Synthesis and X-ray Crystal Structures of Palladium(II) and Platinum(II) Complexes of the PCP-Type Chiral Tridentate Ligand (1*R*,1′*R*)-1,3-Bis[1-(diphenylphosphino)ethyl]benzene. Use in the Asymmetric Aldol Reaction of Methyl Isocyanoacetate and Aldehydes

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Enantiomerically pure (1*R*,1′*R*)-1,3-bis[1-(diphenylphosphino)ethyl]benzene (**4**) has been obtained for the first time. The key step involves in situ tosylation of chiral (1*S*,1′*S*)-dimethyl-1,3-benzenedimethanol (**6**) followed by nucleophilic attack with $LiPPh_2(BH_3)$ to give [(1*R*,1′*R*)-1,3-bis[1-(diphenylphosphino)ethyl]benzene]−bisborane (**7**). The bisborane-protected phosphine can be easily handled and purified before deprotecting with $HBF_4{\cdot}OMe_2$ to give the title compound. [(1*R*,1′*R*)-2,6-bis[1-(diphenylphosphino)ethyl]phenyl]chloropalladium(II) (**9**) and the platinum(II) analogue (**8**) were synthesized through reaction of the chiral PCP-type ligand with $PdCl_2(PhCN)_2$ and $[Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-}CH_2C(CH_3)CH_2)_2]$, respectively, and their X-ray crystal structures were determined. Removal of chloride with AgOTf provided an active catalyst species for the asymmetric aldol reaction of methyl isocyanoacetate and aldehydes.

Introduction

Transition metal complexes with PCP-type tridentate ligands have been studied extensively since the first report in the early 1970s.[1] Metal insertion into the C−H aryl bond can be facilitated by the adjacent phosphines (Figure 1), thus providing structurally well-defined metal complexes with many interesting properties. The PCP tridentate ligands and related NCN and SCS ligands have been reported.[2−4] Metal complexes of these ligands have been used for activation of hydrocarbons,[5] Kharasch addition,[6] dehydrogenation,[7] reduction of CO_2,[8] and even self-assembly of one-dimensional polymeric organometallic structures.[9] Recently, palladium complexes with a PCP ligand have shown remarkable activity for the Heck reaction.[10]

Despite considerable progress, very little attention has been devoted to exploring chiral variants of these tridentate ligands for asymmetric catalytic reactions. Recently, NCN-type ligands containing chiral oxazolines[11] or pyrrolidines[12] have been synthesized (Figure 2). These ligands have been used in several asymmetric transformations such as the Diels−Alder, aldol, and Michael reactions, as well as cyclopropanation and Kharasch addition. However, the enantioselectivities

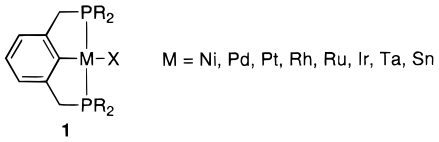

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Figure 1. Metal complexes with PCP ligands.

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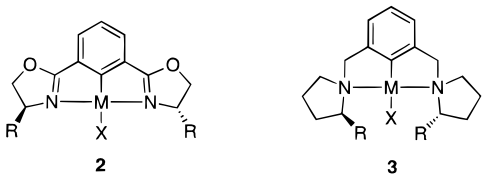


Figure 2. Chiral NCN ligands.

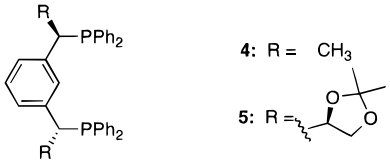


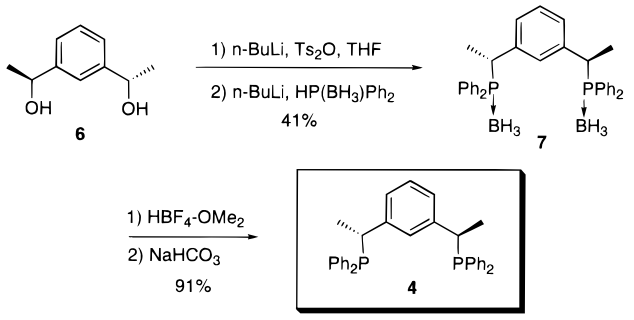
Figure 3. Chiral PCP ligands.

obtained with these ligands have been very low. Attempts directed toward the synthesis of chiral PCP-type ligand **4** (Figure 3) by Venanzi et al. were unsuccessful. Instead they reported the first chiral PCP-type ligand **5** through a tedious synthetic route and used this for the Pt-catalyzed asymmetric aldol reaction.[13] Herein we report the facile synthesis of a chiral PCP ligand **4** based on a general method developed in our laboratory.[14] X-ray crystal structures of Pd(II) and Pt(II) complexes of **4** were determined along with studies of the asymmetric aldol reaction between methylisocyanoacetate and aldehydes.

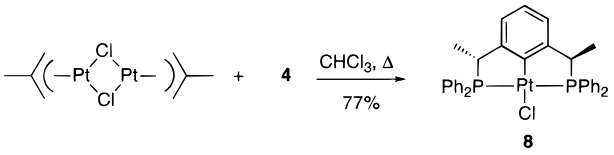
Results and Discussion

Ligand Synthesis. The synthesis of ligand **4** is outlined in Scheme 1. The chiral diol **6** was made by asymmetric reduction of 1,3-diacetylbenzene (>99% ee with ca. 5% meso) according to a procedure reported by H. C. Brown.[15] Chiral diol **6** was then converted to the borane-protected phosphine **7** by in situ tosylation with Ts_2O followed by nucleophilic attack with $LiPPh_2(BH_3)$. The borane-protected phosphine **7** was then recrystallized from EtOAc to remove the meso compound. The BH_3 groups were then cleanly removed to give the enantiomerically pure phosphine **4**.[16]

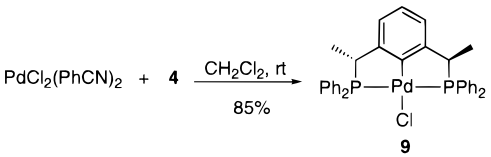
Scheme 1. Synthesis of Ligand 4



Scheme 2. Synthesis of Pt(II) Complex 8



Scheme 3. Synthesis of Pd(II) Complex 9



Preparation of the Pt(II) Complex [4·PtCl], 8, and the Pd(II) Complex [4·PdCl], 9. According to literature reports,[4c] cyclometalation of **4** is quite facile when an appropriate metal precursor is employed. For the formation of complex **8**, refluxing **4** with $[Pt_2(\mu\text{-}Cl)_2(\eta_3\text{-}CH_2C(CH_3)CH_2)_2]$ in $CHCl_3$ for 30 min delivered the desired product as an air-stable white solid (73%, Scheme 2). Single crystals suitable for X-ray analysis were obtained by recrystallization from THF. Complex **9** was easily prepared by mixing ligand **4** with $PdCl_2(PhCN)_2$ in CH_2Cl_2 at room temperature for 24 h.[4a] The desired product was obtained as a yellow air-stable powder (85%, Scheme 3). Single crystals suitable for X-ray analysis were obtained from CH_2Cl_2.

X-ray Crystal Structures of [(1*R*,1′*R*)-2,6-Bis-[1-(diphenyl-phosphino)ethyl]phenyl]chloroplatinum (8) and -palladium (9). The X-ray crystal structures of both Pd(II) and Pt(II) complexes were obtained, and their structural features are almost identical. A summary of selected data is given in Table 1, and ORTEP representations for complexes **8** and **9** are given in Figure 4.

Both the Pd and Pt complexes have a distorted square planar geometry. The P(1)−Pd−P(2) and C(1)−Pd−Cl bond angles are 162.5° and 177.2°, respectively, while the P(1)−Pt−P(2) and C(1)−Pt−Cl bond angles are 164.3° and 176.9°, respectively. The slightly larger P(1)−Pt−P(2) angle is most likely due to the shorter Pt−C bond distance of 2.015 Å compared to 2.030 Å for the Pd−C bond. Two chelated five-membered rings consisting of P(1)−C(13)−C(15)−C(16)−M and P(2)−C(21)−C(17)−C(16)−M exist in compounds **8** and **9**. The methyl groups on C(21) and C(13) located in the axial position of the puckered five-membered chelate rings result in a C_2-symmetric metal complex with the phenyl groups on the phosphines being in pseudoaxial and pseudoequatorial positions, respectively. This struc-

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds 8 and 9

	8	9
M−C(16)	2.030(4)	2.015(4)
M−P(2)	2.2742(11)	2.2702(12)
M−P(1)	2.2864(11)	2.2746(11)
M−Cl	2.3773(12)	2.3855(12)
C(16)−M−P(2)	81.11(12)	82.00(13)
C(16)−M−P(1)	81.49(12)	82.31(12)
P(2)−M−P(1)	162.53(4)	164.25(4)
C(16)−M−Cl	177.22(12)	176.87(12)
P(2)−M−Cl	97.89(5)	96.78(5)
P(1)−M−Cl	99.57(4)	98.96(4)
C(13)−P(1)−M	101.9(2)	102.6(2)
C(15)−C(13)−P(1)	104.9(3)	105.7(3)
C(16)−C(15)−C(13)	120.1(4)	119.5(4)
C(17)−C(16)−M	121.0(3)	121.2(3)
C(15)−C(16)−M	120.2(3)	120.9(3)
C(16)−C(17)−C(21)	119.2(4)	118.6(4)
C(17)−C(21)−P(2)	104.9(3)	105.9(3)
C(21)−P(2)−M	102.8(2)	102.4(2)

tural arrangement is confirmed by the observation of two sets of resonances in the ^{1}H and ^{13}C NMR spectra corresponding to the diastereotopic phenyl groups. The P(1)−M−P(2) angles are 162.5° for **8** and 164.3° for **9**, indicating a trans P−M−P arrangement. The chiral pocket formed by the array of phenyl groups on the phosphines is deeper than most bidentate chiral phosphines (P−M−P angle is ca. 90°), which is key for some asymmetric reactions.

Asymmetric Aldol Reaction between Methyl Isocyanoacetate and Aldehydes.[17] The aldol reaction is one of the fundamental organic transformations for which highly enantioselective catalytic versions have been developed using various strategies. In 1986, Ito, Sawamura, and Hayashi first reported an efficient Au catalyst with a chiral ferrocenylphosphine bearing pendant amines for the asymmetric aldol reaction of isocyanoacetate and aldehydes.[17a] This reaction gave trans isomers of oxazolines as the major product with high enantioselectivities. The secondary interaction between the pendant amines and substrates is important for the high enantioselectivity. Metal complexes with other chiral bidentate phosphine ligands such as CHIRAPHOS, DIOP, and BINAP give almost racemic oxazolines. A rationale for this observation is that enolates derived from isocyanoactetate in the aldol reaction are too far away from the chiral pocket formed by simple cis-bidentate phosphines during bond formation without a pendant chiral amine in the metal complex. Therefore, utilization of chiral PCP-type ligands with a deeper chiral pocket around the metals may perform highly enantioselective aldol reactions without the secondary interaction between ligands and substrate. Indeed, Venanzi et al.[13] have successfully demonstrated that a Pt complex with **5** can facilitate the asymmetric aldol reaction between isocyanoacetate and aldehydes, giving ee's of 13−65% for the trans and 3−32% for the cis oxazolines. Since they have failed to make the simple chiral PCP ligand **4**, it is worthwhile to study the aldol reaction facilitated by metal complexes with this ligand.

Extensive studies were carried out using **9** as the catalyst precursor. Optimizations of the reaction conditions were performed using benzaldehyde as the substrate and diisopropylethylamine as base. The active catalyst species was formed by abstracting the chloride with silver triflate, hence forming a vacant site for binding of methyl isocyanoacetate. Initial studies showed that the Pd catalyst **9** gave much better reactivity and enantioselectivity than the Pt catalyst **8**. Therefore, all results reported herein are with the Pd catalyst **9**.

The effects of solvents on the reaction were investigated. It was discovered that the reaction in THF gave higher enantioselectivity (24% trans, 67% cis) than in CH_2Cl_2 (18% trans, 36% cis) or toluene (9% trans, 49% cis). A variety of organic bases were investigated (i.e., proton sponge, DMAP, pyridine, ethanolamine, morpholine, dipyridyl), and it was found that they had very little effect on the enantioselectivity. Other factors such as concentration, amount of base used, addition rate, and order of substrate addition had no significant effect on the enantioselectivity.

Under optimized conditions (1 mol % **9**, 100 mol % methylisoyanoacetate, 110 mol % aldehyde, and 10 mol % diisopropylethylamine in THF), the asymmetric aldol reaction was performed with a variety of aldehydes (Table 2). For most aromatic aldehydes, the ee's for the cis isomer of oxazolines do not change dramatically and there is no significant trend. The highest ee's (>70%) were obtained with the trisubstituted aromatic aldehyde (entry 17). Interestingly, higher enantioselectivity with aliphatic aldehydes (entries 18 and 19) is observed compared with aromatic aldehydes in their cis product. The trans isomers of oxazolines for most aldehydes are major products and have much lower ee's.

Compared to our system, Venanzi and co-workers obtained higher ee's for the trans isomers of oxazolines (13−65%) and lower ee's for the cis isomers (3−32%) using a Pt complex of **5** as the catalyst.[13] Also their system was influenced more by the rate of addition, solvent, and concentration of substrates. Although ligands **4** and **5** share a similar skeleton, the subtle differences in the ligand structures seem to have a dramatic influence on the stereochemical outcome of the reaction.

In summary, we have developed a general method for the synthesis of chiral PCP-type ligands. This new structural motif can lead to many applications for asymmetric catalytic reactions. Future effort will focus on isolating complexes of ligand **4** with other transition metals and applying these catalysts to various asymmetric transformations. We also continue to develop other tridentate ligands by changing the aromatic backbone so that highly enantioselective C−C bond forming reactions can be realized.

(17) For some reports on the asymmetric aldol reaction of isocyanoacetates and aldehydes see: (a) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405. (b) Ito, Y.; Sawamura, M.; Hayashi, T. *Tetrahedron Lett.* **1987**, *28*, 6215. (c) Ito, Y.; Sawamura, M.; Shirakawa, E.; Hayashizaki, K.; Hayashi, T. *Tetrahedron Lett.* **1988**, *29*, 235. (d) Ito, Y.; Sawamura, M.; Kobayashi, M.; Hayashi, T. *Tetrahedron Lett.* **1988**, *29*, 6321. (e) Ito, Y.; Sawamura, M.; Hamashima, H.; Emura, T.; Hayashi, T. *Tetrahedron Lett.* **1989**, *30*, 4681. (f) Togni, A.; Pastor, S. D. *J. Org. Chem.* **1990**, *55*, 1649. (g) Hayashi, T.; Sawamura, M.; Ito, Y. *Tetrahedron* **1992**, *48*, 1999. (h) Nesper, R.; Pregosin, P. S.; Puntener, K.; Worle, M. *Helv. Chim. Acta* **1993**, *76*, 2239. (i) Soloshonok, V. A.; Hayashi, T. *Tetrahedron Lett.* **1994**, *35*, 2713. (j) Soloshonok, V. A.; Hayashi, T. *Tetrahedron: Asymmetry* **1994**, *5*, 1091. (k) Soloshonok, V. A.; Kacharov, A. D.; Hayashi, T. *Tetrahedron* **1996**, *52*, 245.

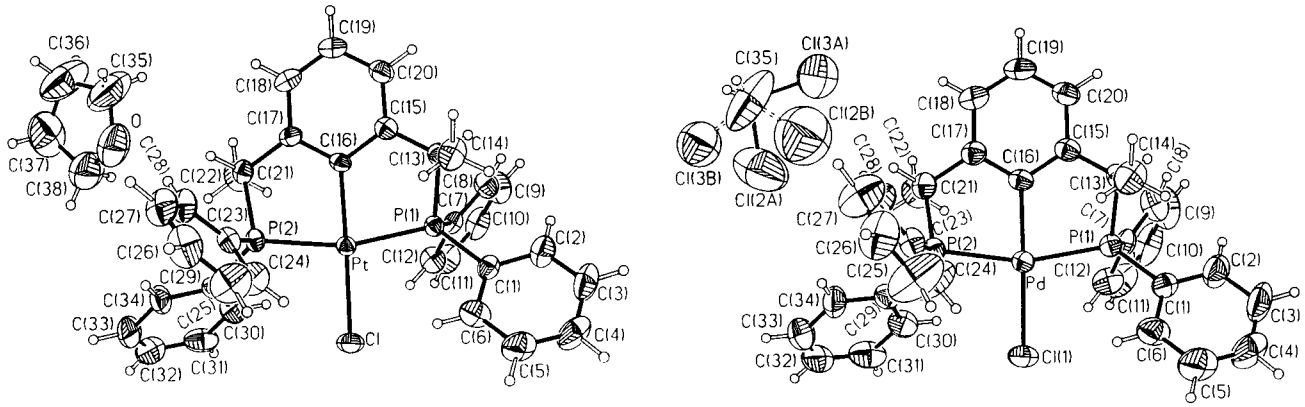
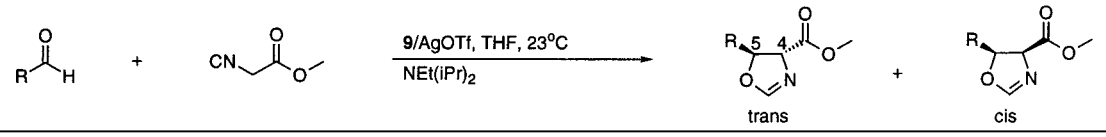
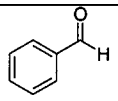
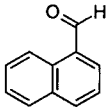
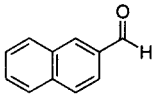
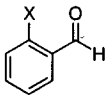
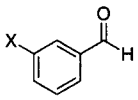
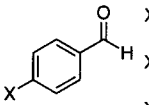
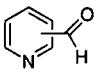
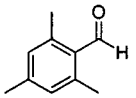
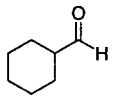
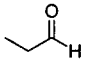


Figure 4. ORTEP representation of complexes **8** and **9**.

Table 2. Aldol Reaction of Methylisocyanoacetate and Aldehydes



Entry	Aldehyde	Yield[%]ᵃ (time[hrs.])	%eeᵇ Trans	%eeᵇ Cis	Trans/Cisᶜ
1[d]		85(12)	24 (4R,5S)	67 (4S,5S)	78/22
2[e]		87(72)	31	77	78/22
3		73(24)	4	53	88/12
4		81(24)	23	66	81/19
5	 X=CH_3	90(12)	3	50	79/21
6	X=Cl	90(6)	19	49	67/33
7	$X=NO_2$	82(6)	1	56	45/55
8	 X=CH_3	87(24)	12	60	80/20
9	X=Cl	91(24)	15	42	83/17
10	$X=NO_2$	73(6)	12	45	72/28
11	 X=CH_3	80(24)	11	61	82/18
12	X=Cl	87(24)	30	65	75/25
13	$X=NO_2$	60(4)	21	57	74/26
14	 *o*	82(8)	0	53	74/26
15	*m*	80(6)	16	61	71/29
16	*p*	82(6)	16	49	79/21
17		84(72)	26	71	86/14
18		97(24)	11	74	72/28
19		91(48)	30	70	91/9

a) Isolated yield by bulb to bulb distillation, See Ref. 18. b) Determined by GC analysis. c) Determined by ^{1}H NMR by integration of the methyl ester protons as well as by G.C. d) See Ref. 19. e) Reaction was run at 0 deg.

Experimental Section

All manipulations were carried out under N_2 using standard Schlenk techniques. Solvents were degassed with N_2 and dried using standard procedures. Column chromatography was performed using 200−400 mesh silica gel supplied by Natland International Corporation. The aldehydes and methylisocyanoacetate were received from Aldrich or Acros and used without further purification. The palladium and platinum catalyst precursors,[20] as well as chiral diol **6**,[15] were made according to reported procedures.

All melting points were determined in open capillary tubes and are uncorrected. ^{1}H NMR spectra were recorded on Bruker WP-200, AM-300, and WM-360 spectrometers. Chemical shifts are reported in ppm downfield of TMS using the solvent as internal standard ($CDCl_3$, δ 7.26). ^{13}C NMR spectra were recorded with complete proton decoupling and are reported in ppm downfield of TMS with solvent as internal standard ($CDCl_3$, δ 77.0). MS data was recorded on a Kratos mass spectrometer MS 9/50 for low and high resolution. GC analysis was carried out on Hewlett-Packard 5890 and 6890

(18) It was observed that during distillation of the oxazoline products slight decomposition occurred. This caused a slightly lower than expected isolated yield. Prior to distillation TLC and ^{1}H NMR showed the reaction proceeded very cleanly and nearly quantitatively to the desired products.

(19) Absolute configuration was determined by separating the trans and cis isomers by silica gel chromatography and comparing the optical rotations with those previously reported. See ref 17a.

(20) (a) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 216. (b) Mabbott, D. J.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 294.

gas chromatographs using a 10 m Supelco Chiral Select 1000, a 30 m β-Dex 225, and a Chirasil-Val III FSOT column.

[(1*R*,1′*R*)-1,3-Bis[1-(diphenylphosphino)ethyl]benzene]−Bisborane, 7. To a stirred solution of diol **6** (1.0 g, 6.0 mmol, 99% ee with 5% meso) in THF (25 mL) at −78 °C was added dropwise a 1.6 M solution of n-BuLi in hexane (8.27 mL, 13.2 mmol). The resulting pink suspension was warmed slowly to −20 °C followed by addition of a Ts_2O (4.32 g, 13.2 mmol) solution in THF (20 mL). The reaction mixture was then allowed to stir at −20 °C for 20 h, resulting in a white suspension. In a separate flask, a solution of $HPPh_2(BH_3)$ (2.65 g, 13.3 mmol) in THF (15 mL) was cooled to −78 °C, and a 1.6 M solution of n-BuLi in hexane (7.52 mL, 12.0 mmol) was added dropwise. The resulting light yellow solution was brought slowly to room temperature and then added dropwise to the previously formed ditosylate solution at −20 °C. The reaction was maintained at −20 °C for 18 h and then warmed to room temperature. Workup required addition of water and extraction with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was loaded on a silica gel column, eluting with CH_2Cl_2/hexane (1:1) to give the desired product. Further purification by recrystallization from EtOAc removed traces of the meso compound and gave enantiomerically pure product **7** as white crystals (1.3 g, 41%): mp 157−159 °C; $[\alpha]_D = +224.44$ ($CHCl_3$, $c = 1.08$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.49 (dd, ^3J(HH) 7.2 Hz, ^3J(PH) 16.2 Hz, 6H, CH_3), 3.69 (qd, ^3J(HH) 7.2 Hz, ^2J(PH) 15.13 Hz, 2H, CH), 6.89−7.88 (m, 24H, C_6H_4 and C_6H_5); ^{13}C NMR (90 MHz, $CDCl_3$) δ 16.9 (s, 2C, CH_3), 37.5 (d, ^1J(PC) 31.7 Hz, 2C, CH), 127.6−138.2 (12 different aromatic C's); ^{31}P NMR (145 MHz, $CDCl_3$) δ 22.03. HRMS calculated for $C_{34}H_{38}B_2P_2$ (M^+) 530.2635; found: 530.2698.

(1*R*,1′*R*)-1,3-Bis[1-(diphenylphosphino)ethyl]benzene, 4. To a solution of **7** (0.58 g, 1.1 mmol) in CH_2Cl_2 (13 mL) at −5 °C was added HBF_4·OMe_2 (1.33 mL, 10.9 mmol). The reaction was warmed slowly to room temperature and stirred for 18 h. The reaction was monitored using ^{31}P NMR of the crude reaction mixture. Workup required addition of CH_2Cl_2 (10 mL) and transfer to a degassed saturated aqueous $NaHCO_3$ solution via cannula. The resulting mixture was stirred vigorously for ca. 15 min, and the organic layer was removed via cannula. The $NaHCO_3$ phase was extracted twice with CH_2Cl_2. The combined organic layers were washed with a brine solution, dried over Na_2SO_4, and removed under reduced pressure to give the product as a sticky white solid (0.55 g, 91%): ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.36 (dd, ^3J(HH) 7.2 Hz, ^3J(PH) 14.8 Hz, 6H, CH_3), 3.46 (qd, ^3J(HH) 7.2 Hz, 2H, CH), 6.98−7.13 (m, 14H), 7.40−7.42 (m, 6H), 7.60−7.64 (m, 4H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 20.2 (d, ^2J(PC) 20.4 Hz, 2C, CH_3), 39.4 (d, ^1J(PC) 12.2 Hz, 2C, CH), 126.3−143.7 (12 different aromatic C's); ^{31}P NMR (145 MHz, $CDCl_3$) δ 2.39.

[(1*R*,1′*R*)-2,6-Bis[1-(diphenylphosphino)ethyl]phenyl]-chloroplatinum(II), 8. To a solution of ligand **4** (100 mg, 0.2 mmol) in $CHCl_3$ (4 mL) was added [$Pt_2(\mu$-Cl)$_2(\eta^3$-$CH_2C(CH_3)CH_2)_2$] (57 mg, 0.1 mmol), and the reaction was heated at reflux for 30 min. After cooling to room temperature, the solvent was removed in vacuo and the crude solid was purified by recrystallization from THF/hexane, giving the desired product as white crystals (0.11 g, 77%): mp 278−279 °C; $[\alpha]_D = -297.8$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.15 (m, 6H, CH_3), 4.07 (m, 2H, CH), 7.10 (m, 3H, C_6H_3), 7.36−7.44 (m, 12H), 7.77−7.92 (m, 8H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 21.2 (s, 2C, CH_3), 46.3 (m, 2C, CH), 122.3−153.1 (12 different aromatic C's); ^{31}P NMR (145 MHz, $CDCl_3$) δ 47.32 (s, ^1J(PtP) = 2975.5 Hz). HRMS calculated for $C_{34}H_{31}P_2PtCl$ (M^+) 731.1237; found 731.1232.

[(1*R*,1′*R*)-2,6-Bis[1-(diphenylphosphino)ethyl]phenyl]-chloropalladium(II), 9. To a solution of ligand **4** (502 mg, 1.0 mmol) in CH_2Cl_2 (15 mL) was added $PdCl_2(PhCN)_2$ (383 mg, 1.0 mmol). The resulting orange solution was stirred at room temperature for 24 h. The reaction was then reduced to one-third of its volume, and absolute ethanol was added to precipitate the product. Filtration gave the desired product as a yellow powder (418 mg, 85%): mp 249−252 °C dec; $[\alpha]_D = -323.6$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.19 (m, 6H, CH_3), 4.04 (m, 2H, CH), 7.10 (m, 3H), 7.34−7.45 (m, 12H), 7.70−7.74 (m, 4H), 7.95−7.97 (m, 4H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 22.1 (s, 2C, CH_3), 46.7 (m, 2H, CH), 122.5−156.8 (12 different aromatic C's); ^{31}P NMR (145 MHz, $CDCl_3$) δ 46.5. HRMS calculated for $C_{34}H_{31}P_2PdCl$ (M^+) 642.0624; found 642.0634.

A Typical Procedure for the Pd(II)-Catalyzed Aldol Reaction. A solution of 7 mg (0.011 mmol, 1.0 mol %) of **9** and 3 mg (0.011 mmol) of AgOTf in CH_2Cl_2 (2 mL) was stirred for ca. 30 min at room temperature. The resulting cloudy solution was filtered through Celite, and the solvent was removed under reduced pressure to give the active catalyst. The catalyst was then dissolved in EtOAc and passed through a plug of silica gel to remove any excess AgOTf. After removal of EtOAc, the catalyst was taken up in THF (6 mL), and methylisocyanoacetate (110 μL, 1.1 mmol) was added followed by introduction of diisopropylethylamine (19 μL, 0.11 mmol) and aldehyde (1.1 mmol). The reaction was monitored by TLC (EtOAc/hexane = 1:1, visualized with $KMnO_4$). After removal of solvent, the pure product was obtained by bulb-to-bulb distillation under reduced pressure (0.1 mmHg).

X-ray Crystallographic Determinations and Refinements. Colorless blocklike crystals of **8**·CH_2Cl_2 suitable for X-ray diffraction were grown from CH_2Cl_2, while those of **9**·THF were grown from THF. All crystals were mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo Ka radiation on an Enraf-Nonius CAD4 computer controlled κ axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $34° < 2\theta < 36°$, measured by the computer-controlled diagonal slit method of centering. As a check on crystal quality, an ω/θ profile analysis of reflections was carried out, which showed that $\Delta\omega$ was less than 0.55° and $\Delta\theta$ was less than 0.60°, indicating good crystal quality. From the following systematic absence, $0k0$, $k = 2n + 1$, and from the results of the final structure refinement, the space group was determined to be $P2_1$.

The data were collected at a temperature of 20 °C using the $\omega/2\theta$ scan technique to a maximum 2θ of 50.0°. The scan range (in deg) was determined as a function of θ to correct for the separation of the Kα doublet; the scan width was calculated as follows: ω scan width = $0.65° + 0.35° \tan\theta$. Moving-crystal static-background counts were made by scanning an additional 25% above and below this range. Thus the ratio of peak counting time to background counting time was 2:1. The counter aperture was also adjusted as a function of θ. The horizontal aperture width ranged from 2.0 to 2.4 mm; the vertical aperture was set at 4.0 mm. The diameter of the incident beam collimator was 0.8 mm, and the crystal-to-detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector; the attenuator factor was 19.455.

As a check on crystal and electronic stability, three representative reflections were measured every 120 min of X-ray exposure. For compound **8** an intensity loss of 65.9% was found for the three standard reflections during 69.1 h of X-ray exposure for the data collection. Compound **9** showed an intensity loss of 27.4% over 42.1 h of X-ray exposure. Therefore a linear decay correction was made to the data.

Table 3. Crystal Data and Structure Refinement for Compounds 8 and 9

	9·CH_2Cl_2	**8**·THF
formula	$C_{35}H_{33}Cl_3P_2Pd$	$C_{38}H_{39}ClOP_2Pt$
fw	728.30	804.17
crys sys	monoclinic	monoclinic
space group	$P2_1$	$P2_1$
unit cell dimensions (Å, deg)	$a = 9.8710(5)$	$a = 9.956(2)$
	$b = 15.1171(11)$	$b = 14.7439(13)$
	$c = 11.5993(8)$	$c = 11.892(2)$
	$\beta = 98.795(5)$	$\beta = 97.810(9)$
volume (Å^3)	1710.5(2)	1729.4(5)
Z	2	2
density (calcd, g/cm^3)	1.414	1.544
F(000)	740	800
wavelength (Å)	0.710 73	0.710 73
abs coeff (mm^{-1})	0.893	4.255
crystal size	0.41 × 0.22 × 0.18 mm	0.40 × 0.28 × 0.25 mm
temp (K)	293(2)	293(2)
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
θ range for data collection	2.09−24.96°	2.06−24.97°
index ranges	−11 h 0, −17 k 17, −13 l 13	−11 h 11, −17 k 17, 0 l 14
scan method	$\theta/2\theta$	$\theta/2\theta$
scan width (in ω)	0.65°+ 0.35° tan θ	0.65° + 0.35° tan θ
no. of total data collected	6371	6374
no. of unique data	6005 [R(int) = 0.0139]	6067 [R(int) = 0.0381]
no. of unique obsd data [$I > 2\sigma(I)$]	5716	5863
max. and min. transmission	0.9980 and 0.9500	0.9988 and 0.8932
weighting scheme	σ weight	σ weight
no. of data/restraints/parameters	6005/7/379	6067/1/388
GOF on F^2	1.262	1.095
final R indices [$I > 2\sigma(I)$]	R1 = 0.0325, wR2 = 0.0820	R1 = 0.0218, wR2 = 0.0551
R indices (all data)	R1 = 0.0355, wR2 = 0.0859	R1 = 0.0234, wR2 = 0.0569
largest diff peak and hole (e Å^{-3})	0.586 and −0.529	0.379 and −0.428

SDP software was used to process intensity data on a VAXstation 3200 computer.[21] Lorentz and polarization corrections were applied to the data. An empirical absorption correction based on a series of ψ-scans was applied to the data.

Structure solution and refinement were performed on a PC by using the SHELXTL package.[22] Most of the nonhydrogen atoms were located by the direct method; the remaining nonhydrogen atoms were found in succeeding difference Fourier syntheses. Least-squares refinement was carried out on F^2 for all reflections. After all nonhydrogen atoms were refined to convergence, difference Fourier synthesis located all hydrogen atoms of the complex molecule. In the final refinement all hydrogen atoms were treated with riding models. All reflections, including those with negative intensities, were included in the refinement, and the $I > 2\sigma(I)$ criterion was used only for calculating R_1. The weighted R factors (wR) are based on F^2 and conventional R factors (R) on F with F set to zero for negative intensities. All esd's were estimated by the use of the full covariance matrix. The cell esd's were included in the estimation of esd's of bond distances and angles.

For compound **8** refinement on its enantiomorph yielded consistently higher values for the above four convergence factors, 0.0367, 0.0949, 0.0397, and 0.0990, and a detrimental value of 1.04(3) for the Flack absolute structure parameter. For compound **9** the convergence factors were 0.0562, 0.1518, 0.058, and 0.1527, with a detrimental value of 1.04(2) for the Flack absolute structure parameter. These data fully confirmed the correctness of the above established enantiomorphs.[23] All relevant crystallographic data and refinements are outlined in Table 3.

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Supporting Information Available: Spectra of new compounds and tables of crystal structure parameters and details of data collection, bond angles and distances, and atomic positional and thermal parameters and ORTEP diagrams of **8** and **9** (47 pages). Ordering information is given on any current masthead page.

OM980461H

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