

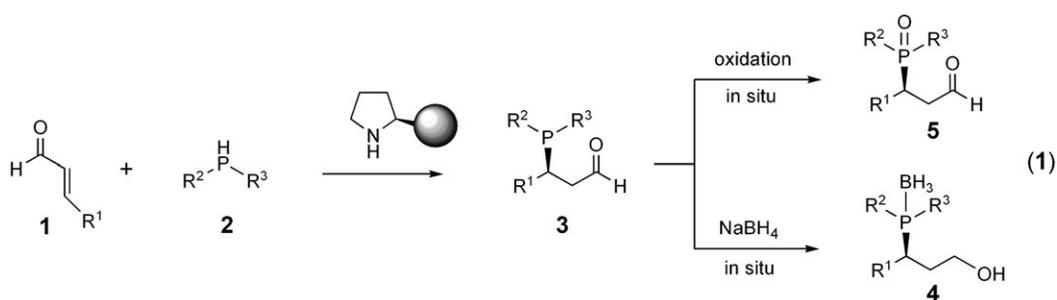
# Enantioselective Organocatalytic Hydrophosphination of $\alpha,\beta$ -Unsaturated Aldehydes\*\*

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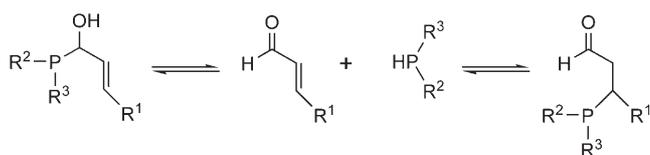
Chiral phosphines are highly valuable ligands for metal-catalyzed enantioselective transformations<sup>[1]</sup> and can be used as catalysts in organocatalytic reactions.<sup>[2]</sup> They are generally prepared by resolution—by employing stoichiometric amounts of chiral auxiliaries or enantiopure substrates.<sup>[3]</sup> Thus, there is an important need for the development of more efficient catalytic methods.<sup>[4]</sup> The asymmetric hydrophosphination (AHP)<sup>[5]</sup> of trivalent phosphine compounds with a P–H bond to electron-deficient olefins provides a direct route to useful chiral phosphine ligands containing different chemical functionalities. However, there are only a few catalytic asymmetric methods for this transformation:<sup>[6–8]</sup> for example, Togni and co-workers reported a highly enantioselective reaction catalyzed by a Lewis acid,<sup>[6]</sup> and, during our initial studies, Melchiorre and co-workers reported an elegant AHP of nitrostyrenes catalyzed by a chiral organic base that proceeds with good enantioselectivity.<sup>[8]</sup>

Aminocatalysis has proven to be a powerful procedure<sup>[9]</sup>

within the field of organocatalysis<sup>[10]</sup> for the enantioselective transformation of carbonyl compounds. In this context, iminium activation<sup>[11a]</sup> has been successfully demonstrated in Michael-type  $\beta$ -functionalizations for carbon-,<sup>[11]</sup> hydrido-,<sup>[12]</sup> sulfur-,<sup>[13]</sup> nitrogen-,<sup>[14]</sup> and oxygen nucleophiles.<sup>[15]</sup> On the basis of this research and the importance of developing AHP reactions, we envisioned a direct route to functionalized optically active  $\beta$ -formyl- and  $\gamma$ -hydroxyphosphines and derivatives thereof by amine-catalyzed stereoselective reactions between trivalent phosphine compounds and enals [Eq. (1), gray sphere = chiral group]. However, there are inherent difficulties in this type of transformation because of the reversibility of the nucleophilic attack and competition between 1,2- and 1,4-addition to the enal (Scheme 1).



Herein we present the highly chemo- and enantioselective organocatalytic  $\beta$ -hydrophosphination of  $\alpha,\beta$ -unsaturated aldehydes.



**Scheme 1.** Difficulties encountered when attempting AHP of enals.

After extensive screening of catalysts and different suitable phosphine sources for the AHP of cinnamic aldehyde (**1a**), we found that diphenylphosphine (**2a**) had the right properties to achieve product formation. Some of the results from the screening of the reaction conditions and catalysts for the enantioselective reaction of enal **1a** and **2a** in  $\text{CHCl}_3$  are shown in Table 1.<sup>[16]</sup> The corresponding  $\beta$ -formylphosphine **3a** was reduced in situ with  $\text{NaBH}_4$  to the air-stable alcohol derivative **4a** to facilitate the purification process as well as to generate a more stable product.<sup>[17]</sup>

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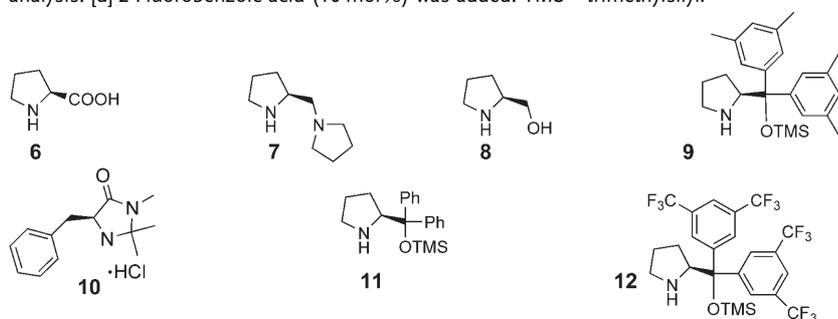
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**Table 1:** Catalyst screen for the reaction between **1a** and **2a**.<sup>[a]</sup>

Entry	Catalyst	T [°C]	t [min]	Conv [%] <sup>[b]</sup>	ee [%] <sup>[c]</sup>
1	<b>6</b>	RT	60	53	0
2	<b>7</b>	RT	60	55	14
3	<b>8</b>	RT	60	59	12
4	<b>9</b>	RT	60	> 99	38
5	<b>10</b>	RT	60	81	18
6	<b>11</b>	RT	60	> 99	50
7	<b>12</b>	RT	60	> 99	56
8	<b>11</b>	RT	10 <sup>[d]</sup>	> 99 <sup>[d]</sup>	40 <sup>[d]</sup>
9	<b>11</b>	4	20 <sup>[d]</sup>	> 99 <sup>[d]</sup>	83 <sup>[d]</sup>
10	<b>12</b>	4	20 <sup>[d]</sup>	> 99 <sup>[d]</sup>	73 <sup>[d]</sup>
11	<b>11</b>	-10	60 <sup>[d]</sup>	45 <sup>[d]</sup>	79 <sup>[d]</sup>

[a] Experimental conditions: A mixture of **1a** (0.25 mmol) and catalyst (20 mol%) in CHCl<sub>3</sub> (1.0 mL) was flushed with argon. Next, **2** (0.30 mmol) was added and the reaction mixture stirred at the temperature for the time indicated. In situ reduction of **3a** with NaBH<sub>4</sub> gave the corresponding  $\gamma$ -alcohol **4a**. [b] Conversion into product **3a** as determined by NMR analysis. [c] Determined by chiral-phase HPLC analysis. [d] 2-Fluorobenzoic acid (10 mol%) was added. TMS = trimethylsilyl.



We found that chiral amines **6–12** catalyzed the AHP of enal **1a** with high efficiency and with *ee* values ranging from 0–56% *ee*. Chiral protected diarylprolinols **7**, **11**,<sup>[18]</sup> and **12**<sup>[11,j,g,13a,c,15a]</sup> were the most efficient catalysts under our reaction conditions and mediated the formation of **3a** with high chemoselectivity (entries 4, 6, and 7). Notably, we found that the reaction was significantly accelerated by the addition of a benzoic acid additive, which probably promoted the formation of the iminium ion. Of the benzoic acids tested, 2-fluorobenzoic acid (10 mol%) gave the best results without significantly affecting the enantioselectivity (entry 8). Under these conditions, chiral amine **11** catalyzed the asymmetric formation of **3a** with 83% *ee* and complete conversion at 4 °C within 20 minutes (entry 9). Decreasing the temperature to -10 °C did not improve the enantioselectivity and reduced the efficiency of the reaction (entry 11). On the basis of

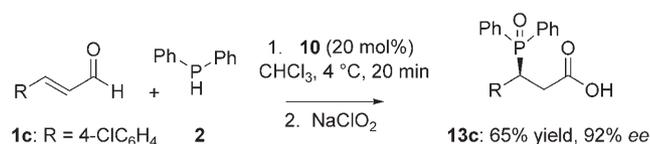
these results we decided to investigate the enantioselective AHP of enals **1** with diphenylphosphine (**2a**) catalyzed by amine **11** and **12** under these conditions (Table 2).

The organocatalytic AHP reactions were highly chemo- and enantioselective and the corresponding formylphosphines **3** were converted in situ into the corresponding alcohols **4** or phosphine oxides **5** by in situ reduction or oxidation, respectively. For example,  $\beta$ -phosphine alcohols **4b–4g** were isolated with 90–99% *ee*. The reaction was efficient and highly enantioselective for  $\alpha,\beta$ -unsaturated aldehydes **1** with either aliphatic or aromatic functional groups. Moreover, the  $\alpha,\beta$ -unsaturated aldehydes **1** could also be converted in a one-pot reaction into the corresponding  $\beta$ -phosphine oxide acids **13** (Scheme 2). For example,  $\beta$ -phosphine oxide carboxylic acid **13c** was obtained in 65% yield and 92% *ee*. If desired, the phosphine oxide derivatives can be readily converted into the hydrophosphines by reduction with silanes.<sup>[19]</sup> The absolute configuration of the phosphorus-containing compounds was 2S (R = Ar), as established by X-ray analysis of a single crystal of the diphosphine oxide derivative **14d** (Figure 1),<sup>[20]</sup> which was formed by decomposition of the isolated pure phosphine oxide aldehyde **3d** after more than 16 h at room temperature.

**Table 2:** Scope of the organocatalytic AHP.<sup>[a]</sup>

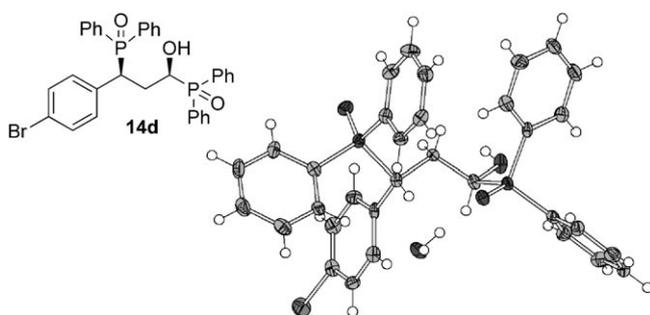
Entry	Catalyst	R	Prod.	Yield [%] <sup>[b]</sup>	ee [%] <sup>[c]</sup>
1	<b>11</b>	Ph	<b>4a</b>	85	83
2	<b>11</b>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>4b</b>	87	99
3	<b>12</b>	4-ClC <sub>6</sub> H <sub>4</sub>	<b>4c</b>	79	92
4	<b>12</b>	4-BrC <sub>6</sub> H <sub>4</sub>	<b>4d</b>	78	90
5	<b>12</b>	2-Naph	<b>4e</b>	85	98
6	<b>12</b>	BnO(CH <sub>2</sub> ) <sub>3</sub> S <sub>2</sub>	<b>4f</b>	70	91
7	<b>12</b>	PhC(=O)O(CH <sub>2</sub> ) <sub>3</sub> S <sub>2</sub>	<b>4g</b>	72	95

[a] Experimental conditions: A mixture of **1** (0.25 mmol), 2-fluorobenzoic acid (10 mol%), and catalyst **11** or **12** (20 mol%) in CHCl<sub>3</sub> (1.0 mL) was flushed with argon. Next, **2** (0.30 mmol) was added and the reaction mixture stirred for 20 min at 4 °C. Next, in situ reduction of **3** with NaBH<sub>4</sub> gave the corresponding alcohol **4**. [b] Yield of isolated pure product aldehyde **5** after in situ oxidation of **3** with I<sub>2</sub>. [c] Determined by chiral-phase HPLC analysis.



**Scheme 2.** One-pot asymmetric synthesis of  $\beta$ -phosphine oxide acid **13c**.

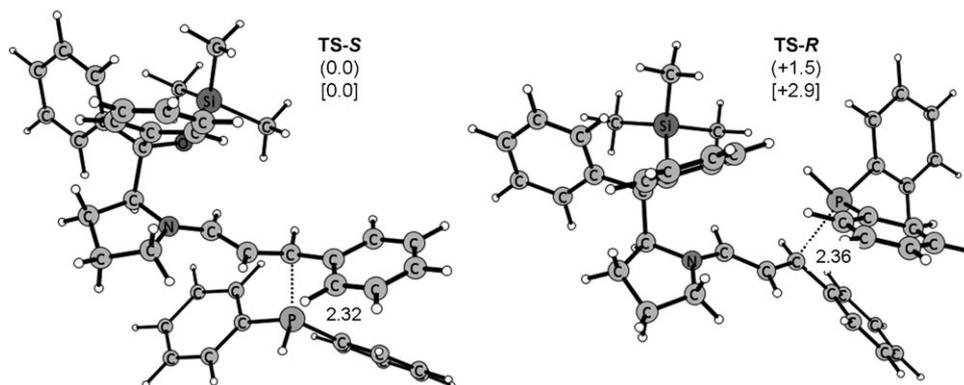
To shed more light on the origin of the enantioselectivity we performed density functional theory (DFT) calculations on the P–C bond-forming step. The calculations were performed using the Gaussian 03 software package<sup>[21]</sup> and the B3LYP functional.<sup>[22]</sup> Geometries were optimized with the 6-31G(d,p) basis set, and characterized with frequency calculations. Final energies were obtained with the larger basis set 6-311+G-(2d,2p) and corrected for zero point effects obtained from the frequency calculations. The effect of solvation in CHCl<sub>3</sub> was calculated using a polarizable conductor model (CPCM).<sup>[23]</sup> As a representative case for the calculations, we considered the reaction of diphenylphosphine (**2a**) with the iminium species formed from cinnamic aldehyde (**1a**) and catalyst **11** (Figure 2).<sup>[24]</sup> The transition state leading to the *S* product (**TS-S**) was calculated to have the lowest energy. The attack takes place at the face of the *E*-iminium ion that is not shielded by the bulky group of the catalyst. The attack on the shielded face of the *E*-iminium ion (**TS-R**), which yields the *2R* product, is 1.5 kcal mol<sup>-1</sup> higher in energy (2.9 kcal mol<sup>-1</sup> including solvation effects). Although the energy difference suggests a somewhat higher enantioselectivity than the one observed experimentally for this specific reaction, it is qualitatively in agreement with the experimental findings and supports the prediction that the bulky group of **11** shields the *Re* face (R = Ar)<sup>[25]</sup> of the *E*-iminium ion, which leads to



**Figure 1.** ORTEP picture of the crystalline di(phosphine oxide) compound **14d**.

*Si* facial attack. The *Z*-iminium ion was previously found to be less stable than the *E*-iminium ion.<sup>[14e]</sup> We have calculated that the different transition states for the phosphine attack on the *Z*-iminium ion have 3–5 kcal mol<sup>-1</sup> higher energies than those formed by attack on the *E*-iminium ion, and are not considered further here. This finding is also in accordance with previous conjugate additions catalyzed by catalysts **11** and **12**.<sup>[13–15]</sup>

In summary, we have reported the unprecedented example of a highly chemo- and enantioselective organocatalytic hydrophosphination of  $\alpha,\beta$ -unsaturated aldehydes. The reaction is catalyzed efficiently by simple chiral pyrrolidine derivatives and gives the corresponding phosphine derivatives



**Figure 2.** Optimized transition-state structures for phosphine attack on an *E*-iminium ion. **TS-S** arises from attack on the unshielded face of the iminium ion and has lower energy than when the attack is on the shielded face (**TS-R**). Relative energies [kcal mol<sup>-1</sup>] in the gas phase (in parentheses) and solvated [in brackets] are given. Distances are in Ångstroms.

in high yields and in up to 99% *ee*. The synthetic utility of the novel catalytic AHP was exemplified by the one-pot asymmetric synthesis of  $\beta$ -phosphine oxide acids. DFT calculations showed that the lowest energy transition state led to the *S* product. Mechanistic studies, synthetic applications of this transformation, as well as development of other enantioselective AHP reactions based on this concept are ongoing.

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