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Asymmetric Conjugate Alkynylation of Cyclic α,β-Unsaturated Carbonyl Compounds with a Chiral Diene Rhodium Catalyst

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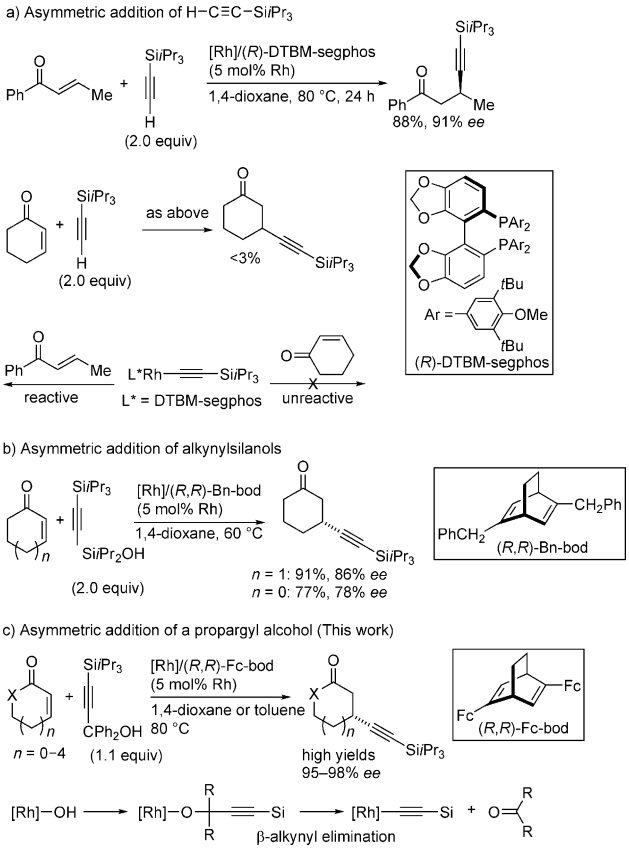
Abstract: *Asymmetric conjugate alkynylation of cyclic α,β-unsaturated carbonyl compounds (ketones, esters, and amides) was realized by use of diphenyl[(triisopropylsilyl)ethynyl]methanol as an alkynylating reagent in the presence of a rhodium catalyst coordinated with a new chiral diene ligand (Fc-bod; bod = bicyclo[2.2.2]octa-2,5-diene, Fc = ferrocenyl) to give high yields of the corresponding β-alkynyl-substituted carbonyl compounds with 95–98% ee.*

Asymmetric conjugate alkynylation of α,β-unsaturated carbonyl compounds is one of the most efficient methods of producing alkynes bearing stereogenic carbon centers at the propargyl position.[1] While a number of efficient reaction systems have been reported on the asymmetric conjugate addition of sp^3- and sp^2-carbon nucleophiles by use of chiral metal catalysts and organocatalysts,[2] the development has been slow on the asymmetric introduction of sp-carbon atoms (alkynyl groups). The catalytic asymmetric conjugate alkynylation has been reported with nickel,[3] copper,[4] rhodium,[5–8] and other metal[9] complexes as catalysts. Although high yields and high enantioselectivities have been reported for some of acyclic α,β-unsaturated carbonyl compounds, there have been only a few reports on successful asymmetric alkynylation of cyclic substrates, typically 2-cyclohexenone and 2-cyclopentenone. One of them is the nickel-catalyzed addition of alkynylaluminum reagents reported by Corey and co-workers, wherein 3-alkynylcyclohexanones were obtained with 85–90% *ee*.[3]

We have previously reported rhodium-catalyzed asymmetric addition of (triisopropylsilyl)acetylene to α,β-unsaturated ketones,[5] where the main side-reaction forming the acetylene dimer[10] was suppressed by use of a bulky chiral bis(phosphine) ligand, DTBM-segphos (Scheme 1a). The rhodium catalyst system consisting of DTBM-segphos and (triisopropylsilyl)acetylene led to high yields and high enantioselectivities for acyclic α,β-unsaturated ketones, typically 1-phenylbut-2-en-1-one and some other reactive substrates,[6] but it is not applicable to less reactive cyclic enones because the alkynylrhodium intermediate with the very bulky ligand, DTBM-segphos, is not reactive toward the cyclic enones (Scheme 1a). Use of alkynylsilanol as an alkynylating reagent and appropriate chiral ligands improved the yield and enantioselectivity for both acyclic and cyclic enones[7,8] (Scheme 1b), but it still has drawbacks in that an excess amount of the alkynylating reagent must be used for a high chemical yield and, more importantly, the substrate scope is not broad. In this context, we have looked for better reaction systems for the asymmetric conjugate alkynylation with a broader substrate scope. Herein we report our recent findings that the asymmetric conjugate alkynylation takes place in high yields with high enantioselectivity by use of an alkynyl(diphenyl)methanol as an alkynylating reagent and a new chiral diene ligand bearing ferrocenyl groups (Scheme 1c). This work is based on the reports that propargyloxy rhodium complexes undergo β-alkynyl elimination to generate alkynyl rhodium species[11] and our expectation is that the acetylene dimerization would be negligible, even with less bulky chiral ligand, because of the low reactivity of the bulky



Scheme 1. Rhodium-catalyzed asymmetric alkynylation of enones.

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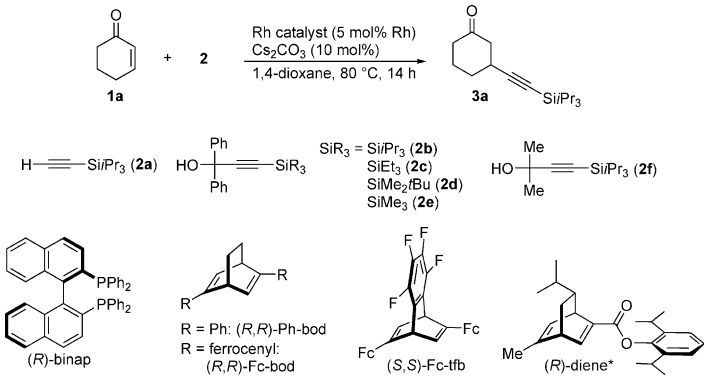
Table 1: Rhodium-catalyzed asymmetric alkynylation of 2-cyclohexenone (**1a**).[a]



Entry	**2** (equiv)	Rh catalyst	Conv [%][b]	Yield [%][c]	*ee* [%][d]
1	**2a** (2.0)	Rh/(*R*)-DTBM-segphos[e]	10	< 3	–
2	**2a** (2.0)	[{RhCl((*R*,*R*)-Ph-bod)}$_2$]	20	< 3	–
3	**2a** (2.0)	[{RhCl((*S*,*S*)-Fc-tfb)}$_2$]	> 95	45	89 (*R*)
4	**2b** (1.0)	[{RhCl(cod)}$_2$]	> 95	93	–
5[f]	**2b** (1.0)	[{RhOH(cod)}$_2$]	> 95	96	–
6	**2b** (1.0)	[{RhCl((*R*,*R*)-Ph-bod)}$_2$]	69	56	93 (*R*)
7	**2b** (1.0)	[{RhCl((*S*,*S*)-Fc-tfb)}$_2$]	73	58	73 (*R*)
8	**2b** (1.0)	[{RhCl((*R*)-diene*)}$_2$]	66	42	90 (*R*)
9	**2b** (1.0)	[{RhCl((*R*)-binap)}$_2$]	> 95	81	23 (*R*)
10	**2b** (1.0)	Rh/(*R*)-DTBM-segphos[e]	29	28	58 (*R*)
11	**2b** (1.0)	[{RhCl((*R*,*R*)-Fc-bod)}$_2$]	> 95	91	97 (*R*)
12	**2b** (1.1)	[{RhCl((*R*,*R*)-Fc-bod)}$_2$]	> 95	94	97 (*R*)
13[g]	**2b** (1.0)	[{RhCl((*R*,*R*)-Fc-bod)}$_2$]	> 95	93	95 (*R*)
14	**2c** (1.0)	[{RhCl((*R*,*R*)-Fc-bod)}$_2$]	86	59[h]	97 (*R*)
15	**2d** (1.0)	[{RhCl((*R*,*R*)-Fc-bod)}$_2$]	65	49[h]	97 (*R*)
16	**2e** (1.0)	[{RhCl((*R*,*R*)-Fc-bod)}$_2$]	27	10[h]	–
17	**2f** (1.0)	[{RhCl((*R*,*R*)-Fc-bod)}$_2$]	53	36	96 (*R*)
18	**2a** (1.0)	[{RhCl((*R*,*R*)-Fc-bod)}$_2$]	> 95	44	92 (*R*)

[a] Reaction conditions: **1a** (0.15 mmol), Rh catalyst (5 mol% of Rh), and Cs_2CO_3 (0.015 mmol) in 1,4-dioxane (0.4 mL). [b] Conversion of **2** determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Yield of the isolated product. [d] The *ee* value was determined by HPLC analysis of the tosylhydrazone (a mixture of *syn*/*anti* isomers) of **3a** on a chiral stationary phase column. For details, see the Supporting Information. The absolute configuration was determined by the optical rotation of **3a**. [e] In situ generation from [{Rh(OH)(cod)}$_2$] and the bis(phosphine). [f] In the absence of Cs_2CO_3. [g] In toluene. [h] The yields of the alkynylation products where Si*i*Pr$_3$ in **3a** is replaced by $SiEt_3$, $SiMe_2tBu$, and $SiMe_3$ in entries 14, 15, and 16, respectively.

alkynyl(diphenyl)carbinol towards the addition of the alkynyl rhodium species.

Table 1 summarizes the results obtained for the rhodium-catalyzed asymmetric alkynylation of 2-cyclohexenone (**1a**) under various reaction conditions, including those reported previously for comparison. In the first set of experiments, the reaction of (triisopropylsilyl)acetylene (**2a**) was examined (entries 1–3). A rhodium catalyst with the bulky bis(phosphine) ligand DTBM-segphos, which has been reported to catalyze the alkynylation of linear enones successfully,[5] gave only a trace amount (< 3%) of the alkynylation product **3a** (entry 1). It is ascribed to the low reactivity of the alkynylrhodium/DTBM-segphos intermediate toward this less reactive enone (see Scheme 1a). The reactivity was not significantly changed by use of Ph-bod[12] (Table 1, entry 2), which is one of the most commonly used chiral diene ligands.[13] Interestingly, the yield of **3a** was increased to 45% with the ferrocene-substituted diene ligand Fc-tfb[14] (entry 3). It was found that the use of diphenyl[(triisopropylsilyl)ethynyl]methanol (**2b**)[11f,15] as an alkynylating reagent greatly improves the yield of **3a**. The reaction of **1a** with 1.0 equivalent of **2b** in the presence of Cs_2CO_3 (10 mol%) and [{RhCl(cod)}$_2$] (5 mol% Rh, cod = 1,5-cyclooctadiene) in 1,4-dioxane at 80 °C for 14 hours gave a 93% yield of **3a** (entry 4). Essentially the same high yield was observed with [{RhOH(cod)}$_2$] as a catalyst in the absence of Cs_2CO_3 (entry 5). However, the yields of **3a** were much lower with rhodium catalysts coordinated with known chiral diene ligands in place of cod. The reaction with the Ph-bod[12] ligand gave 56% yield of **3a**, though the enantioselectivity is high (93% *ee*; entry 6). The yields are also modest with Fc-tfb[14] and the ester-substituted diene (*R*)-diene*[16] (entries 7 and 8), which have been developed recently as more enantioselective ligands for rhodium-catalyzed asymmetric reactions. These low yields are mainly because their rhodium complexes lose their catalytic activity during the reaction. With the bis(phosphine) ligand binap the enantioselectivity was low although the yield of **3a** was high (entry 9). As anticipated, the catalytic activity was low with the bulky bis(phosphine) DTBM-segphos (entry 10).

A high-yielding asymmetric alkynylation was realized with the newly synthesized chiral diene ligand (*R*,*R*)-Fc-bod,[17] which is a chiral bicyclo[2.2.2]octadiene-based ligand substituted with ferrocenyl groups. Thus, the reaction with [{RhCl((*R*,*R*)-Fc-bod)}$_2$] (5 mol% Rh) in 1,4-dioxane under the same reaction conditions as in entry 4 of Table 1, gave 91% yield of **3a**, which is *R* configured, with 97% *ee* (entry 11). The reaction with a small excess (1.1 equiv) of **2b** increased the yield of **3a** to 94% (entry 12). Toluene as a solvent gave a high yield (93%) of **3a** with a slightly lower *ee* value for the alkynylation of **1a** (entry 13). The *i*Pr$_3$Si group at the acetylene terminus in **2b** is essential for the high yield of **3a**. With other propargyl alcohols bearing less bulky silyl groups, Et_3Si (**2c**) and *t*BuMe$_2$Si (**2d**), the yields are modest (59% and 49%, respectively), but high *ee* values were maintained (entries 14 and 15). The smaller substituent, Me_3Si, on the propargyl alcohol **2e** decreased the yield to 10% (entry 16). Replacement of the two phenyl groups on **2b** by two methyl groups also decreased the yield of **3a** (36%; entry 17). The Rh/Fc-

bod catalyst improves the reaction with **2a**, but the yield of **3a** is still moderate (44%; entry 18).

The reaction progress was monitored for the rhodium-catalyzed alkynylation of **1a** with **2b** to compare the catalytic activity of the Rh/Fc-bod catalyst with that of Rh/Ph-bod and Rh/cod (see entries 4, 6, and 11 in Table 1). It was revealed that the lower yield with the Rh/Ph-bod catalyst is due to a shorter lifetime of the catalyst system (Figure 1). Thus, the

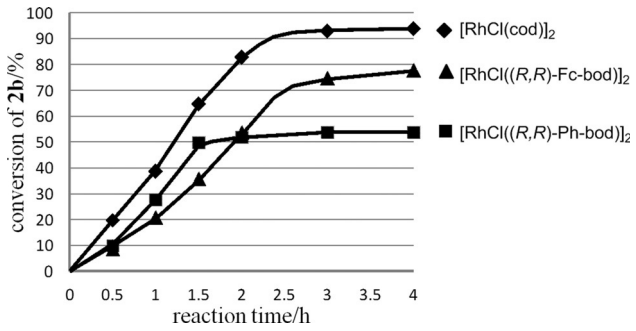


Figure 1. Time-dependent conversion of diphenyl[(triisopropylsilyl)ethynyl]methanol (**2b**) in the reaction of **1a** (0.225 mmol) with **2b** (0.150 mmol) in the presence of Cs_2CO_3 (10 mol%) and either [{RhCl((*R*,*R*)-Fc-bod)}$_2$], [{RhCl((*R*,*R*)-Ph-bod)}$_2$], or [{RhCl(cod)}$_2$] as the catalyst (5 mol% Rh) in 1,4-dioxane (0.6 mL) at 80°C.

reaction with 5 mol% of Rh/Fc-bod proceeds constantly, at least for the initial 4 hours. At this reaction time, the conversion of **2b** and the yield of **3a** reach around 80%. In contrast, Rh/Ph-bod loses its catalytic activity after a reaction time of 1.5 hours. The conversion of **2b** does not change much from 50% after 1.5 hours. It is notable that the color of the reaction mixture with the Rh/Ph-bod catalyst changes from deep red to dark green after a reaction time of 1.5 hours, thus indicating that the deep red and dark green colors are for an active catalyst and for an inactive catalyst, respectively. The color change at around 1 to 2 hours of reaction time was also observed in the reactions catalyzed by Rh/Fc-tfb and Rh/(*R*)-diene*. The reaction with Rh/Fc-bod maintains the deep red color for a longer time. With Rh/cod the red color did not change at all for 14 hours, thus Rh/cod catalyzed the alkynylation faster and did not lose catalytic activity.

Studies on the nonlinear effects gave us significant information on the rhodium intermediates. The large nonlinear effect shown in Figure 2 observed with Rh/Ph-bod catalyst is well understood by assuming that the rhodium complex is in an equilibration between a dimer, which is not catalytically active, and a monomer which is catalytically active, and the equilibration lies towards the dimer.[18] The negative effect is in good agreement with the observation that the homochiral dimer is formed preferentially over the heterochiral dimer in [{RhCl(Ph-bod)}$_2$].[19] The equilibrium constant for the dimer formation is calculated to be $K_{dimer} = 3.6 \times 10^2$, assuming that the homochiral dimer formation is exclusive.[20]

Recently, Fukuzawa reported the synthesis and isolation of the dimeric alkynyl rhodium complex **4**, with a 1,5-cyclooctadiene (cod) ligand (Scheme 2), by treatment of [{RhCl(cod)}$_2$] with the lithium acetylide of **2a**.[21] The same complex **4** was obtained (95%) by mixing [{RhOH(cod)}$_2$] with a stoichiometric amount of **2b** in toluene at 60°C for 4 hours, and by the reaction of [{RhCl(cod)}$_2$] with **2b** in the presence of Cs_2CO_3. The dimer **4** has a deep red color in solution and its catalytic activity is as high as that of [{RhOH(cod)}$_2$] for the alkynylation of **1a**. In contrast, it was difficult to isolate the dimer complex, analogous to **4**, derived from the Ph-bod ligand because of its instability. The reaction of [{RhCl((*R*,*R*)-Ph-bod)}$_2$] with **2b** and Cs_2CO_3 for a long time (80°C, 14 h) gave a dark green complex in 78% yield, which is not catalytically active for the alkynylation. Its ^{13}C NMR resonances at $\delta = 149.2$ (d, $J_{C\text{-}Rh} = 53.8$ Hz) and 108.2 ppm (t, $J_{C\text{-}Rh} = 8.7$ Hz) allow tentative assignment of the complex as the dirhodium species **5**.

It is most likely that the catalytic cycle of the present alkynylation involves the dimer intermediate **A** as a resting state (Scheme 3). Through dimer–monomer equilibration, **A** will provide a minor amount of the catalytically active monomer **C**, which probably enters the catalytic cycle: alkynylrhodation of enone, rhodium enolate–alkoxide exchange, and β-alkynyl elimination. Although the effects of the diene structure on the conversion of **A** into **B** remain to be clarified, the conversion does not take place with the cod ligand and it is slower with Fc-bod than other chiral diene ligands, thus resulting in the longer lifetime of the Fc-bod/Rh catalyst.

The present reaction system consisting of **2b** and Rh/Fc-bod has a broad substrate scope (Table 2). The cyclic enones of five-, seven-, and eight-membered rings gave the corre-

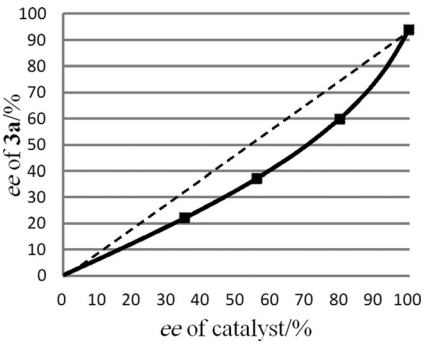
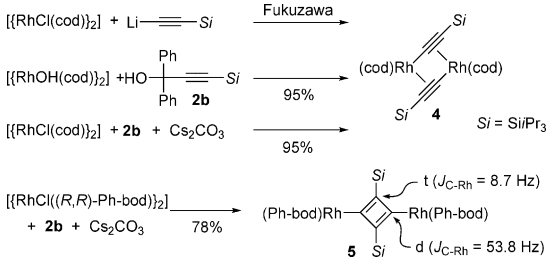
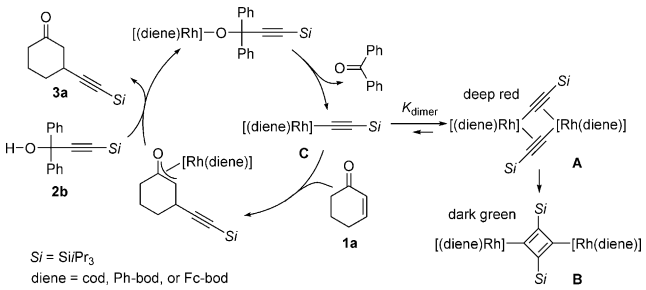


Figure 2. The *ee* value of **3a** versus the *ee* value of the catalyst [{RhCl((*R*,*R*)-Ph-bod)}$_2$] for the reaction of **1a** with **2b**. The *ee* values were obtained for the reactions at a low conversion. The simulation line for $K_{dimer} = 3.6 \times 10^2$ is shown as a solid line.

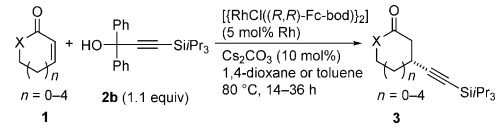


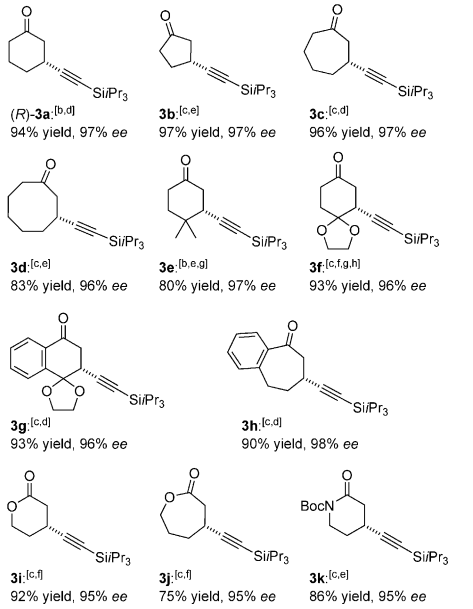
Scheme 2. Stoichiometric reactions of Rh/diene complexes with **2b**.



Scheme 3. A proposed catalytic cycle for the alkynylation of **1a** with **2b** catalyzed by diene rhodium complexes.

Table 2: Rhodium-catalyzed asymmetric alkynylation of cyclic α,β-unsaturated ketones, esters, and amides (**1**) with **2b**.[a]





[a] Reaction conditions: **1** (0.150 mmol), **2b** (0.165 mmol), [{RhCl((*R*,*R*)-Fc-bod)}$_2$] (3.75 μmol, 5 mol% of Rh), and Cs_2CO_3 (0.015 mmol) in 0.4 mL of solvent at 80 °C for a given time. The absolute configurations were determined by stereochemical similarity to the reaction giving (*R*)-**3a**. [b] In 1,4-dioxane. [c] In toluene. [d] For 14 h. [e] For 24 h. [f] For 36 h. [g] With [{RhCl((*R*,*R*)-Fc-bod)}$_2$] (10 mol% of Rh) and 0.030 mmol of Cs_2CO_3. [h] With 0.225 mmol of **2b**. Boc = *tert*-butoxycarbonyl.

sponding alkynylation products **3b**, **3c**, and **3d** in high yields and *ee* values within the range of 96–97%. Those with substituents at the γ-position, and with the benzene-ring-fused structure also gave the products **3e**–**h** with high *ee* values. The asymmetric conjugate alkynylation giving the cyclic esters **3i** and **3j**, and amide **3k** are also possible under the present reaction conditions. For most of the substrates in Table 2, except for those giving **3a** and **3e**, the reaction run in toluene gave higher product yields than those in 1,4-dioxane.[22]

In summary, the combination of diphenyl[(triisopropylsilyl)ethynyl]methanol as an alkynylating reagent and a newly synthesized chiral ferrocenyl diene (Fc-bod) as a chiral ligand realized the rhodium-catalyzed asymmetric conjugate alkynylation of cyclic α,β-unsaturated carbonyl compounds, which are known to be difficult substrates because of their lower reactivity towards the conjugate alkynylation.

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Keywords: alkynes · asymmetric catalysis · diene ligands · rhodium · synthetic methods

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