New Chiral Phosphine−Phosphite Ligands in the Enantioselective Palladium-Catalyzed Allylic Alkylation

Sirik Deerenberg, Henri S. Schrekker, Gino P. F. van Strijdonck, Paul C. J. Kamer, Piet W. N. M. van Leeuwen,* Jan Fraanje, and Kees Goubitz

Contribution from the Institute of Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

kamer@anorg.chem.uva.nl

Received November 8, 1999

A series of chiral phosphine−phosphite ligands **1**−**6** have been synthesized and used in the enantioselective palladium-catalyzed reaction of *rac*-1,3-diphenyl-2-propenyl acetate with dimethyl malonate as nucleophile. Ligands **1a**, **2**, **3**, **5a**, **6a**, and **6b** have been synthesized starting from racemic *tert*-butylphenylphosphinoborane. The use of dynamically resolved Li phosphide (−)-sparteine provided the optically pure ligands. Crystals of the allylpalladium (**6a**) complex were obtained, suitable for X-ray crystal structure determination. The X-ray crystal structure of the allylpalladium (**6a**) complex revealed a longer palladium−carbon bond distance trans to the phosphine moiety indicating that the attack of the nucleophile takes place at the carbon trans to the phosphine moiety. This was confirmed by the fact that the phosphine moiety did not affect the enantioselectivity directly. Under mild reaction conditions, enantioselectivities up to 83% were obtained (25 °C) with ligand **1e**. Systematic variation of the ligand bridge and the phosphite moiety showed that the configuration of the product is controlled by the atropisomerism of the biphenyl substituent at the phosphite moiety. The conformation of the biphenyl group, in turn, is controlled by the substituent at the chiral carbon in the bridge. Ligands with large bite angles yielded higher enantioselectivities.

Introduction

The development of methods for carbon−carbon bond formation is one of the key issues in organic synthesis. A versatile method for achieving this is the palladium-catalyzed allylic substitution with carbon nucleophiles.[1] Therefore, this reaction has been studied extensively over the past few years[2−5] and used in the total synthesis of natural products such as lycorane,[2] carbovir, and aristeromycin.[3] A large number of chiral ligands, mainly diphosphines, have been used and many substrates can be functionalized with high enatiomeric excess (ee). Despite the fact that the reaction mechanism of the allylic alkylation reaction is reasonably well understood, the origin of the enantioselectivity is often unclear. Calculation of the reaction pathway for a C_2-symmetric diphosphine ligand shows that during the nucleophilic attack, the allyl moiety rotates to an alkenelike structure. In a chiral pocket, this rotation can be forced to proceed in one direction only, thus inducing a high ee.[4−6] Currently, the potential of ligands other than diphosphines in the asymmetric catalytic allylic substitutions has been recognized.[7] Among the successful nitrogen-containing ligands that have been employed for the palladium-catalyzed reaction of *rac*-1,3-diphenyl-2-propenyl acetate with dimethyl malonate are ligands that possess either C_2-[8−13] or C_1-symmetry.[14−21] Also, chiral bidentate ligands containing different donor atoms have been found to induce high enantioselectivity. This has recently been demonstrated using phosphinooxazolines,[15−17,22−24] thiophenooxazolines,[19] phosphinosulfoxides,[25] and phosphino-

(1) Buisman, G. J. H.; van der Veen, L. A.; Klootwijk, A.; de Lange, W. G. J.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Vogt, D. *Organometallics* **1997**, *16*, 2929−2939.
(2) Yoshizaki, H.; Satoh, H.; Sato, Y.; Nukui, S.; Shibasaki, M.; Mori, M. *J. Org. Chem.* **1995**, *60*, 2016−2021.
(3) Trost, B. M.; Li, L.; Guile, S. D. *J. Am. Chem. Soc.* **1992**, *114*, 8745−8747.
(4) Dierkes, P.; Ramdeehul, S.; Barloy, L.; de Cian, A.; Fischer, J.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3116.
(5) Blöchl, P. E.; Togni, A. *Organometallics* **1996**, *15*, 4125−4132.
(6) Ramdeehul, S.; Dierkes, P.; Aguado, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3118.
(7) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395−422.
(8) Müller, D.; Umbricht, U.; Weber, B.; Pfaltz, A. *Helv. Chim. Acta* **1991**, *74*, 232.
(9) Leutenegger, U.; Umbricht, U.; Fahrni, C.; von Math, P.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143.
(10) Kubota, H.; Nakajima, M.; Koga, M. *Tetrahedron Lett.* **1993**, *34*, 8135.
(11) Kang, J.; Cho, W. O.; Cho, H. G. *Tetrahedron: Asymmetry* **1994**, *5*, 1347.
(12) Tanner, D.; Andersson, P. G.; Harden, A.; Somfai, P. *Tetrahedron Lett.* **1994**, *35*, 4631.
(13) Chelucci, G.; Caria, V.; Saba, A. *J. Mol. Catal. A* **1998**, *130*, 51.
(14) Togni, A. *Tetrahedron: Asymmetry* **1991**, *2*, 683.
(15) von Math, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566.
(16) Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769.
(17) Dawson, G. J.; Frost, C. G.; Williams, J. M. J.; Coote, S. J. *Tetrahedron Lett.* **1993**, *34*, 3149.
(18) von Math, P.; Loiseleur, O.; Koch, G.; Pfaltz, A.; Lefeber, C.; Feucht, T.; Helmchen, G. *Tetrahedron: Asymmetry* **1994**, *5*, 573.
(19) Allen, V. J.; Bower, J. F.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1994**, *5*, 1895.
(20) Kubota, H.; Koga, M. *Tetrahedron Lett.* **1994**, *35*, 6689.
(21) Wimmer, P.; Widhalm, M. *Tetrahedron: Asymmetry* **1995**, *6*, 657.
(22) Zhang, W.; Yoneda, Y.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron: Asymmetry* **1998**, *9*, 3371.
(23) Sudo, A.; Saigo, K. *J. Org. Chem.* **1997**, *62*, 5508.
(24) Imai, Y.; Zhang, W.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron Lett.* **1998**, *39*, 4343.

10.1021/jo991737d CCC: $19.00
Published on Web 07/07/2000

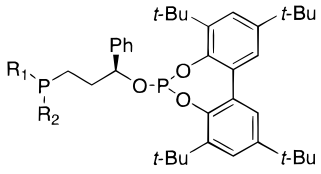
amines[14−21,26−28] as ligands for palladium. Recently, we have shown that the regioselectivity in the palladium-catalyzed allylic alkylation is governed by the relative donor−acceptor strengths of the ligand donor atoms, the steric hindrance in the transition state, the bite angle of the ligand, and the substituents on the allyl moiety.[29]

To elucidate the effects of these parameters on the enantioselectivity in the allylic alkylation reaction, we designed a new class of diastereomeric phosphine−phosphite ligands with a stereogenic phosphine moiety, a chiral backbone, and an atropisomerically chiral phosphite moiety. This type of ligands has the advantage that many structural variations can be made. Systematic variation of the different chiral centers in the ligand can provide information about the origin of the stereochemistry of the reaction. To the best of our knowledge, this is the first example of the use of phosphine−phosphite ligands in the catalytic allylation reaction.

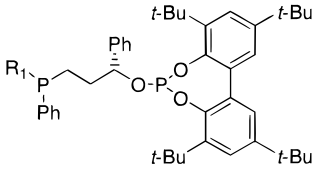
Results and Discussion

Ligand Design. To vary the parameters that are important for the allylic alkylation reaction, we designed a series of ligands. All ligands consisted of two different donor groups, viz., a phosphine and a phosphite. To investigate the effect of the phosphine moiety, it was substituted with different groups. The phosphite moiety was substituted with a bisphenol group that was able to interconvert between its atropisomers.

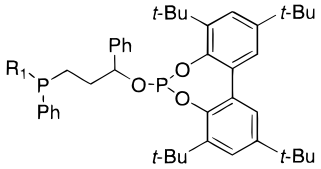
The influence of the group attached to the chiral carbon next to the phosphite moiety on the enantioselectivity was investigated using ligands **1a** and **2**, having opposite



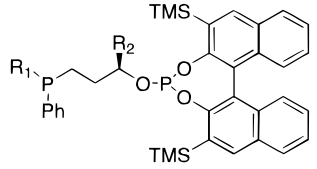
1a (R_P,S_C) R_1=*t*-Butyl, R_2=Ph
1b (S_C) R_1=R_2=*t*-Butyl
1c (S_P,S_C) R_1=1-Napht, R_2=Ph
1d (S_P,S_C) R_1=2-Anisyl, R_2=Ph
1e (S_C) R_1=Ph, R_2=Ph



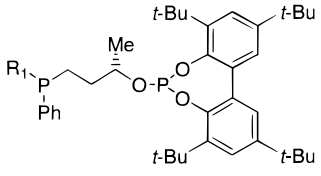
2 (R_P,R_C) R_1=*t*-Butyl



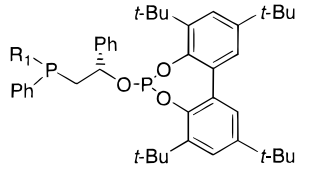
3 (R_P,rac$_C$) R_1=*t*-Butyl



4a (*R*) R_1=Ph, R_2=H
4b (*S*) R_1=Ph, R_2=H
4c (S_P,S_C,*R*) R_1=1-Napht, R_2=Ph
4d (S_P,S_C,*S*) R_1=1-Napht, R_2=Ph



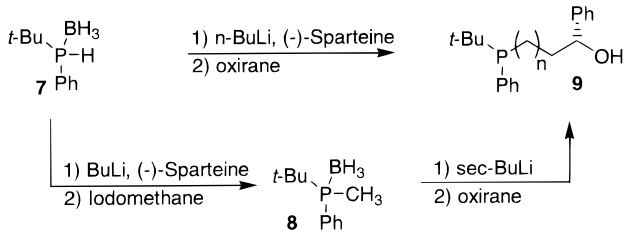
5a (R_P,S_C) R_1=*t*-Butyl
5b (S_C) R_1=Ph



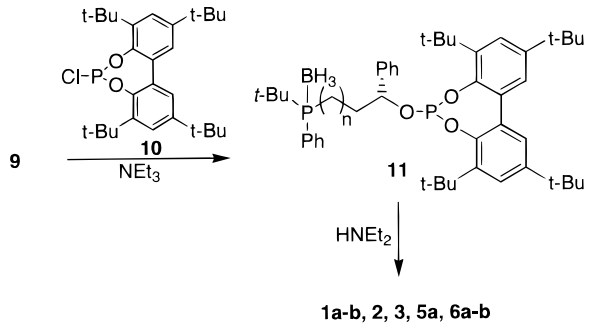
6a (R_P,S_C) R_1=*t*-Butyl
6b (R_P,R_C) R_1=*t*-Butyl

configuration in the bridge, and **3**, being racemic in the bridge.

Scheme 1



Scheme 2



The influence of the bisphenol group on the enantioselectivity was studied using ligands **4a**−**d**. The phosphite moiety is substituted with an atropisomerically pure binaphthol group containing trimethylsilyl groups. The influence of the size of the substituent at the chiral carbon in the bridge was investigated by using ligands **5a** and **5b**. To investigate the effect of the bite angle of the ligand, ligands **6a** and **6b** were synthesized having a shorter bridge length and thus a smaller bite angle.

Ligand Synthesis. The synthesis of ligands with a phosphine moiety consisting of a stereogenic phosphorus atom substituted with a *tert*-butyl group (ligands **1a**, **2**, **3**, **5a**, **6a**, and **6b**) was started from racemic *tert*-butylphenylphosphinoborane **7** (Scheme 1).[30] Dynamic resolution of the lithiated phosphine with (−)-sparteine afforded an enantiopure phosphorus nucleophile, as recently described by Wolfe and Livinghouse.[31] The lithiated phosphine was made to react with methyliodide to obtain **8**.[31] Reaction of methylphosphine **8** with *sec*-butyllithium and the appropriate oxiranes yielded the corresponding phosphino alcohols (**9**). Reaction with bulky 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite **10** afforded the protected phosphine−phosphite ligands (Scheme 2). The boronato group was removed immediately by treatment with diethylamine to give the pure phosphine−phosphite ligands (**1a**, **2**, **3**, and **5a**). Phosphino alcohols **9** with a two-carbon bridge were obtained by direct coupling of the lithiated phosphine **7** with a series of oxiranes. Reaction with **10** followed by decomplexation gave the enantiopure phosphine−phos-

(25) Hiroi, K.; Suzuki, Y.; Kawagishi, R. *Tetrahedron. Lett.* **1999**, *40*, 715.
(26) Cahill, J. P.; Bohnen, F. M.; Goddard, R.; Krüger, C.; Guiry, P. J. *Tetrahedron: Asymmetry* **1998**, *9*, 3831.
(27) Bourghida, M.; Widhalm, M. *Tetrahedron: Asymmetry* **1998**, *9*, 1073.
(28) Suzuki, Y.; Ogata, Y.; Hiroi, K. *Tetrahedron: Asymmetry* **1999**, *10*, 1219.
(29) van Haaren, R. J. H.; van Strijdonck, G. P. F.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **1999**, 1237.
(30) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244.
(31) Wolfe, B.; Livinghouse, T. *J. Am. Chem. Soc.* **1998**, *120*, 5116.

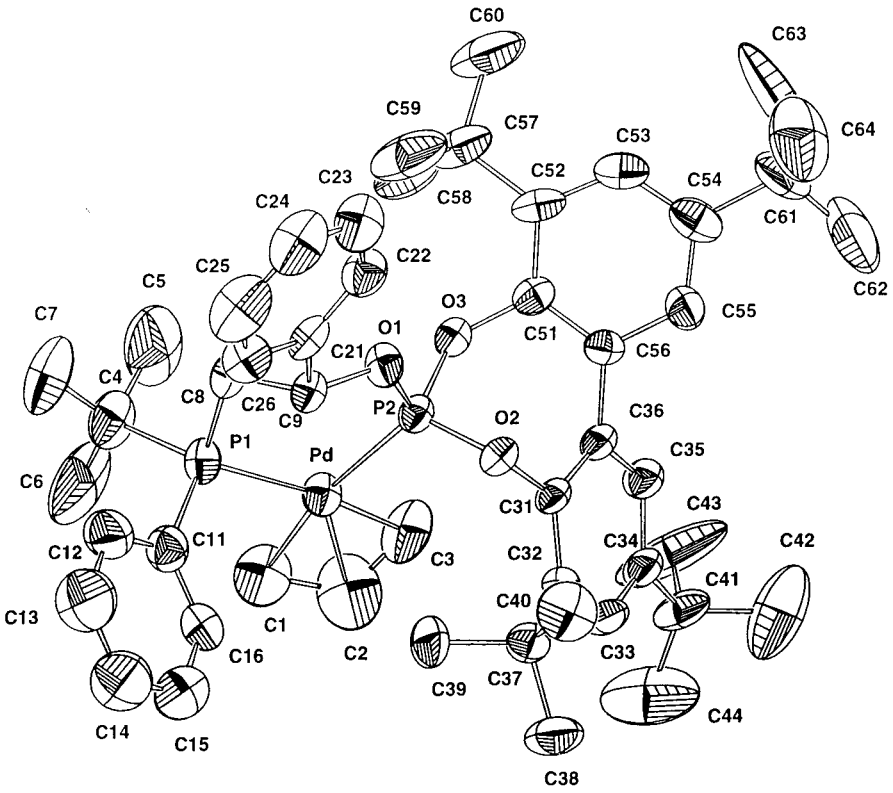


Figure 1. ORTEP plot of palladium(H_3-C_3H_5)(**6a**)BF_4.

phite ligands (**6a** and **6b**). From the ^{1}H NMR spectra, it could be concluded that in none of the preceding reactions were the stereocenters in the ligands affected, since no formation of other diastereomers was observed. As borane decomplexation reactions are known to occur with retention of configuration at the phosphorus atom,[32−34] the absolute configuration at the phosphorus atom was assigned as *R*. Phosphine−phosphite **1b** was prepared following an analogous procedure from di-*tert*-butylmethylphosphinoborane[30] and (*R*)-phenyloxirane. Ligands **4a** and **4b** were synthesized by reaction of 3-phosphinopropanol with enantiomerically pure (*R*)- and (*S*)-3,3′-bis(trimethylsilyl)-2,2′-binaphthol phosphorochloridites, which were synthesized applying a literature method.[1] The synthesis of the other phosphine−phosphites (**1c**−**1e**, **4c**, **4d,** and **5b**) was published previously.[36]

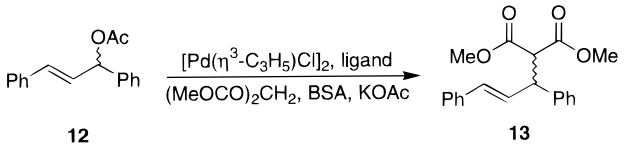
Complex Structure. Since the allylic alkylation proceeds via an (η^3-allyl)palladium species, the cationic (allyl)Pd(ligand) complex was synthesized from ligand **6a** and [(allyl)palladiumchloride]$_2$. The complex was crystallized from dichloromethane and hexanes. We obtained suitable crystals of complex (η^3-allyl)palladium (**6a**) BF_4 for an X-ray crystal structure determination (Figure 1). The complex possesses C_1-symmetry. From the Pd−C1 and Pd−C3 bond distances, 2.176 and 2.220 Å, respectively, it is clear that the allyl moiety is not symmetrically bonded to the palladium center. The Pd−C bond trans to the phosphine is longer caused by the larger trans influence exerted by the phosphine than by the phosphite.[37] Although the phosphite is a better π-acceptor, the σ-donating capacity of the phosphine has a larger influence. In earlier studies, it was suggested that the nucleophilic attack will take place trans to the donor atom with the larger trans influence.[38−40] This implies that, since the nucleophilic attack of the malonate will be far away from the phosphine moiety, the substituents at the phosphine moiety are expected to have a minor influence on the stereoselection, whereas the phosphite moiety is expected to be more important.

The substituent attached to the stereogenic center at the backbone is pointing backward. Since the nucleophilic attack takes place at the front of the allylpalladium complex, the substituent at the backbone is not expected to have a direct influence on the stereoselectivity either. The attack of the nucleophile at the allyl takes place in the vicinity of the biaryl moiety, and it was anticipated that this biaryl moiety would have an influence on the stereoselectivity.

It has been shown by us that the bite angle can have a pronounced effect on the nonsymmetry of the palladium−allyl species.[29] Ligands having a larger bite angle will induce a more distinct embracing of the allyl group by forming a chiral pocket and enhance the steric effects upon attack of the nucleophile. It can thus be anticipated

(32) Jugé, S.; Stéphan, M.; Laffitte, J. A.; Genet, J. P. *Tetrahedron. Lett.* **1990**, *31*, 6357.
(33) Jugé, S.; Merdès, R.; Stéphan, M.; Genet, J. P. *Phosphorus Sulfur Silicon Relat. Elem.* **1993**, *77*, 199.
(34) Jugé, S.; Stéphan, M.; Merdès, R.; Genet, J. P.; Halut-Desportes, D. *J. Chem. Soc., Chem. Commun.* **1993**, 531.
(35) Kyba, E. P.; Rines, S. P. *J. Org. Chem.* **1982**, *47*, 4800.
(36) Deerenberg, S.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **2000**, *19*, 2065.
(37) (a) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089. (b) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. (c) Limaneto, B. S.; Nascimento, J. C.; Franco, D. W. *Polyhedron* **1996**, *15*, 1965.
(38) Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *50*, 4493.
(39) Sprinz, J.; Kiefer, M.; Helmchen, G.; Reggelin, M.; Huttner, G.; Zsolnai, L. *Tetrahedron Lett.* **1994**, *35*, 1523.
(40) von Math, P.; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Rüegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265.

Scheme 3



12 **13**

Table 1. Palladium-Catalyzed Allylic Alkylation of *rac*-1,3-Diphenyl-2-propenyl Acetate[a]

entry	ligand	conv. (%)[b]	ee (%)[c]
1	(R_P,S_C)-**1a**	95	78 (*S*)
2	(S_C)-**1b**	41[d]	64 (*S*)
3	(S_P,S_C)-**1c**	87	69 (*S*)
4	(S_P,S_C)-**1d**	100	65 (*S*)
5	(S_C)-**1e**	100	83 (*S*)
6	(R_P,R_C)-**2**	86	77 (*R*)
7	(R_P,rac$_C$)-**3**	99[e]	11 (S)
8	(R_a)-**4a**	63	43 (*R*)
9	(S_a)-**4b**	64	41 (*S*)
10	(S_P,S_C,R_a)-**4c**	61	21 (*S*)
11	(S_P,S_C,S_a)-**4d**	74	79 (*S*)
12	(R_P,S_C)-**5a**	86	66 (*R*)
13	(S_C)-**5b**	100	82 (*R*)
14	(R_P,S_C)-**6a**	40	15 (*R*)
15	(R_P,R_C)-**6b**	66	35 (*S*)

[a] All reactions were run at an ambient temperature for 1.25 h. Acetate-to-palladium ratio is 100. Malonate-to-palladium ratio is 300. BSA palladium ratio is 300. Ligand-to-palladium ratio is 1. Catalyst preparation time is 0.5. [b] Percentage conversion of acetate determined with GC. [c] Enantiomeric excess determined by HPLC (Daicel OD).[25] Absolute configuration drawn in parentheses. [d] Reaction time was 1 h. [e] Reaction time was 2 h.

that ligands with a larger bite angle will be more enantioselective. Unfortunately, crystal structures of complexes with ligands other than **6a** could not be obtained.

Catalysis. To test the hypothesis proposed in the previous section, the reaction of *rac*-1,3-diphenyl-2-propenyl acetate **12** with dimethyl malonate was performed in CH_2Cl_2 at room temperature in the presence of a catalyst generated in situ from 0.5 mol % of bis[(π-allyl)-palladium chloride] and 1 mol % of the appropriate ligand. The nucleophile was generated from dimethyl malonate in the presence of *N*,*O*-bis(trimethylsilyl)-acetamide (BSA) and a catalytic amount of KOAc (Scheme 3). The results of the catalytic reactions are summarized in Table 1.In general, the reaction proceeds with high conversions (74−100%) within 2 h, as determined by GC, and only the formation of product **13** was observed.

The effects of the stereogenic phosphine moiety are apparent from the enantioselectivities obtained with ligands **1a**−**e**. These ligands all have a phenyl substituent in the backbone, and the configuration of the chiral carbon in the backbone is *S*. The biaryl moiety is a bulky *tert*-butylbisphenol group. Independent of the substituents at the phosphine moiety, either a bulky *tert*-butyl (**1a** and **1b**) or an aryl (**1c**−**1e**), the use of all these ligands yields predominantly the *S* product with similar ee. Ligand **2,** which has the chiral carbon in the *R* configuration, on the contrary, gives the other enantiomer in approximately the same ee as its diastereomeric compound **1a**. These results are in agreement with the expectation that the nucleophilic attack at the allylpalladium takes place trans toward the phosphine and that the phosphine does not effect the enantioselectivity. This is confirmed by the low ee obtained when using ligand **3**, which is racemic at the carbon in the bridge and chiral at the phosphine moiety.

The influence of the phosphite moiety was studied using ligands **4a**−**d** possessing enantiomerically pure bulky binaphthol groups. The use of complexes containing ligands **4a** and **4b**, which are only chiral at the binaphthyl moiety, resulted in 43% and 41% ee, respectively. *R*-configured ligand **4a** afforded the *R* product indicating that the biaryl moiety controls the enantioselectivity of the reaction. The ee obtained using ligands **4a** and **4b** is lower than that using ligand **1e**. Therefore, we conclude that the substituent at the backbone controls not only the configuration of the biphenyl moiety but also affects the position of the phosphite moiety with respect to the Pd center. This is confirmed by the experiments conducted with ligands **4c** and **4d**. The ee's obtained with ligands **4c** and **4d** were 21% and 79%, respectively, and the configuration of the products was *S* in both cases. From these results, we conclude that the biaryl moieties have the same conformations in the palladium complexes of ligands **4d** and **1c**, viz., *S*. [1,41] The stereogenic center at the backbone (*S*) and the chiral binaphthol moiety (*R*) of ligand **4c** give a combination, that causes a different steric surrounding at the Pd complex, yielding a lower ee. Since the configuration of the product is determined by the substituent at the bridge and the bisphenol moiety can interconvert between its atropisomers in the ligand, we propose that in the palladium complex the configuration of the bisphenol moiety is induced by spatial orientation of the substituent at the chiral carbon in the bridge. Thus the configuration of the arylmoiety is controlled by the stereogenic center (*S*) at the backbone. Using ligand **4d** resulted in an increase of the ee compared to **1c**. This is probably due to the bulky trimethylsilyl groups attached to the binaphthyl moiety. We have observed this effect of chiral cooperativity also in the asymmetric hydroformylation reaction using C_2-symmetric chiral diphosphites.[1]

When the phenyl group in the backbone is changed for a methyl substituent (ligands **5a** and **5b**), we obtain the same product enantiomer. The substituent at the backbone is pointing backward and has a minor influence on the stereoselectivity. A methyl group is large enough to control the biphenol moiety, as can be seen for instance from the results obtained using ligands **5a** and **2**. It has to be noted that the substituents hold the same position around the chiral carbon, despite the fact that, according to the Cahn−Ingold−Prelog rules, the absolute configuration of the chiral carbon in the bridge in ligands **5a** and **5b** and **2** is the opposite.[42]

The influence of the bite angle is investigated by using ligands **6a** and **6b**. Compared to **1a** and **2**, ligands **6a** and **6b** have a shorter bridge length and thus a smaller bite angle, and as a result, the nonsymmetry of the alkyl complexes and the steric indications will be smaller.[29] Indeed, the ee in the allylic alkylation is lower. Therefore, a phosphine−phosphite ligand of this type having a smaller bite angle is less enantioselective compared to structurally related ligands with large bite angles.

Conclusions

A series of novel phosphine−phosphite ligands containing a chiral phosphine moiety have been prepared

(41) Nozaki, K.; Sakai, N.; Nanno, T.; Higashijima, T.; Mano, S.; Horiuchi, T.; Takaya, H. *J. Am. Chem. Soc.* **1997**, *119*, 4413−4423.
(42) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

and used as ligands in the palladium catalyzed allylic alkylation reaction. These ligands can be synthesized conveniently and enable systematic investigations of the effect of ligand structure on enantioselectivity. By use of these ligands, moderate to good enantioselectivities are obtained in the reaction of diphenyl-2-propenyl acetate with dimethyl malonate. From results in catalysis, we conclude that the attack of the nucleophile takes place trans toward the phosphine moiety. Therefore, the phosphine moiety has little effect on the chiral induction. The biaryl moiety induces the enantioselectivity controlled by the stereogenic center next to the phosphite moiety. Experiments with ligands having different bridge lengths show that a larger bite angle improves the enantioselectivity.

Experimental Section

General Considerations. All reactions were carried out in flame-dried glasswork using standard Schlenk techniques under an atmosphere of Argon. Toluene was distilled from sodium. THF and Et_2O were distilled from sodium/benzophenone. Triethylamine and diethylamine were distilled from CaH_2. (−)-Sparteine was distilled from CaH_2. Methyliodide was distilled from P_2O_5. PCl_3 was distilled before use. Silica gel 60 (230−400 mesh) was used for column chromatography. Melting points were determined in open capillaries and are uncorrected. NMR spectra were obtained on 300 MHz spectrometers. ^{31}P and ^{13}C spectra were measured ^1H-decoupled unless stated otherwise. Gas chromatographic analyses were conducted with a DB-1 J&W 30m column (split/splitless injector, film thickness 3.0 μm, carrier gas 70 kPa He, FID detector). Enantiomeric excesses were determined using a Daicel OD column.

Allylic Alkylation Experiments. A degassed solution of 0.005 mmol of $[Pd(\eta^3\text{-}C_3H_5)Cl_2]_2$ in CH_2Cl_2 (1.5 mL), 0.01 mmol of ligand, and 0.5 mmol of decane was stirred for 0.5 h. Subsequently, a solution of 1 mmol of *rac*-1,3-diphenyl-2-propenyl acetate in CH_2Cl_2 (0.763 mL; 1.31 M), 3 mmol of dimethyl malonate, 3 mmol of *N,O*-bis(trimethylsilyl)acetamide (BSA), and a pinch of KOAc were added. The reaction mixture was stirred at room temperature. To determine the conversion by GC, a sample was quenched with a dibenzylideneacetone (DBA) solution. To determine the ee by HPLC (Daicel OD, 0.5% 2-propanol/hexane, flow = 0.5 mL/min, t_R = 35.4 min (*R*), t_R = 38.7 min (*S*), λ = 254 nm), a sample was filtered over basic alumina using dichloromethane as eluent.

(R_P,*R*)-3-(*tert*-Butylphenylphosphinoborane)-1-phenyl-1-propanol (9a). Phosphinoborane **8** (1.06 g, 5.48 mmol) was azeotropically dried with toluene (2 × 5 mL), dissolved in THF (10 mL), and the solution was cooled to −25 °C. *sec*-BuLi (4.35 mL, 1.26 M solution in cyclohexane) was added to this solution and stirring was continued for 10 min. The cooling bath was removed, and the solution was stirred at room temperature for 1 h. This solution was added dropwise to a solution of (*S*)-(−)-styrene oxide (0.63 mL, 5.48 mmol) in THF (10 mL) at −60 °C. The reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was quenched with water (15 mL) and extracted with Et_2O (3 × 60 mL). The combined extracts were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (eluents: first, toluene; second, 10% EtOAc in toluene) giving **9a** (1.64 g, 5.23 mmol, 95%) as a white solid: ^1H NMR ($CDCl_3$) δ 7.62 (m, 2H), 7.55−7.40 (m, 3H), 7.37−7.22 (m, 5H), 4.80 (m, 1H), 2.43 (m, 1H), 2.09 (m, 1H), 2.02−1.82 (m, 2H), 1.65 (m, 1H), 1.09 (d, 9H, J = 13.6 Hz), 1.7−0.2 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 143.58 (Cq), 133.27 (d, J = 7.9 Hz, CH), 130.88 (d, J = 2.3 Hz, CH), 128.28 (CH), 128.11 (d, J = 9.2 Hz, CH), 127.47 (CH), 125.47 (CH), 125.35 (d, J = 23.7 Hz, Cq), 74.18 (d, J = 13.0 Hz, CH), 31.99 (CH_3), 28.83 (d, J = 33.0 Hz, CH_2), 25.19 (d, J = 2.0, CH_3), 14.23 (d, J = 35.0 Hz, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 32.34 (m); R_f = 0.09 (toluene); mp = 108 °C; $[\alpha]_D^{21}{}_{589}$ = +29.0 (*c* 1.13; MeOH); MS HR−FAB [found 315.2057; $C_{19}H_{29}BOP$ (MH^+) requires 315.2053]. Anal. Calcd for $C_{19}H_{28}BOP$: C, 72.63; H, 8.98. Found: C, 72.70; H, 9.03.

(R_P,*S*)-3-(*tert*-Butylphenylphosphinoborane)-1-phenyl-1-propanol (9b). This compound was prepared as described for **9a**, using phosphinoborane **8** (1.04 g, 5.34 mmol), *sec*-BuLi (4.24 mL, 1.26 M solution in cyclohexane), and (*R*)-(+)-styrene oxide (610 μL, 5.34 mmol). The product was purified by column chromatography (eluents: first, toluene; second, 10% EtOAc in toluene), giving **9b** (1.48 g, 4.72 mmol, 88%) as a white solid: ^1H NMR ($CDCl_3$) δ 7.63 (m, 2H), 7.54−7.15 (m, 8H), 4.69 (m, 1H), 2.15 (m, 2H), 1.97 (m, 1H), 1.81 (bs, 1H), 1.75 (m, 1H), 1.07 (d, 9H, J = 13.8 Hz), 1.7−0.2 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 143.36 (Cq), 133.16 (d, J = 7.7 Hz, CH), 130.91 (d, J = 2.5 Hz, CH), 128.34 (CH), 128.08 (d, J = 9.2 Hz, CH), 127.60 (CH), 125.75 (d, J = 48.4 Hz, Cq), 125.68 (CH), 74.22 (d, J = 12.7 Hz, CH), 32.05 CH_3), 28.86 (d, J = 32.8 Hz, CH_2), 25.22 (d, J = 2.1 Hz, CH_3), 14.28 (d, J = 34.8 Hz, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 32.39 (m). R_f = 0.13 (eluent: toluene). mp = 93 °C; $[\alpha]_D^{21}{}_{589}$ = −14.1 (*c* 1.03; MeOH); MS HR−FAB [found 315.1873; $C_{19}H_{29}BOP$ (MH^+) requires 315.2053]. Anal. Calcd for $C_{19}H_{28}BOP$: C, 72.63; H, 8.98. Found: C, 72.71; H, 9.10.

(R_P,*S*)-4-(*tert*-Butylphenylphosphinoborane)-2-butanol (9c). This compound was prepared as described for **9a**, using phosphinoborane **8** (881 mg, 4.54 mmol), *sec*-BuLi (3.36 mL, 1.35 M solution in cyclohexane), and (*S*)-(−)-propene oxide (320 μL, 4.54 mmol). The product was purified by column chromatography (eluents: first, toluene; second, 25% EtOAc/toluene), giving **9c** (0.21 g, 0.84 mmol, 18%) as an yellow oil: ^1H NMR ($CDCl_3$) δ 7.72 (m, 2H), 7.55−7.40 (m, 3H), 3.84 (m, 1H), 2.47 (m, 1H), 1.90−1.70 (m, 2H), 1.56−1.40 (m, 2H), 1.19 (d, 3H, J = 6.2 Hz), 1.11 (d, 9H, J = 13.7 Hz), 1.7−0.2 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 133.70 (d, J = 7.3 Hz, CH), 131.33 (CH), 128.56 (d, J = 9.7 Hz, CH), 126.15 (Cq), 68.65 (d, J = 13.4 Hz, CH), 32.43 (CH_3), 29.22 (d, J = 33.0 Hz, CH_2), 25.63 (CH_3), 23.72 (CH_3), 15.20 (CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 32.05 (m); R_f = 0.04 (eluent: toluene); $[\alpha]_D^{21}{}_{589}$ = −21.8 (*c* 1.01; $CHCl_3$); MS HR−FAB [found 251.1732; $C_{14}H_{25}BOP$ (M^+−H) requires 251.1736]. Anal. Calcd for $C_{14}H_{26}BOP$: C, 66.69; H, 10.39. Found: C, 66.81; H, 10.70.

(R_P,*rac*$_C$)-3-(*tert*-Butylphenylphosphinoborane)-1-phenyl-1-propanol (9d). This compound was prepared as described for **9a**, using phosphinoborane **8** (875 mg, 4.51 mmol), *sec*-BuLi (3.34 mL, 1.35M solution in cyclohexane), and (*rac*)-(±)-styrene oxide (515 μL, 4.51 mmol). The product was purified by column chromatography (eluent: toluene), giving **9d** (1.44 g, 4.59 mmol, 100%) as a yellow oil: ^1H NMR ($CDCl_3$) δ 7.62 (t, 4H, J = 7.6 Hz), 7.52−7.15 (m, 16H), 4.80 (dd, 1H, J = 4.1, 8.2 Hz), 4.68 (m, 1H), 2.43 (m, 1H), 2.20−1.50 (m, 9H), 1.10 (d, 9H, J = 5.6 Hz), 1.06 (d, 9H, J = 5.6 Hz), 1.7−0.2 (m, 6H);^{13}C NMR ($CDCl_3$) (R_P,R_C) 143.74 (Cq), 143.55 (Cq), 133.43 (d, J = 7.5 Hz, CH), 133.33 (d, J = 8.1 Hz, CH), 131.48 (d, J = 2.7 Hz, CH), 131.07 (d, J = 2.7 Hz, CH), 128.50 (CH), 128.46 (CH), 128.25 (d, J = 9.2 Hz, CH), 127.70 (d, J = 9.1 Hz, CH), 126.26 (Cq), 125.85 (CH), 125.63 (CH), 125.22 (Cq), 74.38 (d, J = 12.6 Hz, CH), 32.22 (CH_3), 32.16 (CH_3), 29.01 (d, J = 31.6 Hz, CH_2), 25.35 (d, J = 1.6, CH_3), 14.45 (d, J = 35.1 Hz, CH_2), 14.41 (d, J = 35.2 Hz, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 32.60 (m); R_f = 0.14 (eluent: toluene); $[\alpha]_D^{21}{}_{589}$ = +7.6 (*c* 1.06; $CHCl_3$); MS HR−FAB [found 315.2005; $C_{19}H_{29}BOP$ (MH^+) requires 315.2049]. Anal. Calcd for $C_{19}H_{28}BOP$: C, 72.63; H, 8.98. Found: C, 72.65; H, 9.01.

(R_P,*S*)-2-(*tert*-Butylphenylphosphinoborane)-1-phenylethanol (9e). *n*-Buthyllitium (5.11 mL, 2.32M solution in hexane) was added dropwise to a cooled solution (−78 °C) of phosphinoborane **7** (2.14 g, 11.9 mmol) and (−)-sparteine (3.54 mL, 15.4 mmol) in Et_2O (50 mL). The yellow solution was allowed to warm to room temperature. A thick suspension of a white precipitate was formed. After the reaction mixture had been stirred for 1 h at room temperature, it was cooled again to −78 °C and (*S*)-(−)-styrene oxide (1.76 mL, 15.4 mmol) was added. The solution was allowed to warm to −20 °C slowly (2−3 h) and was stirred at −20 °C overnight. The reaction

mixture was washed with 5% H_2SO_4 (aq, 34 mL), and the aqueous phase was extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, and filtered through a short plug of silica gel. Concentration in vacuo and purification by column chromatography (eluents: first, 5% EtOAc/hexanes; second, 20% EtOAc/hexanes) gave **9e** as a white solid (2.42 g, 8.07 mmol, 68%): ^{1}H NMR ($CDCl_3$) δ 7.76 (m, 2H), 7.60−7.40 (m, 3H), 7.35−7.25 (m and d, 5H, J = 4.5 Hz), 4.81 (dt, 1H, J = 1.7, 9.5 Hz), 3.64 (bs, 1H), 2.64 (t, 1H, J = 14.8 Hz), 2.37 (ddd, 1H, J = 3.3, 9.5, 14.9 Hz), 1.13 (d, 9H, J = 14.2 Hz), 1.7−0.2 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 144.34 (d, J = 10.6 Hz, Cq), 133.6 (d, J = 8.3 Hz, CH), 131.77 (CH), 128.78 (d, J = 14.6 Hz, CH), 128.77 (CH), 127.90 (CH), 125.55 (CH), 125.42 (Cq), 69.41 (CH), 30.65 (d, J = 30.1 Hz), 29.41 (d, J = 33.2 Hz), 25.49 (CH_3); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 27.72 (d, J = 70.6 Hz); R_f = 0.06 (eluent: 5% EtOAc/hexane); mp = 107 °C; $[\alpha]_D^{21}{}_{589} = -33.1$ (c 1.14; MeOH); MS HR−FAB [found 301.1879; $C_{18}H_{27}$BOP (MH^+) requires 301.1893]. Anal. Calcd for $C_{18}H_{26}$BOP: C, 72.02; H, 8.73. Found: C, 72.05; H, 8.74.

(R_P,*R*)-2-(*tert*-Butylphenylphosphinoborane)-1-phenylethanol (9f). This compound was prepared as described for **9e**, using *t*-butylphenylphosphinoborane **7** (2.17 g, 12.1 mmol), (−)-sparteine (3.62 mL, 15.6 mmol), *n*-BuLi (5.06 mL, 2.36 M solution in hexane) and (*R*)−(+)-styrene oxide (1.78 mL, 15.6 mmol). Purification by column chromatography (eluents: first, 5% EtOAc/hexanes; second, 20% EtOAc/hexanes) gave **9f** as a colorless oil (2.35 g, 7.80 mmol, 65%): ^{1}H NMR ($CDCl_3$) δ 7.80 (m, 2H), 7.55−7.26 (m, 8H), 5.32 (m, 1H), 2.63 (m, 1H), 2.56 (bs, 1H), 2.30 (ddd, 1H, J = 2.0, 8.6, 14.9 Hz), 1.12 (d, 9H, J = 13.9 Hz), 1.7−0.2 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 144.78 (d, J = 10.6 Hz, Cq), 133.6 (d, J = 8.3 Hz, CH), 131.50 (CH), 128.84 (CH), 128.42 (d, J = 9.1 Hz, CH), 127.93 (CH), 127.19 (d, J = 49.8 Hz, CH), 125.67 (CH), 70.29 (CH), 30.61 (d, J = 30.1 Hz), 29.67 (d, J = 33.4 Hz), 25.67 (CH_3); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 27.03 (m); R_f = 0.08 (eluent: 5% EtOAc/hexane); $[\alpha]_D^{21}{}_{589} = -45.4$ (c 1.20; MeOH); MS HR−FAB [found 323.1690; $C_{18}H_{26}$BOPNa (MNa^+) requires 323.1712]. Anal. Calcd for $C_{18}H_{26}$BOP: C, 72.02; H, 8.73. Found: C, 71.77; H, 8.72.

(*S*)-2-(Di(*tert*-butyl)phosphinoborane)-1-phenyl-1-propanol (9 g). This compound was prepared as described for **9a**, using di-*tert*-butylmethylphosphinoborane (960 mg, 5.52 mmol), *sec*-BuLi (4.09 mL, 1.35 M solution in cyclohexane), and (*R*)-(+)-styrene oxide (630 μL, 5.52 mmol). The product was purified by column chromatography (eluents: first, toluene; second, 10% EtOAc/toluene), giving **9g** (540 mg, 1.84 mmol, 33%) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.38−7.32 (m, 5H), 4.72 (dd, 1H, J = 5.6, 6.9 Hz), 2.15−2.00 (m, 3H), 1.82 (m, 1H), 1.60 (m, 1H), 1.26 (d, 9H, J = 12.3 Hz), 1.22 (d, 9H, J = 11.9 Hz), 1.7−0.2 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 143.63 (Cq), 128.32 (CH), 127.50 (CH), 125.60 (CH), 74.75 (d, J = 11.9 Hz, CH), 33.93 (CH_3), 31.92 (dd, J = 7.5, 27.3 Hz, CH_2), 27.59 (CH_3), 27.35 (CH_3), 13.57 (d, J = 30.4 Hz, CH_2); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 44.55 (m); R_f = 0.35 (eluent: 10% EtOAc/toluene); $[\alpha]_D^{21}{}_{589} = -22.5$ (c 1.01; $CHCl_3$); MS HR−FAB [found 295.2399; $C_{17}H_{33}$BOP (MH^+) requires 295.2365]. Anal. Calcd for $C_{17}H_{32}$BOP: C, 69.40; H, 10.96. Found: C, 69.95; H, 10.98.

(R_P,*R*)-[3-(*tert*-Butylphenylphosphinoborane)-1-phenylpropyl]-1-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite (11a). Phosphino alcohol **9a** (557 mg, 1.77 mmol) was azeotropically dried with toluene (2 × 5 mL) and dissolved in toluene (75 mL) and NEt_3 (0.52 mL, 3.7 mmol), and the solution was cooled to −20 °C. A solution of 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite **10** (883 mg, 1.86 mmol) in toluene (75 mL) was added dropwise, and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was filtered over Celite and concentrated in vacuo. Filtration over a short column of silica gel (eluent: 20% hexane/toluene) afforded **11a** (1.10 g, 1.46 mmol, 82%) as a white foam: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 145.60 (s), 26.03 (m); R_f = 0.75 (eluent: 20% hexane/toluene). Compound **11a** was used immediately.

(R_P,*S*)-[3-(*tert*-Butylphenylphosphinoborane)-1-phenylpropyl]-1-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite (11b). This compound was prepared as described for **11a**, using phosphino alcohol **9b** (556 mg, 1.77 mmol), NEt_3 (0.52 mL, 3.7 mmol), and 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite **10** (881 mg, 1.86 mmol). The product was purified by column chromatography (eluent: 10% hexane/toluene), giving **11b** (1.16 g, 1.54 mmol, 87%) as a white foam: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 141.00 (s), 27.56 (m); R_f = 0.70 (eluent: 20% hexane/toluene). Compound **11b** was used immediately without further purification.

(R_P,*S*)-[4-(*tert*-Butylphenylphosphinoborane)-2-butyl]-2-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite (11c). This compound was prepared as described for **11a**, using phosphino alcohol **9c** (0.21 g, 0.84 mmol), NEt_3 (0.25 mL, 1.76 mmol), and 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite **10** (0.42 g, 0.88 mmol). The product was purified by column chromatography (eluent: 10% hexane/toluene), giving **11c** (553 mg, 0.802 mmol, 95%) as a white foam: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 145.53 (s), 32.50 (m); R_f = 0.91 (20% hexane/toluene). Compound **11c** was used immediately without further purification.

(R_P,rac$_C$)-[3-(*tert*-Butylphenylphosphinoborane)-1-phenylpropyl]-1-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite (11d). This compound was prepared as described for **11a**, using phosphino alcohol **9d** (466 mg, 1.48 mmol), NEt_3 (0.43 mL, 3.1 mmol), and 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite **10** (738 mg, 1.56 mmol). The product was purified by column chromatography (eluent: 10% hexane/toluene), giving **11d** (1.07 g, 1.42 mmol, 96%) as a white foam: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 144.20 (s (*R*,*R*)), 143.26 (s (*R*,*S*)), 32.50 (m); R_f = 0.79 (20% hexane/toluene). Compound **11d** was used immediately without further purification.

(R_P,*S*)-[2-(*tert*-Butylphenylphosphinoborane)-1-phenylethyl]-1-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)-phosphite (11e). This compound was prepared as described for **11a**, using phosphino alcohol **9e** (0.92 g, 3.1 mmol), NEt_3 (0.90 mL, 6.4 mmol), and 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite **10** (1.53 g, 3.22 mmol). The product was purified by column chromatography (eluent: 20% hexane/toluene), giving **11e** (1.89 g, 2.56 mmol, 83%) as a white foam: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 145.52 (s), 26.25 (bs); R_f = 0.83 (eluent: 20% hexane/toluene). Compound **11e** was used immediately without further purification.

(R_P,*R*)-[2-(*tert*-Butylphenylphosphinoborane)-1-phenylethyl]-1-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)-phosphite (11f). This compound was prepared as described for **11a**, using phosphino alcohol **9f** (349 mg, 1.16 mmol), NEt_3 (0.34 mL, 2.4 mmol), and 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite **10** (579 mg, 1.22 mmol). The product was purified by column chromatography (eluent: 10% hexane/toluene), giving **9f** (758 mg, 1.03 mmol, 89%) as a white solid: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 141.04 (s), 27.85 (s); R_f = 0.74 (eluent: 10% hexane/toluene). Compound **11f** was used immediately without further purification.

(R_P,*R*)-[3-(Di(*tert*-butyl)phosphinoborane)-1-phenylpropyl]-1-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)-phosphite (11 g). This compound was prepared as described for **11a**, using phosphino alcohol **9g** (0.30 g, 1.02 mmol), NEt_3 (0.30 mL, 2.14 mmol), and 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite **10** (0.51 g, 1.07 mmol). The product was purified by column chromatography (eluent: 10% hexane/toluene), giving **11g** (0.60 g, 0.82 mmol, 80%) as a white foam: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 143.59 (s), 44.19 (m); R_f = 0.72 (20% hexane/toluene). Compound **11g** was used immediately without further purification.

(R_P,*S*)-[3-(*tert*-Butylphenylphosphino)-1-phenylpropyl]-1-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite (1a). Phosphinoborane **11b** (1.04 g, 1.43 mmol) was dissolved in $HNEt_2$ (35 mL) and stirred overnight at 50 °C. The reaction mixture was concentrated in vacuo. Filtration over silica gel (eluent: toluene) gave **1a** (880 mg, 1.19 mmol, 83%) as a white foam: ^{1}H NMR ($CDCl_3$) δ 7.65 (m, 2H), 7.55−7.32 (m, 12H), 5.49 (m, 1H), 2.55 (m, 1H), 2.37 (m, 1H), 2.10 (m, 1H), 1.91 (m, 1H), 1.63 (s, 9H), 1.60 (s, 9H), 1.59 (s, 9H), 1.54 (s, 9H), 1.08 (d, 9H, J = 11.9 Hz); ^{13}C NMR ($CDCl_3$) δ 146.15 (Cq), 145.59 (Cq), 140.35 (Cq), 139.98 (d, J = 2.7 Hz, Cq), 139.07 (Cq), 134.13 (d, J = 19.8 Hz, CH), 133.46 (Cq),

133.20 (d, J = 2.2 Hz, Cq), 131.93 (d, J = 2.9 Hz, Cq), 128.46 (CH), 127.99 (CH), 127.50 (CH), 127.32 (d, J = 13.3 Hz, CH), 127.11 (d, J = 13.7 Hz, CH), 125.89 (CH), 124.69 (CH), 123.67 (CH), 77.63 (d, J = 18.2 Hz, CH), 35.18 (CH_3), 34.73 (CH_3), 34.48 (CH_3), 34.24 (CH_3), 31.81 (d, J = 17.1 Hz, CH_2), 31.39 (CH_3), 31.20 (CH_3), 31.10 (d, J = 4.7 Hz, CH_3), 30.22 (CH_3), 29.49 (CH_3), 28.45 (d, J = 12.4 Hz, CH_2), 26.87 (d, J = 13.9 Hz, CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 144.25 (s), 3.27 (s). R_f = 0.82 (eluent: toluene); mp = 75 °C; $[\alpha]_D^{21}{}_{589}$ = +41.8 (*c* 1.01; $CHCl_3$); MS HR−FAB [found 739.4401; $C_{47}H_{64}O_3P_2$ (MH^+) requires 739.4409]. Anal. Calcd for $C_{47}H_{64}O_3P_2$: C, 76.39; H, 8.73. Found: C, 76.11; H, 8.89.

(R_P,*R*)-[3-(Di(*tert*-butyl)phosphino)-1-phenylpropyl]-1-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite (1b). This compound was prepared as described for **1a**, using phosphinoborane **11g** (0.60 g, 0.82 mmol) and $HNEt_2$ (30 mL). Filtration over silica gel (eluent: toluene) gave **1b** (0.356 g, 0.50 mmol, 61%) as a white foam: ^1H NMR ($CDCl_3$) δ 7.55−7.43 (m, 3H), 7.42−7.15 (m, 5H), 7.14−6.93 (m, 1H), 5.23 (m, 1H), 3.80 (m, 1H), 2.77 (dd, 1H, J = 7.1, 14.2 Hz), 2.39−2.10 (m, 2H), 1.52−1.35 (m, 36H), 1.20−0.98 (m, 18H), 1.7−0.2 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 146.40−132.53 (Cq), 128.88−123.87 (CH), 78.80 and 78.03 (dd, J = 7.5, 16.5 Hz, dd, J = 7.3, 13.7 Hz, CH), 35.19 (CH_3), 35.12 (CH_3), 35.09 (CH_3), 34.49 (CH_3), 32.07 and 31.71 (d, J = 6.7 Hz, d, J = 7.1 Hz, CH_2), 31.45 (CH_3), 31.19 (CH_3), 31.01 (CH_3), 30.86 (CH_3), 29.44 and 29.26 (d, J = 6.2 Hz, d, J = 6.2 Hz, CH_3), 15.85 and 12.83 (d, J = 19.8 Hz, d, J = 30.0 Hz, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 143.70 (s), 143.57 (s), 32.75 (s), 32.62 (s); R_f = 0.80 (eluent: toluene); mp = 61 °C; $[\alpha]_D^{21}{}_{589}$ = +25.0 (*c* 1.02; $CHCl_3$); MS HR−FAB [found 719.4733; $C_{45}H_{69}O_3P_2$ (MH^+) requires 719.4722]. Anal. Calcd for $C_{45}H_{68}O_3P_2$: C, 75.17; H, 9.53. Found: C, 74.43; H, 9.73.

(R_P,*R*)-[3-(*tert*-Butylphenylphosphino)-1-phenylpropyl]-1-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite (2). This compound was prepared as described for **1a**, using phosphinoborane **11a** (1.07 g, 1.48 mmol) and $HNEt_2$ (35 mL). Filtration over silica gel (eluent: toluene) gave **2** (930 mg, 1.26 mmol, 86%) as a white foam: ^1H NMR ($CDCl_3$) δ 7.55 (dd, 2H, J = 2.4, 6.2 Hz), 7.45−7.20 (m, 12H), 5.32 (m, 1H), 2.45 (m, 1H), 2.10 (m, 1H), 1.97 (m, 2H), 1.51 (s, 9H), 1.48 (s, 9H), 1.47 (s, 9H), 1.46 (s, 9H), 0.97 (d, 9H, J = 11.9 Hz); ^{13}C NMR ($CDCl_3$) δ 146.15 (Cq), 145.99 (Cq), 141.05 (d, J = 1.7 Hz, Cq), 140.12 (d, J = 1.7 Hz, Cq), 139.83 (Cq), 134.62 (d, J = 19.2 Hz, Cq), 133.87 (d, J = 19.3 Hz, CH), 132.77 (d, J = 20.4 Hz, Cq), 132.72 (d, J = 20.2 Hz, Cq), 128.92 (CH), 128.60 (CH), 127.91 (d, J = 31.5 Hz, CH), 127.81 (d, J = 31.6 Hz, CH), 126.78 (CH), 126.37 (CH), 126.30 (CH), 125.20 (CH), 124.04 (d, J = 13.6 Hz, CH), 78.76 (dd, J = 8.7, 14.9 Hz, CH), 35.16 (Cq), 35.13 (Cq), 34.86 (Cq), 34.29 (Cq), 31.49 (CH_3), 30.93 (CH_3), 29.61 (CH_3), 28.67 (d, J = 11.6 Hz, CH_2), 27.22 (d, J = 13.1 Hz, CH_3), 15.27 (d, J = 15.5 Hz, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 144.24 (s), 4.50 (m); R_f = 0.82 (eluent: toluene); mp = 82 °C; $[\alpha]_D^{21}{}_{589}$ = −11.0 (*c* 0.98; $CHCl_3$); MS HR−FAB [found 739.4437; $C_{47}H_{65}BO_3P_2$ (MH^+) requires 739.4409]. Anal. Calcd for $C_{47}H_{64}O_3P_2$: C, 76.39; H, 8.73. Found: C, 76.52; H, 9.02.

(R_P,rac$_C$)-[3-(*tert*-Butylphenylphosphino)-1-phenylpropyl]-1-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)-phosphite (3). This compound was prepared as described for **1a**, using phosphinoborane **11d** (990 mg, 1.32 mmol) and $HNEt_2$ (40 mL). Filtration over silica gel (eluent: toluene) gave **3** (717 mg, 0.972 mmol, 74%) as a white foam: ^1H NMR ($CDCl_3$) δ 7.43−7.36 (m, 6H), 7.35−7.23 (m, 12H), 7.22−7.10 (m, 10H), 5.26−5.17 (m, 2H), 2.18−1.97 (m, 2H), 1.95−1.79 (m, 2H), 1.54−1.25 (m, 4H), 1.41−1.27 (m, 72H), 0.87 (d, 18H, J = 12.1 Hz); ^{13}C NMR ($CDCl_3$) δ 146.02−132.42 (Cq),133.91 (d, J = 18.9 Hz, CH), 133.77 (d, J = 18.9 Hz, CH), 128.83−123.85 (CH), 78.68 (m, CH), 35.02 (CH_3), 34.43 (CH_3), 31.37 (CH_3), 30.75 (CH_3), 28.57 (d, J = 11.2 Hz, CH_2), 28.53 (d, J = 11.5 Hz, CH_2), 27.08 (d, J = 13.2 Hz, (CH_3), 15.57 (d, J = 15.5 Hz, CH_2), 15.13 (d, J = 15.3 Hz, CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 143.78 (s (*R*,*S*)), 143.14 (s (*R*,*R*)), 3.12 (s, (*R*,*S*)), 1.75 (s, (*R*,*R*)); R_f = 0.82 (eluent: toluene); mp = 57 °C; $[\alpha]_D^{21}{}_{589}$ = +23.7 (*c* 1.00; $CHCl_3$); MS HR−FAB [found 739.4401; $C_{47}H_{65}O_3P_2$ (MH^+) requires 739.4409]. Anal. Calcd for $C_{47}H_{64}O_3P_2$: C, 76.39; H, 8.73. Found: C, 76.22; H, 8.86.

(*R*)-[3-(Diphenylphosphino)propyl]-1-(3,3′-bis(trimethylsilyl)-1,1′-binaphthyl-2,2′-diyl)phosphite (4a). A solution of 3-diphenylphosphino-1-propanol (0.122 g, 0.500 mmol) in THF (4 mL) was added dropwise to a solution of freshly prepared (*R*)-3,3′-bis(trimethylsilyl)-2,2′-binaphthol phosphorochloridite (0.50 mmol) and NEt_3 (0.28 mL, 2.0 mmol) in toluene (5 mL) at 0 °C, and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was filtrated and concentrated in vacuo. Filtration over a short column of silica (eluent: toluene/hexanes = 9/1) afforded **4a** (0.180 g, 0.256 mmol, 51%) as an oil: ^1H NMR ($CDCl_3$) δ 8.35 (dd, 1H, J = 4.5 and 7.6 Hz, Ar−H), 8.00−7.75 (m, 6H, Ar−H), 7.46−7.04 (m, 20H, Ar−H), 4.72 (m, 1H, C*H*OP), 1.80 (m, 2H, PCH_2CH_2), 1.52 (m, 2H, PCH_2CH_2), 0.35 (s, 9H, $Si(CH_3)_3$), 0.20 (s, 9H, $Si(CH_3)_3$); ^{31}P NMR ($CDCl_3$) 134.74 (s), −15.49 (s); ^{13}C NMR ($CDCl_3$) δ 153.13 (Cq), 152.19 (Cq), 138.69−122.17 (Cq's), 137.30−125.02 (CH), 65.62 (d, J = 14.6 Hz, CH_2), 27.63 (d, J = 15.9 Hz, CH_2), 24.36 (d, J = 11.0 Hz, CH_2), 0.33 (CH_3), 0.16 (CH_3); $[\alpha]_D^{25}$ = −295 (*c* 1.0, $CHCl_3$); MS HR−FAB [found 703.2324; $C_{41}H_{45}O_3P_2Si_2$ ($M^{+\cdot}$+H) requires 703.2382]. Anal. Calcd for $C_{41}H_{44}O_3P_2Si_2$: C, 70.06; H, 6.31 Found: C, 69.98 C; H, 6.34.

(*S*)-[3-(Diphenylphosphino)propyl]-1-(3,3′-bis(trimethylsilyl)-1,1′-binaphthyl-2,2′-diyl)phosphite (4b). A solution of 3-diphenylphosphino-1-propanol (0.122 g, 0.500 mmol) in THF (4 mL) was added dropwise to a solution of freshly prepared (*S*)-3,3′-bis(trimethylsilyl)-2,2′-binaphthol phosphorochloridite (0.50 mmol) and NEt_3 (0.28 mL, 2.0 mmol) in toluene (5 mL) at 0 °C, and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was filtrated and concentrated in vacuo. Filtration over a short column of silica (eluent: toluene/hexanes = 9/1) afforded **4b** (0.166 g, 0.236 mmol, 47%) as an oil: ^1H NMR ($CDCl_3$) δ 8.35 (dd, 1H, J = 4.5 and 7.6 Hz, Ar−H), 8.00−7.75 (m, 6H, Ar−H), 7.46−7.04 (m, 20H, Ar−H), 4.72 (m, 1H, C*H*OP), 1.80 (m, 2H, PCH_2CH_2), 1.52 (m, 2H, PCH_2CH_2), 0.35 (s, 9H, $Si(CH_3)_3$), 0.20 (s, 9H, $Si(CH_3)_3$); ^{31}P NMR ($CDCl_3$) 134.74 (s), −15.48 (s); ^{13}C NMR ($CDCl_3$) δ 153.17 (Cq), 152.19 (Cq), 138.73−122.24 (Cq's), 137.20−124.15 (CH), 65.65 (d, J = 14.6 Hz, CH_2), 27.61 (d, J = 15.9 Hz, CH_2), 24.34 (d, J = 11.0 Hz, CH_2), 0.32 (CH_3), 0.16 (CH_3); $[\alpha]_D^{25}$ = 302 (*c* 1.2, $CHCl_3$); MS HR−FAB [found 703.2324; $C_{41}H_{45}O_3P_2Si_2$ ($M^{+\cdot}$+H) requires 703.2382]. Anal. Calcd for $C_{41}H_{44}O_3P_2Si_2$: C, 70.06; H, 6.31 Found: C, 69.99; H, 6.36.

(R_P,*S*)-[4-(*tert*-Butylphenylphosphino)-2-butyl]-2-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite (5a). This compound was prepared as described for **1a**, using phosphinoborane **11c** (0.50 g, 0.73 mmol) and $HNEt_2$ (20 mL). Filtration over silica gel (eluent: toluene) gave **5a** (346 mg, 0.512 mmol, 71%) as a white foam: ^1H NMR ($CDCl_3$) δ 7.62−7.37 (m, 5H), 7.31 (m, 1H), 7.21−7.10 (m, 3H), 4.48 (m, 1H), 2.14 (m, 1H), 1.83 (m, 1H), 1.55−1.20 (m, 2H), 1.54−1.30 (m, 36H), 1.25 (m, 3H), 1.00 (m, 9H);^{13}C NMR ($CDCl_3$) δ 146.03 (Cq), 145.64 (Cq), 139.82 (d, J = 6.8 Hz, Cq), 133.94 (d, J = 17.4 Hz, CH), 132.70 (Cq), 132.66 (Cq), 128.12 (CH), 128.00 (m, CH), 126.29 (d, J = 5.3 Hz, CH), 123.91 (CH), 73.00 (m, CH), 35.18 (CH_3), 34.41 (CH_3), 31.32 (CH_3), 31.06 (CH_3), 29.48 (CH_2), 28.81 (CH_2), 26.75 (m, CH_3), 22.05 (CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 146.27 (s), 3.12 (s); R_f = 0.80 (eluent: toluene); mp = 56 °C; $[\alpha]_D^{21}{}_{589}$ = +14.0 (*c* 1.06; $CHCl_3$); MS FAB [found 677.4201; $C_{42}H_{63}O_3P_2$ (MH^+) requires 647.4252]. Anal. Calcd for $C_{42}H_{62}O_3P_2$: C, 74.52; H, 9.23. Found: C, 74.25; H, 9.34.

(R_P,*S*)-[2-(*tert*-Butylphenylphosphino)-1-phenylethyl]-1-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite (6a). This compound was prepared as described for **1a**, using phosphinoborane **11e** (1.89 g, 2.56 mmol) and $HNEt_2$ (15 mL). Filtration over silica gel (eluent: toluene) gave **6a** (489 mg, 0.675 mmol, 26%) as a white solid: ^1H NMR ($CDCl_3$) δ 7.49 (t, 2H, J = 2.7 Hz), 7.37−7.18 (m, 7H), 7.16−7.05 (m, 5H), 5.47 (m, 1H), 2.71 (m, 1H), 2.55 (dd, 1H, J = 5.2, 13.6 Hz), 1.48 (s, 9H), 1.47 (s, 9H), 1.44 (s, 9H), 1.34 (s, 9H), 1.00 (d, 9H, J = 12.1 Hz); ^{13}C NMR ($CDCl_3$) δ 146.20 (d, J = 6.8 Hz, Cq), 146.08 (d, J = 18.1 Hz, Cq) 145.87 (Cq), 140.96 (Cq),

140.00 (m, Cq), 134.58 (d, J = 18.1 Hz, Cq), 134.24 (d, J = 20.4 Hz, CH), 132.95 (dd, J = 3.8, 33.2 Hz, Cq), 128.78 (d, J = 34.0 Hz, CH), 128.22 (CH), 127.54 (d, J = 24.9 Hz, CH), 127.51 (d, J = 24.9 Hz, CH), 126.50 (d, J = 15.1 Hz, CH), 125.32 (CH), 124.15 (d, J = 25.7 Hz, CH), 78.32 (dd, J = 9.9, 31.8 Hz, CH), 35.28 (d, J = 7.1 Hz, CH_3), 34.63 (CH_3), 32.37 (d, J = 17.3 Hz, CH_3), 31.67 (CH_3), 31.14 (CH_3), 29.07 (d, J = 11.6 Hz, CH_3), 27.56 (d, J = 14.1 Hz, (CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 143.97 (d, J = 9.0 Hz), −4.56 (d, J = 9.0 Hz); R_f = 0.82 (eluent: toluene); mp = 76 °C; $[\alpha]_D^{21}{}_{589}$ = −41.2 (c 1.09; $CHCl_3$); MS HR−FAB [found 725.4255; $C_{46}H_{63}O_3P_2$ (MH^+) requires 725.4252]. Anal. Calcd for $C_{46}H_{62}O_3P_2$: C, 76.21; H, 8.62. Found: C, 76.08; H, 8.83.

(R_P,*R*)-[2-(*tert*-Butylphenylphosphino)-1-phenylethyl]-1-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite (6b). This compound was prepared as described for **1a**, using phosphinoborane **11f** (2.15 g, 2.91 mmol) and $HNEt_2$ (30 mL). Filtration over silica gel (eluent: toluene) gave **6b** (1.36 g, 1.87 mmol, 64%) as a white foam: ^1H NMR ($CDCl_3$) δ 7.64 (d, 1H, J = 2.3 Hz), 7.48 (m, 2H), 7.40−7.29 (m, 6H), 7.01−6.91 (m, 3H), 6.83 (m, 2H), 4.99 (m, 1H), 3.13 (dt, 1H, J = 4.1, 12.8 Hz), 2.27 (m, 1H), 1.71 (s, 9H), 1.54 (s, 9H), 1.37 (s, 9H), 1.17 (s, 9H), 0.93 (d, 9H, J = 12.1 Hz); ^{13}C NMR ($CDCl_3$) δ 146.5−132.2 (Cq), 134.02−123.82 (CH), 78.00 (m, CH), 35.09 (Cq), 34.41 (Cq), 31.95 (CH_2), 31.34 (CH_3), 31.20 (CH_3), 30.66 (CH_3), 27.00 (d, J = 20.8 Hz, CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 140.36 (s), −4.88 (s); R_f = 0.78 (eluent: toluene); mp = 113 °C. $[\alpha]_D^{21}{}_{589}$ = +221 (c 1.02; $CHCl_3$); MS HR−FAB [found 725.4225; $C_{46}H_{63}O_3P_2$ (MH^+) requires 725.4252]. Anal. Calcd for $C_{46}H_{62}O_3P_2$: C, 76.21; H, 8.62. Found: C, 76.52; H, 8.97.

Palladium(η^3-C_3H_5)(6a)BF_4 Complex. Phosphine−phosphite **6a** (51.9 mg, 71.6 μmol) and [Pd(η^3-C_3H_5)Cl]$_2$ (13.1 mg, 35.8 μmol) were dissolved in CH_2Cl_2 (6 mL) and stirred for 0.5 h. A solution of $AgBF_4$ (14 mg, 0.072 mmol in benzene) was added. After filtration over Celite, the filtrate was evaporated. Crystallization from CH_2Cl_2 and hexane afforded white crystals. $[C_{49}H_{67}O_3P_2Pd]^+$ BF_4-, M_r = 959.2, orthorhombic, $P2_12_12_1$, a = 10.9847(8), b = 13.0171(12), c = 37.476(7) Å, V = 5358.7(12) Å^3, Z = 4, Dx = 1.189 g cm^{-3}, λ(Cu Kα) = 1.5418 Å, λ(Cu Kα) = 37.6 cm^{-1}, F(000) = 2008, room temperature, final R = 0.066 for 5439 observed reflections.

Acknowledgment. Financial support from CW/STW is gratefully acknowledged.

Supporting Information Available: Crystal structure refinement data for compound palladium(η^3-C_3H_5)(**6a**)BF_4 including atomic coordinates, isotropic and anisotropic displacement parameters, and a complete listing of bond angles and bond lengths. This material is available free of charge via the Internet at http://pubs.org.org.

JO991737D