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Enantioselective Synthesis of Chiral Indane Derivatives by Rhodium-Catalyzed Addition of Arylboron Reagents to Substituted Indenes

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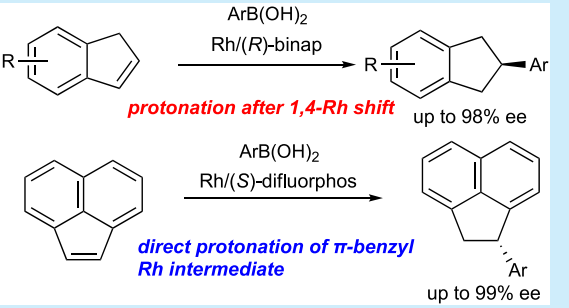
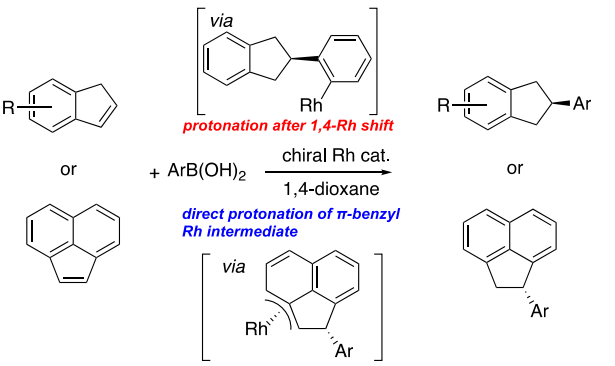
ABSTRACT: Rhodium-catalyzed asymmetric addition of arylboron reagents to indene derivatives proceeded to give 2-arylindanes in good yields with high enantioselectivity. Deuterium-labeling experiments indicated that the present reaction involved a 1,4-Rh shift from an initially formed benzylrhodium to an arylrhodium intermediate before protonation leading to the corresponding addition product. The asymmetric addition was also successful for acenaphthylene, which has a similar skeleton to indene, where it was found that the benzylrhodium intermediate underwent direct protonation without the 1,4-Rh shift.



Rhodium-catalyzed asymmetric addition reaction of arylboron reagents to electron-deficient C−C unsaturated bonds has gained an established position in enantioselective C−C bond formation reactions.[1] In 1998, Hayashi, Miyaura, and co-workers reported the first enantioselective conjugate addition of arylboronic acids to enones.[2] The reaction involves transmetalation of the arylboronic acid with the rhodium complex to give an arylrhodium species, and subsequent alkene insertion generates oxa-π-allyl species, which readily undergoes hydrolysis to form a formal hydroarylation product and to regenerate the Rh catalyst.[3] Following the report, a large number of successful examples of the rhodium-catalyzed asymmetric addition to electron-deficient alkenes have appeared. In contrast, the enantioselective addition to alkenes without electron-deficient substituents has been underdeveloped because of undesired β-hydrogen elimination from an alkylrhodium intermediates. Lautens and co-workers reported that the Rh-catalyzed addition−elimination reaction of styrene proceeded to give *trans*-stilbene, whereas the addition reaction was successful for 2- or 4-vinylpyridine.[4] Lam and co-workers disclosed that introducing an electron-withdrawing NO_2 group at the *para* position of the styrene derivatives enabled the asymmetric addition suppressing β-hydrogen elimination.[5] There have been a few reports on the asymmetric addition to alkenes without particular electron-withdrawing substituents.[6−9] Recently, Wang[7] and we[8] independently reported the asymmetric addition of arylboronic acids to 2*H*-chromene derivatives. Here we report rhodium-catalyzed asymmetric addition of arylboron reagents to indene derivatives giving 2-arylindanes[10] in good yields with high enantioselectivity (Scheme 1).[11] To the best of our knowledge, there have been no reports on the catalytic enantioselective addition of arylmetal reagents to indene derivatives. The reaction involves a 1,4-Rh shift from an initially formed benzylrhodium to an arylrhodium intermediate before protonation leading to the corresponding addition product. The asymmetric addition is also successful for acenaphthylene, where the benzylrhodium intermediate undergoes direct protonation without the 1,4-Rh shift.

Scheme 1. Key Intermediates in This Work



After the reactivity of 1*H*-indene toward Rh-catalyzed addition of arylboronic acids was investigated under several reaction conditions (Table S1), conventional chiral ligands were tested for the enantioselective addition to substituted

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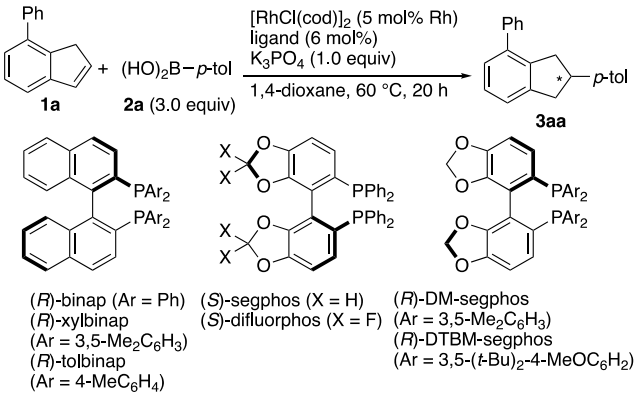
indene derivatives (Table 1). Treatment of 7-phenyl-1*H*-indene (**1a**) with 3.0 equiv of *p*-tolylboronic acid (**2a**) in the presence of $[RhCl(cod)]_2$ (5 mol % of Rh, cod = 1,5-cyclooctadiene), (*R*)-binap[12] (6 mol %), and an equivalent of K_3PO_4 in 1,4-dioxane at 60 °C for 20 h gave the addition product **3aa** in 76% yield, with 95% ee (Table 1, entry 1).

Table 1. Rh-Catalyzed Asymmetric Addition of *p*-Tolylboronic Acid (2a) to 7-Phenylindene (1a)[a]



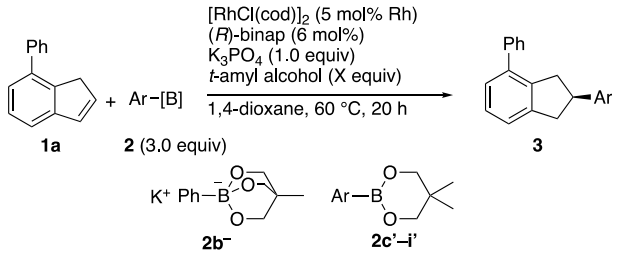
entry	ligand	yield (%)[b]	ee (%)[c]
1	(*R*)-binap	76	95
2	(*R*)-xylbinap	28	66
3	(*R*)-tolbinap	39	81
4	(*S*)-segphos	34	84
5	(*S*)-difluorphos	71	96
6	(*R*)-DM-segphos	52	83
7	(*R*)-DTBM-segphos	11	34
8	—	12	–
9[d]	(*R*)-binap	65	95

[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.30 mmol), $[RhCl(cod)]_2$ (5 mol % of Rh), ligand (6 mol %), and K_3PO_4 (0.10 mmol) in 1,4-dioxane (0.2 mL) at 60 °C for 20 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]$[RhCl(coe)_2]_2$ was used instead of $[RhCl(cod)]_2$.

Binap analogues, xylbinap and tolbinap (entries 2 and 3), and segphos[13] (entry 4) were less effective in terms of both yields and enantioselectivities of **3aa**. (*S*)-Difluorphos,[14] which is known as a relatively electron-deficient ligand, displayed the comparable enantioselectivity of 96% ee with binap (entry 5). The use of bulkier ligands, DM-segphos and DTBM-segphos, did not improve the enantioselectivity (entries 6 and 7). The reaction proceeded without adding the phosphine ligand giving **3aa** in 12% yield, indicating that the 1,5-cyclooctadiene also worked as a ligand to influence the ee when the ligand exchange is incomplete (entry 8). The reaction in the presence of $[RhCl(coe)_2]_2$ (coe = cyclooctene) as a precursor with (*R*)-binap displayed the same enantioselectivity as that observed with $[RhCl(cod)]_2$ (entry 9). The absolute configuration of **3aa** obtained by use of (*R*)-binap was assigned to be *S* by analogy with (*S*)-**3ad** (Table 2, entry 3), which was determined by X-ray crystallography.

The results obtained for the asymmetric addition of *p*-tolylboronic acid (**2a**) to several indene derivatives **1** are summarized in Scheme 2. The addition to indenes substituted with several aryl groups at the 7-position proceeded to give **3ba**–**ga** in moderate to good yields (55–75%), with the enantioselectivity ranging between 79% and 97% ee. A slight decrease of the enantioselectivity (79%

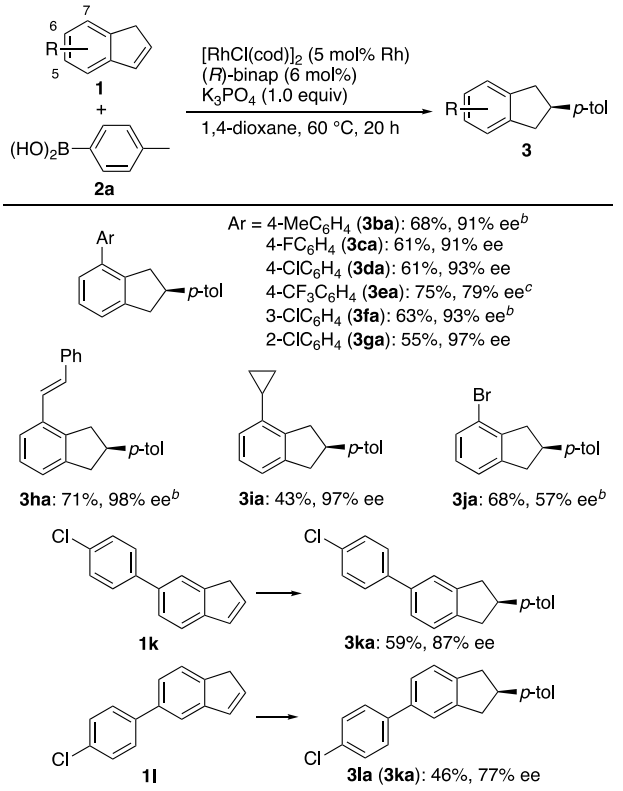
Table 2. Rh-Catalyzed Asymmetric Addition of Arylboron Reagents 2 to 7-Phenylindene (1a)[a]



entry	Ar	X	yield (%)[b]	ee (%)[c]
1	Ph (**2b**$^-$)	2[d]	72 (**3ab**)	92
2	4-PhC_6H_4 (**2c′**)	3	44 (**3ac**)	92
3	4-ClC_6H_4 (**2d′**)	3	64 (**3ad**)	91
4	4-$CF_3C_6H_4$ (**2e′**)	3	94 (**3ae**)	91
5	4-$MeOCOC_6H_4$ (**2f′**)	3	66 (**3af**)	97
6	4-$NO_2C_6H_4$ (**2g′**)	5	67 (**3ag**)	92
7	3-MeC_6H_4 (**2h′**)	5	56 (**3ah**)	93
8	3-ClC_6H_4 (**2i′**)	1.5	79 (**3ai**)	93
9	2-naphthyl (**2j′**)	5	64 (**3aj**)	92

[a]Reaction conditions: **1a** (0.10 mmol), **2** (0.30 mmol), $[RhCl(cod)]_2$ (5 mol % of Rh), (*R*)-binap (6 mol %), and *tert*-amyl alcohol, and K_3PO_4 (0.10 mmol for entries 2–9) in 1,4-dioxane (0.2 mL) at 60 °C for 20 h. [b]Isolated yield. [c]Determined by HPLC analysis with chiral stationary phase columns. [d]H_2O was used instead of *tert*-amyl alcohol without K_3PO_4.

Scheme 2. Rh-Catalyzed Asymmetric Addition of *p*-Tolylboronic Acid to Indene Derivatives[a]



[a]Reaction conditions: **1** (0.10 mmol), **2a** (0.30 mmol), $[RhCl(cod)]_2$ (5 mol % of Rh), (*R*)-binap (6 mol %), and K_3PO_4 (0.10 mmol) in 1,4-dioxane (0.2 mL) at 60 °C for 20 h. [b]$[RhCl(cod)]_2$ (10 mol % of Rh) and (*R*)-binap (12 mol %) were used. [c]At 80 °C.

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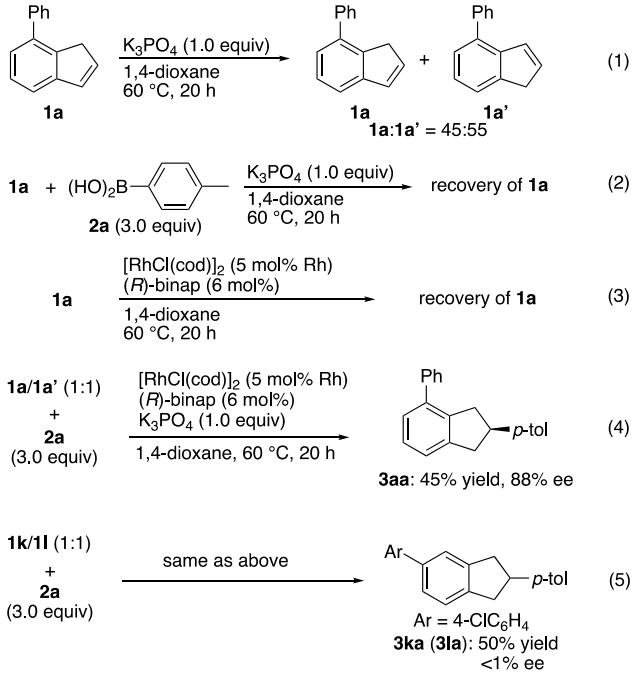
ee) was observed in the addition to **3ea**, which has an electron-withdrawing CF_3 group. Both *m*-chlorophenylindene **1f** and *o*-chlorophenylindene **1g** are also good substrates to give **3fa** and **3ga**, respectively, with high enantioselectivity. Styryl-substituted indene **1h** also participated in the reaction to give **3ha** in 71% yield with 98% ee. The reaction of **3i** having a cyclopropyl group proceeded to give **3ia** with 97% ee. In contrast, the reaction of indene **1j** substituted with a less bulky bromo atom at the 7-position displayed a lower enantioselectivity of 57% ee. The addition to indene **3k** substituted at the 6-position gave the addition product **3ka** in 59% yield with 87% ee. The same product as **3ka** with an opposite absolute configuration (*R*) (**3la**) with 77% ee can be obtained by the reaction of **3l**, which has a *p*-chlorophenyl group at the 5-position, using (*R*)-binap as a ligand.

Table 2 summarizes the results obtained for the addition of several arylboron reagents **2** to 7-phenyl-1*H*-indene (**1a**). The use of arylboron reagents, such as phenylborate ($\mathbf{2b}^-$)[15] in the presence of H_2O (entry 1) and arylboronates (**2′**) with *tert*-amyl alcohol (entries 2−9), brought about higher yields than the corresponding arylboronic acids. Several aryl groups are introduced into **1a** giving the corresponding 2-arylindanes **3** in moderate to good yields with high enantioselectivity. Unfortunately, however, the reaction of *ortho*-substituted aryl groups, such as *o*-tolyl, *o*-chlorophenyl, and *o*-methoxyphenyl, failed to give the corresponding arylation products.

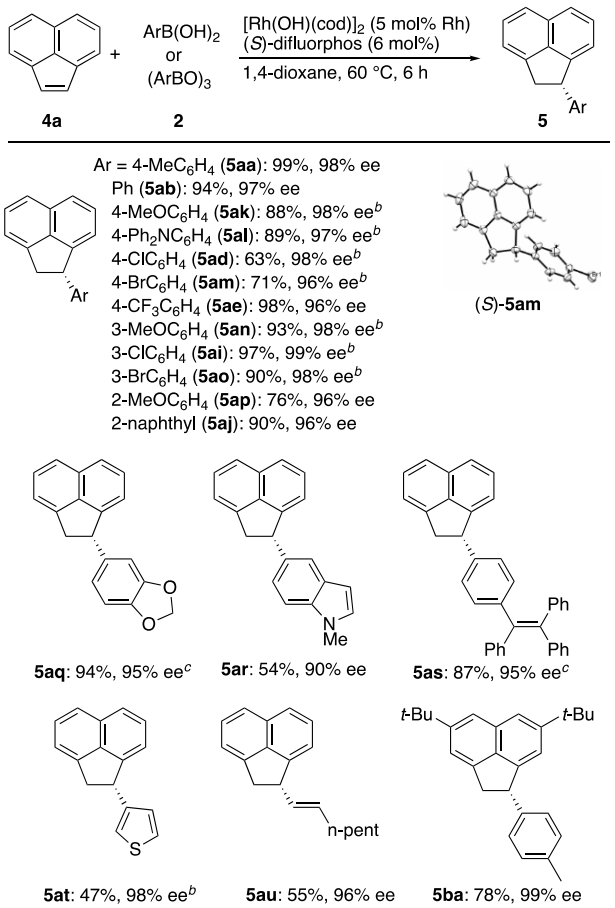
The alkene moiety of indene **1a** easily isomerized into **1a′** in the presence of K_3PO_4 (eq 1). The olefin isomerization, however, was suppressed by *p*-tolylboronic acid (**2a**) even in the presence of the base (eq 2), probably because the basic character was suppressed by the formation of a borate anion. In addition, the chlororhodium catalyst did not isomerize the olefin (eq 3). The reaction of a 1:1 mixture of **1a** and **1a′** gave **3aa** in 45% yield, whose ee was 88% (*S*) (eq 4). The result indicates that the reactivity of **1a** is much higher than **1a′** in consideration of the relatively high enantioselectivity.



The low reactivity of **1a′** might be due to the steric hindrance of the phenyl group located close to the olefin moiety. In sharp contrast, the ee of the product was lost in the reaction of an equimolar mixture of **1k** and **1l** (eq 5), indicating that the substituents far from the olefin moiety do not influence the reactivity. It follows that the same face selectivity of the olefin toward **1k** and **1l** furnishes both enantiomers equally. The result also implies that the olefin isomerization of the indene should be avoided to achieve the high enantioselectivity.

The present catalytic system can also be applied to the asymmetric addition to acenaphthylene as one of the indene derivatives (Scheme 3), which has not been used as an acceptor for Rh-catalyzed addition of arylboron reagents, to the best of our knowledge. After the optimization of the reaction conditions for the asymmetric addition (Table S2), the catalytic system composed of $[Rh(OH)(cod)]_2$ and (*S*)-difluorphos was found to efficiently promote the reaction with high enantioselectivity. Thus, treatment of acenaphthylene (**4a**) with 2.5 equiv of *p*-tolylboronic acid (**2a**) in the presence of $[Rh(OH)(cod)]_2$ (5 mol % of Rh) and (*S*)-difluorphos (6 mol %) in 1,4-dioxane at 60 °C for 6 h gave the addition product **5aa** in 99% yield with 98% ee. The

Scheme 3. Rh-Catalyzed Asymmetric Addition of Arylboron Compounds to Acenaphthylene[a]



[a]Reaction conditions: **4a** (0.20 mmol), **2** (0.50 mmol), $[Rh(OH)(cod)]_2$ (5 mol % of Rh), and (*S*)-difluorphos (6 mol %) in 1,4-dioxane (0.4 mL) at 60 °C for 6 h. [b]Arylboroxine (**2′′**) (2.5 equiv of B) and *tert*-amyl alcohol (3.0 equiv) were used instead of the corresponding arylboronic acids. [c]Arylboroxine (**2′′**) (2.5 equiv of B) and water (5.0 equiv) were used instead of the corresponding arylboronic acids.

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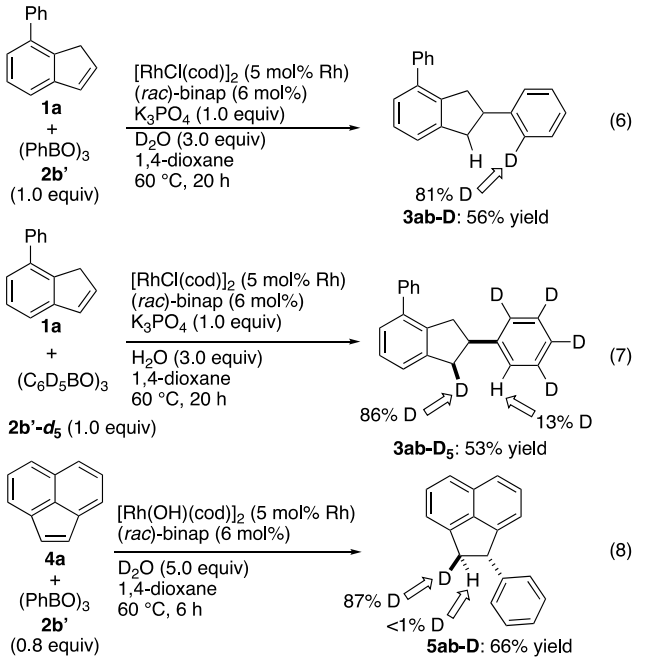
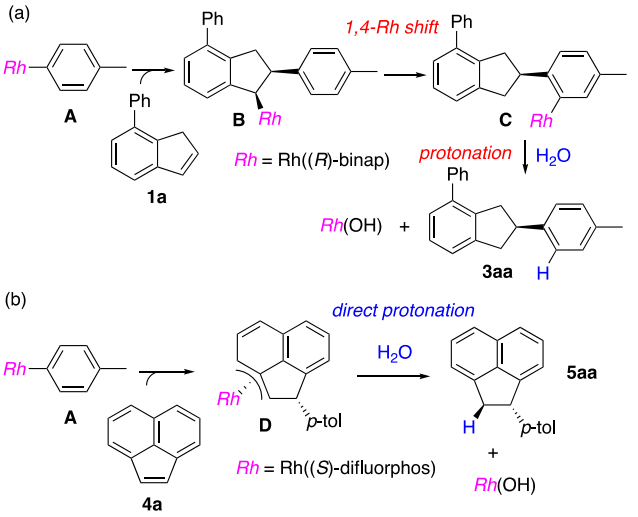
scope of arylboronic acids is fairly broad, and a variety of aryl groups substituted with both electron-donating and -withdrawing groups were introduced into **4a**, thus giving the corresponding addition products **5** in high yield with high enantioselectivity (90−99% ee). 2-Thiopheneboronic acid (**2t**) and alkenylboronic acid **2u** also participated in the reaction to give addition products **5at** and **5au** in 47% and 55% yields, respectively, with high enantioselectivity. The reaction of acenaphthylene **5b** substituted with two *tert*-butyl groups also gave addition product **5ba** in 78% yield with 99% ee. The absolute configuration of the (*S*)-**5am** was determined to be *S* by X-ray crystallographic analysis.

Deuterium-labeling experiments provided mechanistic insight into the protonation step of the present reactions (eqs 6−8). In the reaction of indene **1a** with phenylboroxine **2b′** in the presence of D_2O, where $PhB(OD)_2$ is generated in situ, deuterium incorporation was observed at the 2′-position of the phenyl group (eq 6). The reaction using pentadeuteriophenylboronic acid (**2b**-d_5) generated in situ gave the addition product, where a transfer of deuterium from the phenyl group to a benzylic position of the indane occurred (eq 7). These results indicate that the reaction involves a 1,4-Rh[16] shift before protonation. On the other hand, in the reaction of acenaphthylene (**4a**) with phenylboroxine **2b′** in the presence of D_2O, H/D exchange was observed at the benzylic position (eq 8). It was also confirmed that the deuterium on **5ab-D** was *anti* to the phenyl group. The result indicates that an organorhodium species undergoes direct protonation with inversion of stereochemistry at the rhodium to give the addition product without the 1,4-Rh shift.[17]



Based on the results of the deuterium-labeling experiments and previous studies,[3,16] insertion and protonation steps of the present reactions are proposed as illustrated in Scheme 4. *p*-Tolylrhodium species **A**, generated by transmetalation between *p*-tolylboronic acid (**2a**) and Rh, reacts with indene **1a** to give benzylrhodium intermediate **B**, which undergoes the 1,4-Rh shift to form arylrhodium **C**. Protonation of **C** then gives **3aa** and regenerates a Rh(OH) species. In contrast to the protonation step for indene **1a**, the reaction of

Scheme 4. Protonation Steps via Key Intermediates



acenaphthylene (**4a**) involves direct protonation of the benzylrhodium intermediate as shown in Scheme 4b. The π-benzylrhodium intermediate **D**, which may be stabilized not to receive the 1,4-Rh shift, undergoes the protonation at the benzylic position from the opposite side of rhodium to give **5aa**.

In summary, we have developed Rh-catalyzed asymmetric addition of arylboron reagents to indene derivatives giving 2-arylindanes in good yields with high enantioselectivity. High enantioselectivity was also observed for the addition to acenaphthylene, which has a similar skeleton to indene. Mechanistic investigations indicate that the present Rh-catalyzed addition of arylboronic acids to indene derivatives involves a 1,4-Rh shift before protonation of the benzylrhodium intermediate to release the product and the active Rh species. In contrast, in the reaction of acenaphthylene, direct protonation of the organorhodium species, which may have a π-benzyl form, occurs without the 1,4-Rh shift to give the addition product. Further studies on the asymmetric addition to indene derivatives having a trisubstituted alkene moiety are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03651.

Experimental procedures and compound characterization (PDF)

Accession Codes

CCDC 2031738−2031739 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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