Palladium(0) Olefin Complexes and Enantioselective Allylic Amination/Alkylation with a P,N-Auxiliary

Kumaravel Selvakumar, Massimiliano Valentini, Michael Wörle, and Paul S. Pregosin*

Laboratory of Inorganic Chemistry, ETH Zentrum, 8092 Zürich, Switzerland

Alberto Albinati

Chemical Pharmacy, University of Milan, I-20131 Milan, Italy

Received November 12, 1998

New Pd(0) olefin complexes, **2**−**5**, of a binaphthalene-based chiral P,N(oxazoline) auxiliary, (*S*,*R*)-2-[4-(isopropyl)oxazol-2-yl]-2′-diphenylphosphino-1,1′-binaphthyl, **1**, have been prepared (olefin = fumaronitrile, maleic anhydride, 4-cyclopentene-1,3-dione, and dibenzylideneacetone). These compounds reveal different dynamic behavior in solution as shown by 2-D exchange spectroscopy. Ligand **1** affords excellent enantioselectivity (up to 99% ee) in the allylic amination of a 1,3-diphenyl allyl precursor. The solid-state structure of [Pd(η^3-PhCHCHCHMe)(**1**)]OTf, **15**, has been determined and shows two different diastereomeric cations within one unit cell; that is both the *si* and *re* faces of the allyl crystallize together, the first example of this for a moderately large allyl ligand. The structure of $PdCl_2$(**1**) is also reported and reveals (as does that for **15**) that the oxazoline ring of **1** is twisted relative to the P−Pd−N coordination plane, thus placing this ring substituent above and not below the coordination plane. A more exact solid-state structure for $Pd_2(dba)_3$ has been determined.

Introduction

Several well-known organic transformations involving soluble palladium salts have intermediates that contain the metal in its zero oxidation state, e.g., the cross-coupling,[1] Heck,[2−4] and allylic alkylation[5−7] reactions. Generally, olefins (perhaps in the form of substrate) and/or tertiary phosphorus ligands are well suited to stabilize Pd(0). Recently, Elsevier,[8,9] Vrieze,[9] and their coworkers have found that diimine-type ligands afford quite stable Pd(0) derivatives, and they have studied their electrochemical characteristics. Further, the sulfur donor of a chelating phosphino-thioether can also complex and stabilize Pd(0) compounds.[10]

Enantioselective homogeneous catalysis, using transition metal complexes containing coordinated chiral auxiliaries, is an attractive synthetic methodology in that it provides the opportunity to generate fairly large quantities of enantiopure-products using catalytic amounts of chiral catalysts. A growing literature on chiral P,N-auxiliaries, and specifically those by Helmchen,[11a,12] Pfaltz,[5,11a] Brown,[13] and Togni,[14] testifies to the success of this pair of donors using a variety of metals, including palladium. Several of these enantioselective reactions involve Pd(0) oxazoline intermediates, and Helmchen[15] has recently identified one such species in solution. Fernandez-Galan et al.[16] have successfully prepared several amino-phosphine complexes of Pd(0) using a chiral ferrocene framework.

Given the increasing interest in oxazolines[17] in enantioselective palladium chemistry,[18−20] it seemed worthwhile to investigate the stability of Pd(0) complexes with

(1) (a) Diederich, F.; Stang, P. J. *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998. (b) Calhorda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*, 1431−1438.

(2) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146. Heck, R. F. *Comprehensive Organic Synthesis*; Pergamon: Oxford, 1991; Vol. 4.

(3) Brown, J. M.; Hii, K. K. *Angew. Chem.* **1996**, *108*, 679. Brown, J. M. *Chem. Soc. Rev.* **1993**, 25.

(4) de Meijere, A.; Meyer, F. E. *Angew. Chem.* **1994**, *106*, 2473−2506.

(5) Pfaltz, A. *Acta Chim. Scand.* **1996**, *50*, 189−194.

(6) Reiser, O. *Angew. Chem.* **1993**, *105*, 576.

(7) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395.

(8) Asselt, V.; Elsevier: C. J.; Smeets, W. J. J.; Spek, A. *Inorg. Chem.* **1994**, *33*, 1521−1531.

(9) Rülke, R. E.; Kaasjager, V. E.; Wehman, P.; Elsevier, C. J.; Spek, A.; van Leeuwen, P. W. N.; Vrieze, K.; Fraanje, J.; Goubitz, K.; *Organometallics* **1996**, *15*, 3022−3031.

(10) Tschoerner, M.; Trabesinger, G.; Albinati, A.; Pregosin, P. S. *Organometallics* **1997**, *16*, 3447.

(11) (a) von Matt, P.; Loiseleur, O.; Koch, G.; Pfaltz, A.; Lefeber, C.; Feucht, T.; Helmchen, G. *Tetrahedron Asymmetry* **1994**, *5*, 573. (b) von Matt, P.; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Rüegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265. (c) von Matt, P.; Pfaltz, A. *Angew. Chem.* **1993**, *105*, 614−615.

(12) Rieck, H.; Helmchen, G. *Angew. Chem.* **1995**, *107*, 2881−2883. Sprinz, J.; Kiefer, M.; Helmchen, G.; Reggelein, M.; Huttner, G.; Zsolnai, L. *Tetrahedron Lett.* **1994**, *35*, 1523−1526.

(13) Alcock, N. W.; Brown, J. M.; Hulmes, D. I. *Tetrahedron Asymmetry* **1993**, *4*, 743.

(14) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118* , 1031.

(15) Steinhagen, H.; Reggelin, M.; Helmchen, G. *Angew. Chem.* **1997**, *109*, 2199−2202.

(16) Fernandez-Galan, R.; Jalon, F. A.; Manzano, B. R.; Rodriguez de la Fuente, J.; Vreahami, M.; Jedlicka, B.; Weissensteiner, W.; G., J. *Organometallics* **1997**, *16*, 3758−3768.

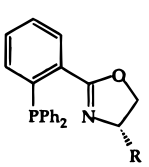
(17) Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron Asymmetry* **1998**, *9*, 1−45. Schaffner, S.; Müller, J. F. K.; Zehnder, M. *Helv. Chim. Acta* **1998**, *81*, 1223.

(18) Johannsen, M.; Jorgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689−1708.

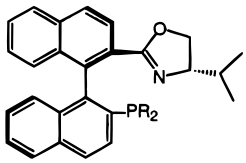
(19) Tanner, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *106*, 625.

(20) Togni, A. *Angew. Chem.* **1996**, *108*, 1581.

10.1021/om980920e CCC: $18.00
Publication on Web 03/05/1999



(from Helmchen and Pfaltz)



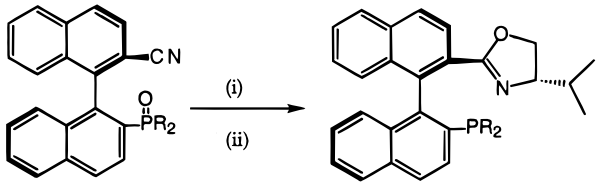
1

related P,N-ligands, e.g., **1**. We report here on the synthesis of new stable olefin complexes using this ligand and also show that **1** is an excellent auxiliary for the enantioselective allylic amination reaction using benzylamines or $CH_3C_6H_4SO_2NH_2$. During the course of this work two independent groups[21,22] have reported on different aspects of **1**.

Results and Discussion

Pd(0) Complexes. Chelate **1** and the new complexes, **2**−**5**, were prepared as shown in Schemes 1 and 2. The

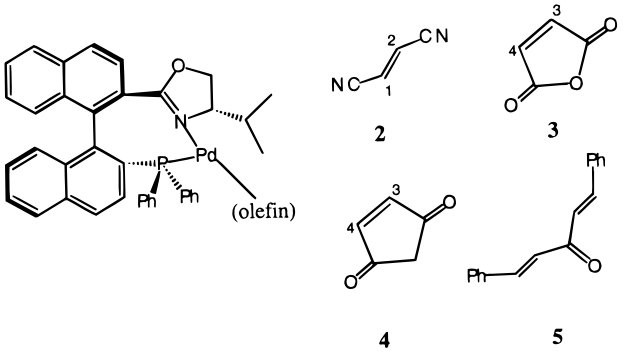
Scheme 1. Synthesis of 1[a]



R = Ph **1**

[a] (i) (*S*)-Valinol and fused $ZnCl_2$ in chlorobenzene, reflux; (ii) $HSiCl_3$ and triethylamine in xylene at 120 °C.

Scheme 2. New Olfin Complexes of Pd(0)[a]

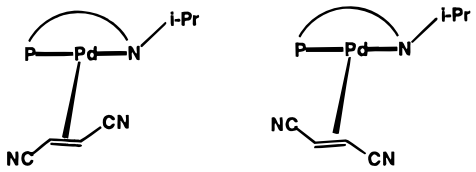


2 **3** **4** **5**

[a] The numbering scheme is relevant for the ^{1}H assignments.

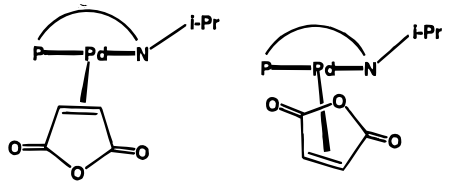
Pd(dba)(**1**) complex, **5**, was prepared by addition of **1** to $Pd_2(dba)_3CHCl_3$. The remaining complexes, **2**−**4**, followed from addition of the appropriate olefin to **5** generated *in situ*. The dba is the largest and, when complexed to Pd(0), the most labile of the olefins, so that its substitution was facile.

The fumaronitrile derivative **2** afforded sharp NMR lines at ambient temperature and exists in two forms, **6** and **7** (in a ca. 1:3 ratio) as a *si* and *re* diastereomeric pair. The maleic anhydride and pentenedione analogues **3** and **4**, respectively, also exist in solution in two forms at ambient temperature, which we assign as the rotational isomers, endo, **8**, and exo, **9** (relative to the i-Pr group of the oxazoline).



6 (minor) **7** (major)

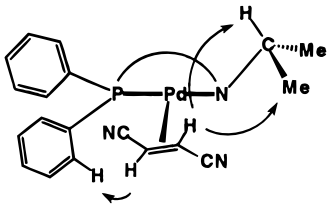
(The position of the i-Pr group will be discussed together with **14**)



8 (exo) **9** (endo)

For the 4-cyclopentene-1,3-dione compound, **4**, there are also two rotational isomers, **10** and **11** (whose structures are not shown).

The dba complex **5** required measurement at 213 K to sharpen its ^{1}H signals. We observe four isomers in solution for **5** and assume (but cannot prove) that these four are due to exo/endo plus the *re* and *si* diastereomeric pair. The overlap in the ^{1}H spectrum does not allow an unequivocal assignment. The assignment of the structures for **2**, however, was readily made via NOE spectroscopy (see Figure 1). The two olefinic protons of the nitrile show selective NOE cross-peaks arising from the different sections of the auxiliary, e.g., as indicated below. The observed selectivity of these and other NOE



measurements confirms that the nitrogen end of the ligand is indeed complexed in solution. The rotation around the Pd−olefin bond in **2** is relatively slow.

In contrast to **2**, the isomeric forms of **3** and **4** exchange via rotation of the olefin as indicated by phase sensitive NOE results (see Figure 2).

There is no exchange between the two olefinic protons within any one isomer; however, one finds a selective exchange of the two protons of one isomer with the corresponding proton in the other rotational isomer; for example, H-4(exo) exchanges with H-3(endo) in **4**.

^{13}C NMR chemical shifts for the new Pd(0) complexes are given in Table 1. Fumaronitrile, whose isomers, **2**, show extremely low-frequency resonances, δ = 22.4−24.0, appears to possess the largest π-back-bonding component. We know that **2** is static on the NMR time scale. The isomers of **3** with maleic anhydride, δ = 44.9−47.9, appear at higher frequency. This olefin is sterically larger than fumaronitrile, due to its cis geometry. The

(21) Imai, Y.; Zhang, W.; Kida, T.; Nakatsuji, Y.; Ikeda, I. *Tetrahedron Lett.* **1998**, *39*, 4343−4346.

(22) Ogasawara, M.; Yoshida, K.; Kamei, H.; Kato, K.; Uozumi, Y.; Hayashi, T. *Tetrahedron Asymmetry* **1998**, *9*, 1779−1787.

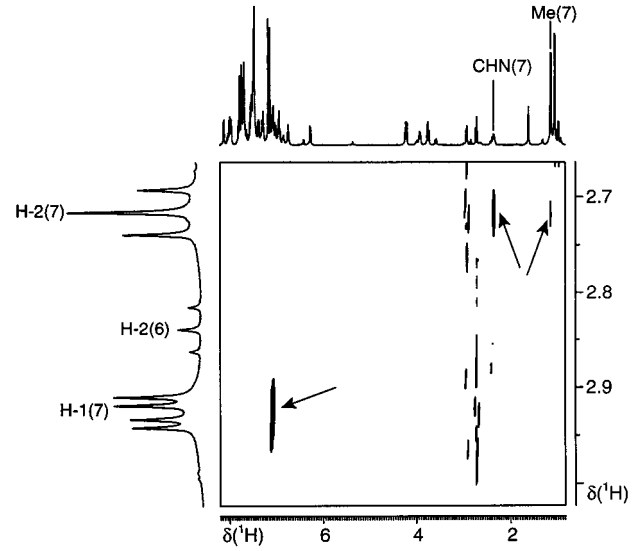


Figure 1. Section of the NOESY spectrum for **2** showing the selective cross-peaks, denoted via arrows, due to the interactions between the olefin ═CH protons (vertical axis) and the i-Pr group (upper right) and phosphine o-protons (lower left). The numbers **6** and **7** refer to the structures in the text (400 MHz, CD_2Cl_2).

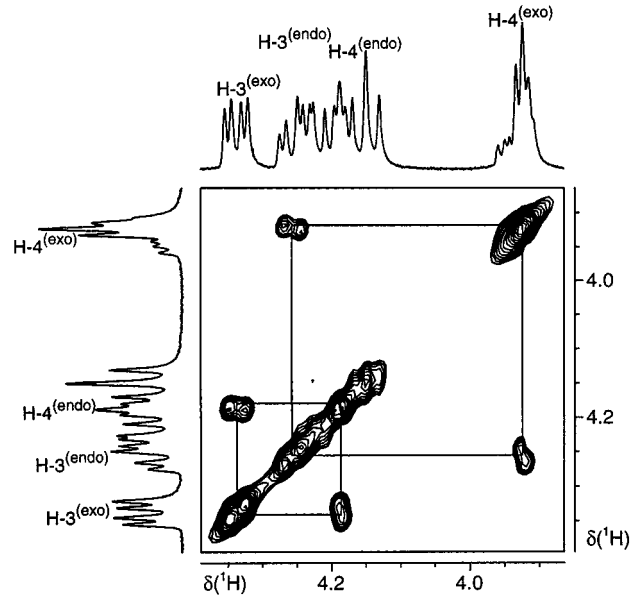


Figure 2. Section of the 2-D exchange spectrum of **4** showing the selective exchange (due to olefin rotation) of H-3 and H-4 of one isomer into H-4 and H-3, respectively, of the second isomer (400 MHz, CD_2Cl_2).

Table 1. δ^{13}C for the Olefin Carbons in 2−5[a]

compound	isomer	δ^{13}C
2	**6**	22.7, 24.0
	7	22.4, 22.9
3	**8** (exo)	45.4, 45.7
	9 (endo)	44.9, 47.9
4	**10** (exo)	68.3, 70.9
	11 (endo)	65.3, 65.8
5		68−72[b]

[a] Measured in CD_2Cl_2. [b] Determined from the ^{13}C, ^{1}H-correlation using the approximate positions of the allyl protons.

isomers with the 4-cyclopentene-1,3-dione, **4**, δ = 65.3−70.9, are found at even higher frequency. This olefin is about the same size as the maleic anhydride in **3**, but has one oxygen less; perhaps the π-component is weakened somewhat. The relatively large dba analogue, **5**, shows the highest ^{13}C frequencies, δ = ca. 68−72 (213 K), for the four observed isomers.

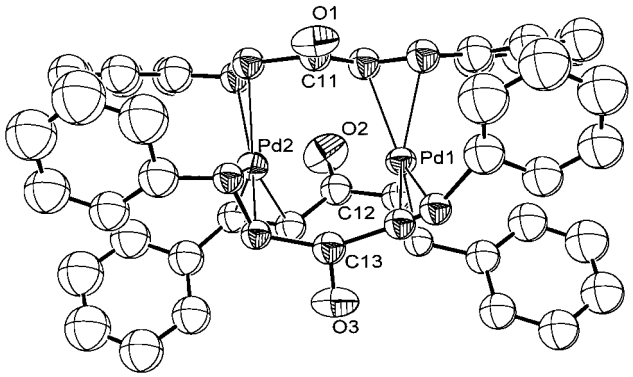
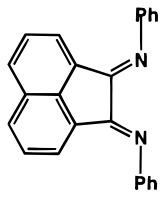
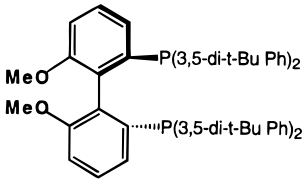


Figure 3. View of the structure of $Pd_2(dba)_3$. Note that each Pd atom has three complexed double bonds from three different dba ligands.

It is useful to compare the ^{13}C values of **2**−**5** with those for known chelate olefin complexes. Pd(fumaronitrile)(**12**)[8] has its ^{13}C absorptions for the olefin carbons at δ = 22.0, quite close to what we find in **2**.



12



13

Further, Pd(4-cyclopentene-1,3-dione)(**13**) and Pd(dba)(**13**), which contain a MeO−Biphep bisphosphine donor,[10] have their ^{13}C-olefin resonances at δ = 70.1, 73.0, and δ = 67.6, 72.4; again, these are not very different from **4** and **5**, respectively. Relative to those for **2**−**5**, these model ^{13}C data do not reflect major bonding differences as a function of the change in chelate donor.

Structure of $Pd_2(dba)_3$. An attempt to obtain a suitable crystal of **5** afforded a good crystal of $Pd_2(dba)_3$ as a CH_2Cl_2 solvate, whose structure was determined without realizing that the crystal no longer contained **1**. This result is interesting in that it shows that, despite our ability to isolate **5**, the molecule can dissociate auxiliary **1** from the Pd(0).

There have been two previous structure determinations of $Pd_2(dba)_3$.[22,23] As both are >20 years old, have *R*-factors around 7%, and are not in agreement with one another, some comment seems called for. The dinuclear complex contains three dba ligands bridging two Pd(0) centers, as found previously (see Figure 3). All of the double bonds have the trans geometry; however, two dba's have the s-trans geometry and one has the s-cis (with respect to the positions of the double bonds relative to one another). One of the two s-trans dba ligands exists in two different conformations in the ratio 1:3. The s-cis dba is disordered over two orientations whose occupancy is 50−50 (see Figures 4, S1, S2, and

(23) Pierpont, C. G.; Mazza, M. C. *J. Chem. Soc., Chem. Commun.* **1973**, 207.

Table 2. Bond Distances (Å) for $Pd_2(dba)_3$

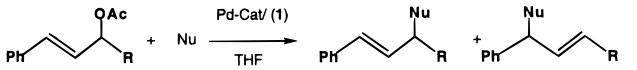
	Pd(1)−Pd(2)	3.1954(4)		
CO[a]	Pd(1)−C(23A)	2.241(7)	C(23A)−C(43)	1.345(10)
	Pd(1)−C(43)	2.294(7)		
CO	Pd(1)−C(23)	2.253(7)	C(23)−C(43A)	1.357(10)
	Pd(1)−C(43A)	2.292(7)		
CO	Pd(1)−C(32)	2.233(4)	C(32)−C(112)	1.352(6)
	Pd(1)−C(112)	2.221(4)		
CO	Pd(1)−C(31A)	2.243(10)	C(31A)−C(11A)	1.327(15)
	Pd(1)−C(11A)	2.275(11)		
CO	Pd(1)−C(31)	2.291(5)	C(31)−C(111)	1.344(8)
	Pd(1)−C(111)	2.324(5)		
CO	Pd(2)−C(41A)	2.202(11)	C(21A)−C(41A)	1.273(16)
	Pd(2)−C(21A)	2.246(11)		
CO	Pd(2)−C(21)	2.238(5)	C(21)−C(41)	1.392(7)
	Pd(2)−C(41)	2.256(5)		
CO	Pd(2)−C(33)	2.268(6)	C(33)−C(113)	1.390(9)
	Pd(2)−C(113)	2.257(7)		
CO	Pd(2)−C(33A)	2.254(8)	C(33A)−C(13A)	1.305(11)
	Pd(2)−C(13A)	2.265(8)		
CO	Pd(2)−C(22)	2.283(4)	C(22)−C(42)	1.286(7)
	Pd(2)−C(42)	2.307(4)		
	O(1)−C(11)	1.222(4)		
	O(2)−C(12)	1.224(5)		
	O(3)−C(13)	1.207(5)		

[a] CO = carbon next to ketone.

S3). The structural result is understandably complicated given these various ligand configurations and results in 10 (and not six) different double bonds (see Table 2). The observed Pd−Pd separation of 3.1954(4) Å is a little shorter than found earlier, but still consistent with two noninteracting Pd atoms. The average Pd−C bond length is 2.26(3) Å, and the average olefin C−C separation is 1.34(3) Å. This latter value does not suggest very strong π-back-bonding.

Concluding this section, Pd(0) olefin complexes with chelating P,N-ligands may prove to be quite stable; nevertheless they may also prove to be labile.

Catalytic Results. Auxiliary **1** was tested in the allylic alkylation and allylic amination reactions with the results summarized in Table 3. These reactions have



The nucleophile, Nu, can be either an amine, or the dimethyl malonate (DMM) anion. R = Ph or Me (1)

been reported successfully by a number of groups,[7,11−14,22] with a variety of auxiliaries recognized to perform well. For R = Ph, Nu = DMM (the classical model), the observed ee, 91%, is high, in keeping with literature expectations.[21,22] For R = Ph, Nu = the anion of *p*-toluenesulfonamide, the observed ee of 98.5% (entry 8) is exceptional and comparable with the best results reported previously in an allylic amination.[11a,14,25] The ee of 92.3% in the amination with benzylamine (entry 3) is very good, with the reaction complete in ca. 15 h. The analogous reactions with 2-methoxybenzylamine, 3 days (entry 4), 4-methoxybenzylamine, 2 days (entry 5), and 2,4-dimethoxybenzylamine, 6 days (entry 6), are much slower. The observed ee's for the first two, 99% and 97%, are excellent, whereas the ee for the disubstituted benzylamine, 74.9%, is not so impressive.

Table 3. Enantioselective Allylic Alkylation and Amination Results

R	nucleophile	time (h)	temp (°C)	yield (%)	ee (%)
1. Ph	DMM/BSA[i]	2	rt	99	91.0 (R)[a]
2. Me	DMM/BSA	1	rt	98	21.0[b]
3. Ph	$C_6H_5CH_2NH_2$	15	40	99	92.3 (S)[c]
4. Ph	2-(MeO)-$C_6H_4CH_2NH_2$	72	40	94	99.0[d]
5. Ph	4-(MeO)-$C_6H_4CH_2NH_2$	48	40	97	97.0[e]
6. Ph	2,4-$(MeO)_2$-$C_6H_3CH_2NH_2$	168	40	73	74.9[f]
7. Me	$C_6H_5CH_2NH_2$	10	40	84	6.9[g]
8. Ph	4-$CH_3C_6H_4SO_2NH_2$/NaH	20	40	94	98.5[h]

[a] Ee was determined by ^{1}H NMR using $Eu(hfc)_3$ as chiral shift reagent. [b] There are two regioisomers arising from attack at the methyl terminus (86% yield, ee 21%) and at the phenyl terminus (14% yield), which were not separated. Ee of the major isomer determined by $Eu(hfc)_3$. [c] Chiracel OD-H column, Hex/i-PrOH, 99.5/0.5; 0.650 mL/min. [d] Chiracel OD-H column, Hex/i-PrOH, 99/1, 0.500 mL/min. [e] Chiracel OD-H column, Hex/i-PrOH/$NHEt_2$, 95/5/0.3, 0.500 mL/min. [f] Chiracel OD-H column, Hex/i-PrOH/$NHEt_2$, 92/8/0.3, 1 mL/min. [g] ≥99% attack at the methyl terminus. Ee was determined by HPLC using Chracel OD-H column, Hex/i-PrOH, 99/1; 0.5 mL/min. [h] The product is the (+) isomer in contrast to ref 11a. Ee was determined by HPLC using chiracel OJ column, Hex/i-PrOH, 75/25; 0.5 mL/min. [i] DMM = dimethyl malonate. BSA = bis(trimethylsilyl)acetamide.

Table 4. Bond Lengths [Å] and Angles [deg] for 14

bond lengths		bond angles	
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)	2.2926(10)	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)−C(27)	1.819(4)	P(1)−Pd(1)−Cl(2)	172.18(4)
P(1)−C(33)	1.821(4)	Cl(1)−Pd(1)−Cl(2)	90.90(4)
P(1)−C(18)	1.850(4)	C(27)−P(1)−C(33)	108.16(17)
N(1)−C(1)	1.270(4)	C(27)−P(1)−C(18)	104.68(16)
N(1)−C(3)	1.499(4)	C(33)−P(1)−C(18)	104.69(16)
O(1)−C(1)	1.334(4)	C(27)−P(1)−Pd(1)	110.22(12)
O(1)−C(2)	1.469(5)	C(33)−P(1)−Pd(1)	110.46(12)

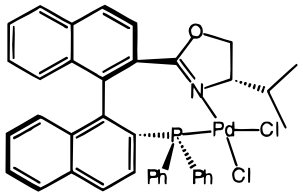
The catalytic reactions with R = Me showed the expected regioselectivity with attack primarily at the methyl terminus. The observed enantioselectivity at this position was minimal. We have also tested **1** in the now classical Heck reaction of phenyl triflate with 2,3-dihydrofuran[4] (see Experimental Section). The observed ee of ca. 74% is only modest based on previous literature results.[26,27]

X-ray Studies on Complexes of 1. To further characterize complexes of **1**, we have determined the structures of the complexes $PdCl_2$(**1**), **14**, and [Pd(η^3-PhCHCHCHMe)(**1**)]OTf, **15**, using X-ray diffraction methods. The structure of the dichloride is well-defined and relatively standard. Appropriate distances and angles are shown in Table 4, and a view of the molecule is shown in Figure 5.

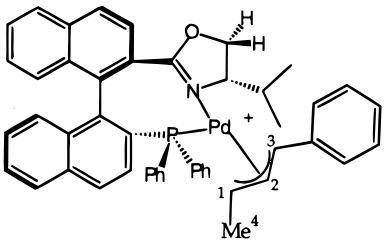
There is one not obvious, but important feature. The naphthyl moiety forces the oxazoline ring to be twisted significantly away from the P−Pd−N coordination plane. This forces the i-Pr group to sit *above* this plane and not below it, and, therefore, the structure is not what one might expect, on the basis of the drawing given for **1**, above. This result has consequences for the proton assignment in **2**−**5**, in that an NOE from a vinylic

(24) Ukai, T.; Kawazura, H.; Ishi, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253−266.
(25) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301.
(26) Ozawa, F.; Kubo. A.; Matsumoto, Y.; Hayashi, T.; Nishioka, I.; Yanagi, K.; Moriguchi, K. *Organometallics* **1993**, *12*, 4188.
(27) Trabesinger,G.; Albinati, A.; Feiken, N.; Kunz, R. W.; Pregosin, P. S.; Tschoerner, M. *J. Am. Chem. Soc.* **1997**, *119*, 6315.

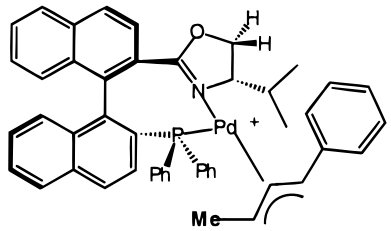
Scheme 3. Additional Complexes of 1



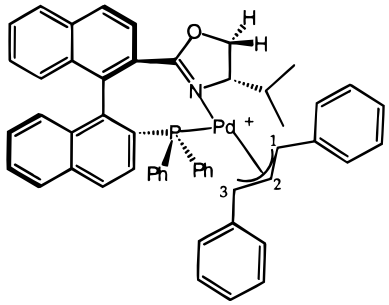
14



15 endo



15 exo



16 (only one of the four isomers is shown)

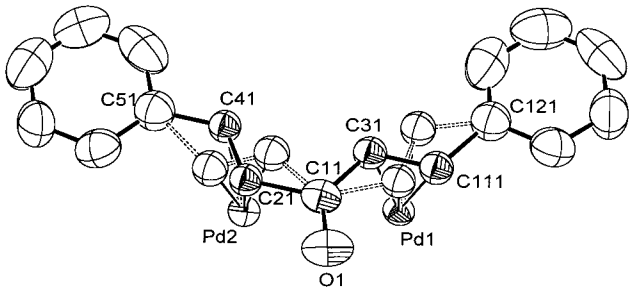


Figure 4. Part of the structure of $Pd_2(dba)_3$ showing the disorder for one of the bridging dba ligands. The solid lines show one ligand configuration, while the dotted lines show a different configuration of the dba within the individual molecules; that is, molecule **1** has the structure with the solid lines, whereas molecule **2** has the structure with the dotted lines.

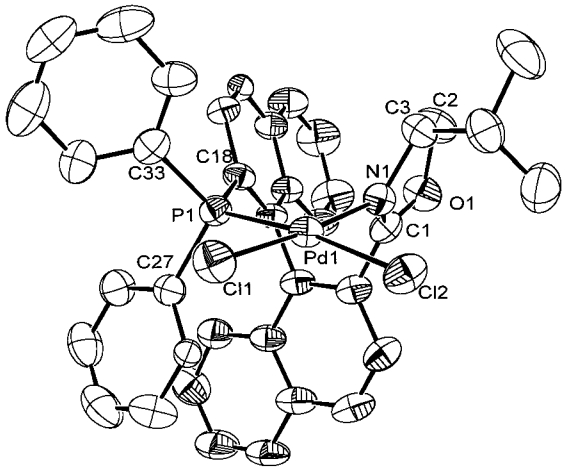


Figure 5. View of the structure of **14** showing the placement of the i-Pr group of complex **1** and the twisting of the oxazoline ring relative to the P−Pd−N plane. The two halogens are coming toward the viewer. Note the almost perpendicular position of the oxazole ring relative to the Cl−Pd−Cl plane.

proton of, for example, fumaronitrile, to an i-Pr proton arises from the =CH moiety "up" rather than "down". Further, this structural feature is also responsible for (i) the change from (S) to (R) in the organic product of the allylic alkylation reaction[21] and (ii) the observation of the (S) product and not the (R) in our amination (Table 3, entry 3). It is useful to know that an auxiliary with an (R) stereogenic center can afford an (S) organic product (or vice versa).

In contrast to **14**, the $[Pd(\eta^3\text{-PhCHCHCHMe})(\mathbf{1})]^+$ structure is quite interesting and reveals *two different diastereomeric cations* within one asymmetric unit; that is, the compounds containing both the *si* and *re* complexed faces of the allyl cocrystallize. Figure 6, shows a superposition of the structures for the two complexes.

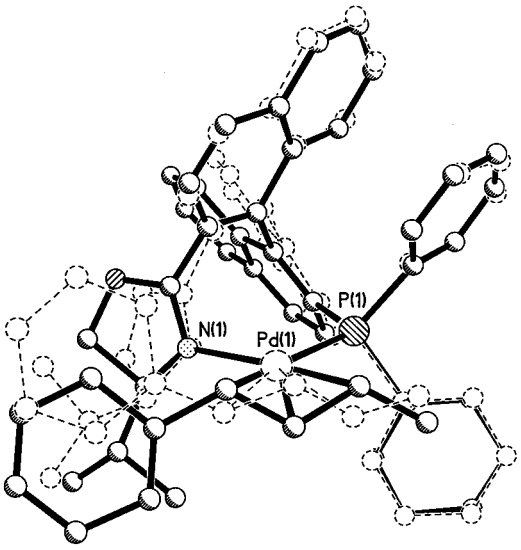


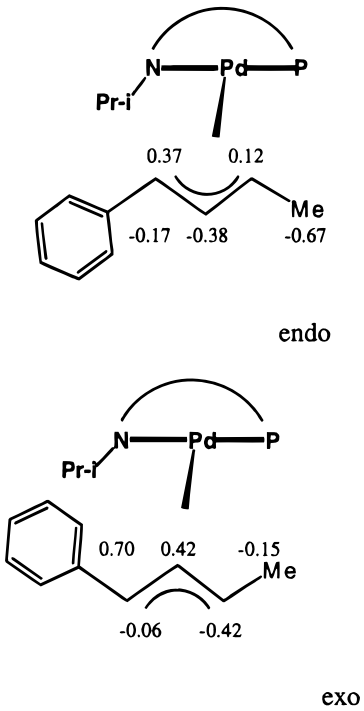
Figure 6. View of the structure of the allyl cation **15** showing the two molecules having the different faces of the η^3-PhCHCHCHMe allyl complexed to the Pd atom.

Although this type of co-crystallization is known[28] for Pd-η^3-C_3H_5 complexes, i.e., relatively small allyl ligands, this is the first example for a significantly larger allyl. The coordination sphere about the Pd consists of the nitrogen and phosphorus donor atoms of the auxiliary plus the η^3-allyl, with the methyl terminus proximate to the P-donor in both cations. Regrettably, the structure is a poor one, so that a detailed discussion of distances and angles is not warranted.[29] Nevertheless, the data are sufficient for an analysis of the positions of the allyl ligand carbons, relative to the P−Pd−N plane. This shows that both η^3-PhCHCHCHMe ligands are strongly clockwise rotated when viewed from behind the allyl looking toward the metal. The details of this rotation are shown in Scheme 4. Clearly, even in the solid state, there is little or no difference in energy between these exo and endo diastereomeric compounds, so that the observed vanishing ee's in the catalytic experiments, due to attack at the less hindered MeCH terminus, are quite understandable.

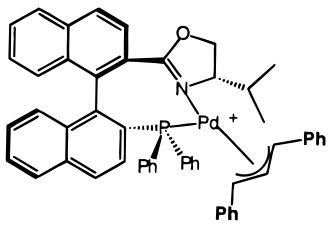
Allyl Complexes. The allyl complexes [Pd(η^3-PhCHCHCHMe)(**1**)]OTf, **15**, and [Pd(η^3-PhCHCHCHPh)(**1**)]OTf, **16**, were studied in solution via 2-D NMR methods.[30,31]

For **16** there are two isomers, **16a** and **16b**, in the ratio 1:3.4. Complex **16b** has the allyl phenyl and the i-Pr on the same side (see discussion of **14** above). The terminal ^{13}C allyl chemical shifts are δ = 82.6 and 89.7 for **16a** and δ = 67.6 and 102.9 for **16b**, suggesting that **16b** has the more electrophilic allyl terminus.[32] Once again[12,14,32] the isomer possessing the largest difference in δ ^{13}C between the two termini leads to the observed product, assuming attack trans to the P-donor. Attack at diastereomer **16b** (or the transition state developing from **16b**[11b]) and not **16a** will now be favored, despite (or perhaps because of) the presence of the i-Pr group on the same side as the allyl phenyl group.

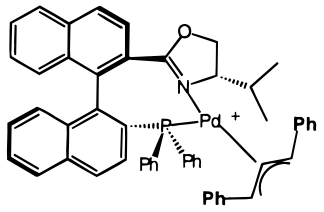
Scheme 4. Positions of the Allyl, Ipso-Phenyl, and Methyl Atoms in 15[a]



[a] Exo and endo refer to the position relative to the oxazoline i-Pr group.



16a



16b

For **15** we find four isomers, in the approximate ratio 2.5:1.5:1.5:1. The three most abundant of these have been identified via ^{1}H NOE spectroscopy: the two syn/syn diastereomers found in the X-ray and one syn/anti isomer (at the CHMe terminus). This type of isomerization is now relatively standard for allyl complexes.[30,32,33] There is considerable overlap in the ^{1}H spectrum, so that not all of the ^{1}H and ^{13}C signals could be unambiguously assigned (see Table 5); however, all of the allyl carbons were located.

(28) Albinati, A.; Eckert, J.; Pregosin, P. S.; Ruegger, H.; Salzmann, R.; Stoessel, C. *Organometallics* **1997**, *16*, 579.
(29) Details of the structure are available as Supporting Information.
(30) Pregosin, P. S.; Salzmann, R. *Coord. Chem. Rev.* **1996**, *155*, 35.
(31) Pregosin, P. S.; Trabesinger, G. *J. Chem. Soc., Dalton Trans.* **1998**, 727−734.
(32) (a) Boog-Wick, K. Pregosin, P. S.; Trabesinger, G. *Organometallics* **1998**, *17*, 3254−3264. (b) Pregosin, P. S.; Salzmann, R.; Togni, A. *Organometallics* **1995**, *14*, 842. (c) Breutel, C.; Pregosin, P. S.; Salzmann, R.; Togni, A. *J. Am. Chem. Soc.* **1994**, *116*, 4067.
(33) Åkermark, B.; Hansson S. *J. Am. Chem. Soc.* **1990**, *112*, 4587.

Table 5. NMR Data for the Diastereomers of 15

	trans/exo syn/syn		trans/endo syn/syn		trans/exo syn/anti	
no.	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	3.46	80.4	3.62	65.2	4.24	71.4
2	5.82	117.0	5.81	112.5	5.90	109.8
3	5.29[a]	89.6	5.49[b]	100.5	5.45	91.3
Me(allyl)	0.72[c]	17.9	0.53[d]	17.3	0.15[i]	14.2
CHO-cis[o]	3.51		3.69		3.16	
CHO-trans	4.00		3.69		3.16	
CHN	4.19		3.23		3.94	
CH(i-Pr)	2.09		0.08		1.95	
Me(i-Pr)	0.92[e]	19.2	0.34[f]	17.1	0.31[j]	14.7
Me(i-Pr)	0.91[g]	14.3	0.85[h]	22.0	1.07[k]	22.1
^{31}P	30.2	30.1		27.5		

[a] (t, $^3J_{PH}$ = 13.3, $^3J_{HH}$ = 11.5). [b] dd, $^3J_{PH}$ = 14.9, $^3J_{HH}$ = 9.9. [c] dd, $^4J_{PH}$ = 8.6, $^3J_{HH}$ = 6.4. [d] (dd, $^4J_{PH}$ = 9.7, $^3J_{HH}$ = 6.2). [e] d, $^3J_{HH}$ = 7.0. [f] d, $^3J_{HH}$ = 6.7. [g] d, $^3J_{HH}$ = 6.9. [h] d, $^3J_{HH}$ = 6.6. [i] t, $^4J_{PH}$ = 9.4, $^3J_{HH}$ = 6.4. [j] d, $^3J_{HH}$ = 6.8. 1d, $^3J_{HH}$ = 6.8. [k] d, $^3J_{HH}$ = 6.5. [n] d, $^3J_{HH}$ = 6.9. [o] C1 trans to N. Cis and trans refer to the i-Pr group.

For **15** there are two additional interesting points: (i) all four isomers have the MeCH allyl terminus pseudo-cis to the P-donor. This is clear via NOEs from the allyl H-3 to the i-Pr group of **1**, plus the local anisotropic effects of the P-phenyl groups on the allyl methyl chemical shifts (see Table 5) and (ii) all four isomers show relatively large spin−spin coupling constants, ca. 8−9 Hz, from the ^{31}P to the allyl methyl, i.e., four-bond interactions. Normally, one might expect large *J*-values when the coupled spins are trans. We considered the possibility that one or more of the isomers might have an η^1-structure; however the allyl ^{13}C data do not support this. The NOESY spectrum does not show an exchange process between these isomers at ambient temperature.

The observed low ee's, in both the amination and alkylation reactions using (*E*)-3-acetoxy-1-phenyl-1-butene, are consistent with (i) the observation that the methyl group on this allyl does not particularly favor either the syn or anti position in **15** and (ii) the solid-state result in which both faces of **15** complex. Given the comparable stability of these diastereomers, it will not prove a simple task to find a suitable enantioselective auxiliary.

Experimental Section

All manipulations were carried out under an argon atmosphere. THF and ether were distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2. Hexane was distilled from sodium. (*E*)-3-Acetoxy-1,3-diphenyl-1-propene and (*E*)-3-acetoxy-1-phenyl-1-butene were prepared by standard procedures. All other chemicals were commercial products and used as received. (*R*)-2,2′-Bis((triflurometh anesulfonyl)-oxy)-1,1′-binaphthyl was purchased from Fluka. (*R*)-(+)-2-Cyano-2′-diphenylphosphinyl-1,1′-binaphthyl was prepared by a reported procedure.[34] The chloro-bridged dimers [PdCl(η^3-PhCHCHCHPh)]$_2$ and [PdCl(η^3-PhCHCHCHCH$_3$)]$_2$ were prepared by standard methods.[35] Routine ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker DPX-250, 300, and 400 MHz spectrometers. Chemical shifts are given in ppm, and coupling constants (*J*) are given in hertz. The two-dimensional ^{1}H NOESY and ^{31}P,^{1}H-correlation experiments were carried out at 400 MHz. Elemental analyses and mass spectroscopic studies were performed at ETHZ.

Table 6. Crystal Data and Structure Refinement for $Pd_2(dba)_3$ and 14

compound	$Pd_2(dba)_3 \cdot CH_2Cl_2$	**14**
formula	$C_{52}H_{44}Cl_2O_3Pd_2$	$C_{43}H_{32}Cl_2NOPPd$
mol wt	1000.67	811.91
data coll. *T*, K	296	293
diffractometer	Siemens Smart CCD	
cryst syst	triclinic	orthorombic
space group	$P\bar{1}$	$P2_12_12_1$
a, Å	12.3960(6)	12.333(2)
b, Å	12.9650(6)	14.286(2)
c, Å	15.2135(7)	20.935(3)
α, deg	115.965(1)	90
β, deg	97.130(1)	90
γ, deg	95.152(1)	90
V, Å^3	2139.1(4)	3688.5(9)
Z	2	4
ρ(calcd), g cm^{-3}	1.553	1.417
μ, cm^{-1}	11.21	13.47
radiation	Mo Kα (graphite-monochromated λ = 0.710 79 Å)	
measured reflns	$\pm h, \pm k, +l$	$\pm h, \pm k, \pm l$
θ range, deg	$1.7 < \theta < 29.8$	$1.7 < \theta < 28.3$
no. of data coll.	26 235	31 733
no. of ind data	10 484	9171
trans coeff	0.9133−1.0000	0.6305−0.918
no. of params refined (n_v)	504	439
R_{av}[a]	0.015	0.063
R (obs, reflns) $[\lvert F_o\rvert > 2.0\sigma(\lvert F\rvert)]$[b]	0.040	0.035
R, R_w^2 (all data)[c]	0.0524, 0.1439	0.0515, 0.085
GOF[d]	0.495	1.004

[a] $R_{av} = \sum\lvert F_o^2 - F_{o,av}^2\rvert/\sum_i\lvert F_o^2\rvert$. [b] $R = \sum(\lvert F_o - (1/k)F_c\rvert)/\sum\lvert F_o\rvert$. [c] $R_w^2 = [\sum w(F_o^2 - (1/k)F_c^2)^2/\sum w\lvert F_o^2\rvert^2]$, where $w = [\sigma^2(F_o^2) + (aP)^2 + P]^{-1}$, and $P = \{[F_o^2 + \max(F_o^2)]/3.0\}$. [d] GOF: $[\sum_w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.

Crystallography. The unit cell constants, space group determination, and the data collection were carried out on a Siemens SMART diffractometer equipped with a CCD detector. The space groups were unambiguously determined from the systematic absences, while the cell constants were refined, at the end of the data collection, using the collected data with the data reduction software SAINT[36] developed by Siemens. Data were corrected for Lorentz and polarization factors and empirically for absorption using the SADABS program.[37] Selected crystallographic and other relevant data are listed in Table 6 and in 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 6.

The structures were solved by direct and Fourier methods and refined by full matrix least squares,[38] minimizing the function $[\sum w(F_o^2 - (1/k)F_c^2)^2]$. The poor quality of the crystals of **15** and the presence of disorder led to a unsatisfactory quality of structural determination; thus, all the relevant crystallographic data are listed only in Supplementary Table S1. During the final refinement of $Pd_2(dba)_3$ anisotropic displacement parameters were used for all atoms except those affected by positional disorder (See Figures S1−S3); for **14** all atoms were treated anisotropically. The contribution of the hydrogen atoms, in their calculated position was included in the refinements using a riding model (C−H = 0.95(Å), *B*(H) = 1.5*B*(C_{bonded})(Å^2)). The handedness was tested by refining

(34) Uozumi, Y.; Suzuki, N.; Ogiwara, A.; Hayashi, T. *Tetrahedron* **1994**, *50*, 4293.
(35) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am.Chem. Soc.* **1985**, *107*, 2033.
(36) *SAINT: SAX Area Detector Integration*; Siemens Analytical Instrumentation, 1996.
(37) Sheldrick, G. M. *SADABS*; Universität Göttingen. To be published.
(38) Sheldrick, G. M *SHELX-97, Structure Solution and Refinement Package*; Universität Göttingen, 1997.

the Flack's parameter.[39] No extinction correction was deemed necessary. Upon convergence (see Table S1) the final Fourier difference map showed no significant peaks. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[40] All calculations were carried out by using the SHELX-97 programs.[38]

Preparation of 1. A mixture of (*R*)-(+)-2-cyano-2′-diphenylphosphinyl-1,1′-binaphthalene (479 mg, 1 mmol), (*S*)-valinol (140 mg, 1.35 mmol), and fused zinc chloride (327 mg, 2.4 mmol) in chlorobenzene (20 mL) was refluxed for 48 h under Ar. The reaction mixture was cooled to room temperature and quenched with saturated NH_4Cl (10 mL) and the resulting mixture extracted with dichloromethane (3 × 20 mL). The dichloromethane solution was washed with water and brine, dried over $MgSO_4$, and then concentrated. The residue obtained was suspended in xylene (15 mL) and then treated with triethylamine (2.8 mL, 20.1 mmol) followed by trichlorosilane (500 μL, 5 mmol) at 0 °C. The resulting mixture was heated slowly to 120 °C and mainained at this temperature for 5 h with stirring. After cooling to room temperature, the solution was diluted with ether and quenched with few drops of $NaHCO_3$. The resulting suspension was filtered through Celite, and the Celite washed with copious amounts of ether. The combined organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue chromatographed on silica gel (elution with 20% ethyl acetate in hexane, R_f = 0.40). The ligand **1**, as a white solid, was crystallized from CH_2Cl_2−ether. Yield: 500 mg, 91%. Mp = 168−170 °C (closed melting point tube). Anal. Calcd for $C_{38}H_{32}NOP$: C, 83.04; H, 5.87; N, 2.55. Found: C, 82.99; H, 5.76; N, 2.37. ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz): 3.72 (dd, $^2J_{HH}$=9.7, $^3J_{HH}$=7.9, cis or trans C*H*O), 3.61 (m, C*H*N), 3.34 (t, $^2J_{HH}$=9.7, $^3J_{HH}$=7.8, trans or cis C*H*O), 1.39 (m, C*H*−i-Pr), 0.59 (d, $^3J_{HH}$=6.8, Me), 0.54 (d, $^3J_{HH}$=6.8, Me). ^{13}C NMR ($CDCl_3$, 298 K, 300 MHz): 72.4 (s), 70.4 (s), 32.8 (s), 19.0 (s), 18.1 (s). ^{31}P NMR ($CDCl_3$, 298 K, 300 MHz): −14.2. MS (EI): 549 (M^+, 16), 479 (74), 402 (34), 365 (53), 352 (100), 183 (38).

Synthesis of Pd(P−N)(Olefin) [2−4]. $Pd_2(dba)_3$ (40.4 mg, 0.04 mmol) and ligand **1** (44 mg, 0.08 mmol) were stirred in THF (3 mL) for 2 h. The appropriate olefin (0.08 mmol) was added to the clear orange solution. Stirring was continued for an additional 2 h. The pale yellow solution that resulted was filtered through Celite and the Celite washed with THF. The combined solution was concentrated under reduced pressure. The residue was washed with hexane (3 × 5) followed by ether (0.5 mL), and the complexes were recrystallized from CH_2Cl_2−hexane to afford yellow solids.

Complex 2. Yield: 30 mg, 52%. MS (FAB): 655 (M^+ − $C_4H_2N_2$, 49), 437 (20), 364 (100).

There are two isomers. Cis and trans C*H*O refer to i-Pr group. ^{1}H NMR (isomer **6**, CD_2Cl_2, 298 K, 400 MHz): 4.21 (m, cis C*H*O), 3.99 (m, C*H*N), 3.57 (t, $^2J_{HH}$=9.5,$^3J_{HH}$=7.9, trans C*H*O), 2.84 (t, $^3J_{PH}$=9.4, $^3J_{HH}$=9.4, *H*-2), 2.64 (m, C*H*−i-Pr), 2.41 (m, *H*-1), 1.05 (Me), 0.92 (d, $^3J_{HH}$=6.8, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 26.5 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 71.3 (s, *C*HN), 69.8 (s, *C*HO), 29.7 (s, *C*H−i-Pr), 24.0 (s, *C*-1), 22.7 (s, *C*-2), 14.4 (s, Me), 14.2 (s, Me). ^{1}H NMR (isomer **7**, CD_2Cl_2, 298 K, 400 MHz): 4.22 (t, $^2J_{HH}$=9.3, $^3J_{HH}$=7.4, cis C*H*O), 3.92 (m, C*H*N), 3.75 (t, $^2J_{HH}$=9.4, $^3J_{HH}$=7.9 trans C*H*O), 2.92 (dd, $^3J_{HH}$=9.3, $^3J_{PH}$=3.5, *H*-1), 2.74 (t, $^3J_{HH}$=9.3, $^3J_{PH}$=9.2, *H*-2), 2.39 (m, C*H*−i-Pr), 1.14 (d, $^3J_{HH}$=6.8, Me), 1.06 (d, $^3J_{HH}$=6.9, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 28.7 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 71.3 (s, *C*HO), 70.7 (s, *C*HN), 31.1 (s, *C*H−i-Pr), 22.9 (s, *C*-1), 22.4 (s, *C*-2), 19.0 (s, Me), 15.7 (s, Me).

Complex 3. Yield: 31 mg, 52%. Anal. Calcd $C_{42}H_{34}NO_4PPd$ (754.13): C, 66.89; H, 4.54; N, 1.86. Found: C, 67.47; H, 5.35; N, 1.74. MS (FAB): 655 (M^+ − $C_4H_2O_3$, 56), 437 (16), 364 (100). There are two isomers.^{1}H NMR (isomer **8**, CD_2Cl_2, 298 K, 400 MHz): 4.18 (dd, $^2J_{HH}$=10.0, $^3J_{HH}$=6.2, cis C*H*O), 3.86 (m, *H*-3), 3.82 (m, *H*-4), 3.81 (td, $^3J_{HH}$=7.4, $^3J_{HH}$=4.7, C*H*N), 3.72 (dd, $^2J_{HH}$=10.1, $^3J_{HH}$=5.7, trans C*H*O), 2.35 (m, C*H*−i-Pr), 1.11 (d, $^3J_{HH}$=7.0, Me), 1.07 (d, $^3J_{HH}$=7.0, Me). ^{31}P NMR: (CD_2Cl_2, 298 K, 400 MHz): 30.8 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 70.9 (s, *C*HO), 45.7 (d,$^2J_{CP}$=2.3, *C*-4), 45.6 (s, *C*HN), 45.4 (s, *C*-3), 30.8 (s, *C*H−i-Pr), 19.2 (s, Me), 15.8 (s, Me). ^{1}H NMR (isomer **9**, CD_2Cl_2, 298 K, 400 MHz): 4.21 (dd, $^2J_{HH}$=8.9, $^3J_{HH}$=7.1, cis C*H*O), 3.92 (td, $^3J_{HH}$=7.1, $^3J_{HH}$=4.0, C*H*N), 3.90 (dd, $^3J_{PH}$=10.2, $^3J_{HH}$=4.2, *H*-3), 3.67 (dd, $^2J_{HH}$=9.1, $^3J_{HH}$=6.3, trans C*H*O), 3.57 (t, $^3J_{PH}$=4.5, $^3J_{HH}$=4.1, *H*-4), 2.39 (m, C*H*-i-Pr), 1.06 (d, $^3J_{HH}$=6.7, Me), 0.97 (d, $^3J_{HH}$=6.9, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 27.1 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 70.3 (s, *C*HO), 47.9 (s, *C*-3), 47.6 (s, *C*HN), 44.9 (d, $^2J_{CP}$=2.4, *C*-4), 29.6 (s, *C*H−i-Pr), 19.1 (s, Me), 14.6 (s, Me).

Complex 4. Yield: 30 mg, 51%. Anal. Calcd for $C_{43}H_{36}NO_3PPd$ (752.16): C, 68.67; H, 4.82; N, 1.86. Found: C, 69.62; H, 5.54: N, 1.72. MS (FAB): 752 (M^+, 6), 655 (M^+ − $C_5H_4O_2$, 100), 437 (20), 364 (84). There are two isomers.^{1}H NMR (isomer **10**, CD_2Cl_2, 263 K, 400 MHz): 4.34 (dd, $^3J_{PH}$=9.6, $^3J_{HH}$=3.9, *H*-3), 4.14 (m, cis and trans C*H*O), 3.94 (t, $^3J_{PH}$=4.1, $^3J_{HH}$=3.7, *H*-4), 3.77 (m, C*H*N), 2.32 (m, C*H*-i-Pr), 1.06 (d, $^3J_{HH}$=6.9, Me), 1.05 (d, $^3J_{HH}$=6.8, Me). ^{31}P NMR (CD_2Cl_2, 263 K, 400 MHz): 24.1 (s). ^{13}C NMR (CD_2Cl_2, 263 K, 400 MHz): 71.4 (s, CHN), 70.9 (s, *C*-4), 70.3 (s,*C*HO), 68.3 (s, *C*-3), 30.6 (s, *C*H−i-Pr), 19.6 (s, Me), 15.7 (s, Me). ^{1}H NMR (isomer **11**, CD_2Cl_2, 263 K, 400 MHz): 4.26 (dd, $^3J_{PH}$=10.4, $^3J_{HH}$=3.9, *H*-3), 4.22 (dd, $^2J_{HH}$= 10.5, $^3J_{HH}$=6.6, trans C*H*O), 4.19 (t, $^3J_{PH}$=3.3, $^3J_{HH}$=3.8, *H*-4), 3.92 (m, C*H*N), 3.69 (dd, $^2J_{HH}$=10.5, $^3J_{HH}$=3.9, cis C*H*O), 2.29 (m, C*H*−i-Pr), 1.02 (d, $^3J_{HH}$=6.9, Me), 0.93 (d, $^3J_{HH}$=7.0, Me). ^{31}P NMR (CD_2Cl_2, 263 K, 400 MHz): 27.4 (s). ^{13}C NMR (CD_2Cl_2, 263 K, 400 MHz): 70.1 (s, *C*HO), 65.8 (s, *C*-3), 65.3 (s, *C*-4), 64.1 (s, *C*HN), 29.2 (s, *C*H−i-Pr), 19.1 (s, Me), 14.4 (s, Me).

Synthesis of Pd(dba)(1), 5. $Pd_2(dba)_3$ (40.4 mg, 0.04 mmol) and **1** (44 mg, 0.08 mmol) were stirred in THF (3 mL) for 1 h. The ^{31}P NMR shows that the substitution was complete. The solution was stirred for an additional 2 h at room temperature. The solution was concentrated under reduced pressure, the residue washed with hexane (3 × 5 mL), and the orange complex, **2**, obtained recrystallized from CH_2Cl_2−hexane. Yield: (25 mg, 36%. Anal. Calcd for $C_{55}H_{46}NO_2PPd$ (890.4): C, 74.19; H, 5.21; N, 1.57. Found: C, 74.69; H, 6.41; N, 1.56. MS (FAB): 890 (M^+, 3), 655 (M^+ − dba, 59), 437 (18), 364 (100). The complex exists as four isomers in solution.

Synthesis of $PdCl_2$(1), 14. $PdCl_2(PhCN)_2$ (19.2 mg, 0.05 mmol) and **1** (27.5 mg, 0.05 mmol) in benzene (4 mL) were stirred at room temperature for 8 h. The solution was concentrated under reduced pressure. The crude product was recrystalized as yellow needles from CH_2Cl_2−hexane. A suitable crystal for X-ray analysis was obtained by the slow diffusion of ether vapor into a CH_2Cl_2 solution of the complex. Yield: (34 mg, 93%. Anal. Calcd for $C_{38}H_{32}NOPCl_2Pd.CH_2Cl_2$ (811.91): C, 57.69; H, 42.22; H, 1.73. Found: C, 57.95; H, 4.47; N, 1.81. MS (FAB): 692 (M^+ − Cl, 68), 655 (M^+ − Cl_2, 14), 437 (11), 364 (100). ^{1}H NMR (CD_2Cl_2, 298 K, 300 MHz): 4.17 (dd, $^2J_{HH}$=10.4, $^3J_{HH}$=8.8, cis or trans C*H*O), 3.75 (m, C*H*N), 3.44 (dd, $^2J_{HH}$=10.3, $^3J_{HH}$=9.0, trans or cis C*H*O), 3.01 (m, C*H*−i-Pr), 1.24 (d, $^3J_{HH}$=6.9, Me), 0.96 (d, $^3J_{HH}$=6.8, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 300 MHz): 25.0.

[Pd(η^3-PhCHCHCHPh)(1)]CF_3SO_3,16. [PdCl(η^3-PhCHCHCHPh)]$_2$ (33.5 mg, 0.05 mmol) and CF_3SO_3Ag (25.7 mg, 0.1 mmol) in acetone (2 mL) were stirred for 1 h in the dark at room temperature. The AgCl formed was filtered through Celite and the Celite washed with acetone. Ligand **1** (55 mg, 0.1 mmol) in CH_2Cl_2 (1 mL) was added to the filtrate with stirring. Stirring was continued for 30 min and then the

(39) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.
(40) *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

solution concentrated. The crude product formed was recrystallized from CH_2Cl_2−hexane. Yield: 80 mg, 80%. Anal. Calcd for $C_{54}H_{45}NO_4F_3PSPd$ (998.41): C, 64.96; H, 4.54; N, 1.40. Found: C, 64.84; H, 4.70; N, 1.32. MS (FAB): 848 ($M^+ - CF_3SO_3$, 100), 655 ($M^+ - (PhCHCHCHPh + CF_3SO_3)$, (14), 437 (15), 364 (21). Major isomer (endo) ^1H NMR (CD_2Cl_2, 298 K, 400 MHz): 6.30 (m, *H*-2), 5.85 (m, *H*-1), 4.52 (d, $^3J_{HH}$=10.5, *H*-3), 3.82 (t, $^2J_{HH}$=9.1, $^3J_{HH}$=5.0, cis C*H*O), 3.69 (t, $^2J_{HH}$=9.0, $^3J_{HH}$=5.4, trans C*H*O), 3.26 (dd, $^3J_{HH}$=9.1, $^3J_{HH}$=6.8, C*H*N), 1.09 (d, $^3J_{HH}$=6.4, Me), 0.38 (d, $^3J_{HH}$=6.6, Me), 0.22 (m, C*H*-i-Pr). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 30.1 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 108.7 (s, *C*-2), 102.9 (s, *C*-1), 74.3 (s, *C*HO), 73.4 (s, *C*HN), 67.6 (s, *C*-3), 30.6 (s,*C*H−i-Pr), 22.3 (s, Me), 17.6 (s, Me). Minor isomer (exo) ^1H NMR (CD_2Cl_2, 298 K, 400 MHz): 6.54 (m, *H*-2), 5.63 (t, $^3J_{HH}$=11.4, $^3J_{PH}$=9.4, *H*-1), 4.62 (d, $^3J_{HH}$=11.7, *H*-3), 4.25 (m, C*H*N), 3.94 (dd, $^2J_{HH}$=9.4, $^3J_{HH}$=5.0, trans C*H*O), 3.09 (t, $^2J_{HH}$=9.5, $^3J_{HH}$=6.3, cis C*H*O), 2.15 (m, C*H*−i-Pr), 0.97 (d, $^3J_{HH}$=6.9, Me), 0.09 (d, $^3J_{HH}$=6.7, Me). ^{31}P NMR (CD_2Cl_2, 298 K, 400 MHz): 29.7 (s). ^{13}C NMR (CD_2Cl_2, 298 K, 400 MHz): 109.9 (s, *C*-2), 89.7 (s, *C*-1), 82.6 (s, *C*-3), 72.3 (s, *C*HN), 71.2 (s, *C*HO), 29.6 (s, *C*H−i-Pr), 19.4 (s, Me), 13.4 (s, Me) Complex **15** was prepared by the same method using $[PdCl(\eta^3\text{-}PhCHCHCHCH_3)]_2$ (27.3 mg, 0.05 mmol). Suitable single crystals were obtained by recrystalization from $CHCl_3$−hexane. Yield: 76 mg, 81%. Anal. Calcd for $C_{49}H_{43}NO_4F_3PSPd$ (936.34): C, 62.86; H, 4.63; N, 1.50. Found: C, 62.57; H, 4.84; N, 1.53. MS (FAB): 786 ($M^+ - CF_3SO_3$, 100), 655 ($M^+ - (PhCHCHCHCH_3 + CF_3SO_3)$ (32), 437 (13), 364 (58).

Allylic Alkylation. $[PdCl(\eta^3\text{-}PhCHCHCHPh)]_2$ (1.34 mg, 0.002 mmol) and **1** (2.75 mg, 0.005 mmol) in CH_2Cl_2 (2 mL) were stirred for 20 min. (*E*)-3-Acetoxy-1−3-diphenyl-1-propene (50.4 mg, 0.2 mmol), dimethyl malonate (68 μL, 0.6 mmol), BSA (148 μL, 0.6 mmol), and KOAc (1 mg) were added, and the reaction mixture was stirred at room temperature for 2 h. The mixture was diluted with ether, washed with water and brine, and then dried ($MgSO_4$). The solvent was evaporated and the oily residue was purified by column chromatography (20% ethyl acetate in hexane) Yield: 64 mg, 99%.

Allylic Amination. $Pd_2(\eta^3\text{-}C_3H_5)_2Cl_2$ (0.74 mg, 0.002 mmol) and **1** (2.75 mg, 0.005 mmol) in THF (0.7 mL) were stirred for 1 h at 40 °C. (*E*)-3-Acetoxy-1,3-diphenyl-1-propene (50.4 mg, 0.2 mmol) and benzylamine (44 μL, 0.4 mmol) in THF (0.7 mL) were added, and the reaction mixture was stirred at 40 °C for 15 h. The resulting mixture was diluted with ether, washed with water and brine, and then dried over $MgSO_4$. The solvent was evaporated and the oily residue purified by column chromatography on silica gel using 20% ethyl acetate in hexane. Yield: 59 mg, 98.6%.

Heck Reaction. Palladium acetate (3.4 mg, 0.015 mol, 3 mol %) and **1** (17 mg, 0.030 mmol) in benzene (3 mL) were stirred for 20 min.[10] Phenyl triflate (81 μL, 0.5 mmol, 1 equiv), *N*,*N*-diisopropylethylamine (261 μL, 1.5 mmol, 3 equiv), and 2,3-dihydrofuran (189 μL, 2.5 mmol, 5 equiv) were added. The solution was stirred at 40 °C for 4 days under argon. The reaction mixture was cooled, diluted with pentane (200 mL), and filtered to remove solid materials. The solution was then washed with 0.1 N HCl and saturated $NaHCO_3$ and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel and eluted with 5% ethyl acetate in hexane. The product is 2-phenyl-3,4-dihydrofuran (R_f = 0.28, 62 mg, 85%). The ee (73.8%) was determined by HPLC using a Chira Grom column (eluent: Hex/i-PrOH, 99:1; flow rate 0.3 mL/min).

Acknowledgment. P.S.P. thanks the Swiss National Science Foundation and the ETH Zurich for financial support. A.A. thanks MURST for partial support. We also thank Johnson Matthey for the loan of $PdCl_2$.

Supporting Information Available: Text giving experimental details and a full listing of crystallographic data for $Pd_2(dba)_3$ and **14** and **15**, including tables of positional and isotropic equivalent displacement parameters, calculated positions of the hydrogen atoms, anisotropic displacement parameters, and bond distances and angles. There are three ORTEP plots showing the disorder of the (dba) ligands. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980920E