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A new electronically deficient atropisomeric diphosphine ligand (*S*)-CF_3O-BiPhep and its application in asymmetric hydrogenation

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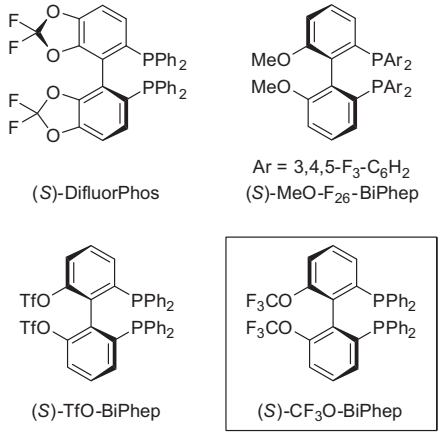
ABSTRACT

A new electronically deficient atropisomeric diphosphine ligand (*S*)-CF_3O-BiPhep was synthesized from 1-bromo-3-(trifluoromethoxy)benzene in high yield. The key steps included oxidative coupling with anhydrous ferric chloride and optical resolution by (+)-DMTA. The ligand afforded high performance for Ir-catalyzed asymmetric hydrogenation of quinolines with ee up to 92% and TON up to 25,000. It was also successfully applied to the Pd-catalyzed asymmetric hydrogenation of simple indoles with ee up to 87% and Rh-catalyzed asymmetric 1,4-addition of phenylboronic acid to 2-cyclohexenone with 97% ee.

Chiral bidentate phosphine ligands play an important role in various homogeneous transition metal-catalyzed reactions.[1] Therefore, design and synthesis of new chiral diphosphine ligands with new scaffold and/or electronic properties were still an attractive area of research.[2] Recently, several studies revealed that electronically deficient atropisomeric diphosphine ligands could often lead to a dramatic variation of the reactivity and enantioselectivity for some transition metal-mediated asymmetric reactions.[3] For example, in 2004, Genêt and co-workers synthesized the DifluorPhos ligand which displayed better reactivity and enantioselectivity than electron-rich diphosphine ligands for several transition metal-catalyzed reactions.[4,5] In 2009, Korenaga group synthesized an electron poor chiral diphosphine ligand MeO-F_{28}-BiPhep which was found to greatly improve the catalytic activity for Rh-catalyzed 1,4-addition at room temperature.[6] Afterward, they found the ligand gave very good catalytic activity in the reaction with TOF up to 53,000 h^{-1} and TON up to 320,000.[7] In the research field of Ir-catalyzed asymmetric hydrogenation of quinolines, the electronically deficient atropisomeric diphosphine ligands also showed very high catalytic activities, such as P-Phos and the aforementioned DifluorPhos.[8] Recently, our group also synthesized a series of electronically deficient atropisomeric bisphosphine ligands based on (*S*)-MeO-BiPhep and studied the effectiveness in the Ir-catalyzed asymmetric hydrogenation of quinolines. We found that these electron-poor chiral diphosphine ligands gave much better catalytic activities than MeO-BiPhep, and the introduction of more electron-withdrawing groups in the biaryl backbone could dramatically improve the catalyst activity. When using the ligand (*S*)-TfO-BiPhep, we achieved the highest 95% ee and TON could be up to 14,600 (Scheme 1).[9] It was known to us that most of the catalytic system for quinoline hydrogenation suffered from low catalytic activity because of the deactivation of iridium catalyst by the formation of catalytically unreactive dimers and trimers through hydride-bridged bonds under hydrogen atmosphere. So we



Scheme 1. Electronically deficient atropisomeric diphosphine ligands.

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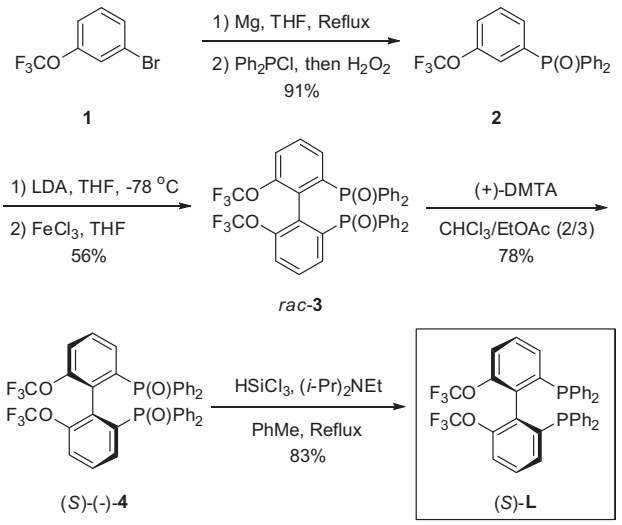
hypothesized that the using of the electronically deficient atropisomeric diphosphine ligands might inhibit the formation of inactive dimmers or trimers and thus the productivity of the catalyst might be enhanced dramatically. Herein, we designed and synthesized a novel electronically deficient atropisomeric diphosphine ligand bearing a trifluoromethoxy at the 6- and 6′-positions of the biaryl backbone. Following the nomenclature for MeO-BiPhep, the ligand was named as CF_3O-BiPhep [2,2′-bis(diphenylphosphino)-6,6′-ditrifluoromethoxy-1,1′-biphenyl].

Our synthetic approach to enantiopure ligand (*S*)-CF_3O-BiPhep was shown in Scheme 2 and the (*R*)-CF_3O-BiPhep was also obtained in the same way.[10] In the first step, treatment of the Grignard reagent of commercially available 1-bromo-3-(trifluoromethoxy)benzene (**1**) with chlorodiphenylphosphine followed by the addition of H_2O_2 to afford the phosphine oxide **2** in 91% yield was performed. *ortho*-Lithiation of **2** by LDA at −78 °C in THF and further oxidative coupling with anhydrous ferric chloride provided the racemic diphosphine dioxide **3** in 56% yield. Effective optical resolution of the *rac*-**3** was achieved by using (+)-di-*p*-methoxybenzoyl-D-tartaric acid [(+)-DMTA] as a resolving agent. Recrystallization of the mixture by a mixed solvent of $CHCl_3$/EtOAc (2:3) gave a complex of (−)-**4** and (+)-DMTA. Treatment of the tartrate complex with aqueous base provided enantiomerically pure (−)-**4** (ee >99%) in 78% yield, based on the amount of (−)-**4** in *rac*-**3**. Finally, $HSiCl_3$ reduction of compound (−)-**4** in the presence of *N*,*N*-diisopropyl-ethylamine afforded the enantiomerically pure ligand in 83% yield (Scheme 2).[11]

The absolute configuration of (−)-**4** was determined by X-ray analysis of the complex of (−)-**4** with (+)-DMTA which was recrystallized from MeOH as a colorless crystal. From the internal comparison with (+)-DMTA, the absolute configuration of (−)-**4** was defined to be *S* (Fig. 1). Therefore, the ligand reduced from (−)-**4** was assigned as (*S*)-CF_3O-BiPhep.

With the ligand in hand, its catalytic performance in the Ir-catalyzed asymmetric hydrogenation of quinolines was firstly investigated.[12,13] Having established the optimal conditions, a variety of substituted quinoline derivatives were tested to explore the scope of the reaction (the S/C molar ratio was 1000/1). As summarized in Table 1, high yields and good enantioselectivities were obtained for several 2-alkyl substituted quinolines and the reaction was relatively insensitive to the length of the alkyl group (Table 1, entries 1–5). It was noted that the C=C double bond in the side chain of **5d** was also completely hydrogenated (Table 1, entry 4). When hydroxyl groups at the side chain, the yield was very excellent but



Scheme 2. Synthesis of the ligand (*S*)-CF_3O-BiPhep.

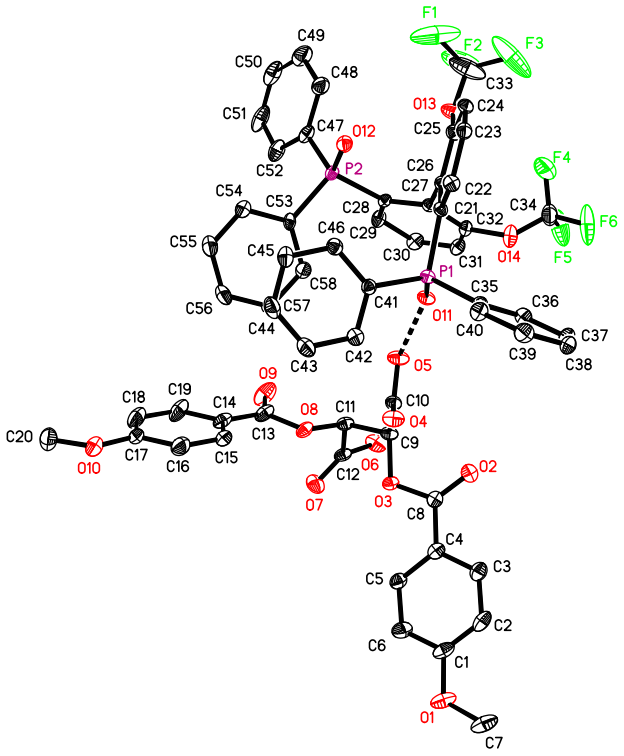
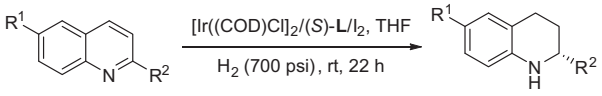


Figure 1. X-ray structure of compound (*S*)-(−)-**4**·(+)-DMTA.

Table 1
Asymmetric hydrogenation of quinoline derivatives[a]



5 **6**

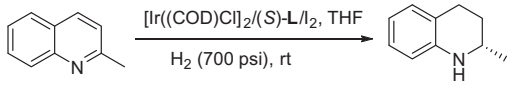
Entry	R^1/R^2	Yield[b] (%)	ee[c] (%)
1	H/Me (**6a**)	98	91 (*S*)
2	H/Et (**6b**)	93	92 (*S*)
3	H/*n*-Pr (**6c**)	97	90 (*S*)
4	H/3-Butenyl (**6d**)	97	87 (*S*)
5	H/*n*-Pentyl (**6e**)	99	88 (*S*)
6	H/$Me_2C(OH)CH_2$–(**6f**)	98	70 (*R*)
7	H/$C_6H_5(CH_2)_2$–(**6g**)	98	86 (*S*)
8	Me/Me (**6h**)	88	79 (*S*)
9	F/Me (**6i**)	95	81 (*S*)
10	H/Ph (**6j**)	98	60 (*R*)

[a] Conditions: **5** (1 mmol), $[Ir(COD)Cl]_2$ (0.0005 mmol), (*S*)-**L** (0.0011 mmol), I_2 (0.0050 mmol), H_2 (700 psi), THF (2 mL), rt, 22 h.
[b] Isolated yields.
[c] Determined by HPLC.

only moderate enantioselectivity was obtained (Table 1, entry 6). With 2-phenethyl substituted quinoline, slightly lower enantioselectivity was obtained (Table 1, entry 7). For the 6-substituted quinolines, the enantioselectivities decreased significantly (Table 1, entries 8 and 9). Replacing the alkyl at 2-position with phenyl group still gave high yield but the enantioselectivity was moderate (Table 1, entry 10).

To evaluate the catalytic efficiency of the system $[Ir(COD)Cl]_2$/**L**/I_2 in asymmetric hydrogenation of quinolines, we investigated the effect of the substrate-to-catalyst (S/C) molar ratio on the conversion and enantioselectivity of this reaction. 2-Methylquinoline was selected as substrate and the results were shown in the Table 2. It

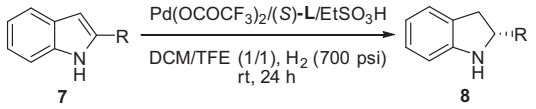
Table 2
The effect of the S/C on conversion and enantioselectivity[a]



5a 6a

Entry	S/C	I_2 (mol %)	Time (h)	Convn.[b] (%)	ee[c] (%)
1	1000/1	0.5	22	>95	91 (*S*)
2	5000/1	1.0	36	>95	93 (*S*)
3	10,000/1	1.0	36	>95	92 (*S*)
4	20,000/1	1.0	72	>95	93 (*S*)
5[d]	50,000/1	2.0	72	50	91 (*S*)

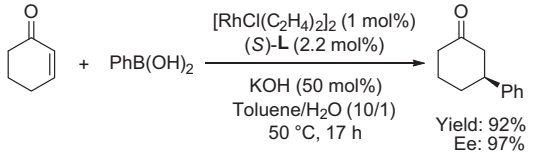
[a] Conditions: **5a** (1 mmol), $[Ir(COD)Cl]_2$/**L** (0.5/1.1), H_2 (700 psi), THF (2 mL), rt.
[b] Determined by ^1H NMR.
[c] Determined by HPLC.
[d] 5 mmol **5a**, 3 mL THF.



7 8

Entry	R	Yield (%)	Ee (%)
1	CH_3	87 (**8a**)	75 (*S*)
2	Bn	98 (**8b**)	87 (*S*)
3	Cyclopentyl	60 (**8c**)	83 (*R*)
4	Cyclohexyl	82 (**8d**)	82 (*R*)

Scheme 3. Asymmetric hydrogenation of simple indoles.



Scheme 4. The addition of phenylboronic acid to cyclohexenone.

was noteworthy that the enantioselectivity changed slightly when the S/C ratio was increased (91–93% ee). When the S/C ratio was increased from 5000/1 to 20,000/1, prolonging the reaction time would facilitate the reaction with full conversion (Table 2, entries 2–4). When S/C ratio further increased to 50,000/1, 50% conversion was observed, providing a high TON value of 25,000 (Table 2, entry 5). It was obvious that our ligand afforded excellent performance for Ir-catalyzed asymmetric hydrogenation of quinolines. It revealed again that the electronically deficient atropisomeric diphosphine ligand showed good catalytic performance in the Ir-catalyzed asymmetric hydrogenation of quinolines.

To further investigate the effectiveness of the ligand in other reactions, we also applied it in the Pd-catalyzed asymmetric hydrogenation of indoles. In contrast to quinolines, the asymmetric hydrogenation of indoles was much less studied, especially the asymmetric hydrogenation of unprotected indoles.[12,14] Very recently, our group developed the first highly enantioselective hydrogenation of unprotected indoles using Pd-H8-BINAP with a Brønsted acid as an activator.[15] Herein, we also applied our ligand in the Pd-catalyzed asymmetric hydrogenation of simple indoles using a Brønsted acid as an activator. To our delight, the ligand also proceeded well in this reaction and the results were shown in Scheme 3. 2-Methyl and 2-benzyl substituted indoles could be hydrogenated smoothly with 75% and 87% ee, respectively (Scheme 3, entries 1 and 2). With the 2-cyclopentyl and 2-cyclohexyl substituted indoles, 83% and 82% ees were obtained, respectively (Scheme 3, entries 3 and 4).

We also applied our ligand in the Rh-catalyzed asymmetric 1,4-addition of phenylboronic acid to 2-cyclohexenone.[16] Gratifyingly, the reaction proceeded well with 97% ee and 92% yield. (Scheme 4)

In summary, we have developed a new electronically deficient atropisomeric diphosphine ligand CF_3O-BiPhep. The ligand afforded high activity in the Ir-catalyzed asymmetric hydrogenation of quinolines with ee up to 92% and TON up to 25,000. It showed again that the electronically deficient atropisomeric diphosphine ligand had good catalytic performance in the Ir-catalyzed asymmetric hydrogenation of quinolines. The CF_3O-BiPhep ligand was also successfully applied in the Pd-catalyzed asymmetric hydrogenation of simple indoles and Rh-catalyzed asymmetric 1,4-addition of phenylboronic acid to 2-cyclohexenone with up to 97% ee. Further study on the detailed reason for the good performance of electronically deficient diphosphine ligand in the Ir-catalyzed asymmetric hydrogenation of quinolines is underway and will be disclosed in due course.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.03.036.

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11. Characterization data of (*S*)-CF_3O-BiPhep: White solid. Mp 194–195 °C. $[\alpha]_D^{27}$ = 87.0 (*c* 0.97, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.35 (m, 14H), 7.14–7.20 (m, 8H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.99–7.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.5, 134.3, 134.2, 133.6, 133.5, 133.4, 131.7, 129.7,

129.0, 128.6, 128.5, 128.4, 117.4, 110.2. ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -13.6$. ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -57.1$.

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