Dialkyl Effect on Enantioselectivity: π-Stacking as a Structural Feature in P,N Complexes of Palladium(II)

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Received April 22, 2002

A phosphino,oxazoline P,N-bidentate ligand, **4**, containing 3,5-di-*tert*-butylphenyl groups has been prepared. In the Heck arylation of dihydrofuran, **4** is shown to afford higher ee's than either **2** or **3**, the unsubstituted and *m*-dimethylphenyl analogues, respectively. Several Pd(0) complexes of **4** are reported. The exchange dynamics of Pd(**4**)(dba) are shown to involve an interconversion of diastereomers via an intramolecular process. The X-ray structure for $PdCl_2$(**4**), **8**, was determined by X-ray diffraction methods. Comparison of data with $PdCl_2$(**2**), **9**, and $PdCl_2$(**3**), **10**, suggests that differing amounts of $\pi-\pi$ stacking influence the structures of these relatively simple Pd complexes, with **9** and **10** revealing the strongest $\pi-\pi$ interactions. An estimation of the van der Waals energies involved in the interaction supports a ca. 4 kcal/mol stabilization via $\pi-\pi$ stacking.

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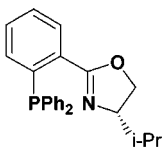
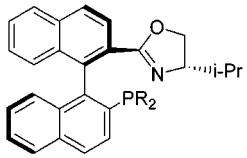
Introduction

Transition metal complexes containing chiral P,N-auxiliaries, and specifically those by Helmchen,[1] Pfaltz,[2] and Togni[3] have proven an attractive addition to enantioselective homogeneous catalysis. Several of these enantioselective reactions involve Pd(II)- and Pd(0)-oxazoline[4] complexes as intermediates, and an increasing number of these derivatives have been isolated and characterized. Helmchen[5] has recently identified a relevant Pd(0)-olefin complex, and X-ray reports on Pd(II)-allyl[6] and -aryl complexes[7] are slowly becoming routine.





(from Helmchen and Pfaltz) **1** **2** R = Ph,

3 R = 3,5-di-methylphenyl

4 R = 3,5-di-t-Bu phenyl

We have recently shown[7,8] that, by extending the chiral backbone from **1** to **2**, the orientation of the oxazoline ring in a Pd complex, e.g., in $PdCl_2$(P,N), changes from coplanar to approximately perpendicular to the Cl−Pd−Cl plane. For the enantioselective allylic alkylation of a 1,3-diphenyl substrate,[7] this structural change induced a change in the observed product enantiomer. Further, by altering the P-phenyl substituents from R = Ph, **2**, to R = 3,5-dimethylphenyl, **3**, we found[8] an increase in the observed enantiomeric excess

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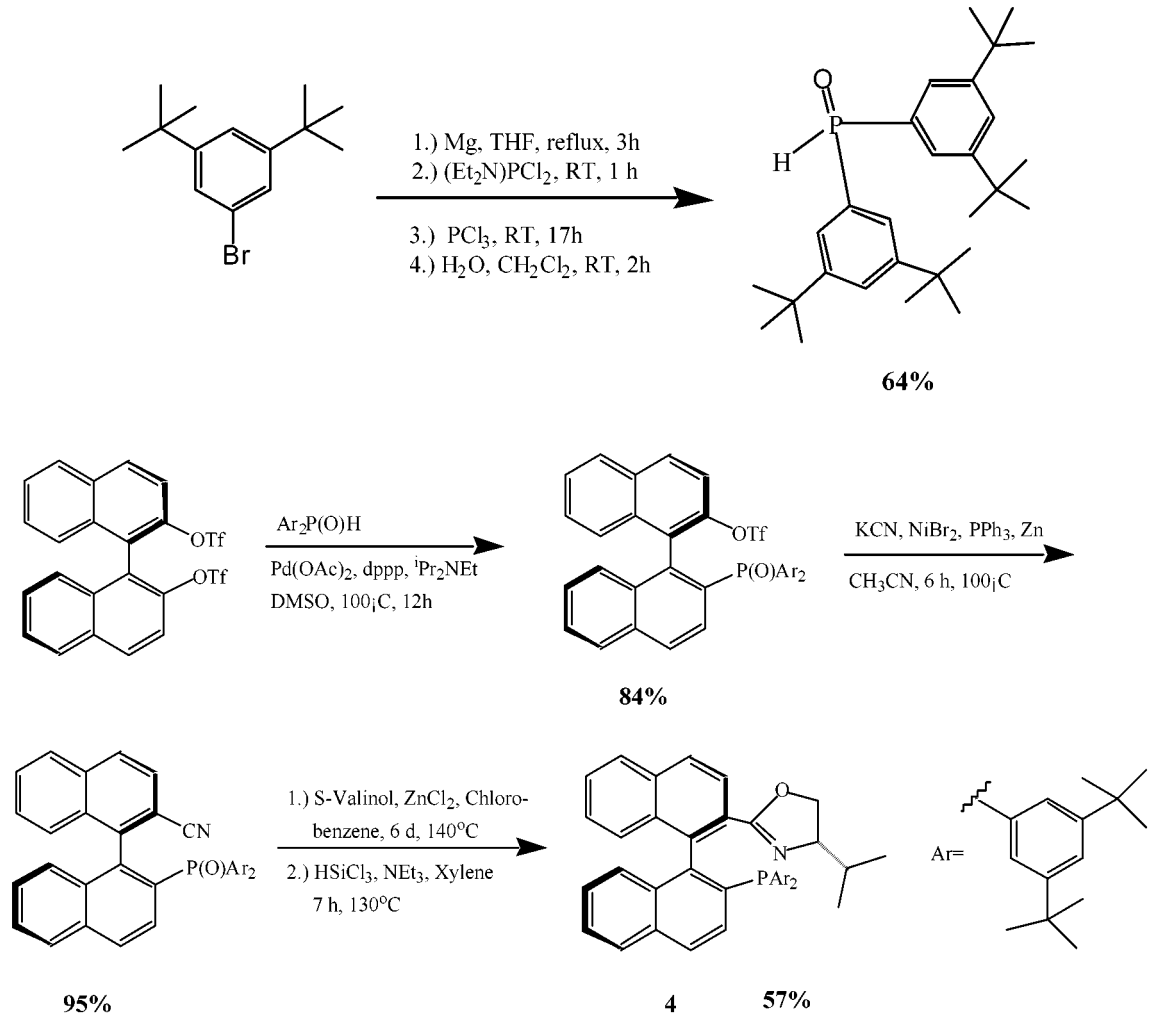
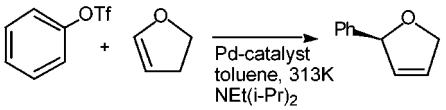
Scheme 1



(ee) in the Heck arylation[9−18] of dihydrofuran with phenyl triflate; see eq 1.



(1)

We report here the synthesis of the 3,5-di-*tert*-butylphenyl analogue of **2**, ligand **4**, the preparation of several Pd(II) and Pd(0) complexes of **4**, and some of the structural and chemical consequences of changing the P substituents.

Results and Discussion

Ligand **4** can be prepared as shown in Scheme 1. There are several organometallic steps, and while the individual yields are good to excellent, the overall yield is ca. 45%.

Heck Arylation. A mixture of **4** together with $Pd(OAc)_2$ slowly catalyzes the Heck arylation of dihydrofuran,[9−18] as shown in eq 1. The new results for **4** together with those noted previously for **2** and **3**, are given in Table 1 and reveal that the enantiomeric excess, ee, increases when the *meta* substituents increase in size. Although the methyl groups of **3** result in a significant improvement in the ee relative to **2**, the best ee results from using **4**. This is yet another manifestation of what we have named the "*meta*-dialkyl effect" on enantioselectivity.[19] This effect arises from

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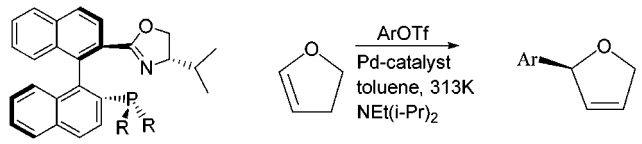
Table 1. Results from the Arylation of Dihydrofuran

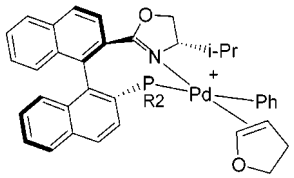


R = phenyl, **2**, 3,5-dimethyl phenyl,3, 3,5-di-t-Bu phenyl, 4

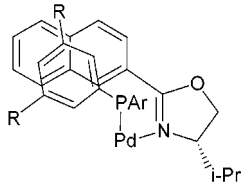
ligand	Ar	ee
2	Ph	74[a] (80)
3	Ph	86[a]
4	Ph	98
2	p-MeO-C_6H_4	80
4	p-MeO-C_6H_4	96

[a] From an earlier report.[7]

restricted rotation around P−C bonds with the resulting chiral pocket becoming slightly more rigid.[19] For the



Heck reaction of eq 1, this restricted rotation is expected to occur in the "[Pd(aryl)(olefin)(**4**)]$^+$" cationic olefin complex (suggested above) and involves one P-3,5-di-*tert*-butylphenyl R-substituent and the backbone biaryl



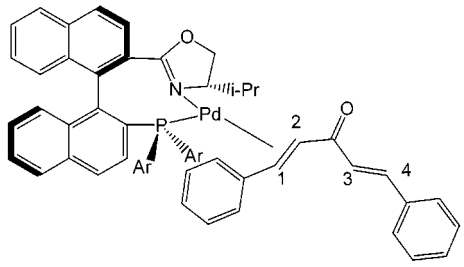
Ar = 3,5 di-t-butyl phenyl
R = t-butyl

of the oxazoline, as indicated above. Analogous steric hindrance has been observed in both an Ru-arene complex[19] and a Pd-aryl complex.[19] The additional rigidity of the chiral pocket increases the correlation with substrate, thus affording a slightly more selective catalyst. There are a number of catalytic reactions for which "*meta*-dialkyl effects" have been shown to be useful.[20−22]

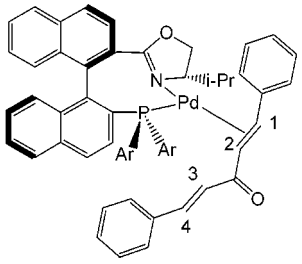
Pd(0) Complexes. Possibly, the effect noted above might also involve electronic changes related to the difference between hydrogen and either methyl or *tert*-butyl. Electronic effects in enantioselective homogeneous catalysis are now well recognized.[3,17] To test this idea, we have prepared several Pd(0) derivatives, **5**−**7**. There are not many well-characterized nitrogen-containing bidentate complexes of Pd(0).[23−25]

The fumaronitrile compound Pd(NCCH=CHCN)(**4**), **5**, the maleic anhydride complex, Pd(maleic anhydride)(**4**), **6**, and the dibenzylidene acetone derivative Pd(dba)(**4**), **7**, were readily synthesized (see Experimental Section), and some of their olefin ^{13}C characteristics, along with those for the analogous complexes of **2**, are given in Tabe 2. If the ligands **2** and **4** were very different electronically, one might expect significant changes in their donor and acceptor properties, and thus changes in the induced ^{13}C chemical shifts. On the basis of the observed ^{13}C NMR data, this seems not to be the case since the differences are <2 ppm. For the fumaronitrile derivative, the two isomers observed arise due to the two diastereomers formed when the two different faces of the olefin complex the Pd atom. For the maleic anhydride analogue one finds two rotational isomers; that is, the isopropyl group can be pseudo-syn or pseudo-anti with respect to the oxygen atoms. In contrast, the nature of the isomers in **7** was not immediately clear.

The ^{31}P NMR spectrum for the dba analogue, **7**, reveals two major components with somewhat broadened resonances at $\delta = 29.9$, **7a**, and $\delta = 32.2$, **7b**, in the ratio ca. 1:0.9. A combination of two-dimensional NMR methods reveals these two complexes to have the following structures:



7a



7b

These structures were assigned (from NMR data at 253 K) on the basis of the following observations:

1. There are two ^{13}C-olefinic resonances for each isomer, $\delta = 56.5$ and $\delta = 69.3$ for **7a**, and $\delta = 56.0$ and $\delta = 67.9$ for **7b**, whose positions are consistent with complexed double bonds.

2. One of the two complexed olefin carbon signals shows a relatively large $^2J(P,C)$ value, 18 Hz for **7a** and 32 Hz for **7b**, thereby identifying the olefinic carbon pseudo-trans to the P atom.

3. The long-range $^3J(C,H)$ from the β-olefinic H-1 to the ortho phenyl carbon distinguishes between the two

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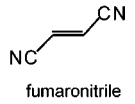
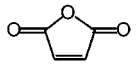
Table 2. ^{13}C Data for the Pd(0)-Olefin Complex



fumaronitrile

Ligand	δ^{13}C first isomer[a]	δ^{13}C second isomer
2	22.7/24.0	22.4/22.9
4	22.1/22.4	22.4/23.4



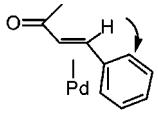
maleic acid anhydride

:

	δ^{13}C first isomer[b]	δ^{13}C second isomer
2	45.4/45.7	44.9/47.9
4	45.2/45.1	44.6/46.9

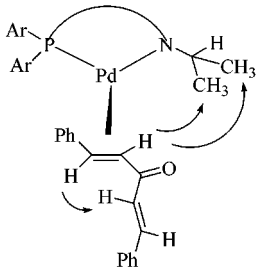
[a] For fumaronitrile the two isomers arise due to the two diastereomers formed when the two different faces of the olefin complex the Pd atom. [b] For the maleic anhydride one finds two rotational isomers; that is, the i-Pr can be pseudo-syn or pseudo-anti with respect to the oxygen atoms.

complexed olefinic proton signals, and a one-bond C,H-correlation connects these protons to their respective carbons. The ^{31}P,^{1}H-correlation helps to assign the two

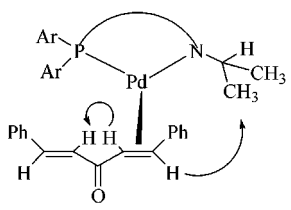


complexed olefinic protons to a single isomer (see Figure 1).

4. There are selective inter-ligand NOEs from the i-Pr methyl groups to different complexed double bond protons in **7a**,**b**; see Figure 2. Specifically two contacts in **7a** and one contact in **7b** suggest the partial structures shown:



7a



7b

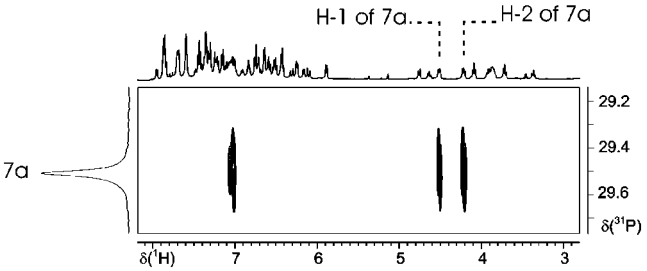


Figure 1. ^{31}P,^{1}H-correlation showing cross-peaks from the two olefinic protons to the P atom of **7a**.

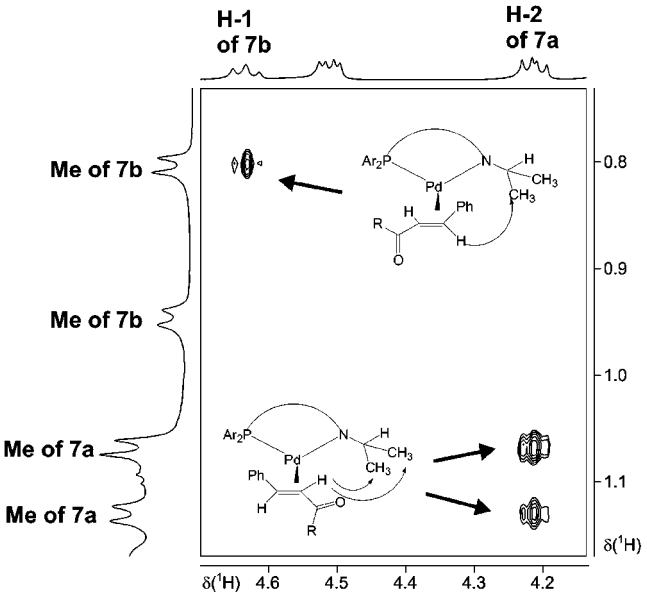


Figure 2. Section of the NOE spectrum for **7**, showing two selective contacts from the i-Pr methyl groups to H-2 of **7a** and one from an i-Pr methyl group to H-1 of **7b**.

Moreover, in **7a**,**b** we find intra-dba olefin NOEs between the two protons indicated via the arrows, suggesting, in **7a**, a rotation of part of the complexed dba, away from the sterically demanding P,N ligand. Therefore we conclude that there are two diastereomeric structures that arise from complexation of the *re* and *si* faces. Of the numerous structural possibilities **7a** and **7b** are preferred.

The ^{31}P two-dimensional exchange spectrum for **7a** and **7b** at ambient temperature reveals that these are in equilibrium (see Figure 3). However, at 253 K the ^{31}P exchange spectrum shows that **7a** is now in equilibrium with a new, weak (ca. 5%), not previously noted species at $\delta = 34.3$, **7c**, but not with **7b**. Complex **7c** has proton and carbon olefinic signals consistent with a complexed dba structure.

In the ^{1}H spectrum at 253 K we find traces (<5%) of free dba which *are not in exchange* with either **7a** or **7b**. At ambient temperature the free dba signals are obscured by other resonances; however, on the basis of the absence of suitable proton exchange cross-peaks it is clear that the dba is not exchanging with **7a**,**b** at this temperature. As expected, addition of another equivalent of dba has no effect on the ^{31}P NMR spectrum.

We conclude that the interconversion of the two diastereomers, **7a**,**b**, proceeds via yet another Pd(dba)-(**4**) type complex, **7c**, and not via dissociation of dba. A possible structure for **7c** is shown below. If this is

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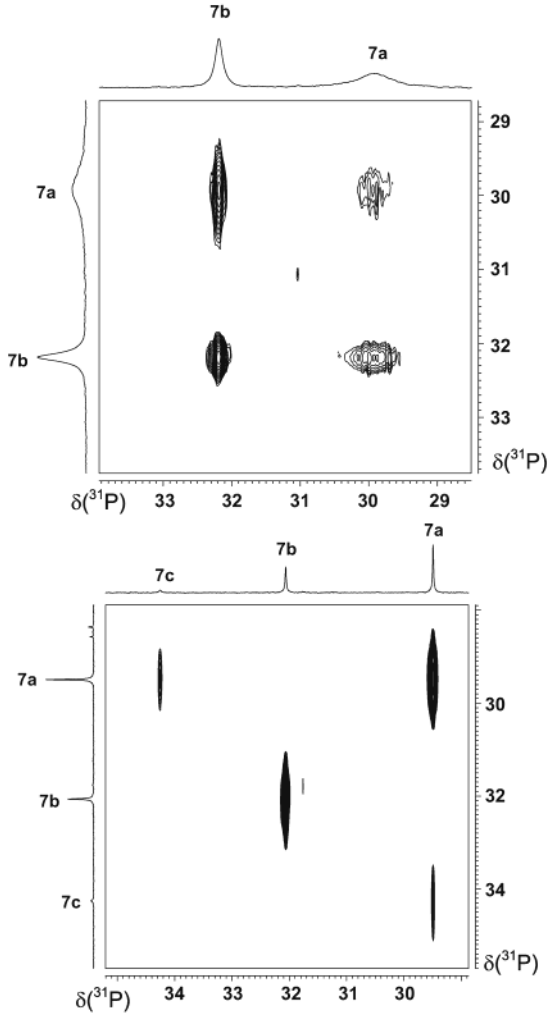
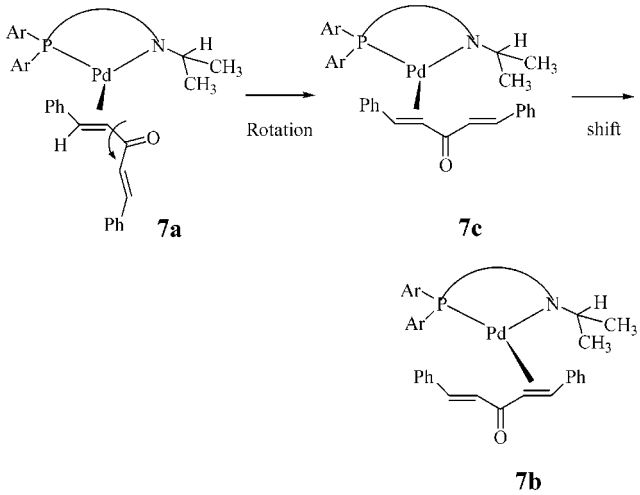


Figure 3. ^{31}P exchange spectrum at ambient temperature (top) showing exchange between **7a** and **7b** and ^{31}P exchange spectrum at 253 K (bottom) showing the new, weak, signal for **7c** and its selective exchange with **7a**.

correct, then the exchange mechanism simply involves rotation around a C−C(O) bond of **7a**, followed by complexation of the second double bond of the dba, to afford **7b**. We do not exclude dba dissociation at higher temperarures.[26]



Structural Studies. The solid-state structure for $PdCl_2$(**4**), **8**, was determined by X-ray diffraction methods. A list of selected bond lengths and bond angles for **8** is given in Table 3, together with comparison data for $PdCl_2$(**2**), **9**, and $PdCl_2$(**3**), **10**. Figure 4 shows an ORTEP plot for **8** and Figure 5 views of **8**−**10**. The immediate coordination sphere for **8** consists of the P and N donor atoms of the chelate and the two chloride ligands. As reported previously,[8] the oxazoline ring is approximately perpendicular to the Cl−P−Cl plane.

Table 3. Bond Lengths (Å) and Angles (deg) for Pd(II) Dichloro Compounds

Bond Lengths		Bond Angles	
		$PdCl_2$(**2**), **10**	
Pd(1)−N(1)	2.028(3)	N(1)−Pd(1)−P(1)	92.19(8)
Pd(1)−P(1)	2.2567(9)	N(1)−Pd(1)−Cl(1)	175.22(8)
Pd(1)−Cl(1)	2.2936(9)	P(1)−Pd(1)−Cl(1)	86.63(4)
Pd(1)−Cl(2)	2.3473(9)	N(1)−Pd(1)−Cl(2)	90.86(8)
		P(1)−Pd(1)−Cl(2)	172.18(4)
		$PdCl_2$(**3**), **9**	
Pd(1)−N(1))	2.030(3)	N(1)−Pd(1)−P(1)	93.16(9)
Pd(1)−P(1)	2.249(1)	N(1)−Pd(1)−Cl(1)	177.8(1)
Pd(1)−Cl(1)	2.289(1)	P(1)−Pd(1)−Cl(1)	85.60(4)
Pd(1)−Cl(2)	2.367(1)	N(1)−Pd(1)−Cl(2)	88.52(9)
		(1)−Pd(1)−Cl(2)	174.88(5)
		$PdCl_2$(**4**), **8**	
Pd(1)−N(1))	2.036(3)	N(1)−Pd(1)−P(1)	91.5(1)
Pd(1)−P(1)	2.273(1)	N(1)−Pd(1)−Cl(1)	173.1(1)
Pd(1)−Cl(1)	2.287(1)	P(1)−Pd(1)−Cl(1)	88.70(3)
Pd(1)−Cl(2)	2.335(1)	N(1)−Pd(1)−Cl(2)	90.0(1)
		P(1)−Pd(1)−Cl(2)	177.35(5)

All of the bond lengths within the three complexes are of a relatively routine nature;[27] however, comparing the Pd−P separations within the three compounds shows some significant differences, with the largest distance found for **8**, 2.273(1) Å. The Pd(1)−Cl(2) separations are also interesting in that, for **8**, 2.287(1) Å represents the shortest of the set. From all three complexes, **8**−**10**, it would appear that as the Pd−P separation increases, the corresponding trans Pd−Cl decreases; that is, the data reflect a modest change in trans influence. The Pd(1)−N(1) bond lengths may be informative; however, the experimental uncertainty is slightly too large. Interestingly, the bond angles P(1)−Pd(1)−Cl (**2**) are observed to be ca. 177°, 175°, and 172° for **8**−**10**, respectively.

If the electronic differences between the P donors in **2**−**4** are minimal, as suggested, what, then, is the source of the observed changes in bond lengths?

Inspection of the arene−arene ring separations from the X-ray data suggests that these simple Pd complexes may be experiencing differing π-stacking interactions, with that for **9** and **10** the strongest and that for **8** the weakest. The observed ring−ring separations of ca. 3.5 Å in **9** and **10** and >4.0 Å in **8** (vida infra) support this conclusion. We have been studying[28] attractive, stabilizing π-stacking interactions in palladium complexes of biaryl phosphines and found that these can easily amount to −3 to −4 kcal. One consequence of such a π-stacking is that the local square-planar coordination geometry can distort markedly,[28] so as to accommodate this stabilizing influence. In PdBr(p-NCC_6H_4)({S}-MeO-

(26) Reid, S. M.; Mague, J. T.; Fink, M. J. *J. Organomet. Chem.* **2000**, *616*, 10−18.
(27) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.
(28) Magistrato, A.; Merlin, M.; Pregosin, P. S.; Rothlisberger, U.; Albinati, A. *Organometallics* **2000**, *19*, 3591−3596. Magistrato, A.; Pregosin, P. S.; Albinati, A.; Rothlisberger, U. *Organometallics* **2001**, *20*, 4178−4184.

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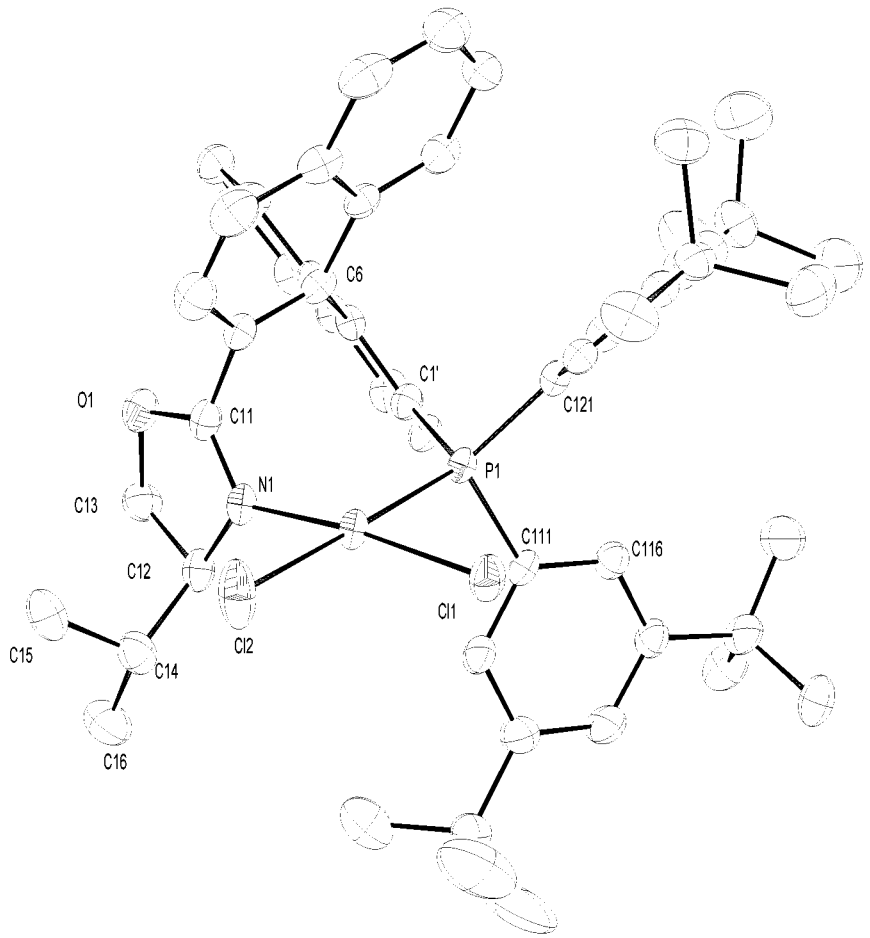


Figure 4. ORTEP plot for **8**; note the relatively large separation between the arene moieties due to the *tert*-butyl groups.

Biphep), **11**, the P−Pd−Br trans angle falls to ca. 159°, partially as a result of the π-stacking. We suggest that the relative bond length changes in **9** and **10**, as noted above, derive primarily from such an interaction. In **9** and **10**, the stacking is favored; however, when the large *meta tert*-butyl groups make it more difficult to achieve the desired π-effect, the molecule relaxes toward the expected structure with a trans angle close to 180°.

Relative Strength of the $\pi-\pi$ Interactions. With a view to refining our understanding of the observed structural differences, we have attempted to quantify the relative strengths of the $\pi-\pi$ stacking interactions of the complexes **8**−**10** by an estimation of the van der Waals energies[30] of the naphthalene moiety and the P-phenyl ring parallel to it. The calculated values (Table 4), at the relative distances observed in the X-ray structures, are −4.3, −6.5, and −2.0 kcal/mol for complexes **10**, **9**, and **8**, respectively. The distances[31] between the rings involved in the $\pi-\pi$ stacking are 3.58 and 3.48 Å for **10** and **9**, respectively. Taken together, these data indicate the presence of strong $\pi-\pi$ stacking interactions in complexes **9** and **10**. However, in complex **8** the large ring separation of ∼4.5 Å and the relatively modest −2.0 kcal/mol value of the corresponding van der Waals energy suggest that the nonbonded interaction between the 3,5-*tert*-butylphenyl ring and the naphthalene moiety should not be classified as a "stacking" effect.

From Table 4, it appears that the nonbonded interaction is stronger in the dimethyl complex **9** than in **10**, even if the stacking separations for the two are quite similar. In fact, the calculations show that the contribution from the *meta* methyl groups of the P-phenyl ring of **9** to the total van der Waals energy is −2.6 kcal/mol, while the two *meta* hydrogen atoms of the P-phenyl ring of **10** contribute to the $\pi-\pi$ interaction by only −0.4 kcal/mol. This suggests that the difference in the total van der Waals energy between complexes **9** and **10** (6.5−4.3 = 2.2 kcal/mol) is mainly[32] due to the additional contribution of the *meta*-methyl substituents. In any case, as noted previously,[28] the $\pi-\pi$ stacking stabilization is on the order of 4 kcal/mol.

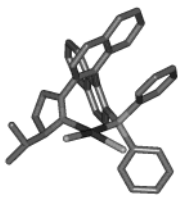
(29) Drago, D.; Pregosin, P. S.; Tschoerner, M.; Albinati, A. *J. Chem. Soc., Dalton Trans.* **1999**, 2279−2280.

(30) van der Waals energies have been estimated based on the empirical Lennard-Jones parameters of the Tripos force field (Clark, M.; Cramer, R. D., III; van Opdenbosh, N. *J. Comput. Chem.* **1989**, *10*, 982), according to the formula for the Lennard-Jones 12−6 potential $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ where σ (Å) represents the van der Waals bond length and ϵ (kcal/mol) well depth.

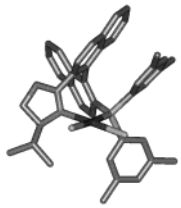
	ε	σ
H	0.042	3.00
C	0.107	3.40

(31) These distances are defined as the distance between the center of the P-phenyl and the center of the naphthalene rings.

(32) Our computational approach does not explicitly take into account electronic effects; therefore the observed energy differences can be attributed to the purely additive van der Waals interactions of the *meta* substituents with the parallel displaced naphthalene ring.



9



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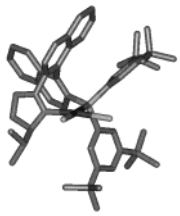

8

Figure 5. Views of complexes **8**−**10**; note the relatively large separation between the binaphthyl moiety and the P-aryl group in **8** compared to **9** and **10**.

Table 4. Van Der Waals Energies (kcal/mol) of 8, 9, and 10

	8	**9**	**10**
van der Waals energies	−4.3	−6.5	−2.0

Since the differences in the relative strengths of the $\pi-\pi$ interactions between **9** and **10** are relatively small, factors, such as differences in the crystal packing and the variation of the intermolecular interactions in the solid state, may be responsible for the observed slightly different values of the P(1)−Pd(1)t−Cl(2) trans angles (172° vs 175° for complex **10** and **9**, respectively). However, the ca. 4 kcal/mol $\pi-\pi$ stacking stabilization is certainly large enough to affect structural changes.

Comment. There is no contradiction between the suggested source of the "*meta*-dialkyl effect" on enantioselectivity in the catalysis section and the structural π-stacking in **9** and **10**. In a more crowded environment with two organic ligands, e.g., "[Pd(aryl)(olefin)(**4**)]$^+$", perhaps both the electronic π-interaction combined with the restricted rotation will be in play. In any case, the π-stacking interactions (and consequently the structures) change as a function of the P-substituent so that it is worth re-emphasizing that the structures of phenyl phosphine chelating complexes containing suitable biaryl backbones (with or without a second P donor) can be influenced by π-interactions between proximate rings.

Experimental Section

All manipulations were carried out under an argon atmosphere. Pentane and ether were distilled from NaK, THF and toluene from potassium, and CH_2Cl_2 from CaH_2. 3,5-Di-*tert*-butylbromobenzene and (*R*)-2,2′-bis((trifluoromethanesulfonyl)oxy)-1,1′-binaphthyl were prepared by standard procedures. (*R*)-1,1′-Bi(2-naphthol) was purchased from Fluka.

NMR spectra were recorded with Bruker DPX-300, -400, and -500 MHz spectrometers at room temperature unless otherwise noted. Chemical shifts are given in ppm, coupling constants (*J*) in Hz. Elemental analyses and mass spectroscopic studies were performed at ETHZ.

Table 5. Experimental Data for the X-ray Diffraction Study of $PdCl_2$(4)·$(CH_2)_2Cl_2$, [8]·$(CH_2)_2Cl_2$

formula	$C_{56}H_{68}Cl_4NOPPd$
mol wt	1050.28
data coll *T*, K	200(2)
diffractometer	SMART CCD
cryst syst	monoclinic
space group (no.)	$P2_1$ (4)
a, Å	16.9656(1)
b, Å	10.8266(1)
c, Å	18.4585(2)
β, deg	112.579(1)
V, Å^3	3130.58(5)
Z	2
$\rho_{(calcd)}$, g cm^{-3}	1.114
μ, cm^{-1}	5.25
radiation	Mo Kα (graphite monochromated, $\lambda = 0.71073$ Å)
θ range, deg	$2.08 < \theta < 27.48$
no. independent data	14 241
no. obsd reflns (n_o) $[\lvert F_o\rvert^2 > 2.0\sigma(\lvert F\rvert^2)]$	12 358
transmn coeff	0.70−0.95
no. of params refined (n_v)	577
R (obsd reflns)[a]	0.0461
R_w^2 (obsd reflns)[b]	0.1271
GOF[c]	1.044

[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 $= [\sum_w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.

Structural Study of $PdCl_2$(4)·$(CH_2)_2Cl_2$, [8]·$Cl(CH_2)_2Cl$. Air-stable, yellow crystals of $PdCl_2$(**4**)·$Cl(CH_2)_2Cl$, [**8**]·$Cl(CH_2)_2$-Cl, suitable for X-ray diffraction, were obtained by the slow diffusion of pentane into a $(CH_2)_2Cl_2$ solution of the complex. A prismatic single crystal was mounted, for the data collection, on a glass fiber at a random orientation, on a Bruker SMART CCD diffractometer at 200(2) K. The space groups was determined from the systematic absences, while the cell constants were refined at the end of the data collection with the data reduction software SAINT.[33] Data were collected by using ω scans in steps of 0.3 deg; a list of experimental conditions for the data collection is given in Supplementary Table S1. The collected intensities were corrected for Lorentz and polarization factors[33] and empirically for absorption using the SADABS program.[34] Selected crystallographic and other relevant data are listed in Table 1 and in Supplementary Table S1. The standard deviations on intensities were calculated in term of statistics alone, while those on F_o^2 were calculated as shown in Table 5 and S1.

The structure was solved by direct and Fourier methods and refined by full matrix least squares,[35] minimizing the function $[\sum w(F_o^2 - (1/k)F_c^2)^2]$ and using anisotropic displacement parameters for all atoms. A chlathrated solvent molecule ($(CH_2)_2Cl_2$) was found from difference Fourier maps and included in the refinement. Anisotropic displacement parameters were used for all atoms.

No extinction correction was deemed necessary. Upon convergence (see Supplementary Table S1), the final Fourier difference map showed no significant peaks. The contribution of the hydrogen atoms, in their calculated position (C−H = 0.95 Å, B(H) = 1.5×B(C_{bonded}) Å^2), was included in the refinement using a riding model. Refining the Flack parameter[36]

(33) *SAINT: SAX Area Detector Integration*; Siemens Analytical Instrumentation, 1996.

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tested the handedness of the structure. All calculations were carried out by using the PC version of the SHELX-97 and ORTEP programs.[35] The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[37]

Synthesis of Bis(3,5-di-*tert*-butylphenyl)phosphine Oxide. 3,5-Di-*tert*-butylbromobenzene (7.20 g, 26.7 mmol) in 30 mL of THF was added slowly to 683 mg (28.1 mmol) of magnesium turnings in 15 mL of THF. Small amounts of iodine were used to start the reaction. The reaction mixture was refluxed for 3 h and then cooled to 0 °C. $(Et_2N)PCl_2$ (2.23 g, 12.8 mmol) in 20 mL of THF was added carefully, followed by stirring for 15 min at 0 °C. The cooling bath was removed and the solution stirred for another 60 min. The solution was concentrated under reduced pressure, and 20 mL pentane was added. The mixture was filtrated over Celite and the Celite washed with copious amounts of pentane and ether. The solvents were evaporated to give a pale yellow solid, which was dissolved in 20 mL of phosphorus trichloride at 0 °C and stirred for 17 h at room temperature. PCl_3 was removed under reduced pressure and the resulting oil dissolved in 30 mL of CH_2Cl_2. H_2O (5 mL) was slowly added at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Another 20 mL of CH_2Cl_2 and 15 mL of brine were added. The aqueous phase was extracted twice with 15 mL of CH_2Cl_2, and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent gave an orange solid, which was chromatographed on silica gel (hexane/ethyl acetate, 2:1) to give 3.57 g (8.37 mmol, 64%) of the product as a white powder. Anal. Calcd for $C_{28}H_{43}OP$: C, 78.83; H, 10.16. Found: C, 78.61; H, 10.09. ^{1}H NMR ($CDCl_3$, 300 MHz): 8.10 (d, J_{PH} = 475, P*H*), 7.64 (d, J = 1.4, 2 H), 7.58 (d, J = 1.6, 2 H), 7.53 (d, J = 1.6, 2 H), 1.33 (s, 36 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): 151.8 (d, $^3J_{PC}$ = 12.3), 131.1 (d, J_{PC} = 101), 126.0 (s), 125.3 (d, $^2J_{PC}$ = 12.1), 35.5 (s, *C*$(CH_3)_3$), 31.7 (s, C(*C*$H_3)_3$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): 25.0 (s). MS (EI): 426 (M^+, 47), 411 (100).

Synthesis of (*R*)-2-(Bis(3,5-di-*tert*-butylphenyl)phosphinyl)-2′-((trifluoromethanesulfonyl)oxy)-1,1′-binaphthyl. To a mixture of 3.78 g of (*R*)-2,2′-bis((trifluoromethanesulfonyl)oxy)-1,1′-binaphthyl (6.9 mmol), 3.58 g of bis(3,5-di-*tert*-butylphenyl)phosphine oxide (8.4 mmol, 1.2 equiv), 77 mg of palladium diacetate (0.34 mmol), and 143 mg of 1,4-bis-(diphenylphosphino)propane (dppp, 0.35 mmol) were added 34 mL of DMSO and 4.7 mL of diisopropylethylamine, and the mixture was heated with stirring at 100 °C for 19 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure to give a red residue. The residue was diluted with ethyl acetate, washed twice with water, dried over Na_2SO_4, concentrated under reduced pressure, and chromatographed on silica gel (elution with hexane/ethyl acetate, 7:2) to give 4.97 g (6.0 mmol, 84%) of the product. Anal. Calcd for $C_{49}H_{54}O_4F_3PS$: C, 71.17; H, 6.58. Found: C, 71.28; H, 6.71. ^{1}H NMR ($CDCl_3$, 300 MHz): 6.8−8.0 (m, aromatic, 18 H), 1.29 (s, C$(CH_3)_3$, 18 H), 1.17 (s, C$(CH_3)_3$, 18 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): 35.4 (s, *C*$(CH_3)_3$), 35.2 (s, *C*$(CH_3)_3$), 31.7 (s, C(*C*$H_3)_3$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): 29.4 (s). MS(MALDI): 827 (M^+, 40), 677 (100), 426 (16).

Synthesis of (*R*)-2-Cyano-2′-(bis(3,5-di-*tert*-butylphenyl)phosphinyl)-1,1′-binaphthyl. A mixture of 4.70 g of (*R*)-2-(bis(3,5-di-*tert*-butylphenyl)phosphinyl)-2′-((trifluoromethanesulfonyl)oxy)-1,1′-binaphthyl (5.7 mmol), 3.83 g of potassium cyanide (59 mmol), 572 mg of nickel dibromide (2.6 mmol), 3.06 g of triphenylphosphine (11.7 mmol), and 538 mg of activated zinc powder (8.2 mmol) in 40 mL of acetonitrile was stirred under Ar for 6 h at 80 °C. After being cooled to room temperature, the reaction mixture was diluted by ethyl acetate and washed with water (2×) and brine. The organic phase was dried over Na_2SO_4, concentrated under reduced pressure, and chromatographed on silica gel (hexane/ethyl acetate, 2:1) to give 3.81 g (5.4 mmol, 95%) of the product. Anal. Calcd for $C_{49}H_{54}NOP$: C, 83.61; H, 7.73; N, 1.99. Found: C, 82.59; H, 7.68; N 2.03. ^{1}H NMR ($CDCl_3$, 300 MHz): 6.96−8.02 (m, aromatic, 18 H), 1.26 (s, C$(CH_3)_3$, 18 H), 1.24 (s, C$(CH_3)_3$, 18 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): 35.3 (s, *C*$(CH_3)_3$), 31.7 (s, C(*C*$H_3)_3$), 31.6 (s, C(*C*$H_3)_3$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): 29.4 (s). MS(EI): 703 (M^+, 100).

Synthesis of (*S,R*)-2-[4-(Isopropyl)oxazol-2-yl]-2′-[bis-(3,5-di-*tert*-butylphenyl)phosphino)]-1,1′-binaphthyl, 4. A mixture of 2.70 g of (*R*)-2-cyano-2′-(bis(3,5-di-*tert*-butylphenyl)phosphinyl)-1,1′-binaphthyl (3.84 mmol), 0.99 g of (*S*)-valinol (9.6 mmol), and 1.23 g of fused zinc chloride (9.0 mmol) in 50 mL of chlorobenzene was refluxed for 6 days at 140 °C. The reaction mixture was cooled to room temperature and quenched with 50 mL of saturated NH_4Cl and the resulting mixture extracted with dichloromethane (3 × 100 mL). The dichloromethane solution was washed with water and brine, dried over Na_2SO_4, and then concentrated. The residue obtained was dissolved in 60 mL of xylene and treated with 10.64 mL of triethylamine (76.4 mmol) and 1.9 mL of trichlorosilane (19 mmol). The resulting mixture was heated slowly to 130 °C and maintained at this temperature for 7 h. After cooling to room temperature, the solution was diluted with ether and quenched with 1.5 mL of saturated $NaHCO_3$. The resulting suspension was filtered through Celite and the Celite washed with copious amounts of ether. The combined organic layer was dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue chromatographed on silica gel (hexane/ethyl acetate, 9:1). The product (1.68 g, 57%) was obtained as a white solid. Mp = 80 °C. Anal. Calcd for $C_{54}H_{64}NOP$: C, 83.79; H, 8.33; N, 1.81. Found: C, 83.70; H, 8.16; N, 1.77. ^{1}H NMR (CD_2Cl_2, 300 MHz): 6.74−8.17 (m, aromatic, 18 H), 3.75 (dd, $^2J_{HH}$ = 9.7, $^3J_{HH}$ = 7.9, C*H*O), 3.56 (m, *CH*N), 3.36 (t, $^2J_{HH}$ = 8.9, $^3J_{HH}$ = 7.9, C*H*O), 1.30 (m, C*H*$(CH_3)_2$), 1.27 (s, C$(CH_3)_3$, 18 H), 1.15 (s, C$(CH_3)_3$, 18 H), 0.58 (d, $^3J_{HH}$ = 5.4, CH(C*H*$_3)_2$), 0.56 (d, $^3J_{HH}$ = 5.4, CH(C*H*$_3)_2$). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): 72.8 (s), 70.8 (s), 35.1 (s), 35.0 (s), 33.2 (s), 31.6 (s), 31.5 (s), 18.7 (s), 18.3 (s). ^{31}P NMR (CD_2Cl_2, 121.5 MHz): −12.6 (s). MS(ESI): 774 (M^+, 100).

Synthesis of $PdCl_2$(4), 8. $PdCl_2(PhCN)_2$ (35 mg, 0.09 mmol) and 70 mg of **4** (0.09 mmol) in 5 mL of dichloromethane were stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue washed with 4 mL of ether and 4 mL of pentane. The product (64 mg, 0.068 mmol, 76%) was obtained as a yellow solid. Crystals suitable for X-ray analysis were obtained by the slow diffusion of pentane into a $Cl(CH_2)_2Cl$ solution of the complex. Anal. Calcd for $C_{54}H_{64}NOPCl_2Pd\cdot 0.5CH_2Cl_2$: C, 65.86; H, 6.59; N, 1.41. Found: C, 65.87; H, 6.80; N, 1.52. ^{1}H NMR (CD_2Cl_2, 300 MHz): 6.28−8.27 (m, aromatic, 18 H), 3.75 (dd, $^2J_{HH}$ = 9.7, $^3J_{HH}$ = 7.9, C*H*O), 3.56 (m, *CH*N), 3.36 (t, $^2J_{HH}$ = 8.9, $^3J_{HH}$ = 7.9, C*H*O), 1.30 (m, C*H*$(CH_3)_2$), 1.27 (s, C$(CH_3)_3$, 18 H), 1.15 (s, C$(CH_3)_3$, 18 H), 0.58 (d, $^3J_{HH}$ = 5.4, CH(C*H*$_3)_2$), 0.56 (d, $^3J_{HH}$ = 5.4, CH(C*H*$_3)_2$). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): 72.8 (s), 70.8 (s), 35.1 (s), 35.0 (s), 33.2 (s), 31.6 (s), 31.5 (s), 18.7 (s), 18.3 (s). ^{31}P NMR (CD_2Cl_2, 121.5 MHz): 27.9 (s). MS(ESI): 774 (M^+, 100).

Synthesis of Pd(dba)(4), 7. $Pd(dba)_2$ (66.9 mg, 0.12 mmol) and 90 mg of **4** (0.12 mmol) were stirred for 3 h in 5 mL of THF. The solvent was removed under reduced pressure and the residue chromatographed on silica gel (ether/pentane, 4:1) to give 80 mg (0.073 mmol, 62%) of the orange product. Anal. Calcd for $C_{71}H_{78}NO_2PPd$: C, 76.50; H, 7.05; N, 1.26. Found: C, 76.39; H, 7.04; N, 1.24. At 253 K, there is mixture of three isomers: two major isomers (**7a**/**7b**, ratio 1.7:1) and a minor isomer (**7c**, ca. 5%).

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7a: ^{1}H NMR (CD_2Cl_2, 500 MHz, 253 K): 7.70 (d, $^3J_{HH}$ = ca. 16, *H*-4), 6.72 (d, $^3J_{HH}$ = ca. 16, *H*-3), 4.51 (dd, $^3J_{HH}$ = 10.9, $^3J_{PH}$ = 4.5, *H*-1), 4.21 (dd, $^3J_{HH}$ = 10.9, $^3J_{PH}$ = 7.3, *H*-2), 4.09 (t, $^3J_{HH}$ = 8.6, $^2J_{HH}$ = 10.5, trans C*H*O), 3.87 (m, C*H*N), 3.71 (t, $^3J_{HH}$ = 9.4, $^2J_{HH}$ = 11.3, cis C*H*O), 2.48 (m, C*H*(CH_3)$_2$), 1.13 (d, $^3J_{HH}$ = 7.0, CH(C*H*$_3$)$_2$), 1.07 (d, $^3J_{HH}$ = 6.6, CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2, 125.8 MHz, 253 K): 187.1 (s, *C*═O), 135.9 (s, *C*-4), 125.7 (s, *C*-3), 71.9 (s, *C*HN), 70.8 (s, *C*HO), 69.3 (d, $^2J_{PC}$ = 18, *C*-2), 56.5 (s, *C*-1), 31.4 (s, *C*H(CH_3)$_2$), 19.9 (s, CH(*C*H$_3$)$_2$), 16.4 (s, CH(*C*H$_3$)$_2$). ^{31}P NMR (CD_2Cl_2, 202.5 MHz, 253 K): 29.5 (s).

7b: ^{1}H NMR (CD_2Cl_2, 500 MHz, 253 K): 6.31 (d, $^3J_{HH}$ = 15.6, *H*-4), 6.10 (d, $^3J_{HH}$ = 15.6, *H*-3), 4.76 (d, $^3J_{HH}$ = 10.5, *H*-2), 4.63 (t, $^3J_{HH}$ = 11.1, $^3J_{PH}$ = 9.4, *H*-1), 3.92 (t, trans C*H*O), 3.87 (m, C*H*N), 3.37 (t, $^3J_{HH}$ = 9.2, $^2J_{HH}$ = 11.5, cis C*H*O), 2.52 (m, C*H*(CH_3)$_2$), 0.95 (d, $^3J_{HH}$ = 7.0, CH(C*H*$_3$)$_2$), 0.80 (d, $^3J_{HH}$ = 6.8, CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2, 125.8 MHz, 253 K): 183.1 (s, *C*═O), 134.5 (s, *C*-4), 130.8 (s, *C*-3), 71.7 (s, *C*HN), 70.0 (s, *C*HO), 67.9 (s, *C*-2), 56.0 (d, $^2J_{PC}$ = 32, *C*-1), 30.4 (s, *C*H(CH_3)$_2$), 19.5 (s, CH(*C*H$_3$)$_2$), 15.9 (s, CH(*C*H$_3$)$_2$). ^{31}P NMR (CD_2Cl_2, 202.5 MHz, 253 K): 32.1 (s).

7c: ^{1}H NMR (CD_2Cl_2, 300 MHz, 253 K): 4.86 (b, β-H of complexed olefin of dba), 3.57 (b, α-H of complexed olefin of dba). ^{13}C NMR (CD_2Cl_2, 125.8 MHz, 253 K): 67.0 (s, α-C of complexed olefin of dba), 54.3 (s, β-C of complexed olefin of dba). ^{31}P NMR (CD_2Cl_2, 202.5 MHz, 253 K): 34.2 (b). MS-(FAB): 879 (M^+ − dba, 100), 661 (26), 364 (87).

Synthesis of Pd(fumaronitrile)(4), 5. $Pd(dba)_2$ (46 mg, 0.08 mmol) and 61.9 mg of **4** (0.08 mmol) were stirred for 4 h in 3 mL of THF. Fumaronitrile (6.3 mg, 0.08 mmol) was added, which caused a fast change in color from red to yellow. Stirring was continued for an additional 2 h. The solution was concentrated under reduced pressure and the residue chromatographed on silica gel (pentane/ether, 3:1) to give 48 mg (0.05 mmol, 63%) of the product as a yellow powder. Anal. Calcd for $C_{58}H_{66}N_3OPPd$: C, 72.67; H, 6.94; N, 4.38. Found: C, 72.58; H, 7.06; N, 4.28. There are two isomers in a ratio of 3.6:1. Major isomer: ^{1}H NMR (CD_2Cl_2, 300 MHz): 4.21 (t, J_{HH} = 8.5, 8.2, C*H*O), 3.89 (m, CHN), 3.78 (t, J_{HH} = 9.7, 8.5, C*H*O), 2.88 (dd, $^3J_{HH}$ = 9.2, $^3J_{PH}$ = 2.8, NCC*H*═CHCN trans to N), 2.67 (t, $^3J_{HH}$ = 9.2, $^3J_{PH}$ = 9.2, NCCH═C*H*CN trans to P), 2.34 (m, C*H*(CH_3)$_2$), 1.31 (s, C(C*H*$_3$)$_3$), 1.16 (d, $^3J_{HH}$ = 6.9, CH(C*H*$_3$)$_2$), 1.13 (s, C(C*H*$_3$)$_3$), 1.04 (d, $^3J_{HH}$ = 7.1, CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): 71.2 (s, *C*HN), 70.9 (s *C*HO), 31.5 (s, C(*C*H$_3$)$_3$), 31.4 (s, C(*C*H$_3$)$_3$), 31.2 (s, *C*H(CH_3)$_2$), 22.4 (d, $^2J_{PC}$ = 2.7, NC*C*H═CHCN trans to N), 22.1 (d, $^2J_{PC}$ = 41.4, NCCH═*C*HCN trans to P), 19.0 (s, CH(*C*H$_3$)$_2$), 15.9 (s, CH(*C*H$_3$)$_2$). ^{31}P NMR (CD_2Cl_2, 121.5 MHz): 31.1 (s). Minor isomer: ^{1}H NMR (CD_2Cl_2, 300 MHz): 4.23 (C*H*O), 4.00 (m, C*H*N), 3.61 (t, J_{HH} = 9.2, 10.8, C*H*O), 2.26 (dd, $^3J_{HH}$ = 9.2, $^3J_{PH}$ = 4.4, NCC*H*═CHCN trans to N), 2.76 (t, $^3J_{HH}$ = 9.2, $^3J_{PH}$ = 9.2, NCCH═C*H*CN trans to P), 2.34 (m, C*H*(CH_3)$_2$), 1.31 (s, C(C*H*$_3$)$_3$), 1.12 (s, C(C*H*$_3$)$_3$), 1.08 (d, $^3J_{HH}$ = 7.2, CH(C*H*$_3$)$_2$), 0.93 (d, $^3J_{HH}$ = 7.1, CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): 71.4 (s, *C*HN), 69.6 (s *C*HO), 31.5 (s, *C*(CH$_3$)$_3$), 31.4 (s, C(*C*H$_3$)$_3$), 31.2 (s, CH-(*C*H$_3$)$_2$), 23.4 (d, $^2J_{PC}$ = 2.7, NC*C*H═CHCN trans to N), 22.4 (d, $^2J_{PC}$ = 41.4, NCCH═*C*HCN trans to P), 19.1 (s, CH(*C*H$_3$)$_2$), 14.1 (s, CH(*C*H$_3$)$_2$). ^{31}P NMR (CD_2Cl_2, 121.5 MHz): 26.5 (s). MS(FAB): 879 (M^+ − fumaronitrile, 57), 661 (14), 364 (100).

Synthesis of Pd(maleic acid anhydride)(4), 6. $Pd(dba)_2$ (11.8 mg, 0.02 mmol) and 15.8 mg of **4** (0.02 mmol) were stirred for 2 h in 1 mL of THF. Fumaronitrile (2.4 mg, 0.024 mmol) was added, which caused a fast change in color from red to yellow. Stirring was continued for an additional hour. The solution was concentrated under reduced pressure and the residue chromatographed on silica gel (pentane/ether, 2:1) to give 14.3 mg (0.015 mmol, 73%) of the product as a yellow powder. The complex was only characterized by its NMR data. There are two isomers in a ratio of 1.8:1. Major isomer: ^{1}H NMR (CD_2Cl_2, 300 MHz): 4.19 (C*H*O), 3.87 (CHN), 3.83 (2H, C*H*═C*H*C_2O_3) 3.65 (C*H*O), 2.39 (m, C*H*(CH_3)$_2$), 1.32 (s, C(C*H*$_3$)$_3$), 1.13 (s, C(C*H*$_3$)$_3$), 1.08 (d, $^3J_{HH}$ = 6.7, CH(C*H*$_3$)$_2$), 0.93 (d, $^3J_{HH}$ = 7.2, CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): 71.8 (s, *C*HN), 70.1 (s, *C*HO), 45.2 (d, $^2J_{PC}$ = 32, *C*H═CHC_2O_3 trans to P), 45.1 (s, CH═*C*HC_2O_3 trans to N), 31.5 (s, C(*C*H$_3$)$_3$), 31.2 (s, C(*C*H$_3$)$_3$), 29.5 (s, *C*H(CH_3)$_2$), 19.2 (s, CH(*C*H$_3$)$_2$), 14.5 (s, CH-(*C*H$_3$)$_2$). ^{31}P NMR (CD_2Cl_2, 121.5 MHz): 32.6 (s). Minor isomer: ^{1}H NMR (CD_2Cl_2, 300 MHz): 4.16 (C*H*O), 3.91 (C*H*═CHC_2O_3), 3.79 (CHN), 3.60 (C*H*O), 3.54 (CH═C*H*C_2O_3), 2.45 (m, C*H*(CH_3)$_2$), 1.30 (s, C(C*H*$_3$)$_3$), 1.13 (s, C(C*H*$_3$)$_3$), 1.11 (CH-(C*H*$_3$)$_2$), 0.98 (d, $^3J_{HH}$ = 6.9, CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): 71.5 (s, *C*HN), 70.1 (s, *C*HO), 46.9 (d, $^2J_{PC}$ = 32, *C*H═CHC_2O_3 trans to P), 44.6 (s, CH═*C*HC_2O_3 trans to N), 31.5 (s, C(*C*H$_3$)$_3$), 31.2 (s, C(*C*H$_3$)$_3$), 30.3 (s, *C*H(CH_3)$_2$), 19.3 (s, CH-(*C*H$_3$)$_2$), 14.9 (s, CH(*C*H$_3$)$_2$). ^{31}P NMR (CD_2Cl_2, 121.5 MHz): 28.3 (s).

Heck Reaction. Palladium acetate (3.4 mg, 0.015 mmol, 3 mol %) and 23.2 mg of **4** (0.030 mmol, 6 mol %) in 3 mL of toluene were stirred for 20 min. Phenyl triflate (81 μL, 0.5 mmol, 1 equiv), 261 μL of *N*,*N*-diisopropylethylamine (1.5 mmol, 3 equiv), and 189 μL of 2,3-dihydrofuran (2.5 mmol, 5 equiv) were added. The solution was stirred at 40 °C for 7.5 days. The mixture was cooled, diluted with pentane, washed with 0.1 N HCl and saturated $NaHCO_3$, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue chromatographed on silica gel (hexane/ethyl acetate, 19:1) to give 20 mg of 2-phenyl-3,4-dihydrofuran (26%). The ee (98%) was determined by GC using a Supelco γ-Dex 120 column.

For the *p*-methoxyphenyltriflate, the ee was determined by HPLC using a Chiracel OD-H column.

Acknowledgment. P.S.P. thanks the Bundesamt für Bildung und Wissenschaft, and A.A. thanks MURST (Cofinanziamento 2000-2002) for financial support. We also thank Johnson Matthey for the loan of precious metals.

Supporting Information Available: Text giving experimental details and a full listing of crystallographic data for compound **8**, including tables of positional and isotropic equivalent displacement parameters, calculated positions of the hydrogen atoms, anisotropic displacement parameters, and bond distances and angles. ORTEP figure showing the full numbering schemes. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020314Q

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Published on June 13, 2002 on http://pubs.acs.org | doi: 10.1021/om020314q