Substrate and Catalyst Screening in Platinum-Catalyzed Asymmetric Alkylation of Bis(secondary) Phosphines. Synthesis of an Enantiomerically Pure C_2-Symmetric Diphosphine

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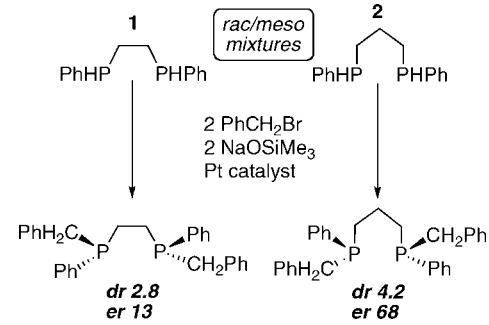
Platinum-catalyzed asymmetric alkylation of bis(secondary) phosphines was investigated. The modular design of the catalyst precursor Pt(diphos*)(R′)(Cl) and the substrates, a bis(secondary) phosphine HRP∼PHR and a benzyl halide, along with an efficient ^{31}P NMR screening method, enabled rapid evaluation of the rate and diastereoselectivity of these reactions. These experiments identified a selective catalyst, Pt(DuPhos)(Ph)(Cl), and showed that the alkylation of PhHP(CH$_2$)$_3$PHPh (**2**) was faster and more selective than that of PhHP(CH$_2$)$_2$PHPh (**1**), MesHP(CH$_2$)$_3$PHMes (**3**), or 1,1′-(C$_5$H$_4$PHPh)$_2$Fe (**4**). Alkylation of **1** with *o*-CF$_3$C$_6$H$_4$CH$_2$Br using the base NaOSiMe$_3$ and the catalyst precursor Pt((*R*,*R*)-*i*-Pr-DuPhos)(Ph)(Cl), or the analogous Me-DuPhos complex, gave the diphosphine Ph(CH$_2$*o*-CF$_3$C$_6$H$_4$)P(CH$_2$)$_2$P(CH$_2$*o*-CF$_3$C$_6$H$_4$)Ph (**7**), which was prepared on a multigram scale and isolated as a borane adduct (**6**). The rac and meso diastereomers of **6** were separated by recrystallization, and enantiomerically pure **6** was isolated. Both (*R*,*R*)- and (*S*,*S*)-**6**, prepared separately in high ee using appropriate catalyst precursors, were characterized by X-ray crystallography, as was *meso*-**7**. Separate treatment of (*S*,*S*)-**7** and *meso*-**7** with Pt(COD)(Ph)(Cl) gave the complexes Pt((*S*,*S*)-**7**)(Ph)(Cl) ((*S*,*S*)-**8**) and Pt(*meso*-**7**)(Ph)(Cl) (*meso*-**8**). Both diastereomers of **8** were catalyst precursors for synthesis of **7** by alkylation of **1** with *o*-CF$_3$C$_6$H$_4$CH$_2$Br, but these reactions were unselective, because ligand **7** was rapidly displaced from its complex, **8**.

Introduction

We recently reported a new approach to catalytic asymmetric synthesis of chiral phosphines[1] via Pt-catalyzed asymmetric alkylation of racemic secondary phosphines with benzyl halides in the presence of base.[2] Alkylation of bis(secondary) phosphine substrates **1** and **2** gave significantly enantioenriched C_2-symmetric (rac) products, although diastereoselectivity was modest (rac/meso ratio (dr) ∼3−4:1, Scheme 1).[2,3]

Such reactions might be synthetically useful if it was possible to separate the rac and meso diphosphines and to increase the ee of the rac isomer by recrystallization.[4] Analogous C_2-symmetric *P*-stereogenic diphosphines, such as DiPAMP,[5] are important ligands in asymmetric catalysis.[6] Pt-catalyzed asymmetric alkylation is also attractive as a potential route to libraries of chiral diphosphines, taking advantage of the modular nature

Scheme 1.[a] Pt-Catalyzed Asymmetric Alkylation of Bis(secondary) Phosphines[2,3]



[a] The catalyst precursor was Pt((*R*,*R*)-*i*-Pr-DuPhos)(Ph)(Cl) (for **1**) or Pt((*R*,*R*)-Me-DuPhos)(Ph)(Cl) (for **2**); reactions were done at room temperature in THF with 10 mol % catalyst precursor per diphosphine (5 mol % in terms of the P−H bonds). Diastereomeric (rac/meso) ratio = dr; enantiomeric ratio = er. The absolute configurations of the products, which have not been determined, are drawn arbitrarily.

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[†] Dartmouth College.
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(1) (a) Glueck, D. S. *Synlett* **2007**, 2627–2634. (b) Glueck, D. S. *Coord. Chem. Rev.* **2008**, in press (doi:10.1016/j.ccr.2007.12.023). (a) Glueck, D. S. *Chem.−Eur. J.* **2008**, *14*, 7108–7117. (d) Glueck, D. S. *Dalton Trans.* **2008**, in press (doi:10.1039/b806138f).

(2) (a) Scriban, C.; Glueck, D. S. *J. Am. Chem. Soc.* **2006**, *128*, 2788–2789. (b) Scriban, C.; Glueck, D. S.; Golen, J. A.; Rheingold, A. L. *Organometallics* **2007**, *26*, 1788–1800 (Addition/Correction: *Organometallics* **2007**, *26*, 5124). For analogous Ru-catalyzed reactions, see: (c) Chan, V. S.; Stewart, I. C.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 2786–2787.

(3) The dr and er in the Pt-catalyzed alkylation of **2** with benzyl bromide were originally reported to be 3.9 and 26 (93% ee), respectively.[2a] Subsequent duplicate experiments showed that the average diastereoselectivity (dr = 4.2 ± 0.3) was reproducibly similar to the first report, while the enantioselectivity (er = 68 ± 12 (∼97% ee)) was even higher (Anderson, B. J. Ph.D. Thesis, Dartmouth College, 2008; manuscript in preparation).

(4) Imamoto, T.; Watanabe, J.; Wada, Y.; Masuda, H.; Yamada, H.; Tsuruta, H.; Matsukawa, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 1635–1636.

(5) Knowles, W. S. *Angew. Chem., Int. Ed.* **2002**, *41*, 1998–2007.

(6) (a) Blaser, H.-U., Schmidt, E., Eds. *Asymmetric Catalysis on Industrial Scale. Challenges, Approaches, and Solutions*; Wiley-VCH: Weinheim, Germany, 2004. For recent reviews of *P*-stereogenic phosphines, see: (b) Grabulosa, A.; Granell, J.; Muller, G. *Coord. Chem. Rev.* **2007**, *251*, 25–90. (c) *Phosphorus Ligands in Asymmetric Catalysis. Synthesis and Applications*; Börner, A., Ed.; Wiley-VCH: Weinheim, 2008.

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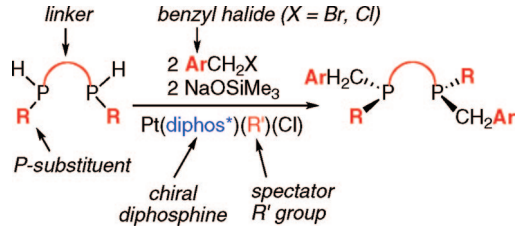
Scheme 2. Diversity Elements in Pt-Catalyzed Asymmetric Alkylation of Bis(secondary) Phosphines



of the substrates.[7] Thus, bis(secondary) phosphine substrates can be modified by changing either the phosphorus substituent or the linker, while many sterically and electronically varied benzyl halides are commercially available. Finally, a family of Pt catalyst precursors may be prepared readily by changing either the chiral diphosphine ligand or the ancillary Pt-R′ group (Scheme 2).[8]

Results and Discussion

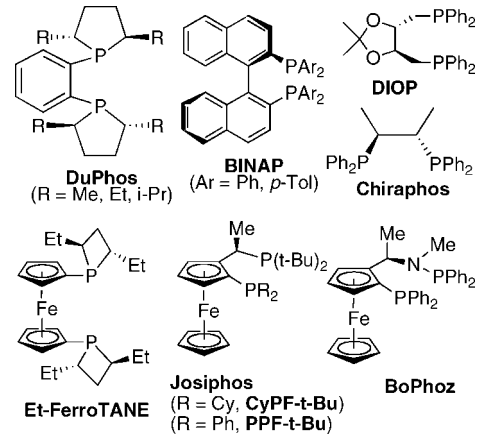
Because it is difficult to rationally predict what combination of bis(secondary) phosphine, benzyl halide, and catalyst will lead to highly enantioenriched products, we developed a simple screening process. Stock solutions of the phosphine, $NaOSiMe_3$ base, and catalyst precursor were prepared and combined in NMR tubes. After addition of benzyl halides, reactions were monitored by ^{31}P NMR spectroscopy and the dr was determined by integration; in most cases, ^{31}P NMR signals due to the rac and meso diastereomers of the diphosphine products were well separated. This approach enabled the screening of about 20 catalytic reactions per day and provided information on both the rate and the diastereoselectivity of reaction. Synthetically valuable processes would have a high dr (rac/meso ratio), which may be associated with high er of the rac isomers, as in Scheme 1.[9] In principle, er values could also be measured for each substrate, or at least for those with high dr. However, we avoided this extra step, which would make the screening process much slower.

The first screens sought to find the best catalyst, which could be prepared *in situ* from a variety of chiral diphosphine ligands (Chart 1) and Pt(COD)(R′)(Cl) (R′ = Ph, Me).[10] The catalysts generated were screened in the alkylation of 1,2-bis(phenylphosphino)ethane (**1**), using $NaOSiMe_3$ and benzyl bromide (Scheme 3). As shown in Table 1, DuPhos ligands gave the highest dr values; we also observed that Pt-Ph catalyst precursors mediated faster and more selective reactions than those with a Pt-Me substituent. The major products were always the desired bis(tertiary) phosphines, but in several cases byproducts were also observed, typically for the less diastereoselective catalysts.

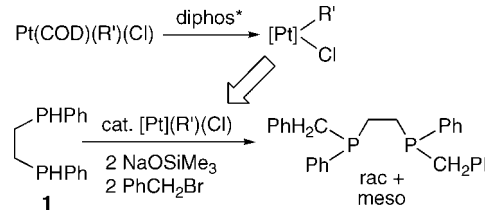
Qualitatively, these results showed that the original catalyst precursors, Pt(DuPhos)(Ph)(Cl), were the best for the alkylation of **1** with benzyl bromide. Although the reactions were done under similar conditions, the dr value in the screening process using (*R*,*R*)-*i*-Pr-DuPhos (1.9, Table 1) was somewhat less than that using isolated Pt((*R*,*R*)-*i*-Pr-DuPhos)(Ph)(Cl) (2.8, Scheme 1). These differences may result from catalyst generation *in situ* or the use, in the screening experiments, of 1.0 M $NaOSiMe_3$ in THF instead of solid sodium silanolate. Finally, the dr value in Table 1 was measured on the crude reaction mixture, while that in Scheme 1 was obtained after workup and purification of the product. Despite the quantitative disagreement, the screening results confirmed that this combination of catalyst precursor and substrate yielded diastereoselectivity worthy of further investigation.

To investigate the generality of this process, Pt((*R*,*R*)-Me-DuPhos)(Ph)(Cl) was used as a catalyst precursor in alkylation of four different bis(secondary) phosphines (Scheme 4) with 18 commercially available benzyl halides; see the Experimental Section and the Supporting Information for details. Integration

Chart 1. Chiral Diphosphines Screened in Pt-Catalyzed Alkylation of 1 with Benzyl Bromide



Scheme 3. Pt-Catalyzed Asymmetric Alkylation of 1 Using Precursors Pt(diphos*)(R′)(Cl) Prepared *in situ*[a]



[a] [Pt] = Pt(diphos*); see Chart 1 for structures of the chiral diphosphines. R′ = Ph or Me, COD = cyclooctadiene.

Table 1. Diastereomer Product Ratios in Pt-Catalyzed Asymmetric Alkylation of 1 with Benzyl Bromide Using Catalysts Generated *in Situ* from Pt(COD)(R′)(Cl) (R′ = Ph, Me) and a Chiral Diphosphine (diphos*)[a]

diphos*	dr (R′ = Ph)	dr (R′ = Me)
(*R*,*R*)-Me-DuPhos	2	1.2[b]
(*R*,*R*)-Et-DuPhos	2.1	1.2
(*R*,*R*)-*i*-Pr-DuPhos	1.9	1.2
(*R*,*S*)-CyPF-t-Bu	1.2	1.1
(*R*,*S*)-PPF-t-Bu	0.9[b]	1.1[b]
(*S*)-BoPhoz	1[b]	1.1[b]
(*S*,*S*)-Et-FerroTANE	1[b]	1.1[b]
(*S*,*S*)-Chiraphos	0.9[b]	1.1
(*S*)-Tol-BINAP	0.9[b]	0.9[b]
(*R*)-BINAP	0.9[b]	1.1
(*S*,*S*)-DIOP	0.9[b]	1.1[b]

[a] Time for complete conversion of the bis(secondary) phosphine substrate (typically ca. 1−2 h) and the dr (rac/meso product ratio) were determined by ^{31}P NMR spectroscopy. [b] Additional products also formed.

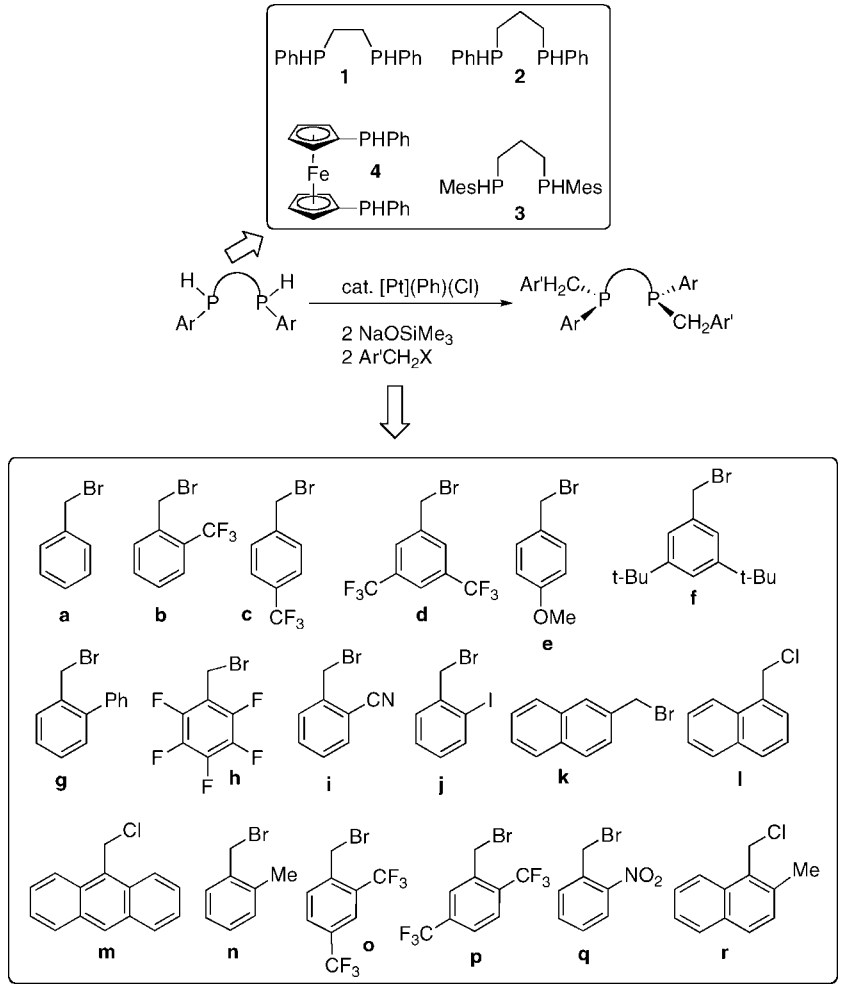
(7) (a) Lennon, I. C.; Pilkington, C. J. *Synthesis* **2003**, *11*, 1639–1642. (b) de Vries, J. G.; Lefort, L. *Chem.−Eur. J.* **2006**, *12*, 4722–4734. (c) Dolhem, F.; Johansson, M. J.; Antonsson, T.; Kann, N. *J. Comb. Chem.* **2007**, *9*, 477–486. (d) Landis, C. R.; Clark, T. P. *Proc. Nat. Acad. Sci.* **2004**, *101*, 5428–5432.

(8) Some of the results in this article were reported in preliminary form in a patent application: Scriban, C.; Glueck, D. S. WO2007016264, 2007.

(9) (a) Fleming, I.; Ghosh, S. K. *J. Chem. Soc., Chem. Commun.* **1994**, 99–100. (b) Muci, A. R.; Campos, K. R.; Evans, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9075–9076. (c) Negishi, E. *Dalton Trans.* **2005**, 827–848.

(10) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411–428.

Scheme 4. Screening Benzyl Halides in Pt-Catalyzed Asymmetric Alkylation of Bis(secondary) Phosphines[a]



[a] ([Pt] = Pt((*R*,*R*)-Me-DuPhos), Mes = 2,4,6-$Me_3C_6H_2$).

of ^{31}P NMR spectra of the crude reaction mixtures gave the diastereomer ratios in Table 2, although selectivity was difficult to measure reliably in some cases, where reaction was incomplete, byproducts were formed, or P−F coupling produced broad ^{31}P NMR multiplet signals. We hoped that these dr values reflected preference for the rac isomer, as in the selective alkylation of **1** and **2** with benzyl bromide, but note that false positives (high dr associated with a meso-selective catalyst) are possible.

How reliable are the results in Table 2? The dr values for alkylation of **1** with benzyl bromide using isolated Pt((*R*,*R*)-Me-DuPhos)(Ph)(Cl) (Table 2, entry **1a**, dr = 1.6) and a catalyst precursor generated *in situ* (Table 1, row 1, dr = 2) were qualitatively similar, despite the differences in preparation of the catalyst. The reproducibility of the dr in alkylation of **2** with benzyl bromide was investigated in more detail. The dr value from the reaction mixture in the screening process (4.3, Table 2) was similar to that determined after workup and purification (4.2, Scheme 1).[3]

Analysis of the data in Table 2 revealed some structure/reactivity/selectivity relationships for the catalytic alkylations. Reactions of propane-bridged bis(phenylphosphine) **2** occurred fastest and with the highest diastereoselectivity. The qualitative order of reaction rates was **2** > **1** > **3** ∼ **4**, while diastereoselectivity varied in the order **2** > **1** ∼ **3** > **4**. Among the benzyl halides, no direct structure/selectivity relationship was apparent. However, most reactions of benzyl chloride substrates were slower than those of the bromides, especially with the bulkier diphosphines **3** and **4** (see the Supporting Information for details).

The anomalously high diastereoselectivity observed in alkylation of **1** with 9-chloromethylanthracene (Table 2, entry **1m**, dr = 75) was investigated by scaling up this reaction (Scheme 5). A single diastereomer of **5** was readily isolated, but in only 30% yield and 70% ee. As described in more detail in the Experimental Section, it appears that *meso*-**5** was much less soluble than the rac isomer; its precipitation led to the apparent high dr and the low yield. This is consistent with observations from the original screening experiment, in which the dr was 5.7 at incomplete conversion, but much higher at the end of the reaction. This demonstrated a drawback of the screening process, which requires solubility of all the products to ensure a reliable assay.

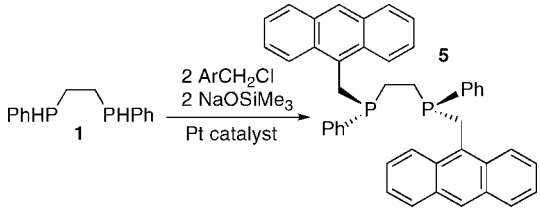
The alkylation of **1** with *o*-trifluorobenzyl bromide (Table 2, entry **1b**) was also examined in detail. We originally thought that this reaction was highly diastereoselective, because a ^{19}F NMR signal due to an impurity was mistakenly assigned to *meso*-**7**; this illustrates a liability of screening crude reaction mixtures.[8] In fact, the dr of **7** was relatively low (1.4). Conveniently, however, the diastereomers of phosphine-borane **6** could be separated by recrystallization. Unusually for this class of compounds, the racemic diastereomer was less soluble than the meso one.[4,9b] A series of recrystallizations, which were monitored by ^{19}F and ^{1}H NMR spectroscopy, gave *rac*-**6** in pure

Table 2. Diastereomeric Product Ratios in Pt-Catalyzed Asymmetric Alkylation of Bis(secondary) Phosphines with Benzyl Halides[a]

	diphosphine			
benzyl halide	**1**	**2**	**3**	**4**
a	1.6	4.3	1.7	1.3
b	1.4	[b]	2.2	[b]
c	1.1	4.4	1.5	1.4
d	1.1	1.5	[b]	1.6
e	1.5	[c]	1.9	[b]
f	1.3	2.3	1.4	1.4
g	1.1	4.0	1.3	1.8
h	2.1	[b]	1.6	1.2
i	2.2	2.6	[b]	2.3
j	1.7	2.3	1.5	1.1
k	2.0	2.9	1.6	1.1
l	1.7	2.2	1.6	1.4
m	75[d]	1.4	2.4	3
n	1.8	1.4	1.4	1
o	[b]	[b]	[b]	[b]
p	[b]	[b]	[b]	[b]
q	[b]	[b]	[b]	[b]
r	1.8	2.2	1.9	[b]

[a] Reactions were carried out at room temperature in THF with 10 mol % of the catalyst precursor Pt((*R*,*R*)-Me-DuPhos)(Ph)(Cl) (5 mol % per P−H bond). The product diastereomer ratio (dr) was determined by integration of ^{31}P NMR spectra of crude reaction mixtures. See the Experimental Section and the Supporting Information for details. [b] The dr was not readily determined when reaction was incomplete, byproducts were formed or P−F coupling produced broad ^{31}P NMR multiplet signals. See the Supporting Information for details on individual reactions. [c] Not performed. [d] The meso diastereomer precipitated during catalysis; the actual dr was significantly lower (see discussion in the text).

Scheme 5. Pt-Catalyzed Asymmetric Alkylation of 1 with 9-Chloromethylanthracene[a]



[a] Pt catalyst precursor = Pt((*R*,*R*)-Me-Duphos)(Ph)(Cl).

form; deprotection using either an amine or HBF_4 gave **7** (Scheme 6).[11]

Under optimized conditions (Table 3), using the catalyst precursor Pt((*R*,*R*)-*i*-Pr-DuPhos)(Ph)(Cl) in THF at 0 °C, diphosphine **7** was prepared on a large scale, then converted to **6**. Recrystallization gave 1.24 g (32%) of (*S*,*S*)-**6** (>99% ee; see the Experimental Section for ee determination), along with 0.55 g (14%) of *meso*-**6** and 0.91 g of a mixture of *rac*- and *meso*-**6** (total 2.7 g, 70% yield). Similarly, (*R*,*R*)-**6** was isolated using the catalyst precursor Pt((*R*,*R*)-(Me-DuPhos)(Ph)(Cl).[12]

The crystal structures of both enantiomers of *rac*-**6** (determined separately) and of *meso*-**7** are shown in Figures 1 and 2. Table 4 summarizes the crystallographic data; see the Supporting Information for more details.

The ^{31}P and ^{19}F NMR spectra of **7** were complicated by long-range coupling, which was not observed in the borane adduct

Scheme 6. Pt-Catalyzed Asymmetric Alkylation of 1 and Synthesis of Diphosphine 7

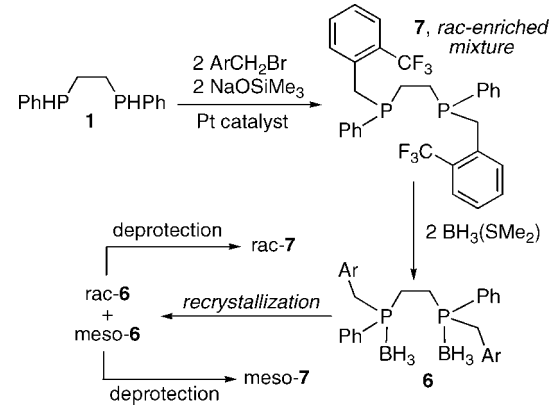


Table 3. Effect of Reaction Conditions on Selectivity in Pt-Catalyzed Asymmetric Synthesis of Diphosphine 7[a]

entry	temp (°C)	time	yield (%)[b]	dr	er
1	−20	4 days	80 (∼2.2 g)	1.7	11
2	0	<12 h		2.2	14
3	rt	<12 h		1.8	12
4	40	2 h	88 (∼1.8 g)	1.2	6
5	rt[c]	12 h		1.7	[d]
6	rt[e]	4 h		2.2	8.4

[a] Reactions were performed with 5 mol % catalyst precursor in THF. For entries 1−4, the precursor was Pt((*R*,*R*)-*i*-Pr-DuPhos)(Ph)(Cl). The reported temperatures are those of the cooling/heating bath; rt = room temperature. [b] Isolated yields of phosphine-borane **6**. [c] Pt((*R*,*R*)-Me-DuPhos)(Ph)(Cl) was used as catalyst precursor. [d] The er was not determined. [e] Pt((*R*,*R*)-Me-DuPhos)(9-phenanthryl)(Br) was used as catalyst precursor.

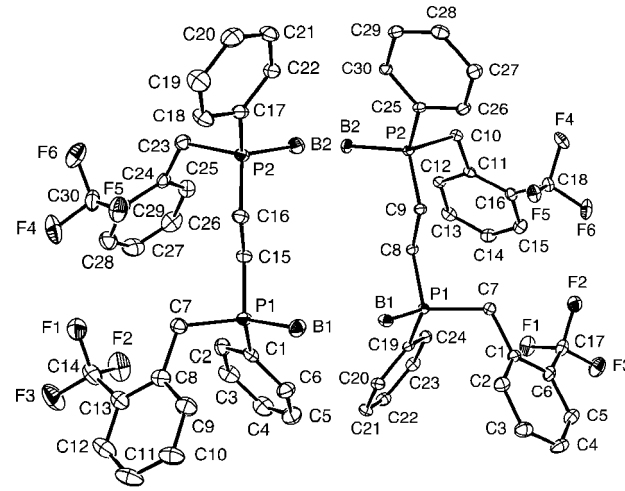


Figure 1. ORTEP diagrams of (*S*,*S*)-**6** (left) and (*R*,*R*)-**6** (right).

6. Experimental and simulated spectra are shown in Figure 3 for *rac*-**7** (AA′X$_3$X$_3$′ spin system).[13] The coupling constants J_{PP} and J_{PF} were 31 and 15 Hz, respectively, as in similar phosphines (Chart 2).[14−16] The spectra for *meso*-**7** were essentially identical.[17]

The enantiomeric purity of diphosphine **7** was determined by ^{31}P NMR spectroscopy after binding it to a chiral Pd reporter complex (see the Experimental Section and Table 4 for details).[1b,18] Because signals due to the diastereomeric Pd

(11) (a) Brunel, J. M.; Faure, B.; Maffei, M. *Coord. Chem. Rev.* **1998**, 178–180, 665−698. (b) McKinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, *35*, 9319–9322.

(12) As described elsewhere,[1,2a] as a result of the conventions for assigning absolute configuration, (*R*,*R*)-Me-DuPhos and (*R*,*R*)-*i*-Pr-DuPhos have opposite configurations. See: Burk, M. J.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10125–10138.

(13) Budzelaar, P. *gNMR* v3.6.5; Cherwell Scientific, 1992−1996.

(14) NMR data for dppe: Hersh, W. H. *J. Chem. Educ.* **1997**, *74*, 1485–1488.

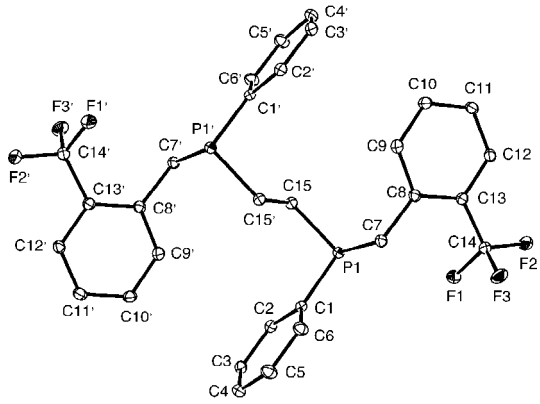


Figure 2. ORTEP diagram of *meso*-**7**.

Table 4. Crystallographic Data for Phosphine-Boranes (*S*,*S*)-6 and (*R*,*R*)-6, and the Phosphine *meso*-7

	(*S*,*S*)-**6**	(*R*,*R*)-**6**	*meso*-**7**
formula	$C_{30}H_{32}B_2F_6P_2$	$C_{30}H_{32}B_2F_6P_2$	$C_{30}H_{26}F_6P_2$
fw	590.12	590.12	562.45
space group	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)	*C*2/*c*
a, Å	10.3800(16)	10.3469(7)	14.5330(18)
b, Å	13.920(2)	13.8409(9)	15.6300(19)
c, Å	20.209(3)	20.1361(13)	11.6520(14)
α, deg	90	90	90
β, deg	90	90	94.356(2)
γ, deg	90	90	90
V, Å^3	2920.0(8)	2883.7(3)	2639.1(6)
Z	4	4	4
D(calc), g/cm^3	1.342	1.345	1.416
μ(Mo Kα), mm^{-1}	0.206	0.209	0.226
temp, K	208(2)	100(2)	100(2)
R(*F*), %[a]	5.64	4.44	3.42
R(*wF*^{2}), %[a]	11.73	12.10	9.14
absolute struct param	0.12(12)	−0.01(9)	

[a] Quantity minimized: $R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o^2,0)]/3$. A Bruker CCD diffractometer was used in all cases.

complexes of (*R*,*R*)-**7** and (*S*,*S*)-**7** could be distinguished readily, these spectra showed that **7** was highly enantioenriched. The ^{13}C satellite peaks[19] in the ^{19}F NMR spectrum of (*S*,*S*)-**7-Pd** enabled quantification of the enantiomeric purity. Under conditions where these satellite signals (2% of the intensity of the central peak) were observed, the ^{19}F NMR signal of (*R*,*R*)-**7-Pd** was not, suggesting that the enantiomeric purity was >99%.[20]

Attempted Chirality Breeding. The availability of enantiomerically pure **7** suggested the possibility of using it in "chirality breeding"[21] as a ligand in a Pt complex that could catalyze asymmetric alkylation of **1** with *o*-$CF_3C_6H_4CH_2Br$ to yield **7**.[22] Separate reactions of (*S*,*S*)-**7** and *meso*-**7** with Pt(COD)(Ph)(Cl) gave the rac and meso diastereomers of Pt(**7**)(Ph)(Cl) (**8**, Scheme 7).

The diastereomers of **8** were then used separately as catalyst precursors in alkylation of **1** with *o*-trifluorobenzyl bromide.

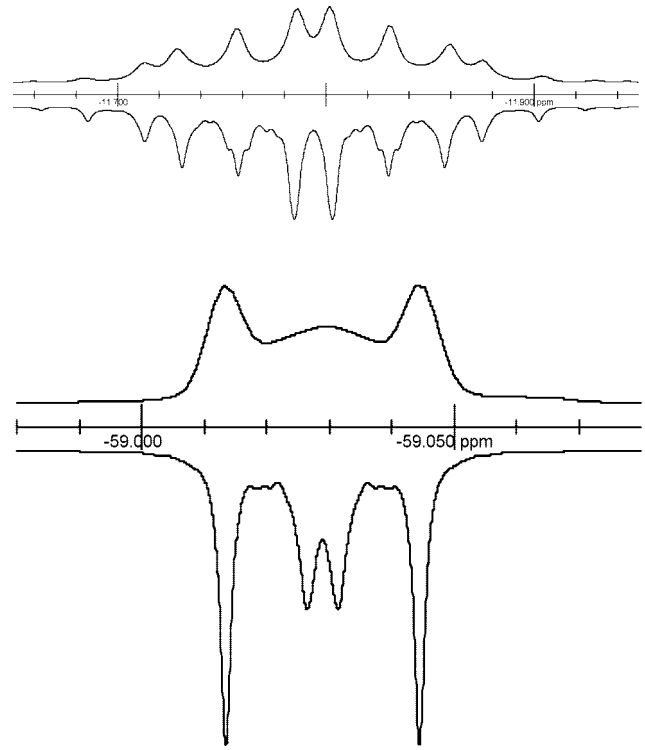
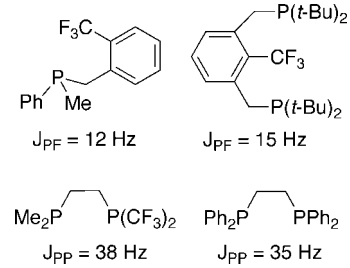
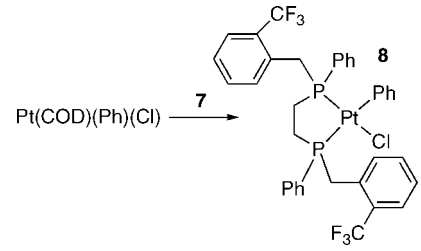


Figure 3. Experimental (in C_6D_6, above) and simulated (below) ^{31}P (top) and ^{19}F (bottom) NMR spectra of *rac*-**7**. Coupling constants (in Hz) used in the simulation: $J_{PP} = 30.8$, $J_{PF} = 15.0$, -0.4, $J_{FF} = -3.3$.

Chart 2. NMR Coupling Constants in Phosphines Related to 7



Scheme 7. Synthesis of Pt Complexes 8



(15) NMR data for $Me_2PCH_2CH_2P(CF_3)_2$: Field, L. D.; Wilkinson, M. P. *Tetrahedron Lett.* **1997**, *38*, 2779–2782.

(16) NMR data for 1-CF_3,2,6$(CH_2P(t\text{-}Bu)_2)_2C_6H_3$: van der Boom, M. E.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 6652–6656.

(17) In the diphosphine oxides and sulfides $PhHP(E)CH_2CH_2PHPh(E)$ (E = O or S, Grossmann, G.; Walther, B.; Gastrock-Mey, U. *Phosphorus Sulfur* **1981**, *11*, 259–272.) J_{PP} values for the rac and meso diastereomers were the same, and the J_{PC} values for these diastereomers were also very similar.

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Scheme 8. Attempted Chirality Breeding: Pt-Catalyzed Synthesis of 7 using Precursors 8, which Contain (*S*,*S*)-7 or *meso*-7

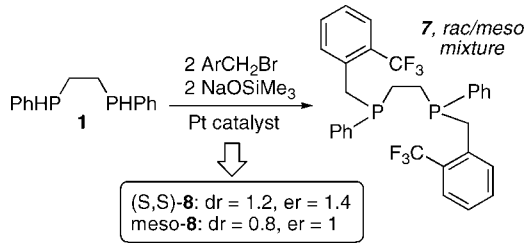

Table 5. Synthesis of 7 from 1 Using the Catalyst Precursors (*S*,*S*)-8 and *meso*-8

entry	catalyst precursor	dr of **7**	er of **7**	time (h)	yield (%)
1	(*S*,*S*)-**8**	1.1	1.5	<1	86
2	(*S*,*S*)-**8**	1.3	1.4	<1	84
3	(*S*,*S*)-**8**	1.4	1.9	<4	[a]
4	*meso*-**8**	0.9	1.06	<4	80
5	*meso*-**8**	0.7	1.10	<4	78
6	*meso*-**8**	0.6	1.13	<4	[b]

[a] Approximately 50% conversion to **7** with 10% oxide formation (δ 24.7 (d, J = 42), 24.2 (d, J = 43), −10.3 to −10.7 (m)), and 29% monoalkylated P(Ph)(*o*-$CF_3C_6H_4CH_2$)$(CH_2)_2$PHPh (δ (THF) −12.1 to −12.4 (m), −12.8 to −12.9 (m), −44.2, −45.9). [b] Approximately 60% conversion to **7** with 15% oxide formation and 24% monoalkylated P(Ph)(*o*-$CF_3C_6H_4CH_2$)$(CH_2)_2$PHPh.

Table 6. ^{31}P and ^{19}F NMR Data for Diastereomeric Complexes of the Diphosphine PhP(CH_2*o*-$C_6H_4CF_3$)CH_2CH_2PPh(CH_2*o*-$C_6H_4CF_3$) (7) with (*S*)-(Pd($NMe_2CH(Me)C_{10}H_6$)(μ-Cl))$_2$[a]

monodentate complex	*RR*	*SS*	*meso*
δ (^{31}P) (C_6D_6)	38.6	38.7	39.2, 38.0[b]
δ (^{31}P) (CD_2Cl_2)	38.2	37.8	38.5, 36.4[c]
δ (^{19}F) (C_6D_6)	−57.9[d]	−58.5[e]	−57.5, −59.3
δ (^{19}F) (CD_2Cl_2)	−58.5[f]	−59.0[g]	−58.1, −59.7

chelate complex	*RR*	*SS*	*meso*[j]
δ (^{31}P) (CD_2Cl_2)	65.4, 35.5[h]	65.0, 37.2[i]	66.2, 39.2[k] 65.0, 37.4[l]
δ (^{19}F) (CD_2Cl_2)	−58.1, −59.1	−58.1, −59.1	−57.9, −58.2[k] −58.0, −58.3

[a] Chemical shifts are in ppm, coupling constants in Hz. [b] AB pattern; both peaks are doublets with J = 52. [c] AB pattern; both peaks are doublets with J = 51. [d] The ^{13}C satellite peak was observed at δ −58.0 (d, J = 274). [e] The ^{13}C satellite peak was observed at δ −58.7 (d, J = 274). [f] The ^{13}C satellite peak was observed at δ −58.0 (d, J = 274). [g] The ^{13}C satellite peak was observed at δ −59.1 (d, J = 274). [h] Broad doublets, J = 22. [i] Doublets, J = 24. [j] Two diastereomers of the meso chelate complex were observed. [k] Broad peaks. [l] doublets, J = 23.

With (*S*,*S*)-**8**, the product was enriched in the diphosphine (*S*,*S*)-**7** (dr = 1.2, er = 1.4). In contrast, **7** formed using catalyst precursor *meso*-**8**, was meso-enriched (dr = 0.8, Scheme 8). These results are consistent with displacement of the original diphosphine ligand, which was present from the 10 mol % catalyst loading. Addition of 10 mol % of (*S*,*S*)-**7** to a 1:1 racemic/meso mixture of **7** formed by an unselective catalyst would give a dr of 1.2 and an er of 1.4, as observed. Similarly, adding 10 mol % of *meso*-**7** to a 1:1 mixture yields a dr of 0.8. Consistent with these results, treatment of either (*S*,*S*)-**8** or *meso*-**8** with 1,2-bis(phenylphosphino)ethane and $NaOSiMe_3$ caused rapid displacement of **7**, as observed by ^{31}P NMR spectroscopy.

Conclusions

A rapid process for screening rate and diastereoselectivity in the Pt-catalyzed asymmetric alkylation of bis(secondary) phosphines with benzyl halides has been developed. Using this approach, the alkylation of **1** with *o*-$CF_3C_6H_4CH_2Br$ was scaled up and enantiopure diphosphine **7** was prepared on a multigram scale. We expect that related diphosphines can be prepared in a similar way. The diphosphine (*S*,*S*)-**7** was used as a ligand in a platinum complex to breed itself, but without any selectivity, because it was displaced rapidly. This approach may be more successful with more tightly binding diphosphines, and we are currently examining this possibility.

Experimental Section

General Experimental Details. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20 °C in a drybox or using standard Schlenk techniques. Petroleum ether (bp 38−53 °C), CH_2Cl_2, ether, THF, and toluene were dried over alumina columns similar to those described by Grubbs.[23] NMR spectra were recorded using Varian 300 or 500 MHz spectrometers. ^{1}H or ^{13}C NMR chemical shifts are reported versus Me_4Si and were determined by reference to the residual ^{1}H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported versus H_3PO_4 (85%) used as an external reference. Coupling constants are reported in Hz as absolute values unless noted otherwise. Unless indicated, peaks in NMR spectra are singlets. Instead of the expected quartet resonances[11a] in the ^{31}P NMR spectra of the phosphine-boranes, poorly resolved multiplets were often observed; in some cases the signal was an apparent doublet. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory or Quantitative Technologies Inc. Mass spectra were recorded at the University of Illinois, Urbana−Champaign (http://www.scs.uiuc.edu/~msweb).

Reagents were from commercial suppliers, except for these compounds, which were made by the literature procedures: Pt(COD)(R)Cl) (COD = cyclooctadiene, R = Me or Ph),[10] Pt((*R*,*R*)-Me-DuPhos)(Ph)(Cl),[24] Pt((*R*,*R*)-*i*-Pr-DuPhos)(Ph)(Cl),[2a,b] (*S*)-(Pd(Me_2-$NCH(Me)C_6H_4$)(μ-Cl))$_2$,[25] (*S*)-(Pd($Me_2NCH(Me)C_{10}H_6$)(μ-Cl))$_2$,[26] $MesPH(CH_2)_3PHMes$.[27] The complex Pt((*R*,*R*)-Me-DuPhos)(9-phenanthryl)(Br) (see Table 3) was prepared from Pt((*R*,*R*)(Me-DuPhos)Cl_2 and (9-phenanthryl)MgBr; details will be reported separately.

PhPH(CH_2)$_2$PHPh (1) via PhP(O)(O-*i*-Pr)(CH_2)$_2$PPh(O)(O-*i*-Pr). In a modification of the literature method,[28] PhP(O-*i*-Pr)$_2$ (10 g, 0.04 mmol, bp 112−114 °C) and 1,2-dibromoethane (1.9 mL, 0.022 mmol, bp 131 °C) were combined under N_2 in a Kugelrohr apparatus and heated under vacuum at 140 °C for 3 h, although this temperature was higher than the boiling points of both reactants. About 5 mL of distillate was collected, leaving behind a white solid. Cyclohexane (40 mL) was added to the solid, and the resulting slurry was heated to a boil for 5 min. The slurry was allowed to cool to room temperature and filtered to give a white solid, which was again boiled with 40 mL of cyclohexane. Filtration after cooling to room temperature gave 5.65 g (65% yield) of a mixture of two diastereomers; an impurity (^{31}P NMR: δ 23.4) remained in the filtrate. Boiling this mixture with 30 mL of

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cyclohexane, then filtering the hot slurry, gave one diastereomer as a white solid; the filtrate was enriched in the other diastereomer. The product is a known compound,[28] for which we report additional characterization data.

Anal. Calcd for $C_{20}H_{28}O_4P_2$: C, 60.91; H, 7.16. Found: C, 60.75; H, 7.21. HRMS: *m/z* calcd for $C_{20}H_{28}O_4P_2$ *m/z* 394.1463, found *m/z* 394.1468. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.02 (a), 43.00 (b), 1:1 ratio of diastereomers. For pure diastereomer a, ^1H NMR ($CDCl_3$): δ 7.80−7.75 (m, 4H, Ar), 7.57 (t, $J = 7$, 2H, Ar), 7.49 (t, $J = 7$, 4H, Ar), 4.50−4.47 (m, 2H, O-CH), 2.06−2.05 (m, 4H, CH_2), 1.32 (d, $J = 6$, 6H, CH_3), 1.12 (d, $J = 6$, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 132.6 (Ar), 132.0 (t, $J = 5$, Ar), 128.9 (t, $J = 6$, Ar), 70.2, 24.7, 24.1 (t, $J = 3$), 22.7 (5-line pattern, $J_{PP} = 67$, $J_{PC} = 104$, −6).[29] One of the expected aryl carbon signals was not observed. For the mixture of diastereomers a and b, ^1H NMR ($CDCl_3$): δ 7.78−7.69 (m, 4H a, 4H b, Ar), 7.58−7.42 (m, 6H a, 6H b, Ar), 4.54−4.44 (m, 2H a, 2H b, O-CH), 2.21−2.13 (m, 2H, b), 2.05−2.04 (m, 4H a, CH_2), 1.94−1.86 (m, 2H b), 1.36 (d, $J = 6$, 6H b, CH_3), 1.31 (d, $J = 6$, 6H a, CH_3), 1.14 (d, $J = 6$, 6H b, CH_3), 1.11 (d, $J = 6$, 6H a, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 132.63 (a, Ar), 132.59 (b, Ar), 132.0−131.9 (m, a, b), 128.9−128.8 (m, a, b), 70.2 (m, a, b), 24.8−24.7 (m, a, b), 24.1 (m, a, b), 22.7 (m, overlapping five-line patterns, a, b).[29]

Synthesis of **1** by reduction of this Arbuzov product with $LiAlH_4$ was reported earlier.[30] However, we found the procedure with $LiAlH_4/Me_3SiCl$ to be more convenient.[31] A slurry of $LiAlH_4$ (1.39 g, 36.7 mmol) in 50 mL of dry THF was cooled to −78 °C, and Me_3SiCl (4.70 mL, 36.7 mmol) was added via a syringe. The gray slurry was slowly allowed to warm to room temperature and stirred for an additional 2 h. The resulting mixture was cooled to −40 °C, and a solution of the Arbuzov product above (2.14 g, 6.1 mmol), in 100 mL of anhydrous THF under N_2, was added via cannula. The mixture was stirred at room temperature overnight. In the morning, degassed water (100 mL, added dropwise until the fizzing ceased) and ether (100 mL) were added and the organic layer was separated. The aqueous layer was extracted with 2 × 50 mL of ether, and the organic layers were combined and dried with $MgSO_4$. The ether was then removed *in vacuo*, yielding a pale yellow oil, which was stored under N_2 at −40 °C overnight to give 1.01 g (67% yield) of a white solid.

Screening Chiral Diphosphine Ligands with *in Situ* Precatalyst Formation in the Catalytic Reaction of Benzyl Bromide with 1. To a solution of diphosphine **1** (0.2 mL of 0.05 M THF solution, 0.01 mmol) was added Pt(COD)(R)(Cl) (100 μL of a 0.1 M solution in THF, 0.01 mmol, R = Me or Ph). After 15 min, 1,2-bis(phenylphosphino)ethane (**1**, 50 μL of 2.0 M solution in THF, 0.1 mmol) was added and the solution became cloudy. $NaOSiMe_3$ (0.2 mL of 1.0 M solution in THF, 0.2 mmol) was added and the solution became yellow. The reaction mixture was transferred to an NMR tube. Benzyl bromide (24 μL, 34 mg, 0.2 mmol) was added via microliter syringe, and a white precipitate immediately formed. The reaction mixture was monitored by ^{31}P NMR spectroscopy, which enabled determination of the extent of conversion and the rac/meso ratio of the product diphosphine (Table 1). ^{31}P NMR data (THF) for 1,2-bis(benzylphenylphosphino)ethane: δ −13.1 (meso), −13.6 (rac).

Screening Benzyl Halides in Pt-Catalyzed Asymmetric Alkylation of 1. A 50 μL (0.01 mmol) amount of a stock solution of 0.2 M Pt((*R*,*R*)-Me-Duphos)(Ph)(Cl) in THF was charged to an NMR tube. The disecondary phosphine (50 μL of a 2.0 M solution in THF, 0.1 mmol) was added via syringe and a white precipitate formed. $NaOSiMe_3$ (200 μL of a 1.0 M solution in THF (Aldrich), 0.2 mmol) was added; the precipitate dissolved and the solution turned yellow. The benzyl halide (0.2 mmol) was added (neat, for liquids, or as a solution in the minimum amount of dry THF, about 100 μL) and a white precipitate formed. The reaction was monitored by ^{31}P NMR spectroscopy. See Table 2 for diastereomeric product ratios and the Supporting Information for additional data. Analogous screening experiments with diphosphines **2**, **3**, and **4** were carried out similarly (see the Supporting Information for details).

Pt-Catalyzed Asymmetric Synthesis of 1,2-Bis((anthracen-9-methyl)(phenyl)phosphino)ethane (5). A solution of 1,2-bis(phenylphosphino)ethane (**1**, 197 mg, 0.8 mmol) in 2 mL of THF was treated with $NaOSiMe_3$ (1.6 mL of a 1.0 M solution in THF, 1.6 mmol) and Pt((*R*,*R*)-Me-Duphos)(Ph)(Cl) (49 mg, 0.10 mmol, 12 mol %); the solution turned yellow. A solution of 9-(chloromethyl)-anthracene (363 mg, 1.6 mmol) in 2 mL of THF was added. The solution immediately turned orange, and a white precipitate formed within 5 min. The mixture was stirred overnight, then filtered through Celite to remove the salt, washing with THF. However, the Celite remained yellow even after washing. The solvent was removed from the filtrate *in vacuo* to give approximately 300 mg of an orange solid, which was dissolved in a 1:1 mixture of petroleum ether/THF and passed through a 35 mm wide frit filled 25 mm high with silica gel. The pale yellow filtrate was concentrated under vacuum, and the resulting solid was recrystallized from THF/petroleum ether at −40 °C. The pale yellow supernatant was decanted to give 130 mg of yellow solid. The silica plug was washed with 20 mL (each) of THF, petroleum ether, toluene, CH_2Cl_2, and ether to give, after removal of the solvent, 20 mg more yellow solid (total yield 150 mg, 30%, of a single diastereomer). However, the silica plug remained yellow even after the sequential washings, suggesting that some product may remain insoluble, explaining the low yield.

The mass spectrum of the air-sensitive diphosphine was consistent with oxidation at both P centers. HRMS: *m/z* calcd for $C_{44}H_{37}O_2P_2$ $(MO_2H)^+$ 659.2269, found *m/z* 659.2274. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −11.1. ^1H NMR ($CDCl_3$): δ 8.28 (2H, Ar), 8.03 (d, $J = 8$, 4H, Ar), 7.94 (d, $J = 7$, 4H, Ar), 7.42−7.32 (m, 14H, Ar), 7.29−7.26 (m, 4H, Ar), 3.99 (d, $J = 14$, 2H, benzyl H), 3.77 (d, $J = 14$, 2H, benzyl H), 1.89−1.84 (m, 2H, CH_2), 1.59−1.54 (m, 2H, CH_2). $^1H\{^{31}P\}$ NMR (C_6D_6): δ 8.04 (2H, Ar), 8.00 (m, 4H, Ar), 7.75 (m, 4H, Ar), 7.21 (m, 8H, Ar), 7.14 (d, $J = 8$, 4H, Ar), 7.01 (m, 2H, Ar), 6.91 (t, $J = 8$, 4H, Ar), 3.72 (d, $J = 14$, 2H), 3.53 (d, $J = 14$, 2H), 1.91−1.86 (m, 2H), 1.65−1.58 (m, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 138.5 (m, Ar), 133.0 (m, Ar), 132.0 (Ar), 130.8 (m, Ar), 130.4 (m, Ar), 129.3 (Ar), 129.1 (Ar), 128.5 (t, $J = 3$, Ar), 126.3 (Ar), 125.5 (Ar), 125.2 (Ar), 125.0 (Ar), 29.8 (m, benzyl C), 24.2 (apparent t, $J = 34$, CH_2). For ee determination, the product (30 mg, 0.048 mmol) was dissolved in 1 mL of CH_2Cl_2 and a solution of the reporter complex (*S*)-$(Pd(NMe_2CH(Me)C_{10}H_6)(\mu\text{-}Cl))_2$ (35 mg, 0.053 mmol) in 1 mL of CH_2Cl_2 was added. Integration of the $^{31}P\{^1H\}$ NMR spectrum showed the ee to be 70%: δ 38.6 (major), 34.6 (minor).

Effect of Reaction Conditions on the Selectivity of Formation of 7 (Sample Procedure, Table 3). A solution of 1,2-bis(phenylphosphino)ethane (1.2 g, 4.7 mmol) in 10 mL of THF was treated with a solution of $NaOSiMe_3$ (1.0 g, 9.3 mmol) in 10 mL of THF and a solution of Pt((*R*,*R*)-*i*-Pr-Duphos)(Ph)(Cl) (169 mg, 0.23 mmol, 5 mol %) in 10 mL of THF, and the bright yellow solution was stirred at −20 °C. A solution of 1-(bromomethyl)-2-(trifluoromethyl)benzene (2.2 g, 9.3 mmol) in 5 mL of THF was added to the mixture, and within 5 min, the solution turned a darker yellow-orange and a white precipitate was observed. The progress of the reaction was monitored by removing an aliquot (0.5 mL) for ^{31}P NMR spectroscopy. Once the reaction was complete, the sample from the NMR tube was filtered through silica, eluting with

(29) This signal was similar to that reported for analogous AXX′ spin systems; see: Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727–733. The coupling constants were obtained from simulations using gNMR.

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10% THF/petroleum ether. The solvent was removed under vacuum to give ~30 mg of a colorless oil. The selectivity was determined by treatment of the diphosphine with (*S*)-(Pd(NMe$_2$CH(Me)C$_{10}$H$_6$)(μ-Cl))$_2$ (1.1 equiv) in CD_2Cl_2 and integration of the ^{31}P NMR spectrum (see below).

Pt-Catalyzed Asymmetric Synthesis of 1,2-Bis((*o*-trifluorobenzyl)(phenyl)phosphino)ethane (7) and Separation of rac and meso Diphosphine-Borane 6. A solution of 1,2-bis(phenylphosphino)ethane (1.64 g, 6.6 mmol) in 50 mL of THF was treated with a solution of $NaOSiMe_3$ (1.49 g, 13.3 mmol) in 50 mL of THF and a solution of Pt((*R*,*R*)-*i*-Pr-Duphos)(Ph)(Cl) (240 mg, 0.33 mmol, 5 mol %) in 50 mL of THF, and the bright yellow solution was stirred at 0 °C. A solution of 1-(bromomethyl)-2-(trifluoromethyl)benzene (3.2 g, 13.3 mmol) in 20 mL of THF was added to the mixture, and within 5 min, the solution turned a darker yellow-orange and a white precipitate was observed. After 4 h the reaction was complete as determined by ^{31}P NMR spectroscopy. While still at 0 °C, $BH_3(SMe_2)$ (7.3 mL of a 2.0 M solution in THF, 14.5 mmol) was added and the mixture was stirred overnight, then filtered through Celite to remove insoluble salts. The solvent was removed *in vacuo* to yield a yellow oil. The crude product dr was 1.6 (23% de), according to ^{19}F NMR spectroscopy in C_6D_6 (δ −58.4 (rac, major), −58.5 (meso, minor)). The two diastereomers were separated by a series of recrystallizations from CH_2Cl_2 layered with petroleum ether at 0 °C for 12 h, giving the rac diastereomer as white solid. After one recrystallization the dr was improved to 6:1 (70% de). Repeated recrystallization gave steady enrichment of the rac diastereomer, which was isolated after four recrystallizations. The solutions from these recrystallizations were concentrated and then recrystallized in a similar manner to give more isolated rac compound. A total of 1.24 g of the rac diastereomer was isolated (32% yield, > 99% ee, (*S*,*S*)-**6**), as well as 550 mg (14%) of the meso diastereomer, plus an additional 910 mg of rac/meso mixtures (total yield 2.7 g, 70%). A similar experiment using Pt((*R*,*R*)-Me-DuPhos)(Ph)(Cl) gave enrichment of (*R*,*R*)-**6**.

Anal. Calcd for $C_{30}H_{32}B_2F_6P_2$: C, 61.06; H, 5.47. Found: C, 60.86; H, 5.64. HRMS: *m*/*z* calcd for $C_{30}H_{32}B_2F_6P_2$ (M^+) 590.2070, found 590.2053. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 22.8 (br). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −58.6, −58.8 (d, J_{CF} = 274, ^{13}C satellite); minor (impurity) peaks were observed in some samples at δ −58.68, −58.71, and −59.1. ^{1}H NMR ($CDCl_3$): δ 7.57 (d, J = 8, 2H, Ar), 7.52−7.46 (m, 8H, Ar), 7.39 (t, J = 7, 6H, Ar), 7.35 (t, J = 8, 2H, Ar), 3.51−3.46 (m, 2H, benzyl CH_2), 3.40−3.35 (m, 2H, benzyl CH_2), 1.97−1.92 (m, 2H, CH_2), 1.88−1.85 (m, 2H, CH_2) 1.1−0.4 (br, 6H, BH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 132.7 (t, J = 2, Ar), 132.5 (t, J = 5, Ar), 131.8 (Ar), 131.7 (Ar), 131.4 (Ar), 129.0 (t, J = 5, Ar), 128.3 (Ar), 127.5 (d, J = 51, Ar), 127.2 (Ar), 126.4 (q, J = 6), 124.7 (q, J = 274, CF_3), 30.8 (filled-in d,[32] J = 29, benzyl C), 18.7 (filled-in d,[32] J = 35, CH_2).

Data for *meso*-6. HRMS: *m*/*z* calcd for $C_{30}H_{31}B_2F_6P_2$ $(M - H)^+$ 589.1991, found 589.1995. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 22.9 (br). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −58.4, −58.6 (d, J = 274, ^{13}C satellite). ^{1}H NMR (C_6D_6): δ 7.61−7.57 (m, 4H, Ar), 7.13 (d, J = 8, 2H, Ar), 7.09 (d, J = 8, 2H, Ar), 6.98−6.84 (m, 8H, Ar), 6.64 (t, J = 8, 2H, Ar), 3.15−3.10 (m, 2H, benzyl CH_2), 2.98−2.93 (m, 2H, benzyl CH_2), 2.50−2.46 (m, 2H, CH_2), 1.67−1.65 (m, 2H, CH_2), 1.8−1.2 (br m, 6H, BH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 132.6 (t, J = 5, Ar), 132.5 (m, Ar), 132.4−132.3 (m, Ar), 132.2−131.8 (m, Ar), 131.76 (Ar), 130.9 (Ar), 129.1 (t, J = 5, Ar), 129.0 (Ar), 127.46 (Ar), 126.6−126.4 (m, Ar), 126.2 (Ar), 125.8 (Ar), 124.1 (q, J = 274, CF_3), 31.3−31.1 (m, benzyl C), 18.2−17.6 (m, CH_2).

Deprotection of Diphosphine-Borane 6. On addition of $HBF_4(OMe_2)$ (322 mg, 2.4 mmol, 10 equiv) to a stirred solution of (*S*,*S*)-**6** (142 mg, 0.24 mmol) in 2 mL of CH_2Cl_2, gas evolution was observed.[11b] The mixture was stirred for 12 h, and then 10 mL of degassed aqueous $NaHCO_3$ was added and the mixture was stirred for another 12 h. The mixture was extracted with ether (2 × 30 mL) and dried with $MgSO_4$, and the solvent was removed *in vacuo* to give a white solid. The solid was eluted over silica with 50/50 THF/petroleum ether, and the solvent was removed *in vacuo* to give 103 mg (76% yield) of **7** as a white solid. A similar procedure, or deprotection with DABCO (see below), was used to isolate *meso*-**7**.

Data for *rac*-7. Mass spectroscopic results were consistent with oxidation at both P centers. HRMS: *m*/*z* calcd for $C_{30}H_{27}F_6O_2P_2$ $(MO_2H)^+$ 595.1391, found 595.1387. Alternatively, a solution of crude **7** (430 mg, 0.76 mmol, dr = 1.8) in 10 mL of THF was treated with sulfur (78 mg, 2.4 mmol, 3.2 equiv). The bright yellow slurry was stirred for 1 h, then filtered through Celite, eluting with CH_2Cl_2. The solvent was removed under vacuum to give a yellow solid, which was dissolved in ether and filtered through Celite again. The ether was removed under vacuum to give the product as a yellow solid. The dr remained unchanged and was easily measured from integration of the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$). HRMS: *m*/*z* calcd for $C_{30}H_{27}S_2F_6P_2$ $(MH)^+$ 627.0934, found 627.0927. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 49.3 (minor), 49.0 (major). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −58.5 (major), −58.6 (minor).

$^{31}P\{^1H\}$ NMR (C_6D_6): δ −11.6 to −12.0 (m, J_{PP} = 30.8, J_{PF} = 15.0, −0.4, J_{FF} = −3.3). $^{31}P\{^{19}F\}$ NMR (C_6D_6): δ −11.8. $^{19}F\{^1H\}$ NMR (C_6D_6): δ −59.0 (m, J_{PP} = 30.8, J_{PF} = 15.0, −0.4, J_{FF} = −3.3), −59.1 (d of m, J_{CF} = 275, ^{13}C satellites). ^{1}H NMR (C_6D_6): δ 7.38−7.31 (m, 6H, Ar), 7.09−7.04 (m, 6H, Ar), 6.94−6.83 (m, 4H, Ar), 6.73 (q, J = 7, 2H, Ar), 3.11 (d, AB pattern, J = 14, CH_2, 2H), 2.95 (d, AB pattern, J = 14, CH_2, 2H), 1.87−1.83 (m, 2H), 1.75−1.73 (m, CH_2, 4H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.7−137.5 (m, Ar), 133.4−133.2 (m, Ar), 131.8−131.7 (m, Ar), 131.5 (Ar), 129.6 (Ar), 128.73−128.68 (m, Ar), 128.3 (overlapping with solvent peaks, Ar), 126.3 (q, J = 6, Ar), 126.0 (Ar), 125.2 (q, J = 274, CF_3), 33.9 (filled-in d,[32] J = 19, CH_2), 24.1 (br, CH_2).

***meso*-7.** A solution of *meso*-**6** (190 mg, 0.32 mmol) was stirred in 5 mL of THF, and a solution of DABCO (109 mg, 0.97 mmol) in 5 mL of THF was added. The mixture was stirred for 48 h and monitored by ^{31}P NMR spectroscopy; deprotection was not complete after 24 h. The THF was removed *in vacuo*, and the resulting oil was dissolved in petroleum ether and filtered through a silica column (15 by 1 mm) eluting with 7 × 15 mL fractions of petroleum ether to remove excess amine. Then the phosphine was eluted with 3 × 15 mL fractions of CH_2Cl_2. The solvent was removed *in vacuo* to give 150 mg (83% yield) of a white solid. Crystals of *meso*-**7** were obtained by slow evaporation of petroleum ether.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ −11.8 to −11.9 (m). $^{31}P\{^{19}F\}$ NMR (C_6D_6): δ −11.8 (br). $^{19}F\{^{31}P\}$ NMR (C_6D_6): δ −59.0, −59.1 (d, J = 273, ^{13}C satellite). ^{1}H NMR (C_6D_6): δ 7.38−7.34 (m, 6H, Ar), 7.08−7.03 (m, 6H, Ar), 6.93 (d, J = 7, 2H, Ar), 6.84 (t, J = 7, 2H, Ar), 6.72 (t, J = 7, 2H, Ar), 3.14 (d, AB pattern, J = 14, 2H, CH_2), 3.00 (d, AB pattern, J = 14, 2H, CH_2), 1.88−1.83 (m, 2H, CH_2), 1.74−1.69 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.8−137.6 (m, Ar), 133.3−133.1 (m, Ar), 131.8−131.7 (m, Ar), 131.5 (Ar), 129.5 (Ar), 128.8−128.7 (m, Ar), 126.3 (quintet, J = 6, Ar), 126.0 (Ar), 125.2 (q, J = 274, CF_3), 33.5 (filled-in d,[32] J = 18, CH_2), 24.1 (m, CH_2).

Nonselective Synthesis of 6. $BH_3(SMe_2)$ (1.0 mL of a 2 M solution in THF, 2.0 mmol) was added via a syringe to a solution of **1** (225 mg, 0.91 mmol) in 10 mL of DMF at 0 °C. The mixture was stirred for 1 h at 0 °C, then stirred at room temperature overnight. The mixture was cooled to −40 °C, *n*-BuLi (0.91 mL of a 2.0 M solution in cyclohexane, 1.83 mmol) was added via a syringe, and the solution was stirred for 1 h. A solution of degassed 1-(bromomethyl)-2-(trifluoromethyl)benzene (437 mg, 1.83 mmol) in 10 mL of dry DMF was added to the reaction mixture, which

(32) Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 50–59.

was stirred for 2 h at −40 °C, then overnight at room temperature. Water and CH_2Cl_2 (50 mL) were added, and the organic layer was separated. The aqueous layer was extracted with 4 × 10 mL of CH_2Cl_2. The organic layers were combined and dried with $MgSO_4$. The solvent was removed *in vacuo* to give 500 mg of a pale yellow oil. Column chromatography (7 in. tall, 1 in. wide silica column, 10% ethyl acetate/petroleum ether) was used to isolate the product, R_f 0.2, as 150 mg (28%) of colorless oil.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ 22.9 (br). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −58.3 (rac), −58.4 (meso), −58.5 (d, J = 273, ^{13}C satellite, rac), −58.6 (d, J = 274, ^{13}C satellite, meso). ^1H NMR (C_6D_6): δ 7.61−7.57 (m, 4H, Ar, meso), 7.50−7.46 (m, 4H, Ar, rac), 7.30 (d, J = 8, 2H, Ar, rac), 7.24 (d, J = 8, 2H, Ar, rac), 7.13 (d, J = 8, 2H, Ar, meso), 7.09 (d, J = 8, 2H, Ar, meso), 6.98−6.84 (m, 16H, 8H rac, 8H meso, Ar), 6.71 (t, J = 8, 2H, rac, Ar), 6.64 (t, J = 8, 2H, meso, Ar), 3.30−3.25 (m, 2H, rac, benzyl), 3.15−3.10 (m, 2H, meso, benzyl), 3.05−2.99 (m, 2H, rac, benzyl), 2.98−2.93 (m, 2H, meso, benzyl), 2.50−2.46 (m, 2H, CH_2, meso), 2.19−2.14 (m, 2H, rac CH_2), 2.07−2.01 (m, 2H, rac CH_2), 1.67−1.65 (m, 2H, meso CH_2), 1.8−1.2 (12H, br m, BH_3). $^1H\{^{31}P\}$ NMR (C_6D_6): δ 7.59 (d, J = 8, 4H, Ar, meso), 7.48 (d, J = 8, 4H, Ar, rac), 7.30 (d, J = 8, 2H, Ar, rac), 7.24 (d, J = 8, 2H, Ar, rac), 7.14 (d, J = 8, 2H, Ar, meso), 7.09 (d, J = 8, 2H, Ar, meso), 6.98−6.84 (m, 16H, 8H rac, 8H meso, Ar), 6.71 (t, J = 8, 2H, rac Ar), 6.64 (t, J = 8, 2H, meso Ar), 3.28 (d, J = 15, 2H, rac benzyl, AB pattern), 3.12 (d, J = 15, 2H, meso benzyl, AB pattern), 3.02 (d, J = 15, 2H, rac benzyl, AB pattern), 2.96 (d, J = 15, 2H, meso benzyl, AB pattern), 2.50−2.46 (m, 2H, meso CH_2), 2.19−2.13 (m, 2H, rac CH_2), 2.08−2.01 (m, 2H, rac CH_2), 1.68−1.64 (m, 2H, meso CH_2), 1.8−1.2 (m, 12H, BH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 132.6 (t, J = 5, Ar, meso), 132.5 (t, J = 2, Ar, rac, overlapping with meso), 132.4−132.3 (m, Ar), 132.2−131.8 (m, Ar), 131.83 (rac, Ar), 131.76 (meso, Ar), 130.9 (Ar), 129.1 (t, J = 5, Ar), 129.0 (meso, Ar), 127.53 (rac, Ar), 127.46 (meso, Ar), 126.8 (rac, Ar), 126.6−126.4 (m, Ar), 126.2 (meso, Ar), 125.8 (meso, Ar), 124.14 (q, J = 274, rac, CF_3), 124.06 (q, J = 274, meso, CF_3), 31.3−31.1 (m, meso, benzyl C), 30.9−30.7 (m, rac, benzyl C), 18.2−17.6 (m, rac and meso overlapping, CH_2).

Determination of the ee for 7. The ee of the diphosphine was determined using either a slight excess of the Pd reporter complex (*S*)-(Pd(NMe$_2$CH(Me)C$_{10}$H$_6$)(μ-Cl))$_2$ in C_6D_6, to ensure monodentate coordination of the diphosphine, or 0.5 equiv of the Pd complex in CD_2Cl_2, to favor bidentate coordination (some monodentate coordination also occurred under these conditions). Integration of the ^{31}P and ^{19}F NMR spectra gave the ee of the diphosphine (see Table 6 for the NMR data). Using highly rac-enriched diphosphine-borane gave material of >99% de and ee.

Pt-Catalyzed Asymmetric Synthesis of PMePh(CH$_2$C$_6$H$_4$-*o*-CF$_3$). A solution of methylphenylphosphine (2.1 mmol, 264 mg) in 5 mL of THF was treated with a solution of $NaOSiMe_3$ (2.1 mmol, 239 mg) in 2 mL of THF and a solution of Pt((*R*,*R*)-*i*-Pr-DuPhos)(Ph)(Cl) (77 mg, 0.11 mmol, 5 mol %) in 3 mL of THF, and the solution turned yellow. A solution of 1-(bromomethyl)-2-(trifluoromethyl)benzene (509 mg, 2.1 mmol) in 10 mL of THF was added slowly to the mixture via cannula. The mixture showed a hint of orange before turning bright yellow followed by the formation of a white precipitate. After 3 h, the reaction was observed to be complete by ^{31}P NMR spectroscopy, and the white slurry was filtered through Celite to remove the insoluble salt. The orange filtrate was pumped down to give an orange oil, which was loaded onto a 5 mm wide, 50 mm high silica column with a 1:3 mixture of THF/petroleum ether, leaving an orange precipitate behind. The column was eluted with 30 mL of petroleum ether; the solution was concentrated to yield the product (360 mg, 60%) as a colorless oil. The ee was determined to be 21% by treating the phosphine (25 mg, 0.089 mmol) with the chiral Pd reporter compound (*S*)-Pd(Me$_2$NCH(Me)C$_6$H$_4$)(μ-Cl))$_2$ (31 mg, 0.053 mmol) in 1 mL of CD_2Cl_2 ($^{31}P\{^1H\}$ NMR: major peak δ 24.0, minor peak δ 22.5; by ^{19}F NMR integration the ee was 24%, major peak δ −56.8, minor δ −56.6).

HRMS: m/z calcd for $C_{15}H_{15}F_3PO$ $(MOH)^+$ m/z 299.0813, found 299.0818. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −24.9 (q, J = 12). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −59.0 (d, J = 12), −59.1 (dd, J = 274, 12, ^{13}C satellites). ^1H NMR ($CDCl_3$): δ 7.67 (d, J = 7, 1H, Ar), 7.60−7.54 (m, 2H, Ar), 7.43−7.38 (m, 4H, Ar), 7.32−7.22 (m, 2H, Ar), 3.27 (m, 2H), 1.38 (d, J = 4, 3H). Selected $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 3.30 (d, J = 14, 1H, AB), 3.24 (dd, J = 14, 1, 1H, AB). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.6 (d, J = 16, Ar), 137.2 (m, Ar), 131.9 (Ar), 131.8 (Ar), 131.7 (Ar), 131.6 (Ar), 129.1 (Ar), 128.6 (d, J = 6, with low-intensity shoulders (d, J = 3)), 126.3 (q, J = 6, Ar), 126.1 (d, J = 2, Ar), 124.7 (q, J = 274, CF_3), 35.2 (d, J = 21, CH_2), 10.9 (d, J = 16, Me).

Pt(*meso*-7)(Ph)(Cl) (*meso*-8). A solution of Pt(COD)(Ph)(Cl) (70 mg, 0.17 mmol) in 1 mL of CH_2Cl_2 was treated with a solution of *meso*-**7** (95 mg, 0.17 mmol) in 1 mL of CH_2Cl_2. The mixture was stirred for 20 min, and then the solvent was removed *in vacuo*. The resulting white solid was washed with petroleum ether (3 × 2 mL), and the remaining solvent was removed *in vacuo* to give 135 mg (91%) of a white solid, which could be recrystallized from THF/ether.

Anal. Calcd for $C_{36}H_{31}ClF_6P_2Pt$: C, 49.69; H, 3.59. Found: C, 49.91, H, 3.48. HRMS: m/z calcd for $C_{36}H_{31}F_6P_2Pt$ $(M - Cl)^+$ 834.1453, found 834.1428. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.0 (J_{Pt-P} = 1657), 40.8 (J_{Pt-P} = 4230). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −58.1, −58.2. ^1H NMR ($CDCl_3$): δ 8.19 (d, J = 8, 1H), 7.94 (t, J = 9, 2H), 7.85 (d, J = 8, 1H), 7.72−7.69 (m, 2H), 7.66−7.59 (m, 4H), 7.47−7.22 (m, 10H), 7.12 (t, J = 7, 2H), 6.95 (t, J = 7, 1H), 4.10 (dd, J_{HH} = 14, J_{PH} = 10, 1H, CH_2), 3.81 (apparent t, J_{HH} = 14, J_{PH} = 14, 1H, CH_2), 3.66 (d, J_{PH} = 14, 2H, CH_2), 1.85−1.70 (m, 2H, CH_2), 1.48−1.26 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.2 (br m, Ar), 136.1 (Ar), 133.8 (d, J = 5, Ar), 133.4 (d, J = 11, Ar), 133.2 (d, J = 12, Ar), 132.6 (br m, Ar), 132.4 (d, J = 6, Ar), 132.3 (br m, Ar), 132.1 (br, Ar), 132.0 (d, J = 3, Ar), 131.5 (d, J = 2, Ar), 130.9 (d, J = 41, Ar), 129.1 (t, J = 10, Ar), 128.7 (br m, Ar), 128.5 (d, J = 7, Ar), 127.2 (d, J = 26, Ar), 127.1 (d, J = 26, Ar), 126.7−126.6 (br m, Ar), 126.4−126.3 (br m, Ar), 125.5 (d, J = 14, Ar), 123.8 (Ar), 29.4 (dm, J = 27, CH_2), 29.0 (dd, J = 40, 21, CH_2), 26.8 (d, J = 36, CH_2), 22.7 (dm, J = 36, CH_2). The CF_3 signals and some aryl peaks were not observed.

Pt((*S*,*S*)-7)(Ph)(Cl) ((*S*,*S*)-8). A solution of Pt(COD)(Ph)(Cl) (39 mg, 0.09 mmol) in 1 mL of CH_2Cl_2 was treated with a solution of (*S*,*S*)-**7** (53 mg, 0.09 mmol) in 1 mL of CH_2Cl_2. The mixture was stirred for 20 min, and then the solvent was removed *in vacuo*. The resulting white solid was washed with petroleum ether (3 × 2 mL), dried under vacuum, and recrystallized from 1:1 ether/petroleum ether to give 85 mg (67%) of a white solid.

Anal. Calcd for $C_{36}H_{31}ClF_6P_2Pt$: C, 49.69; H, 3.59. Found: C, 50.14, H, 3.60. HRMS: m/z calcd for $C_{36}H_{31}F_6P_2Pt$ $(M - Cl)^+$ 834.1453, found 834.1442. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 50.5 (J_{Pt-P} = 1682), 43.2 (J_{Pt-P} = 4263). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −58.4, −58.7. ^1H NMR ($CDCl_3$): δ 8.73 (d, J = 8, 1H), 8.30 (d, J = 8, 1H), 7.98−7.94 (m, 2H), 7.73−7.68 (m, 3H), 7.64 (t, J = 7, 2H), 7.58 (d, J = 8, 1H), 7.49−7.40 (m, 6H), 7.34−7.28 (m, 3H), 7.17 (t, J = 8, 1H), 7.11 (t, J = 7, 2H), 6.96 (t, J = 7, 1H), 4.39−4.34 (m, 1H, CH_2), 3.82 (t, J = 14, 1H, CH_2), 3.72 (t, J = 15, 1H, CH_2), 3.63 (t, J = 14, 1H, CH_2), 1.99−1.73 (m, 2H, CH_2), 1.33−1.12 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.2 (d, J = 7, Ar), 160.2 (d, J = 7, Ar), 137.2 (br m, Ar), 134.1 (d, J = 5, Ar), 133.5 (t, J = 11, Ar), 133.6−133.4 (br, overlapping previous peak, Ar), 132.8 (br, Ar), 132.5 (Ar), 132.3 (Ar), 132.2−132.1 (m, Ar), 131.7 (br, Ar), 131.6 (d, J = 2, Ar), 129.6 (d, J = 40, Ar), 129.10 (d, J = 10, Ar), 129.08 (d, J = 11, Ar), 128.5 (d, J = 7, Ar), 127.9 (d, J = 55, Ar), 127.1 (t, J = 3, Ar), 126.3−126.2 (m, Ar), 125.6 (d, J = 12, Ar), 123.9

(Ar), 123.4 (d, $J = 14$, Ar), 28.5 (d, $J = 23$, CH_2), 27.0 (dd, $J = 40$, 17, CH_2), 25.5 (d, $J = 37$, CH_2), 21.4 (br d, $J = 34$, CH_2). The CF_3 signals were not observed.

Attempted Chirality Breeding. The following procedure was used for entries 1, 2, 4, and 5 in Table 5. A solution of **1** (25 mg, 0.1 mmol) in 0.5 mL of THF was treated with $NaOSiMe_3$ (23 mg, 0.2 mmol) and either (*S*,*S*)-**8** or *meso*-**8** (8 mg, 0.01 mmol). The resulting yellow solution was treated with 1-(bromomethyl)-2-(trifluoromethyl)benzene (24 μL, 0.2 mmol); the solution slowly became colorless, and a white precipitate was observed. When the reaction was complete, as determined by ^{31}P NMR spectroscopy, petroleum ether was added (4 mL) and the mixture was filtered through silica eluting with 50% THF/petroleum ether. The solvent was removed under vacuum to give the product as a colorless oil. The selectivity was determined by binding the diphosphine to the Pd reporter complex (*S*)-$[Pd(NMe_2CH(Me)C_{10}H_6)(\mu\text{-}Cl)]_2$. In entries 3 and 6, before the addition of benzyl bromide, ^{31}P NMR spectroscopy showed the formation of diphosphine **7**; the original Pt complex was not observed. The benzyl bromide was added approximately 30 min later; the catalytic reactions did not go to completion under these conditions. The workup was the same as described above.

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Supporting Information Available: Additional experimental and crystallographic data (CIF) is available free of charge via the Internet at http://pubs.acs.org.

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