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双功能配体促进的钯催化不对称醚化和胺化反应

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摘要　研究双亚砜膦配体(BiSO-P)亚砜基团的 Bronsted 碱性在协同催化反应中的作用. ^{1}H NMR 研究表明双亚砜膦与醇和胺等质子试剂形成氢键; 并将此类配体应用于钯催化的不对称醚化和胺化反应, 最高获得 99% *ee*. 研究发现氢键的存在能有效提高反应的 *ee* 值, 配体亚砜基团在反应过程中同时起着 Lewis 和 Bronsted 碱的作用.

关键词　手性双亚砜膦配体; 双功能; 氢键; 钯催化; 烯丙基醚化和胺化

Bifunctional Ligand Promoted Pd-Catalyzed Asymmetric Allylic Etherification/Amination

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Abstract　A serious of bissulfoxide-phosphine ligands are examined on the Bronsted basicity of sulfinyl moiety. The effect of secondary binding property of the ligand is demostrated in Pd-catalyzed asymmetric allylic etherification and amination (up to 99% *ee*). And the application scope of this methodology to hydrogen-donor nucleophiles is investigated.

Keywords　chiral bissulfoxide-phosphine ligands; bifunctional; hydrogen bond; Pd-catalysis; allylic etherification and amination

1　Introduction

Bifunctional catalysis, which able to simultaneously activate two reaction partners like enzyme catalysis,[1] commonly features mild reaction condition, excellent selectivity and unexpected performance. The design and application of bifunctional catalysts in the asymmetric catalysis is highlighted recent years.[2] Growing efforts for the development of efficient asymmetric catalysts have been attracted on the concept of cooperative activation, such as bimetallic catalysts,[3] bifunctional organocatalysts[4] and bifunctional metal-organocatalysts[5] and so on. Among these, more attentions are focused on metal-tethered terminal functional group catalysts and the ligand skeleton including ferrocenylphosphine,[6] binol,[7] salen,[8] cinchonine.[9] Generally, the terminal functional groups of ligands play two kinds of roles in the asymmetric catalysis: (1) acidic site (Lewis acid or hydrogen-bond donor); (2) basic site (Lewis base or hydrogen-bond acceptor).

Very recently, we designed a new type of chiral bifunctional bissulfoxide-phosphine (BiSO-P) ligands which performed cooperative effects in a Pd-catalyzed asymmetric allylic alkylation (carbon-carbon bond formation), and showed unique stereocontrolling ability.[10] In fact, the additional sulfoxide moiety in BiSO-P serves as hydrogen bond acceptor (attracting N—H of indole) to make reaction from inter- to intramolecular attack. In the earlier reports, the *tert*-butyl sulfinyl groups were also found to form hydrogen bond with protonated imine[11] or binol.[12] Herein, we continuously investigated the ability of this type of chiral bissulfoxide-phosphine ligands interacting with alcohol and amine, and examined the efficacy of hydrogen bond interaction in Pd-catalyzed asymmetric etherification and amination (C—X bond formation).[13]

2　Results and discussion

The ligands used in this context including bifunctional **L1**～**L5** and non-bifunctional **L6** were outlined in Figure 1. Ligands **L3**～**L5** were obtained according to the same procedure for the synthesis of **L1**～**L2**.[10]

We choose two representative bissulfoxide-phophines **L1** (1-pyrrolyl) and **L4** (Phenyl) to interact with some proton reagents. As shown in Table 1, **L1** shifted down the chemical shift of proton of benzyl alcohol (**1a**) by 0.26 ppm (Table 1, Entry 1). The larger $\Delta\delta$ (+0.27 ppm) of proton affected by **L4** was detected (Table 1, Entry 3), which excluded the interaction between nitrogen atom in **L1** and the proton reagent. Controling experiments showed that triphenyl phosphine was found no effects on the

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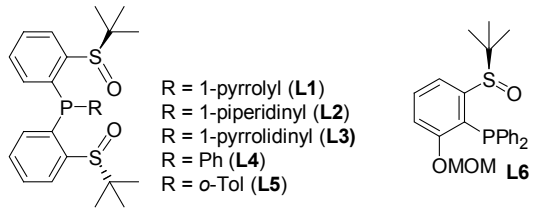
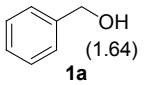
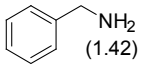
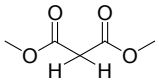


Figure 1 Chiral sulfoxide-phosphine ligands

chemical shift of proton reagents to exclude the interaction between phosphorous atom and proton. So, it is reasonable to believe that the *tert*-butyl sulfinyl group in sufoxide-phosphine ligands served as hydrogen-bond acceptor to interact with proton reagents. Notably, the *in-situ* formed Pd(II)-complex also showed such hydrogen-bond interaction ability (Table 1, Entries 2 and 4). We further observed weaker hydrogen-bond interaction between benzyl amine (**2a**) and bissulfoxide-phophines ($\Delta\delta$ +0.16 ppm for **L1** and +0.05 ppm for **L4**) (Table 1, Entries 5～6). As expected, diethyl malonate **3** was found no hydrogen bond interaction with neither of sulfoxide-phosphine ligands (Table 1, Entries 7～8).

Table 1 The investigation of hydrogen-bond interaction between ligands and proton reagents by NMR[a]

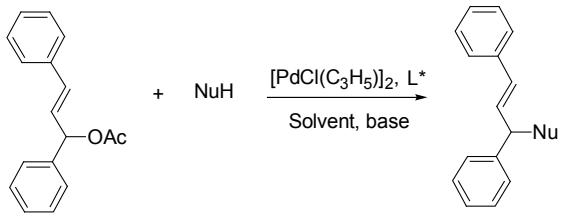
Entry	H-Bond donor[b]	Ligand	δ[c]	$\Delta\delta$[d]
1		**L1**	1.90	+0.26
2	 (1.64) **1a**	**L1**+Pd(II)[e]	1.93	+0.29
3		**L4**	1.91	+0.27
4		**L4**+Pd(II)[e]	2.43	+0.77
5	 (1.42) **2a**	**L1**	1.58	+0.16
6		**L4**	1.47	+0.05
7	 **3** (3.39)	**L1**	3.39	0
8		**L4**	3.39	0

[a] The solution of hydrogen-bond donor (0.02 mmol) and ligand (0.02 mmol) in 0.5 mL $CDCl_3$ was monitored by 400 MHz NMR at room temperature. [b] The value in the parenthesis is chemical shift of proton. [c] Chemical shift of proton of the mixed solution. [d] The changing value of proton's chemical shift after mixing the hydrogen-bond donors with the ligand. [e] The *in situ* formed complex of the ligand and $[Pd(C_3H_5)Cl]_2$ was added.

Since bissulfoxide-phosphine ligands can play dual roles of Lewis base and Bronsted base, we decide to test them (**L1**～**L5**) in the transition-metal mediated asymmetric catalysis. Asymmetric allylic substitution was chosen as the model reaction,[14] because it was demonstrated that some modified ferrocenylphosphine ligands show the cooperative effect in this transformation. For example, Ito and coworkers[15] found crown ether-modified chiral ferrocenylphosphine ligands are effective for the palladium-catalyzed asymmetric allylation of 8-diketones, owing to the attractive interaction between crown ether group and enolate salts. In the Pd-catalyzed asymmetric allylic amination, Hayashi[16] and Hou[17] found chiral ferrocenylphosphine ligands with a pendant side chain bearing hydroxyl group could remarkably improve the enantio- and regioselectivities of products. To our surprise, none of effective ligands was reported in Pd-catalyzed asymmetric allylic etherification before 2007, although a few ligands have promoted this transformation now.[18]

We initially tested sulfoxide-phosphine ligands in the asymmetric allylic etherification of 1,3-diphenylallyl acetate. As shown in Table 2, bissulfoxide-phosphines **L1**～**L4** gave much better enantioselectivities (Table 2, Entries 1～4) than monosulfoxide-phosphine **L6** (Table 2, Entry 8). Stereo hindrance group on bissulfoxide-phosphine (**L5**) eroded the *ee* value (Table 2, Entry 5). All results indicated that the additional sulfinyl group improved the enantioselectivity of the reaction not through the steric effect, but serving as hydrogen-bond acceptor. This effect was also applicable in the asymmetric amination (Table 2, Entry 7). In the asymmetric allylation of dimethyl manolate which has no hydrogen bond interaction with sulfinyl group, bissulfoxide-phophine gave similar *ee* value to monosulfoxide-phosphine (Table 2, Entry 9 vs. Entry 10). So, we believe that such hydrogen bond interaction benefits to the enantioselectivities of the reaction, which make the reaction from an inter- to intramolecular attack.

Table 2 The effects of ligands on asymmetric allylic alkylation of 1,3-diphenylallyl acetate[a]



4

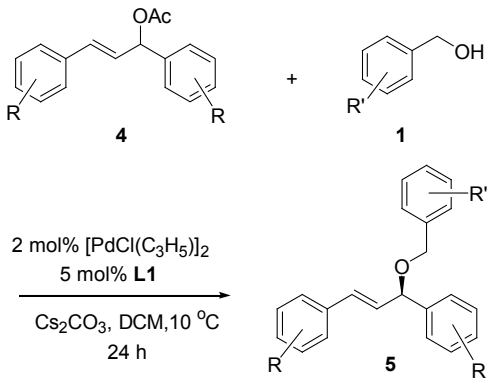
Entry	NuH	L	Yield[b]/%	*ee*[c]/%
1	**1a**	**L1**	94	90
2	**1a**	**L2**	83	85
3	**1a**	**L3**	92	83
4	**1a**	**L4**	92	89
5	**1a**	**L5**	79	56
6	**1a**	**L6**	56	63
7[d,e]	**2a**	**L2**	95	89
8	**2a**	**L6**	99	63[f]
9[d,g]	**3**	**L1**	89	84
10	**3**	**L6**	99	81[f]

[a] Reaction conditions: **4** (0.2 mmol), NuH (0.6 mmol), $[Pd(C_3H_5)Cl]_2$ (0.004 mmol), **L** (0.01 mmol), Cs_2CO_3 (0.6 mmol), CH_3CN (1 mL), 10 ℃, 24 h. [b] Isolated yield. [c] Determined by chiral HPLC. [d] BSA (0.6 mmol)+LiOAc (1 mg) instead of Cs_2CO_3. [e] Reacted at 15 ℃. [f] data from lit. [13a]. [g] Reacted at r.t.

In the next, we went on to investigate the substrate scope (for condition screening, see supporting information) for asymmetric etherification (Table 3) and amination (Table 4) of symmetrical 1,3-disubstituted allylic acetates. Bissulfoxide-phosphine ligands were found to be mostly effective for most of diaromatic allylic acetates. And variety

of allylic ethers and sencondary amines were obtained with excellent optical activities (90%～99% *ee* for etherification and 73%～99% *ee* for amination). Particularly, in the allylic etherification, there is little electronic effect of allylic acetates or alcohol substrates on the reactivities as well as enantioselectivities of the reaction.

Table 3 Pd-catalyzed allylic etherification of symmetric 1,3-disubstituted allylic acetates[a]



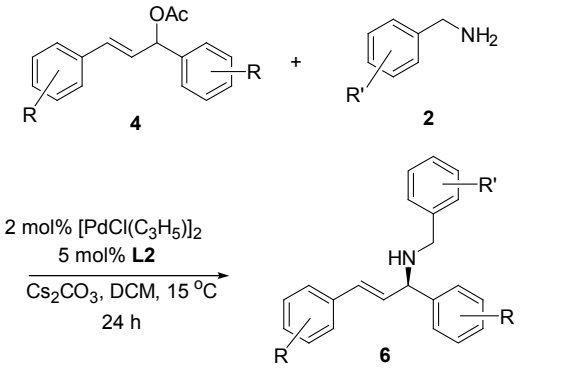
Entry	R	R'	5	Yield[b]/%	*ee*[c]/%
1	H (**4a**)	H (**1a**)	**5a**	94	95
2	H (**4a**)	*m*-MeO (**1b**)	**5b**	96	93
3	H (**4a**)	*p*-MeO (**1c**)	**5c**	97	94
4	H (**4a**)	*o*-Me (**1d**)	**5d**	93	95
5	H (**4a**)	*m*-Me (**1e**)	**5e**	93	94
6	H (**4a**)	*p*-Me (**1f**)	**5f**	95	93
7	H (**4a**)	*o*-F (**1g**)	**5g**	95	92
8	H (**4a**)	*o*-Cl (**1h**)	**5h**	95	92
9	H (**4a**)	*o*-Br (**1i**)	**5i**	93	93
10	H (**4a**)	*p*-NO_2 (**1j**)	**5j**	93	90
11	H (**4a**)	1-naphthyl (**1k**)	**5k**	90	94
12	H (**4a**)	MeOH (**1l**)	**5l**	94	94
13	*o*-MeO (**4b**)	H (**1a**)	**5m**	92	94
14	*p*-MeO (**4c**)	H (**1a**)	**5n**	95	93
15	*o*-Me (**4d**)	H (**1a**)	**5o**	95	97
16	*m*-Me (**4e**)	H (**1a**)	**5p**	96	95
17	*o*-Cl (**4f**)	H (**1a**)	**5q**	92	99
18	*m*-Cl (**4g**)	H (**1a**)	**5r**	90	91
19	*p*-Cl (**4h**)	H (**1a**)	**5s**	93	99

[a] Reaction conditions: **4** (0.2 mmol), **1** (0.3 mmol), $[Pd(C_3H_5)Cl]_2$ (0.004 mmol), **L1** (0.01 mmol), Cs_2CO_3 (0.6 mmol), DCM (2 mL), 10 ℃, 24 h. [b] Isolated yield. [c] Determined by chiral HPLC.

3 Conclusion

In summary, based on the concept of cooperative catalysis, a serious of bissulfoxide-phophine ligands which possess both Lewis base and Bronsted base sites were applied in Pd-catalyzed asymmetric allylic etherification and amination. The Bronsted basicity of these ligands was observed by ^{1}H NMR spectrum to show the existence of hydrogen bond interaction between *tert*-butyl sulfinyl group and several proton reagents. Meanwhile, this weak interaction was found to be beneficial in the Pd-catalyzed asymmetric etherification and amination of symmetric 1,3-disubstituted allylic acetates. Allylic ethers and amines adducts were obtained with excellent yields and *ee*s. Further application of these new bifunctional ligands in other asymmetric catalyzed reactions is going on in our laboratory.

Table 4 Pd-catalyzed allylic amination of symmetric 1,3-disubstituted allylic acetates [a]



Entry	R	R'	6	Yield[b]/%	*ee*[c]/%
1	H (**4a**)	H (**2a**)	**6a**	95	93
2	H (**4a**)	*o*-MeO (**2b**)	**6b**	90	92
3	H (**4a**)	*m*-MeO (**2c**)	**6c**	94	92
4	H (**4a**)	*p*-MeO (**2d**)	**6d**	92	92
5	H (**4a**)	*o*-Me (**2e**)	**6e**	91	93
6	H (**4a**)	*m*-Me (**2f**)	**6f**	93	90
7	H (**4a**)	*p*-Me (**2g**)	**6g**	95	91
8	H (**4a**)	*o*-Br (**2h**)	**6h**	93	94
9	H (**4a**)	*p*-Br (**2i**)	**6i**	90	91
10	H (**4a**)	*p*-Cl (**2j**)	**6j**	93	91
11	H (**4a**)	*p*-F (**2k**)	**6k**	93	92
12	H (**4a**)	*p*-OH (**2l**)	**6l**	87	89
13	H (**4a**)	*o*-F (**2m**)	**6m**	90	92
14	*o*-MeO (**4b**)	*o*-Br (**2h**)	**6n**	92	99
15	*m*-MeO (**4i**)	*o*-Br (**2h**)	**6o**	88	89
16	*o*-Me (**4d**)	*o*-Br (**2h**)	**6p**	91	96
17	*m*-Me (**4e**)	*o*-Br (**2h**)	**6q**	90	95
18	*p*-Me (**4j**)	*o*-Br (**2h**)	**6r**	90	94
19	1-naphthyl (**4k**)	*o*-Br (**2h**)	**6s**	86	98

[a] Reaction conditions: **4** (0.2 mmol), **2** (0.6 mmol), $[Pd(C_3H_5)Cl]_2$ (0.004 mmol), **L2** (0.01 mmol), Cs_2CO_3 (0.6 mmol), DCM (2 mL), 15 ℃, 24 h. [b] Isolated yield. [c] Determined by chiral HPLC.

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