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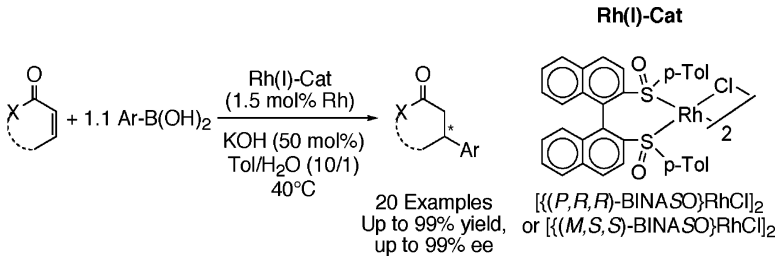

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A Chiral Bis-Sulfoxide Ligand in Late-Transition Metal Catalysis; Rhodium-Catalyzed Asymmetric Addition of Arylboronic Acids to Electron-Deficient Olefins

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Asymmetric metal catalysis has seen tremendous developments in the last decades.[1] The overwhelming majority of successful chiral chelate ligands in late-transition metal catalysis are based on phosphorus and/or nitrogen. Recently, Hayashi and Carreira have developed alternative chiral diene ligands for asymmetric rhodium and iridium catalysis.[2,3] Synthesis of these new dienes as well as the more traditional P/N ligands requires multistep synthetic procedures with often tedious separation of the enantiomers. A potentially very readily available chiral ligand class with a well-known coordination chemistry is represented by sulfoxides.[4] Considering that these compounds play an important role as chiral auxiliaries in asymmetric synthesis,[5] it is surprising that few examples exist in which this ligand class participates in homogeneous metal catalysis.[6−8] The use of rhodium bis-sulfoxide compounds in catalysis is unknown,[9] and successful applications of bis-sulfoxide ligands in asymmetric transformations have not been reported.[7,8]

We recently decided to investigate chiral bis-sulfoxides as ligands in LTM catalysis. In this report, we describe our results on the preparation of a chiral bis-sulfoxide rhodium(I) complex and its use as a precatalyst in the asymmetric 1,4-addition of arylboronic acids to cyclic α,β-unsaturated ketones and esters.[10]

The bis-sulfoxide ligand used in our first catalytic application is a 1,1′-binaphthyl derivative similar to the well-known BINAP (1,1′-binaphthalene-2,2′-diyl-bis-diphenylphosphine) ligand developed by Noyori et al.[11] Compared to BINAP, synthesis of the bis-sulfoxide analogue is extremely straightforward and can be done in one single step from commercially available starting materials according to Scheme 1.[12] Following the nomenclature for BINAP and its derivatives, we name this ligand *p*-tol-BINASO (1,1′-binaphthalene-2,2′-diyl-bis-(*p*-tolylsulfoxide, **1**). The two atropisomers of the diastereoisomeric BINASO compounds were easily separated via column chromatography, independently from whether *S*- or *R*-sulfinates were employed, giving four pure ligands (Scheme 1) in good overall yield (>70% based on *rac*-DBBN).[13]

(*P*,*R*,*R*)-*p*-tol-BINASO [(*P*,*R*,*R*)-**1**] (2 equiv) ligand reacts readily with $[RhCl(C_2H_4)_2]_2$ in a methylene chloride solution at room temperature.[14] Subsequent filtration, concentration and layering with THF followed by crystallization at −35 °C afforded burgundy crystals of [{(*P*,*R*,*R*)-*p*-tol-BINASO}RhCl]$_2$ (**2**) in high yield (>90%).

Figure 1 shows the ORTEP drawings of both (*M*,*R*,*R*)-*p*-tol-BINASO (left, **1**) and [{(*P*,*R*,*R*)-*p*-tol-BINASO}RhCl]$_2$ (right, **2**). Coordination of *p*-tol-BINASO to the metal leads to the expected sulfur−oxygen bond contraction [S−O in **1**, 1.4922(16) Å; S−O in **2**, 1.466(4) and 1.473(4) Å], indicating efficient σ-donation of the sulfoxide moiety. Comparing the solid-state structure of **2** with its phosphine analogue [{(*R*)-BINAP}RhCl]$_2$,[15] reveals a significant increase in bite angle for BINASO (98.1°) over BINAP (90.5°), whereas the dihedral angle between the planes of the two naphthyl

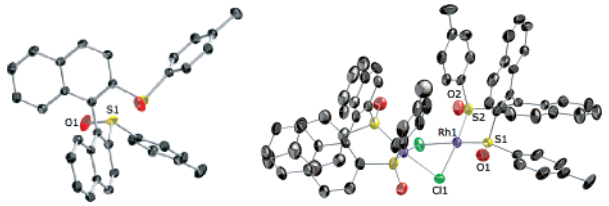
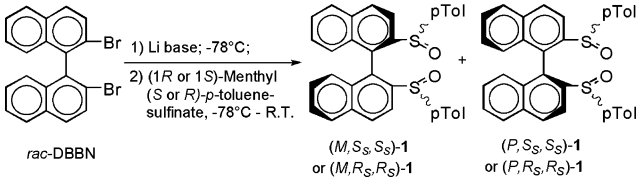


Figure 1. ORTEP drawings (50% probability) of (*M*,*R*,*R*)-*p*-tol-BINASO (left, **1**) and [{(*P*,*R*,*R*)-*p*-tol-BINASO}RhCl]$_2$ (right, **2**).

Scheme 1. Synthesis of *p*-tol-BINASO Ligands



units remains very similar (74.1° BINASO; 76.0° BINAP). A comparison of the Rh···Rh distances in **2**, in [{(*R*)-BINAP}RhCl]$_2$, and in Hayashi's similarly bulky diene complex [{(*S*,*S*)-Ph-bod*}-RhCl]$_2$,[16] indicates that the ligating properties of bis-sulfoxides might lie somewhere between diene and bis-arylphosphine ligand systems.[17]

With catalyst precursor **2** at hand, we evaluated its performance in the 1,4-addition of phenylboronic acid to 2-cyclohexenone. Experiments carried out in a mixture of dioxane/water/KOH following Hayashi's procedure gave excellent selectivities, but low overall yields. Gratifyingly, substituting dioxane with toluene led to complete conversion to the product within 30 min at room temperature while maintaining high ee values (see Supporting Information for details). Subsequent studies showed that catalyst loadings could be diminished to 1.5 mol % Rh without significant loss of reactivity (In general, 3 mol % Rh have to be used with phosphine or diene ligands). More importantly, our catalytic system does not require excess of expensive boronic acid (normally 2−5 equiv have to be used) and can be run conveniently with stoichiometric (1.1 equiv) amounts. This is all the more surprising since throughout our catalytic studies, commercially available starting materials were used without purification.

Table 1 shows that the catalytic activity of **2** is excellent with complete conversion normally achieved within a couple of hours at 40 °C. The enantioselectivities observed here are among the highest for the rhodium-catalyzed asymmetric 1,4-addition, the selectivity being 90% ee and higher in all but one of the reactions examined (entry 18). Virtually complete selectivity was obtained with a number of substrates. Using [{(*M*,*S*,*S*)-*p*-tol-BINASO}RhCl]$_2$ (**2**) gave the opposite enantiomer with equally high selectivity (entry 2). An interesting possibility arises with chiral, racemic 6-methyl-2-cyclohexen-1-one (**3e**). Addition of 2-naphthylboronic acid (**4y**)

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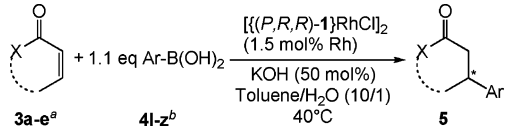
Table 1. Catalytic Results with [{(*P*,*R*,*R*)-*p*-tol-BINA*SO*}RhCl]$_2$ (**2**)



3a-e[a] **4l-z**[b] **5**

entry	3	4	time (h)	yield[c] (%) of 5	% ee[d]
1	**3a**	**4l**	1	99 (**5al**)	98 (*S*)
2[e]	**3a**	**4l**	1	99 (**5al**)	98 (*R*)
3	**3a**	**4m**	1	97 (**5am**)	96
4	**3a**	**4n**	1.5	86 (**5an**)	98
5	**3a**	**4o**	1.5	90 (**5ao**)	98
6	**3a**	**4p**	1	92 (**5ap**)	99
7	**3a**	**4q**	1.5	93 (**5aq**)	99
8	**3a**	**4r**	1	94 (**5ar**)	97
9	**3a**	**4s**	1.5	93 (**5as**)	99
10	**3a**	**4t**	1	91 (**5at**)	97
11[f]	**3a**	**4u**	1	55 (**5au**)	97
12	**3a**	**4v**	2	98 (**5av**)	90
13[f]	**3a**	**4w**	1	60 (**5aw**)	99
14	**3a**	**4x**	1	99 (**5ax**)	90
15	**3a**	**4y**	1	89 (**5ay**)	96
16	**3a**	**4z**	1	90 (**5az**)	95
17	**3b**	**4l**	0.5	99 (**5bl**)	96
18[g]	**3c**	**4l**	3	98 (**5cl**)	66
19	**3d**	**4l**	1	98 (**5dl**)	91
20[g]	**3e**	**4y**	1	49 (***cis*-5ey**)	94
				49 (***trans*-5ey**)	94

[a] **3a** = 2-cylcohexen-1-one, **3b** = 2-cyclopenten-1-one, **3c** = 2-cyclohepten-1-one, **3d** = 5,6-dihydro-2*H*-pyran-2-one, **3e** = 6-methyl-2-cyclohexen-1-one. [b] Ar = Ph (**4l**), 4-$CH_3C_6H_4$ (**4m**), 4-ClC_6H_4 (**4n**), 4-FC_6H_4 (**4o**), 4-$CH_3OC_6H_4$ (**4p**), 3-$CH_3C_6H_4$ (**4q**), 3-$CF_3C_6H_4$ (**4r**), 3-ClC_6H_4 (**4s**), 3- FC_6H_4 (**4t**), 3-$CH_3OC_6H_4$ (**4u**), 2-$CH_3C_6H_4$ (**4v**), 2-FC_6H_4 (**4w**), 1-naphthyl (**4x**), 2-naphthyl (**4y**), 1-pyrene (**4z**). [c] Isolated yields. [d] Determined by HPLC analysis with chiral columns (Daicel Chiralcel OD, OD−H, OJ-H, OB−H or Chiralpak IA). [e] Using [{(*M*,*S*,*S*)-*p*-tol-BINA*SO*}RhCl]$_2$ (**2**) as catalyst. [f] Using 2 equiv of the boronic acid gives better yields (70−80%). [g] Reaction run using 3 mol % of catalyst and 2 equiv of boronic acid.

to **3e** gave cis and trans diastereomers in equal amounts and equal selectivities after separation through silica gel chromatography (entry 20), a result that is in contrast to the copper-catalyzed 1,4-addition of alkyl−zinc reagents to **3e**.[18] More intriguingly, epimerization of the methyl group in *cis*-**5ey** under thermodynamic control (NaOMe/MeOH or HCl/MeOH) to give the trans diastereomer does not occur (see Supporting Information).

Finally, we should note that derivatives of [{*p*-tol-BINA*SO*}-RhCl]$_2$ (**2**), namely (*p*-tol-BINA*SO*)Rh(acac) as well as the cationic, coordinatively saturated η^6-tolylsulfoxide bound dimer [{*p*-tol-BINA*SO*}Rh]$_2$(PF_6)$_2$, are equally effective catalysts for the present transformation.

In conclusion, we have shown that chiral bis-sulfoxides can be used successfully as ligands in asymmetric late-transition metal catalysis. Precatalyst [{(*P*,*R*,*R*)-*p*-tol-BINA*SO*}RhCl]$_2$ (**2**) shows high reactivities and excellent selectivities in the 1,4-addition of arylboronic acids to cyclic, electron-poor double bonds and we are currently expanding the scope of our catalyst system to other substrates. In the present protocol, catalyst loadings can be kept low and excess boronic acid is not required for efficient catalysis. The key advantage of *p*-tol-BINASO over known chiral ligands for this transformation (and for asymmetric LTM catalysis in general) lies in its extraordinarily easy synthesis. In addition, *p*-tol-BINASO and other bis-sulfoxides should be more versatile than diene ligands and be able to support catalysis involving oxidative addition processes (H_2, $HSiR_3$, etc.) or carbon monoxide. Furthermore, examples of achiral oxidation catalysis with sulfoxide−palladium compounds[6c−f] show that this ligand class might overcome limitations associated with phosphines. Studies pertinent to the above transformations are underway.

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Supporting Information Available: Experimental procedures and CIFs for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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