Palladium-Catalyzed Asymmetric Phosphination. Enantioselective Synthesis of PAMP−BH_3, Ligand Effects on Catalysis, and Direct Observation of the Stereochemistry of Transmetalation and Reductive Elimination

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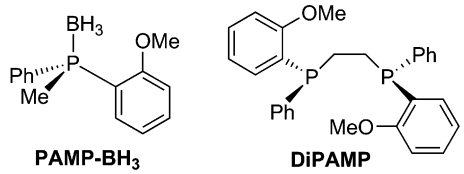
Received February 28, 2003

The complexes Pd(diphos)(*o*-An)(I) (*o*-An = *o*-$MeOC_6H_4$; diphos = dppe (**3**), (*S*,*S*)-Chiraphos (**4**), (*R*,*R*)-Me-Duphos (**5**), (*R*,*S*)-*t*-Bu-Josiphos (**6**), (*R*)-Tol-Binap (**7**)) were prepared. Complex **6** catalyzed the coupling of PH(Me)(Ph)(BH_3) (**2**) with *o*-AnI in the presence of base to yield PAMP−BH_3 (P(Me)(Ph)(*o*-An)(BH_3) (**1**)) in low enantiomeric excess. The course of stoichiometric reactions of **3**−**7** with **2** and $NaOSiMe_3$ depended on the diphosphine ligand. Complexes **6** and **7** gave PAMP−BH_3 (**1**) and Pd(0) species; no intermediates were observed. With **3**, the intermediate Pd(dppe)(*o*-An)(P(Me)(Ph)(BH_3)) (**10**) was observed by ^{31}P NMR, while **4** gave the isolable diastereomeric palladium complexes (S_P)-Pd((*S*,*S*)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (**11a**) and (R_P)-Pd((*S*,*S*)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (**11b**), whose absolute configurations were determined by X-ray crystallography after separation. The analogous Pd((*R*,*R*)-Me-Duphos)(*o*-An)(P(Me)(Ph)(BH_3)) diastereomers (**12a**,**b**) were also separated and isolated. Treatment of **4** with highly enantioenriched **2** (*R* or *S*) gave **11a** or **11b** in high diastereomeric excess with retention of configuration at phosphorus. P−C reductive elimination from either isomer of highly diastereoenriched **11** in the presence of excess diphenylacetylene yielded Pd((*S*,*S*)-Chiraphos)(PhC≡CPh) (**14**) and highly enantioenriched PAMP−BH_3 (**1**), with retention of configuration.

Introduction

The historical and industrial importance of the chiral phosphine−borane P(Me)(Ph)(*o*-An)(BH_3) (PAMP−BH_3, **1**; *o*-An = *o*-$MeOC_6H_4$), a precursor to the useful DiPAMP ligand[1] (Chart 1), is reflected by the variety of different syntheses reported.[2] Like most preparations of enantiopure P-chirogenic phosphines, these all require a stoichiometric amount of chiral reagent.[3] A metal-catalyzed asymmetric synthesis would be an attractive alternative, and some observations in the literature suggested this approach would be possible.

Chart 1



P-chirogenic substrates containing the P(=O)(H) moiety undergo palladium-catalyzed coupling with aryl or

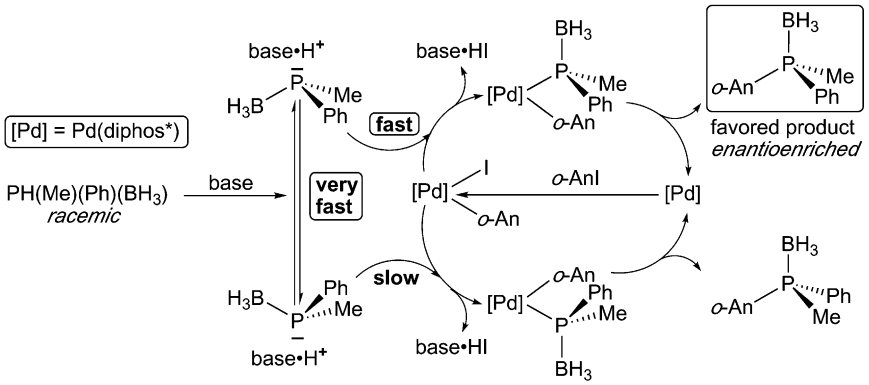
(1) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946−5952.

(2) (a) Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985**, *107*, 5301−5303. (b) Juge, S.; Stephan, M.; Laffitte, J. A.; Genet, J. P. *Tetrahedron Lett.* **1990**, *31*, 6357−6360. (c) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244−5252. (d) Schmidt, U.; Riedl, B.; Griesser, H.; Fitz, C. *Synthesis* **1991**, 655−657. (e) Imamoto, T.; Oshiki, T.; Onozawa, T.; Matsuo, M.; Hikosaka, T.; Yanagawa, M. *Heteroat. Chem.* **1992**, *3*, 563−575. (f) Corey, E. J.; Chen, Z.; Tanoury, G. J. *J. Am. Chem. Soc.* **1993**, *115*, 11000−11001. (g) Uziel, J.; Stephan, M.; Kaloun, E. B.; Genet, J. P.; Juge, S. *Bull. Soc. Chim. Fr.* **1997**, *134*, 379−389. (h) Vedejs, E.; Donde, Y. *J. Am. Chem. Soc.* **1997**, *119*, 9293−9294. (i) Al-Masum, M.; Kumaraswamy, G.; Livinghouse, T. *J. Org. Chem.* **2000**, *65*, 4776−4778.

(3) (a) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375−1411. (b) Kagan, H. B.; Sasaki, M. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: Chichester, U.K., 1990; Vol. 1, pp 51−102. (c) This statement refers to asymmetric synthesis, but biocatalytic resolution of racemic P-chirogenic phosphines, or their derivatives, yields chiral products using a catalytic amount of chiral material (enzyme). For examples, see: Shioji, K.; Tashiro, A.; Shibata, S.; Okuma, K. *Tetrahedron Lett.* **2003**, *44*, 1103−1105. Shioji, K.; Ueno, Y.; Kurauchi, Y.; Okuma, K. *Tetrahedron Lett.* **2001**, *42*, 6569. Serreqi, A. N.; Kazlauskas, R. J. *J. Org. Chem.* **1994**, *59*, 7609−7615. Kielbasinski, P.; Zurawinski, R.; Pietrusiewicz, K. M.; Zablocka, M.; Mikolajczyk, M. *Tetrahedron Lett.* **1994**, *35*, 7081−7084.

10.1021/om030144x CCC: $25.00
Publication on Web 06/27/2003

Scheme 1



vinyl halides or triflates with retention of configuration at phosphorus.[4] With phosphine−boranes, however, Imamoto observed that coupling of enantiopure PH(Me)(Ph)(BH_3) (**2**) with *o*-AnI to give **1** led to retention or inversion of P stereochemistry, depending on base, solvent, and temperature.[5] More recently, Livinghouse showed that adding Cu(I) to similar reaction mixtures gave tertiary phosphine−boranes in high enantiomeric excess (ee) with retention of configuration at phosphorus.[2i] P−C bond formation presumably occurs via oxidative addition of *o*-AnI to Pd(0), replacement of the iodide with $(P(Me)(Ph)(BH_3))^-$, and reductive elimination to yield the product and regenerate Pd(0); Brown and Gaumont have directly observed these steps in related cross-couplings.[6]

Both Imamoto and Livinghouse have reported that loss of P stereochemistry is possible in the formation of PAMP−BH_3 from enantiopure **2**, presumably because the anion $(P(Me)(Ph)(BH_3))^-$, formed by deprotonation of the secondary phosphine−borane, can racemize before Pd−P bond formation.[7] If this racemization occurs more quickly than Pd−P bond formation with a *chiral* Pd catalyst, and if one enantiomer of the anion reacts more quickly than the other with the intermediate Pd(diphos*)(*o*-An)(I) (diphos* = chiral diphosphine), dynamic kinetic resolution[8] might afford enantioenriched PAMP−BH_3 via the mechanism of Scheme 1. Here we report the successful development of a catalytic asymmetric synthesis of PAMP−BH_3 according to this scheme, albeit in low enantiomeric excess (ee).[9]

Testing a range of diphosphines as chiral auxiliaries revealed important ligand effects on the individual steps in the catalytic cycle and enabled direct observation of the stereochemistry of Pd−P bond formation (transmetalation) and P−C bond formation (reductive elimination).[10] Both steps proceed with *retention* of configuration at phosphorus, and the effect of reaction conditions on transmetalation stereochemistry was observed directly.

These observations are significant because stereocontrol in such reactions has been ascribed to the transmetalation step, assuming that reductive elimination proceeds with retention of configuration at phosphorus.[4,5] However, these steps could not be separated and observed directly. More generally, such fundamental information on the stereochemistry of organometallic reactions, while important in asymmetric catalysis, is incompletely documented.[11] For example, a standard textbook states that "A great deal of evidence suggests that the formation of C−C, C−H, and C−X bonds by reductive elimination always proceeds with retention of stereochemistry at carbon, although no case has been reported in which an isolated starting material of known stereochemistry has eliminated a product of known stereochemistry."[12] Recently, Hillhouse showed that C−N bond formation at a Ni center led to inversion at carbon, but in this oxidatively induced reductive elimination, the nature of the Ni(III) intermediate could not be determined.[13]

Results and Discussion

The catalyst precursors Pd(diphos*)(*o*-An)(I) (diphos* = dppe (**3**), (*S*,*S*)-Chiraphos (**4**), (*R*,*R*)-Me-Duphos (**5**), (*R*,*S*)-*t*-Bu-Josiphos (**6**), (*R*)-Tol-Binap (**7**)) were prepared as shown in Scheme 2. The reaction between *trans*-Pd-

(4) (a) Xu, Y.; Zhang, J. *J. Chem. Soc., Chem. Commun.* **1986**, 1606 and references therein. (b) Johansson, T.; Stawinski, J. *Chem. Commun.* **2001**, 2564−2565.

(5) (a) Reference 2e. (b) For analogous results with another secondary phosphine−borane, see: Oshiki, T.; Imamoto, T. *J. Am. Chem. Soc.* **1992**, *114*, 3975−3977.

(6) Gaumont, A.-C.; Hursthouse, M. B.; Coles, S. J.; Brown, J. M. *Chem. Commun.* **1999**, 63−64.

(7) For related studies, see: (a) Reference 5b. (b) Miura, T.; Yamada, H.; Kikuchi, S.; Imamoto, T. *J. Org. Chem.* **2000**, *65*, 1877−1880. (c) Wolfe, B.; Livinghouse, T. *J. Am. Chem. Soc.* **1998**, *120*, 5116−5117.

(8) (a) Hoveyda, A. H.; Didiuk, M. T. *Curr. Org. Chem.* **1998**, *2*, 489−526. (b) Ward, R. S. *Tetrahedron: Asymmetry* **1995**, *6*, 1475−1490. (c) Noyori, R.; Tokunaga, M.; Kitamura, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 36−56.

(9) During the course of this work, John Brown (Oxford) informed us that he had prepared enantioenriched chiral triarylphosphine−boranes by a similar pathway using a Pd(Tol-Binap) catalyst: Gaumont, A.-C.; Brown, J. M. Unpublished results, 1998.

(10) For a preliminary communication of some of these results, see: Moncarz, J. R.; Brunker, T. J.; Glueck, D. S.; Sommer, R. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 1180−1181.

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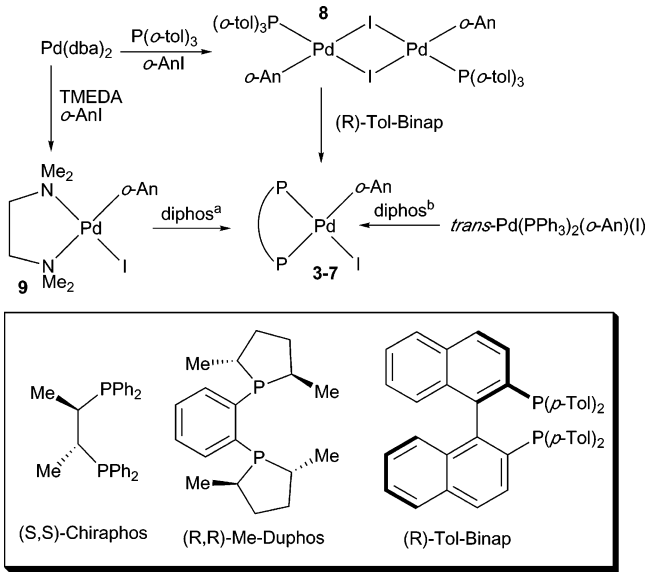
(12) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 333. (b) As described in more detail in Flood's review,[11a] conclusions about the stereochemistry of organometallic reaction steps are often based on indirect evidence, such as the stereochemical results of a multistep transformation, without observation, isolation, or knowledge of stereochemistry of the intermediates.

(13) Lin, B. L.; Clough, C. R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 2890−2891.

Scheme 2



[a] Legend and conditions: diphos = (*S*,*S*)-Chiraphos, (*R*,*R*)-Me-Duphos, (*R*,*S*)-*t*-Bu-Josiphos, (*R*)-Tol-Binap. [b]Legend and conditions: diphos = dppe, Chiraphos. dppe = $Ph_2PCH_2CH_2PPh_2$. See Scheme 3 for the structure of *t*-Bu-Josiphos.

$(PPh_3)_2$(*o*-An)(I)[14] and dppe to yield **3** was rapid at room temperature, but analogous reactions with more hindered diphosphines were less convenient. For example, using Chiraphos instead of dppe required 3 days and gave **4** in only 48% yield. With (*R*)-Tol-Binap, no reaction occurred at room temperature and a mixture of products was obtained upon heating at 50 °C. Instead, **7** was synthesized following chemistry developed by Hartwig[15] and Buchwald,[16] whereby $Pd(dba)_2$ was treated with P(*o*-Tol)$_3$ and *o*-iodoanisole to give the sparingly soluble dimer {Pd(P(*o*-Tol)$_3$)(*o*-An)(I)}$_2$ (**8**). Subsequent addition of (*R*)-Tol-Binap yielded **7** in moderate yields, compromised by the formation of a purple impurity that was removed upon recrystallization.

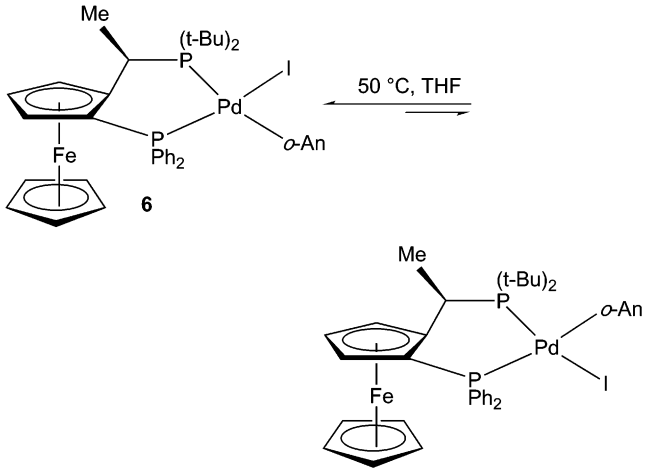
In a more convenient synthesis, diphosphines readily displaced TMEDA in Pd(TMEDA)(*o*-An)(I) (**9**)[17] to yield complexes **3**−**7** as thermally robust, air-stable solids. Reaction of **9** at room temperature in THF with (*R*,*S*)-*t*-Bu-Josiphos was slow. After 24 h, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed a 1:1 mixture of regioisomers of **6**, as well as some of the free ligand. Heating to 50 °C promoted interconversion of the isomers, one of which precipitated from THF (Scheme 3). The insolubility of this isomer drove the reaction to completion, and **6** was isolated as a single isomer with the PPh_2 group trans to iodide, as established by X-ray crystallography (see below). Once isolated, no further isomerization occurred.

Complexes **3**−**7** were characterized by NMR spectroscopy (Table 1), by elemental analysis and, for **3**−**6**, by X-ray crystallography (see below). The $^{31}P\{^1H\}$ NMR spectra showed the expected AX patterns with J_{PP} ranging from 24 to 38 Hz. The OMe group gave rise to a sharp singlet (δ 3.1−3.9 in the ^1H NMR spectrum and δ 53−57 in the $^{13}C\{^1H\}$ NMR spectrum).

The NMR spectra of complexes **4**−**7** indicated the presence of a second, minor atropisomer arising from restricted rotation about the Pd−C bond, which was also observed in the ^1H NMR spectrum of **9**. In that case, rapid Pd−C(*o*-An) rotation on the NMR time scale would make the two methyl groups on a given N equivalent, because the aryl group passes through a molecular plane of symmetry as it rotates. However, four sharp NMe signals were observed, consistent with slow Pd−C rotation on the NMR time scale. Similar behavior was reported for Pd(TMEDA)(*o*-Tol)(Br)[18] and Pd(dppf)(*o*-Tol)(NHNCPh$_2$)[19] (dppf = $Ph_2PC_5H_4FeC_5H_4PPh_2$) and in the closely related Pt(Diop)(*o*-An)(I) and Pt(Binap)(*o*-An)(Br).[20]

Barriers to Pd−C rotation were measured for complexes **4** and **7** by variable-temperature $^{31}P\{^1H\}$ and ^1H

Scheme 3[a]



[a] Heating the initially formed mixture gives a single isomer of **6**.

Table 1. Selected NMR Data for the Complexes Pd(diphos)(*o*-An)(I) (3−7)[a]

diphos	compd	δ (^1H)[b]	δ (^{13}C)[b]	δ (^{31}P)	J_{PP}
dppe	**3**	3.22	54.5	51.9, 36.7	26
(*S*,*S*)-Chiraphos	**4a**[c]	3.14	54.5	55.8, 42.4	37
	4b	3.35	*d*	57.1, 43.0	38
(*R*,*R*)-Me-Duphos	**5a**[c]	3.72	56.1	74.8, 69.0	24
	5b[c]	3.74	53.7	73.8, 68.6	25
(*R*,*S*)-*t*-Bu-Josiphos	**6a**[e,c]	3.46	53.7	78.5, 15.9	37
	6b[e]	3.20	53.2	70.2, 21.5	36
(*R*,*S*)-*t*-Bu-Josiphos	**6c**[f]	*g*	*g*	76.5, 4.7	37
	6d[f]	*g*	*g*	81.8, 5.7	36
(*R*)-Tol-Binap	**7a**[c]	3.64	56.0	23.8, 12.3	37
	7b	3.67	55.9	23.4, 10.4	38

[a] The solvent was $CDCl_3$ for **3** (except $^{13}C\{^1H\}$ NMR spectrum), **5**, and **6**, CD_2Cl_2 for **4** and the $^{13}C\{^1H\}$ NMR spectrum of **3**, and C_6D_6 for **7**. Chemical shifts are given in ppm, with coupling constants in Hz. For **4**−**7**, **a** (or **c**) refers to the major atropisomer and **b** (or **d**) to the minor one. [b] OMe resonance. [c] Ratio of atropisomers: **4**, 6:1; **5**, 4.5:1; **6** (major isomer), 5:1; **7**, 1.8:1. [d] Not observed. [e] Isolated isomer, PPh_2 trans to I. [f] Minor isomer, solvent THF, ratio of atropisomers not measured. [g] Not measured.

(14) Wallow, T. I.; Goodson, F. E.; Novak, B. M. *Organometallics* **1996**, *15*, 3708−3716.
(15) Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030−3039.
(16) (a) Widenhoefer, R. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2755−2763. (b) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215−7216.
(17) Kruis, D.; Markies, B. A.; Canty, A. J.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1997**, *532*, 235−242.
(18) Alsters, P. L.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1639−1647.
(19) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2090−2093.
(20) Diop = *O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane: Brown, J. M.; Perez-Torrente, J. J.; Alcock, N. W. *Organometallics* **1995**, *14*, 1195−1203.

Table 2. Variable-Temperature NMR Data for the Atropisomeric Pd Complexes Pd(Diphos*)(*o*-An)(I) (4−7)[a]

complex (diphos)	resonance	δ (ppm)	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_c^{\ddagger}$ (kcal/mol)
4 ((*S*,*S*)-Chiraphos)	^{1}H (OMe)	3.25, 3.19	19	323	16.5
5 ((*R*,*R*)-Me-Duphos)	^{1}H (OMe)	3.67, 3.63	12	>368	>19.3[b]
6 ((*R*,*S*)-*t*-Bu-Josiphos)	^{1}H (Cp)	4.15, 4.00	43	>373	>18.6[c]
7 ((*R*)-Tol-Binap)	^{1}H (Tol-Me)	2.10, 2.08	5	302	16.3
	^{31}P	23.8, 23.4	47	318	15.6
	^{31}P	12.3, 10.4	227	>343	>15.9

[a] Chemical shifts and $\Delta\nu$ values from slow-exchange spectra at 21 °C. Estimated errors are different for each resonance; "typical" errors are 5 Hz in $\Delta\nu$, 10 °C in T_c, and 0.5 kcal/mol in $\Delta G_c^{\ddagger}$. Solvents: C_6D_5Cl for **4** and **6**, C_7D_8 for **5**, and C_6D_6 for **7**. [b] Consistent results were obtained from the ^{31}P NMR spectrum, where larger $\Delta\nu$ values gave reduced lower bounds for the rotational barrier. [c] Consistent results were obtained from the OMe ^{1}H NMR signal and from the ^{31}P NMR spectrum, where larger $\Delta\nu$ values gave reduced lower bounds for the rotational barrier.

NMR spectroscopy; because coalescence was not observed for **5** and **6**, only lower bounds to the rotational barriers could be established in those cases (Table 2).[21] Summarizing related studies of atropisomerism in square-planar Pd(II) and Pt(II) complexes of chiral diphosphines, both Stang and Siehl[22] and Brown[20] noted that diphosphines with a larger bite angle give rise to higher rotation barriers. However, our results show that bite angle is not the only factor affecting the rotational barrier, since both the Duphos complex **5** (bite angle 87°) and *t*-Bu-Josiphos complex **6** (bite angle 95.6°) had rotational barriers higher than that of the (*R*)-Tol-Binap complex **7** (the average Binap bite angle is 92.8°).[23] Presumably, the steric and electronic differences in the groups on phosphorus also play a role in the energetics of rotation.

Crystallographic Studies. The structures of complexes **3**−**6** and **9** were determined by X-ray crystallography. ORTEP diagrams are shown in Figures1−5, data collection and structure refinement details are summarized in Table 3, selected bond lengths and angles for **3**−**6** are given in Table 4, and additional information appears in the Experimental Section and the Supporting Information. These complexes all adopt a near-square-planar geometry at palladium, with the aryl group oriented orthogonal to the square plane of the molecule. The Me-Duphos and Josiphos complexes **5** and **6** show the greatest distortions from planarity, as judged by the distances of ligand atoms from the P_2-PdIC plane (up to 0.25 Å for P_1 in **5** and 0.41 Å for I in **6**). Despite steric and electronic differences between the diphosphines, there was no significant difference in Pd−C bond lengths. There was, however, a slight difference in Pd−I bond lengths, with that in *t*-Bu-Josiphos complex **6** being the longest. This result is consistent with the greater steric congestion caused by P(*t*-Bu)$_2$ in comparison to PPh_2.

Comparison of the crystal structures of Pd(TMEDA)(*o*-An)(I) (**9**), Pd(TMEDA)(*p*-An)(I) (see the Supporting Information),[17] and the previously reported Pd(TMEDA)(Ph)(I) (Table 5)[24] suggest that methoxy substitution has little steric or electronic effect on the structure of these Pd aryl complexes.

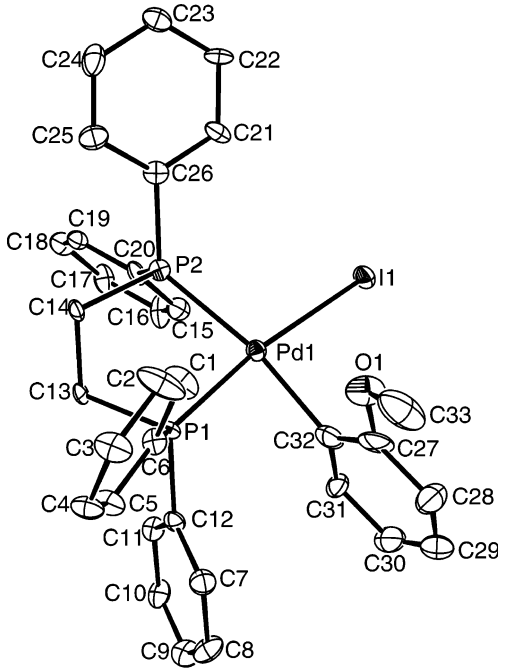


Figure 1. ORTEP diagram of Pd(dppe)(*o*-An)(I) (**3**), with thermal ellipsoids at the 30% probability level and hydrogen atoms omitted for clarity.

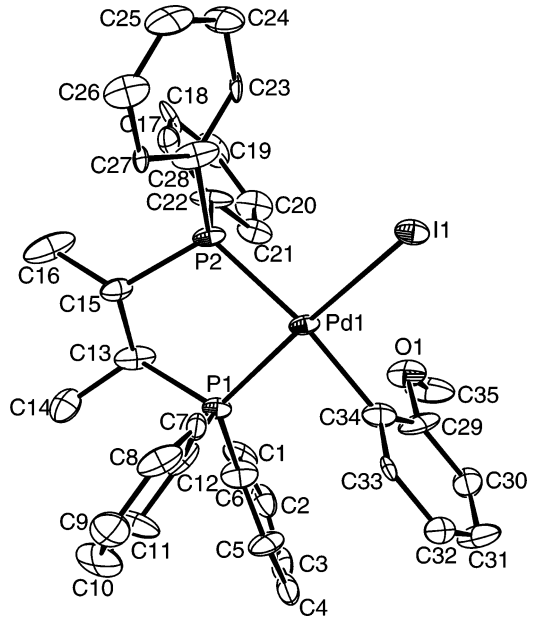


Figure 2. ORTEP diagram of Pd((*S*,*S*)-Chiraphos)(*o*-An)(I) (**4**), with thermal ellipsoids at the 30% probability level and hydrogen atoms omitted for clarity.

Catalysis. Complexes **3**−**7** were screened as catalyst precursors for coupling of PH(Me)(Ph)(BH_3) and *o*-AnI in the presence of base to make PAMP−BH_3. Many of the bases tested (BuLi, $NaOSiMe_3$, *i*-Pr_2NEt, K_2CO_3, Cs_2CO_3, KOH, pentamethylpiperidine) caused deprotection of the secondary phosphine−borane and/or the

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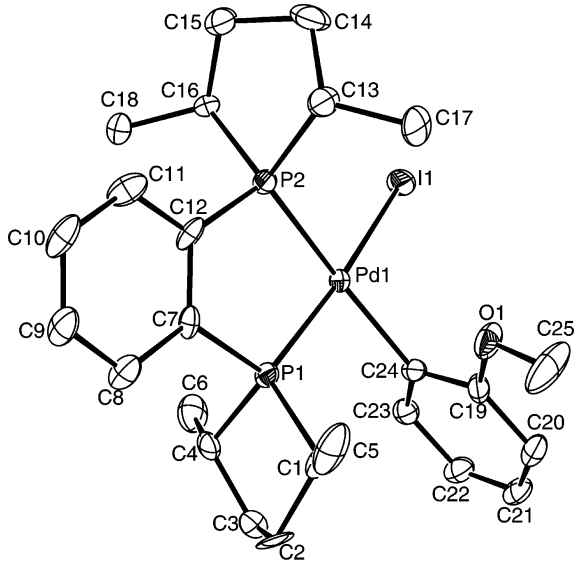


Figure 3. ORTEP diagram of Pd((*R*,*R*)-Me-Duphos)(*o*-An)(I)·CH_2Cl_2 (**5**·CH_2Cl_2), with thermal ellipsoids at the 30% probability level. Hydrogen atoms and the solvent molecule are omitted for clarity.

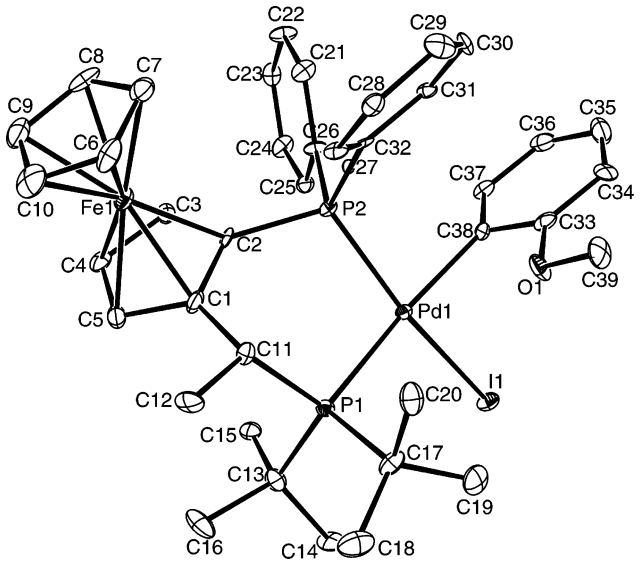


Figure 4. ORTEP diagram of Pd((*R*,*S*)-*t*-Bu-Josiphos)(*o*-An)(I) (**6**), with thermal ellipsoids at the 30% probability level and hydrogen atoms omitted for clarity.

tertiary phosphine−borane product or led to other undesirable side reactions. Catalytic turnover was observed only for tol-Binap and Josiphos complexes **6** and **7**; since free tol-Binap and other decomposition products were often observed during catalysis with **7**, the more robust Josiphos complex **6** was preferred. Under optimized conditions (THF, 40 °C, Proton Sponge as base; Scheme 4), PAMP−BH_3 was formed in good yield and isolated after workup by column chromatography.

Unfortunately, the catalytic reaction was very slow (ca. 5 turnovers per day), excess Proton Sponge was required, and the enantiomeric excess (ee) of the product, as determined by HPLC on a chiral column, was low, 10% at best (the R enantiomer was favored). Using the more kinetically active base $NaOSiMe_3$ led to formation of unidentified phosphine−borane byproducts, but the combination of a catalytic amount of

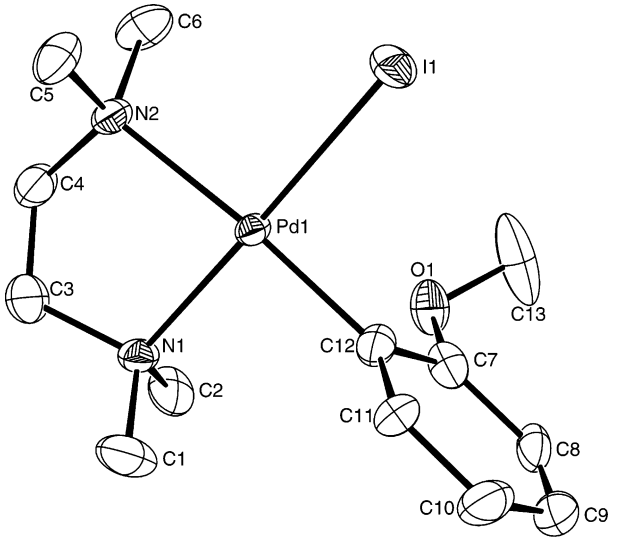


Figure 5. ORTEP diagram of Pd(TMEDA)(*o*-An)(I) (**9**), with thermal ellipsoids at the 30% probability level and hydrogen atoms omitted for clarity.

$NaOSiMe_3$ and stoichiometric Proton Sponge gave a cleaner reaction with increased rate (ca. 8 turnovers per day) without affecting the product ee.[25] Details of the catalysis are given in Table 6 and the Experimental Section.

Stoichiometric versions of the catalytic reactions provided more information on the reaction mechanism and on the pronounced ligand effects on catalyst turnover (Scheme 5). Treatment of Pd((*R*,*S*)-*t*-Bu-Josiphos)(*o*-An)(I) (**6**) with 1 equiv of PH(Me)(Ph)(BH_3) (**2**) and $NaOSiMe_3$ in the presence of *o*-AnI led to the clean formation of P(Me)(Ph)(*o*-An)(BH_3) (**1**); no intermediate was observed. Although initially a single isomer of **6** was used, oxidative addition of *o*-AnI to Pd(0) yielded a 5:1 mixture of isomers of **6**. Similarly, treatment of Pd((*R*)-Tol-Binap)(*o*-An)(I) (**7**) with 1 equiv of **2** and $NaOSiMe_3$ at room temperature in the presence of 1 equiv of (*R*)-Tol-Binap gave P(Me)(Ph)(*o*-An)(BH_3) (**1**) and Pd((*R*)-Tol-Binap)$_2$.[26] When this reaction was carried out at −78 °C, the PAMP−BH_3 product was observed by ^{31}P NMR even at −80 °C, and no intermediate could be identified.

In contrast, reaction of Pd(dppe)(*o*-An)(I) (**3**) with PH(Me)(Ph)(BH_3) and $NaOSiMe_3$ in THF in the presence of *o*-AnI gave the unstable (see below) intermediate Pd(dppe)(*o*-An)(P(Me)(Ph)(BH_3)) (**10**) as a 1:1 mixture of atropisomers (Table 7). The related intermediates Pd(diphos*)(*o*-An)(P(Me)(Ph)(BH_3)) with Chiraphos and Duphos ligands could be isolated. Treatment of Pd((*S*,*S*)-Chiraphos)(*o*-An)(I) (**4**) and Pd((*R*,*R*)-Me-Duphos)(*o*-An)(I) (**5**) with PH(Me)(Ph)(BH_3) and $NaOSiMe_3$ led to the clean formation of a mixture of diastereomers **11a** and **11b** (the ratio depends on reaction conditions; see below) and a 1:1 ratio of diastereomers **12a** and **12b**, respectively (Scheme 5, Table 7). The phosphido−borane complexes **10**−**12** show a characteristic broad ^{31}P NMR signal due to the P(Me)(Ph)(BH_3) group and J_{PP}(trans) values of ca. 300 Hz, similar to related complexes prepared by Gaumont and Brown.[6]

(25) Taggi, A. E.; Hafez, A. M.; Wack, H.; Young, B.; Ferraris, D.; Lectka, T. *J. Am. Chem. Soc.* **2002**, *124*, 6626−6635.

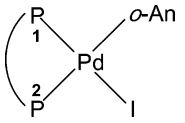
(26) Alcazar-Roman, L. M.; Hartwig, J. F.; Rheingold, A. L.; Liable-Sands, L. M.; Guzei, I. A. *J. Am. Chem. Soc.* **2000**, *122*, 4618−4630.

Table 3. Crystallographic Data for Complexes 3−6, 9, 14, and 17

	3	4	5·CH_2Cl_2	6	9	14	17
formula	$C_{33}H_{31}IOP_2Pd$	$C_{35}H_{35}IOP_2Pd$	$C_{26}H_{37}Cl_2IOP_2Pd$	$C_{39}H_{47}FeIOP_2Pd$	$C_{13}H_{23}IN_2OPd$	$C_{42}H_{38}P_2Pd$	$C_{36}H_{56}P_4Pd$
fw	738.82	766.87	729.68	882.86	456.63	711.06	719.09
space group	$P\bar{1}$	$P2_1$	$P2_12_12_1$	$P2_1$	$P2_1/n$	$P2_1$	$P2_1$
a, Å	9.836(2)	9.0397(2)	12.8392(2)	9.7440(2)	8.2681(2)	9.9491(8)	10.5573(7)
b, Å	11.496(3)	14.2113(3)	15.1191(2)	11.9220(2)	17.4132(2)	22.4313(19)	18.1364(11)
c, Å	14.168(3)	12.5971(2)	15.9153(2)	15.9338(3)	11.9951(2)	16.2199(14)	19.6534(12)
α, deg	81.340(4)	90	90	90	90	90	90
β, deg	80.800(4)	101.237(2)	90	97.6465(10)	108.4800(8)	97.677(2)	103.7100(10)
γ, deg	68.620(4)	90	90	90	90	90	90
V, Å^3	1465.2(6)	1587.27(4)	3089.43(4)	1834.54(9)	1637.93(3)	3587.4(5)	3655.8(4)
Z	2	2	4	2	4	4	4
D(calcd), g/cm^3	1.675	1.605	1.569	1.598	1.852	1.317	1.306
μ(Mo Kα), mm^{-1}	1.821	1.684	1.893	1.844	3.010	0.634	0.706
temp, K	173(2)	198(2)	173(2)	173(2)	173(2)	150(2)	173(2)
radiation				Mo Kα (0.71073 Å)			
R(*F*), %[a]	0.0529	0.0714	0.0420	0.0384	0.0412	0.0674	0.0259
$R_w(F^2)$, %[a]	0.1350	0.2029	0.1333	0.1237	0.1225	0.1437	0.0649

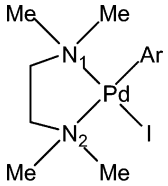
[a] Quantity minimized = $R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o,0)]/3$.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in Pd(diphos)(*o*-An)(I) Complexes 3−6



	3	4	5·CH_2Cl_2	6
diphos	dppe	(*S*,*S*)-Chiraphos	(*R*,*R*)-Me-Duphos	(*R*,*S*)-*t*-Bu-Josiphos
Pd−C	2.078(5)	2.067(9)	2.083(6)	2.064(9)
Pd−I	2.6668(9)	2.6201(19)	2.6675(6)	2.7063(8)
Pd−P_1	2.238(2)	2.209(5)	2.2515(15)	2.245(2)
Pd−P_2	2.359(2)	2.313(5)	2.3184(16)	2.44(2)
C−Pd−I	87.15(17)	91.0(4)	91.74(17)	82.4(2)
P_1−Pd−P_2	86.32(8)	85.43(18)	86.88(6)	95.67(7)
P_1−Pd−C	85.60(18)	86.1(4)	88.51(17)	84.4(2)
P_2−Pd−I	100.21(6)	97.88(13)	94.93(5)	102.56(5)

Table 5. Selected Bond Lengths (Å) and Angles (deg) in Pd(TMEDA)(Ar)(I) Complexes

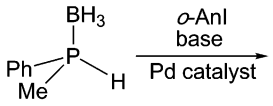


	Ar		
	o-$MeOC_6H_4$ (**9**)	*p*-$MeOC_6H_4$[a]	Ph[b]
Pd−C	1.980(6)	2.036(9)	1.992(7)
Pd−I	2.5735(6)	2.5954(7)	2.5703(8)
C−Pd−I	88.79(17)	89.7(2)	87.4(2)
N−Pd−N	83.63(19)	84.2(2)	84.0(2)
Pd−N_1	2.125(5)	2.156(7)	2.127(6)
Pd−N_2	2.176(5)	2.208(7)	2.193(6)
N_1−Pd−C	92.0(2)	91.1(3)	92.8(3)
N_2−Pd−I	95.56(13)	95.00(17)	95.8(2)

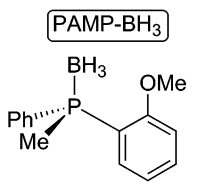
[a] Kruis, D.; Markies, B. A.; Canty, A. J.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1997**, *532*, 235−242. For details of the crystal structure determination, see the Supporting Information. [b] Markies, B. A.; Canty, A. J.; de Graaf, W.; Boersma, J.; Janssen, M. D.; Hogerheide, M. P.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1994**, *482*, 191−199.

Because of their differing solubilities in ether, Chiraphos complexes **11a** and **11b** could be separated and isolated as single diastereomers or as samples highly enriched in one diastereomer. For the Duphos complex

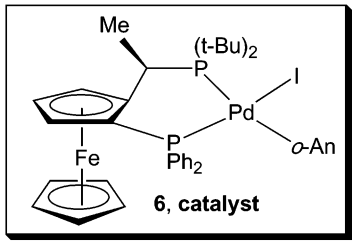
Scheme 4



2, *racemic*



1, *enantioenriched*



6, **catalyst**

Table 6. Pd-Catalyzed Asymmetric Synthesis of PAMP−BH_3[a]

method[b]	*T* (°C)	time (days)	conversn (%)[c]	yield (%)[d,e]	ee (%)[f]
1	25	10	88	76	10
1	40	5	95	76	2
2	25	7	89	68	7
2	40	3	80	65	9

[a] For the general procedure, including workup details, see the Experimental Section. *rac*-PH(Me)(Ph)(BH_3) (**2**) was treated with *o*-AnI (2.1 equiv), a base (1.1 equiv), and complex **6** (4 mol %) in THF, and the mixture was heated to 40 °C. Reactions were monitored by ^{31}P NMR spectroscopy. [b] Method 1: base, Proton Sponge. Method 2: base, Proton Sponge (1.1 equiv) plus $NaOSiMe_3$ (0.04 equiv). [c] By ^{31}P NMR integration of **2** and PAMP−BH_3 signals. [d] Based on amount of starting **2**. [e] Isolated yields after recrystallization from hexane/CH_2Cl_2. [f] Determined by HPLC (ChiralPak AD column) in comparison with racemic material.

12, recrystallization from THF/petroleum ether at −25 °C yielded a 2:1 mixture of diastereomers. However, precipitation from THF at −25 °C yielded only **12a**, according to ^{31}P{^{1}H} NMR. A MeO signal due to a second, minor isomer was observed in the ^{1}H NMR spectrum (δ 3.63, CD_2Cl_2, major to minor ratio 16:1), but it was unclear whether this was the other diastereomer or an atropisomer, since a corresponding signal was not observed in the ^{31}P{^{1}H} NMR spectrum.

The Chiraphos and Me-Duphos complexes were further characterized by ^{1}H and ^{13}C NMR spectroscopy (Table 8). These techniques, as well as ^{31}P NMR spectra, showed that minor atropisomers of **11** and **12** are

Scheme 5

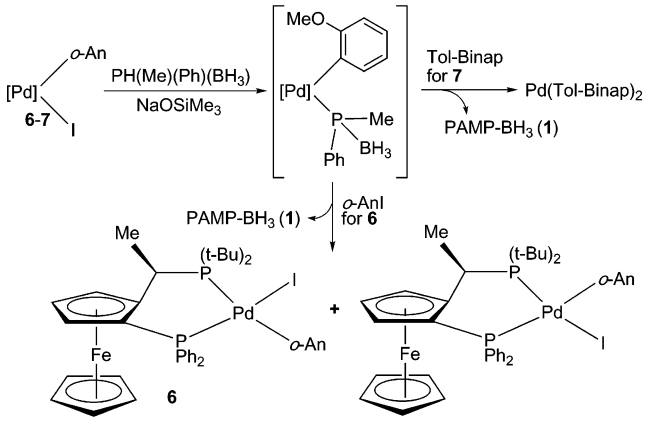
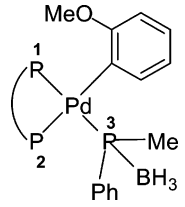


Table 7. $^{31}P\{^1H\}$ NMR Data for Pd(diphos)(*o*-An)(P(Me)(Ph)(BH_3)) Complexes 10−12[a]

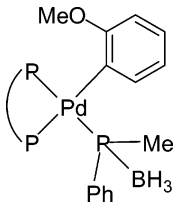


diphos	compd	$\delta(P_1)$	$\delta(P_2)$	$\delta(P_3)$	J_{12}	J_{13}	J_{23}
dppe	**10a**	44.8	41.9	−2.5	23	293	28
dppe	**10b**	42.7	42.3	−14.9	24	301	28
(*S*,*S*)-Chiraphos	**11a**[b]	46.6	45.4	1.9	38	291	18
(*S*,*S*)-Chiraphos	**11b**[c]	49.0	44.1	−14.4	37	293	27
(*S*,*S*)-Chiraphos	**11c**[d,e]	47.2	45.1	−5.0	37	292	27
(*S*,*S*)-Chiraphos	**11d**[d,e]	48.4	45.5[f]	−12.6	36	292	*g*
(*R*,*R*)-Me-Duphos	**12a**[d]	71.4	73.1	−20.2	26	287	27
(*R*,*R*)-Me-Duphos	**12b**[d]	70.4	70.0	−9.6	27	310	27
(*R*,*R*)-Me-Duphos	**12c**[d,h]	67.1	69.6	−14.5	27	298	26
(*R*,*R*)-Me-Duphos	**12d**[d,h]	67.4	69.0	*g*	25	297	26

[a] Solvent: THF/THF-d_8 for **10**, THF-d_8 for **11**, THF with the signal locked to a DMSO-d_6 insert for **12**. The chemical shift is referenced to external 85% H_3PO_4; *J* values are given in Hz. [b] S_P (X-ray crystallography, see below). [c] R_P (X-ray crystallography, see below). [d] Absolute configuration not determined. [e] Minor atropisomers: **11a** is associated with **11d** and **11b** with **11c**. See the text for details. [f] Doublet of doublets partially obscured by signals due to **11a**. [g] Not observed. [h] Minor atropisomers: ratio **12a**:**12b**:**12c**:**12d** ca. 10:10:2:1.

present in solution. Isolated samples of **11a** contained atropisomer **11d**, and **11b** contained **11c**. The **11b**:**11c** ratio was consistently ca. 30:1 in isolated samples but varied from ca. 10 to 20 in the crude material, depending on reaction conditions for the transmetalation, being larger when Pd−P bond formation was done at lower temperature. Purified samples of **11a**, and those formed in situ by reaction of **4** with **2**, contained small amounts of atropisomer **11d**. The **11a**:**11d** ratio ranged from ca. 10:1 to 40:1 and seemed to depend on conditions, being larger when Pd−P bond formation was done at higher temperature. From these observations, we cannot determine if these atropisomer ratios represent kinetic or thermodynamic preferences or depend on other solution components (such as $NaOSiMe_3$ and NaI in transmetalation experiments). For determination of the diastereomeric excess of a sample of **11** (important in studies of the stereochemistry of reductive elimination and transmetalation described below), the small amounts of

Table 8. Selected ^1H NMR Data for Pd(diphos)(*o*-An)(P(Me)(Ph)(BH_3)) Complexes 11a,b and 12a,b[a−c]



		$\delta(^1H)$		
diphos	compd	OMe	PMe	J_{PH}
(*S*,*S*)-Chiraphos	**11a**	3.23	0.44	9, 3
(*S*,*S*)-Chiraphos	**11b**	3.11	0.59	8, 3
(*S*,*S*)-Chiraphos	**11c**[d]	3.41	0.44	8, 3
(*S*,*S*)-Chiraphos	**11d**[d]	3.29	0.67	8, 4
(*R*,*R*)-Me-Duphos	**12a**	3.59	0.85	9, 3
(*R*,*R*)-Me-Duphos	**12b**[f]	3.66	0.79	*e*

[a] Chemical shifts in ppm and coupling constants in Hz. [b] Solvent: CD_2Cl_2 for **11a** and **12a**; THF-d_8 for **11b**−**d**; acetone-d_6 for **12b**. [c] Temperature 21 °C. [d] **11c** is an atropisomer of **11b**; **11d** is an atropisomer of **11a**. [e] Obscured due to peak overlap. [f] Complexes **12** were not obtained analytically pure; therefore, ^1H NMR signals due to the minor atropisomers **12c** and **12d** could not be confidently assigned.

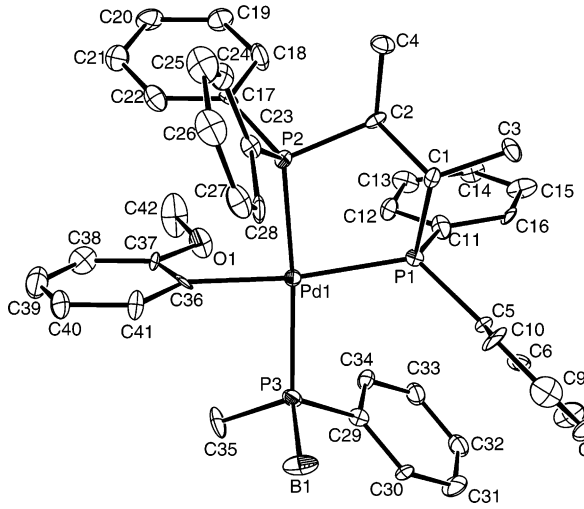


Figure 6. ORTEP diagram of (S_P)-Pd((*S*,*S*)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (**11a**), with thermal ellipsoids at the 30% probability level and hydrogen atoms omitted for clarity.

11c and **11d** present were quantified by ^1H NMR integration and grouped with their parent isomers.

Crystallographic Studies. Crystals of **11a** were obtained by slow diffusion of petroleum ether into a concentrated THF solution of diastereomerically pure material at −25 °C, and small crystals of **11b** crystallized out of the diethyl ether mother liquor obtained after initial separation of **11a**. ORTEP diagrams are shown in Figures 6 and 7, selected bond lengths and angles are given in Table 9, and data collection and structure refinement details are summarized in Table 3.

The structures of the diastereomers, with square-planar Pd and a distorted-tetrahedral phosphido−borane group, are similar to each other and to that of the related complex Pd(dppp)(C_6F_5)((PPh_2)(BH_3)).[6] The crystal structures provided the absolute configuration of the P(Me)(Ph)(BH_3) group (*S* in **11a** and *R* in **11b**).

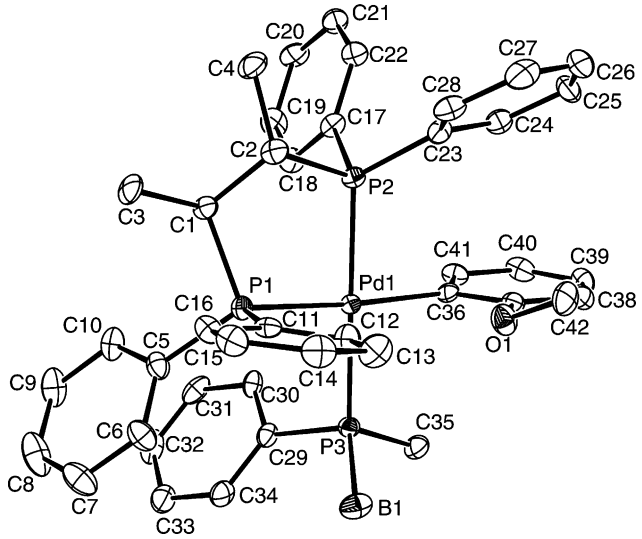


Figure 7. ORTEP diagram of (R_P)-Pd((*S*,*S*)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (**11b**), with thermal ellipsoids at the 30% probability level and hydrogen atoms omitted for clarity.

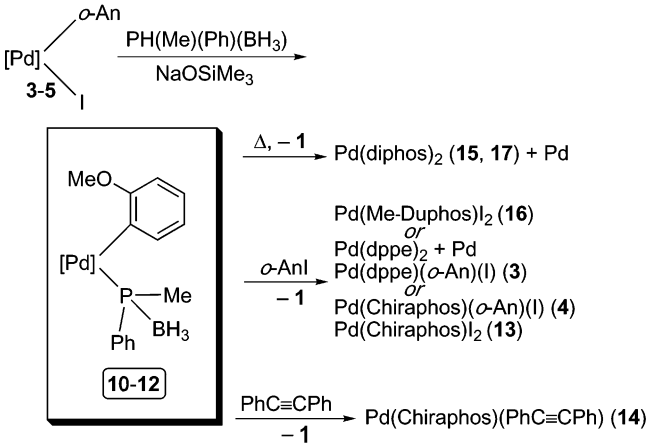
Table 9. Selected Bond Lengths (Å) and Angles (deg) for Diastereomeric Pd((*S*,*S*)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) Complexes 11a and 11b

	11a	11b
P_3 confign	*S*	*R*
Pd−P_1	2.312(2)	2.315(2)
Pd−P_2	2.302(2)	2.3118(18)
Pd−P_3	2.333(2)	2.3338(19)
Pd−C_{36}	2.038(7)	2.038(8)
P_1−Pd−P_2	84.98(7)	85.07(7)
P_1−Pd−P_3	99.70(7)	97.11(7)
P_2−Pd−P_3	172.64(7)	176.91(8)
P_3−Pd−C_{36}	87.5(2)	88.88(19)
P_1−Pd−C_{36}	172.7(2)	171.7(2)
P_2−Pd−C_{36}	88.0(2)	89.2(2)
Pd−P_3−B	112.8(3)	116.8(3)
Pd−P_3−C_{29}	112.3(2)	105.8(2)
Pd−P_3−C_{35}	113.7(3)	114.4(4)
B−P_3−C_{29}	108.9(4)	111.9(4)
B−P_3−C_{35}	108.8(4)	106.6(4)
C_{29}−P_3−C_{35}	99.4(4)	100.2(4)
P_3−B	1.944(9)	1.929(9)
P_3−C_{35}	1.807(8)	1.831(9)
P_3−C_{29}	1.796(7)	1.837(8)

Due to the similarity in the scattering factors of the BH_3 and Me groups, it was difficult to differentiate these two fragments, especially in the lower quality structure of **11a**. However, both the P−BH_3 and the P−Me bond lengths in **11a** and **11b** are in close agreement with the average values found in the literature (1.825(25) and 1.914(34) Å, respectively).[27]

The absolute configurations of **11a** and **11b** were correlated with their respective NMR spectra by obtaining a ^{1}H NMR spectrum at 0 °C of the single crystal used for the X-ray analysis of **11b**. Unfortunately, we were unable to obtain any NMR data on the crystal used to obtain the crystal structure of **11a**, perhaps due to the very small size (0.08 × 0.06 × 0.04 mm) of the crystal.

Scheme 6



[a] Legend: [Pd] = Pd(diphos); diphos = dppe (**3**, **10**), (*S*,*S*)-Chiraphos (**4**, **11**, **13**−**15**), (*R*,*R*)-Me-Duphos (**5**, **12**, **16**, **17**).

Reductive Elimination. Qualitatively, there was a correlation between the P−Pd−P bite angles of the ligands in Pd(diphos)(*o*-An)(I) complexes **3**−**7** (Table 4) and the striking difference in the rates of P−C reductive elimination from Pd(diphos)(*o*-An)(P(Me)(Ph)(BH_3)). As observed previously, larger bite angles (t-Bu-Josiphos, Tol-Binap)[23] are correlated with faster reductive elimination.[28] Although the bite angles of dppe and Chiraphos are nearly identical, the dppe complex reacted much more quickly at room temperature. This could be ascribed to the superior donor properties of Chiraphos, stabilizing Pd(II),[29] or to the greater structural rigidity of the Chiraphos complex, which could retard the motion required to reach the transition state to reductive elimination.

For dppe complex **10**, reductive elimination occurred over 48 h at room temperature in the presence of *o*-AnI to give P(Me)(Ph)(*o*-An)(BH_3) (**1**), complex **3**, and Pd(dppe)$_2$;[30] the solution became dark, presumably due to formation of Pd metal (Scheme 6). In some cases, Pd(dppe)I_2 was also formed; we have not investigated the potential effect of light on appearance of this byproduct.[31]

Similarly, Chiraphos complex **11** and Me-Duphos complex **12** underwent reductive elimination to produce **1**. The major Pd products depended on the trapping agent (Scheme 6) and the temperature. For **11**, with 2.5 equiv of *o*-AnI, reductive elimination was complete after 25 h at 55 °C. The major palladium products were Pd((*S*,*S*)-Chiraphos)(*o*-An)(I) (**4**) and Pd((*S*,*S*)-Chiraphos)I_2 (**13**) in a ca. 2:1 ratio. At room temperature, in the presence of *o*-AnI (1 equiv), the major Pd product was **13**. When diphenylacetylene (DPA) was used as a trap (T = 50 °C), after 48 h, the major Pd product was Pd((*S*,*S*)-Chiraphos)(DPA) (**14**), with a small amount of Pd-

(27) (a) For the average P−BH_3 bond length see: Brunel, J. M.; Faure, B.; Maffei, M. *Coord. Chem. Rev.* **1998**, *178*−*180*, 665−698. (b) For the average P−Me bond length (in $PPhMe_2$ complexes), see: Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S84. (c) For crystallographic characterization of several related P(Me)(Ar)(BH_3) compounds, see: Stoop, R. M.; Mezzetti, A.; Spindler, F. *Organometallics* **1998**, *17*, 668−675. Moulin, D.; Bago, S.; Bauduin, C.; Darcel, C.; Jugé, S. *Tetrahedron: Asymmetry* **2000**, *11*, 3939−3956. Vedejs, E.; Daugulis, O.; Diver, S. T.; Powell, D. R. *J. Org. Chem.* **1998**, *63*, 2338−2341.

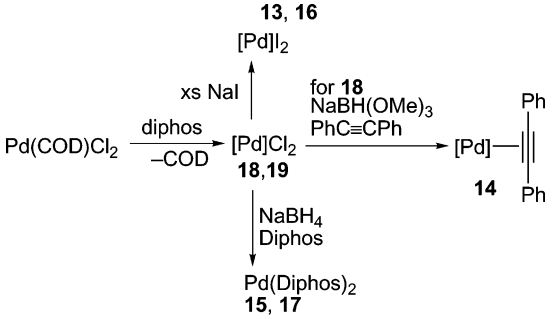
(28) Brown, J. M.; Guiry, P. J. *Inorg. Chim. Acta* **1994**, *220*, 249−259.

(29) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933−4941.

(30) Broadwood-Strong, G. T. L.; Chaloner, P. A.; Hitchcock, P. B. *Polyhedron* **1993**, *12*, 721−729.

(31) Oberhauser, W.; Bachmann, C.; Stampfl, T.; Haid, R.; Bruggeller, P. *Polyhedron* **1997**, *16*, 2827−2835.

Scheme 7



[a] Legend: [Pd] = Pd(diphos); diphos = (*S*,*S*)-Chiraphos (**13**−**15**, **18**), (*R*,*R*)-Me-Duphos (**16**, **17**, **19**).

((*S*,*S*)-Chiraphos)$_2$ (**15**).[32] When no trap was present, **15** and metallic palladium were observed. Reductive elimination of **12** in the presence of *o*-AnI gave mostly Pd((*R*,*R*)-Me-Duphos)I_2 (**16**), and in the absence of *o*-AnI, Pd((*R*,*R*)-Me-Duphos)$_2$ (**17**) and Pd metal were formed.

The products **13**−**17** were synthesized independently (Scheme 7). Reaction of Pd(COD)Cl_2 with 1 equiv of the appropriate chiral diphosphine produced Pd((*S*,*S*)-Chiraphos)Cl_2 (**18**) and Pd((*R*,*R*)-Me-Duphos)Cl_2 (**19**). Treatment of **18** and **19** with an excess of NaI afforded **13** and **16**, respectively. The bis(diphosphine) complexes **15** and **17** were prepared by $NaBH_4$ reduction of dichlorides **18** and **19** in the presence of Chiraphos or Duphos, respectively. Similar treatment of **18** with $NaBH(OMe)_3$ in the presence of diphenylacetylene gave **14**.[33]

The dihalide complexes **13**, **16**, and **19** were characterized crystallographically as CH_2Cl_2 solvates (see the Supporting Information for ORTEP diagrams and other details). As expected, the Pd−P bonds in diiodide complex **16** (2.2649(12) and 2.2591(13) Å) are longer than those in dichloride **19** (2.2243(15) and 2.2122(15) Å), reflecting the trans influence of the halide.[34] Although Me-Duphos complexes **16** and **19** show negligible deviations from square-planar geometry, several of the ligating atoms in Chiraphos complex **13** are displaced from the PdP_2IC plane, up to 0.25 Å for P_1.

The crystal structures of Pd(0) complexes **14** and **17** were also determined (Figures 8 and 9, Table 3). The diphenylacetylene in **14** occupies the Pd(Chiraphos) plane (the dihedral angle between the PdP_2 and PdC_2 planes is 8.5°), and the C−C bond length in complexed diphenylacetylene (1.405(11) Å) is longer than that in the free ligand (1.198(4) Å).[35] Complex **17** adopts a distorted-tetrahedral structure, with a dihedral angle between the two PdP_2 planes of 80.4°.

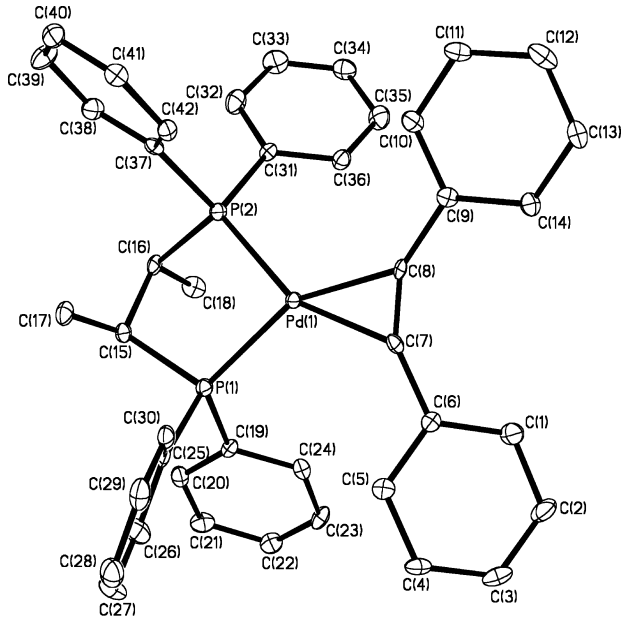


Figure 8. ORTEP diagram of Pd((*S*,*S*)-Chiraphos)(PhC≡CPh) (**14**), with thermal ellipsoids at the 30% probability level and H atoms omitted for clarity. Selected bond lengths (Å): Pd1−C7 = 2.052(7), Pd1−C8 = 2.076(7), Pd1−P2 = 2.322(2), Pd1−P1 = 2.323(2). Selected bond angles (deg): C7−Pd1−C8 = 36.1(3), C7−Pd1−P2 = 155.9(2), C8−Pd1−P2 = 120.7(2), C7−Pd1−P1 = 116.4(2), C8−Pd1−P1 = 152.5(2), P2−Pd1−P1 = 86.70(7).

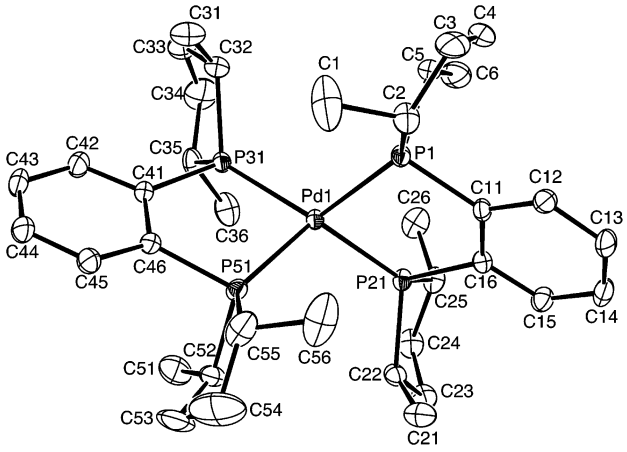


Figure 9. ORTEP diagram of Pd((*R*,*R*)-Me-Duphos)$_2$ (**17**) with thermal ellipsoids at the 30% probability level and hydrogen atoms omitted for clarity. One of the two molecules in the unit cell is shown. Selected bond lengths (Å): Pd1−P51 = 2.3001(7), Pd1−P1 = 2.3036(8), Pd1−P31 = 2.3127(8), Pd1−P21 = 2.3194(7). Selected bond angles (deg): P51−Pd1−P1 119.90(3), P51−Pd1−P31 = 87.09(3), P1−Pd1−P31 = 118.37(3), P51−Pd1−P21 = 113.08(3), P1−Pd1−P21 = 86.83(3), P31−Pd1−P21 = 135.13(3).

Stereochemistry of Reductive Elimination. Knowledge of the absolute configurations of **11a** and **11b** and of the enantiomers of PAMP−BH_3 (**1**) allowed direct observation of the stereochemistry of reductive elimination. In analogous C−X (X = N, S, O) reductive eliminations from Pd(II), adding a trap for Pd(0) improved the yield and/or selectivity of the reaction.[36] Similarly, after screening several trapping agents (none, *o*-AnI, (*S*,*S*)-Chiraphos), we found that using an excess of diphenyl-

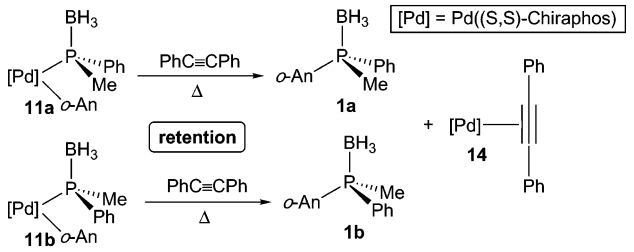
(32) (a) Visentin, G.; Piccolo, O.; Consiglio, G. *J. Mol. Catal.* **1990**, *61*, L1-L5. (b) Genet, J.-P.; Grisoni, S. *Tetrahedron Lett.* **1988**, *29*, 4543−4546. (c) Elmes, P. S.; Jackson, W. R. *Ann. N. Y. Acad. Sci.* **1980**, 225−228.

(33) For analogous Pd(diphos)(PhC≡CPh) and Pd(PR_3)$_2$(PhC≡CPh) complexes, see: (a) Reference 19. (b) Tanaka, Y.; Yamashita, H.; Shimada, S.; Tanaka, M. *Organometallics* **1997**, *16*, 3246−3248. (c) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237−3243. (d) Portnoy, M.; Milstein, D. *Organometallics* **1994**, *13*, 600−609. (e) Pan, Y.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 3842−3843. (f) Schager, F.; Bonrath, W.; Pörschke, K.-R.; Kessler, M.; Krüger, C.; Seevogel, K. *Organometallics* **1997**, *16*, 4276−4286. (g) Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* **1985**, *4*, 647−657.

(34) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738−747. For an earlier report of the structure of **19**·CH_2Cl_2, see: Malaisé, G.; Barloy, L.; Osborn, J.; Kyritsakas, N. *C. R. Chim.* **2002**, *5*, 289−296.

(35) Mavridis, A.; Moustakali-Mavridis, I. *Acta Crystallogr.* **1977**, *B33*, 3612.

Scheme 8



acetylene resulted in the cleanest reductive elimination. Heating either diastereomer of **11** to 50 °C in the presence of 4 equiv of diphenylacetylene gave PAMP−BH_3 and Pd((*S*,*S*)-Chiraphos)(PhC≡CPh) (**14**) as the major products, along with anisole and other unidentified MeO-containing byproducts (Scheme 8). Some Pd((*S*,*S*)-Chiraphos)$_2$ (**15**) was observed by ^{31}P NMR, as well as formation of small amounts of solid, presumably Pd metal. Since continued heating led to further decomposition, thermolyses were not run to complete conversion (Table 10).

Workup by preparative TLC gave pure PAMP−BH_3 in high ee (chiral HPLC), with *retention* of configuration at phosphorus. Diastereomers **11a** and **11b** undergo reductive elimination at different rates; approximate half-lives under these conditions are 30 and 10 h, respectively. Interestingly, when a smaller excess (1.1 equiv) of diphenylacetylene was present to trap Pd(0), some erosion in the stereochemistry was observed. The origin of anisole and the other unidentified byproducts remains unclear; likewise, the mechanism of formation of the arene byproduct in Pd-catalyzed aryl amination could not be elucidated.[37]

Stereochemistry of Transmetalation. Treatment of **4** with highly enantioenriched (S_P)- or (R_P)-**2**[38] and $NaOSiMe_3$ in THF-d_8 at −78 °C gave (R_P)-**11b** or (S_P)-**11a,** respectively, in high de, with *retention* of configuration at phosphorus (Scheme 9 and Table 11, entries 1 and 2; the apparent inversion is due to the change in priority for assigning absolute configuration). The erosion of stereochemistry in room-temperature transmetalation (entries 7 and 8) is presumably due to inversion of the phosphido−borane anion before reaction with the Pd complex occurs (Scheme 10, see also Scheme 1).[39] Study of transmetalation at a variety of temperatures provided qualitative information on the relative rates of inversion and Pd−P bond formation (entries 3−6). With racemic **2**, dynamic kinetic resolution was observed (Scheme 10 and Table 11, entry 9); one enantiomer of the anion $(P(Me)(Ph)(BH_3))^-$ appears to react more quickly with chiral **4** than the other ($k_R > k_S$), and anion interconversion can occur before transmetalation. This is consistent with the greater loss of stereochemical information in entry 7 vs entry 8 and suggests that transmetalation occurs somewhat more quickly than P inversion under these conditions, but the rates of these processes are competitive.

Similar dynamic kinetic resolution (26% de) was observed in toluene on a larger scale. Because of the limited solubility of **4** in toluene, NMR-scale experiments such as those in Table 11 were not possible in this solvent. On a preparative scale, however, these observations provided a convenient, high-yield route to **11a** without requiring synthesis of enantiopure (R_P)-**2**. Thus, treatment of **4** with 2 equiv of racemic **2** in toluene gave **11a** in 80% isolated yield; as expected, unreacted **2**, isolated by chromatography, was enriched in the *S* enantiomer (ee ca. 30% by chiral HPLC).

These observations show that Pd complex **4** is a highly reactive electrophile, since transmetalation occurs before racemization of enantioenriched $(P(Me)(Ph)(BH_3))^-$ at −78 °C. Livinghouse reported similar behavior of this anion and closely related ones with the potent alkylating agent 2-(chloromethyl)benzothiophene.[38a] Our brief survey of reaction conditions for transmetalation of **4** showed that temperature and solvent both affected the diastereoselectivity. To study similar behavior with an organic electrophile, we used *p*-methoxybenzyl chloride. This compound is commercially available, in contrast to the benzothiophene derivative,[40] and the ee of the product (**19**, Scheme 11) was readily determined by chiral HPLC. Alkylations were performed in THF at −78 °C with a variety of bases. The results (Table 12) confirm the sensitivity of such reactions to the nature of the base, to the resulting counterion, and to additives such as HMPA and provide another benchmark for the reactivity of Chiraphos complex **4**.

Conclusion. Several Pd(diphos)(*o*-An)(I) complexes were prepared and tested in the catalytic asymmetric synthesis of P(Me)(Ph)(*o*-An)(BH_3). Although Pd((*R*,*S*)-t-Bu-Josiphos)(*o*-An)(I) (**6**) was a robust catalyst, the reaction was slow and the enantioselectivity (≤10% ee) was poor. However, both these observations and Brown's related work[9] demonstrate that chiral phosphine−boranes can be successfully prepared via Pd-catalyzed asymmetric phosphination.

Our results provide two targets for rational improvement of these reactions. First, the direct observations of transmetalation stereochemistry for Chiraphos complex **4** show that interconversion of the enantiomeric phosphido−borane anions $(P(Me)(Ph)(BH_3))^-$ is competitive in rate with transmetalation, not much faster, as desired (Scheme 1). Second, these experiments also show that the rates of transmetalation of these enantiomers are not strikingly different, again unlike the idealized Scheme 1. Although this system is not catalytically active, it is plausible that these ideas are relevant to catalysis with other complexes. Therefore, P inversion (anion interconversion) could be accelerated by using bulkier P substituents and/or by replacing the P−Me with a P−Ar group,[7] and transmetalation selectivity could be improved by employing P substituents more sterically different than Me and BH_3. We are currently investigating these approaches.

Studies of the stoichiometric steps in the asymmetric phosphination led to separation, isolation, and determination of the absolute configuration of the Pd phos-

(36) (a) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232−8245. (b) Mann, G.; Baranano, D.; Hartwig, J. F.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 9205−9219. (c) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787−6795.

(37) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 3694−3703.

(38) (a) Wolfe, B.; Livinghouse, T. *J. Org. Chem.* **2001**, *66*, 1514−1516. (b) References 2c and 5.

(39) (a) Oshiki, T.; Hikosaka, T.; Imamoto, T. *Tetrahedron Lett.* **1991**, *32*, 3371−3374. (b) Reference 7b.

(40) ***Caution!*** We found that 2-(chloromethyl)benzothiophene caused severe contact dermatitis and suggest that special care be used in handling this compound.

Table 10. Stereochemistry of Reductive Elimination of PAMP−BH_3 from Pd((*S*,*S*)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (11a and 11b)[a]

isomer (de (%))[b]	amt of DPA (equiv)	time (h)	conversn (%)[c]	PAMP−BH_3 yield (%)[d]	ee (%)[e]	other product yield (%)[f]	dec (%)[g]
11a (89)	1.2	72	79	39 (20) (*48*, *25*)	75 (85)	4, 6, 4	31
11a (88)	1.2	72	55	36 (18) (*65*, *32*)	69 (80)	0, 3, 3	15
11a (94)	4	72	84	51 (21) (*61*, *25*)	91 (93)	4, 4, 0	27
11a (94)	4	96	87	73 (20) (*83*, *23*)	87 (93)	3, 3, 0	10
11b (100)	1.5	42	98	62 (20) (*63*, *20*)	77	1, 3, 8	24
11b (100)	1.2	42	98	62 (27) (*64*, *28*)	77	6, 0, 9	21
11b (100)	4	37	96	54 (20) (*56*, *21*)	98	2, 1, 0	40
11b (88)	4	48	91	70 (21) (*78*, *24*)	93 (92)	3, 5, 0	12

[a] For details, see the Experimental Section. [b] The de value was determined by integration of the MeO signals in the initial ^{1}H NMR spectrum, including the atropisomers **11c** and **11d**. [c] Conversion of **11** was determined by integration of its MeO signals at the beginning and end of the reaction. [d] Yields of PAMP−BH_3 were determined by NMR integration (MeO resonance). Isolated yields are in parentheses. The figures in italics are NMR and isolated yields corrected for incomplete conversion. [e] The ee value was determined by chiral HPLC (Chiralpak AD; see the Experimental Section). Because the diastereomers of **11** undergo reductive elimination at different rates, experiments involving incomplete conversion and in which **11** is not diastereopure are expected to lead to PAMP−BH_3 products with ee values different from the initial de of **11**. In these cases, the theoretical maximum ee of **11** is given in parentheses, as determined by NMR integration (MeO signals). [f] Several MeO-containing products were observed. These include unknown impurities with MeO signals at δ 3.84 (X) and 3.65 (Z) and anisole (Y, δ 3.74). Their NMR yields were determined by integration. [g] The extent of decomposition was measured by comparing the integration of the initial MeO signals of **11** with the integrals of the products (PAMP−BH_3 and other products). The incomplete mass balance is reflected in the percent decomposition. In some cases, the sum of the yields of PAMP−BH_3 and X, Y, and Z is not 100%, due to rounding errors.

Scheme 9

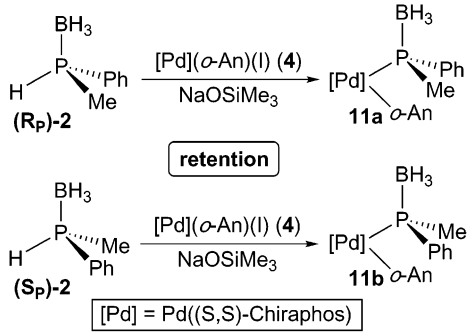


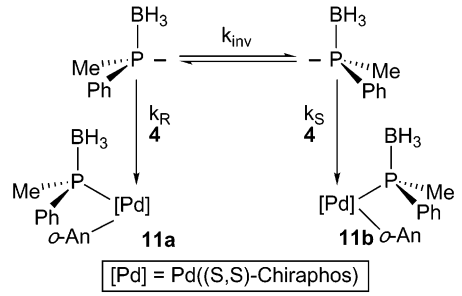
Table 11. Stereochemistry of Pd−P Bond Formation (Transmetalation) in Reaction of 4 with 2 and $NaOSiMe_3$ in THF-d_8

entry	temp (°C)	ee of **2** (%)[a]	de of **11** (%)[b]
1	−78	95 (*R*)	94 (*S*)[c]
2	−78	99 (*S*)	94 (*R*)
3	−60	99 (*S*)	94 (*R*)
4	−45	97 (*S*)	93 (*R*)
5	−15	97 (*S*)	88 (*R*)
6	0	97 (*S*)	80 (*R*)
7	21	97 (*S*)	63 (*R*)
8	21	95 (*R*)	86 (*S*)[d]
9	21	0	23 (*S*)[d]

[a] From chiral HPLC (Chiralpak OJ-H). [b] From integration of the ^{1}H NMR spectrum; the ee and de values obtained at −78 °C (entries 1 and 2) are the same, within experimental error. [c] Average of two runs. [d] Average of three runs.

phido−borane complexes Pd((*S*,*S*)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (**11a** and **11b**). Treatment of Pd((*S*,*S*)-Chiraphos)(*o*-An)(I) (**4**) with highly enantioenriched **1** and $NaOSiMe_3$ yielded highly diastereoenriched Pd((*S*,*S*)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (**11**), which formed highly enantioenriched PAMP−BH_3 (**2**) by reductive elimination; both reactions proceed with *retention* of configuration at phosphorus. These observations provide detailed mechanistic information on this useful class of Pd-mediated reactions and have more general significance in confirming long-held assumptions about the stereochemistry of reductive elimination, while suggesting that the reactions of M−P and M−C bonds are similar in stereochemistry.

Scheme 10



Scheme 11

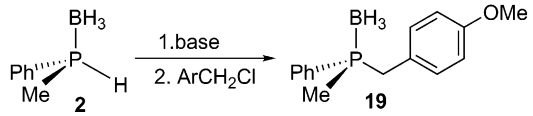


Table 12. Formation of 19 by Alkylation of (S_P)-PH(Me)(Ph)(BH_3) (2) with *p*-Methoxybenzyl Chloride in THF at −78 °C: Dependence of Product Stereochemistry on the Base

entry	ee of **2** (%)[a]	base	ee of **19** (%)[b]
1	99	n-BuLi/2 equiv HMPA[c]	0
2	97	n-BuLi[c]	30
3	97	$NaOSiMe_3$	76
4	94	$KN(SiMe_3)_2$	12

[a] From chiral HPLC (Chiralpak OJ-H). [b] From chiral HPLC (Chiralpak AD). [c] n-BuLi was used as a solution in hexanes.

Experimental Section

General Details. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at room temperature in a drybox or using standard Schlenk techniques. Petroleum ether (bp 38−53 °C), ether, THF, CH_2Cl_2, and toluene were dried and degassed using columns containing activated alumina[41] or dried and distilled before use from Na/benzophenone (CH_2Cl_2 was distilled from CaH_2).

Unless otherwise noted, all NMR spectra were recorded on a Varian 500 MHz spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported relative to Me_4Si and were determined by reference to the residual ^{1}H or ^{13}C solvent peaks. ^{31}P NMR

(41) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

chemical shifts are reported relative to H_3PO_4 (85%) used as an external reference. Unless otherwise noted, peaks in NMR spectra are singlets; *J* values are given in Hz. Infrared spectra were recorded on KBr pellets with a Perkin-Elmer 1600 series FTIR instrument and are reported in cm^{-1}. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory. Mass spectra were obtained at the University of Illinois Urbana-Champaign.

The following compounds were prepared using previously reported procedures: $Pd(dba)_2$,[42] $Pd(PPh_3)_4$,[43] $Pd(COD)Cl_2$,[44] PH(Me)(Ph),[45] and (S_P)-PH(Me)(Ph)(BH_3).[38a] (R_P)-PH(Me)(Ph)-(BH_3) was prepared using a modification of the literature method; (−)-menthol gave (S_P)-PH(Me)(Ph)(BH_3) as the major product as reported, but (+)-menthol yielded (R_P)-PH(Me)(Ph)-(BH_3) as the major product.[2c,e] The ee of PH(Me)(Ph)(BH_3) was determined by chiral HPLC (Chiralcel OJ-H, 10% i-PrOH/hexane, flow rate 1 mL/min; retention times are 12.1 (*R*) and 12.9 min (*S*)).

PH(Me)(Ph)(BH_3) (1). PH(Me)(Ph) (3.18 g, 0.026 mol) was slowly transferred by cannula to a stirred solution of BH_3·THF (27.8 mL of a 1.0 M solution in THF, 0.028 mol). The solvent was removed in vacuo, and petroleum ether was added to the cloudy oil. The mixture was filtered over a fine frit loaded with silica gel, and the silica gel was rinsed with petroleum ether (300 mL). The mixture was concentrated in vacuo to ca. 25 mL and filtered through Celite. The rest of the solvent was removed in vacuo to yield a clear oil, which should be stored under nitrogen to prevent decomposition. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −14 (br).

***trans*-Pd(PPh_3)$_2$(*o*-An)(I).** This complex was prepared by a modification of a literature procedure.[14] To a bright yellow stirred suspension of $Pd(PPh_3)_4$ (2.00 g, 1.73 mmol) in toluene (10 mL) was added *o*-AnI (343 μL, 2.64 mmol, 1.5 equiv), which caused the suspension to become pale yellow. The suspension was stirred under N_2 for 1 h and was then filtered. The pale yellow solid was washed with diethyl ether (3 × 15 mL) to yield 1.20 g (80%) of crude product, which was used in subsequent reactions without further purification. $^{31}P\{^1H\}$ NMR (THF): δ 25.1.[14]

{Pd[P(*o*-Tol)$_3$](*o*-An)(μ-I)}$_2$ (8). To a suspension of $Pd(dba)_2$ (1.00 g, 1.75 mmol) in toluene (15 mL) was added a solution of P(*o*-Tol)$_3$ (1.07 g, 3.50 mmol, 2 equiv) in toluene (10 mL) and a solution of *o*-AnI (1.14 mL, 8.75 mmol, 5 equiv) in toluene (5 mL). The purple-brown suspension was diluted to 60 mL with toluene. The mixture was stirred for 75 min and filtered. The orange filtrate was concentrated to 20 mL, and diethyl ether (200 mL) was added. Cooling to −25 °C for 7 days precipitated an air-stable orange solid, which was collected on a fine frit and washed with petroleum ether (10 mL) to give 572 mg (51%) of crude, sparingly soluble product. A sample could be purified for elemental analysis by recrystallization from CH_2Cl_2/diethyl ether at −25 °C.

$^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 27.6 (broad). IR: 3044, 2923, 1455, 1384, 1228, 1022, 748, 698, 535, 467. Anal. Calcd for $C_{56}H_{56}I_2O_2P_2Pd_2$: C, 52.16; H, 4.38. Found: C, 52.12; H, 4.21.

Pd(TMEDA)(*o*-An)(I) (9). To a stirred suspension of $Pd(dba)_2$ (2.03 g, 3.55 mmol) in toluene (20 mL) were added TMEDA (697 μL, 4.62 mmol) and *o*-iodoanisole (660 μL, 5.08 mmol) under N_2. The reaction mixture was heated to 55 °C, at which point it turned green and became homogeneous. Once cooled back to room temperature, the reaction mixture was filtered to remove suspended Pd metal particles. The solvent was then removed from the filtrate in vacuo to yield an air-stable yellow solid. This product was washed with diethyl ether (3 × 10 mL) and collected on a fine frit. The diethyl ether fraction was concentrated to ca. 20 mL and cooled to −25 °C. At this temperature, both dba and the product precipitated from solution. As the solution was warmed to room temperature, however, the dba redissolved and more product was collected as a yellow solid. Recrystallization from CH_2Cl_2/diethyl ether afforded yellow crystals suitable for crystallographic and elemental analysis. Three crops of product were obtained (total yield: 1.21 g, 75% yield).

^1H NMR (300 MHz, $CDCl_3$): δ 7.21−7.18 (m, 1H, Ar), 6.88−6.83 (m, 1H, Ar), 6.82−6.64 (m, 1H, Ar), 6.52−6.49 (m, 1H, Ar), 3.85 (3H, OMe), 2.82−2.53 (m, 4H, CH_2), 2.73 (3H, Me), 2.72 (3H, Me), 2.39 (3H, Me), 2.34 (3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.7 (quat, Ar), 137.4 (Ar), 130.0 (quat, Ar), 123.4 (Ar), 119.7 (Ar), 109.7 (Ar), 61.9 (CH_2), 58.3 (CH_2), 55.6 (OMe), 50.0 (Me), 49.9 (Me), 49.6 (Me), 49.1 (Me). IR: 2911, 2879, 1728, 1556, 1450, 1283, 1222, 1172, 1117, 1050, 1022, 950, 800, 750, 722, 694, 500, 472. Anal. Calcd for $C_{13}H_{23}IN_2OPd$·0.36CH_2Cl_2: C, 32.94; H, 4.91; N, 5.75. Found: C, 32.91; H, 4.90; N, 5.70 (the presence of solvent was quantitatively confirmed by NMR).

Pd(dppe)(*o*-An)(I) (3). To a solution of *trans*-Pd(PPh_3)$_2$(*o*-An)(I) (536 mg, 0.620 mmol) in toluene (4 mL) was added a solution of dppe (272 mg, 0.682 mmol) in toluene (4 mL). The pale yellow suspension was stirred for 45 min, and the toluene was removed in vacuo. Petroleum ether (7 mL) was added, and the solution was stirred for 12 h. The air-stable, pale yellow solid was collected on a fine frit and dried to yield 289 mg (63%) of crude product. A sample was purified for analysis by recrystallization from $CHCl_3$/ether at −25 °C; recrystallization from THF at −25 °C afforded crystals for crystallographic analysis.

^1H NMR ($CDCl_3$): δ 8.07−7.80 (broad m, 7H, Ar), 7.48 (broad m, 10H, Ar), 7.22−6.90 (m, 4H, Ar), 6.75−6.71 (m, 1H, Ar), 6.57−6.52 (m, 1H, Ar), 6.19−6.15 (m, 1H, Ar), 3.22 (3H, OMe), 2.42 (broad m, 4H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 161.5 (Ar, quat), 141.6 (d, J = 128, Ar, quat), 138.2 (d, J = 2, Ar), 134.5−128.2 (m, br, Ar), 124.3 (Ar), 120.4 (d, J = 5, Ar), 109.8 (d, J = 3, Ar), 54.5 (OMe), 29.0 (dd, J = 17, 13, CH_2), 25.0 (dd, J = 16, 8, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 50.5 (d, J = 26), 35.2 (d, J = 26). IR: 3044, 2922, 2811, 1556, 1483, 1456, 1428, 1306, 1222, 1178, 1100, 1050, 1017, 994, 878, 817, 739, 693, 530, 487. Anal. Calcd for $C_{33}H_{31}IOP_2Pd$: C, 53.65; H, 4.23. Found: C, 53.59; H, 4.22.

Pd((S,S)-Chiraphos)(*o*-An)(I) (4). Method 1. To a solution of *trans*-Pd(PPh_3)$_2$(*o*-An)(I) (203 mg, 0.234 mmol) in toluene (6 mL) was added a solution of (*S*,*S*)-Chiraphos (100 mg, 0.234 mmol) in toluene (6 mL). The pale yellow suspension was stirred at room temperature for 72 h. The toluene was removed in vacuo. Petroleum ether (12 mL) was added, and the suspension was stirred for 24 h. The air-stable, yellow solid was collected on a fine frit and dried to yield 80 mg (48%) of crude product.

Method 2. To a stirred solution of Pd(TMEDA)(*o*-An)(I) (**9**; 1.000 g, 2.19 mmol) in THF (5 mL) was added, dropwise, a solution of (*S*,*S*)-Chiraphos (934 mg, 2.19 mmol) in THF (5 mL). The solution was stirred for 24 h, and a yellow solid precipitated. The solid was collected on a fine frit, rinsed with THF (0.5 mL) and petroleum ether (20 mL), and dried on the frit to yield 1.212 g (72% yield) of analytically pure product. The washes were combined with the original mother liquor, and a second crop precipitated at room temperature (total yield 1.437 g, 85% yield).

NMR spectra showed two atropisomers (A and B) in a 6:1 ratio. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.10−8.04 (m, 1H A, 5H B, Ar), 7.89−7.83 (m, 3H A, Ar), 7.70−7.47 (m, 11H A, 8H B, Ar), 7.37−7.32 (m, 1H A, 2H B, Ar), 7.25−7.23 (m, 3H B, Ar), 7.18−7.14 (m, 2H A, Ar), 6.99−6.94 (m, 1H A, 2H B, Ar), 6.83−6.70 (m, 3H A, 3H B, Ar), 6.50−6.45 (m, 1H A, 1H B, Ar), 6.12−6.08 (m, 1H A, Ar), 3.35 (3H B, OMe), 3.14 (3H A, OMe), 2.44−2.33 (m, 1H A, 1H B, CH), 2.19−2.04 (m, 1H A, 1H B, CH), 1.10−0.97 (m, 6H A, 6H B, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 161.7 (Ar), 143.1 (d, J = 127, Ar, quat), 137.5 (Ar), 137.2 (d, J

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= 13, Ar), 136.8 (d, J = 13, Ar), 132.9 (d, J = 9, Ar), 132.3 (d, J = 3, Ar), 131.9 (d, J = 8, Ar), 131.7 (Ar), 130.4 (d, J = 2, Ar), 130.0 (d, J = 3, Ar), 129.8 (d, J = 57, Ar, quat), 129.0 (Ar), 128.9 (Ar), 128.8 (Ar), 128.7 (d, J = 3, Ar), 128.58 (d, J = 2, Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.03 (Ar), 127.7 (Ar), 126.1 (d, J = 45, Ar, quat), 124.2 (Ar), 120.0 (d, J = 8, Ar), 109.9 (d, J = 5, Ar), 54.5 (OMe), 36.8 (dd, J = 27, 23, CH), 34.0 (dd, J = 24, 15, CH), 14.4−13.9 (m, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 56.5 (d, J = 39, B), 55.4 (d, J = 36, A), 42.5 (d, J = 39, B), 41.8 (d, J = 36, A). IR: 3036, 2966, 2907, 1560, 1482, 1449, 1431, 1219, 1102, 1055, 1020, 743, 690, 544, 520. Anal. Calcd for $C_{35}H_{35}IOP_2Pd$: C, 54.82; H, 4.60. Found: C, 54.83; H, 4.71.

Pd((R,R)-Me-Duphos)(*o*-An)(I) (5). A solution of Pd(TMEDA)(*o*-An)(I) (**9**; 255 mg, 0.558 mmol) and (*R*,*R*)-Me-Duphos (171 mg, 0.558 mmol) in THF (3 mL) was stirred at room temperature for 24 h. The yellow product was precipitated by the addition of petroleum ether, collected, and further washed with petroleum ether. Yield: 235 mg (65%). A sample was prepared for elemental and crystallographic analysis by recrystallization from CH_2Cl_2/Et_2O at −25 °C. Complex **5** cocrystallized with 1 equiv of CH_2Cl_2 according to X-ray crystallography. Desolvation occurred prior to elemental analysis to yield a final Pd:CH_2Cl_2 ratio of 10:1. A 4.5:1 ratio of atropisomers A and B was observed by NMR.

^1H NMR ($CDCl_3$): δ 7.75−7.67 (m, 1H A, 1H B, Ar), 7.64−7.58 (m, 4H A, 3H B, Ar), 7.24−7.21 (m, 1H B, Ar), 6.97−6.92 (m, 1H A, 1H B, Ar), 6.83−6.80 (m, 1H A, 1H B, Ar), 6.67−6.63 (m, 1H A, 1H B, Ar), 3.78−3.70 (m, 1H A, 1H B, CH), 3.74 (3H B, OMe), 3.72 (3H A, OMe), 3.16−3.09 (m, 1H B, CH), 2.89−2.78 (m, 1H A, CH), 2.65−2.60 (m, 1H B, CH), 2.57−2.45 (m, 2H A, CH_2), 2.39−2.29 (m, 1H A, 1H B, CH), 2.25−1.80 (m, 6H A, $3CH_2$), 1.67−1.54 (9H B, Me + $3CH_2$), 1.57 (dd, J_{PH} = 20, J_{HH} = 7, 3H A, Me), 1.44 (dd, J_{PH} = 19, J_{HH} = 7, 3H A, Me), 1.24 (dd, J_{PH} = 20, J_{HH} = 7, 3H B, Me), 1.02−0.87 (m, 7H A, 2Me +CH; 6H B, 2Me), 0.81−0.77 (m, 2H B, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 163.5 (B, Ar), 162.0 (A, Ar), 144.7 (d, J = 130, A, Ar, quat), 144.5 (dd, J = 44, 34, A, Ar, quat), 143.0 (dd, J = 33, 27, A, Ar, quat), 140.7 (A, Ar), 136.5 (B, Ar), 133.42 (d, J = 9, B, Ar), 133.36 (d, J = 15, A, Ar), 132.7 (d, J = 16, A, Ar), 132.6 (B, Ar), 131.5−131.3 (m, A, Ar), 124.4 (A, Ar), 120.8 (d, J = 5, A, Ar), 111.5 (d, J = 5, A, Ar), 109.6 (d, J = 5, B, Ar), 56.1 (A, OMe), 53.7 (B, OMe), 44.4 (d, J = 29, A, CH), 43.0 (d, J = 22, A, CH), 42.8 (d, J = 23, B, CH), 42.7 (d, J = 28, B, CH), 38.0 (d, J = 1, A, CH_2), 37.8 (B, CH_2), 37.5 (d, J = 21, B, CH), 36.8 (A, CH_2), 36.7 (d, J = 21, A, CH), 36.5 (B, CH_2), 36.3 (d, J = 3, A, CH_2), 35.9 (d, J = 27, A, CH), 35.5 (d, J = 5, A, CH_2), 35.4 (B, CH_2), 33.6 (d, J = 27, B, CH), 17.7 (d, J = 10, B, Me), 17.3 (d, J = 11, A, Me), 16.1 (d, J = 8, A, Me), 15.5 (B, Me), 15.0 (d, J = 5, B, Me), 14.8 (A, Me), 14.7 (d, J = 18, B, Me), 14.2 (A, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 74.8 (d, J = 24, A), 73.8 (d, J = 25, B), 69.0 (d, J = 24, A), 68.6 (d, J = 25, B). IR: 3047, 2926, 2864, 1559, 1451, 1424, 1243, 1218, 1170, 1115, 1054, 1019, 753, 715, 698, 643, 545, 455. Anal. Calcd for $C_{25}H_{35}IOP_2Pd\cdot 0.1CH_2Cl_2$: C, 46.01; H, 5.41. Found: C, 45.94; H, 5.34.

Pd((*R*,*S*)-t-Bu-Josiphos)(*o*-An)(I) (6). A 50 mL ampule was charged with Pd(TMEDA)(*o*-An)(I) (**9**; 250 mg, 0.547 mmol) and (*R*,*S*)-*t*-Bu-Josiphos (297 mg, 0.547 mmol) in 5 mL of THF. The reaction flask was heated at 50 °C with stirring under N_2. The reaction was monitored by $^{31}P\{^1H\}$ NMR. After 24 h, the orange product precipitated out of solution. It was collected and washed with petroleum ether. The mother liquor was pumped dry, fresh THF was added, and heating was continued. In this manner, the product was periodically collected until its formation ceased (3 days). Yield: 414 mg (85%). A sample was purified for elemental and crystallographic analysis by recrystallization from CH_2Cl_2/Et_2O at −25 °C. Two atropisomers (A and B) were observed by NMR in a 5:1 ratio.

^1H NMR ($CDCl_3$): δ 8.47−8.42 (m, 1H B, Ar), 7.90−7.84 (m, 2H A, Ar), 7.66−7.59 (m, 3H B, Ar), 7.48−7.34 (m, 8H A, Ar), 7.17−7.12 (m, 1H B, Ar), 6.98−6.92 (m, 2H B, Ar), 6.91−6.83 (m, 2H B, Ar), 6.75−6.69 (m, 1H B, Ar), 6.67−6.60 (m, 1H A, Ar), 6.48−6.44 (m, 1H B, Ar), 6.32−6.22 (m, 1H A, 1H B, Ar), 6.15−6.10 (m, 2H A, Ar), 5.74−5.69 (m, 1H B, Ar), 4.62−4.60 (m, 1H B, Cp), 4.54−4.51 (m, 1H A, Cp), 4.38−4.36 (m, 1H B, Cp), 4.34−4.33 (m, 1H B, Cp), 4.26−4.25 (m, 1H A, Cp), 3.82−3.78 (m, 6H A, Cp), 3.70 (5H B, Cp), 3.49−3.40 (m, 4H A, OMe, C*H*Me), 3.20 (3H B, OMe), 3.17 (q, J_{HH} = 4, 1H B, C*H*Me), 2.14−2.09 (m, 3H A, Me), 2.10−2.06 (m, 3H B, Me), 1.76 (d, J_{PH} = 12, 9H A, 9H B, *t*-Bu), 1.47 (d, J_{PH} = 13, 9H B, *t*-Bu), 1.38 (d, J_{PH} = 13, 9H A, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.7 (B, Ar, quat), 160.6 (d, J = 3, A, Ar, quat), 141.4 (A, Ar), 138.0 (dd, J = 138, 6, A, Ar, quat), 136.8 (d, J = 15, B, Ar), 134.4 (d, J = 13, A, Ar), 134.0 (d, J = 10, A, Ar), 132.8 (d, J = 9, B, Ar), 132.3 (d, J = 47, A, Ar, quat), 131.9 (d, J = 63, A, Ar, quat), 130.1 (d, J = 2, A, Ar), 129.6 (d, J = 3, A, Ar), 128.2 (d, J = 11, B, Ar), 128.0 (B, Ar), 127.6 (d, J = 20, A, Ar), 127.3 (d, J = 11, A, Ar), 125.6 (d, J = 10, B, Ar), 123.8 (B, Ar), 123.5 (A, Ar), 120.3 (d, J = 9, A, Ar), 108.6 (B, Ar), 107.9 (d, J = 4, A, Ar), 96.2 (dd, J = 18, 7, A, Cp, quat), 79.1 (dd, J = 35, 10, A, Cp, quat), 74.8 (d, J = 4, A, Cp, CH), 70.4 (B, Cp), 70.1 (A, Cp), 69.3 (d, J = 8, A, Cp, CH), 67.8 (A, Cp, CH), 53.7 (A, OMe), 53.2 (B, OMe), 39.5 (B, *C*Me_3), 38.8 (A, *C*Me_3), 38.3 (B, *C*Me_3), 36.7 (d, J = 2, A, *C*Me_3), 33.7 (d, J = 8, A, CH), 33.2 (br, B, C*Me*$_3$), 32.6 (d, J = 4, A, C*Me*$_3$), 31.4 (d, J = 4, A, C*Me*$_3$), 31.3 (B, C*Me*$_3$), 19.0 (d, J = 6, B, Me), 18.2 (d, J = 6, A, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78.5 (d, J = 38, A), 70.2 (d, J = 36, B), 21.5 (d, J = 36, B), 15.9 (d, J = 38, A). IR: 2921, 2852, 1734, 1560, 1492, 1453, 1385, 1223, 1176, 1162, 1100, 1051, 1018, 746, 697. Anal. Calcd for $C_{39}H_{47}FeIOP_2Pd$: C, 53.06; H, 5.37. Found: C, 53.12; H, 5.39.

Pd((*R*)-Tol-Binap)(*o*-An)(I) (7). To a suspension of {Pd[P(*o*-Tol)$_3$](*o*-An)(I)}$_2$ (**8**; 390 mg, 0.302 mmol) in toluene (20 mL) was added a solution of (*R*)-Tol-Binap (410 mg, 0.605 mmol) in toluene (5 mL). The orange-brown suspension was stirred at room temperature for 24−30 h, at which point it appeared to be homogeneous. The solution was filtered by cannula, and the filtrate was pumped dry. The granular off-white solid contained a small amount of a purple impurity, which was removed by washing with petroleum ether. Trituration with ether (75 mL) gave a yellow solid product. The solid was then collected and recrystallized from THF/petroleum ether at −25 °C to yield 308 mg of product (49%). Two atropisomers (A and B), whose ^1H NMR spectra were not resolved in the aryl region, were observed in a 1.8:1 ratio.

^1H NMR (C_6D_6): δ 8.65−8.63 (m, 1H B, Ar), 8.25−8.05 (m, 3H A, 3H B, Ar), 7.74 (m, 2H A, 2H B, Ar), 7.60−7.57 (m, 1H A, 2H B, Ar), 7.33−7.20 (m, 2H A, 2H B, Ar), 7.12−6.90 (m, 11H A, 11H B, Ar), 6.82−6.77 (m, 2H A, 2H B, Ar), 6.65−6.53 (m, 6H A, 6H B, Ar), 6.23−6.21 (m, 3H A, 3H B, Ar) 6.10 (br, 2H A, 2H B, Ar), 3.67 (3H, B, OMe), 3.64 (3H, A, OMe), 2.09 (3H A, Me; 3H B, Me), 1.79−1.64 (overlapping s, 9H, A, Me; 9H, B, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.9 (Ar), 140.4 (m, Ar), 139.9−139.5 (m, Ar), 138.0−137.2 (m, Ar), 136.6 (m, Ar), 135.6−133.6 (m, Ar), 131.0−130.1 (m, Ar), 129.8 (Ar), 129.6−129.4 (m, Ar), 127.0 (Ar), 126.8 (Ar), 126.4 (Ar), 124.6 (Ar), 123.9 (Ar), 122.6 (Ar), 121.0 (Ar), 114.0 (Ar), 111.7 (Ar), 110.5 (Ar), 56.0 (A, OMe), 55.9 (B, OMe), 21.7−21.3 (overlapping s, tol-Me). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 23.8 (d, J = 37, A), 23.4 (d, J = 38, B), 12.3 (d, J = 37, A), 10.4 (d, J = 38, B). IR: 3044, 2933, 1556, 1494, 1450, 1256, 1217, 1189, 1094, 1022, 800, 744, 700, 633, 522, 500. Anal. Calcd for $C_{55}H_{47}IOP_2Pd$: C, 64.81; H, 4.65. Found: C, 64.91; H, 4.63.

Separation of the Diastereomers of Pd((*S*,*S*)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH$_3$)) (11) and Isolation of Pure Pd((*S*,*S*)-Chiraphos)(*o*-An)(*S*$_P$-P(Me)(Ph)(BH$_3$)) (11a). Pd((*S*,*S*)-Chiraphos)(*o*-An)(I) (**4**; 300 mg, 0.391 mmol) was suspended in toluene (4 mL) with vigorous stirring, and *rac*-PH(Me)(Ph)(BH_3) (**2**, 54 mg, 0.39 mmol) was added as a

solution in toluene (2 mL). $NaOSiMe_3$ (0.371 mL, 1.0 M solution in THF, 0.37 mmol) was then added slowly by syringe. The mixture became somewhat darker, and the slurry was stirred for 30 min at room temperature and then filtered through Celite to remove NaI. The Celite was washed with several portions of toluene (total 5 mL), giving a golden yellow solution. (Exhaustive extraction of the Celite/solid is necessary to ensure complete extraction of all of the less soluble diastereomer.) Removal of all volatiles in vacuo left a sticky orange solid, to which Et_2O (5 mL) was added with vigorous stirring, causing a white solid to precipitate. The mixture was stirred for 10 min, and then the white solid was isolated by filtration on a frit, washed with Et_2O (3 mL), and dried in vacuo. NMR spectroscopy revealed this solid to be highly enriched in **11a** and its atropisomer **11d** (typically greater than 90% de), and it was found to be analytically pure. The Et_2O-soluble fraction was pumped down to give a sticky orange solid. NMR analysis of this material showed it contained mainly **11b** but also significant quantities of siloxy-containing byproducts. Typical yield of **11a**: 100 mg (33%, 0.131 mmol). Crystals that were suitable for X-ray analysis were obtained by slow (11 months) diffusion of petroleum ether into a concentrated THF solution of diastereomerically pure **11a** at −25 °C.

Anal. Calcd for $C_{42}H_{46}P_3BOPd$: C, 64.93; H, 5.97. Found: C, 64.60; H, 5.78. ^{1}H NMR (THF-d_8): δ 8.12−8.08 (m, 2H, Ar), 7.95−7.91 (m, 2H, Ar), 7.63−7.50 (m, 6H, Ar), 7.35−7.17 (m, 7H, Ar), 7.15−7.11 (m, 2H, Ar), 6.83−6.82 (m, 1H, Ar), 6.77−6.72 (m, 3H, Ar), 6.70−6.64 (m, 4H, Ar), 6.48−6.45 (m, 1H, Ar), 6.21−6.18 (m, 1H, Ar), 3.23 (OMe), 2.12−2.01 (m, 2H, CH), 0.93−0.87 (m, 6H, Chiraphos Me), 0.44 (dd, J_{PH} = 9, 2, 3H, P−Me). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 161.6 (Ar), 150.0 (Ar), 149.2 (Ar), 143.1 (d, J = 26, Ar), 137.8−137.7 (m, Ar), 137.6 (d, J = 13, Ar), 137.4 (d, J = 13, Ar), 134.4−134.3 (m, Ar), 132.8 (d, J = 10, Ar), 132.2 (d, J = 2, Ar), 132.1−132.0 (m, Ar), 131.9 (Ar), 129.3 (d, J = 11, Ar), 129.2 (Ar), 128.9 (d, J = 9, Ar), 128.8 (d, J = 10, Ar), 128.5 (d, J = 9, Ar), 128.2 (Ar), 127.9 (Ar), 127.6−127.5 (m, Ar), 127.3 (Ar), 127.0 (d, J = 8, Ar), 124.3 (Ar), 120.5 (d, J = 7, Ar), 109.8 (Ar), 54.7 (OMe), 38.5−38.2 (m, CH), 33.6−33.3 (m, CH), 16.7 (d, J = 24, P-Me), 14.6−14.4 (m, Chiraphos Me), 14.0−13.8 (m, Chiraphos Me). ^{31}P{^{1}H} NMR (THF-d_8): δ 52.1 (dd, J = 291, 38), 50.9 (dd, J = 38, 16), 7.0 (broad d, J = 291). FAB-MS (Magic Bullet): m/z 775 $(M - H)^+$, 762, 685, 655, 532 $[Pd(Chiraphos)]^+$, 476, 455, 398, 371, 309, 291, 263, 243, 195, 155, 135, 119.

Purified samples of **11a**, and those formed in situ by reaction of **4** with **2**, contained small amounts of atropisomer **11d**, which was identified by ^{31}P{^{1}H} NMR and ^{1}H NMR. The **11a**:**11d** ratio ranged from ca. 10:1 to 40:1 and seemed to depend on conditions. Data for **11d** are as follows. ^{31}P{^{1}H} NMR (THF-d_8): δ 48.4 (dd, J = 292, 36), 45.5 (dd, J = 36, obscured by signals of **11a**, so that the other coupling could not be measured), −12.6 (br d, J = 292). ^{1}H NMR (THF-d_8): δ 3.29 (OMe), 0.67 (dd, J_{PH} = 8, 4, P*Me*).

Diastereoselective Synthesis of Pd((*S*,*S*)-Chiraphos)(*o*-An)((*R*$_P$)-P(Me)(Ph)(BH$_3$)) (11b). Pd((*S*,*S*)-Chiraphos)(*o*-An)(I) (**4**; 250 mg, 0.326 mmol) and (S_P)-PH(Me)(Ph)(BH_3) (**2**; 45 mg, 0.33 mmol) were weighed in the glovebox and transferred to a Schlenk flask with THF (total 5 mL). The flask was removed from the glovebox and cooled to −78 °C, and $NaOSiMe_3$ (0.326 mL, 1.0 M solution in THF, 0.33 mmol) was added by syringe under N_2. The mixture was stirred at −78 °C for 2 h, and then the cold bath was removed and the mixture warmed to room temperature. All volatiles were then removed in vacuo to yield a pale orange sticky solid, which darkened over time. The residue was washed with Et_2O (5 mL) and the washings stripped in vacuo to give a sticky red solid. ^{1}H NMR (THF-d_8) analysis of the solid revealed small amounts of **11b** and **11a** (in approximate ratio 92:8) and large quantities of a $OSiMe_3$-containing impurity. The Et_2O-insoluble material was then extracted with toluene (total 15 mL), filtered through Celite, and reduced in volume to ca. 3 mL in vacuo. The brown-purple solution was layered with petroleum ether (10 mL) and stored at −25 °C for 24 h. A pale pink solid was isolated by decantation, washed with petroleum ether (2 mL), and dried in vacuo. ^{1}H NMR spectroscopy revealed this solid to contain **11b** (and its atropisomer **11c**) with de >99%. Yield: 175 mg (0.229 mmol, 70%).

Crystals that were suitable for X-ray analysis were obtained from ether at −25 °C. After the structure of **11b** was determined by X-ray crystallography, the single crystal used for the structure determination was dissolved in THF-d_8 and its ^{1}H NMR spectrum was obtained, to correlate the NMR data for **11a** and **11b** with their absolute configurations.

Anal. Calcd for $C_{42}H_{46}P_3BOPd$: C, 64.93; H, 5.97. Found: C, 64.58; H, 5.83. ^{1}H NMR (THF-d_8): δ 8.34−8.30 (m, 2H, Ar), 7.82−7.79 (m, 2H, Ar), 7.63−7.45 (m, 8H, Ar), 7.35−7.32 (m, 1H, Ar), 7.26−7.17 (m, 5H, Ar), 7.13−7.05 (m, 3H, Ar), 6.91−6.88 (m, 1H, Ar), 6.84−6.81 (m, 2H, Ar), 6.67−6.65 (m, 3H, Ar), 6.46−6.43 (m, 1H, Ar), 6.00−5.97 (m, 1H, Ar), 3.11 (OMe), 2.11−2.05 (m, 1H, CH), 1.98−1.94 (m, 1H, CH), 0.98 (dd, J = 10, 7, 3H, Me), 0.90 (dd, J = 10, 7, 3H, Me), 0.59 (dd, J_{PH} = 8, 3, P−Me). ^{31}P{^{1}H} NMR (THF-d_8): δ 54.3 (dd, J = 287, 36), 49.5 (dd, J = 36, 27), −9.1 (broad d, J = 287).

Purified samples of **11b**, and those formed in situ by reaction of **4** with **2**, contained small amounts of atropisomer **11c**, which was identified by ^{31}P{^{1}H} NMR and ^{1}H NMR. The **11b**:**11c** ratio was consistently ca. 30:1 in isolated samples but varied from ca. 10:1 to 20:1 in the crude material, depending on reaction conditions for the transmetalation. Data for **11c** are as follows. ^{31}P{^{1}H} NMR (THF-d_8): δ 47.2 (dd, J = 292, 37), 45.1 (dd, J = 37, 27), −5.0 (br d, J = 292). ^{1}H NMR (THF-d_8): δ 3.41 (OMe), 1.33−1.28 (m, Me), 0.44 (dd, J_{PH} = 8, 3, PMe).

Kinetic Resolution. Synthesis of 11a. Pd((*S*,*S*)-Chiraphos)(*o*-An)(I) (**4**; 139 mg, 0.181 mmol) was weighed into a vial and slurried in toluene (2 mL), and a solution of *rac*-PH(Me)(Ph)(BH_3) (**2**; 50 mg, 0.36 mmol, 2 equiv) in toluene (2 mL) was added. $NaOSiMe_3$ (181 μL, 1.0 M solution in THF, 0.18 mmol) was then added via microliter syringe and the yellow slurry stirred for 30 min at room temperature. All volatiles were removed in vacuo to leave a sticky pale yellow residue. ^{1}H NMR spectroscopic analysis of this solid (THF-d_8) indicated the ratio of diastereomers (and accompanying atropisomers) of Pd((*S*,*S*)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) **11a**:**11b** = 5.84:1, giving an overall de of 70% (the same result was obtained in a second run). The resultant solid was extracted with Et_2O (10 mL), and the yellow extracts were pumped down to give a sticky yellow solid, containing **11b**, PH(Me)(Ph)(BH_3), and siloxy-containing impurities. The residual PH(Me)(Ph)(BH_3) was isolated by chromatography of this solid on silica gel with 1:1 hexane/CH_2Cl_2 as eluent. Chiral HPLC analysis (Chiralcel OJ-H) of the isolated PH(Me)(Ph)(BH_3) showed it to be enriched in (S_P)-PH(Me)(Ph)(BH_3) with an ee of approximately 30%.

The Et_2O-insoluble material was dissolved in toluene (total 15 mL), and the solution was filtered and reduced in volume to ca. 4 mL, at which point white solid started to precipitate. The solution was layered with pentane (10 mL) and stored at −25 °C for 3 days to yield 111 mg (0.145 mmol, 80% yield) of Pd((*S*,*S*)-Chiraphos)(*o*-An)((S_P)-P(Me)(Ph)(BH_3)) (**11a**) with >99% de (as shown by ^{1}H NMR in THF-d_8).

Pd((*R*,*R*)-Me-Duphos)(*o*-An)(P(Me)(Ph)(BH$_3$)) (12a,b). Method 1. To a stirred solution of Pd((*R*,*R*)-Me-Duphos)(*o*-An)(I) (**5**; 50 mg, 0.077 mmol) in THF (8 mL) were added PH(Me)(Ph)(BH_3) (11 mg, 0.077 mmol) and $NaOSiMe_3$ (77 μL of a 1.0 M THF solution, 0.077 mmol). The mixture was stirred for 10 min and concentrated to 1 mL by removal of the solvent in vacuo. The ^{31}P{^{1}H} NMR spectrum of this crude reaction mixture showed four species: two major diastereomers (**12a, 12b**) in a 1:1 ratio and two minor rotamers (**12c**, **12d**) in a 2:1 ratio. This reaction mixture was characterized by ^{31}P{^{1}H} COSY NMR spectroscopy. ^{31}P{^{1}H} NMR (THF with a DMSO-d_6 insert): δ 73.1 (dd, J = 31, 26, **12a**), 71.4 (dd, J = 287, 26,

12a), 70.4 (dd, J = 310, 27, **12b**), 70.0 (apparent t, J = 27, **12b**), 69.6 (apparent t, J = 27, **12c**), 69.0 (dd, J = 26, 25, **12d**), 67.4 (dd, J = 297, 25, **12d**), 67.1 (dd, J = 298, 26, **12c**), −9.6 (broad d, J = 310, **12b**), −14.5 (broad d, J = 298, **12c**), −20.2 (broad d, J = 287, **12a**). Note that the phosphido−borane resonance for **12d** was not observed.

Method 2. To a stirred slurry of Pd((*R*,*R*)-Me-Duphos)(*o*-An)(I) (**10**; 200 mg, 0.31 mmol) in toluene (4 mL) were added PH(Me)(Ph)(BH_3) (43 mg, 0.31 mmol) and $NaOSiMe_3$ (309 μL of a 1.0 M THF solution, 0.309 mmol). The mixture became homogeneous, and then a white solid precipitated. The solvent was removed in vacuo, and the residue was redissolved in minimal THF and cooled at −25 °C for 2 weeks. The white precipitate was washed with minimal THF (which caused a small amount of dissolution) followed by a generous wash with petroleum ether and dried in vacuo (yield: ca. 40 mg, 20% yield). This product was shown to be a single diastereomer (**12a**) by $^{31}P\{^1H\}$ NMR spectroscopy. A second, minor, isomer was observed in the ^1H NMR spectrum, but it was unclear whether this was **12b** or a rotational conformer. Only the easily assigned OMe signal is reported here; integrals of this peak with that of **12a** showed an 18:1 ratio. ^1H NMR (CD_2Cl_2): δ 7.69−7.66 (m, 1H, Ar), 7.61−7.53 (m, 6H, Ar), 7.20−7.17 (m, 2H, Ar), 7.15−7.11 (m, 1H, Ar), 6.99−6.96 (m, 1H, Ar), 6.79−6.76 (m, 1H, Ar), 6.54−6.52 (m, 1H, Ar), 3.63 (OMe, minor), 3.59 (3H, OMe), 2.51−2.33 (m, 3H, CH_2 + CH), 2.14−2.05 (m, 1H, CH), 1.96−1.85 (m, 2H, CH_2), 1.79−1.69 (m, 3H, CH_2 + CH), 1.61−1.51 (m, 1H, CH), 1.41 (dd, J_{PH} = 18, J_{HH} = 7, 3H, Me), 1.15 (dd, J_{PH} = 19, J_{HH} = 7, 3H, Me), 1.04 (dd, J_{PH} = 15, J_{HH} = 7, 3H, Me), 0.89 (dd, J_{PH} = 15, J_{HH} = 7, 3H, Me), 0.85 (dd, J_{PH} = 9, 3, 3H, P−Me), 0.69−0.57 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 161.8 (Ar, quat), 149.0 (d, J = 106, Ar, quat), 145.9 (ddd, J = 39, 28, 3, Ar, quat), 144.9 (dm, J = 24, Ar, quat), 142.6 (ddd, J = 38, 27, 3, Ar, quat), 139.8 (Ar, CH), 133.9 (d, J = 15, Ar, CH), 133.15 (d, J = 8, Ar, CH), 133.14 (d, J = 8, Ar, CH), 133.1 (Ar, CH), 131.2 (m, Ar, CH), 130.8 (m, Ar, CH), 127.3 (d, J = 8, Ar, CH), 124.6 (Ar, CH), 120.1 (d, J = 7, Ar, CH), 109.2 (Ar, CH), 54.5 (OMe), 45.1 (d, J = 22, CH), 44.9 (d, J = 26, CH), 37.7 (CH_2), 37.3 (CH_2), 35.7 (d, J = 4, CH_2), 35.2 (d, J = 18, CH), 34.8 (d, J = 4, CH_2), 34.78 (d, J = 22, CH), 16.6 (d, J = 12, Me), 15.7 (d, J = 9, Me), 15.1 (d, J = 25, P−Me), 14.3 (d, J = 2, Me), 14.2 (d, J = 2, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 65.0 (dd, J = 314, 27), 64.5 (apparent t, J = 26), −20.1 (br d, J = 314). Anal. Calcd for $C_{32}H_{46}BOP_3Pd$: C, 58.51; H, 7.06. Found: C, 57.62; H, 7.48.

Pd((*S*,*S*)-Chiraphos)Cl_2 (18). This compound was previously synthesized by a different method.[46] To a stirred slurry of Pd(COD)Cl_2 (150 mg, 0.52 mmol) in CH_2Cl_2 (2 mL) was added a solution of (*S*,*S*)-Chiraphos (224 mg, 0.52 mmol) in CH_2Cl_2. The mixture became homogeneous, and then a white solid precipitated. The reaction mixture was stirred for 25 min. The solid was collected on a fine frit, rinsed with diethyl ether, and dried on the frit to yield 240 mg of product. The ether was added to the CH_2Cl_2 mother liquor to yield a second crop of product (35 mg, total yield: 275 mg, 87%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 66.6.

Pd((*S*,*S*)-Chiraphos)I_2 (13). To a clear, colorless, stirred solution of Pd((*S*,*S*)-Chiraphos)Cl_2 (**18**; 56 mg, 0.17 mmol) in acetone (3 mL) was added a slurry of NaI (56 mg, 0.66 mmol, 4 equiv) in acetone (2 mL). The reaction mixture turned bright yellow and was stirred for 1 h. The acetone was removed in vacuo, and distilled water (7 mL) was added. The yellow product was collected on a fine frit, washed three times with water (10 mL), and dried on the frit to yield 50 mg (83%). A sample was recrystallized from CH_2Cl_2 for elemental and crystallographic analysis.

^1H NMR ($CDCl_3$): δ 8.02−7.98 (m, 4H, Ar), 7.77−7.73 (m, 4H, Ar), 7.69−7.66 (m, 2H, Ar), 7.58−7.49 (m, 10H, Ar), 2.32−2.30 (m, 2H, CH), 1.06 (dd, J_{PH} = 4, J_{HH} = 8, 6H, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.0. Anal. Calcd for $C_{28}H_{28}I_2P_2Pd\cdot 0.8CH_2Cl_2$: C, 40.48; H, 3.49. Found: C, 40.08; H, 3.26. The presence of solvent was quantitatively confirmed by ^1H NMR spectroscopy.

Pd((*R*,*R*)-Me-Duphos)Cl_2 (19). This complex was prepared previously by a different method.[47] To a stirred yellow slurry of Pd(COD)Cl_2 (200 mg, 0.70 mmol) in CH_2Cl_2 (2 mL) was added a solution of (*R*,*R*)-Me-Duphos (214 mg, 0.70 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred for 1 h, and a white solid precipitated. The solid was collected on a fine frit and washed with ether (3 × 5 mL) to yield analytically pure product (287 mg, 85%).

^1H NMR ($CDCl_3$): δ 7.75−7.65 (m, 4H, Ar), 3.75−3.62 (m, 2H, CH), 2.71−2.22 (m, 8H, CH_2), 1.82−1.69 (m, 2H, CH), 1.62 (dd, J_{PH} = 7, J_{HH} = 9, 6H, Me), 0.95 (dd, J_{PH} = 7, J_{HH} = 17, 6H, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 96.2. Anal. Calcd for $C_{18}H_{28}Cl_2P_2Pd\cdot 0.9CH_2Cl_2$: C, 40.53; H, 5.36. Found: C, 40.89; H, 5.26. The presence of solvent was confirmed quantitatively by ^1H NMR spectroscopy.

Pd((*R*,*R*)-Me-Duphos)I_2 (16). To a stirred solution of Pd((*R*,*R*)-Me-Duphos)Cl_2 (**19**; 200 mg, 0.41 mmol) in acetone (5 mL) was added a slurry of NaI (248 mg, 1.65 mmol, 4 equiv) in acetone (3 mL). A yellow solid immediately precipitated, and the acetone was removed in vacuo. Distilled water (7 mL) was added, and the yellow product was collected on a fine frit, washed with water (3 × 10 mL), and dried on the frit to yield 210 mg (75%). A sample was recrystallized from CH_2Cl_2/diethyl ether for elemental and crystallographic analysis.

^1H NMR ($CDCl_3$): δ 7.74 (broad, 4H, Ar), 4.24−4.12 (m, 2H, CH), 2.59−2.14 (m, 8H, CH_2), 1.96−1.85 (m, 2H, CH), 1.56 (dd, J_{PH} = 6, J_{HH} = 20, 6H, Me), 0.91 (dd, J_{PH} = 7, J_{HH} = 16, 6H, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 95.1. Anal. Calcd for $C_{18}H_{28}I_2P_2Pd$: C, 32.43; H, 4.23. Found: C, 32.55; H, 4.49.

Pd((*S*,*S*)-Chiraphos)$_2$ (15). This complex was synthesized previously by a different method.[32] To a vigorously stirred slurry of Pd((*S*,*S*)-Chiraphos)Cl_2 (**18**; 200 mg, 0.33 mmol) and (*S*,*S*)-Chiraphos (134 mg, 0.31 mmol, 0.95 equiv) in degassed ethanol (15 mL) was added a solution of $NaBH_4$ (50 mg, 1.3 mmol, 4 equiv) in degassed, distilled H_2O. The reaction mixture immediately turned bright yellow and was stirred for 45 min. The product was fully precipitated by cooling to 0 °C and was filtered by cannula. The air-sensitive yellow solid was washed with degassed water (3 × 10 mL) and left under a flow of N_2 for several days to dry before being brought into the drybox. The yellow solid was dissolved in THF (2 mL), and the solution was filtered through Celite. The THF was removed in vacuo, and the residue was extracted with Et_2O, concentrated, and placed in the refrigerator at −25 °C to precipitate analytically pure yellow crystals (140 mg, 46% yield).

^1H NMR (C_6D_6): δ 7.68 (br, 8H, Ar), 7.37 (br, 8H, Ar), 7.14−7.11 (m, 4H, Ar), 7.05 (m, 8H, Ar), 6.91−6.88 (m, 12H, Ar), 1.88 (br, 4H, CH), 0.78 (12H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.5−140.3 (m, Ar), 136.5−136.4 (m, Ar), 136.2−136.0 (m, Ar), 131.6−131.5 (m, Ar), 128.9 (m, Ar), 128.6 (Ar, CH), 127.4 (m, Ar), 126.7 (Ar, CH), 38.8−38.3 (m, CH), 15.9−15.7 (m, Me). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 43.8. Anal. Calcd for $C_{56}H_{56}P_4Pd\cdot 0.35Et_2O$: C, 69.97; H, 6.09. Found: C, 69.86; H, 6.55. The presence of solvent was quantitatively confirmed by ^1H NMR spectroscopy.

Pd((*R*,*R*)-Me-Duphos)$_2$ (17). To a vigorously stirred slurry of Pd((*R*,*R*)-Me-Duphos)Cl_2 (**19**; 200 mg, 0.41 mmol) and (*R*,*R*)-Me-Duphos (120 mg, 0.39 mmol, 0.95 equiv) in degassed ethanol (15 mL) was added a solution of $NaBH_4$ (62 mg, 1.6 mmol, 4 equiv) in degassed H_2O. The reaction mixture immediately turned bright orange and was stirred for 20 min. The product was fully precipitated by cooling to 0 °C and was filtered by cannula. The air-sensitive orange solid was washed with degassed water (3 × 10 mL) and dried under a stream of

(46) Morandini, F.; Consiglio, G.; Piccolo, O. *Inorg. Chim. Acta* **1982**, *57*, 15−19.

(47) Drago, D.; Pregosin, P. S. *Organometallics* **2002**, *21*, 1208−1215.

N_2 for several days before being brought into the drybox. Recrystallization from petroleum ether at −25 °C yielded 210 mg (71% yield) of orange crystals. Analytically pure material was obtained after a second recrystallization from petroleum ether at −25 °C.

$^1H\{^{31}P\}$ NMR (C_6D_6): δ 7.62−7.60 (m, 4H, Ar), 7.14−7.12 (m, 4H, Ar), 2.60−2.52 (m, 4H, CH), 2.33−2.24 (m, 8H, CH, CH_2), 2.00−1.93 (m, 4H, CH_2), 1.69−1.61 (m, 4H, CH_2), 1.56−1.48 (m, 4H, CH_2), 1.32 (d, J_{HH} = 8, 12H, Me), 0.85 (d, J_{HH} = 6, 12H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 149.8−149.2 (m, Ar), 132.2 (Ar), 127.6 (d, J = 7, Ar), 42.2−42.0 (m, CH), 37.3 (CH_2), 37.0−36.9 (m, CH), 36.8 (CH_2), 22.8−22.5 (m, Me), 15.5 (m, Me). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 57.5. Anal. Calcd for $C_{36}H_{56}P_4Pd$: C, 60.13; H, 7.85. Found: C, 59.76; H, 8.12.

General Procedure for Catalysis with Pd((*R*,*S*)-t-Bu-Josiphos)(*o*-An)(I) (6). Method 1. Pd((*R*,*S*)-t-Bu-Josiphos)(*o*-An)(I) (**6**; 5 mg, 0.006 mmol, 0.04 equiv) was weighed into a vial in the glovebox and dissolved in THF (0.5 mL), and *o*-AnI (38 μL, 0.29 mmol) and PH(Me)(Ph)(BH_3) (20 mg, 0.14 mmol) were added to the solution. Proton Sponge (31 mg, 0.15 mmol) was dissolved in THF (0.5 mL), and this solution was added to the catalyst solution. The mixture was then transferred to an NMR tube, the vials were rinsed with a further small amount of THF, and the washings were added to the tube. The mixture was allowed to stand at room temperature or placed in an oil bath at 40 °C, during which time it slowly deposited large colorless crystals of protonated Proton Sponge (according to ^1H NMR after isolation). The reaction was monitored by ^{31}P NMR spectroscopy every 24 h. When the ratio of product to starting material (as determined by integration of the signals in the ^{31}P spectrum) was approximately 45:55, no further reaction occurred. The NMR tube was returned to the glovebox, a second equivalent of base was added, and the tube was returned to the oil bath (if required). The reaction was then found to proceed smoothly to a ratio of approximately 90:10 product to starting material. The contents of the NMR tube were then filtered and the solids washed with THF (ca. 2 mL). The filtrate and washings were pumped to dryness in vacuo, and the residue was purified by column chromatography on silica gel (acid washed, 230−400 mesh), with 2:1 hexanes/ethyl acetate as eluent (PAMP−BH_3 R_f = 0.64). The product was isolated as a pale yellow solid and its identity confirmed by ^1H and ^{31}P NMR spectroscopy ($CDCl_3$). Further purification was achieved by recrystallization from hexanes/CH_2Cl_2 at −60 °C. The ee was determined by chiral HPLC (Chiralpak AD, 1% *i*-PrOH/hexane, flow rate 1 mL/min; retention times are 11.8 (*S*) and 13.4 min (*R*)). Retention times were compared to those of the racemate and authentic (R_P)-PAMP−BH_3 (prepared by the method of Livinghouse) run under identical conditions.[2i]

Method 2. An NMR tube was prepared as in method 1. $NaOSiMe_3$ (6 μL, 1.0 M solution in THF, 6 μmol) was then added to the tube via microliter syringe. The mixture was allowed to stand at room temperature or placed in an oil bath at 40 °C, during which time it slowly deposited large colorless crystals of protonated Proton Sponge (^1H NMR); formation of unidentified bubbles also occurred. The reaction was monitored by ^{31}P NMR spectroscopy every 24 h; although the rate slowed over time, it was not necessary to add more base. Workup and ee assay were performed as described in Method 1.

Stoichiometric Reaction of Pd((*R*,*S*)-t-Bu-Josiphos)(*o*-An)(I) (6), PH(Me)(Ph)(BH_3), $NaOSiMe_3$, and *o*-AnI. To a solution of Pd((*R*,*S*)-t-Bu-Josiphos)(*o*-An)(I) (**6**; 128 mg, 0.15 mmol) in THF (10 mL) was added *o*-AnI (38 μL, 0.29 mmol, 2 equiv), PH(Me)(Ph)(BH_3) (20 mg, 0.15 mmol), and then $NaOSiMe_3$ (145 μL of a 1.0 M solution in THF, 0.145 mmol). The mixture was stirred for 1 h, and the $^{31}P\{^1H\}$ NMR spectrum showed signals for PAMP−BH_3, a small amount of PAMP, the two atropisomers of **6**, and its regioisomer (see Table 1).

Reaction of Pd((*R*)-Tol-Binap)(*o*-An)(I) (7), PH(Me)(Ph)(BH_3), and $NaOSiMe_3$. To a solution of Pd((*R*)-Tol-Binap)(*o*-An)(I) (**7**; 74 mg, 0.07 mmol) and (*R*)-Tol-Binap (49 mg, 0.07 mmol) in THF (2 mL) was transferred a solution of PH(Me)(Ph)(BH_3) (10 mg, 0.07 mmol) and $NaOSiMe_3$ (73 mL of 1.0 M solution in THF, 0.073 mmol) in THF (1 mL). The mixture turned bright red and then dark purple. $^{31}P\{^1H\}$ NMR (THF): δ 24.1 (Pd((*R*)-Tol-Binap)$_2$), 9.2 (br, PAMP−BH_3), −16.5.

Reaction of Pd(dppe)(*o*-An)(I) (3), PH(Me)(Ph)(BH_3), and $NaOSiMe_3$. To a solution of Pd(dppe)(*o*-An)(I) (**3**; 20 mg, 0.027 mmol) in THF (1.75 mL) was added enantioenriched PH(Me)(Ph)(BH_3) (**2**; 6.0 μL, 0.027 mmol, about 75% ee (R_P)) and *o*-AnI (3.4 μL, 0.027 mmol), to give a pale yellow solution. $NaOSiMe_3$ (27 μL of a 1.0 M solution in THF, 0.027 mmol) was added. The solution briefly became salmon colored and upon mixing turned a light orange-yellow. THF-d_8 (about 5 drops) was added to enable NMR locking. The reaction was monitored by ^{31}P NMR after 30 min, which showed that Pd(dppe)(*o*-An)(P(Me)(Ph)(BH_3)) (**10**) was formed as a 1:1 mixture of atropisomers: δ 44.795 (dd, J = 293.01, 22.87), 42.710 (dd, J = 300.70, 22.87), 42.318 (overlapped dd, J = 27.70, 24.38), 41.922 (dd, J = 27.52, 22.87), −2.4 (broad d, $J \approx$ 290), −14.9 (broad d, $J \approx$ 300). The reductive elimination product Pd(dppe)$_2$ (δ 31.3) was also observed; over 48 h further decomposition gave more of this product as well as **1**, **3**, and in some cases Pd(dppe)I_2 (see the text for more details). Similar results were observed with racemic **2**.

General Procedure for Transmetalation Experiments with Chiraphos Complex 4. In the glovebox, Pd((*S*,*S*)-Chiraphos)(*o*-An)(I) (**4**; 28 mg, 0.037 mmol) was transferred to an NMR tube as a slurry in THF-d_8 (1 mL) along with a solution of (S_P)-PH(Me)(Ph)(BH_3) (**2**; 5 mg, 0.036 mmol) of known ee in THF-d_8 (0.5 mL). The tube was fitted with a rubber septum and cooled to −78 °C in a dry ice/acetone bath. $NaOSiMe_3$ (36.2 μL, 1.0 M solution in THF, 0.036 mmol) was then added by microliter syringe. After 1 min, the tube was inverted to ensure complete mixing; the tube was kept in the bath for a further 15 min and inverted every 5 min. It was then warmed to room temperature, and the ^1H and ^{31}P NMR spectra were recorded. The de of the product was calculated from integration of the OMe signals of both diastereomers and their respective atropisomers in the ^1H NMR spectrum.

Alkylation of PH(Me)(Ph)(BH_3) (2) with *p*-Methoxybenzyl Chloride. n-BuLi (986 μL of a 1.6 M solution in hexanes, 1.58 mmol) was added dropwise to a solution of *rac*-PH(Me)(Ph)(BH_3) (200 mg, 1.45 mmol) and HMPA (492 μL) in dry THF (2 mL) at −78 °C. The resultant yellow solution was stirred for 15 min at −78 °C, and then 4-methoxybenzyl chloride (214 μL, 1.58 mmol) was added by syringe. The solution was stirred for a further 3 h at −78 °C and then warmed to room temperature and stirred overnight. Water (3 mL) was added, the layers were separated, and the aqueous layer was extracted with Et_2O (3 × 3 mL). The combined organic extracts were washed with brine (2 × 3 mL), dried over $MgSO_4$, filtered, and pumped to dryness in vacuo. The crude product was purified by gravity column chromatography on silica with CH_2Cl_2/hexanes as eluent (2:1, R_f = 0.33), yielding P(Me)(Ph)(CH_2-*p*-$MeOC_6H_4$)(BH_3) (**19**) as a colorless, viscous oil that solidified on standing. Yield: 244 mg (0.945 mmol, 65%).

Anal. Calcd for $C_{15}H_{20}POB$: C, 69.80; H, 7.81. Found: C, 69.84; H, 7.81. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.4 (br q, J_{P-B} = 58). ^1H NMR ($CDCl_3$): δ 7.59−7.40 (m, 5H, Ar), 6.86−6.81 (m, 2H, Ar), 6.78−6.74 (m, 2H, A), 3.78 (3H, OMe), 3.17−3.13 (m, 2H, CH_2), 1.49 (d, J = 10, 3H, PMe), 1.2−0.2 (v br q, 3H, BH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.8 (d, J = 2.5, quat Ar), 131.9 (d, J = 9, Ar), 131.5 (d, J = 2, Ar), 130.9 (d, J = 4, Ar), 129.0 (d, J = 53, quat Ar), 128.7 (d, J = 10, Ar), 113.9 (d, J = 3, Ar), 124.3 (d, J = 7, quat Ar), 55.4 (OMe), 35.1 (d, J = 32, CH_2), 9.0 (d, J = 39, PMe). HPLC (Chiralpak AD, 3% i-PrOH in hexanes, flow rate 1 mL min^{-1}): retention times are 10.4 (*S*) and 12.4 (*R*) min.

Alkylation of Enantioenriched PH(Me)(Ph)(BH_3) (2) with *p*-Methoxybenzyl Chloride. Highly enantioenriched (S_P)-PH(Me)(Ph)(BH_3) (60 mg, 0.43 mmol, ee determined by chiral HPLC) was weighed in the glovebox, dissolved in THF (1 mL), and transferred to a Schlenk flask. The solution was cooled to −78 °C, and n-BuLi (296 μL, 1.6 M in hexanes, 0.474 mmol) was added by syringe. A yellow color instantly formed, and the solution was stirred for 10 min. 4-Methoxybenzyl chloride (64.3 μL, 0.474 mmol) was then added by microliter syringe and the mixture stirred at −78 °C for 6 h. The solution was warmed to room temperature and then quenched with H_2O (1 mL). The organic layer was separated and the aqueous layer extracted with Et_2O (3 × 2 mL). The organic extracts were combined, washed with brine (3 mL), dried over $MgSO_4$, and stripped to dryness in vacuo. The crude product (**19**) was purified by gravity column chromatography on silica, as described above. The ee of **19** was determined by chiral HPLC.

General Procedure for Reductive Elimination Reactions with Chiraphos Complex 11. A solution of highly diastereomerically enriched Pd((*S*,*S*)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (typical scale 50 mg) in THF-d_8 was transferred to an NMR tube, along with a solution of $FeCp_2$ (ca. 5 mg) and diphenylacetylene (4 equiv) in THF-d_8. (Use of a smaller excess of diphenylacetylene was found to result in lower ee's and increased OMe-containing impurities.) Initial ^{1}H and ^{31}P NMR spectra were recorded, and the initial de (ratio of **11a** + **11d** to **11b** + **11c**) determined by integration of the OMe signals in the ^{1}H NMR spectra; similarly, the initial ratio of Pd (total OMe signals) to $FeCp_2$ was also determined.

The NMR tube was then placed in an oil bath at 50 °C and monitored by NMR spectroscopy periodically. A small amount of solid was seen to deposit during the course of the reaction. Reactions were typically run for 42 h (**11b**) and 72 h (**11a**), since the rates of reductive elimination were different for the two diastereomers. The use of longer reaction times to effect near-complete conversion generally resulted in the appearance of extra unidentified signals in the spectra, indicating decomposition by other pathways. Formation of PAMP−BH_3 was indicated by the appearance of a singlet at 3.67 ppm in the ^{1}H NMR spectrum (and a quartet at 10.2 ppm in the ^{31}P NMR spectrum) and of Pd((*S*,*S*)-Chiraphos)(PhC≡CPh) by a singlet at 49.9 ppm in the ^{31}P NMR spectrum (see below). Other significant byproducts observed in these reactions are detailed in Table 10.

The reaction mixture was then transferred to a vial in air, the tube washed with additional THF, and the solvent removed in vacuo. The residue was extracted with Et_2O in several portions (total 10 mL), and again the solvent was removed in vacuo. PAMP−BH_3 was then isolated by preparative TLC on silica, with the residue loaded as a solution in CH_2Cl_2 and with hexanes/ethyl acetate as eluent (2:1). NMR yields of PAMP−BH_3 ranged from 50 to 70%, and isolated yields were typically 20%. The identity of the product was confirmed by ^{1}H NMR ($CDCl_3$ or C_6D_6), and the ee was determined by chiral HPLC (Chiralpak AD, 1% i-PrOH/hexane, flow rate 1 mL/min, retention times are 11.8 (*S*) and 13.4 min (*R*)). Retention times were compared to those of the racemate and authentic (R_P)-PAMP−BH_3 (prepared by the method of Livinghouse) run under identical conditions.[2i]

Pd((*S*,*S*)-Chiraphos)(PhC≡CPh) (14). Pd((*S*,*S*)-Chiraphos)Cl_2 (**18**; 110 mg, 0.182 mmol) and diphenylacetylene (65 mg, 0.36 mmol) were stirred as a slurry in dry THF (4 mL), and a solution of NaBH(OMe)$_3$ (93 mg, 0.73 mmol) in THF (3 mL) was added dropwise. During the addition the reaction mixture instantly darkened, and at the end of the addition it was yellow-brown. The mixture was stirred for a further 20 min to give a dark brown slurry, and then all volatiles were removed in vacuo. The residue was extracted repeatedly with toluene (total 10 mL), and the resulting solution was filtered through Celite and concentrated to ca. 2 mL. This solution was layered with petroleum ether (5 mL) and cooled to −25 °C for 24 h, after which time a dirty yellow solid was isolated and dried in vacuo. Isolated yield: 50 mg (0.07 mmol, 39%).

^{1}H NMR (THF-d_8): δ 7.89−7.75 (m, 8H, Ar), 7.49−7.34 (m, 4H, Ar), 7.31−6.97 (m, 18H, Ar), 2.62 (br, 2H, CH), 0.84 (br, 6H, Me). ^{13}C{^{1}H) NMR (THF-d_8): 137.7−137.4 (m), 136.5 (apparent t, J = 8), 135.5 (apparent t, J = 11), 135.1−134.8 (m), 134.0 (apparent t, J = 7), 131.6 (apparent t, J = 3), 130.8, 130.0, 129.8, 129.4 (apparent t, J = 4), 129.1, 128.8 (apparent t, J = 5), 128.5, 126.3, 126.2, 124.5, 123.7, 40.2 (apparent t, J = 21, CH), 17.5 (apparent t, J = 4, Me). ^{31}P{^{1}H} NMR (THF-d_8): δ 49.9. IR: 3056, 2956, 2922, 1800, 1644, 1583, 1478, 1433, 1256, 1094, 1022, 800, 750, 689, 528. Anal. Calcd for $C_{42}H_{38}P_2$-Pd: C, 70.94; H, 5.39. Found: C, 70.57; H, 5.34.

Crystallographic Structure Determinations. A summary of the crystallographic data is given in Table 3, with additional details in the Supporting Information. Structural data for complexes **11a** and **11b** were reported previously.[10] The systematic absences in the diffraction data are uniquely consistent for the reported space group for **5** and **9** and consistent for the space groups $P2_1$ and $P2_1/m$ for **6** and **4**. No evidence of symmetry higher than triclinic was observed in the diffraction data of **3**. *E* statistics and the value of *Z* suggested the centrosymmetric option of **3**, and the absence of mirror plane symmetry in **6** and **4** precluded the centrosymmetric option. These choices yielded chemically reasonable and computationally stable refinements. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. DIFABS[48] absorption correction was applied to **3**−**5**. Platon/Squeeze[49] was applied to **5** to resolve a dichloromethane molecule (42 electrons) per Pd complex. Within the 631.9 Å^3 void space occupied by solvent molecules per unit cell, a total of 172 electrons (43 electrons/complex) was found. In this treatment of solvent, the contribution of the solvent molecule is treated collectively and is not refined as individual atoms. Structure **5** is an 87:13 racemic mixture, and the absolute configurations of **6** and **4** were determined (Flack parameters are 0.03(3) and 0.01(7), respectively). The phenyl rings of **3** and **4** were refined as rigid planar groups. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and all hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Acknowledgment. We thank the National Science Foundation, Union Carbide (Innovation Recognition Program), and DuPont for support. We are grateful to Professors Tsuneo Imamoto (Chiba University) and Tom Livinghouse (Montana State University) for advice and for sharing unpublished results on the preparation of enantiopure **2** and to Professor John Brown (University of Oxford) for sharing his related results before publication.

Supporting Information Available: Details of the X-ray crystallographic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030144X

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