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Bicyclic Bridgehead Phosphoramidite (Briphos) Ligands with Tunable π-Acceptor Ability and Catalytic Activity in the Rhodium-Catalyzed Conjugate Additions

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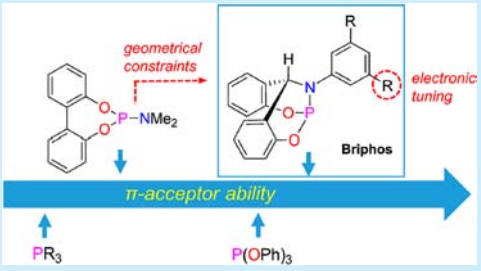
Supporting Information

ABSTRACT: A new type of bicyclic bridgehead phosphoramidites (briphos) is reported, where the geometrical constraints significantly enhance the π-acceptor ability compared with its monocyclic analogs. The briphos is shown to be highly efficient and tunable for Rh(I)-catalyzed conjugate additions of aryl boronic acids to α,β-unsaturated ketones and *N*-tosyl ketimines.



A continuing goal in the field of transition-metal catalysis is to develop highly active and selective catalysts for the pharmaceutical and fine chemical industries.[1] One major research direction is to improve the catalytic performance of given transition metals by controlling various ligand effects.[2] The phosphorus (P) ligand is a logical first choice to study such ligand effects due to its wide availability and diversity.[3] The reported methods in this regard include chelate control as well as steric and electronic control, which were systematically demonstrated in terms of the bite angle[4] and the Tolman cone angle and electronic parameter.[5] Indeed, the concept of tuning the P ligands has successfully led to the development of highly efficient transition metal catalysts.[1−3]

In addition, the geometrical constraints have been used to modulate the ligand effect. In bicyclic or cage-shaped P ligands, compared with their acyclic analogs, interesting features such as increased π−acceptor and decreased σ−donor ability as well as reduced steric demand have been reported (Figure 1a).[6−9]

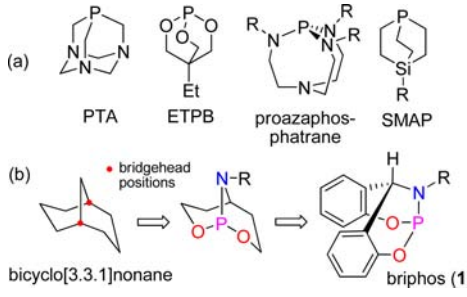


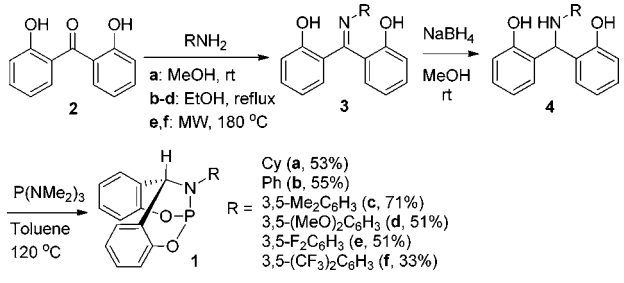
Figure 1. (a) Representative bicyclic or caged phosphorus ligands (b) design of briphos (**1**).

Although beneficial effects of geometrical constraints have been widely used in transition metal catalysis especially with commercially available PTA,[7] ETPB,[8] and proazaphosphatranes,[9] further modifications such as chiral ligand design[10] or steric and electronic tuning are difficult for the given bicyclic or cage-shaped P ligands.

We here report a new class of bicyclic bridgehead phosphoramidite (briphos) ligands (**1**) based on the bicyclo[3.3.1]nonane structure (Figure 1b). The geometrical constraints in briphos with respect to its monocyclic analogs enhance π-acceptor ability. Furthermore, facile tuning of briphos leads to (a) highly efficient ligands with dramatic ligand acceleration effect (LAE), (b) new catalytic reactivity, and (c) asymmetric induction in Rh(I)-catalyzed conjugate additions of aryl boronic acids.

A series of briphos (**1**) compounds were efficiently prepared by a three-step procedure, as shown in Scheme 1. Commercially

Scheme 1. Preparation of Briphos (1)



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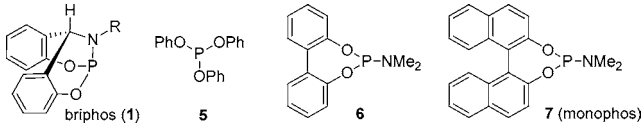
available 2,2′-dihydroxybenzophenone (**2**) was reacted with primary amines to form the corresponding imines (**3**). We have demonstrated that the internal hydrogen bonding in **2** significantly accelerates the imine formation, and the imine products have been used for stereoselective generation of axial compounds[11] and chiral-at-metal complexes.[12] The imine formation smoothly proceeded with a primary alkyl amine, cyclohexyl amine at ambient temperature, but required elevated temperature with aniline. For electron-deficient anilines, we applied microwave radiation in order to improve the product yields. The resulting imines were conveniently reduced by $NaBH_4$ to form secondary amines (**4**), and a series of briphos compounds (**1**) were prepared by reaction with **4** and hexamethylphosphorous triamide (HMPT) in good to moderate overall yields (33−71%). Briphos **1b** was also prepared in multigram scale (45.8 g) in 31% yield using a modified procedure (Supporting Information (SI)). In addition to the mild and scalable reaction conditions, the synthetic procedure for briphos (**1**) allows facile tuning of the ligand structures by variation of the primary amines.

In order to examine the ligand property of briphos, we measured the electronic properties of a series of briphos ligands (**1**), as well as their monocyclic analogs **6** and monophos (**7**), with results as summarized in Table 1. The σ-donor ability has

Table 1. Ligand Properties



entry	L	R in briphos (**1**)	δ [ppm][a]	^1J [Hz][b]	ν_{CO} [cm^{-1}][c]
1	**5**	–	128.6	1025	2016
2	**6**	–	149.8	968	2006
3	**7**	–	149.4	972	2010
4	**1a**	Cy	98.0	1015	2016
5	**1b**	Ph	90.5	1039	2018
6	**1c**	3,5-$Me_2C_6H_3$	90.5	1037	2011
7	**1d**	3,5-$(MeO)_2C_6H_3$	90.1	1040	2013
8	**1e**	3,5-$F_2C_6H_3$	88.7	1048	2019
9	**1f**	3,5-$(CF_3)_2C_6H_3$	88.3	1051	2029

[a] ^{31}P NMR spectra in $CDCl_3$. [b] ^{31}P−^{77}Se. [c] [RhCl(L)$_2$(CO)].

been scaled by the coupling constant of ^{31}P−^{77}Se bonds,[13] and the π-acceptor ability has been determined by CO stretch frequencies of metal complexes.[5] Indeed, Cy-briphos (**1a**) was characterized to be a weaker σ-donor and stronger π-acceptor than the monocyclic phosphoramidites **6** and **7** (entries 2−4). The increased π-acceptor ability of **1a** is quite comparable with that of $P(OPh)_3$ (**5**) (entry 1). Since Cy-briphos (**1a**) and **6** have similar functional groups attached to the P atom, it is quite remarkable that the electronic properties of phosphoramidite ligands can be modulated solely using geometrical constraints (Δ^1J (^{31}P−^{77}Se) = 47 Hz, $\Delta\nu_{CO}$ = 10 cm^{-1}).

Moreover, electronic tuning of briphos ligands was performed using substituted anilines at the meta-position. An electron-withdrawing group, CF_3, greatly enhanced the π-acceptor ability and lowered the σ-donor ability (Δ^1J (^{31}P−^{77}Se) = 12 Hz, $\Delta\nu_{CO}$ = 11 cm^{-1}), consistent with previous studies[14] (entries 5 and 9 for **1b** and **1f**). For other aryl substituted briphos ligands (**1c**−**e**), subtle changes in electronic properties were observed depending on the electronic nature of the substituents (entries 6−8). Here we note that the increase of π-acceptor ability by the geometric constraints ($\Delta\nu_{CO}$ = 10 cm^{-1}) is compatible with that of strong electron-withdrawing substituents, CF_3 ($\Delta\nu_{CO}$ = 11 cm^{-1}), which suggests that geometric control of ligands can be an efficient route to modulate ligand properties apart from the conventional electronic tuning. Decreased basicity of bicyclic phosphites compared to their monocyclic or acyclic analogs has been reported.[6b,d,8a,c] This work represents the first example of bicyclic phosphoramidite ligands as a platform of geometry-induced tunable π-acceptor ligands.

Tolman's electronic parameter, determined by measuring the CO A_1 vibrational frequency of Ni(CO)$_3$L [ν_{CO} (A_1)], has been used as an indicator of the donor/acceptor ability of a ligand.[5] Perrin et al. showed a linear correlation between computational ν_{CO} (A_1) of P ligands in the gas phase and corresponding experimental values.[15a] Recently Gusev generalized such a linear relationship for a series of two-electron ligands.[15b] In this regard, we computed ν_{CO} (A_1) of briphos to investigate their relative donor/acceptor properties with respect to other known ligands. In order for direct comparison, we used GAUSSIAN09 at the same level of DFT with that in ref 15b: the MPW1PW91 functional and 6-311+G(2d) for Ni and 6-311+G(d,p) for all others.[16]

Figure 2 shows the computational results. Relative ν_{CO} (A_1) values between **1a**, **1b**, **1f**, **5**, **6**, and **7** for Ni(CO)$_3$L are consistent

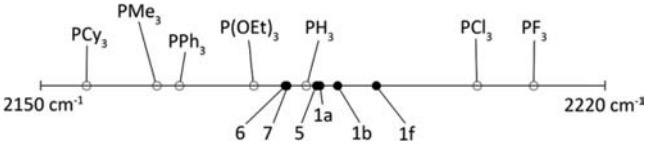


Figure 2. Calculated ν_{CO} (A_1) data for Ni(CO)$_3$L.

with those for [RhCl(L)$_2$(CO)] in Table 1, indicating that the enhanced π-acceptor ability of briphos can be generalized to other metal complexes. Both monophos (**7**) and **6** are weaker π-acceptors than PH_3, whereas the three briphos ligands (**1a**, **1b**, and **1f**) as well as **5** turn out to be stronger π-acceptors than PH_3. We stress that briphos, by varying its N-substituent, spans a wide range of the Tolman electron parameters, which promises its diverse applicability as a tunable π-acceptor ligand.

In order to verify the geometrical features of the briphos, we compared the crystal structures of briphos (**1c**) with monophos (**7**)[17] (Figure 3a and 3b). The sum of three P-centered angles for briphos is 300.0°, while that for monophos is 303.2°. Despite the similar total angles, the individual angles for briphos (**1c**) are symmetric (100.8°, 99.4°, and 99.8°), whereas those for monophos (**7**) are asymmetric (96.0°, 109.5°, and 97.7°). Moreover, the geometry of briphos is conserved in [Rh(**1a**)$_2$Cl]$_2$, where the average total angle is 301.6° and the average individual angles are 101.0°, 101.5°, and 99.1° (Figure 3c). On the basis of the variable hybridization calculations of the P atom using the crystal structures **1c** and **7**, the geometrical constraints in briphos result in an increase of the s-character of the P lone pair (SI). Thus, briphos can be a weaker σ-donor and stronger π-acceptor than its monocyclic analogs in agreement with experiments and DFT computations.[18]

Since π-acceptor ligands are known to facilitate low-valent metal catalysis, we selected the Rh(I)-catalyzed conjugate addition of phenyl boronic acid to cyclohexenone as a benchmark reaction.[19] When the reaction was monitored for 1 h at 50 °C, the briphos ligands (**1a** and **1b**) showed a significant

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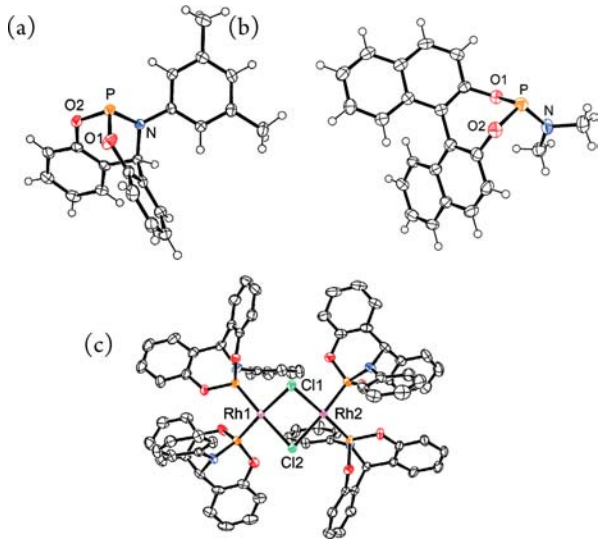


Figure 3. Crystal structures of (a) briphos (**1c**), (b) monophos (**7**), and (c) $[Rh(\mathbf{1b})_2Cl]_2$.

ligand acceleration effect (LAE), while the monocyclic phosphoramidites (**6** and **7**) as well as mono- or bidentate phosphines were inefficient or even inactive (SI).[20] In our P ligand screening, only $P(OPh)_3$ (**6**) was found to be as effective as briphos in reasonable agreement with the measured electronic properties. Remarkably, the tuning of briphos structure showed a highly efficient ligand as **1e** when only 0.1 mol % of $Rh(acac)(C_2H_4)_2$ and 0.25 mol % of ligand were used at ambient temperature (Figure 4).

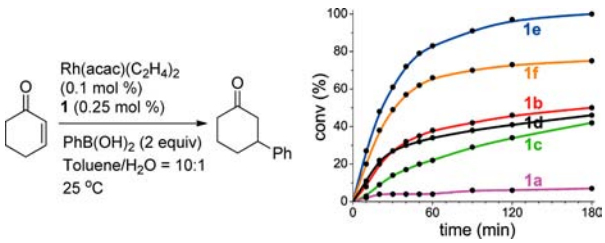
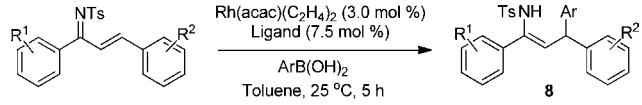


Figure 4. Tuning of briphos ligands for the Rh(I)-catalyzed conjugate addition of phenylboronic acid under neutral conditions.

The applications of briphos, a tunable π-acceptor ligand, can be extended to explore new catalytic reactivity. *N*-Tosyl ketimines were used to make α-tertiary amines by Rh(I)-catalyzed 1,2-addition of arylboronic acids,[21] arylboroxines,[22] potassium organotrifluoroborates,[23] or other boron reagents.[24] However, 1,2- or 1,4-addition of boronic acids to α,β-unsaturated *N*-tosyl ketimines has not been reported despite the structural similarity of substrates. Only reactive organoaluminum reagents were used to react with cyclic *N*-tosyl ketimines in Rh(I) catalysis.[25] Indeed, in our ligand screening, most monodentate or bidentate phosphorus ligands including phosphoramidite (**6**) and phosphite (**5**) were not active while briphos ligands selectively promoted 1,4-addition of 4-methoxyphenyl boronic acid to a *N*-tosyl ketimine of 1,3-diphenyl-2-propen-1-one (Table 2, entries 1−6). Further tuning of briphos ligands showed that **1c** is the most active ligand, and thus 1,4-addition of aryl boronic acids to α,β-unsaturated *N*-tosyl ketimines was successfully demonstrated as shown in Table 2.

Table 2. Rh-Catalyzed Conjugate Addition of Aryl Boronic Acids to α,β-Unsaturated *N*-Tosyl Ketimines[a]

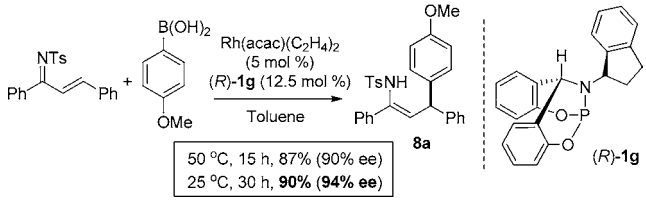


entry	L	8	R^1	R^2	Ar	yield (%)[b]
1	**5**	**8a**	H	H	4-$MeOC_6H_4$	0
2	**7**	**8a**	H	H	4-$MeOC_6H_4$	0
3	**1a**	**8a**	H	H	4-$MeOC_6H_4$	<5
4	**1b**	**8a**	H	H	4-$MeOC_6H_4$	65
5	**1c**	**8a**	H	H	4-$MeOC_6H_4$	88
6	**1e**	**8a**	H	H	4-$MeOC_6H_4$	21
7	**1c**	**8b**	H	H	3-$MeOC_6H_4$	81
8	**1c**	**8c**	H	H	4-MeC_6H_4	>99
9	**1c**	**8d**	H	H	3-MeC_6H_4	80
10	**1c**	**8e**	H	H	Ph	85[c]
11	**1c**	**8f**	H	H	2-naphthyl	89[c]
12	**1c**	**8g**	H	H	4-ClC_6H_4	59[c,d]
13	**1c**	**8h**	4-F	H	Ph	75
14	**1c**	**8i**	H	4-F	Ph	88
15	**1c**	**8j**	4-F	4-F	Ph	99
16	**1c**	**8k**	4-Me	4-F	Ph	87
17	**1c**	**8l**	H	3-NO_2	Ph	65

[a]Conditions: Imine (0.2 mmol), $ArB(OH)_2$ (3.0 equiv), [Rh] (3.0 mol %), and **1c** (7.5 mol %) in 2.0 mL of toluene. [b]Isolated yields. [c]The reaction was performed at 50 °C. [d]The reaction was performed for 10 h.

The utility of briphos is finally verified by asymmetric Rh-catalyzed conjugate addition of an α,β-unsaturated *N*-tosyl ketimine (Scheme 2). A chiral briphos (*R*)-**1g**, prepared from

Scheme 2. Asymmetric Conjugate Addition by Chiral Briphos (1g)



(*R*)-1-aminoindane, provided the product with up to 90% yield and 94% ee. It is remarkable that only one chiral carbon center in the monodentate P ligand showed such a high level of stereoinduction. Thus, the briphos can be a new type of chiral template.

In summary, we prepared a new class of bicyclic bridgehead phosphoramidite (briphos) ligands under mild, scalable, and tunable reaction conditions. Owing to geometrical constraints, the briphos ligands showed enhanced π-acceptor ligand properties compared with its monocyclic analogs supported by X-ray crystallography and DFT computations. We demonstrated that the electronic tuning of briphos ligands provided the significant ligand acceleration effect (LAE) and new catalytic reactivity for Rh(I)-catalyzed conjugate additions and the briphos can be a template for chiral ligand design. The concept of controlling the ligand property by geometrical constraints will be applicable to the development of new ligands or catalysts as exemplified by briphos.

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■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectroscopic, calculation, and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(20) P ligands showed no significant additive effect of base (KOH), while both $[Rh(OH)(COD)]_2$ and $[Rh(COD)Cl]_2$ with the base were found to be active (Table S1, Supporting Information).

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