JOC*Note*

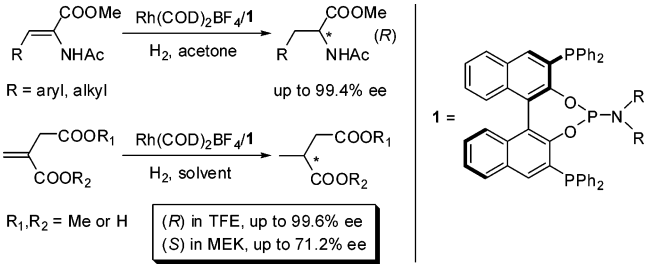
Highly Enantioselective Hydrogenation of α-Dehydroamino Esters and Itaconates with Triphosphorous Bidentate Ligands and the Unprecedented Solvent Effect Thereof

Weicheng Zhang and Xumu Zhang*

Department of Chemistry, 104 Chemistry Building, The Pennsylvania State University, University Park, Pennsylvania 16802

xumu@chem.psu.edu

Received October 30, 2006



An X-ray diffraction experiment revealed an interesting triphosphorous bidentate coordination in a Pd(II) complex of a phosphine-phosphoramidite ligand **1**, which showed excellent enantioselectivity (up to 99.4% ee) in Rh-catalyzed hydrogenation of α-dehydroamino esters in acetone. A dramatic solvent effect was found in the hydrogenation of itaconates, which induces opposite chiralities of the product with the same catalytic system by the use of different solvents (e.g., 99.6% ee (*R*) in TFE vs 71.2% ee (*S*) in methyl ethyl ketone).

The exploration of new effective ligands is a continuous challenge in transition-metal-mediated asymmetric hydrogenation.[1] Recent mechanistic investigation of monodentate ligands,[2] in association with the successful application of combinatorial strategy in catalyst screening,[3] inspired us to develop a new family of air-stable modular phosphine-phosphoramidite ligands **1**.[4,5] In this communication, we presented structural characterization of a Pd/**1a** complex by X-ray diffraction and the expanded synthesis of **1** for highly enantioselective hydrogenation of α-dehydroamino esters and itaconates (up to 99.6% ee). Interestingly, we have observed a strong solvent effect in the present catalytic system, in that a change of solvent could result in opposite chiralities of the product.

Previously, we demonstrated that **1** are excellent ligands for Rh-catalyzed hydrogenation of aryl enamides, especially the challenging ortho-substituted phenyl enamides and 1-naphthyl enamide.[4] NMR spectroscopy analysis revealed a highly preferential chelating of rhodium with only two phosphorus donors, leaving a third uncoordinated phosphine. Although computational study provided an approximate description of such a configuration, direct structural information is necessary to establish the proposed "triphosphorous-bidentate" feature and gain insight into the chiral coordination environment around the metal center. Thus, a single crystal of the $PdCl_2$·**1a** complex was grown from CH_2Cl_2/hexane and subject to an X-ray diffraction experiment.[6] Consistent with NMR and computational results, the solved structure (Figure 1) revealed a well-defined chiral coordination environment around the square-planar d^8 palladium (Pd(1)), which incorporates two properly oriented P donors (P(1) and P(2)) within a six-membered chelation ring in the presence of a third spectator phosphine (P(3)). Fused to the chelation ring is a neighboring seven-membered ring (P(2)−O(2)−C(3)−C(12)−C(14)−C(13)−O(1)) that imposes the spatial arrangement of the two substituents (O(2) and N(1)) on P(2). As a consequence, O(2) is pulled back from the top right quadrant whereas the dimethylamino group ($Me_2N(1)$−) protrudes forward to block the bottom right quadrant. On the other side, two phenyl groups on P(1) accommodate quasiequatorial and quasiaxial conformations, respectively, the former occupying the top left quadrant and the latter leaving the bottom left quadrant accessible. According to the quadrant diagram rule,[7] such a chiral environment, albeit with C_1-symmetry, would lead to *R* selectivity in the hydrogenation of dehydroamino acids. Moreover, given the substitutes on the phosphoramidite site of more steric hindrance (such as the diisopropylamino group compared with the dimethylamino group) or restricted conformational mobility (such as the piperidyl group compared with the diethylamino group), the chiral environment could be modified. To testify this point, we have prepared a series of **1** in two standard methods (Scheme 1). ^{31}P NMR spectroscopy analysis confirmed that each ligand forms a well-defined triphosphorous bidentate complex with an equivalent amount of $Rh(COD)_2BF_4$ in various solvents, which were then applied in Rh-catalyzed hydrogenation of α-dehydroamino esters and itaconates.

(1) (a) Zhang, X. *Enantiomer* **1999**, *4*, 541. (b) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029.

(2) Reetz, M. T.; Meiswinkel, A.; Mehler, G.; Angermund, K.; Graf, M.; Thiel, W.; Mynott, R.; Blackmond, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 10305.

(3) (a) Reetz, M. T.; Sell, T.; Meiswinkel, A.; Mehler, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 790. (b) Reetz, M. T.; Mehler, G. *Tetrahedron Lett.* **2003**, *44*, 4593. (c) Reetz, M. T.; Mehler, G.; Meiswinkel, A. *Tetrahedron: Asymmetry* **2004**, *15*, 2165. (d) Reetz, M. T.; Li, X. *Tetrahedron* **2004**, *60*, 9709. (e) Reetz, M. T.; Ma, J.-A.; Goddard, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 412. (f) Pena, D.; Minnaard, A. J.; Boogers, J. A. F.; de Vries, A. H. M.; de Vries, J. G.; Feringa, B. L. *Org. Biomol. Chem.* **2003**, *1*, 1087. (g) Hoen, R.; Boogers, J. A. F.; Bernsmann, H.; Minnaard, A. J.; Meetsma, A.; Tiemersma-Wegman, T. D.; de Vries, A. H. M.; de Vries, J. G.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4209.

(4) Zhang, W.; Zhang, X. *Angew. Chem., Int. Ed.* **2006**, *45*, 5515.

(5) For other representative phosphine-phosphoramidite ligands in hydrogenation, see: (a) Francio, G.; Faraone, F.; Leitner, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 1428. (b) Hu, H.-P.; Zheng, Z. *Org. Lett.* **2004**, *6*, 3585. (c) Hu, H.-P.; Zheng, Z. *Org. Lett.* **2005**, *7*, 419. (d) Huang, J.-D.; Hu, X.-P.; Duan, Z.-C.; Zeng, Q.-H.; Yu, S.-B.; Deng, J.; Wang, D.-Y.; Zheng, Z. *Org. Lett.* **2006**, *8*, 4367.

(6) So far, we have not been able to obtain a suitable single crystal of Rh/**1** for the X-ray diffraction experiment. However, the structure of an isoelectronic Pd(II) complex may provide valuable coordination information as well. See, for example: Bayer, A.; Murszat, P.; Thewalt, U.; Rieger, B. *Eur. J. Inorg. Chem.* **2002**, 2614.

(7) (a) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106. (b) Gridnev, I. D.; Imamoto, T. *Acc. Chem. Res.* **2004**, *37*, 633.

10.1021/jo0622429 CCC: $37.00
Published on Web 12/29/2006

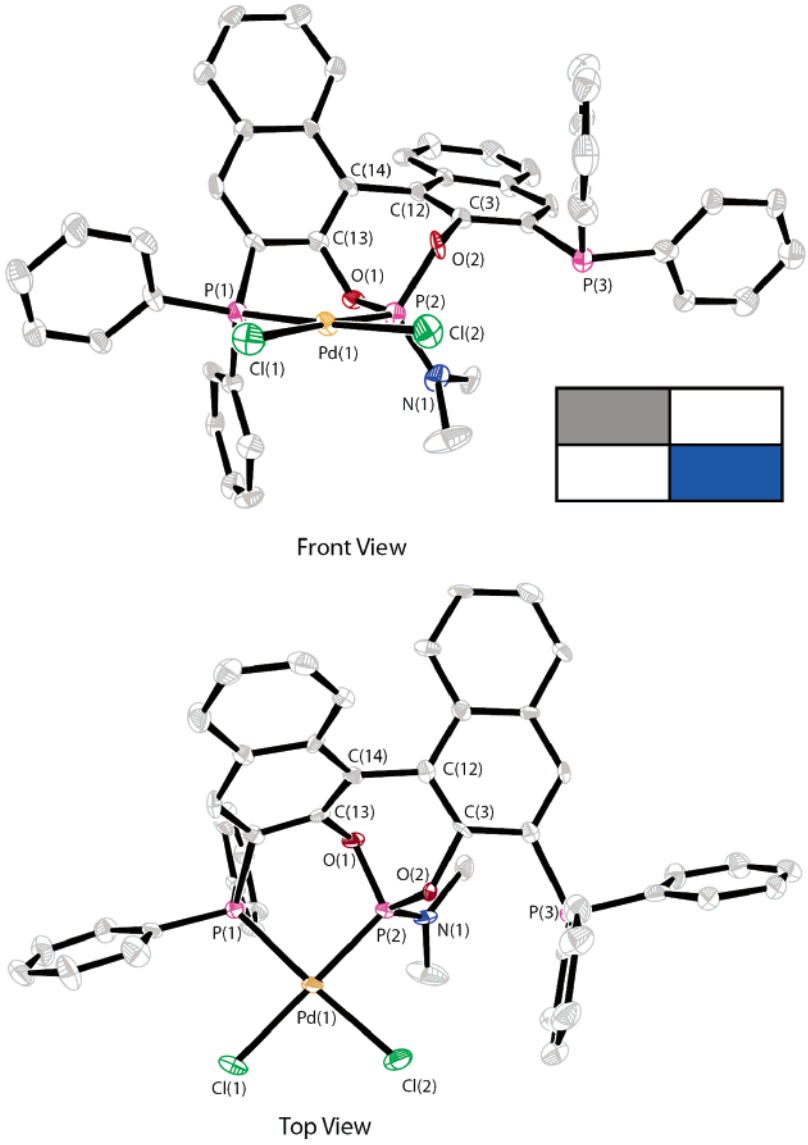
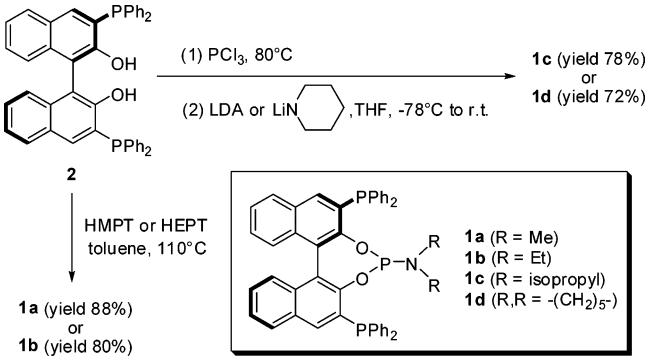


FIGURE 1. ORTEP representation of $PdCl_2$·**1a** at 50% probability for the drawing of thermal ellipsoids (solvents and hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Pd(1)−Cl(1) 2.319, Pd(1)−Cl(2) 2.355, Pd(1)−P(1) 2.281, Pd(1)−P(2) 2.212.

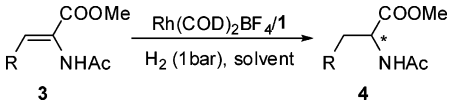
SCHEME 1



In Rh-catalyzed hydrogenation of α-dehydroamino esters and itaconate derivatives, CH_2Cl_2 is the solvent of choice for most bidentate[5] and monodentate[8] phosphoramidite ligands. For the present catalytic system, desirable performance was also found in the hydrogenation of enamides if CH_2Cl_2 or 2,2,2-trifluoroethanol (TFE) is used as solvent.[4] Interestingly, hydrogenation of the benchmark substrate **3a** with $Rh(COD)_2BF_4$/**1a** revealed a distinct solvent effect. Both CH_2Cl_2 and TFE gave only poor enantioselectivities (Table 1, entries 1 and 8 by **1a**, 48.6% ee and 54.6% ee, respectively), whereas remarkable improvement was seen in toluene, THF, EtOAc, and MeOH (entries 2−4 and 7 by **1a**). To our surprise, excellent enantioselectivities were obtained in ketonic solvents such as acetone and methyl ethyl ketone (MEK) (entries 5 and 6 by **1a**, 97.4% ee and 98.2% ee, respectively). Thus, acetone was chosen as the solvent for the subsequent hydrogenation of **3b**−**k** with **1a**−**d**. As shown in

(8) (a) van den Berg, M.; Minnaard, A. J.; Schudde, E. P.; van Esch, J.; de Vries, A. H. M.; de Vries, J. G.; Feringa, B. L. *J. Am. Chem. Soc.* **2000**, *122*, 11539. (b) Berg, M. v. d.; Minnaard, A. J.; Haak, R. M.; Leeman, M.; Schedde, E. P.; Meetsma, A.; Feringa, B. L.; de Vries, A. H. M.; Maljaars, C. E. P.; Williams, C. E.; Hyett, D.; Boogers, J. A. F.; Henderickx, H. J. W.; de Vries, J. G. *Adv. Synth. Catal.* **2003**, *345*, 308. (c) Bernsmann, H.; Berg, M. v. d.; Hoen, R.; Minnaard, A. J.; Mehler, G.; Reetz, M. T.; de Vries, J. G.; Feringa, B. L. *J. Org. Chem.* **2005**, *70*, 943. (d) Fu, Y.; Xie, J.-H.; Hu, A.-G.; Zhou, H.; Wang, L.-X.; Zhou, Q.-L. *Chem. Commun.* **2002**, 480. (e) Wu, S.; Zhang, W.; Zhang, Z.; Zhang, X. *Org. Lett.* **2004**, *6*, 3565. (f) Liu, Y.; Ding, K. *J. Am. Chem. Soc.* **2005**, *127*, 10488.

TABLE 1. Rh-Catalyzed Asymmetric Hydrogenation of α-Dehydroamino Esters 3[a]



3 4

				Rh−**1** system/ee (%) (configuration)[b]			
entry	substrate	R	solvent	**1a**	**1b**	**1c**	**1d**
1	**3a**	Ph	CH_2Cl_2	48.6 (*R*)	−	−	−
2	**3a**	Ph	toluene	86.6 (*R*)	−	−	−
3	**3a**	Ph	THF	86.8 (*R*)	−	−	−
4	**3a**	Ph	EtOAc	85.4 (*R*)	−	−	−
5	**3a**	Ph	acetone	97.4 (*R*)	95.8 (*R*)	98.8 (*R*)	98.4 (*R*)
6	**3a**	Ph	MEK	98.2 (*R*)	−	−	−
7	**3a**	Ph	MeOH	85.2 (*R*)	−	−	−
8	**3a**	Ph	TFE	54.6 (*R*)	−	−	−
9	**3b**	H	acetone	91.2 (*R*)	96.8 (*R*)	98.6 (*R*)	99.2 (*R*)
10	**3c**	4-F-Ph	acetone	98.2 (*R*)	97.4 (*R*)	98.4 (*R*)	97.0 (*R*)
11	**3d**	2-Cl−Ph	acetone	94.4 (*R*)	97.0 (*R*)	95.6 (*R*)	96.6 (*R*)
12	**3e**	4-Cl-Ph	acetone	97.4 (*R*)	97.4 (*R*)	98.0 (*R*)	98.2 (*R*)
13	**3f**	3-Br-Ph	acetone	98.0 (*R*)	98.0 (*R*)	98.4 (*R*)	97.2 (*R*)
14	**3g**	4-MeO-Ph	acetone	96.4 (*R*)	98.2 (*R*)	99.4 (*R*)	98.6 (*R*)
15	**3h**	4-CF_3-Ph	acetone	97.4 (*R*)	97.2 (*R*)	97.2 (*R*)	96.6 (*R*)
16	**3i**	thiophenyl	acetone	91.8 (*R*)	95.6 (*R*)	96.6 (*R*)	96.8 (*R*)
17	**3j**	*n*-propyl	acetone	97.2 (*R*)	98.4 (*R*)	99.0 (*R*)	99.2 (*R*)
18	**3k**	CH_3OCH_2	acetone	95.6 (*R*)	96.2 (*R*)	92.6 (*R*)	96.8 (*R*)

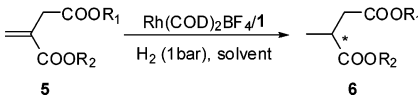
[a] All reactions were carried out under 1 bar of hydrogen pressure with an S/C ratio of 100:1 at room temperature for 18 h at 100% conversion. [b]Determined by chiral GC equipped with a Chirasil-L-Val column. The absolute configuration was assigned by comparing the observed optical rotation with the literature data.

Table 1, **1c** and **1d** outperform **1a** and **1b** in most cases, which tends to support the initial assumption that increasing steric hindrance or conformational rigidity on the phosphoramidite site could enhance enantioselectivity. However, no ligand gives consistently superior results and occasionally **1a** or **1b** showed the best selectivity among the whole series (entries 11 by **1b** and 15 by **1a**). This phenomenon indicated that chiral induction by **1** is still substrate-dependent. In other words, the ligand structure has to match the steric requirements of the substrate to achieve high enantioselectivity. Generally, excellent results (96.8%∼99.4% ee) were attained for both aromatic (**3a**−**i**) and aliphatic (**3j**,**k**) substrates, which is comparable to the results given by other bidentate[5] and monodentate[8] phosphoramidite ligands.

Hydrogenation of itaconate derivatives **5a**−**d** with **1a** revealed a more dramatic solvent effect. In the case of dimethyl itaconate **5a**, both CH_2Cl_2 and TFE gave excellent enantioselectivities (Table 2, entries 1 and 8 of **6a**, 96.6% and 99.2% ee, respectively), whereas an abrupt drop in the ee value was seen in toluene, THF, and MeOH. It is unexpected that reversed enantioselectivities were observed by the use of EtOAc, acetone, and MEK, leading to the opposite *S* configuration in the product **6a** (entries 4−6 of **6a**, 11.6%, 39.6%, and 30.4% ee, respectively). A similar trend was found in the hydrogenation of **5b**, showing the reversed *S* selectivity with up to 71.2% ee by the use of MEK (entry 6 of **6b**). Such a strong *S* preference is in sharp contrast to the nearly perfect *R* selectivity provided by CH_2Cl_2 and TFE (entries 1 and 8 of **6b**, 99.6% and 99.4% ee, respectively). For the other two substrates **5c** and **5d**, opposite enantioselectivities were also obtained. Not limited to **1a**, the other ligands **1b**−**d** also gave reversed stereoselection in MEK, though in a less remarkable degree.

Homogeneous asymmetric hydrogenation transfers the chirality of the catalyst into the reduced product, with one handedness of the catalyst corresponding to one stereochemical configuration of the product and the other handedness to the opposite configuration. If both enantiomers of the product are to be prepared, both enantiomers of the ligand have to be available.[9] An alternative approach can be conceived if a catalytic system

TABLE 2. Rh-Catalyzed Asymmetric Hydrogenation of Itaconates 5[a]



5 6

			product/ee (%) (configuration)[b]			
entry	ligand	solvent	**6a**	**6b**	**6c**	**6d**
1	**1a**	CH_2Cl_2	96.6 (*R*)	99.6 (*R*)	96.8 (*R*)	97.0 (*R*)[c]
2	**1a**	toluene	3.0 (*R*)[c]	75.8 (*R*)[c]	92.8 (*R*)	92.2 (*R*)
3	**1a**	THF	10.4 (*R*)	25.4 (*S*)[c]	6.6 (*R*)	39.4 (*R*)
4	**1a**	EtOAc	11.6 (*S*)[c]	43.4 (*R*)[c]	51.6 (*R*)	41.4 (*R*)
5	**1a**	acetone	39.6 (*S*)	51.8 (*S*)[c]	17.0 (*R*)	25.4 (*S*)
6	**1a**	MEK	30.4 (*S*)	71.2 (*S*)	30.8 (*S*)	32.6 (*S*)
7	**1a**	MeOH	32.0 (*R*)[c]	4.6 (*S*)	86.6 (*R*)	12.8 (*R*)
8	**1a**	TFE	99.2 (*R*)	99.4 (*R*)	98.8 (*R*)	99.4 (*R*)
9	**1b**	TFE	97.0 (*R*)	97.6 (*R*)	88.6 (*R*)	94.2 (*R*)
10	**1b**	MEK	30.0 (*R*)	45.6 (*S*)	19.4 (*R*)	17.4 (*S*)
11	**1c**	TFE	97.4 (*R*)	98.6 (*R*)	97.4 (*R*)	99.4 (*R*)
12	**1c**	MEK	35.6 (*R*)	10.8 (*S*)[c]	90.6 (*R*)	84.6 (*R*)
13	**1d**	TFE	99.2 (*R*)	99.6 (*R*)	97.4 (*R*)	99.6 (*R*)
14	**1d**	MEK	9.4 (*R*)	28.0 (*S*)	19.8 (*R*)	13.2 (*R*)

[a] Unless mentioned otherwise, all reactions were carried out under 1 bar of hydrogen pressure with an S/C ratio of 100:1 at room temperature for 18 h at 100% conversion. [b]Determined by chiral GC equipped with a γ-dex 225 column. The absolute configuration was assigned by comparing the observed optical rotation with the literature data. **6b**−**6d** were converted to the corresponding dimethyl ester **6a** with $TMSCHN_2$ or HCl in MeOH before GC analysis. [c]Incomplete conversions (<100%) were observed. See Supporting Information for details.

(9) Aware of this issue, our group recently developed DuanPhos as both enantiomers compared with the previously reported TangPhos, which exists as only one enantiomer. See: Liu, D.; Zhang, X. *Eur. J. Org. Chem.* **2005**, 646.

is capable of generating opposite chiralities in the product. Theoretically, reversal of enantioselectivity[10] is not impossible if the key enantiodifferentiating step is influenced significantly by modified transition states or if an entirely different mechanism is involved. In practice, both ammonium halides[11] and achiral monodentate ligands[3b] have been found to trigger such an effect. Nevertheless, it is rare that the same metal/ligand system induces opposite chiralities in the product simply due to the use of different solvents.[12] It can be reasoned that the solvent may have participated in enantiodifferentiating steps that are critical to the stereochemical outcome of the product, instead of serving merely as spectator molecules. In addition, the uncoordinated phosphine is situated close to the coordination sphere.[13] Whether it would have any effect during hydrogenation is still unclear. The correct correlation between the quadrant diagram of **1** and the observed *R* selectivity in the hydrogenation of dehydroamino esters in ketonic solvents and itaconates in CH_2Cl_2 and TFE suggests that hydrogenation under these conditions may follow a mechanism[7b] that works for most C_2-symmetric ligands. Meanwhile, the discrepancy found in the hydrogenation of itaconates in ketonic solvents may point to a different mechanism. This result further demonstrates that solvent screening is extremely important for a given catalytic system and that catalyst optimization is critical for the development of new ligands.

Experimental Section

General Procedure for the Synthesis of Phosphine-phosphoramidite Ligands 1. Synthesis of **2**, **1a**, and **1b** has been reported in ref 4. To a 50 mL Schlenk flask equipped with a condenser were charged **2** (1.71 g, 2.61 mmol) and 20 mL of PCl_3. The mixture was stirred at 80 °C overnight and then cooled to room temperature. The excessive PCl_3 was removed in a vacuum. Azeotropic distillation with toluene (10 mL) three times afforded the intermediate chlorophosphite as a white powder, which was used directly in the following step without purification. To a solution of this intermediate (1 equiv) in THF (25 mL) was added freshly prepared LDA or lithiated piperidine (2 equiv) in THF dropwise at −78 °C over 10 min. Then the reaction mixture was stirred overnight and warmed slowly to room temperature. The solvent was then evaporated, and the mixture was subjected to flash column chromatography on silica gel (EtOAc/hexane = 1:15) to afford the product as a white powder (78% yield for **1c**, 72% yield for **1d**).

(*R*)-*O*,*O*′-(3,3′-Bis(diphenylphosphino)-1,1′-dinaphthyl-2,2′-diyl)-*N*,*N*-diisopropylphosphorous Amidite (1c). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.91 (s, 6H), 1.29−1.42 (m, 6H), 3.25−3.37 (m, 2H), 7.16−7.61 (m, 30H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 23.38, 24.16, 24.85, 45.64, 45.82, 124.77, 128.71, 128.74, 128.81, 128.84, 129.00, 129.06, 129.09, 129.15, 129.40, 129.51, 133.65, 133.93, 133.98, 134.25, 134.98, 135.25, 151.91, 152.14, 152.48. ^{31}P NMR (146 MHz, CD_2Cl_2): δ = −14.38 (d, J_{P-P} = 29.7 Hz), −12.65 (s), 151.70 (d, J_{P-P} = 30.9 Hz). HRMS (M + H$^+$): calcd, 784.2663; found, 784.2680.

(*R*)-*O*,*O*′-(3,3′-Bis(diphenylphosphino)-1,1′-dinaphthyl-2,2′-diyl)-*N*,*N*-piperidylphosphorous Amidite (1d). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.21 (s, br, 4H), 1.51 (s, br, 2H), 2.98 (m, 4H), 7.27−7.69 (m, 30H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 25.14, 27.09, 27.14, 29.93, 45.27, 45.32, 45,60, 124.78, 126.48, 128.55, 128.60, 128.64, 128.70, 128.83, 128.88, 128.94, 128.96, 128.98, 129.03, 133.31, 133.58, 134.95, 135.23, 136.94, 151.35, 151.37, 152.06. ^{31}P NMR (146 MHz, CD_2Cl_2): δ = −14.43 (d, J_{P-P} = 24.5 Hz), −12.49 (d, J_{P-P} = 4.3 Hz), 145.17 (dd, J^1_{P-P} = 22.7 Hz, J^2_{P-P} = 3.6 Hz). HRMS (M + H$^+$): calcd, 768.2350; found, 768.2350.

General Procedure for Asymmetric Hydrogenation. The stock solution of the Rh/**1** complex (2×10^{-3} mol/L) was made by stirring $Rh(COD)_2BF_4$ and **1a**−**d** at a 1:1 molar ratio in desired solvents at room temperature for 1 h in a nitrogen-filled glovebox. Then, an aliquot of catalyst solution (0.5 mL, 0.001 mmol) was added into the vial charged with substrate (0.1 mmol) dissolved in the desired solvent (2.5 mL). All the vials were then placed in a steel autoclave into which hydrogen gas was charged at 1 bar of pressure after three "charge-release" cycles. After stirring at room temperature for 18 h, hydrogen gas was released carefully and the solution was concentrated and subjected to a short silica gel column to remove the metal complex. The purified sample was analyzed by chiral GC to determine ee and conversion. The itaconates **6b**−**d** were first converted to dimethyl ester **6a** before column purification and GC analysis.

Acknowledgment. Financial support from the National Institutes of Health is appreciated (NIH-GM58832). We thank Dr. Yennawar for assistance with X-ray diffraction experiments (NSF CHE-0131112).

Supporting Information Available: ^{1}H, ^{13}C, and ^{31}P NMR spectra of compounds **1c** and **1d** and X-ray crystal structure files (.cif) for the $PdCl_2$·**1a** complex. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0622429

(10) (a) In heterogeneous hydrogenation, reversal of enantioselectivity is under active study. See, for example: Bonalumi, N.; Vargas, A.; Ferri, D.; Burgi, T.; Mallat, T.; Baiker, A. *J. Am. Chem. Soc.* **2005**, *127*, 8467. (b) In asymmetric transfer hydrogenation, it was shown very recently that a subtle change in ligand structure can result in a switch of the product's absolute configurations. See: Zaitsev, A. B.; Adolfsson, H. *Org. Lett.* **2006**, *8*, 5129.

(11) Buriak, J. M.; Osborn, J. A. *Organometallics* **1996**, *15*, 3161.

(12) (a) A Rh complex of an α-glucosidic bisphosphinite ligand gave 73% ee (*S*) in ethanol but 6% ee (*R*) in benzene during the hydrogenation of dehydroamino esters. See: Selke, R. *J. Prakt. Chem.* **1987**, *329*, 717. (b) A Rh/PipPhos system gave 90% ee (*R*) in CH_2Cl_2 but 26% ee (*S*) in MeOH during the hydrogenation of an enol acetate. See: Panella, L.; Feringa, B. L.; de Vires, J. G.; Minnaard, A. J. *Org. Lett.* **2005**, *7*, 4177.

(13) According to the crystal structure of $PdCl_2$·**1a**, the distance from P(3) to P(2) is 3.906 Å, from P(3) to N(1) is 3.779 Å, and from P(3) to Pd(1) is 5.499 Å.