DOI: 10.1002/adsc.201500975

Advanced Synthesis & Catalysis

Very Important Publication

A Chiral Disulfoxide Ligand for the Efficient Rhodium-Catalyzed 1,2-Addition of Arylboroxines to *N*-Tosylarylimines

Guang-Zhen Zhao,[a] Gellért Sipos,[a] Alvaro Salvador,[a] Arnold Ou,[a] Pengchao Gao,[a] Brian W. Skelton,[b] and Reto Dorta[a,*]

[a] School of Chemistry and Biochemistry, University of Western Australia, 35 Stirling Highway, 6009 Crawley, Western Australia, Australia
Fax: (+61)-8-6488-7330; phone: (+61)-8-6488-3161; e-mail: reto.dorta@uwa.edu.au
[b] Centre for Microscopy, Characterisation and Analysis, University of Western Australia, 35 Stirling Highway, 6009 Crawley, Western Australia, Australia

Received: October 22, 2015; Revised: November 23, 2015; Published online: January 26, 2016

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201500975.

Abstract: Enantiomerically pure diarylmethylamines are important building blocks in active pharmaceutical ingredients. Herein, we report a rhodium precatalyst with a chiral disulfoxide ligand that effects the 1,2-addition of arylboroxines to aromatic imines to give high yields and high enantioselectivities of these products. The present paper describes a system that is very simple, where the ease of synthesis of the chiral ligand is combined with low catalyst loadings and reaction conditions that do not need any additives or external base.

Keywords: 1,2-additions; chiral disulfoxide ligands; diarylmethylamines; rhodium catalysis

Introduction

Chiral diarylmethylamines are molecular frameworks that are frequently found in pharmacologically active compounds and their synthetic access in enantiopure form is therefore of high interest.[1–5] One of the most successful strategies that has emerged to access these compounds is the arylation of aldimines. For example, the asymmetric addition of highly reactive organometallic reagents to imino compounds with enantioselectivity controlled by chiral O/N-coordinating ligands[6] or chiral auxiliaries[2b,c,4c,7] is a fast and reliable method for asymmetric synthesis of this scaffold.[8] Useful chiral diarylmethylamines with high enantiomeric excess were successfully obtained with this method, although it is normally more efficient for the synthesis of dialkylmethylamine or alkylarylmethylamine synthesis.[9]

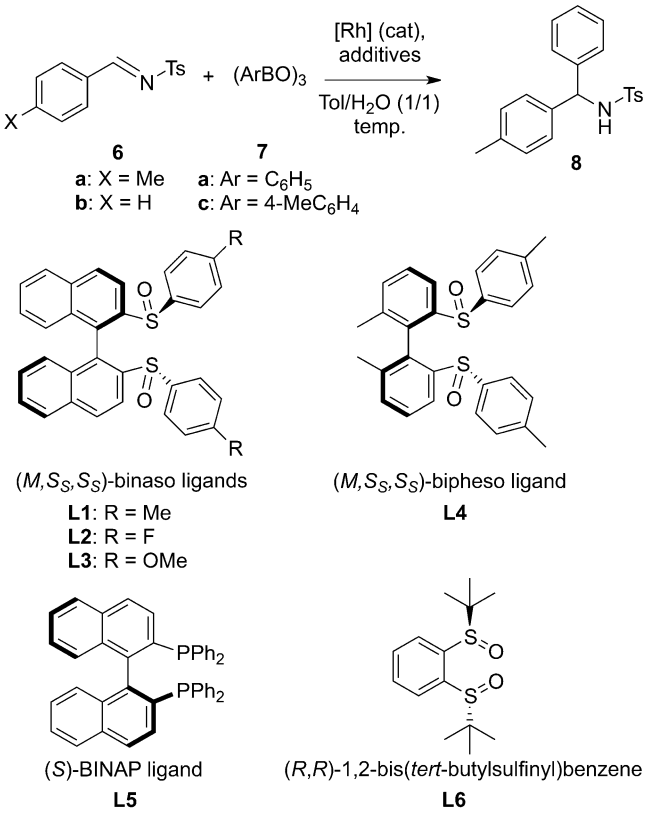
Asymmetric addition processes that employ chiral transition metal catalysts represent another entry to these building blocks. As a main advantage to the above-mentioned more traditional methods, they offer the possibility of using milder, less reactive arylation agents.[10] Among them, arylboron reagents are particularly appealing as they are readily available, highly functional group compatible, and much less toxic and hazardous than other arylation reagents. These advantages make them, when paired with (chiral) Rh and Pd catalysts, the most widely used aryl sources for asymmetric arylation reactions of imines.[11] To date, a wide range of chiral ligands have been described in these reactions and include phosphine(s), olefin(s), phosphoramidite(s), and phosphate(s), which in conjunction with the appropriate rhodium precursor, give the corresponding chiral amine products in good yields and high enantiomeric excess.[12] It is therefore surprising to note that among the impressive array of chiral ligand systems described for this important reaction, there are very few reports that work at catalyst loadings lower than 1 mol%,[12h,p] which given the high price of the metal/ligand combinations used would be a prerequisite for successful applications on a larger scale. A possible problem that may be at least in part responsible for the lack of reactivity of most catalysts is the fact that these reactions are oftentimes plagued by competing imine hydrolysis.[12k]

In 2008, our group showed that a chiral chelating disulfoxide ligand can be employed successfully in a Rh-catalyzed addition reaction, namely the 1,4-addition of boronic acids to α,β-unsaturated compounds (Hayashi–Miyaura reaction).[13] The ligand design was based on a simple mimic of the very successful chiral binap ligand, where the two phosphine moieties were

substituted by chiral sulfoxides. This work and following ligand designs by other groups all suggest that at least for such rhodium-catalyzed addition reactions, S-bound, sulfinyl-based ligands can indeed be used successfully in asymmetric catalysis.[14] Of the many chiral ligand designs available, one of the main advantages of using sulfoxides is their easy access in enantiopure form, which renders ligand syntheses straightforward, cheap and practical.

To extend the reactivity of our binaso-type family of disulfoxides, we herein report the employment of these C_2-symmetric S-chiral disulfoxide ligands in the 1,2-addition of arylboroxines to *N*-tosylaldimines. At the outset of this study, it was not clear whether these ligands would be successful in the 1,2-addition, as it is well known that ligand requirements between the 1,4-addition to α,β-unsaturated compounds and the 1,2-addition to imines are different and distinct and very few examples exist where the same ligand is able to promote both these reactions.[12n,p,q,u] Indeed, the report here is the first that shows that a disulfoxide ligand system can be used in the 1,2-addition reaction. A careful optimization study on the reaction conditions also led to a system where hydrolysis was not observed for the imine substrates,[11f,12k,15] while mild reaction conditions in aqueous toluene were maintained giving high yields and enantioselectivities at catalyst loadings that are among the lowest reported.[16]

Table 1. Asymmetric arylation of *N*-tosylimine **6** with arylboroxine **7**: optimization of reaction conditions.[a]



Entry	Catalyst [mol%]		6	7	Additives [mol%]	*T* [°C]	Yield [%][b]	*ee* [%][c]
1	[(**L1**)RhCl]$_2$	[1.25]	**6a**	**7a**	KF [400]	35	99	96 (*S*)
2	[(**L2**)RhCl]$_2$	[1.25]	**6a**	**7a**	KF [400]	35	87	94 (*S*)
3	[(**L3**)RhCl]$_2$	[1.25]	**6a**	**7a**	KF [400]	35	50	97 (*S*)
4	[(**L4**)RhCl]$_2$	[1.25]	**6a**	**7a**	KF [400]	35	54	95 (*S*)
5	[(**L5**)RhCl]$_2$	[1.25]	**6a**	**7a**	KF [400]	35	11	31 (*R*)
6	none		**6a**	**7a**	KF [400]	35	NR	
7	[(**L1**)RhCl]$_2$	[0.75]	**6b**	**7c**	KF [400]	35	92	97 (*R*)
8	[(**L1**)RhCl]$_2$	[0.75]	**6b**	**7c**	NaOH [3]	35	67	96 (*R*)
9	[(**L1**)RhCl]$_2$	[1.25]	**6b**	**7c**	K_3PO_4 [20]	35	91	96 (*R*)
10	[(**L5**)RhCl]$_2$	[0.75]	**6b**	**7c**	KF [400]	35	19	31 (*S*)
11	[(**L6**)RhCl]$_2$	[0.75]	**6b**	**7c**	KF [400]	35	40	97 (*S*)
12	[(**L5**)Rh(OH)]$_2$	[0.75]	**6b**	**7c**	KF [400]	35	21	24 (*S*)
13	[(**L1**)Rh(OH)]$_2$	[0.75]	**6b**	**7c**	KF [400]	35	99	96 (*R*)
14	[(**L6**)Rh(OH)]$_2$	[0.75]	**6b**	**7c**	KF [400]	35	49	97 (*S*)
15[d]	[(**L1**)Rh(OH)]$_2$	[0.50]	**6b**	**7c**	none	25	96	97 (*R*)
16[e]	[(**L1**)Rh(OH)]$_2$	[0.75]	**6b**	**7c**	4 Å MS	35	NR	
17[e]	[(**L1**)Rh(OH)]$_2$	[1.50]	**6b**	**7c**	4 Å MS	35	24	95 (*R*)
18[d,f]	[(**L1**)Rh(OH)]$_2$	[0.35]	**6b**	**7c**	none	25	97	96 (*R*)
19[g]	[(**L1**)Rh(OH)]$_2$	[0.25]	**6b**	**7c**	none	25	96	97 (*R*)

Results and Discussion

Initial studies were carried out with 4-methylbenzaldehyde *N*-tosylimine **6a** and phenylboroxine **7a** reactants with rhodium catalysts containing various binaso-type ligands under reaction conditions reported in the literature that include using excess KF as a base additive (Table 1, entries 1–4). The chloro-bridged rhodium dimer [(**L1**)RhCl]$_2$, which was successfully utilized in our initial report on 1,4-addition reactions,[13a] was tested first (entry 1) using a toluene/water mixture (1:1) to which were added the catalyst (2.5 mol% Rh) and KF (4 equivalents). The mixture was heated to 35 °C for 18 h giving a high isolated yield of phenyl(4-methylphenyl)methylamine tosylamide **8aa** (95% yield) after chromatography on silica gel. Gratifyingly, the enantiomeric purity was determined to be 96% *ee* by HPLC analysis. Varying the *para*-substituents of the phenyl group on the binaso ligands did not improve the outcome with 4-fluoro-sub-

[a] *Reaction conditions:* imine **6** (0.30 mmol), boroxine **7** (0.6 mmol B), rhodium catalyst and additives were stirred in toluene/H_2O (2.0 mL/2.0 mL) for 12–18 h.
[b] Isolated yields after column chromatography.
[c] Determined by HPLC analysis; absolute stereochemistry assigned by comparison with results reported in refs.[12g,l]
[d] **6** (0.45 mmol), **7** (0.9 mmol) in toluene/H_2O (4.5 mL/2.5 mL).
[e] Toluene as solvent, no H_2O.
[f] 1.4 equiv. B (0.42 mmol) were used.
[g] **6** (0.45 mmol), **7** (0.9 mmol) in toluene/H_2O (6.0 mL/1.0 mL).

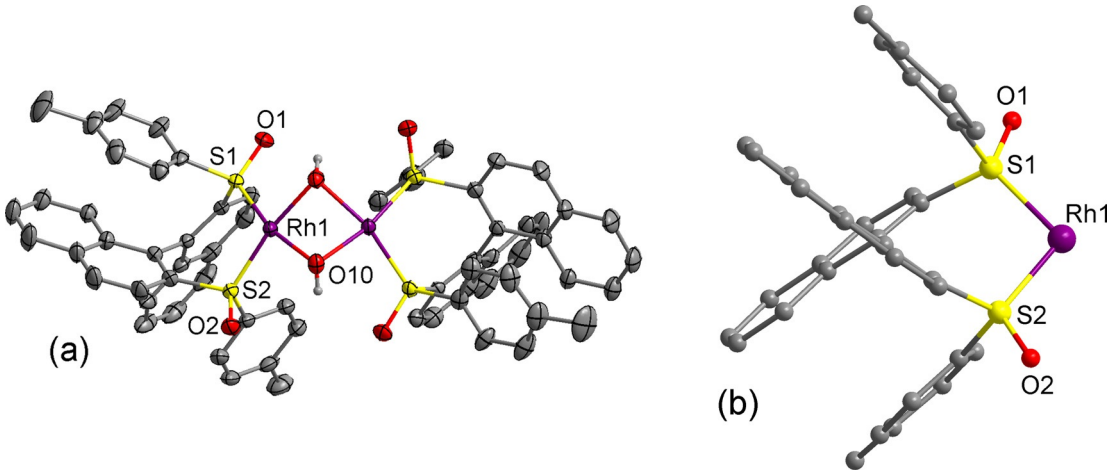


Figure 1. (a) Molecular structure of [{(*M*,*S*,*S*)-*p*-Tol-binaso}Rh(OH)]$_2$ (30% probability ellipsoids; only O–H hydrogen atoms shown). Selected bond lengths (Å) and angles (deg): Rh1–O10′, 2.049(3) and 2.061(3); Rh1–S1, 2.1563(9); Rh1–S2, 2.1598(9); S1–O1, 1.477(3); S2–O2, 1.481(3); S1–Rh1–S2, 98.87(3); O10–Rh1–S2, 93.86(8); O10–Rh1–S2′, 168.61(8); O10–Rh1–S1, 166.31(8); O10–Rh1–S1′, 92.45(8); O10–Rh1–O10′, 74.75(14). The prime refers to the atom at x,1–y,1/2–*z*. (b): Half-view, ball-and-stick model of the {(*M*,*S*,*S*)-*p*-Tol-binaso}[Rh] fragment.

stituted binaso **L2** giving a slightly lower yield and enantioselectivity (entry 2). Excellent enantiocontrol was observed when electron-donating 4-methoxy-substituted binaso **L3** was used (97% *ee*), but the isolated yield dropped significantly (50% yield). When modifying the backbone structure of the ligand (**L4**), which in our earlier studies on the 1,4-addition reaction led to the most active and selective catalyst,[13b] **8aa** was again obtained in good enantiomeric excess (95% *ee*) but in just 50% yield (entry 4). This underlines the fact that 1,4-addition and 1,2-addition reactions have distinct ligand requirements and indeed, classical chiral diphosphine binap, one of the preferred ligands for the 1,4-addition reaction, performs very poorly in the 1,2-addition reaction to imines (entry 5). Not surprisingly, omitting the catalyst does not lead to any product formation (entry 6).

After having identified **L1** as the proper ligand, we proceeded to optimize the reaction conditions using benzaldehyde *N*-tosylimine **6b** and arylboroxine **7c**. The choice of these substrates also highlights the fact that both enantiomers of the amine product(s) may be synthesized using a single catalyst by simply switching the two substrate components (entry 1 *vs.* entry 7). We began our optimization of the reaction conditions by testing different bases in the reaction, as KF is relatively expensive, especially given the fact that a large amount (4 equiv.) is required. As a first attempt, we switched to stronger NaOH as a base, that even when used in catalytic amounts (entry 8) incurred significant hydrolysis of the imine substrate.[11f,12k] Gratifyingly, a catalytic amount of K_3PO_4 (0.2 equiv.) gave a high yield of product (91% yield) while maintaining the excellent selectivity seen with KF (96% *ee*, entry 9). Binap was again not a good ligand for these substrates (entry 10), and more importantly, the bis-sulfoxide ligand (*R*,*R*)-1,2-bis(*tert*-butylsulfinyl)benzene,[14c] reported by Liao as an excellent ligand in the 1,4-addition reaction, led to a catalyst system that showed high enantioselectivity (entry 11), but was not very active.

In the hope to increase reactivity further and because Hayashi et al. had previously established that a relatively big reactivity difference existed between the dimeric Cl- and OH-bridged catalyst precursors in the related 1,4-addition reaction,[17] we next set out to synthesize [(**L1**)Rh(OH)]$_2$. This new Rh complex was obtained in high yield by treatment of the disulfoxide coordinated Cl-bridged [(**L1**)RhCl]$_2$ with potassium hydroxide in aqueous acetone at room temperature, which after appropriate washing and work-up gave [(**L1**)Rh(OH)]$_2$ as a well-divided orange powder. When this new catalyst was tested in the model reaction and compared to [(**L1**)RhCl]$_2$, (entries 13 and 7, respectively), we noted a cleaner reaction outcome resulting in increased yield of **8bc**. More importantly, by switching to the hydroxo-bridged precatalyst, addition of base was not necessary anymore and as an added bonus, reactivity was such that the reactions could be run at ambient temperature (entry 15). Entries 16 and 17 show that reaction conditions that completely remove water did not lead to generation of the product in significant amounts. It should though be noted that the low product yield seen when using a higher catalyst loading (entry 17) indicates that direct transmetallation between the rhodium amido species and arylboroxine (avoiding the [Rh]-OH intermediates) is indeed happening,[12b] albeit at a much slower rate (see also discussion of Figure 2 below).

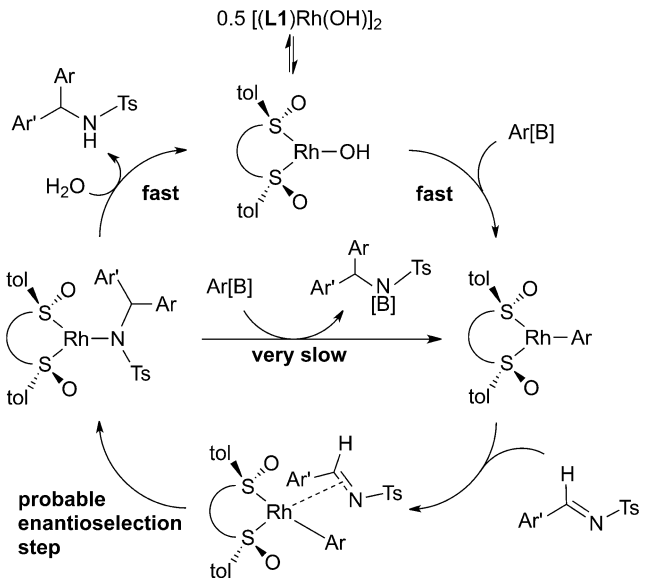
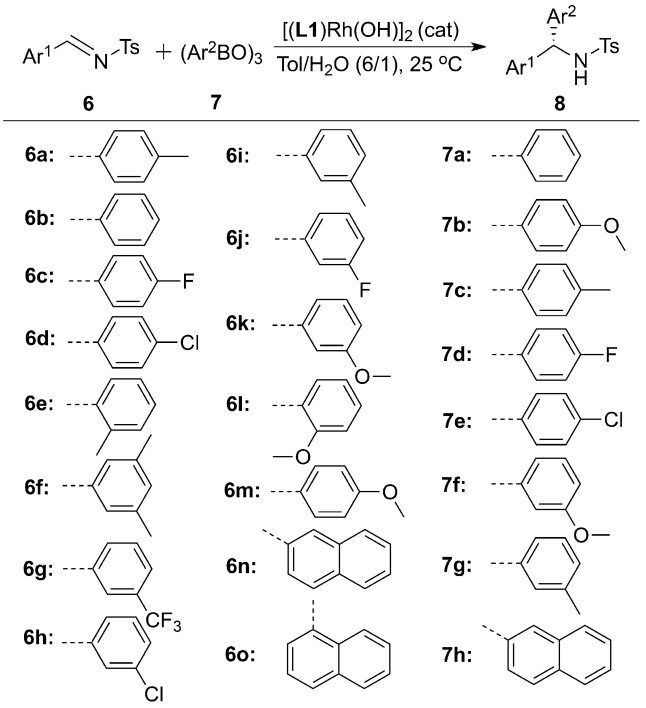


Figure 2. Possible catalytic cycle starting from $[(\mathbf{L1})Rh(OH)]_2$.

When only 1.4 equivalents of the arylboroxine coupling partner were employed (based on B), the reaction still proceeded smoothly (entry 18). Finally, we were able to lower the catalyst loading further by running the reaction under slightly more dilute conditions (entry 19).

Having established the correct reaction conditions, precatalyst $[(\mathbf{L1})Rh(OH)]_2$ was then tested in the arylation of *N*-tosylarylimines with a variety of arylboroxines (Table 2). To our delight, the low catalyst loadings (0.25 mol%) and simple (no addition of base or other additives) as well as mild reaction conditions (room temperature) worked for a variety of substrates as shown in Table 2. The recorded enantioselectivities throughout are excellent, and the desired products were all obtained in 94–99% *ee*. As can be seen, arylboroxines bearing electron-donating or electron-withdrawing groups are well tolerated for the arylation of benzaldehyde *N*-tosylimine **6b** with products obtained in 58–99% yield with 95–99% *ee* (entries 1–9). Good yields were also achieved when nucleophiles with electron-withdrawing functional groups (4-Cl, 4-F) were employed (entries 4–6). The *para*- and *meta*-substituted arylimines were all arylated with phenylboroxine **7a** to give the desired products in 77–98% yield with 96–99% *ee* (entries 10, 11, 13–18). The *ortho*-substituted arylimines **6e**, **6l** and **6o** also reacted swiftly with different boroxines to give the corresponding addition products in good yields and enantioselectivities (entries 12, 21, 23). Overall and as far as we are aware, the catalytic results in Table 2 report a reaction system that is among the simplest and most efficient for the synthesis of chiral diarylmethylamines.

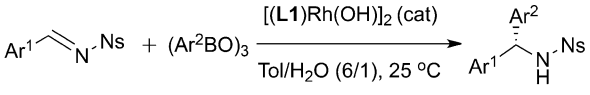
Table 2. Asymmetric arylation of *N*-tosylimines **6** with arylboroxines **7**.[a]



Entry	Ar^1	Ar^2	$[(\mathbf{L1})Rh(OH)]_2$ [mol%]	Yield [%][b]	*ee* [%][c]
1	**6a**	**7a**	0.25	77 (**8aa**)	96 (*S*)
2	**6b**	**7b**	0.25	99 (**8bb**)	95 (*R*)
3	**6b**	**7c**	0.25	98 (**8bc**)	97 (*R*)
4	**6b**	**7d**	0.25	58 (**8bd**)	96 (*R*)
5[d]	**6b**	**7d**	0.25	70 (**8bd**)	96 (*R*)
6	**6b**	**7e**	0.50	58 (**8be**)	97 (*R*)
7	**6b**	**7f**	0.25	86 (**8bf**)	99 (*R*)
8	**6b**	**7g**	0.25	92 (**8bg**)	97 (*R*)
9	**6b**	**7h**	0.25	91 (**8bh**)	96 (*R*)
10	**6c**	**7a**	0.50	96 (**8ca**)	97 (*S*)
11	**6d**	**7a**	0.50	97 (**8da**)	97 (*S*)
12	**6e**	**7a**	0.25	94 (**8ea**)	98 (*S*)
13	**6f**	**7a**	0.25	96 (**8fa**)	98 (*S*)
14	**6g**	**7a**	0.25	87 (**8ga**)	98 (*S*)
15	**6h**	**7a**	0.25	95 (**8ha**)	99 (*S*)
16	**6i**	**7a**	0.25	92 (**8ia**)	97 (*S*)
17	**6j**	**7a**	0.25	84 (**8ja**)	99 (*S*)
18	**6k**	**7a**	0.50	86 (**8ka**)	97 (*S*)
19	**6e**	**7c**	0.25	97 (**8ec**)	96 (*S*)
20	**6m**	**7c**	0.25	89 (**8mc**)	97 (*S*)
21	**6l**	**7b**	0.25	92 (**8lb**)	95 (*S*)
22	**6n**	**7b**	0.25	99 (**8nb**)	94 (*S*)
23	**6o**	**7b**	0.25	67 (**8ob**)	95 (*S*)

[a] *Reaction conditions:* A mixture of **6** (0.45 mmol), **7** (0.9 mmol B) and $[(\mathbf{L1})Rh(OH)]_2$ was stirred in toluene (6.0 mL) and H_2O (1.0 mL) at 25 °C for 14–15 h.
[b] Isolated yields after column chromatography.
[c] Determined by HPLC analysis; absolute stereochemistry assigned by comparison with results reported in refs.[12g,l]
[d] Reaction was run at 35 °C.

Table 3. Asymmetric arylation of *N*-nosylimines **9** with arylboroxines **7**.



9 **7** **10**

Entry	Ar^1	Ar^2	[(**L1**)Rh(OH)]$_2$ [mol%]	Yield [%][b]	*ee* [%][c]
1	C_6H_5	3-MeC_6H_4	0.25	96 (**10a**)	96 (*R*)
2	C_6H_5	4-MeC_6H_4	0.25	97 (**10b**)	98 (*R*)
3	C_6H_5	4-ClC_6H_4	0.25	97 (**10c**)	96 (*R*)
4	C_6H_5	4-FC_6H_4	0.25	93 (**10d**)	96 (*R*)
5	2-MeOC_6H_4	4-MeC_6H_4	0.25	96 (**10e**)	96 (*S*)
6	2-MeOC_6H_4	4-MeOC_6H_4	0.25	94 (**10f**)	91 (*S*)
7	2-thiophenyl	4-MeOC_6H_4	0.50	95 (**10g**)	95 (*S*)

[a] *Reaction conditions:* a mixture of **9** (0.45 mmol), **7** (0.9 mmol B) and rhodium complex was stirred in toluene (6.0 mL) and H_2O (1.0 mL) at 25 °C for 14–15 h.
[b] Isolated yields after column chromatography.
[c] Determined by HPLC analysis; absolute stereochemistry assigned by comparison with results reported in ref.[12m]

While modern deprotection methods for the tosylated products **8** shown in Table 2 are very mild and straightforward,[18] we deemed it important to extend our chemistry to the related 4-nitrophenylsulfonylaldimines. This was also done in view of the fact that according to some previous reports, nosyl-protected substrates do not behave analogously to the tosyl-protected ones in these 1,2-addition reaction.[10a,12m,o] Under the exact same reaction conditions established above, we found that the products of representative substrates were transformed to the amine products with excellent enantioselectivities (91–98% *ee*) and yields (93–97%), outlining the excellent behaviour of the catalyst system for these reactions (Table 3).[19]

The very high activity and selectivity of the new [(**L1**)Rh(OH)]$_2$ precatalyst in these 1,2-addition reactions strongly indicate that a similar, unusual mechanism to the 1,4-addition mechanism with [(**L1**)RhCl]$_2$ takes place.[13c,d] There, we were able to show that the high reactivity was likely due to the fact that substrate approach and binding to the metal is less difficult than in other chiral chelating ligands because of the relative lack of bulk protruding from our ligand structure, and where electronic factors originating from the use of the sulfinyl moieties were at least partially responsible for transferring the chiral information to the products. To test and underline the validity of these arguments in the present system, the structure of the precatalyst was ascertained by an X-ray crystal structure analysis of suitable crystals of [(**L1**)Rh(OH)]$_2$ (Figure 1).[20] The Rh center adopts the expected square planar geometry with the sulfur atoms coordinated to the metal center. Not surprisingly, the dihedral angles of the two naphthyl units and S–Rh–S bond angles in [(**L1**)Rh(OH)]$_2$ are very similar to the values measured for the previously reported [(**L1**)RhCl]$_2$ complex, with the main difference between the two complexes being seen in the bond lengths for Rh–OH which is shorter than that of Rh–Cl [Rh–OH, 2.049(3) and 2.061(3) Å; Rh–Cl, 2.3650(12) and 2.3847(12) Å].

The Rh–S bond lengths in [(**L1**)Rh(OH)]$_2$ and [(**L1**)RhCl]$_2$ are very similar, with slightly shorter values (on average, 0.033 Å shorter) for the OH-bridged complex due to its lower *trans* influence. In terms of overall Rh–OH bond length, we compared the values found for [(**L1**)Rh(OH)]$_2$ with the other, crystallographically characterized complexes of the same type. Quite surprisingly, only 7 other compounds have been characterized so far and include either alkene or phosphorus coordinated (μ-OH)$_2$ bridged square-planar rhodium(I) dimers (Cambridge Structural Database).[12k,21] Within this limited dataset, we notice that the mean Rh–OH bond length for our sulfoxide bound complex [2.055(3) Å] is at the lower limit of the range reported so far (2.047–2.116 Å). The dihedral angle between the two coordination planes defined by two groups of O—Rh—O of the four-membered 'RhORhO' ring is 120.1(1)°, which is the largest among the reported (μ-OH)$_2$ bridged rhodium(I) dimers. Accordingly, it possesses the smallest intermetallic separation [2.82960(5) Å].

Again comparing the solid-state structure of [(**L1**)Rh(OH)]$_2$ with [(**L1**)RhCl]$_2$, the S–O bond lengths of [(**L1**)Rh(OH)]$_2$ are slightly longer [S–O in free ligand, 1.4922(16) Å; S–O in Cl-bridged complex, 1.466(4) and 1.473(4) Å; S–O in OH-bridged complex, 1.477(3) and 1.481(3) Å], reflecting the σ-donating properties of the hydroxo bridges.

Most important to the discussion of possible reaction pathways during catalysis and in line with what we saw for [(**L1**)RhCl]$_2$, the *p*-tolyl groups in [(**L1**)Rh(OH)]$_2$ that are connected to the sulfoxide units are oriented parallel to the other half of the naphthalenic backbone with bond lengths within the range of π–π stacking interactions. It therefore indicates again that the normal model for enantioselection, which assumes that the substrates approach the metal so as to minimize steric interactions with protruding groups placed on the chiral ligand, is not operative in this case.[22] As outlined in Figure 2, it is most probable that enantioselection occurs at the subsequent insertion step, although favourable/unfavourable interactions between the tosyl group and the sulfinyl moiety of the ligand during the imine approach might be operative in this case. Finally and as determined experimentally, the direct path depicted in the center of the catalytic cycle of Figure 2 is very minor.

Conclusions

Herein, we have shown, for the first time, that a chiral disulfoxide ligand can be used as an ancillary ligand in the rhodium-catalyzed asymmetric 1,2-addition of arylboroxines to *N*-tosylarylimines. Results gathered here show that the binaso ligand, as already evidenced in the related 1,4-addition reaction, combines excellent reactivity with high enantioselectivity that compare very favourably with the best data available in the literature. Especially by introducing the new μ-OH-bridged rhodium complex of binaso, we have been able to avoid complicated reaction conditions and taken together with the fact that the chiral ligand is very readily available (1 step synthesis from commercially available starting materials), the results presented here might well represent the simplest catalytic system available for this important transformation.

Experimental Section

Preparation of [{(M,S_S,S_S)-*p*-Tol-binaso}-Rh(OH)]$_2$:

A solution of [{(M,S_S,S_S)-*p*-Tol-binaso}RhCl]$_2$ (600 mg, 0.45 mmol) in acetone (60 mL) was prepared in a Schlenk tube inside the glove-box. The Schlenk tube was taken outside, connected to a Schlenk line and aqueous KOH (2.2 mL, 2.5 M) was added under stirring. The solution was stirred at room temperature for 1.5 h and then the solvent was removed under vacuum. Dichloromethane (40 mL) was added to the crude solid in the Schlenk flask, and the organic layer was washed and decanted with degassed water (3× 15 mL). Anhydrous Na_2SO_4 was added to the flask and the organic layer was then concentrated to a small volume (~ 1.5 mL). At this point, the Schlenk flask was reintroduced into the glove-box and the content was filtered through Celite® and the cake was washed with a small amount of CH_2Cl_2. Crystals were obtained by layering with THF (20 mL) and cooling the mixture at −30 °C overnight. The supernatant solution was decanted and the crystals were washed with cold THF (2×4 mL). The burgundy crystals were redissolved in 0.5 mL DCM and 10 mL pentane was added drop by drop to precipitate the product, which was dried under vacuum for 5 h to afford the corresponding complex as an orange-red finely divided powder. The yield of [{(M,S_S,S_S)-*p*-Tol-binaso}Rh(OH)]$_2$ was 445 mg (76%) after a second recrystallization/precipitation sequence of the mother liquor. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.32 (d, J = 8.8 Hz, 4H), 8.06 (d, J = 8.8 Hz, 4H), 8.02–7.77 (br, 8H), 7.74 (d, J = 8.3 Hz, 4H), 7.37 (ddd, J = 8.2, 6.9, 1.2 Hz, 4H), 6.96 (ddd, J = 8.5, 6.8, 1.3 Hz, 4H), 6.58 (d, J = 7.9 Hz, 8H), 6.33 (d, J = 8.6 Hz, 4H), 2.00 (s, 12H), 0.22 (s, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 145.61, 141.93, 141.59, 134.57, 131.91, 130.28, 129.09, 128.36, 127.55, 127.51, 127.48, 126.9–127.4 (br), 126.79, 121.07, 21.25; anal. calcd. for $C_{68}H_{54}O_6Rh_2S_4$: C 62.77, H 4.18; found: C 62.61, H 4.23; $[\alpha]_D^{20}$: +295.45 (*c* 2.20, $CDCl_3$).

Typical Catalytic Procedure

A stock solution of [{(M,S_S,S_S)-*p*-Tol-binaso}Rh(OH)]$_2$ (9 mg, 0.069 mmol) was stirred in toluene (18 mL) inside the glove-box in a screw-cap vial. During the mixing time, a septum-capped reaction vial was charged with imine **6** or **9** (0.45 mmol) and the corresponding arylboroxine **7** (0.30 mmol). To this vial was added the required amount of the stock solution of the catalyst [2.9 mL containing 1.46 mg (0.0011 mmol) for 0.25 mol% runs]. Then toluene (3.1 mL) was added to make up for a total volume of 6 mL. After this, a stir bar was added, the vial was sealed and was brought out from the glove-box. H_2O (1 mL, degassed, Milli-Q) was then added with a syringe and the mixture was stirred for 14 h. After this, the solvent was removed under vacuum. The residue was dissolved in a minimum amount of dichloromethane and charged on top of a silica gel column and purified by column chromatography (hexane/ethyl acetate or diethyl ether as eluent). Products **8** or **10** where then dried under vacuum and analyzed.

Characterization data of the compounds can be found in the Supporting Information of this article.

Acknowledgements

RD thanks the Australian Research Council (ARC) for generous funding (FT130101713). GZZ, GS and PG thank the University of Western Australia for an International Postgraduate Research Scholarship, an Australian Postgraduate Award and a Safety-Net Top-Up Scholarship. AS thanks the Swiss National Science Foundation for a postdoctoral fellowship. AO thanks the University of Western Australia for an Australian Postgraduate Award and a Safety-Net Top-Up Scholarship. The Centre for Microscopy, Characterisation & Analysis at UWA is thanked for providing facilities and assistance.

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