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Enamine–Metal Lewis Acid Bifunctional Catalysis: Application to Direct Asymmetric Aldol Reaction of Ketones

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Keywords: Organocatalysis / Aldol reactions / Lewis acids / Lewis bases / Amino acids / Tridendate ligands

Unprecedented bifunctional enamine–metal Lewis acid catalysts have been developed. In this bifunctional catalytic system, a tridentate ligand tethered with a chiral secondary amine was designed to solve the acid–base self-quenching problem leading to catalyst inactivation. This new bifunctional enamine–metal Lewis acid catalyst was found to catalyze aldol reactions of ketones efficiently in high yields and good to excellent diastereoselectivities and enantioselectivities.

Introduction

Since the rebirth of organic catalysis in 2000,[1] asymmetric organocatalysis has been growing at a breathtaking pace. A large number of asymmetric carbon–carbon and carbon–heteroatom bond-forming reactions, such as the aldol reaction, Mannich reaction, Michael reaction, and even complicated cascade reactions have been achieved with unprecedented ease.[2] Proline has been playing a major role in enamine-based catalysis.[1–4] Mechanistic studies suggest that both the pyrrolidine ring and the carboxylic acid group are essential to the reaction. In this view proline can be regarded as a Lewis base/Brønsted acid "bifunctional catalyst".[5] In the past several years, major efforts on modifying proline catalysts have been focused on modification of the carboxylic acid group by introducing electronic and/or steric factors to optimize the interaction between the Brønsted acid and the aldol acceptor through hydrogen bonding. We want to "replace" the Brønsted acid with a metal Lewis acid and develop a novel class of metal Lewis acid–enamine bifunctional catalysts with the intention to bridge more traditional transition-metal catalysis with the newly established prosperous area of organocatalysis.

Multifunctional catalytic systems for asymmetric organic reactions have the potential to bring higher reactivity, selectivity, and versatility.[6] Partly due to their inherent complexity, few Lewis acid/Lewis base bifunctional systems have been well defined. The major challenge lies in the acid–base self-quenching reaction leading to catalyst inactivation. The general approach to solve this problem is to finetune the reaction conditions and catalysts, such as using a "hard" Lewis acid and a "soft" Lewis base. Several examples of this sort have been reported,[7] in which a proline/pyrrolidine molecule was mixed with a transition metal to establish the bi/multifunctional catalytic system. We are using a different strategy to solve this problem. In our approach, the Lewis acid and Lewis base are incorporated into one molecule. To achieve this, we use a tridentate ligand (Figure 1, **1**, **2**, and **3**) tethered with a chiral secondary amine, for example, L-proline, in combination with transition metals. We envision that the tridentate ligand will "trap" the incoming metal preventing the coordination of the secondary amine to the metal, so that the bifunctional system is built up within one molecule. The metal introduced into the chiral tridentate scaffold will act as a Lewis

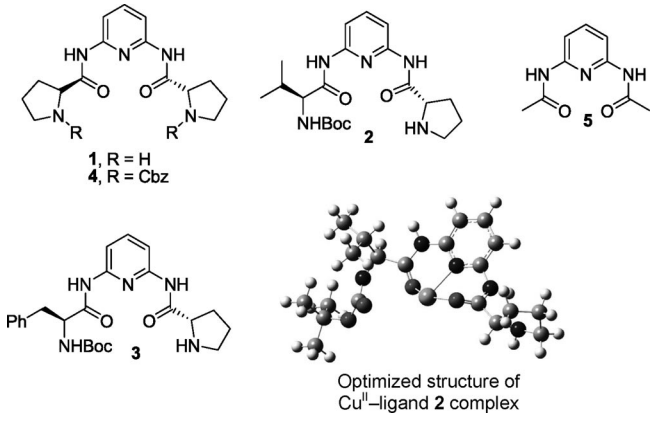

Figure 1. Tridentate ligands.

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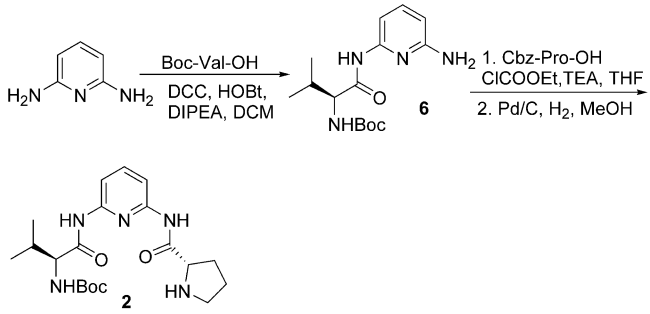
acid, and it will also serve to assemble the molecule into a relatively rigid structure, a desired property for bifunctional catalysts. Furthermore, the Lewis acidity and the secondary structure for substrate interaction can be easily tuned by introducing different metals. Herein we wish to report the preliminary results of the first example of enamine–metal Lewis acid bifunctional catalysts for the direct asymmetric aldol reactions of ketones.

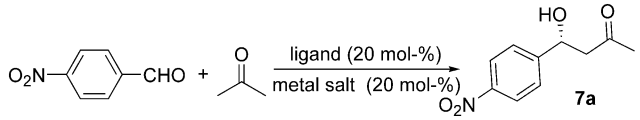
Results and Discussion

Three tridentate ligands (**1**, **2** and **3**) were prepared (Figure 1). These ligands can be obtained from pyridine-2,6-diamine (Scheme 1, see Supporting Information for the synthesis of **1**–**3**). Ligand **1** with C_2 symmetry has two L-proline moieties incorporated, and ligand **2** and **3** have C_1 symmetry and carry only one L-proline moiety. To prove the principle, we decided to use the intermolecular aldol reaction as the model reaction. Preliminary experiments focused on benchmark screening of different metals in combination with ligand **1** (Table 1). The reaction between acetone (excess) and 4-nitrobenzaldehye was carried out at room temperature. The bifunctional catalysts were prepared by stirring ligand **1** with metal salts in a molar ratio of 1:1 in corresponding solvent(s) for 2–4 h at room temperature. All the bifunctional catalysts showed activities. $Co(ClO_4)_2$ and $Zn(OAc)_2$ displayed high activities in terms of yield and reaction time. However, the enantioselectivities were modest (42 and 53% *ee*; Table 1, Entries 2 & 6). Counteranions of the metal salts also played a role in determining the yield and enantioselectivity. Whereas $Cu(SbF_6)_2$ and $Cu(NO_3)_2$ gave reasonable *ee* values of 75 and 70% in modest yield, $Cu(OTf)_2$ and $Cu(ClO_4)_2$ resulted in enantioselectivities of 48 and 47%, respectively, albeit in high yields (Table 1, Entries 7–10). These results strongly suggest that metals participate in the reactions. To further prove the bifunctional nature of this catalytic system, we prepared *N*-Cbz-protected ligand **4** and ligand **5** bearing no pyrrolidine moiety (Figure 1). The aldol reactions carried out with **4** and **5** in the presence of $Cu(SbF_6)_2$ did not give any aldol products after 72 h, suggesting that the pyrrolidine ring is critical for the reaction (Table 1, Entries 11 & 12). When **5**, $Cu(SbF_6)_2$, and pyrrolidine were mixed in a 1:1:1 molar ratio, the aldol reaction proceeded very slowly due to the coordination of the free pyrrolidine to the copper, and the aldol product was obtained in only 20% yield (Table 1, Entry 13), in sharp contrast to the reactions carried out with **1**/metal systems (Table 1, Entries 2–10) and free ligand **1**[8] (Table 1, Entry 1), indicating that the tethered pyrrolidine moiety in ligand **1** did not participate in the coordination to the metal and the acid–base self-quenching reaction did not happen as expected. To gain more understanding of the catalyst structure, the structure of the Cu^{II} complex was optimized with the DFT variant hybrid density functional theory (B3LYP) in conjunction with the 6-31+G(d) basis set by using the Gaussian 03 program package. The optimized structure shows that coordination of the secondary amine on the pyrrolidine moiety of ligand **2** to the metal would be very difficult due to its distance (Figure 1).



Scheme 1. Synthesis of ligand **2**.

Table 1. Metal screening.[a]



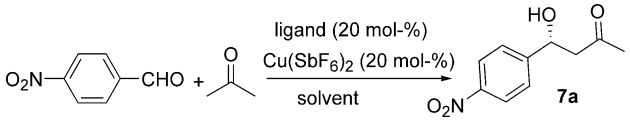
Entry	Metal	Ligand	Time [h]	Yield [%][c]	*ee* [%][d]
1[8]	–	**1**	48	74	43
2	$Zn(OAc)_2$	**1**	24	73	53
3	$Zn(ClO_4)_2$	**1**	36	45	28
4[b]	$Ni(OAc)_2$	**1**	48	84	38
5[b]	$Ni(ClO_4)_2$	**1**	48	63	58
6	$Co(ClO_4)_2$	**1**	24	83	42
7	$Cu(OTf)_2$	**1**	48	85	48
8	$Cu(ClO_4)_2$	**1**	72	81	47
9[b]	$Cu(NO_3)_2$	**1**	48	48	70
10	$Cu(SbF_6)_2$	**1**	48	58	75
11	$Cu(SbF_6)_2$	**4**	72	0	≈
12	$Cu(SbF_6)_2$	**5**	72	0	≈
13[e]	$Cu(SbF_6)_2$	**5**	60	20	≈

[a] Reactions were carried out with acetone (2 mL) and aldehyde (0.2 mmol). [b] DMSO (1 mL) was added. [c] Isolated yield. [d] Determined by chiral HPLC. [e] Pyrrolidine (20 mol-%) was added.

Having established the bifunctional nature of the catalytic system, we decided to optimize the reaction conditions of the aldol reaction catalyzed by ligand **1** with $Cu(SbF_6)_2$, as it gives the highest enantioselectivity (75% *ee*; Table 1, Entry 10). Higher asymmetric induction was achieved when THF was used as solvent (Table 2, Entries 1–4; see Supporting Information for a full list of reaction conditions). When 2 mL of THF and 0.5 mL of acetone were used, a good *ee* value of 83% was obtained, albeit with a longer reaction time (72 h) and low yield (31%). When 2 mL/1 mL of THF/acetone was used, the yield increased to 51% without sacrificing the *ee* value; addition of a small amount of water helped increase the yield, but the *ee* value decreased slightly. Using a higher concentration largely increased the yield, but to our disappointment, the *ee* value was also lowered slightly (Table 2, Entry 4). On the basis of these observations, ligand **1** was modified by replacing one of the L-proline moieties with a sterically more bulky L-valine (**2**) and a

benzene carrying L-phenylalanine (**3**) to optimize the catalytic performance. The asymmetric catalytic aldol reactions carried out with both **2** and **3** resulted in much higher yields and *ee* values in shorter reaction times, with **2** displaying slightly superior enantioselectivity to **3** (Table 2, Entries 5–8). Even though it is not clear why C_2 ligand **1** displayed both poorer activity and enantioselectivity, we speculate that it may arise from a competition between the two proline moieties. When lower loading of **2** (10 mol-%) was used, both activity and enantioselectivity decreased (Table 2, Entry 9). Lowering the temperature (0 °C) helped increase the *ee* value slightly (90% *ee*; Table 2, Entry 7).

Table 2. Optimization of the model reaction conditions.[a]

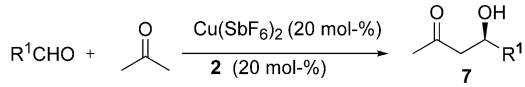


Entry	Ligand	THF [mL]	Acetone [mL]	Time [h]	Yield [%][e]	*ee* [%][f]
1	**1**	2	0.5	72	31	83
2	**1**	2	1	60	51	82
3[b]	**1**	2	1	60	61	79
4	**1**	0.6	0.3	48	84	75
5	**2**	2	1	48	93	88
6	**2**	0.6	0.3	24	93	87
7[c]	**2**	0.6	0.3	48	75	90
8	**3**	0.6	0.3	48	92	85
9[d]	**2**	0.6	0.3	72	95	83

[a] Reactions were performed with 0.2 mmol aldehyde. [b] H_2O (0.3 mL) was added. [c] At 0 °C. [d] 10 mol-% of catalyst. [e] Isolated yield. [f] Determined by chiral HPLC.

Compound **2** was then selected in conjunction with $Cu(SbF_6)_2$ as the bifunctional catalytic system for further investigation, and the aldehyde scope was examined for the asymmetric aldol reactions of acetone (Table 3). Under optimized conditions both electron-rich and electron-poor aromatic aldehydes reacted smoothly with acetone to give desired aldol products **7**. The aldol products were obtained in high yields (60–95%) and good enantioselectivity (85–91% *ee*) for electron-deficient aldehydes (Table 3, Entries 1–7); electron-rich aldehydes (Table 3, Entries 8 & 9), however, gave decreased yields (48–73%) and enantioselectivity (58–74% *ee*).

Table 3. Aldehyde scope of the direct aldol reaction of acetone.[a]

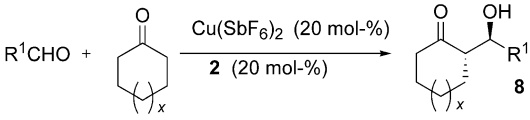


Entry	R^1	Product, Yield [%][c]	*ee* [%][d]
1[b]	4-$NO_2C_6H_4$	**7a**, 75	90
2[b]	3-$NO_2C_6H_4$	**7b**, 75	89
3[b]	2-$NO_2C_6H_4$	**7c**, 71	93
4	4-CNC_6H_4	**7d**, 95	87
5	4-$COOMeC_6H_4$	**7e**, 92	87
6	4-ClC_6H_4	**7f**, 60	85
7	2,6-$Cl_2C_6H_3$	**7g**, 73	91
8	2-naphthyl	**7h**, 73	74
9	4-MeC_6H_4	**7i**, 48	58

[a] The reactions were carried out with aldehyde (0.2 mmol) and acetone (0.3 mL) in THF (0.6 mL) at r.t. for 24–72 h. [b] At 0 °C. [c] Isolated yield. [d] Determined by chiral HPLC.

When cyclohexone was used as the aldol donor (Table 4), the same trend was observed. In general, the reactions of electron-deficient aldehydes proceeded in very high yields (80–96%), good to excellent diastereoselectivity (*anti*/*syn*,

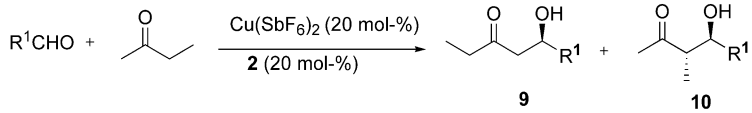
Table 4. Aldehyde scope of the direct aldol reaction of cyclic ketones.[a]



Entry	R^1	*x*	*anti*/*syn*[b]	Product, Yield [%][c]	*ee* [%][d] (*anti*)
1	4-$NO_2C_6H_4$	1	8:1	**8a**, 96	91
2	3-$NO_2C_6H_4$	1	9:1	**8b**, 96	81
3	2-$NO_2C_6H_4$	1	8:1	**8c**, 96	83
4	4-CNC_6H_4	1	10:1	**8d**, 91	84
5	4-$COOMeC_6H_4$	1	8:1	**8e**, 82	80
6	4-ClC_6H_4	1	6:1	**8f**, 80	82
7	2,6-$Cl_2C_6H_3$	1	>30:1	**8g**, 95	86
8	2-naphthyl	1	6:1	**8h**, 71	76
9	C_6H_5	1	5:1	**8i**, 70	71
10	4-$NO_2C_6H_4$	0	4:1	**8j**, 96	92

[a] The reactions were carried out with aldehyde (0.2 mmol) and ketone (0.3 mL) in THF (0.6 mL) at r.t. for 24–72 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Combined yield. [d] Determined by chiral HPLC.

Table 5. Examples of the direct aldol reaction of 2-butanone.[a]



Entry	R^1	Product, Yield [%][c]	*ee* [%][d]	Product, Yield [%][c]	*anti*/*syn*[b]	*ee* [%][d] (*anti*)
1	4-$NO_2C_6H_4$	**9a**, 36	88	**10a**, 59	>30:1	>99
2	3-$NO_2C_6H_4$	**9b**, 34	85	**10b**, 54	>30:1	>99
3	2-$NO_2C_6H_4$	**9c**, 20	84	**10c**, 40	25:1	99

[a] The reactions were carried out with aldehyde (0.2 mmol) and ketone (0.3 mL) in THF (0.6 mL) at r.t. for 24–48 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield. [d] Determined by chiral HPLC.

6:1→30:1), and good enantioselectivity (80–91%*ee*; Table 4, Entries 1–7). Cyclopentanone (Table 4, Entry 10) was also examined with 4-nitrobenzaldehyde furnishing 96% yield and 92%*ee*, in lower diastereoselectivity (*anti*/*syn*, 4:1).

When 2-butanone served as the aldol donor, excellent enantioselectivity (99%*ee*) and diastereoselectivity (*anti*/*syn*, >30:1) were obtained with branched product **10** (Table 5). Linear product **9** was generated in good enantioselectivities (84–88%*ee*).

These reactions gave predominately (*R*)-aldol products. The absolute configuration predicted from the proposed transition state model (Figure 2) matches the experimental results. Even though the detailed mechanism needs further investigation, on the basis of the data obtained we speculate that the metal (Cu^{II}) serves as a Lewis acid activating the aldehyde, and the pyrrolidine ring serves as a Lewis base and forms an enamine with the ketone. The enamine attacks from the *Re* face of the aldehyde to give the (*R*)-aldol product.

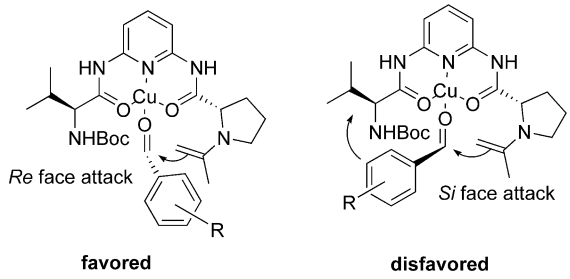


Figure 2. Proposed transition state.

Conclusions

In summary, we have developed a new class of enamine–metal Lewis acid cooperative bifunctional catalysts and successfully applied them to the direct asymmetric aldol reactions of ketones with aldehydes. The aldol products were obtained in good yields and good to excellent diastereoselectivity and enantioselectivity. In this bifunctional catalytic system, a new type of tridentate ligand was incorporated to bring the chiral secondary amine (Lewis base) and metal Lewis acid in close proximity without self-quenching each other, which causes catalyst inactivation. This strategy can be used to develop other new bifunctional catalysts. Application of these catalysts to other important reactions is underway.

Experimental Section

General Procedure for the Enantioselective Aldol Reaction: A mixture of $CuCl_2$ (0.04 mmol), $AgSbF_6$ (0.08 mmol), ligand (0.04 mmol), and ketone (0.3 mL) in THF (0.6 mL) was stirred at room temperature for 4 h. The aldehyde (0.2 mmol) was then added. The resulting mixture was stirred at room temperature for 24–72 h. After the reaction was complete (monitored by TLC), the reaction mixture was treated with aqueous NH_4Cl (S) and extracted with EtOAc. After removal of the solvent, the residue (the mixture was analyzed by ^1H NMR spectroscopy to determine diastereoselectivity where applicable) was purified by column chromatography on silica gel (hexane/ethyl acetate) to give the pure products. All aldol products are known compounds, and their spectroscopic data are identical to those reported in the literature. The *ee* values were determined by chiral HPLC analysis.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures, characterization data for all new compounds, and HPLC data.

Acknowledgments

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