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Applications of 4,4′-$(Me_3Si)_2$-BINAP in Transition-Metal-Catalyzed Asymmetric Carbon–Carbon Bond-Forming Reactions

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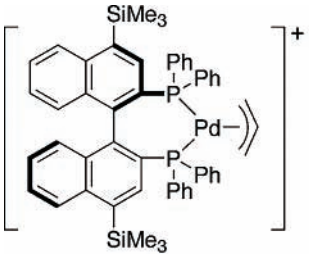
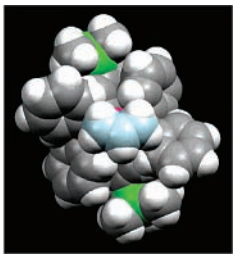
ABSTRACT





A recently developed BINAP derivative with trimethylsilyl substituents on the 4- and 4′-positions of the binaphthyl skeleton, 2,2′-bis(diphenylphosphino)-4,4′-bis(trimethylsilyl)-1,1′-binaphthyl (tms-BINAP), was used in a variety of transition-metal-catalyzed asymmetric carbon–carbon bond-forming reactions. In π-allylpalladium-mediated reactions, tms-BINAP gave better enantioselectivity than the unsubstituted BINAP, and the origin of the improved enantioselectivity was gained from an X-ray structural study of [Pd(η^3-C_3H_5)((*R*)-tms-BINAP)]ClO_4.

Design of chiral ligands is central to the development of transition-metal-catalyzed asymmetric reactions. Among numerous reported chiral ligands, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) is arguably the most successful one to date.[1] Since the first report of BINAP on the rhodium-catalyzed asymmetric hydrogenation in 1980,[1a] transition-metal/BINAP complexes have been used for a wide range of asymmetric reactions with good enantioselectivity, which include Rh-catalyzed isomerization of allylamines,[2] Ru-catalyzed hydrogenation of carbonyl groups,[3] Pd-catalyzed Heck reaction,[4] Rh-catalyzed conjugate addition of aryl- or alkenyl-nucleophiles,[5] Ir-catalyzed Pauson−Khand type cyclization,[6] and Ag-catalyzed allylation of carbonyl

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groups.[7] Structural modification of BINAP has been extensively examined to improve enantioselectivity of the asymmetric reactions catalyzed by transition-metal/BINAP complexes. Notable examples include modifications of the phenyl groups of the $-PPh_2$ moieties of BINAP[8] and the development of atropisomeric bisphosphines based on modified biaryls such as H_8-BINAP,[9] MeO-biphep,[10] biphemp,[11] and segphos.[12]

Recently, we have reported a novel strategy of BINAP modification by introducing sterically encumbered substituents at the 4- and 4′-positions of the binaphthyl skeleton, which drastically enhances enantioselectivity in the Ru-catalyzed asymmetric hydrogenation of a variety of carbonyl compounds.[13] Herein, we wish to report the effectiveness of this novel class of modified BINAPs in transition-metal-catalyzed asymmetric carbon−carbon bond-forming reactions. Four different asymmetric carbon−carbon bond-forming reactions were examined in this work: (1) Pd-catalyzed asymmetric synthesis of axially chiral allenes from 2-bromo-1,3-dienes,[14] (2) Pd-catalyzed asymmetric allylation of prochiral nucleophiles,[15] (3) Rh-catalyzed conjugate addition of $ArB(OH)_2$ to α,β-unsaturated carboxylic esters,[5b−c,16] and (4) Pd-catalyzed asymmetric allylic alkylation reactions.[17] In the first three reactions, BINAP has shown superiority over other chiral phosphines; however, the reported enantioselectivity still has room for further improvement.

Among the 4,4′-disubstituted BINAPs, those with Me_3Si- or $(HO)_2P(O)$-substituents have been shown to give the highest enantioselectivity in Ru-catalyzed asymmetric hydrogenation reactions.[13] Since some of the reactions examined here require aprotic conditions, 4,4′-$(Me_3Si)_2$-BINAP (tms-BINAP) was chosen as a representative of the 4,4′-disubstituted BINAPs for the present study (Figure 1).

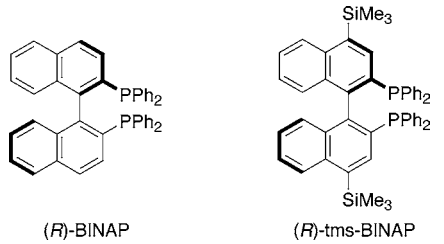
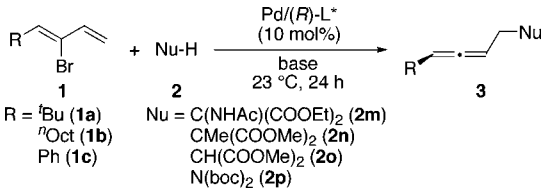


Figure 1. BINAP and 4,4′-$(Me_3Si)_2$-BINAP (tms-BINAP).

The effect of tms-substituents was first examined in the Pd-catalyzed asymmetric synthesis of axially chiral allenes.[14] For a direct comparison between BINAP and tms-BINAP, two reactions, one with BINAP and the other with tms-BINAP, were set up simultaneously and carried out side by side under identical conditions. The results are summarized in Table 1. In the previous report on the asymmetric allene synthesis, malonate derivatives, such as **2m** and **2n**, were used as pronucleophiles.[14c,d] While the Pd/BINAP catalyst gave the axially chiral allene **3am** with 74% ee for the reaction of the ^{t}Bu-substituted bromodiene **1a** with **2m** (entry

Table 1. Pd-Catalyzed Asymmetric Synthesis of Axially Chiral Allenes[a]



entry	1	2	base	L*	solvent	yield[b]/%	% ee[c] (config)[d]
1a	**1a**	**2m**	CsO^{t}Bu	(*R*)-BINAP	CH_2Cl_2	70 (**3am**)	74 (*R*)
1b				(*R*)-tms-BINAP		72 (**3am**)	85 (*R*)
2a	**1a**	**2n**	NaH	(*R*)-BINAP	THF	80 (**3an**)	70 (*R*)
2b				(*R*)-tms-BINAP		82 (**3an**)	80 (*R*)
3a[e,f]	**1b**	**2o**	CsO^{t}Bu	(*R*)-BINAP	THF	73 (**3bo**)	53 (*R*)
3b[e,f]				(*R*)-tms-BINAP		83 (**3bo**)	61 (*R*)
4a	**1c**	**2p**	KH	(*R*)-BINAP	THF	76 (**3cp**)	62 (*R*)
4b				(*R*)-tms-BINAP		98 (**3cp**)	77 (*R*)

[a] All the reaction were carried out with **1** (0.50 mmol), **2** (0.55 mmol), and base (0.55 mmol) in a given solvent (5.0 mL) for 24 h in the presence of a Pd catalyst (10 mol %) generated from $Pd(dba)_2$ and the chiral phosphine. [b] Isolated yield by chromatography on alumina. [c] Determined by chiral HPLC (Chiralpak AD-H (**3am** and **3an**), Chiralcel OD-H (**3bo** and **3cp**)). [d] The absolute configurations were deduced by the Lowe−Brewster rule (ref 19). [e] With 5 equiv of **2o** with respect to **1b**. [f] At 0 °C.

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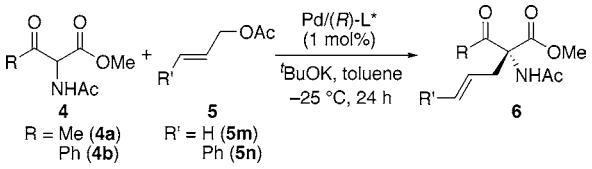
1a), the Pd/tms-BINAP catalyst afforded **3am** in 85% ee under the identical conditions except the ligand (entry 1b). Similarly, tms-BINAP gave higher ee's than BINAP for the reaction of **1a** and **2n** to give **3an** (80% ee vs 70% ee; entries 2a and 2b) and **1b** and **2o** to give **3bo** (61% ee vs 53% ee; entries 3a and 3b). An N-nucleophile generated from HN(boc)$_2$ (**2o**) and KH was found to be effective for the asymmetric reaction.[18] The asymmetric amination product **3cp** of 62% ee was obtained in 76% yield using BINAP (entry 4a). In comparison, the Pd/tms-BINAP system afforded **3cp** with 77% ee in 98% yield under the same conditions (entry 4b).

Encouraged by these results, we have examined the effects of tms-BINAP on Pd-catalyzed allylations of prochiral nucleophiles.[15] BINAP was reported to be a particularly effective chiral ligand for the reactions using α-acetamido-β-ketoesters as pronucleophiles. As shown in Table 2, the Pd-catalyst with tms-BINAP gave higher ee's for these reactions. For instance, the allylation product **6am** of 68% ee was obtained by a Pd/BINAP-catalyzed reaction of **4a** and **5m** in toluene at −25 °C (entry 1a).[20] In comparison, the Pd/tms-BINAP catalyst afforded **6am** of 77% ee under the same conditions (entry 1b). Analogously, the Pd/tms-BINAP catalyst exhibited higher ee's than the Pd/BINAP catalyst for the reactions of **4a** and **5n**, giving **6am** (93% ee vs 90% ee; entries 2a and 2b), and **4b** and **5m**, giving **6bm** (84% ee vs 72% ee; entries 3a and 3b).

Table 2. Pd-Catalyzed Asymmetric Allylation of Prochiral Nucleophiles[a]



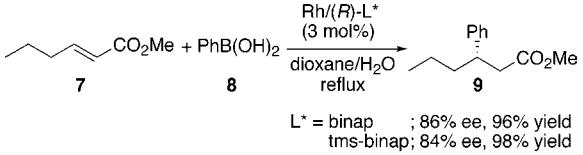
entry	4	5	L*	yield[b]/%	% ee[c] (config)[d]
1a	**4a**	**5m**	(*R*)-BINAP	87 (**6am**)	68 (*R*)
1b			(*R*)-tms-BINAP	75 (**6am**)	77 (*R*)
2a	**4a**	**5n**	(*R*)-BINAP	78 (**6an**)	90 (*R*)
2b			(*R*)-tms-BINAP	68 (**6an**)	93 (*R*)
3a	**4b**	**5m**	(*R*)-BINAP	93 (**6bm**)	72 (*R*)
3b			(*R*)-tms-BINAP	90 (**6bm**)	84 (*R*)

[a] All the reactions were carried out with **4** (0.50 mmol) and **5** (0.80 mmol) at −25 °C[20] in toluene (2.5 mL) in the presence of a Pd catalyst (1 mol %) generated from [PdCl(π-allyl)]$_2$ and the chiral phosphine. [b] Isolated yield by silica gel chromatography. [c] Determined by chiral HPLC (Chiralcel OD-H (**6am** and **6an**), Chiralcel OJ-H (**6bm**)). [d] Determined on the basis of the sign of the specific rotations of the products.

Contrary to the above-mentioned Pd-catalyzed reactions, tms-BINAP did not give ee enhancement for the Rh-catalyzed conjugate addition of arylboronic acids to α,β-unsaturated carboxylic esters.[16] A representative example was shown in Scheme 1. For the reaction of methyl 2-hexenoate (**7**) with PhB(OH)$_2$ (**8**), the Rh/BINAP catalyst gave methyl 3-phenylhexanoate (**9**) of 86% ee in 96% yield. The enantioselectivity of the Rh/tms-BINAP was slightly lower for the same reaction, and the addition product **9** was obtained in 98% yield with 84% ee.

It is known that the key intermediates for the two Pd-catalyzed reactions in which tms-BINAP are effective are quite similar to each other. The reactions in Table 2 proceeded via a well-known π-allylpalladium intermediate.[15a] The intermediate for the Pd-catalyzed allene formation process (Table 1) is a (1,2,3-η^3-butadien-3-yl)palladium species,[14a,c] which possesses a π-allylpalladium substructure as well. Apparently, the effect of the Me$_3$Si substituents was not operative in the Rh-catalyzed reaction (Scheme 1), of which the catalytic cycle[21] as well as the structure of the suggested stereodetermining intermediates[5a,16] were different from the above-mentioned π-allylpalladium-mediated reactions.

Scheme 1



To gain insight into the origin of the interesting enantioenhancement of the tms-BINAP ligand in the π-allylpalladium-mediated asymmetric reactions, we have prepared [Pd(η^3-C$_3$H$_5$)((*R*)-tms-BINAP)]ClO$_4$ and determined its structure by single-crystal X-ray diffraction studies.[22] As shown in Figure 2 for the space-filling model of the [Pd(η^3-C$_3$H$_5$)((*R*)-tms-BINAP)]$^+$ ion, there is steric interaction between the SiMe$_3$ substituents on the binaphthyl skeleton and the phenyl groups of the diphenylphosphino moieties. Consequently, the average dihedral angle of 76.7° between the naphthyl rings in [Pd(η^3-C$_3$H$_5$)((*R*)-tms-BINAP)](ClO$_4$) is smaller than that between the naphthyl rings in the BINAP analogue (79.9°).[15a] This change in the dihedral angle can in effect tilt the equatorial phenyl groups toward the coordinating η^3-allyl moiety to presumably lead to a better stereodiscrimination between the favored and disfavored

(18) Recently, Imada et al. reported dynamic kinetic resolution of racemic allenylmethyl esters by the Pd-catalyzed amination giving allenic amines; see Nishida, M.; Kutsuwa, K.; Imada, Y.; Murahashi, S.-I. Naota, T. In *Abstracts*; 51st Symposium on Organometallic Chemistry, October 2−3, 2004, Toyko, Japan; Kinki Chemical Society: Japan, 2004; PB153. Also see Imada, Y.; Ueno, K.; Kutsuwa, K.; Murahashi, S.-I. *Chem. Lett.* **2002**, 140.

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(20) In the original report by Kuwano and Ito,[15a] the reactions were performed at −30 °C. Because of a limitation of the equipment available in our laboratory, we carried out the reactions at −25 °C.

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(22) [Pd(η^3-C$_3$H$_5$)((*R*)-tms-BINAP)]ClO$_4$ was prepared according to the literature procedure for its BINAP analogue and crystallizes (from slow evaporation of a CH$_2$Cl$_2$/2-propanol solution) in the chiral space group $P2_1$ with two molecules in each asymmetric unit. See Pregosin, P. S.; Ruegger, H.; Salzmann, R.; Albinati, A.; Lianza, F.; Kunz, R. W. *Organometallics* **1994**, *13*, 83.

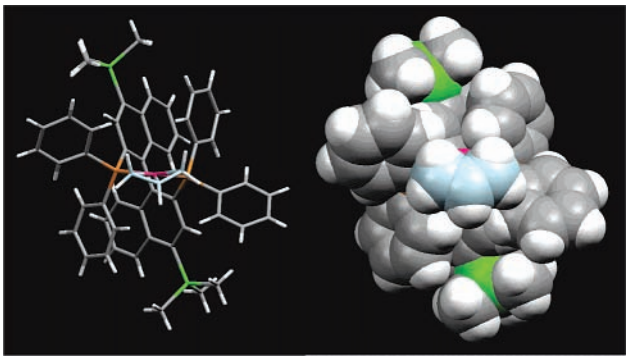

Figure 2. Capped stick and space-filling models of single-crystal X-ray structure of [Pd(η^3-allyl)((*R*)-tms-BINAP)]ClO_4. Red, Ru; orange, P; green, Si; gray, C; white, H. The allyl carbon atoms are highlighted in light blue color. The ClO_4^- anion is omitted for clarity.

diastereomeric transition states during the subsequent step of nucleophilic attack on the π-allyl group.

The X-ray structure study as well as the results in Tables 1 and 2 prompted us to explore the effect of tms-BINAP on Pd-catalyzed asymmetric allylic alkylations.[17] The allylic alkylation reactions shown in Table 3 proceed via an essentially identical intermediate to that of the reactions in Table 2, with the key difference of generating a stereogenic center on the electrophile fragment. Previous studies indicated that BINAP was not a suitable ligand for this asymmetric reaction, and the Pd/BINAP catalyst showed only modest enantioselectivity for most cases.[23] As shown in Table 3, while the Pd/BINAP catalyst gave the alkylated product **12am** with only 25% ee for the reaction of 1,3-diphenyl-2-propenyl acetate (**10a**) with sodium dimethyl methylmalonate (**11m**) (entry 1a), the Pd/tms-BINAP catalyst afforded **12am** of a much higher 80% ee under the same conditions (entry 1b). Similarly, tms-BINAP showed a better enantioselectivity than BINAP for reactions of **10a** and **11n**, giving **12an** (94% ee vs 84% ee; entries 2a and 2b), and **10b** and **11m**, giving **12bm** (57% ee vs 40% ee; entries 3a and 3b).

In summary, we have applied 4,4′-$(Me_3Si)_2$-BINAP in several Pd- and Rh-catalyzed asymmetric carbon−carbon bond-forming reactions. It was found that tms-BINAP was more enantioselective than the unsubstituted BINAP in the π-allylpalladium-mediated reactions; however, the effect of the Me_3Si-substituents was not operative in the Rh-catalyzed conjugate addition of phenyboronic acid to an α,β-unsaturated ester. A comprehensive survey of the scope and the limitation of the 4,4′-substituted-BINAP in other transition-metal-catalyzed asymmetric transformations is currently under investigation.

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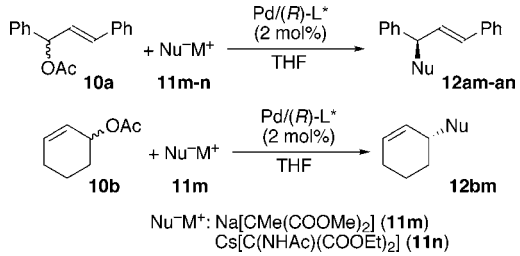
Table 3. Pd-Catalyzed Asymmetric Allylic Alkylations[a]



entry	10	11	L*	conditions	yield[b]/%	% ee[c] (config)[d]
1a	**10a**	**11m**	(*R*)-BINAP	rt, 12 h	85 (**12am**)	25 (*R*)
1b			(*R*)-tms-BINAP		96 (**12am**)	80 (*R*)
2a	**10a**	**11n**	(*R*)-BINAP	0 °C, 24 h	89 (**12an**)	84 (*R*)
2b			(*R*)-tms-BINAP		>99 (**12an**)	94 (*R*)
3a	**10b**	**11m**	(*R*)-BINAP	0 °C, 24 h	91 (**12bm**)	40 (*S*)
3b			(*R*)-tms-BINAP		94 (**12bm**)	57 (*S*)

[a] All the reactions were carried out with **10** (0.50 mmol) and **11** (0.55 mmol) in THF (5.0 mL) in the presence of a palladium catalyst (2 mol %) generated from [PdCl(π-allyl)]$_2$ and the chiral phosphine. [b] Isolated yield by silica gel chromatography. [c] Determined by chiral HPLC on a Chiralpak AD-H column. [d] Determined on the basis of the sign of the specific rotations of the products.

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Supporting Information Available: Detailed experimental procedures, compound characterization data, and crystallographic data (CIF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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