3,5-Dialkyl Effect on Enantioselectivity in Pd Chemistry: Applications Involving Both Bidentate and Monodentate Auxiliaries

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The structural 3,5-dialkylphenyl effect on enantioselectivity is demonstrated for several Pd-catalyzed reactions including a ring-opening transmetalation, Heck arylation, and allylic alkylation. For these homogeneously catalyzed reactions the observed enantiomeric excesses (ee's) are found to improve by more than 15%. The ligands tested include MeO-Biphep and a P,N-phosphino-oxazoline-bidentate ligand containing 3,5-di-*tert*-butylphenyl substituents. Further, several derivatives of the monodentate auxiliary MOP ((*R*)-2-diarylphosphino-1,1′-binaphthyl) have been modified to include 3,5-dialkylphenyl substituents and these auxiliaries have been tested in Pd-catalyzed enantioselective hydrosilylation chemistry. For some, but not all of these MOP ligands, enhanced ee's of the order of 40−50% are found. Variable-temperature and 2-D NMR studies have been carried out on new model complexes and reveal selected restricted rotation around a number of the P−C(*ipso*) aryl bonds. Solid-state structures for two of the new complexes, PdBr(p-NCC_6H_4)(phosphino-oxazoline, **2b**), **8b**, and PdCl($C_6H_4CH_2NMe_2$)(MOP, **4b**), **9b**, have been determined.

Introduction

There are now a number of readily available bidentate chiral auxiliaries capable of achieving enantiomeric excesses (ee's) in excess of 90%, for a variety of enantioselective transformations. The ligands Duphos[1−3] and Binap[4] have been relatively successful in enantioselective homogeneous hydrogenation, whereas the TADDOL[5] series has been employed successfully in C−C bond making reactions. Many chelating oxazoline derivatives,[6−11] with and without tertiary phosphine donors, are now widely employed in a variety of catalytic reactions.

In several studies,[12−14] we have shown that introducing 3,5-di-*tert*-butylphenyl groups onto the P-donor of the auxiliary (instead of the routine phenyl substituent) enhances the ee's in Heck and allylic alkylation chemistry. Specifically, we have used MeO-Biphep, **1**,[12] and the phosphino-oxazolines, **2** (see Scheme 1),[13,14] in the

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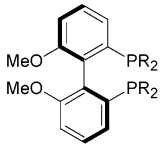
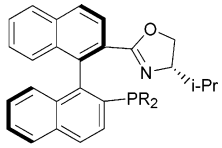
Scheme 1



1a, R = Ph

1b R = 3,5-di-*t*-butylphenyl



2a, R = Ph

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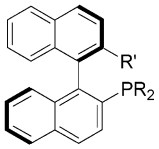


4a, R = Ph, R' = H

4b, R =3,5-di-*t*-butylphenyl, R' = H

4c, R =3,5-di-methylphenyl, R' = H

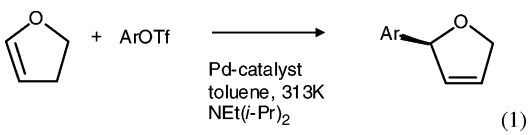
5a, R = Ph, R' = MeO

5b, R =3,5-di-*t*-butylphenyl, R' = MeO

6a, R = Ph, R' = CN

6b, R =3,5-di-*t*-butylphenyl, R' = CN

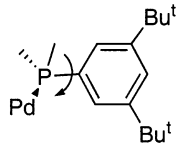
enantioselective Heck arylation of dihydrofuran (e.g., as shown in eq 1), and found that **1b** and **2b** are signifi-



(1)

cantly better than **1a** and **2a** in terms of enantioselectivity with improvements of 10−20% rather routine. Several other groups[15−19] have found that both 3,5-di-*tert*-butylphenyl and 3,5-dimethylphenyl substituents can be effective and that Ru, Rh, and Ir catalysts also show this 3,5-dialkyl effect on enantioselectivity.

For complexes of MeO-Biphep, **1**,[12] we have suggested that this enhanced enantioselectivity arises due to restricted rotation around the P−C(*ipso*) bonds of the P(3,5-di-*tert*-butylphenyl) groups, as indicated in fragment **3**. This decrease in molecular freedom derives from



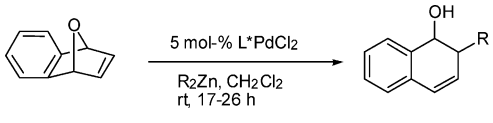
fragment **3**

the restricted rotation due to the interaction of the P-aryl substituent with the biaryl backbone and results in a more rigid chiral pocket and thus improved correlation between substrate and catalyst.

We report here (a) several new examples of this 3,5-dialkyl effect on ee, involving palladium chemistry of the ligands **1** and **2**, (b) that the effect can be extended to the monodentate auxiliary, MOP,[20] **4**, and (c) new detailed NMR and X-ray studies relevant to the P−C restricted rotation for new complexes of **2** and MOP.

Results

Reactions with 1a,b and 2a,b. Lautens and coworkers[21] have reported in detail on the Pd-catalyzed ring-opening alkylation of the oxabenzonorbornadiene shown in eq 2. The reaction is thought to involve a



(2)

transmetalation from the dialkyl zinc to palladium, followed by alkyl insertion into the complexed double bond and Zn-assisted ring opening. One diastereomer is strongly favored. The reaction conditions are mild and yields are good. For dimethyl zinc, using (R)-Binap, (R)-

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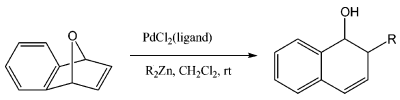
Table 1. Results in Alkylating Ring Opening of Oxabenzonorbornadiene[a]



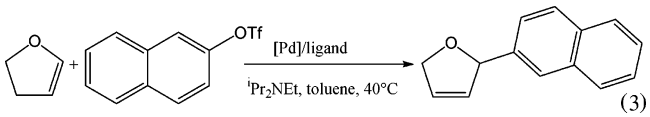
entry	R	ligand	reaction time (h)	yield (%)	ee (%)
1	Me	(*S*)-**1a**	26	93	82.7
2	Me	(*R*)-**1a**	18	73	81.6
3	Me	(*R*)-**1b**	22	73	97.7
4	Et	(*R*)-**1a**	20	87	95.0
5	Et	(*R*)-**1b**	20	49[c]	97.4
6	Me	**2a**	17	57[b]	92.5
7	Me	**2b**	17	86	93.1

[a] Catalyst loading: 5 mol % $PdCl_2$(ligand). [b] Formation of side products. [c] Reaction not run to completion.

Tol-Binap, and the Pfaltz/Helmchen phosphino-oxazoline *i*-Pr-PHOX, Lautens reports ee's of 67%, 76%, and 89%, respectively.

Using the two MeO-Biphep ligands, **1a,b**, with the latter having the 3,5-di-*tert*-butylphenyl groups, we find ee's of ca. 81.6% and 97.7%, respectively, and show our results in Table 1 (entries 2 and 3). Clearly, the effect is working in this chemistry and the observed increase lies within the range we have previously noted. The same reaction with the P,N-auxiliaries **2a**,**b** gave ee's of 92.5% and 93.1% (entries 6 and 7), i.e, almost no improvement. Similarly, using diethyl zinc[22] and **1a**,**b**, we find ee's of 95.0% and 97.4% (entries 4 and 5). It would appear that the effect is more pronounced where there is more room for improvement.

The enantioselective Heck reaction has been the subject of considerable interest. The classical test substrate, suggested by Hayashi,[23] is dihydrofuran, dhf, although Overman and co-workers[24] have reported on several elegant intramolecular versions. For the Pd-catalyzed Heck reaction of 2-naphthyl triflate with dihydrofuran, i.e., eq 3, we find 79% ee with **2a** and 98%



(3)

ee with **2b**. Interestingly, $Pd_2(dba)_3$ is the preferred Pd-precursor, relative to $Pd(OAc)_2$, in that the yields with the former are much better. This was somewhat surprising for us.[12b,25] Using the dba precursor, one avoids the reduction step; nevertheless, the reaction is still quite slow. However, the observed ee with **2b**, 98% (19% more than with **2a**), is gratifying.

(22) Using diethyl zinc and **2a**,**b**, we find little or no reaction.

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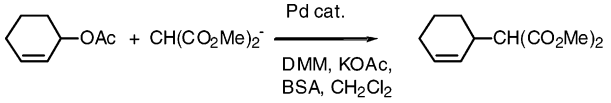
(25) ^{31}P and ^{19}F NMR experiments with stoichiometric amounts of the 2-naphthyl triflate substrate and $Pd(OAc)_2$ and P,N-ligand, or Pd-$(dba)_2$ and P,N-ligand, suggest not much difference between these two with respect to the rate of formation of the Pd-aryl and free triflate. Consequently, the observed rate difference as a function of catalyst is most likely not related to the oxidative addition reaction.

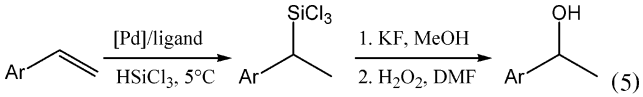
The allylic alkylation of cyclohexenyl acetate with dimethyl malonate (eq 4) has been reported previously.[26]



(4)

Although many auxiliaries do not work well with this substrate, presumably because the Pd-allyl intermediate formed (vida infra) is rather small and symmetric, Trost[26] has developed a ligand set that carries out this transformation with high ee's. Using [Pd(η^3-C_3H_5)(**2a**,**b**)]-OTf as precursor, we find 36% ee with **2a** and 56% ee with **2b**. While these data confirm that the 3,5-dialkyl effect is present, they are a far cry from the 90% ee known in the literature.

MOP Chemistry. The monodentate auxiliary MOP ((*R*)-2-diarylphosphino-1,1′-binaphthyl), **4a**−**6a**, introduced by Hayashi,[20] has proven to be an interesting ligand. While it has been used successfully in allylic alkylation chemistry, much effort has been devoted to its application to enantioselective hydrosilylation reactions,[20a,b,h] e.g., the chemistry of eq 5.



(5)

A **B** **C**

The standard MOP compounds, **4a**−**6a**, were synthesized according to the literature. In addition, we have prepared the new MOP derivatives **4b**−**6b** (with 3,5-di-*tert*-butylphenyl groups).

Using these various auxiliaries, together with the allyl complex [Pd(μ-Cl)(η^3-C_3H_5)]$_2$, gave quantitative yields of the trichlorosilane, **B**, and good yields of the alcohol, **C**, after oxidative workup with KF, and then H_2O_2. In contrast to the Heck chemistry, the amount of catalyst precursor employed was relatively small, usually 0.1%. The ee's from the hydrosilylation reactions with styrene (entries 1−7), 2-vinylnaphthalene (entries 8−12), and *p*-methoxystyrene (entries 13−15) are shown in Table 2. The data, and related observations, reveal a number of interesting points:

(a) For styrene, using the MeO-MOP, **5b** (entries 3 and 4), and CN-MOP, **6b** (entries 5 and 6), containing the 3,5-di-substituted *tert*-butyl groups, there are >39% improvements in the ee, relative to **5a** and **6a**. Nevertheless, the maximum ee is still modest. However, for the unsubstituted H-MOP, **4b**, there is a slight decrease in ee, relative to **4a** (entries 1 and 2), and both of these ee values are much larger than for either MeO-MOP or CN-MOP.[27]

(b) For the 2-vinyl naphthalene and *p*-methoxy styrene substrates, the use of the 3,5-*dimethylphenyl* groups can be advantageous, e.g., there is a ca. 13%

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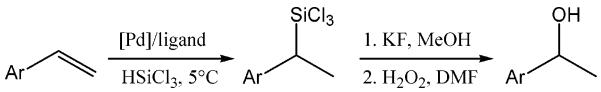
(27) We note that there is a change of enantiomer on going from **4** or **5** to **6**. We believe this is related to differences in how these ligands bind the Pd-atom and studies to support this idea on suitable models are in progress.

Table 2. Catalytic Results[a] from the Hydrosilylation Reaction with MOP Ligands



A		B			C
entry	Ar	ligand	time (h)	yield[b] of **B** (%)	ee of **C** (%)
1	Ph	**4a**	20	100	92 (*R*)
2	Ph	**4b**	16	100	88 (*R*)
3	Ph	**5a**	16	100	7 (*R*)
4	Ph	**5b**	43	100	57 (*R*)
5	Ph	**6a**	2	100	42 (*S*)
6	Ph	**6b**	2	100	81 (*S*)
7[c]	Ph	**6b**	21	100	86 (*S*)
8[c,d]	2-naphthyl	**4a**	66	100	77 (*R*)
9[c,d]	2-naphthyl	**4b**	88	100	55 (*R*)
10[c,d]	2-naphthyl	**4c**	138	95	80 (*R*)
11[c,d]	2-naphthyl	**6a**	21	100	32 (*S*)
12[c,d]	2-naphthyl	**6b**	68	100	66 (*S*)
13[c]	4-MeO-Ph	**4a**	15	100	67 (*R*)
14[c]	4-MeO-Ph	**4b**	65	99	38 (*R*)
15[c]	4-MeO-Ph	**4c**	65	100	80 (*R*)

[a] Catalyst loading: 0.05 mol % [Pd(μ-Cl)(η^3-C_3H_5)]$_2$, 0.2 mol % ligand unless otherwise stated. [b] Determined by NMR. [c] Run in toluene (1 M). [d] 0.2 mol % [Pd(μ-Cl)(η^3-C_3H_5)]$_2$, 0.8 mol % ligand used.

increase in ee for the *p*-methoxy styrene with the 3,5-dimethylphenyl groups (entry15), but the 3,5-di-*tert*-butylphenyl groups result in marked *decreases* in ee. For the 2-vinyl naphthalene, the results are mixed.

(c) When using the standard H-MOP, changing from styrene to *p*-methoxy styrene results in decreased ee's (entries 1 and 2 vs 13 and 14), i.e., the substrate is important.

(d) The reactions with the *meta*-substituted auxiliaries are usually slower.

Clearly, the choice of MOP ligand is important. Further, although the 3,5-di-*tert*-butylphenyl substituent on the phosphine donor can be helpful, this ligand modification is not always the best choice in terms of improving the selectivity, i.e., in some cases the 3,5-dimethylphenyl compound is better. Earlier, in the Pd-catalyzed *phenylation* of dihydrofuran with phenyl triflate,[14a] using **2a**−**c** (**2c** is not shown in the scheme), the observed ee increased "as expected": phenyl (74%) < 3,5-di-methylphenyl (86%) < 3,5-di-*tert*-butylphenyl (98%).

NMR and Structural Studies for the P,N Complexes. The effect on the solution dynamics of introducing the 3,5-di-*tert*-butylphenyl groups on the phosphorus donor of **2b** in the simple P,N complex, $PdCl_2$(**2b**), **7b**, is shown in Figure 1. In the ^{1}H NMR spectrum at 273 K one begins to see the effects of the P−C hindered rotation on the *tert*-butyl proton signals of one of the P-aryl rings. At 233 K the two *tert*-butyl groups are clearly nonequivalent and well resolved (as are the *ortho* protons, not shown). An analogous set of temperature-dependent spectra for $PdCl_2$(**2a**), **7a**, do not reveal any restricted rotation at 233 K. At 213 K (at which temperature the second P-aryl ring begins to experience slow rotation around its P−C bond) the first set of *tert*-butyl resonances are sharp. At 199 K, all four *tert*-butyl groups are nonequivalent and resolved. Figure 2 shows

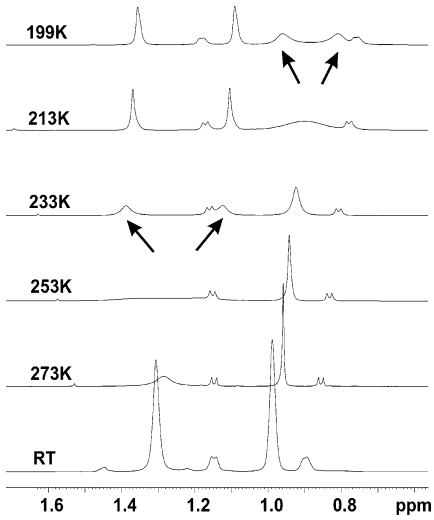


Figure 1. A section of the variable-temperature ^{1}H NMR spectra measured for **7b**. The pseudoaxial 3,5-di-*tert*-butylphenyl group demonstrates a higher barrier to rotation than the pseudoequatorial analogue. The two weaker doublets stem from the nonequivalent methyl groups of the *i*-Pr group (CD_2Cl_2).

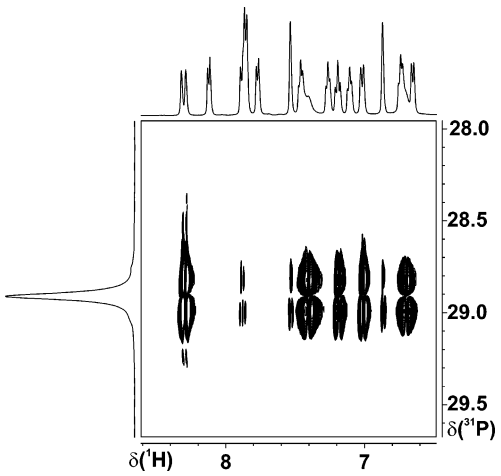


Figure 2. ^{31}P,^{1}H correlation at 199 K for **7b** showing the five nonequivalent *ortho* protons (one from the naphthyl backbone, four from the two rings) as a consequence of the restricted rotation. Two of the three weaker correlations stem from *J* values to the *para* protons, i.e, $^5J(^{31}P,^1H)$-(CD_2Cl_2).

the aromatic region of the ^{31}P,^{1}H correlation at this temperature. Apart from the four strong cross-peaks from the now nonequivalent *ortho* protons (five, counting the *o*-naphthyl analogue), three additional weak cross-peaks are observed. Two of these (δ ca. 6.8 and ca. 7.5) arise from the slightly broadened singlets due to the *para* protons of the 3,5-di-*tert*-butylphenyl groups, i.e., we are observing a rare example of a readily detectable five-bond, $^5J(^{31}P,^1H)$, spin−spin interaction.

We also recorded variable-temperature ^{1}H NMR spectra for the aryl complexes PdBr(*p*-NC-C_6H_4)(**2a** and **2b**), **8a**,**b**, which stem from substitution reactions on Pd(Br)-(*p*-NCC_6H_4)(TMEDA). Interestingly, we find *no* evidence for significant differences in the barriers to rotation about the P−C bonds in these two complexes. Given the improved ee's noted in the text, above, this observation seemed strange. This NMR finding prompted us to measure the structure of **8b** in the solid state, via X-ray

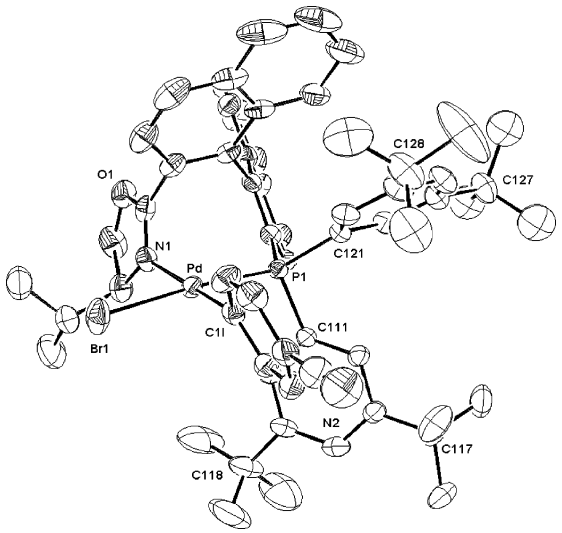


Figure 3. An ORTEP view of the structure of the complex PdBr(*p*-NCC_6H_4) (**2b**), **8b**. Ellipsoids are drawn at 50% probability.

diffraction, and an ORTEP view of this molecule is given in Figure 3.

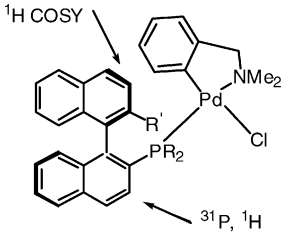
Solid-State Structure of 8b. Complex **8b** reveals a slightly distorted square-planar structure with the bromide ligand in a trans position to the P-donor and the *p*-cyano aryl η^1 carbon atom trans to the oxazoline nitrogen. As expected, On the basis of previous structures[13,14a] for complexes of **2**, the oxazoline ring is rotated ca. +98° with respect to the Br−Pd−N−P plane. In conventional complexed PHOX ligands, the oxazoline is approximately *in* the coordination plane. Further, the *p*-cyano-aryl ligand is rotated ca. −71° with respect to this same coordination plane. This is important in that this aryl ligand now occupies space fairly remote from the closest 3,5-di-*tert*-butylphenyl group, thereby explaining why no restricted rotation is found in solution.

The immediate bonding distances about the Pd-atom are fairly routine,[28] allowing for the differing *trans* influences of the four donors, e.g., the Pd−P separation, 2.277(1) Å, lies toward the lower end of the range for this bond distance, due to the modest *trans* influence of the bromide ligand, while the Pd−N bond length, 2.141(4) Å, is slightly long, due to the *trans* carbon-donor. We note that the Br−Pd−C(1L) angle, at ca. 86°, is rather small, suggesting that the *p*-cyano-aryl ligand prefers a position remote from the relatively large P-aryl substituents. A summary of the most relevant distances and angle is given in Table 3.

NMR and Structural Studies for the MOP Complexes. To better understand the results from the catalytic experiments using MOP, we have prepared several simple MOP complexes, **9**, derived from the well-known chloro-bridged cyclometalated *N*,*N*′-dimethylbenzylamine.[29−31]

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 8b and 9b

		8b	
Pd−C(1L)	1.989(4)	C(1L)−Pd−N(1)	176.6(2)
Pd−N(1)	2.141(4)	C(1L)−Pd−P(1)	91.4(1)
Pd−P(1)	2.277(1)	N(1)−Pd−P(1)	91.5(1)
Pd−Br(1)	2.469(1)	C(1L)−Pd−Br(1)	85.8(1)
P(1)−C(111)	1.822(4)	N(1)−Pd−Br(1)	91.5(1)
P(1)−C(121)	1.816(4)	P(1)−Pd−Br(1)	174.7(1)
P(1)−C(6)	1.837(4)	N(2)−C(7L)	1.149(7)
		9b	
Pd−C(1L)	2.007(4)	P(1)−C(121)	1.834(4)
Pd−N(1)	2.167(4)	P(1)−C(111)	1.840(4)
Pd−P(1)	2.256(1)	C(1L)−Pd−N(1)	81.1(2)
Pd−Cl(1)	2.416(1)	C(1L)−Pd−P(1)	97.7(1)
N(1)−C(8L)	1.455(6)	N(1)−Pd−P(1)	176.8(1)
N(1)−C(9L)	1.490(6)	C(1L)−Pd−Cl(1)	165.1(1)
N(1)−C(7L)	1.492(6)	N(1)−Pd−Cl(1)	91.8(1)
P(1)−C(6)	1.835(4)	P(1)−Pd−Cl(1)	90.1(1)



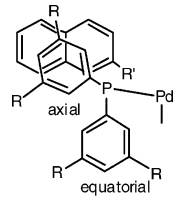
9

a, = R = Ph, R' = H

b, R = 3,5-di-*t*-butylphenyl, R' = H

c, = R = 3,5-dimethylphenyl

The ^{31}P, ^1H, and ^{13}C assignments for the two different P(3,5-dialkylphenyl) rings in **9b**,**c** were made by first assigning both of the two spin systems (indicated by arrows in **9**), using proton−proton and phosphorus−proton correlations, followed by NOE's to assign the remaining protons. Once the protons are assigned, the two P-aryl rings can be distinguished via NOE's. Figure 4 shows a slice through the NOESY spectrum for the 3,5-methylphenyl complex, **9c**. The pseudoaxial ring in the molecule is proximate to the binaphthyl backbone, see fragment **10**, and reveals eight different NOE's



fragment **10**

arising from the methyl groups, six from the backbone plus two strong interactions involving the immediately adjacent *ortho* and *para* protons. The pseudoequatorial ring shows only four NOE's from the methyl groups, two very weak interactions to the backbone and, again, two strong interactions involving the proximate *ortho* and *para* protons.

The *cis* chloride ligand in **9** is not very bulky; however, the aryl moiety associated with the cyclometalated ring

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(31) Newcome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451−489.

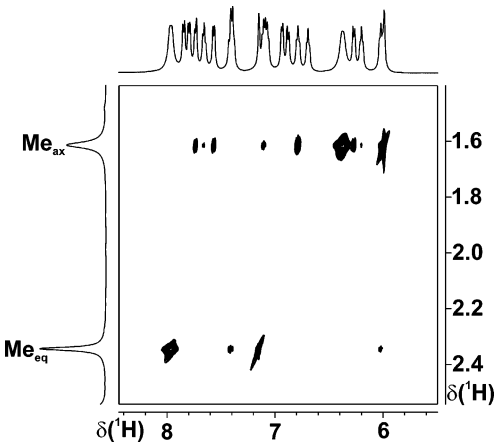


Figure 4. A slice through the ^{1}H,^{1}H NOESY spectrum of the 3,5-dimethylphenyl MOP analogue, **9c**. The pseudoaxial aryl ring, associated with the low-frequency methyl signal, reveals many more contacts to the aromatic backbone than does the pseudoequatorial analogue. Indeed, for the methyl group at higher frequency, the two most intense contacts stem from the adjacent *ortho* and *para* protons of the 3,5-dimethylphenyl moiety and not from the interring NOE's (CD_2Cl_2).

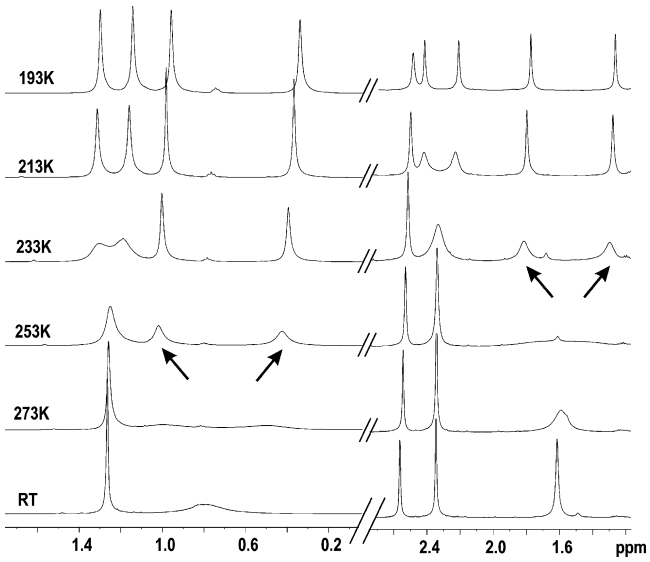


Figure 5. ^{1}H NMR spectra measured as a function of temperature for the complexes **9b** and **9c** in the methyl region. For the 3,5-di-*tert*-butylphenyl complex (left) the restricted rotation is clearly visible at 253 K, whereas for the 3,5-dimethylphenyl compound (right) the restricted rotation is recognized at 233 K; for **9c**, the ca. 2.55 ppm resonance stems from a *N*-methyl group (CD_2Cl_2).

lies approximately *in* the coordination plane and is thus sterically significant with respect to the proximate MOP ligand. Figure 5 shows sections of the appropriate variable temperature ^{1}H spectra for **9b** (left side) and **9c** (right side). At ambient temperature, the 18-proton *tert*-butyl signal of the pseudoaxial ring in **9b** is quite broad, and at 273 K, broad but resolved. At 233 K all four 9-proton signals are resolved. The spectra for the dimethyl analogue, **9c**, reveal the first set of resolved methyl signals at 233 K, i.e., the barrier to rotation is lower. The aryl protons of **9a** begin to show well-resolved *ortho* proton resonances from the P-aryl moieties below 200 K. Once again there is selective restricted rotation induced by the presence of the 3,5-dialkyl groups.

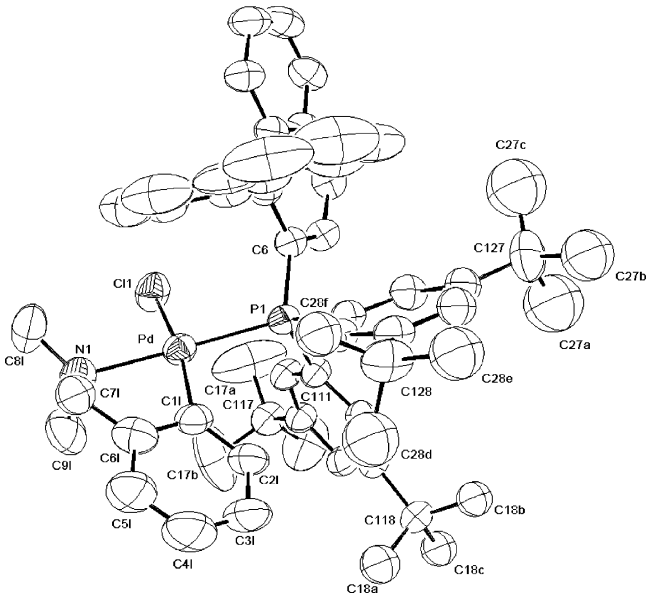


Figure 6. An ORTEP view of the structure of the cyclometalated Pd complex, **9b**. Ellipsoids are drawn at 50% probability.

To complement these NMR studies we have determined the solid-state structure of **9b** using X-ray diffraction methods.

Solid-State Structure of 9b. Figure 6 shows an ORTEP view of the new MOP complex. Complex **9b** reveals a distorted square-planar structure with the chloride ligand in a *trans* position to the C-donor and the MOP P-donor *trans* to the dimethylamino nitrogen. The coordination distances are fairly standard, although both the Pd−N, 2.167(4) Å, and Pd−Cl, 2.416(1) Å, separations are on the longish side,[28] due to the relatively strong *trans* influences of the P- and C-donors, respectively.

The pseudoaxial P(3,5-di-*tert*-butylphenyl) group, identified via the torsion angle Cl(1)−Pd−P(1)−C(111) = ca. −83°, is found closest to the C,N-chelate ring in agreement with the NMR studies. Interestingly, the binaphthyl backbone is positioned closest to the chloride ligand (the torsion angle Cl(1)−Pd−P(1)−C(6) is ca. 34°). This observation serves as a reminder that one is not certain as to which of the possible MOP substituent fragments actually approaches the position occupied by potential substrate.

The bond angles about the Pd atom are interesting. The C(1L)−Pd−N(1) angle at 81.1(2)° is, as expected, fairly small, due to the five-membered ring. Consequently, the remaining two ligands, Cl^- and MOP, will have a little more space. The N(1)−Pd−Cl(1) angle, 91.8(1)°, is only slightly opened; however, the C(1L)−Pd−P(1) angle, 97.7(1)°, is relatively large. Since the sum of the four angles from the various *cis*-positioned ligands is 360.7°, it seems reasonable that the larger 97.7(1)° angle arises from steric crowding between the MOP and the cyclometalated aromatic ring, again in agreement with the NMR experiments. Indeed, the ORTEP view suggests that the molecule is somewhat congested in the area between the MOP and the C,N-chelate ring. Despite the congestion, we note that the three C−P−C angles are all fairly normal: C(6)−P(1)−C(121) = 100.3(2)°, C(6)−P(1)−C(111) = 107.1(2)°, and C(121)−P(1)−C(111) = 104.0(2)°.

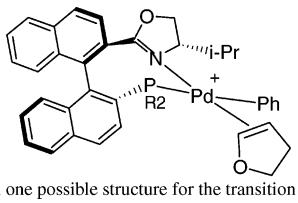
Discussion

The catalytic results support a substantial 3,5-dialkyl effect on enantioselectivity based on the four different Pd-catalyzed reactions presented. Moreover, given that some few earlier studies on Ru(II),[15a] Rh(I),[17] and Ir(I)[15b] catalyzed hydrogenation, using 3,5-dialkyl-substituted auxiliaries, all showed improved ee's, we feel justified in suggesting that the effect has some generality. It is also noteworthy that the effect is operative for MOP, a presumed monodentate auxiliary.

The >20% improvements in ee observed seem associated with reactions which, initially, gave only moderate-to-poor ee's. Moreover, it is not always the case that the 3,5-di-*tert*-butylphenyl groups on the phosphorus afford the largest increases. In one or two examples, the 3,5-dimethylphenyl substituents could be shown to induce the desired improvement, whereas the *tert*-butyl analogues proved to be worse in terms of ee. This brings us to the solution studies.

The variable-temperature ^{1}H NMR studies on the model complexes, **7** and **9**, which have additional ligands occupying space on or near the coordination plane, suggest that the 3,5-di-*tert*-butylphenyl groups induce selective restricted rotation around the pseudoaxial aryl P−C(*ipso*) bond. We suggest that the additional crowding due to the *meta* substituents will move part of the tertiary phosphine toward the remaining ligands. This will, in turn, make the ligand more intrusive with respect to complexed olefin substrate, and thus, the chiral pocket more selective. For complexes of the P,N ligand, **2**, a 3,5-dialkylphenyl substituent moves closer; however, for MOP it is not yet certain which of the three P-substituents is involved.

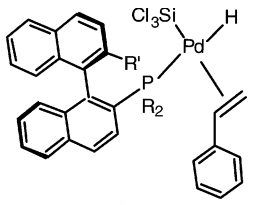
The observed normal barriers to rotation found in **8b** are not surprising since the aryl ligand is rotated away from the coordination plane. For a hypothetical complex related to **8b**, but containing an in-plane olefin (a possible transition state in the Heck reaction, see **10**),



10, one possible structure for the transition state

the crowding would increase. If, instead, a five-coordinate transition state were correct, e.g., Pd(Br or triflate)(phenyl or 2-naphthyl)(dhf)(**2b**), there would again be increased steric interactions. For both coordination numbers, we expect that higher barriers should be observed. Unfortunately, we have never been able to detect a dhf complex related to **10**.

However, one can have too much of a good thing. In the MOP hydrosilylation chemistry, the 3,5-di-*tert*-butylphenyl groups are not advantageous. In **11**, which might be a relevant structure since the hydride migrates to the methylene group, the styrene phenyl moiety might well interact with the pseudoequatorial P-aryl substituent (or the naphthyl backbone). If the P-substituent moves too close to the remaining ligands and interferes with complexation and/or induces a change in the transition state structure, then a reduced ee may result. This is likely to be the reason the 3,5-dimethylphenyl analogue will occasionally be superior. The energy difference, $\Delta\Delta G^{\ddagger}$, associated with a 10% ee improvement between ca. 80% and 90% is known to be of the order of 1 kcal.[32] Consequently, small structural changes can be important. Undoubtedly, our structural 3,5-dialkyl effect on enantioselectivity is quite subtle, but useful.



11

Experimental Section

All water- or air-sensitive manipulations were carried out under a nitrogen atmosphere. Pentane and ether were distilled from NaK, THF and toluene from potassium, and CH_2Cl_2 from CaH_2. The MeO-Biphep ligands **1a** and **1b** were a gift from F. Hoffmann-La Roche AG. The phosphino-oxazoline ligands **2a**[33] and **2b**,[14] the MOP ligands, **4a**,[34] **4c**,[35] **5a**,[36] and **6a**,[34] the intermediates (*R*)-2-(bis(3,5-di-*tert*-butylphenyl)phosphinyl)-2′-((trifluoromethane-sulfonyl)oxy)-1,1′-binaphthyl[14] and (*R*)-2-(bis(3,5-di-*tert*-butylphenyl)phosphinyl)-2′-(cyano)-1,1′-binaphthyl,[14] and the complexes **7a**,[32] **7b**,[14] and **8a**[13] were synthesized according to the literature. NMR spectra were recorded with Bruker DPX-250, -300, -400, and -500 MHz spectrometers at room temperature unless otherwise noted. Chemical shifts are given in ppm, coupling constants (*J*) in Hertz. Elemental analyses and mass spectroscopic studies were performed at ETHZ.

Crystallography. Colorless crystals of PdBr(*p*-CN-C_6H_4)(**2b**), **8b**, suitable for X-ray diffraction, were obtained by diffusion from a CH_2Cl_2/pentane mixture and are air stable. Air-stable, yellow crystals of ($C_6H_4CH_2NMe_2$)Pd(**4b**)Cl, **9b**, were obtained from a methanol/water solution.

Crystals were mounted on a Bruker SMART diffractometer, equipped with a CCD detector, for the unit cell and space group determinations. Crystals of **8b** were cooled, using a cold nitrogen stream, to 200(2) K for the data collection; for **9b** data were collected at room temperature. Selected crystallographic and other relevant data are listed in Table 4 and in the Supporting Information (Table S1).

Data were corrected for Lorentz and polarization factors with the data reduction software SAINT[37] and empirically for absorption with the SADABS program.[38]

The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares[39] (the function minimized being $\sum[w(F_o^2 - (1/k)F_c^2)]$). For both structures, no extinction correction was deemed necessary. The scattering factors used, corrected for the real and imaginary parts of the

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(39) Sheldrick, G. M. *SHELX-97*, Structure Solution and Refinement Package; Universität Göttingen: Göttingen, Germany, 1997.

Table 4. Experimental Data for the X-ray Diffraction Study of 8b·H_2Cl_2 and 9b[a]

compd	**8b**·CH_2Cl_2	**9b**
formula	$C_{62}H_{70}BrCl_2N_2OPPd$	$C_{57}H_{67}ClNPPd$
mol wt	1147.38	938.94
collection T, K	200(2)	293(2)
diffractometer	Bruker SMART CCD	
cryst syst	monoclinic	monoclinic
space group (no.)	$P2_1$ (no. 4)	$P2_1$ (no. 4)
a, Å	14.6172(2)	15.193(2)
b, Å	12.7682(1)	10.700(1)
c, Å	17.5686(3)	15.882(2)
β, deg	111.713(1)	92.449(3)
V, Å^3	3046.28(7)	2579.5(5)
Z	2	2
$\rho_{(calcd)}$, g cm^{-3}	1.251	1.209
μ, cm^{-1}	11.13	4.78
radiation	Mo Kα graphite monochrom., $\lambda = 0.71073$ Å	
θ range, (deg)	$1.56 < \theta < 27.46$	$1.82 < \theta < 26.02$
no. data collected	31530	24512
no. independent data	13850	10137
no. obsd reflns (n_o) $[\lvert F_o\rvert^2 > 2.0\sigma(\lvert F\rvert^2)]$	10925	8019
no. of param refined (n_v)	652	544
abs structure (Flack's) param	0.008(8)	0.04(2)
R_{int}	0.0580	0.0367
R (obsd reflns)[a]	0.0448	0.0379
R_w^2 (obsd reflns)[b]	0.1079	0.0884
GOF[c]	0.820	0.979

[a] $R = \sum(\lvert F_o - (1/k)F_c\rvert)/\sum\lvert F_o\rvert$. [b] $R_w^2 = [\sum w(F_o^2 - (1/k)F_c^2)^2/\sum w\ \lvert F_o^2\rvert^2]$. [c] GOF $= [\sum_w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.

anomalous dispersion, were taken from the literature.[40] The standard deviations on intensities were calculated in term of statistics alone. Refining the Flack's parameter tested the handedness of the structure (cf. Table 4).[41] All calculations were carried out by using the PC version of SHELX-97[39] and ORTEP programs.[42]

Structural Study of PdBr(*p*-CN-C_6H_4)(2b)·CH_2Cl_2, 8b·CH_2Cl_2. The space group was unambiguously determined from the systematic absences, while the cell constants were refined by least squares, at the end of the data collection, using 2414 reflections ($\theta_{max} \leq 22.5°$). The data were collected (up to $\sin(\theta/\lambda) = 0.649$) by using ω scans, in steps of 0.3 deg. For each of the 2142 collected frames, counting time was 20 s.

The *t*-Bu substituents on the phenyl rings show large amplitude vibrational displacements that, nonetheless, could be modeled satisfactorily by using anisotropic displacements for the C atoms. However, for the carbons bound to atom C127, two different orientations were clearly shown in the difference Fourier maps. Thus, the two orientations were refined by using isotropic displacement parameters for the disordered C atoms. The occupancy factors, for the two orientations, are approximately equal (0.59 and 0.41, respectively). All other atoms were refined by using anisotropic displacement parameters.

Toward the end of refinement, a highly disordered chlatrated solvent molecule (CH_2Cl_2) was found in the difference Fourier maps. Two different orientations were refined but the resulting solvent geometry is poorly defined.

The contribution of the hydrogen atoms, in their calculated positions (C−H = 0.95 Å, B(H) = 1.3/1.5 × B(C_{bonded}) Å^2), was included in the refinement by using a riding model. Upon convergence (see Table S1) no significant features were found in the difference Fourier map.

Structural Study of ($C_6H_4CH_2NMe_2$)Pd(4b)Cl, 9b. The space group was unambiguously determined from the systematic absences, while the cell constants were refined by least squares, at the end of the data collection, using 991 reflections ($\theta_{max} \leq 21.7°$). The data were collected (up to $\sin(\theta/\lambda) = 0.617$) by using ω scans, in steps of 0.3 deg. For each of the 1878 collected frames, counting time was 15 s.

As in the previous case, the *t*-Bu substituents are disordered. Two different orientations (with approximately equal weights) for the carbon atoms bound respectively to atoms C118, C127, and C128 were clearly shown in the difference Fourier maps, and a disorder model was refined, as above. The remaining *t*-Bu group was satisfactorily refined anisotropically.

Anisotropic displacement parameters were used for all other atoms. The contribution of the hydrogen atoms, in their calculated positions (C−H = 0.95 Å, B(H) = 1.3/1.5 × B(C_{bonded}) Å^2), was included in the refinement by using a riding model. Upon convergence (see Table S1) the final Fourier difference map showed no significant peaks.

Synthesis of the Phosphine Oxide (*S*)-2-(Bis(3,5-di-*tert*-butylphenyl)phosphinyl)-1,1′-binaphthyl. To a mixture of (*S*)-2-trifluoromethanesulfonyloxy-1,1′-binaphthyl (1.38 g 3.43 mmol), palladium acetate (39 mg, 0.085 mmol), 1,4-bis-(diphenylphosphino)butane (73 mg, 0.085 mmol), and bis(3,5-di-*tert*-butylphenyl)phosphine oxide (1.76 g, 4.13 mmol) was added 12 mL of DMSO and 2.35 mL of diisopropylethylamine (1.77 g, 13.7 mmol). The mixture was heated with stirring at 100 °C for 20 h. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was diluted with EtOAc, washed twice with water, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatography on silica gel (hexane/EtOAc = 3:1) gave 2.33 g (100%) of the product as a white solid. Anal. Calcd for $C_{48}H_{55}OP$: C, 84.92; H, 8.16. Found: C, 84.99; H, 8.09. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.78−7.99 (m, aromatic, 2H), 7.38−7.74 (m, aromatic, 8H), 7.17−7.29 (m, aromatic, 5H), 7.02−7.08 (m, aromatic, 2H), 6.91 (d, $^3J_{HH}$ = 8.0, aromatic, 1 H), 1.31 (s, $C(CH_3)_3$, 18 H), 1.17 (s, $C(CH_3)_3$, 18 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 35.0 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 31.4 (s, $C(CH_3)_3$), 31.2 ($C(CH_3)_3$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): δ 27.9 (s). MS (ESI): 679.1 (M^+, 100%).

Synthesis of (*S*)-2-(Bis(3,5-di-*tert*-butylphenyl)phosphino)-1,1′-binaphthyl, 4b. To a mixture of (*S*)-2-(bis(3,5-di-*tert*-butylphenyl)phosphinyl)-1,1′-binaphthyl (2.32 g, 3.42 mmol) and triethylamine (9.7 mL, 69 mmol) in 50 mL of xylene was added $HSiCl_3$ (1.8 mL, 18.4 mmol). The mixture was heated to 130 °C for 6 h. After being cooled to room temperature, the mixture was diluted with ether and quenched with

(40) *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1992; Vol. C.
(41) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.
(42) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

a small amount of saturated $NaHCO_3$. The resulting suspension was filtrated over Celite and the Celite washed with copious amounts of ether. After removal of the solvent, the crude product was purified by chromatography on silica gel (hexane/EtOAc = 30:1) to give 2.20 g (97%) of the product as a white solid. Anal. Calcd for $C_{48}H_{55}P$: C, 86.97; H, 8.36. Found: C, 86.87; H, 8.25. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.91−8.03 (m, aromatic, 4H), 7.03−7.60 (m, aromatic, 15 H), 1.37 (s, $C(CH_3)_3$, 18 H), 1.25 (s, $C(CH_3)_3$, 18 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 34.9 ($C(CH_3)_3$), 34.8 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 31.4 ($C(CH_3)_3$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): δ −11.6 (s). MS (ESI): 663.1 (M^+, 100%).

Synthesis of (*R*)-2-(Bis(3,5-di-*tert*-butylphenyl)phosphinyl)-2′-(hydroxy)-1,1′-binaphthyl. To a stirred solution of 2.07 g of (*R*)-2-(bis(3,5-di-*tert*-butylphenyl)phosphinyl)-2′-((trifluoromethane-sulfonyl)oxy)-1,1′-binaphthyl (2.50 mmol) in a 2/1 mixture of 1,4-dioxane and methanol (15 mL) was added 2 mL of an aqueous 3 M NaOH solution. The solution was stirred for 24 h at room temperature. After addition of 3 mL of 3 M HCl and 100 mL of EtOAc, the organic phase was separated and washed with water. Another 3 mL of 3 M HCl was added to the aqueous phase, which was extracted once again with EtOAc. The combined organic phases were dried over $MgSO_4$. Evaporation of the solvent followed by chromatography (silica gel, hexane/EtOAc = 5:1) gave 1.566 g (90%) of the product as a white solid. Anal. Calcd for $C_{48}H_{55}O_2P$: C, 82.96; H, 7.98. Found: C, 83.07; H, 8.16. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ 9.73 (s, OH, 1H), 6.85−8.05 (m, aromatic, 17 H), 6.37 (d, $^3J_{HH}$ = 8.3, aromatic, 1H), 1.40 (s, $C(CH_3)_3$, 18 H), 1.14 (s, $C(CH_3)_3$, 18 H). ^{13}C NMR (CD_2Cl_2, 62.9 MHz): δ 35.1 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), 30.8 ($C(CH_3)_3$). ^{31}P NMR (CD_2Cl_2, 101.3 MHz): δ 31.0 (s). MS (ESI): 695.2 (M^+, 100%).

Synthesis of (*R*)-2-(Bis(3,5-di-*tert*-butylphenyl)phosphinyl)-2′-(methoxy)-1,1′-binaphthyl. To a suspension of (*R*)-2-(bis(3,5-di-*tert*-butylphenyl)phosphinyl)-2′-(hydroxy)-1,1′-binaphthyl (1.56 g, 2.24 mmol) and potassium carbonate (1.23 g, 8.9 mmol) in acetone (15 mL) was added MeI (1.28 g, 9.0 mmol). The mixture was heated to 60 °C and stirred for 5 h at which point another 0.68 g of MeI was added followed by stirring for 16 h at 60 °C. After being cooled to room temperature, the reaction mixture was filtrated over Celite and the Celite washed with CH_2Cl_2. The solvents were evaporated and the residue chromatographed on silica gel (hexane/EtOAc = 3:2) to give 1.45 g (91%) of the product as a white solid. Anal. Calcd for $C_{49}H_{57}O_2P$: C, 83.01; H, 8.10. Found: C, 83.09; H, 8.10. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.96−7.91 (m, aromatic, 2 H), 7.80 (d, $^3J_{HH}$ = 9.1 Hz, aromatic, 1 H), 7.72−7.66 (m, aromatic, 2 H), 7.54−7.44 (m, aromatic, 4 H), 7.33−7.12 (m, aromatic, 7 H), 6.94 (m, aromatic, 1 H), 6.73 (d, $^3J_{HH}$ = 8.4 Hz, aromatic, 1 H), 1.27 (s, $C(CH_3)_3$, 18 H), 1.20 (s, $C(CH_3)_3$, 18 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 57.0 (OCH_3), 35.3 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 31.8 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 29.4 (s). MS (ESI): 709.1 (M^+, 100%).

Synthesis of (*R*)-2-(Bis(3,5-di-*tert*-butylphenyl)phosphino)-2′-(methoxy)-1,1′-binaphthyl, 5b. To a mixture of (*R*)-2-(bis(3,5-di-*tert*-butylphenyl)phosphinyl)-2′-(methoxy)-1,1′-binaphthyl (1.45 g, 2.03 mmol) and triethylamine (5.8 mL, 41.3 mmol) in 40 mL of xylene was added $HSiCl_3$ (1.1 mL, 11 mmol). The mixture was heated to 130 °C for 6 h. After being cooled to room temperature, the mixture was diluted with ether and quenched with a small amount of saturated $NaHCO_3$. The resulting suspension was filtrated over Celite and the Celite washed with copious amounts of ether. After removal of the solvent, the crude product was purified by chromatography on silica gel (hexane/EtOAc = 25:1) to give 1.43 g (100%) of the product as a white solid. Anal. Calcd for $C_{49}H_{57}O_2P$: C, 84.93; H, 8.29. Found: C, 84.91; H, 8.22. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.05 (d, $^3J_{HH}$ = 9.0, aromatic, 1H), 7.87−7.96 (m, aromatic, 3H), 6.90−7.56 (m, aromatic, 14 H), 3.57 (s, OCH_3, 3H), 1.29 (s, $C(CH_3)_3$, 18 H), 1.21 (s, $C(CH_3)_3$, 18 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 56.0 (OCH_3), 34.9 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 31.4 ($C(CH_3)_3$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): δ −11.4 (s). MS (HiResMALDI): calcd 693.4220, found 693.4195 (M^+, 100%).

Synthesis of (*R*)-2-(Bis(3,5-di-*tert*-butylphenyl)phosphino)-2′-(cyano)-1,1′-binaphthyl, 6b. To a mixture of (*R*)-2-(bis(3,5-di-*tert*-butylphenyl)phosphinyl)-2′-(cyano)-1,1′-binaphthyl (0.42 g, 0.60 mmol) and triethylamine (1.7 mL, 12.1 mmol) in 12 mL of xylene was added $HSiCl_3$ (0.31 mL, 3.1 mmol). The mixture was heated to 130 °C for 6 h. After being cooled to room temperature, the mixture was diluted with ether and quenched with a small amount of saturated $NaHCO_3$. The resulting suspension was filtrated over Celite and the Celite washed with copious amounts of ether. After removal of the solvent, the crude product was purified by chromatography on silica gel (hexane/EtOAc = 9:1) to give 0.41 g (99%) of the product as a white solid. Anal. Calcd for $C_{49}H_{54}NP$: C, 85.55; H, 7.91; N, 2.04. Found: C, 85.51; H, 7.91; N, 1.92. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.87−8.07 (m, aromatic, 4H), 7.81 (d, $^3J_{HH}$ = 8.5, aromatic, 1H), 6.92−7.55 (m, aromatic, 13 H), 1.26 (s, $C(CH_3)_3$, 18 H), 1.17 (s, $C(CH_3)_3$, 18 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 34.9 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 31.3 ($C(CH_3)_3$), 31.3 ($C(CH_3)_3$). ^{31}P NMR ($CDCl_3$, 101.3 MHz): δ −12.6 (s). MS (HiResMALDI): 688.4060 (M^+, 100%).

Synthesis of PdBr(*p*-CN-C_6H_4)(2b), 8b. To a mixture of 30 mg of PdBr(*p*-CN-C_6H_4)(TMEDA) (0.074 mmol) and 57.4 mg of **2b** (0.074 mmol) was added 3 mL of THF. The solution was stirred at 65°C for 18 h. After the solution was cooled to room temperature, the solvent was evaporated and the residue chromatographed on silica gel (CH_2Cl_2/acetone = 100:1). Recrystallization from CH_2Cl_2/pentane gave 59 mg (75%) of the product as a white solid. Anal. Calcd for $C_{61}H_{68}N_2OPBrPd$: C, 68.96; H, 6.45; N, 2.64. Found: C, 68.69; H, 6.69; N, 2.55. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 4.01 (t, $^3J_{HH}$ = 8.5, 1H, OCH_2), 3.55 (m, 1H, NC*H*), 3.34 (t, $^3J_{HH}$ = 9.5, 1H, OCH_2), 2.74 (m, 1H, $CH(CH_3)_2$), 1.24 (s, 18H, $C(CH_3)_3$), 1.06 (d, $^3J_{HH}$ = 7, 3H, $CH(CH_3)_2$), 0.87 (d, $^3J_{HH}$ = 6.5, 3H, $CH(CH_3)_2$), 0.85 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 72.7 (NCH), 71.7 (CH_2O), 35.4 ($C(CH_3)_3$), 34.8 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 29.6 ($CH(CH_3)_2$), 21.4 ($CH(CH_3)_2$), 16.6 ($CH(CH_3)_2$). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 25.6 (s). MS (FAB): 981.5 (M^+ − Br, 40%). For a more detailed NMR assignment see the Supporting Information.

Synthesis of ($C_6H_4CH_2NMe_2$)Pd(4a)Cl, 9a. To a mixture of [Pd(μ-Cl)][($C_6H_4CH_2NMe_2$)]$_2$ (30 mg, 0.054 mmol) and **4a** (47.7 mg, 0.109 mmol) was added 3 mL of CH_2Cl_2. The solution was stirred for 30 min at room temperature. After removal of the solvent, the crude product was recrystallized from toluene/pentane to give 114 mg (74%) of the product. Anal. Calcd for $C_{41}H_{35}NPClPd$: C, 68.91; H, 4.94; N, 1.96. Found: C, 68.71; H, 4.98; N, 2.03. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 4.52 (d, $^3J_{HH}$ = 13, 1H, NCH_2), 3.48 (dd, $^3J_{HH}$ = 13, $^4J_{PH}$ = 3.5, 1H, NCH_2), 3.05 (d, $^4J_{PH}$ = 2.5, 3H, NCH_3), 3.05 (s, 3H, NCH_3). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 73.8 (NCH_2), 52.4 (NCH_3), 49.0 (NCH_3). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 39.1 (s). MS (HiResMALDI): calcd 678.1550, found 678.1544 (M^+ − Cl, 100%). For a more detailed NMR assignment see the Supporting Information.

Synthesis of ($C_6H_4CH_2NMe_2$)Pd(4b)Cl, 9b. To a mixture of [Pd(μ-Cl)][($C_6H_4CH_2NMe_2$)]$_2$ (30 mg, 0.054 mmol) and **4b** (72.1 mg, 0.109 mmol) was added 3 mL of CH_2Cl_2. The solution was stirred for 30 min at room temperature. After removal of the solvent, the residue was dissolved in 2 mL of pentane. After a few seconds, the product precipitated from the solution and was removed by filtration. Yield: 76 mg (74%). Anal. Calcd for $C_{57}H_{67}NPClPd$: C, 72.91; H, 7.19; N, 1.49. Found: C, 72.33; H, 7.17; N, 1.59. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 4.54 (b, 1H, NCH_2), 3.42 (dd, $^3J_{HH}$ = 13, $^4J_{PH}$ = 3, 1H, NCH_2), 3.06 (s, 3H,

NCH_3), 2.46 (s, 3H, NCH_3), 1.26 (s, 18H, $C(CH_3)_3$), 0.81 (br, 18H, $C(CH_3)_3$). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 73.7 (NCH_2), 52.1 (NCH_3), 48.4 (NCH_3), 35.6 ($C(CH_3)_3$), 34.8 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 30.8 ($C(CH_3)_3$). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 40.4 (s). MS (HiResMALDI): 902.4031 ($M^+ - Cl$, 100%). For a more detailed NMR assignment see the Supporting Information. Crystals suitable for X-ray diffraction were obtained from a methanol solution of **9b** by adding a few drops of water.

Synthesis of $PdCl(C_6H_4CH_2NMe_2)$(4c), 9c. To a mixture of $[Pd(\mu\text{-}Cl)][(C_6H_4CH_2NMe_2)]_2$ (55.8 mg, 0.101 mmol) and **4c** (100 mg, 0.202 mmol) was added 3 mL of CH_2Cl_2. The solution was stirred for 30 min at room temperature. After removal of the solvent, the residue was recrystallized from toluene/pentane and washed twice with pentane. Yield: 86 mg (56%). Anal. Calcd for $C_{45}H_{43}NPClPd$: C, 70.13; H, 5.62; N, 1.82. Found: C, 70.23; H, 5.68; N, 1.76. ^1H NMR (CD_2Cl_2, 500 MHz): δ 4.66 (d, $^3J_{HH} = 13$, 1H, NCH_2), 3.49 (d, $^3J_{HH} = 13$, 1H, NCH_2), 3.09 (s, 3H, NCH_3), 2.56 (s, 3H, NCH_3), 2.34 (s, 6H, CH_3), 1.62 (s, 6H, CH_3). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 73.8 (NCH_2), 52.4 (NCH_3), 48.6 (NCH_3), 21.6 (CH_3), 20.8 (CH_3). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 40.0 (s). MS (HiResMALDI): calcd 734.2178, found 734.2204 ($M^+ - Cl$, 64%). For a more detailed NMR assignment see the Supporting Information.

Alkylating Ring Opening of Oxabenzonorbornadiene. To a mixture of Pd(ligand)Cl_2 (17 μmol) and 50 mg of oxabenzonorbornadiene (0.35 mmol) were added 10 mL of CH_2Cl_2 and a solution of dialkylzinc (0.26 mL of 2 M $ZnMe_2$ in toluene or 0.52 mL of 1 M $ZnEt_2$ in hexane, 0.52 mmol). The resulting solution was stirred at room temperature. The reaction was worked up by addition of a few drops of water, stirring for half an hour, filtration over Celite, and evaporation of the solvent. The crude product was purified by silica gel chromatography (hexane/EtOAc = 5:1). The ee was determined by HPLC: (R = Me) Chiracel OB-H, hexane/^{i}PrOH = 98:2, 0.5 mL/min, $t_R = 21.5$ min (major isomer for **2**), $t_R = 24.1$ min (major isomer (*R*)-**1**); (R = Et) Chiracel OD-H, hexane/^{i}PrOH = 98:2, 0.5 mL/min, $t_R = 20.2$ min (major isomer for (*R*)-**1**), $t_R = 18.7$ min (minor isomer (*R*)-**1**).

Heck Chemistry. To a mixture of the catalyst (15 μmol of $Pd(OAc)_2$ and 30 μmol of ligand **4** or 15 μmol of $Pd(dba)_2$ and 16.5 μmol of ligand **4**) and 138.1 mg of 2-naphthyltriflat (0.5 mmol) were added 3 mL of toluene, 261 μL of NEt^iPr_2 (1.5 mmol) and 189 μL of 3,4-dihydrofuran (2.5 mmol). The solution was stirred at 40 °C. Addition of 100 mL of pentane, washing with 0.1 M HCl and saturated $NaHCO_3$, drying over Na_2SO_4, and chromatography on silica gel (hexane/EtOAc = 19:1) gave the product as a white solid. The ee was determined by HPLC with a Chiracel OD-H column (hexane/^{i}PrOH = 99:1, 0.5 mL/min), $t_R = 19.6$ min (minor isomer), $t_R = 17.3$ min (major isomer).

ligand	Pd source	reaction time (h)	yield (%)	ee (%)
2a	$Pd(OAc)_2$	96	71	79
2b	$Pd(OAc)_2$	300	14	97
2a	$Pd(dba)_2$	71	87	79
2b	$Pd(dba)_2$	89	80	98

Allylic Alkylation. To 4 μmol of $[Pd(\eta^3\text{-}C_3H_5)($ **2a** or **2b**$)]$-(OTf) in 2 mL of CH_2Cl_2 were added 28 μL of cyclohexenyl acetate (0.2 mmol), 68 μL of dimethylmalonate (0.6 mmol), 148 μL of BSA (0.6 mmol), and 1 mg of KOAc. The reaction mixture was stirred at 40 °C, followed by addition of 50 mL of ether. The organic phase was washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by chromatography on silica gel (hexane/EtOAc = 9:1) to give the product as a colorless oil. The ee was determined by HPLC with a Chiracel OB-H column (hexane/^{i}PrOH = 90:10, 0.3 mL/min), $t_R = 30.0$ min (minor isomer), $t_R = 23.5$ min (major isomer).

catalyst	reaction time (h)	yield (%)	ee (%)
$[Pd($**2a**$)(\eta^3\text{-}C_3H_5)](OTf)$	3	66	36
$[Pd($**2b**$)(\eta^3\text{-}C_3H_5)](OTf)$	20	36	56

Hydrosilylation Chemistry. In a typical procedure, to a mixture of 0.8 mg of $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ (2.1 μmol) and 3.8 mg of ligand **4a** (8.2 μmol) was added 0.5 mL of styrene (4.33 mmol). The solution was cooled to 5 °C and 0.53 mL of $HSiCl_3$ (5.3 mmol) was added. The reaction solution was stirred at 5 °C for 20 h. NMR analysis confirmed complete disappearance of the signals of styrene. The product was carefully poured into a suspension of KF (4.3 g) in MeOH (40 mL) and stirred for 30 min. The solvent was removed in vacuo, after which DMF (50 mL) and H_2O_2 (35% water solution, 4.5 mL) were added and the mixture was heated for 1 h at 60−70 °C. The suspension was filtrated over Celite and the Celite washed with 100 mL of CH_2Cl_2. The organic phase was washed with water and dried over Na_2SO_4. Evaporation of the solvent and chromatography on silica gel (hexane/EtOAc = 4:1) gave 370 mg (70%) of 1-phenylethanol. The ee (92%) was determined by HPLC: (1-phenylethanol) Chiracel OB-H, hexane/^{i}PrOH = 90:10, 0.5 mL/min, $t_R = 16.7$ min ((*S*)-enantiomer), $t_R = 12.5$ min ((*R*)-enantiomer); (1-(4-MeO-phenyl)ethanol) Chiracel OB-H, hexane/^{i}PrOH = 90:10, 0.5 mL/min, $t_R = 31.9$ min ((*R*)-enantiomer), $t_R = 23.8$ min ((*S*)-enantiomer); (1-naphthylethanol) Chiracel OD-H, hexane/^{i}PrOH = 90:10, 0.5 mL/min, $t_R = 20.7$ min ((*R*)-enantiomer), $t_R = 18.4$ min ((*S*)-enantiomer).

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Supporting Information Available: Full listing of crystallographic data for **8b**·CH_2Cl_2 and **9b**, including tables of positional and isotropic equivalent displacement parameters, anisotropic displacement parameters, calculated positions of the hydrogen atoms, bond distances, bond angles, and torsional angles; figures showing the full numbering schemes; and NMR details for **8b** and **9a**−**c** (Table S13). This material is available free of charge via the Internet at http://pubs.acs.org.

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