Tetrahedron: *Asymmetry* 23 (2012) 655–658

Contents lists available at SciVerse ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Rhodium/chiral diene-catalyzed asymmetric methylation of *N*-sulfonylarylimines with trimethylboroxine

Takahiro Nishimura *, Akram Ashouri, Yusuke Ebe, Yuko Maeda, Tamio Hayashi *

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan

ARTICLE INFO

Article history:
Received 21 March 2012
Accepted 27 April 2012
Available online 12 June 2012

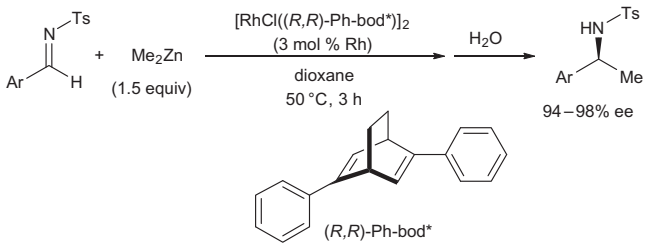
ABSTRACT

A hydroxorhodium complex coordinated with a chiral diene ligand catalyzed the asymmetric addition of trimethylboroxine to *N*-sulfonylarylimines to give high yields of chiral 1-aryl-1-ethylamines with high enantioselectivity.

1. Introduction

α-Chiral amines are important structural motifs in several chiral drugs and natural products, and their enantioselective synthesis has attracted much attention from organic chemists.[1] Of the many approaches for the synthesis of α-chiral amines, the catalytic enantioselective addition of dialkylzinc reagents to imines has been developed by using chiral copper catalysts;[1c] most of the studies reported so far have focused on the catalytic ethylation of imines because of its high reactivity and selectivity. Conversely, efficient methods for the asymmetric methylation of imines have been limited due to the lower reactivity of dimethylzinc, and the large amount of dimethylzinc often required for high yielding methylations.[2–5] Leading studies of the asymmetric methylation of imines with dimethylzinc have been developed in copper-catalyzed asymmetric methylations of *N*-tosylimines with an amidophosphine ligand (Tomioka)[2b] and of *N*-phosphinoylimines with a chiral bis(phosphine) monoxide ligand (Charette),[3a,b,f] and in methylations catalyzed by a Lewis acid complexed with chiral amino acid–based ligands (Hoveyda/Snapper).[4] We have also reported the rhodium-catalyzed asymmetric methylation of *N*-sulfonylarylimines with dimethylzinc, which was realized by the use of a rhodium/chiral diene catalyst (Scheme 1).[6,7]

Organoboronic acids and their derivatives are attractive carbon nucleophiles because of their wide availability and stability,[8] while aryl- and alkenylboron compounds have frequently been used in the rhodium-catalyzed asymmetric addition to electron-deficient alkenes and imines.[9] On the other hand, although methylboronic acid and its derivatives are stable in air and moisture and are easy to handle, there have been only a few examples of their use as methylating reagents in rhodium catalysis.[10] Herein we report the first example of a rhodium-catalyzed asymmetric methylation of *N*-sulfonylarylimines by using trimethylboroxine.



Scheme 1. Asymmetric addition of dimethylzinc to *N*-tosylarylimines catalyzed by Rh/(*R*,*R*)-Ph-bod*.

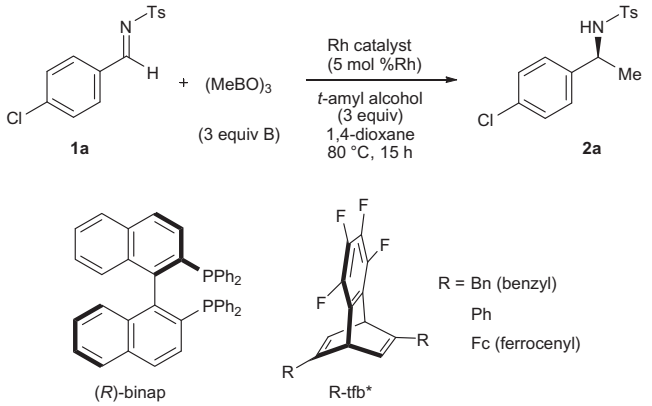
2. Results and discussion

We found that a hydroxorhodium complex coordinated with a diene ligand has high catalytic activity in the addition of trimethylboroxine to *N*-tosylarylimines (Table 1). Thus, treatment of *N*-tosylimine **1a** with trimethylboroxine (3 equiv B) in the presence of $[Rh(OH)(cod)]_2$ (5 mol % of Rh) and *tert*-amyl alcohol (3 equiv) in 1,4-dioxane at 80 °C for 15 h gave the methylation product **2a** in 74% yield (entry 1). The reaction of **1a** with methylboronic acid instead of trimethylboroxine gave a lower yield (22%) of **2a** (entry 2). When carrying out the reaction by using a chlororhodium complex $[RhCl(cod)]_2$ combined with aqueous KOH, which are typical reaction conditions for the addition of arylboronic acids,[11] it did not give **2a** at all, either in the addition of trimethylboroxine (entry 3) or methylboronic acid (entry 4). The hydroxorhodium/bisphosphine complex [Rh(OH)((*R*)-binap)]$_2$,[12] which is one of the most efficient catalysts in the addition of arylboronic acids to α,β-unsaturated ketones, had no catalytic

* Corresponding authors.
E-mail addresses: tnishi@kuchem.kyoto-u.ac.jp (T. Nishimura), thayashi@kuchem.kyoto-u.ac.jp (T. Hayashi).

0957-4166/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetasy.2012.04.021

Table 1
Rhodium-catalyzed asymmetric methylation of **1a**[a]



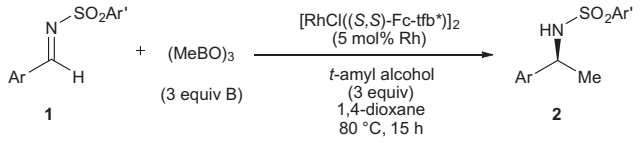
Entry	Catalyst	Isolated yield (%)	ee[b] (%)
1	$[Rh(OH)(cod)]_2$	74	—
2[c]	$[Rh(OH)(cod)]_2$	22[d]	—
3[e]	$[RhCl(cod)]_2$	0	—
4[c,e]	$[RhCl(cod)]_2$	0	—
5	$[Rh(OH)((R)\text{-binap})]_2$	0	—
6	$[Rh(OH)((R,R)\text{-Bn-tfb}^*)]_2$	79	65
7	$[Rh(OH)((R,R)\text{-Ph-tfb}^*)]_2$	90	96
8	$[Rh(OH)((S,S)\text{-Fc-tfb}^*)]_2$	96	98

[a] Reaction conditions: **1a** (0.10 mmol), $[RhCl\mathbf{L}^*]_2$ (5 mol % of Rh), $(MeBO)_3$ (0.10 mmol), *t*-amyl alcohol (0.30 mmol) in 1,4-dioxane (0.4 mL) at 80 °C for 15 h.
[b] Determined by HPLC analysis with a chiral stationary phase column: Chiralcel OD-H.
[c] Performed with $MeB(OH)_2$ (0.30 mmol) instead of $(MeBO)_3$ in the absence of *t*-amyl alcohol.
[d] Determined by ^1H NMR.
[e] Performed in the presence of 1.5 M KOH (aq) (20 mol %) in the absence of *t*-amyl alcohol.

activity (entry 5). These results prompted us to use a hydroxorhodium complex coordinated with a chiral diene ligand[13] for the development of the asymmetric reaction. We have recently developed stable hydroxorhodium complexes coordinated with a chiral diene based on a tetrafluorobenzobarrelene (tfb*) skeleton;[14] in the present reaction we found them to display high catalytic activity and enantioselectivity. Thus, the reactions using hydroxorhodium complexes coordinated with (*R*,*R*)-Bn-tfb* (Bn = benzyl),[14b] (*R*,*R*)-Ph-tfb*,[14c] and (*S*,*S*)-Fc-tfb*[14e] (Fc = ferrocenyl) gave **2a** in 79%, 90%, and 96% yield, respectively (entries 6–8), where (*S*,*S*)-Fc-tfb* displayed the highest enantioselectivity (98% ee, entry 8). The absolute configuration of **2a** obtained when using (*S*,*S*)-Fc-tfb* was determined to be (*S*) by comparison of its specific rotation $\{[\alpha]_D^{20} = -79$ (*c* 0.55, $CHCl_3$) with 99% ee; lit. [6] $([\alpha]_D^{20} = -70.7$ (*c* 1.02, $CHCl_3$) with 96% ee (*S*)}.

Table 2 summarizes the results obtained for the methylation of several *N*-sulfonylarylimines **1**, where the yields and ee of **2** were higher than those observed in our previous studies on the addition of dimethylzinc.[6] The methylation of arylimines substituted with not only *para*-**1a** but also *meta*-**1b** and *ortho*-chloro **1c** proceeded to give the corresponding addition products **2a**–**2c** in high yields with high enantioselectivity (entries 1–3). The arylimines having bromo **1d**, trifluoromethyl **1e**, and methoxy at *para* **1f** and *ortho* **1g** gave the corresponding addition products **2d**–**2g** in high yields (91–97%) with over 98% ee (entries 4–7). Naphthylimines **1h** and **1i** were also good substrates and gave **2h** and **2i** in high yields and with 97% and 98% ee, respectively (entries 8 and 9). The present catalytic system can also be applied to the methylation of *N*-nosylarylimines (Ns = *p*-nitrobenzenesulfonyl) with high enantioselectivity. Thus, the reaction of *N*-nosylimines **1j** and **1k** gave *N*-nosylamides **2j** and **2k** in 92% and 89% yields, respectively (98% ee, entries 10 and 11).

Table 2
Rhodium-catalyzed asymmetric methylation of *N*-sulfonylarylimines **1**[a]



Entry	Ar	SO_2Ar'	Isolated yield (%)	ee[b] (%)
1	$4\text{-}ClC_6H_4$	Ts, **1a**	96, **2a**	99
2	$3\text{-}ClC_6H_4$	Ts, **1b**	95, **2b**	98
3	$2\text{-}ClC_6H_4$	Ts, **1c**	96, **2c**	99
4	$4\text{-}BrC_6H_4$	Ts, **1d**	91, **2d**	98
5	$4\text{-}CF_3C_6H_4$	Ts, **1e**	96, **2e**	99
6	$4\text{-}MeOC_6H_4$	Ts, **1f**	91, **2f**	99
7	$2\text{-}MeOC_6H_4$	Ts, **1g**	97, **2g**	98
8	1-Naphthyl	Ts, **1h**	91, **2h**	97
9	2-Naphthyl	Ts, **1i**	95, **2i**	98
10	$4\text{-}ClC_6H_4$	Ns, **1j**	92, **2j**	98
11	$4\text{-}MeOC_6H_4$	Ns, **1k**	89, **2k**	98

[a] Reaction conditions: **1** (0.20 mmol), $[RhCl((S,S)\text{-Fc-tfb}^*)]_2$ (5 mol % of Rh), $(MeBO)_3$ (0.20 mmol), *t*-amyl alcohol (0.60 mmol) in 1,4-dioxane (0.8 mL) at 80 °C for 15 h.
[b] Determined by chiral HPLC analysis.

3. Conclusion

In conclusion, we have developed a rhodium-catalyzed asymmetric methylation of *N*-sulfonylarylimines by using trimethylboroxine as a methylating reagent to give chiral 1-aryl-1-ethylamines in high yields and with high enantioselectivity; this was achieved by using hydroxorhodium/chiral diene catalyst.

4. Experimental

4.1. General and materials

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen. NMR spectra were recorded on a JEOL JNM ECA-600 spectrometer (600 MHz for ^1H, 150 MHz for ^{13}C). Chemical shifts are reported in δ (ppm) referenced to the residual peaks of $CDCl_3$ (δ 7.26) for ^1H NMR and $CDCl_3$ (δ 77.00) for ^{13}C NMR. Optical rotations were measured on a JASCO P-2200 polarimeter. Flash column chromatography was performed with Silica Gel 60 N (spherical, neutral) (Cica-Reagent). 1,4-Dioxane was purified by passing through a neutral alumina column under N_2. Rhodium complexes, $[RhCl(cod)]_2$,[15] $[Rh(OH)(cod)]_2$,[16] $[Rh(OH)((R)\text{-binap})]_2$,[12] $[Rh(OH)((R,R)\text{-Bn-tfb}^*)]_2$,[14b] $[Rh(OH)((R,R)\text{-Ph-tfb}^*)]_2$,[14c] and $[Rh(OH)((S,S)\text{-Fc-tfb}^*)]_2$[14e] were prepared according to reported procedures. Trimethylboroxine and methylboronic acids (Aldrich) were purchased and used as received. *N*-Sulfonylarylimines were prepared from aldehydes and arenesulfonamides according to reported procedures.[17]

4.2. A general procedure for the asymmetric addition of trimethylboroxine to imines 1 (Table 2)

To a mixture of $[Rh(OH)((S,S)\text{-Fc-tfb}^*)]_2$ (0.0050 mmol, 7.2 mg, 5 mol % of Rh), imine **1** (0.20 mmol), and *t*-amyl alcohol (66 μL, 0.60 mmol) in 1,4-dioxane (0.8 mL) was added trimethylboroxine (28 μL, 0.20 mmol) under N_2, and the mixture was stirred at

80 °C for 15 h. The mixture was passed through a short column of silica gel with ethyl acetate and concentrated on a rotary evaporator. The residue was subjected to flash column chromatography on silica gel with hexane/ethyl acetate to give **2**.

4.3. Characterization of the products

All products are known compounds and were characterized by comparison of the spectroscopic data with those reported previously. Conditions for HPLC analysis and specific rotation values are shown below.

4.3.1. (*S*)-*N*-(1-(4-Chlorophenyl)ethyl)-4-methylbenzenesulfonamide 2a [6]

The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.3 mL/min, 254 nm, t_1 = 25.7 min (*R*), t_2 = 28.6 min (*S*); $[\alpha]_D^{20} = -79$ (*c* 0.55, $CHCl_3$) with 99% ee (*S*).

4.3.2. (*S*)-*N*-(1-(3-Chlorophenyl)ethyl)-4-methylbenzenesulfonamide 2b [6]

The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.3 mL/min, 254 nm, t_1 = 23.1 min (*R*), t_2 = 26.4 min (*S*); $[\alpha]_D^{20} = -73$ (*c* 0.50, $CHCl_3$) with 98% ee (*S*).

4.3.3. (*S*)-*N*-(1-(2-Chlorophenyl)ethyl)-4-methylbenzenesulfonamide 2c [18]

The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.5 mL/min, 254 nm, t_1 = 14.5 min (*R*), t_2 = 16.6 min (*S*); $[\alpha]_D^{20} = -53$ (*c* 0.40, $CHCl_3$) with 99% ee (*S*).

4.3.4. (*S*)-*N*-(1-(4-Bromophenyl)ethyl)-4-methylbenzenesulfonamide 2d [18]

The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.3 mL/min, 254 nm, t_1 = 25.8 min (*R*), t_2 = 29.8 min (*S*); $[\alpha]_D^{20} = -62$ (*c* 0.33, $CHCl_3$) with 98% ee (*S*).

4.3.5. (*S*)-4-Methyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide 2e [6]

The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.3 mL/min, 254 nm, t_1 = 22.4 min (*R*), t_2 = 24.9 min (*S*); $[\alpha]_D^{20} = -49$ (*c* 0.51, $CHCl_3$) with 99% ee (*S*).

4.3.6. (*S*)-*N*-(1-(4-Methoxyphenyl)ethyl)-4-methylbenzenesulfonamide 2f [19]

The ee was measured by HPLC (Chiralcel OD-H column × 2, hexane/2-propanol = 4/1, flow 0.3 mL/min, 254 nm, t_1 = 64.5 min (*R*), t_2 = 68.7 min (*S*); $[\alpha]_D^{20} = -82$ (*c* 0.51, $CHCl_3$) with 99% ee (*S*).

4.3.7. (*S*)-*N*-(1-(2-Methoxyphenyl)ethyl)-4-methylbenzenesulfonamide 2g [19]

The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.3 mL/min, 254 nm, t_1 = 25.4 min (*R*), t_2 = 28.4 min (*S*); $[\alpha]_D^{20} = -66$ (*c* 0.42, $CHCl_3$) with 98% ee (*S*).

4.3.8. (*S*)-4-Methyl-*N*-(1-(naphthalen-1-yl)ethyl)benzenesulfonamide 2h [18]

The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.3 mL/min, 254 nm, t_1 = 29.8 min (*R*), t_2 = 39.3 min (*S*); $[\alpha]_D^{20} = +14$ (*c* 0.52, $CHCl_3$) with 97% ee (*S*).

4.3.9. (*S*)-4-Methyl-*N*-(1-(naphthalen-2-yl)ethyl)benzenesulfonamide 2i [6]

The ee was measured by HPLC (Chiralcel OD-H column, hexane/2-propanol = 4/1, flow 0.5 mL/min, 254 nm, t_1 = 19.0 min (*R*), t_2 = 23.1 min (*S*); $[\alpha]_D^{20} = -79$ (*c* 0.46, $CHCl_3$) with 98% ee (*S*).

4.3.10. (*S*)-*N*-(1-(4-Chlorophenyl)ethyl)-4-nitrobenzenesulfonamide 2j [20]

The ee was measured by HPLC (Chiralcel OJ-H column, hexane/2-propanol = 1/1, flow 0.3 mL/min, 230 nm, t_1 = 36.9 min (*S*), t_2 = 42.0 min (*R*); $[\alpha]_D^{20} = -37$ (*c* 0.56, $CHCl_3$) with 98% ee (*S*).

4.3.11. (*S*)-*N*-(1-(4-Methoxyphenyl)ethyl)-4-nitrobenzenesulfonamide 2k [20]

The ee was measured by HPLC (Chiralcel OJ-H column, hexane/2-propanol = 1/1, flow 0.3 mL/min, 230 nm, t_1 = 46.5 min (*S*), t_2 = 60.6 min (*R*); $[\alpha]_D^{20} = -32$ (*c* 0.47, $CHCl_3$) with 98% ee (*S*).

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research from the MEXT, Japan. AA thanks the Iran Ministry of Science Research and Technology for an academic scholarship.

References

1. For reviews, see: (a) Kobayashi, S.; Mori, Y.; Fossey, J. S.; Salter, M. M. *Chem. Rev.* **2011**, *111*, 2626; (b) Marques, C. S.; Burke, A. J. *Chem. Cat. Chem.* **2011**, *3*, 635; (c) Yamada, K.; Tomioka, K. *Chem. Rev.* **2008**, *108*, 2874; (d) Friestad, G. K.; Mathies, A. K. *Tetrahedron* **2007**, *63*, 2541; (e) Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999**, *99*, 1069; (f) Bloch, R. *Chem. Rev.* **1998**, *98*, 1407.
2. (a) Fujihara, H.; Nagai, K.; Tomioka, K. *J. Am. Chem. Soc.* **2000**, *122*, 12055; (b) Soeta, T.; Nagai, K.; Fujihara, H.; Kuriyama, M.; Tomioka, K. *J. Org. Chem.* **2003**, *68*, 9723.
3. (a) Boezio, A. A.; Charette, A. B. *J. Am. Chem. Soc.* **2003**, *125*, 1692; (b) Boezio, A. A.; Pytkowicz, J.; Côté, A.; Charette, A. B. *J. Am. Chem. Soc.* **2003**, *125*, 14260; (c) Côté, A.; Boezio, A. A.; Charette, A. B. *Angew. Chem., Int. Ed.* **2004**, *43*, 6525; (d) Côté, A.; Boezio, A. A.; Charette, A. B. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5405; (e) Charette, A. B.; Boezio, A. A.; Côté, A.; Moreau, E.; Pytkowicz, J.; Desrosiers, J.-N.; Legault, C. *Pure Appl. Chem.* **2005**, *77*, 1259; (f) Lauzon, C.; Charette, A. B. *Org. Lett.* **2006**, *8*, 2743.
4. (a) Porter, J. R.; Traverse, J. F.; Hoveyda, A. H.; Snapper, M. L. *J. Am. Chem. Soc.* **2001**, *123*, 984; (b) Porter, J. R.; Traverse, J. F.; Hoveyda, A. H.; Snapper, M. L. *J. Am. Chem. Soc.* **2001**, *123*, 10409; (c) Akullian, L. C.; Snapper, M. L.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4244; (d) Akullian, L. C.; Porter, J. R.; Traverse, J. F.; Snapper, M. L.; Hoveyda, A. H. *Adv. Synth. Catal.* **2005**, *347*, 417; (e) Fu, P.; Snapper, M. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2008**, *130*, 5530.
5. For selected examples of catalytic enantioselective methylations of imines with dimethylzinc or trimethylaluminium, see: (a) Soai, K.; Hatanaka, T.; Miyazawa, T. *J. Chem. Soc., Chem. Commun.* **1992**, 1097; (b) Dahmen, S.; Bräse, S. *J. Am. Chem. Soc.* **2002**, *124*, 5940; (c) Almansa, R.; Guijarro, D.; Yus, M. *Tetrahedron: Asymmetry* **2007**, *18*, 2828; (d) Pizzuti, M. G.; Minnaard, A. J.; Feringa, B. L. *J. Org. Chem.* **2008**, *73*, 940.
6. Nishimura, T.; Yasuhara, Y.; Hayashi, T. *Org. Lett.* **2006**, *8*, 979.
7. For examples of rhodium-catalyzed asymmetric 1,2-additions of dimethylzinc or trimethylaluminium, see: (a) Crampton, R. H.; Hajjaji, S. E.; Fox, M. E.; Woodward, S. *Tetrahedron: Asymmetry* **2009**, *20*, 2497; (b) Yoshida, K.; Akashi, N.; Yanagisawa, A. *Tetrahedron: Asymmetry* **2011**, *22*, 1225; (c) Siewert, J.; Sandmann, R.; von Zezschwitz, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 7122.
8. *Boronic Acids*; Hall, D. G., Ed.; Wiley-VCH: Weinheim, 2005.
9. For reviews, see: (a) Sibi, M. P. Ed.; Manyem, S. *Tetrahedron* **2000**, *56*, 8033; (b) Krause, N.; Hoffmann-Röder, A. *Synthesis* **2001**, 171; (c) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169; (d) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829; (e) Darses, S.; Genet, J.-P. *Eur. J. Org. Chem.* **2003**, 4313; (f) Christoffers, J.; Koripelly, G.; Rosiak, A.; Rössle, M. *Synthesis* **2007**, 1279; (g) Miyaura, N. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1535; (h) Berthon, G.; Hayashi, T. In *Catalytic Asymmetric Conjugate Reactions*; Córdova, A., Ed.; Wiley-VCH: Weinheim, 2010; p 1; (i) Hargrave, J. D.; Allen, J. C.; Frost, C. G. *Chem. Asian J.* **2010**, *5*, 386; (j) Edwards, H. J.; Hargrave, J. D.; Penrose, S. D.; Frost, C. G. *Chem. Soc. Rev.* **2010**, *39*, 2093; (k) Tian, P.; Dong, H.-Q.; Lin, G.-Q. *ACS Catal.* **2012**, *2*, 95.
10. For an example of rhodium-catalyzed additions of methylboronic acid to alkynoates, see: (a) Yasuhara, Y.; Nishimura, T.; Hayashi, T. *Chem. Commun.* **2010**, *46*, 2130; For an example of rhodium-catalyzed 1,2-additions of chiral secondary and tertiary benzylic potassium trifluoroborate salts to aldehydes, see: (b) Ros, A.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 6289.
11. Itooka, R.; Iguchi, Y.; Miyaura, N. *J. Org. Chem.* **2003**, *68*, 6000.
12. Hayashi, T.; Takahashi, M.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **2002**, *124*, 5052.
13. For reviews, see: (a) Defieber, C.; Grützmacher, H.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4482; (b) Shintani, R.; Hayashi, T. *Aldrichim. Acta* **2009**, *42*, 31; (c) Feng, C. G.; Xu, M.-H.; Lin, G.-Q. *Synlett* **2011**, 1345; For selected examples of chiral diene ligands, see: (d) Hayashi, T.; Ueyama, K.; Tokunaga, N.; Yoshida, K. *J. Am. Chem. Soc.* **2003**, *125*, 11508; (e) Otomaru, Y.; Okamoto, K.; Shintani, R.; Hayashi, T. *J. Org. Chem.* **2005**, *70*, 2503; (f) Okamoto, K.; Hayashi, T.; Rawal, V. H. *Chem. Commun.* **2009**, 4815; (g) Fischer, C.; Defieber, C.; Suzuki, T.; Carreira, E. M. *J. Am. Chem. Soc.* **2003**, *126*, 1628; (h) Paquin, J.-F.; Defieber, C.;

Stephenson, C. R. J.; Carreira, E. M. *J. Am. Chem. Soc.* **2005**, *127*, 10850; (i) Läng, F.; Breher, F.; Stein, D.; Grützmacher, H. *Organometallics* **2005**, *24*, 2997; (j) Helbig, S.; Sauer, S.; Cramer, N.; Laschat, S.; Baro, A.; Frey, W. *Adv. Synth. Catal.* **2007**, *349*, 2331; (k) Wang, Z.-Q.; Feng, C.-G.; Xu, M.-H.; Lin, G.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 5336; (l) Noël, T.; Vandyck, K.; Van der Eycken, J. *Tetrahedron* **2007**, *63*, 12961; (m) Gendrineau, T.; Chuzel, O.; Eijsberg, H.; Genet, J.-P.; Darses, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 7669; (n) Hu, X.; Zhuang, M.; Cao, Z.; Du, H. *Org. Lett.* **2009**, *11*, 4744; (o) Brown, M. K.; Corey, E. J. *Org. Lett.* **2010**, *12*, 172; (p) Luo, Y.; Carnell, A. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 2750; (q) Pattison, G.; Piraux, G.; Lam, H. W. *J. Am. Chem. Soc.* **2010**, *132*, 14373.

14. (a) Nishimura, T.; Kumamoto, H.; Nagaosa, M.; Hayashi, T. *Chem. Commun.* **2009**, 5713; (b) Nishimura, T.; Wang, J.; Nagaosa, M.; Okamoto, K.; Shintani, R.; Kwong, F.; Yu, W.; Chan, A. S. C.; Hayashi, T. *J. Am. Chem. Soc.* **2009**, *132*, 464; (c) Shintani, R.; Takeda, M.; Nishimura, T.; Hayashi, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 3969; (d) Nishimura, T.; Makino, H.; Nagaosa, M.; Hayashi, T. *J. Am. Chem. Soc.* **2010**, *132*, 12865; (e) Nishimura, T.; Kasai, A.; Nagaosa, M.; Hayashi, T. *Chem. Commun.* **2011**, *47*, 10488; (f) Nishimura, T.; Noishiki, A.; Hayashi, T. *Chem. Commun.* **2012**, *48*, 973.
15. Usón, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126.
16. Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.
17. (a) Love, B. E.; Raje, P. S.; Williams, T. C., II *Synlett* **1994**, 493; (b) Jin, T.-S.; Yu, M.-J.; Liu, L. B.; Zhao, Y.; Li, T. S. *Synth. Commun.* **2006**, *36*, 2339.
18. Liu, C.-R.; Yang, F.-L.; Jin, Y.-Z.; Ma, X. T.; Cheng, D.-J.; Li, N.; Tian, S. K. *Org. Lett.* **2010**, *12*, 3832.
19. Wang, Y.-Q.; Lu, S. M.; Zhou, Y. G. *J. Org. Chem.* **2007**, *72*, 3729.
20. Taylor, J. G.; Whittall, N.; Hii, K. K. *Org. Lett.* **2006**, *8*, 3561.