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(*R*)-3,5-diCF_3-SYNPHOS and (*R*)-*p*-CF_3-SYNPHOS, Electron-Poor Diphosphines for Efficient Room Temperature Rh-Catalyzed Asymmetric Conjugate Addition of Arylboronic Acids

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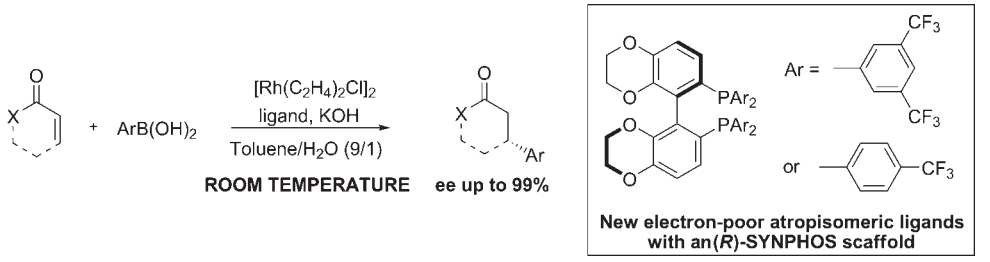
ABSTRACT



Two new atropisomeric electron-poor chiral diphosphine ligand analogues of SYNPHOS were prepared, and their electronic properties are described. These two ligands afforded high performance for the Rh-catalyzed asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated carbonyl compounds at room temperature.

Chiral bidentate phosphine ligands play an important role in various homogeneous transition-metal-catalyzed reactions,[1] thereby making the design and synthesis of novel chiral diphosphine ligands an attractive area of research. Among the chiral phosphorus ligands that have been reported over the past three decades, atropisomeric C_2-symmetric diphosphine ligands have proven to be highly efficient chiral inducers in many enantioselective transformations.[2] The great majority of axially chiral ligands reported to date are more electron-rich with respect to triphenylphosphine, despite the fact that several studies revealed that electron-poor diphosphine ligands can often lead to a dramatic variation of the reactivity and enantioselectivity for some transition-metal-mediated asymmetric reactions.[3] For example, Achiwa et al.[4] described the synthesis of FUPMOP and BIFUP, two biphenyl-based ligands, which proved to be very efficient in the Ru-catalyzed asymmetric hydrogenation of methyl 3-oxobutanoate with ee values up to 99%. Keay et al.[5] reported the use of BINAPFu, a biheteroaryl ligand, in an asymmetric Heck reaction between 2,3-dihydrofuran and phenyl

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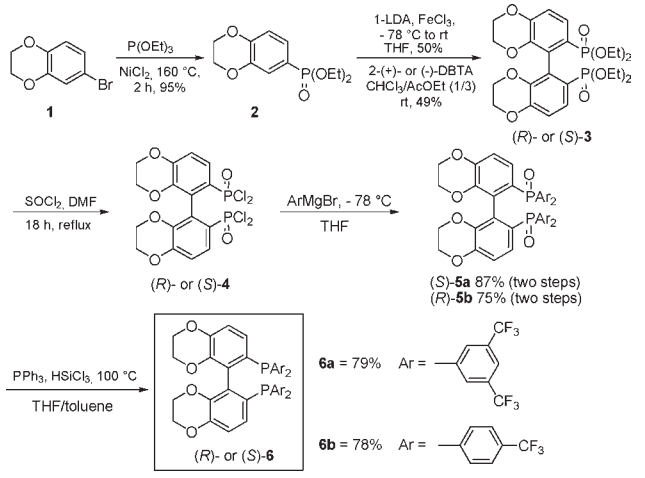
triflate. Recently, Sakai et al.[6] demonstrated that the catalytic activity for Rh-catalyzed 1,4-addition of arylboronic acids at room temperature could be significantly improved by using an MeO-F_{12}-BIPHEP ligand. Another representative example of an electron-poor atropisomeric diphosphine, which displays better activity and enantioselectivity compared to electron-rich diphosphines for several transition-metal-catalyzed C−C[7] and C−H[8] bond formations, is the DIFLUORPHOS[9] ligand bearing a bi(difluorobenzodioxole)backbone that has been developed in our group. These results, in conjunction with our continued interest in ligand design,[9,10] led us to develop two new electron-poor chelating diphosphines derived from SYNPHOS[11] containing one or two trifluoromethyl functional groups on each of the phosphorus phenyl rings: (*R*)-3,5-diCF_3-SYNPHOS **6a** and (*R*)-*p*-CF_3-SYNPHOS **6b**. We report herein a concise synthesis of the title compounds, the evaluation of their electronic properties, and their applications in Hayashi−Miyaura Rh-catalyzed enantioselective conjugate addition of arylboronic acids to α,β-unsaturated carbonyl compounds[12] under very mild reaction conditions.

Our synthetic approach to enantiopure ligands **6a** and **6b** is outlined in Scheme 1.

Scheme 1. Synthesis of Electron-Poor Ligands **6a** and **6b**



In the first step, commercially available bromobenzo-1,4-dioxane **1** was readily phosphorylated using an Arbuzov type reaction in the presence of triethyl phosphite and a catalytic amount of nickel dichloride at a constant temperature of 160 °C for 2 h to give diethyl phosphonate **2** in 95% yield. *Ortho*-lithiation of **2** by LDA at −78 °C in THF and further oxidative coupling with anhydrous ferric chloride furnished the racemic bis(diethyl) phosphonate **3** in a 50% unoptimized yield. The optical resolution of racemic **3** was carried out in a mixture of $CHCl_3$/AcOEt (1:3) at room temperature. Both enantiomers **3a** and **3b** can be obtained on a multigram scale with enantiomeric excesses up to 99% by using 2,3-dibenzoyltartaric acid ((+)- or (−)-DBTA) as the resolving reagents. The bis(phosphine oxide) **5** was then obtained in 87% yield using a one-pot two-step procedure involving conversion of **3** into the corresponding bis(phosphonic dichloride) derivative **4** followed by treatment with an excess of the required aryl Grignard reagents. Finally, $HSiCl_3$ reduction of compound **5** in the presence of PPh_3 as an oxygen acceptor[13] afforded the enantiomerically pure ligands **6a** and **6b**, respectively, in 79% and 78% yields. The configuration of (*R*)-**6** was assigned as *R* by comparison of its hydrogenation products with those obtained with its parent compound, (*R*)-SYNPHOS.[11]

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Having ligands **6a** and **6b** in hand, attention was then focused on the evaluation of their electronic properties, since subtle changes in the electronic properties of the chiral ligand can often lead to a dramatic variation of the catalytic activity in metal-catalyzed asymmetric reactions. The electronic coordination mode of diphosphine ligands to a transition metal involves σ-donation from the ligand to the metal and π-retrodonation from the ligand to the metal. A valuable method for the evaluation of the σ-donation ability of a phosphine group is to measure the magnitude of the $^1J_{P,Se}$ coupling constant of the corresponding diphosphine(V) selenide.[14] Indeed, Allen and Taylor have reported[14a] that phosphorus(V) selenides incorporating electron-withdrawing groups exhibit larger coupling constants than those for phosphorus(V) selenides bearing electron-donating groups, which indicates an increase in the s character of the phosphorus lone-pair orbital (*i.e.*, a less basic phosphine). To estimate the donor ability of phosphorus centers in ligands **6a** and **6b**, we therefore prepared the diselenide derivatives by the oxidation of the corresponding diphosphines with elemental selenium in refluxing chloroform and compared it with other SYNPHOS-derived ligands. The results depicted in Table 1 clearly show that (*R*)-3,5-diCF$_3$-SYNPHOS **6a** (Table 1, entry 1, 773.9 Hz) and (*R*)-*p*-CF$_3$-SYNPHOS **6b** (Table 1, entry 2, 758.1 Hz) have significantly higher $^1J_{P,Se}$ coupling constant values among all the SYNPHOS ligand family (Table 1, entries 3−5), including the electron-poor DIFLUORPHOS (Table 1, entry 6, 749 Hz), which indicates a lower σ-donor ability.

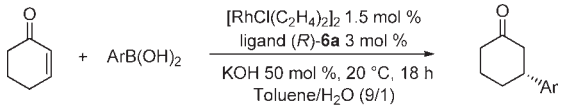
Table 1. Electronic Properties of Ligands **6a** and **6b**

entry	diphosphine (L*)	$^1J(^{31}P-^{77}Se)$ in (Hz)	ν_{CO} of [RhCl(L*)(CO)] (cm^{-1})
1	(*R*)-3,5-diCF$_3$-SYNPHOS **6a**	773.9	2032
2	(*R*)-*p*-CF$_3$-SYNPHOS **6b**	758.1	2015
3	(*R*)-SYNPHOS	740	2001
4	(*R*)-3,5-CH$_3$-SYNPHOS	734	2000
5	(*R*)-*p*-CH$_3$-SYNPHOS	733	1997
6	(*R*)-DIFLUORPHOS	749	2015

Electronic donor−acceptor properties of new diphosphines **6a** and **6b** have also been estimated by studying the carbonyl stretching frequencies of the corresponding [RhCl(diphosphine)(CO)] complexes, which were prepared by the reaction of $[RhCl(CO)_2]_2$ with diphosphine ligands (Table 1).[15] The higher the carbonyl stretching frequency (ν_{CO}), the lower the electronic density on the rhodium center, and the higher the π-acidic character of the ligand. From this electronic comparative study, we can conclude that the new diphosphines (*R*)-3,5-diCF$_3$-SYNPHOS **6a** and (*R*)-*p*-CF$_3$-SYNPHOS **6b** containing one or two trifluoromethyl functional groups, respectively, on each phosphorus phenyl ring are the best π-acceptors compared to nonfluorinated SYNPHOS ligands (compare entries 1−2 vs 3−5).

To evaluate the potential of our ligands **6a** and **6b**, the Rh-catalyzed asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated carbonyl compounds[12] was chosen as a model reaction since it has been demonstrated that electron-poor ligands would accelerate both transmetalation[16] and insertion[17] steps in the catalytic cycle.[12] In the first set of experiments, we studied the addition of arylboronic acids **8** to 2-cyclohexenone **7a** using 1.5 mol % of $[RhCl(C_2H_4)_2]_2$ and 3 mol % of the more electron-deficient ligand (*R*)-**6a** in the presence of KOH in toluene/H$_2$O (9/1) at 20 °C. The results are summarized in Table 2.

Table 2. Rhodium Catalyzed 1,4-Addition of Arylboronic Acids to Cyclohexenone



7a **8** **9**

entry	Ar of boronic acid **8**	product	yield (%)[a]	ee (%)[b]
1[c]	C_6H_5 (**8a**)	**9aa**	20	98
2	C_6H_5 (**8a**)	**9aa**	95	99
3	4-MeC_6H_4 (**8b**)	**9ab**	90	99
4	3,5-diMeC_6H_3 (**8c**)	**9ac**	90	99
5	4-MeOC_6H_4 (**8d**)	**9ad**	84	99
6	3-MeOC_6H_4 (**8e**)	**9ae**	50	96
7	4-BrC_6H_4 (**8f**)	**9af**	81	99
8	3-ClC_6H_4 (**8g**)	**9ag**	82	99
9	2-MeC_6H_4 (**8h**)	**9ah**	86	93
10	1-Naphthyl (**8i**)	**9ai**	81	90

[a] Isolated yield. [b] Determined by stationary phase chiral HPLC analysis. [c] (*R*)-SYNPHOS was used instead of (*R*)-**6a**.

A high chemical yield and excellent enantioselectivity up to 99% for the 1,4-adduct **9aa** was obtained in the reaction between phenylboronic acid **8a** and 2-cyclohexenone **7a**. This excellent result suggests that the strong electron-withdrawing effect of the trifluoromethyl groups probably plays a crucial role in the reactivity of the reaction since, under similar reaction conditions, only a 20% yield was obtained when the parent (*R*)-SYNPHOS ligand was used (Table 2, entry 1 vs 2). The data of Table 2 clearly show that the electron-donating substituents on the phenyl ring of the boronic acids did not affect the selectivity of the reaction, providing the expected products **9ab**−**9ae** in high enantioselectivity (Table 2, entries 3−6). A similarly high selectivity was obtained when arylboronic acids bearing electron-withdrawing groups were employed (Table 2, entries 7 and 8). In contrast, the use of sterically more hindered arylboronic

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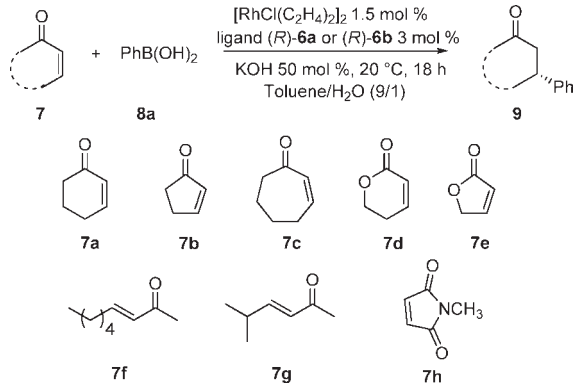
acids, such as 2-tolylboronic acid and 1-naphthylboronic acid, gave **9ah** and **9ai**, respectively, in good yields but with slightly lower enantioselectivity, probably due to steric hindrance (Table 2, entries 9 and 10).

In the next stage, the substrate scope of this Rh-catalyzed asymmetric 1,4-addition reaction was examined. Several cyclic and acyclic α,β-unsaturated carbonyl compounds were allowed to react with phenylboronic acid, using 1.5 mol % of a rhodium catalyst bearing (*R*)-**6a** or (*R*)-**6b** as ligands in the presence of KOH in toluene/H_2O (9/1) at 20 °C.

Table 3. Rhodium Catalyzed 1,4-Addition of Phenylboronic Acid to α,β-Unsaturated Carbonyl Compounds



entry	substrate	ligand	product	yield (%)[a]	ee (%)[b]
1	**7a**	(*R*)-**6a**	**9aa**	95	99
2		(*R*)-**6b**	**9aa**	92	99
3	**7b**	(*R*)-**6a**	**9ba**	84	96
4		(*R*)-**6b**	**9ba**	69	88
5	**7c**	(*R*)-**6a**	**9ca**	84	99
6		(*R*)-**6b**	**9ca**	80	96
7	**7d**	(*R*)-**6a**	**9da**	70	90
8		(*R*)-**6b**	**9da**	80	97
9	**7e**	(*R*)-**6a**	**9ea**	48	77
10		(*R*)-**6b**	**9ea**	77	97
11[c]	**7f**	(*R*)-**6a**	**9fa**	92	93
12[c]		(*R*)-**6b**	**9fa**	57	93
13	**7g**	(*R*)-**6a**	**9ga**	76	97
14		(*R*)-**6b**	**9ga**	65	99
15[d]	**7h**	(*R*)-**6a**	**9ha**	93	88

[a] Isolated yield. [b] Determined by stationary phase chiral HPLC analysis. [c] Reaction run for 60 h using 3 mol % of $[Rh(C_2H_4)_2Cl]_2$ and 6 mol % of ligand. [d] Reaction run in dioxane/H_2O (9/1) at 50 °C.

From the results listed in Table 3, we can see that better catalytic activity in terms of both yield and enantioselectivity was obtained in the reaction between phenylboronic acid **8a** and cyclic α,β-unsaturated ketones **7a**−**c** when ligand (*R*)-**6a** was employed (Table 3, entries 1−6). In contrast, (*R*)-**6b** proves to be a much more efficient ligand for this reaction when cyclic α,β-unsaturated lactones **7d**−**e** were used as substrates (Table 3, entries 7−10). In the cases of acyclic α,β-unsaturated ketones **7f** and **7g**, no significant difference between the two ligands was observed regarding the enantioselectivity, although the 1,4-adducts **9fa** and **9ga** were isolated in higher yields when the reaction was run in the presence of (*R*)-**6a** (Table 3, entries 11−14). Remarkably, enantioselectivity up to 88% with a 93% yield was obtained with (*R*)-3,5-diCF_3-SYNPHOS **6a** for the reaction of phenylboronic acid **8a** with *N*-methylmaleimide **7h**, which is one of the trickiest substrates of particular interest because the 1,4-adducts are synthetically and biologically important α-substituted succinimides.[18] It should be noted that this result represents by far the best selectivity obtained for these types of compounds compared to other atropisomeric diphosphine ligands.[19]

In summary, we have synthesized new electron-poor atropisomeric diphosphines containing one or two trifluoromethyl functional groups on each diphenylphosphine substituent. A comparative study of their electronic properties showed that (*R*)-3,5-diCF_3-SYNPHOS and (*R*)-*p*-CF_3-SYNPHOS possess a lower σ-donor ability and the best π-acceptor ability compared to nonfluorinated SYNPHOS ligands. These ligands proved to be highly effective in the Rh-catalyzed asymmetric 1,4-addition of arylboronic acids to a variety of α,β-unsaturated carbonyl compounds at room temperature. Studies on the applications of these new diphosphines to various transition-metal-catalyzed asymmetric processes are ongoing.

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Supporting Information Available. Experimental procedures and compound characterization data. This material is available free of charge via Internet at http://pubs.acs.org.

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