-P} = 5.7 Hz), 128.2, 128.3 (d, J_{C-P} = 2.3 Hz), 128.9 (d, J_{C-P} = 10.6 Hz), 137.3 (d, J_{C-P} = 74.6 Hz), 142.7, 164.1 (d, J_{C-P} = 2.6 Hz), 164.5 (d, J_{C-P} = 1.1 Hz); δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +61.2 (br m).

(R_P)-[(1*S*,2*R*)-(*N*-Ephedrino)](2-methoxynaphth-1-yl)(phenyl)-phosphine-*P*-borane (2d). To an Et_2O (7 mL) solution of 1-bromo-2-methoxynaphthalene (570 mg, 3.6 mmol) was added *n*-BuLi (3.6 mmol) at 0 °C. The mixture was left to stir for 3 h at rt, and a solution of (−)-**1** (855 mg, 3.0 mmol) in THF (7 mL) was added at 0 °C. After stirring at rt for 24 h, the reaction was quenched with H_2O. The concentrated residue was partitioned between CH_2Cl_2 (30 mL) and H_2O (10 mL), and the organic layer was dried over Na_2SO_4 then concentrated. ^{1}H and ^{31}P NMR revealed **2d**/**3** ratio of 52:48. The crude was purified on silica gel eluting with toluene/EtOAc 9:1 (R_f 0.1 in toluene) to yield **2d** as yellowish oil (505 mg, 38%, ∼95% purity according to ^{1}H NMR): δ_H (300 MHz, $CDCl_3$, TMS) 0.50−1.58 (br m, 3H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.72 (br d, *J* = 3.8 Hz, 1H), 2.72 (d, *J* = 8.0 Hz, 3H), 3.31 (s, 3H), 4.50 (m, 1H), 4.96 (m, 1H), 7.11−7.50 (m, 13H), 7.79 (m, 1H), 7.97 (d, *J* = 9.1 Hz, 1H), 8.66 (d, *J* = 8.7 Hz, 1H); δ_C (75 MHz, $CDCl_3$) 11.3 (d, J_{C-P} = 4.2 Hz), 31.4 (d, J_{C-P} = 3.3 Hz), 55.5, 58.5 (d, J_{C-P} = 9.7 Hz), 79.0 (d, J_{C-P} = 3.3 Hz), 110.2 (d, J_{C-P} = 60.9 Hz), 113.6 (d, J_{C-P} = 5.1 Hz), 123.9, 125.9, 126.0 (d, J_{C-P} =

(24) Brandsma, L.; Verkruijsse, H. D. In *Preparative Polar Organometallic Chemistry*; Springer-Verlag: Berlin, Heidelberg, 1987; Vol. 1, pp 203−204.

7.2 Hz), 126.8, 127.2, 127.9 (d, J_{C-P} = 10.9 Hz), 128.2, 128.5 (d, J_{C-P} = 1.2 Hz), 129.00 (d, J_{C-P} = 10.7 Hz), 129.02 (d, J_{C-P} = 2.0 Hz), 129.4 (d, J_{C-P} = 7.6 Hz), 134.7 (d, J_{C-P} = 1.9 Hz), 135.4 (d, J_{C-P} = 9.1 Hz), 137.6 (d, J_{C-P} = 67.7 Hz), 142.6, 160.5 (d, J_{C-P} = 1.1 Hz); δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +64.0 (br s); HRMS (ESI) *m*/*z* calcd for $C_{27}H_{32}BNO_2P$ [M^+ + H] 444.226, found 444.227.

(R_P)-[(1*S*,2*R*)-(*N*-Ephedrino)](9-anthryl)(phenyl)phosphine-*P*-borane (2e). To a THF (5 mL) solution of 9-bromoanthracene (668 mg, 2.6 mmol) was added *t*-BuLi (5.2 mmol) at −78 °C.[25] The mixture was left to stir for 15 min at this temperature, then brought up to rt, and a solution of (−)-**1** (570 mg, 2.0 mmol) in THF (5 mL) was added. After stirring at rt for 1 h, the reaction was quenched with H_2O. The concentrated residue was partitioned between CH_2Cl_2 (30 mL) and H_2O (10 mL), and the organic layer was dried over Na_2SO_4 then concentrated. ^1H and ^{31}P NMR revealed **2e**/**3** ratio of 5:95. The crude was purified on silica gel eluting with hexane/EtOAc 9:1 (R_f 0.15). Product **2e** was isolated as a yellow powder (37 mg, 4%, ∼95% purity according to ^1H NMR): δ_H (300 MHz, $CDCl_3$, TMS) 0.50−2.15 (br m, 3H), 1.18 (d, *J* = 7.0 Hz, 3H), 1.75 (br s, 1H), 2.40 (d, *J* = 7.5 Hz, 3H), 4.60 (m, 1H), 5.11 (d, *J* = 2.4 Hz, 1H), 7.17−7.45 (m, 12 H), 7.58 (m, 2H), 8.00 (dm, *J* = 8.5 Hz, 2H), 8.27 (dm, *J* = 9.1 Hz, 2H), 8.59 (s, 1H); δ_C (75 MHz, $CDCl_3$) 9.7 (d, J_{C-P} = 6.7 Hz), 30.9 (d, J_{C-P} = 3.3 Hz), 58.4 (d, J_{C-P} = 10.1 Hz), 78.7, 119.1 (d, J_{C-P} = 64.1 Hz), 124.9, 125.3, 125.7, 126.6 (d, J_{C-P} = 7.1 Hz), 127.2, 128.2, 128.5 (d, J_{C-P} = 10.5 Hz), 129.0, 130.5 (d, J_{C-P} = 2.2 Hz), 130.8 (d, J_{C-P} = 10.7 Hz), 131.2 (d, J_{C-P} = 8.4 Hz), 133.0 (d, J_{C-P} = 2.8 Hz), 134.1 (d, J_{C-P} = 7.2 Hz), 134.4 (d, J_{C-P} = 60.1 Hz), 142.3; δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +68.5 (br m).

(R_P)-[(1*S*,2*R*)-(*N*-Ephedrino)](2,6-dimethylphenyl)(phenyl)-phosphine-*P*-borane (2f). To a cold (−20 °C) solution of (−)-**1** (570 mg, 2.0 mmol) in THF (4 mL) was added 2,6-dimethylphenyllithium[26] (2.3 mmol in Et_2O). After stirring at rt for 2 h, the reaction was quenched with H_2O. The concentrated residue was partitioned between CH_2Cl_2 (30 mL) and H_2O (10 mL), and the organic layer was dried over Na_2SO_4 then concentrated. ^1H and ^{31}P NMR revealed **2f**/**3** ratio of 50:50. The crude was purified on silica gel eluting with toluene (R_f 0.35) to yield **2f** as a colorless oil (360 mg, 46%): $[\alpha]^{25}_D$ −141.6 (*c* 1.0, $CHCl_3$); δ_H (300 MHz, $CDCl_3$, TMS) 0.60−1.95 (br m, 3H), 1.02 (d, *J* = 7.0 Hz, 3H), 1.41 (br d, *J* = 3.6 Hz, 1H), 2.17 (s, 6H), 2.61 (d, *J* = 7.1 Hz, 3H), 4.34 (m, 1H), 4.86 (s, 1H), 7.00 (m, *J* = 3.5 Hz, 2H), 7.15−7.48 (m, 9H), 7.80 (m, 2H); δ_C (75 MHz, $CDCl_3$) 9.4 (d, J_{C-P} = 6.8 Hz), 23.6 (d, J_{C-P} = 4.4 Hz), 31.2 (d, J_{C-P} = 4.2 Hz), 58.3 (d, J_{C-P} = 10.4 Hz), 78.5, 125.4, 126.9 (d, J_{C-P} = 66.9 Hz), 127.0, 128.1, 128.5 (d, J_{C-P} = 10.0 Hz), 130.1 (d, J_{C-P} = 2.0 Hz), 130.3 (d, J_{C-P} = 8.8 Hz), 130.5 (d, J_{C-P} = 2.3 Hz), 130.7 (d, J_{C-P} = 10.2 Hz), 134.3 (d, J_{C-P} = 57.2 Hz), 142.5, 142.9 (d, J_{C-P} = 9.2 Hz); δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +67.0 (br m); HRMS (ESI) *m*/*z* calcd for $C_{24}H_{32}BNOP$ [M^+ + H] 392.232, found 392.232. Anal. Calcd for $C_{24}H_{31}BNOP$: C, 74.08; H, 8.21; N, 3.46. Found: C, 74.43; H, 8.29; N, 3.49.

(R_P)-[(1*S*,2*R*)-(*N*-Ephedrino)](2-mesityl)(phenyl)phosphine-*P*-borane (2g). To a THF (4 mL) solution of 2-bromomesitylene (500 mg, 2.5 mmol) was added *t*-BuLi (5.0 mmol) at −78 °C.[27] The mixture was left to stir for 15 min at this temperature, then brought up to rt and stirred for 15 min. To this mixture at −40 °C was added a solution of (−)-**1** (570 mg, 2.0 mmol) in THF (5 mL). After stirring at rt for 2 h, the reaction was quenched with H_2O. The concentrated residue was partitioned between CH_2Cl_2 (30 mL) and H_2O (10 mL), and the organic layer was dried over Na_2SO_4 then concentrated. ^1H and ^{31}P NMR revealed **2g**/**3** ratio of 68:32. The crude was purified on silica gel eluting with toluene (R_f 0.3) to yield **2g** as a colorless oil (465 mg, 57%): $[\alpha]^{25}_D$ −128.9 (*c* 1.0, $CHCl_3$); δ_H (300 MHz, $CDCl_3$, TMS) 0.55−1.95 (br m, 3H), 1.04 (d, *J* = 7.0 Hz, 3H), 1.36 (br d, *J* = 2.9 Hz, 1H), 2.15 (s, 6H), 2.27 (s, 3H), 2.64 (d, *J* = 7.3 Hz, 3H), 4.35 (m, 1H), 4.91 (s, 1H), 6.84 (d, *J* = 3.5 Hz, 2H), 7.18−7.49 (m, 8H), 7.81 (m, 2H); δ_C (75 MHz, $CDCl_3$) 9.5 (d, J_{C-P} = 6.8 Hz), 20.8 (d, J_{C-P} = 1.1 Hz), 23.6 (d, J_{C-P} = 4.3 Hz), 31.2 (d, J_{C-P} = 4.0 Hz), 58.4 (d, J_{C-P} = 10.2 Hz), 78.6, 123.5 (d, J_{C-P} = 68.9 Hz), 125.5, 127.1, 128.2, 128.5 (d, J_{C-P} = 10.2 Hz), 130.5 (d, J_{C-P} = 2.1 Hz), 130.8 (d, J_{C-P} = 10.1 Hz), 131.3 (d, J_{C-P} = 9.1 Hz), 134.4 (d, J_{C-P} = 57.0 Hz), 140.3 (d, J_{C-P} = 2.5 Hz), 142.8 (d, J_{C-P} = 28.8 Hz), 142.9; δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +67.2 (br m); HRMS (ESI) *m*/*z* calcd for $C_{25}H_{34}BNOP$ [M^+ + H] 406.2471, found 406.2472. Anal. Calcd for $C_{25}H_{33}BNOP$: C, 74.08; H, 8.21; N, 3.46. Found: C, 74.43; H, 8.29; N, 3.49.

***trans*-(S_P)-(*N*-Methylamino)(phenyl)(1-phenyl-1-propenyloxy)phosphine-*P*-borane (3).** This product derives from the reaction of 2,6-dimethoxyphenyllithium (45 mmol) with (−)-**1** (9.10 g, 31.9 mmol) and was purified on silica gel eluting with toluene (R_f 0.6). It was recrystallized from hexane (5.10 g, 56%) as colorless crystals: mp 65−69 °C; $[\alpha]^{25}_D$ −69.6 (*c* 1.0, $CHCl_3$); δ_H (300 MHz, $CDCl_3$, TMS) 0.03−1.40 (br m, 3H), 1.78 (dd, *J* = 7.3, 2.7 Hz, 2H), 2.29 (dd, *J* = 10.7, 5.7 Hz, 3H), 2.92 (m, 1H), 5.67 (qd, *J* = 7.3, 2.7 Hz, 1H), 7.27−7.52 (m, 8H), 7.74−7.83 (m, 2H); δ_C (75 MHz, $CDCl_3$) 12.9 (d, J_{C-P} = 1.1 Hz), 27.3 (d, J_{C-P} = 6.8 Hz), 112.2 (d, J_{C-P} = 6.1 Hz), 127.9, 128.1, 128.5 (d, J_{C-P} = 11.0 Hz), 128.6 (d, J_{C-P} = 1.1 Hz), 130.8 (d, J_{C-P} = 90.4 Hz), 131.2 (d, J_{C-P} = 11.2 Hz), 131.5 (d, J_{C-P} = 2.2 Hz), 135.1 (d, J_{C-P} = 2.2 Hz), 147.2 (d, J_{C-P} = 6.6 Hz); δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +105.8 (br m); HRMS (ESI) *m*/*z* calcd for $C_{16}H_{21}BNNaOP$ [M^+ + Na] 308.135, found 308.136. Anal. Calcd for $C_{16}H_{21}BNOP$: C, 67.40; H, 7.42; N, 4.91. Found: C, 67.53; H, 7.54; N, 4.78.

OxazaPB (1) Ring Opening with 2,2′-Dilithio-1,1′-biarenes (i,j). General Procedure: To a cold (−20 °C) solution of 2,2′-dilithio-1,1′-biarene[18] (0.48 mmol) was added a solution of (+)-**1** (342 mg, 1.2 mmol), and the mixture was stirred at rt overnight. The reaction was quenched with H_2O and concentrated. The residue was partitioned between CH_2Cl_2 (30 mL) and H_2O (10 mL), and the organic layer was dried over Na_2SO_4 then concentrated. The crude was purified on silica gel eluting with hexane/CH_2Cl_2 (10:1 to 4:1).

***P*-Phenyl-5*H*-dibenzophosphole (4i):** R_f 0.45 in hexane/CH_2Cl_2 9:1; δ_H (300 MHz, $CDCl_3$, TMS) 7.19−7.37 (m, 7H), 7.43−7.50 (m, 2H), 7.70 (m, 2H), 7.95 (d, *J* = 7.8 Hz, 2H); δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) −9.5 (s).

***P*-Phenyl-7*H*-dinaphtho[2,1-*b*:1′,2′-*d*]phosphole (4j):** R_f 0.45 in hexane/CH_2Cl_2 9:1; δ_H (300 MHz, $CDCl_3$, TMS) 7.16−7.35 (m, 5H), 7.46−7.55 (m, 4H), 7.75−7.90 (m, 4H), 7.96 (m, 2H), 8.47 (m, 2H); δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) −4.1 (s).

Bis[(1*R*,2*S*)-*N*-ephedrino](phenyl)phosphine-*P*-borane (5). To a THF (2 mL) solution of (−)-ephedrine (165 mg, 1.0 mmol) was added *n*-BuLi (2 mmol) at −50 °C. The mixture was stirred at this temperature for 30 min then at 0 °C for 10 min. Then, a solution of (+)-**1** (285 mg, 1.0 mmol) in THF (2 mL) was added. After stirring at rt for 16 h, the reaction was quenched with H_2O. The concentrated residue was partitioned between CH_2Cl_2 (10 mL) and H_2O (10 mL), and the organic layer was dried over Na_2SO_4 then concentrated. The crude was purified on silica gel eluting with toluene (R_f 0.3 in toluene/EtOAc 9:1), then precipitated from hexane to yield **5** as viscous oil (365 mg, 81%): $[\alpha]^{25}_D$ +16.2 (*c* 1.0, $CHCl_3$); δ_H (300 MHz, $CDCl_3$, TMS) 0.10−1.80 (m, 6H), 1.11 and 1.14 (2d, *J* = 6.9 Hz, 6H), 2.15 and 2.21 (2d, *J* = 3.7 Hz, 2H), 2.52 (d, *J* = 7.8 Hz, 3H), 2.62 (d, *J* = 7.6 Hz, 3H), 4.06 (m, 2H), 4.91 (m, 2H), 7.17−7.43 (m, 15H); δ_C (75 MHz, $CDCl_3$) 11.1 (d, J_{C-P} = 4.5 Hz), 12.2 (d, J_{C-P} = 1.8 Hz), 30.7 (d, J_{C-P} = 3.9 Hz), 30.9 (d, J_{C-P} = 2.8 Hz), 57.0 (d, J_{C-P} = 10.9 Hz), 57.4 (d, J_{C-P} = 9.4 Hz), 78.7 (d, J_{C-P} = 6.6 Hz), 78.8 (d, J_{C-P} = 2.8 Hz),

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125.8, 126.3, 127.4, 127.5, 128.1, 128.2, 128.4, 128.5, 130.4, 130.4, 131.8, 131.9, 132.1 (d, J_{C-P} = 87.1 Hz), 142.5, 142.8; δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +93.8 (br m). Anal. Calcd for $C_{26}H_{36}BN_2O_2P$: C, 69.34; H, 8.06; N, 6.22. Found: C, 69.51; H, 8.21; N, 6.08.

Bis[(1*R*,2*S*)-*N*-(*O*-methylephedrino)](phenyl)phosphine-*P*-borane (5a). To a THF (1 mL) solution of **5** (90 mg, 0.20 mmol) was added NaH (12 mg, 0.5 mmol) followed by MeI (0.61 mL, 10 mmol). After stirring at rt for 16 h, the reaction was quenched with H_2O. The concentrated residue was purified on silica gel eluting with toluene (R_f 0.8 in toluene/EtOAc 9:1), then recrystallized from hexane to yield **5a** as colorless crystals (87 mg, 91%): mp 146−148 °C; $[\alpha]^{25}_D$ −28.1 (*c* 0.4, $CHCl_3$); δ_H (300 MHz, $CDCl_3$, TMS) 0.10−1.60 (m, 6H), 1.14 and 1.19 (2d, *J* = 6.9 Hz, 6H), 2.65 and 2.67 (2d, *J* = 4.2 Hz, 6H), 3.25 and 3.29 (2s, 6H), 3.90−4.15 (m, 2H), 4.42 (d, *J* = 3.5 Hz, 1H), 4.50 (d, *J* = 4.2 Hz, 1H), 7.17−7.45 (m, 15H); δ_C (75 MHz, $CDCl_3$) 11.2 (d, J_{C-P} = 5.0 Hz), 12.3 (d, J_{C-P} = 2.4 Hz), 30.9 (m), 56.9 (d, J_{C-P} = 8.2 Hz), 57.0 (d, J_{C-P} = 11.4 Hz), 57.5 (d, J_{C-P} = 10.4 Hz), 88.8 (d, J_{C-P} = 5.8 Hz), 89.0 (d, J_{C-P} = 2.6 Hz), 126.7, 127.2, 127.3, 127.4, 128.19, 128.24, 128.5, 128.6, 130.46, 130.49, 131.7, 131.9, 132.5 (d, J_{C-P} = 86.3 Hz), 139.8, 140.0; δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +93.6 (br m). Anal. Calcd for $C_{28}H_{40}BN_2O_2P$: C, 70.29; H, 8.43; N, 5.86. Found: C, 70.52; H, 8.58; N, 5.54.

OxazaPB (1) Ring Opening with 1,1′-Dilithioferrocene (k) and -ruthenocene (l): (R_P,R_P)-1,1′-Bis{[(1*S*,2*R*)-(*N*-ephedrino)](phenyl)phosphino-*P*-borane}ferrocene (2k) and (R_P,S_P)-1,1′-Bis-{[(1*S*,2*R*)-(*N*-ephedrino)](phenyl)phosphino-*P*-borane}-ferrocene (2k′). To a cold (−50 °C) THF (5 mL) solution of 1,1′-dibromoferrocene (688 mg, 2 mmol) was added *n*-BuLi (4.2 mmol) and stirred at −30 °C for 1 h, then at 0 °C for 10 min. To this mixture at −20 °C was added a solution of (−)-**1** (1.26 g, 4.4 mmol) in THF (10 mL) and stirred at rt for 4 h. The reaction was quenched with H_2O, concentrated, and the residue was partitioned between CH_2Cl_2 (30 mL) and H_2O (20 mL). The organic layer was dried over Na_2SO_4 and concentrated. ^{1}H NMR of the crude showed a dr **2k**/**2k′** = 82:18. Products were purified on silica gel eluting with toluene/EtOAc 95:5 to yield **2k** (980 mg, 64%) and **2k′** (150 mg, 10%).

Major diastereomer (**2k**): orange needles (R_f 0.25 in toluene/EtOAc 9:1), mp 151−153 °C (hexane/CH_2Cl_2); $[\alpha]^{25}_D$ +72.7 (*c* 0.7, $CHCl_3$); δ_H (300 MHz, $CDCl_3$, TMS) 0.45−1.65 (m, 6H), 1.22 (d, *J* = 6.8 Hz, 6H), 1.85 (d, *J* = 3.8 Hz, 2H), 2.35 (d, *J* = 8.3 Hz, 6H), 4.12−4.20 (m, 4H), 4.60, 4.65 and 4.73 (3m, 6H), 4.87 (m, 2H), 7.26−7.40 (m, 20H); δ_C (75 MHz, $CDCl_3$) 13.0, 30.5 (d, J_{C-P} = 2.4 Hz), 57.7 (d, J_{C-P} = 9.0 Hz), 72.9 (m), 73.9 (m), 74.8 (d, J_{C-P} = 6.6 Hz), 78.7 (d, J_{C-P} = 5.3 Hz), 126.5, 127.6, 128.2 (d, J_{C-P} = 10.4 Hz), 128.4, 130.6, 131.3 (d, J_{C-P} = 9.7 Hz), 132.4 (d, J_{C-P} = 69.9 Hz), 142.5; δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +68.8 (br m). Anal. Calcd for $C_{42}H_{52}B_2FeN_2O_2P_2$: C, 66.70; H, 6.93; N, 3.70. Found: C, 66.84; H, 7.09; N, 3.56.

Minor diastereomer (**2k′**): viscous brown oil (R_f 0.3 in toluene/EtOAc 9:1); $[\alpha]^{25}_D$ +2.5 (*c* 1.0, $CHCl_3$); δ_H (300 MHz, $CDCl_3$, TMS) 0.35−1.65 (br m, 6H), 1.12 and 1.16 (2d, *J* = 6.8 Hz, 6H), 1.85 (br d, *J* = 11.7 Hz, 2H), 2.27 (d, *J* = 8.4 Hz, 3H), 2.43 (d, *J* = 9.7 Hz, 3H), 3.59 (m, 1H), 4.05−4.14 (m, 2H), 4.26−4.34 (m, 3H), 4.50, 4.54, 4.58, and 4.66 (4m, 4H), 4.71 and 4.81 (2m, 2H), 7.12−7.60 (m, 20H); δ_C (75 MHz, $CDCl_3$) 12.4 (d, J_{C-P} = 1.6 Hz), 12.9 (d, J_{C-P} = 2.2 Hz), 30.2 (d, J_{C-P} = 2.6 Hz), 30.5 (d, J_{C-P} = 2.8 Hz), 57.6 (d, J_{C-P} = 2.2 Hz), 57.7 (d, J_{C-P} = 5.8 Hz), 71.0−74.8 (m), 78.1 (d, J_{C-P} = 4.7 Hz), 78.7 (d, J_{C-P} = 5.3 Hz), 126.3, 126.4, 127.6, 127.7, 128.2, 128.3, 128.36, 128.39, 130.6 (d, J_{C-P} = 2.2 Hz), 131.1 (d, J_{C-P} = 2.2 Hz), 131.3 (d, J_{C-P} = 10.3 Hz), 131.8 (d, J_{C-P} = 12.1 Hz), 131.9 (d, J_{C-P} = 10.5 Hz), 132.7 (d, J_{C-P} = 17.24 Hz), 142.5, 142.8; δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +68.8 (br m).

(R_P,R_P)-1,1′-Bis{[(1*S*,2*R*)-*N*-(*O*-methylephedrino)](phenyl)-phosphino-*P*-borane}ferrocene (2ka). To a THF (2 mL) solution of **2k** (378 mg, 0.5 mmol) was added NaH (20 mg, 0.8 mmol), followed by MeI (310 μL, 5 mmol). After stirring at rt for 20 h, the reaction was quenched with H_2O. The concentrated residue was purified on silica gel eluting with toluene (R_f 0.35) and recrystallized from hexane/CH_2Cl_2 to yield amber colored crystals (373 mg, 95%): mp 163−167 °C; $[\alpha]^{25}_D$ +75.5 (*c* 0.5, $CHCl_3$); δ_H (300 MHz, $CDCl_3$, TMS) 0.23−1.70 (m, 6H), 1.18 (d, *J* = 6.9 Hz, 6H), 2.38 (d, *J* = 8.2 Hz, 6H), 3.21 (s, 6H), 4.07 (m, 2H), 4.20 (m, 2H), 4.30 (d, *J* = 5.4 Hz, 2H), 4.58, 4.63, and 4.71 (3m, 6H), 7.23−7.42 (m, 20H); δ_C (75 MHz, $CDCl_3$) 13.1 (d, J_{C-P} = 2.3 Hz), 30.6 (d, J_{C-P} = 2.7 Hz), 56.9, 57.5 (d, J_{C-P} = 10.0 Hz), 72.8−74.7 (m), 88.5 (d, J_{C-P} = 5.2 Hz), 127.3, 127.5, 128.2 (d, J_{C-P} = 10.2 Hz), 128.3, 130.5 (d, J_{C-P} = 2.3 Hz), 131.3 (d, J_{C-P} = 10.2 Hz), 132.7 (d, J_{C-P} = 69.5 Hz), 139.8; δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +69.1 (br m). Anal. Calcd for $C_{44}H_{56}B_2FeN_2O_2P_2$: C, 67.38; H, 7.20; N, 3.57. Found: C, 67.72; H, 7.47; N, 3.28.

(R_P,R_P)-1,1′-Bis{[(1*S*,2*R*)-(*N*-ephedrino)](phenyl)phosphino-*P*-borane}ruthenocene (2l). To a cold (0 °C) solution of ruthenocene (925 mg, 4.0 mmol) in hexane (30 mL) was added *n*-BuLi (8.0 mmol) followed by TMEDA (1.2 mL, 8.0 mmol), and the mixture was stirred at rt overnight.[23] The beige colored precipitate was washed with hexane (2 × 10 mL), and to it was added a solution of (−)-**1** (2.44 g, 8.5 mmol) in THF (20 mL) at 0 °C. The mixture was stirred at rt for 2 h, quenched with H_2O, concentrated, and the residue was partitioned between CH_2Cl_2 (30 mL) and H_2O (20 mL). The organic layer was dried over Na_2SO_4 and concentrated. ^{1}H NMR of the crude showed **2l**/**2l′** = 80:20. This was purified on silica gel eluting with a gradient of toluene/EtOAc (100:0 to 95:5).

Major diastereomer (**2l**): 1.09 g (34%), beige powder (R_f 0.25 in toluene/EtOAc 9:1); mp 145−146 °C (hexane/CH_2Cl_2); $[\alpha]^{25}_D$ +95.2 (*c* 1.0, $CHCl_3$); δ_H (300 MHz, $CDCl_3$, TMS) 0.25−1.35 (m, 6H), 1.25 (d, *J* = 6.8 Hz, 6H), 1.83 (br s, 2H), 2.41 (d, *J* = 8.4 Hz, 6H), 4.15 (m, 2H), 4.54 (m, 2H), 4.81−4.86 (m, 4H), 4.94 and 4.99 (2m, 4H), 7.18−7.45 (m, 20H); δ_C (75 MHz, $CDCl_3$) 13.4 (d, J_{C-P} = 1.2 Hz), 30.4 (d, J_{C-P} = 3.3 Hz), 57.7 (d, J_{C-P} = 9.6 Hz), 75.0 (d, J_{C-P} = 13.5 Hz), 76.5−77.4 (m), 77.6 (d, J_{C-P} = 5.9 Hz), 78.5 (d, J_{C-P} = 13.5 Hz), 126.6 127.7, 128.1 (d, J_{C-P} = 10.4 Hz), 128.4, 130.5 (d, J_{C-P} = 2.2 Hz), 131.4 (d, J_{C-P} = 10.0 Hz), 131.9 (d, J_{C-P} = 71.5 Hz), 142.4; δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +68.99 (br s). Anal. Calcd for $C_{42}H_{52}B_2N_2O_2P_2Ru$: C, 62.94; H, 6.54; N, 3.50. Found: C, 62.86; H, 6.50; N, 3.63.

Minor diastereomer **2l′**: 0.39 g, yellowish oil (R_f 0.3 in toluene/EtOAc 9:1), containing 30% of **2l**; δ_H (300 MHz, $CDCl_3$, TMS) 0.35−1.50 (m, 6H), 1.17 and 1.20 (2d, *J* = 6.9 Hz, 6H), 1.85 (br d, *J* = 11.7 Hz, 2H), 2.35 (d, *J* = 9.5 Hz, 3H), 2.49 (d, *J* = 8.2 Hz, 3H), 3.80 and 4.10 (2m, 2H), 4.47 (m, 1H), 4.62 (m, 2H), 4.72 (m, 1H), 4.76−4.87 (m, 6H), 7.18−7.46 (m, 18H), 7.57 (m, 2H); δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +69.0 (br m). **2m**: 0.25 g (12%); containing 3% of its (S_P)-diastereomer.

A compound consisting of a ruthenocene three-times substituted with (*N*-ephedrino)(phenyl)phosphino-*P*-borane group according to ^{1}H NMR and to preparation of 1,1′-dilithioruthenocene (**l**)·2 TMEDA:[23] 0.27 g (6%).

(R_P)-[(1*S*,2*R*)-(*N*-ephedrino)](ruthenocenyl)(phenyl)phosphine-*P*-borane (2m). To a cold (0 °C) solution of ruthenocene (231 mg, 1.0 mmol) in THF (3 mL) was added *t*-BuLi (0.67 mL, 1.0 mmol) and stirred for 5 min.[28] Hexane (3 mL) was added, the reaction mixture cooled to −70 °C, the precipitated beige solid decanted, and washed with hexane (3 × 3 mL). To this solid was added a solution of (−)-**1** (340 mg, 1.2 mmol) in THF (3 mL) at 0 °C, slowly warmed to rt, stirred for 3 h, quenched with H_2O, concentrated, and partitioned between CH_2Cl_2 (20 mL) and H_2O (10 mL). The residue was purified on silica gel eluting with toluene/EtOAc 9:1 (R_f 0.5) to yield **2m** (139 mg, 27%) as a yellowish foam: ^{1}H NMR revealed the presence of 4% of the (S_P)-

(28) (a) Rausch, M. D.; Fischer, E. O.; Grubert, H. *J. Am. Chem. Soc.* **1960**, *82*, 76−82. (b) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Suszko, P. R.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2337−2347.

diastereomer (δ_H 2.54 (d, J = 7.7 Hz, 3H); $[\alpha]^{25}_D$ +112.7 (*c* 1.0, $CHCl_3$); δ_H (300 MHz, $CDCl_3$, TMS) 0.20−1.45 (br m, 3H), 1.24 (d, J = 6.8 Hz, 3H), 2.06 (br s, 1H), 2.38 (d, J = 8.3 Hz, 3H), 4.17 (m, 1H), 4.50 (m, 1H), 4.60 (s, 5H), 4.72−4.81 (m, 3H), 4.89 (m, 1H), 7.17−7.44 (m, 10H); δ_C (75 MHz, $CDCl_3$) 13.4, 30.3 (d, J_{C-P} = 3.3 Hz), 57.6 (d, J_{C-P} = 9.4 Hz), 72.6 (d, J_{C-P} = 2.2 Hz), 72.7, 73.6 (d, J_{C-P} = 14.3 Hz), 74.4 (d, J_{C-P} = 7.4 Hz), 75.5 (d, J_{C-P} = 64.9 Hz), 78.5 (d, J_{C-P} = 6.5 Hz), 126.6, 127.7 (d, J_{C-P} = 18.6 Hz), 128.0, 128.3, 130.2 (d, J_{C-P} = 2.2 Hz), 131.5 (d, J_{C-P} = 10.0 Hz), 132.3 (d, J_{C-P} = 71.4 Hz), 142.5; δ_P (120 MHz, $CDCl_3$, 85% H_3PO_4) +69.3 (br m); HRMS (ESI) *m*/*z* calcd for $C_{26}H_{32}BNOPRu$ $[M^+ + H]$ 518.136, found 518.136. Anal. Calcd for $C_{26}H_{31}BNOPRu$: C, 60.47; H, 6.05; N, 2.71. Found: C, 60.37; H, 6.19; N, 2.83.

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Supporting Information Available: Experimental procedure for **2n**, ^1H and ^{13}C NMR spectra of all new compounds, X-ray crystallographic data for **2b**, **2ka**, **3**, and **5a** (cif files). This material is available free of charge via the Internet at http://pubs.acs.org.

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