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Catalytic asymmetric Michael reactions using a chiral rhodium complex

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Abstract—Catalytic asymmetric Michael reaction of β-keto esters and methyl vinyl ketone was achieved using a chiral diamine-based Rh complex to give the Michael adducts in up to 75% e.e.

1. Introduction

The asymmetric Michael reaction is one of the most important carbon–carbon bond-forming synthetic methods.[1] Although the catalytic asymmetric Michael reaction between β-keto esters and α,β-unsaturated ketones has been reported, there are only a few synthetically valuable examples.[2–6] *Cinchona* alkaloids (1 mol%, −21°C, 185 h) were found to catalyze the reaction of methyl 1-oxo-2-indanecarboxylate **1a** and methyl vinyl ketone **2**, giving the Michael addition product (*S*)-**3a** in 76% e.e.[2] A chiral crown ether catalyst was used in the presence of *tert*-BuOK to promote the same reaction (4 mol%, −78°C, 120 h), giving (*S*)-**3a** in 48% yield with e.e. of 99%.[3] The complex formed from $Co(acac)_2$ and (*S*,*S*)-1,2-diphenyl-1,2-ethylenediamine (5 mol%, −50°C, 64 h) was first reported by Brunner to give (*R*)-**3a** in 50% yield with 66% e.e.[4] The dimeric Cu complex derived from (*S*)-2-(2-hydroxybenzylideneamino)-1,4-butandiol (1 mol%, −20°C, 3 days) also catalyzed the reaction, giving (*S*)-**3a** quantitatively with e.e. of 75%,[5] and the chiral shift reagent $Eu(tfc)_3$ (10 mol%) was reported to promote the reaction of acyclic β-keto esters and **2** to give Michael adducts in 23–36% e.e.[6] To date the most successful example, reported by Shibasaki, involved the use of a chiral heterobimetallic binaphthol–La/Na catalyst (5–20 mol%, −50°C, 12–20 h) in the reaction of a variety of β-keto esters with **2** to afford the addition products with yields of 73–98% and e.e.s of 73–91%.[7] Although several successful results have been reported, there is clearly much room for improvement in terms of the stereoselectivity of the reactions and the catalyst efficiency and applicability.[8,9] Herein we report a new protocol using a simple diamine-based Rh catalyst to give chiral Michael addition products with e.e.s of up to 75% (Scheme 1).

2. Results and discussion

Stirring a mixture of tetrachlorobis(pentamethylcyclopentadienyl)dirhodium $[Cp^*RhCl_2]_2$ **4a** with (*R*,*R*)-*N*-(4-*tert*-butylbenzenesulfonyl)-1,2-diphenylethylenediamine (*R*,*R*)-**5b** and KOH (mol ratio 1:2:10) in CH_2Cl_2 at room temperature for 2 hours under argon gave a deep blue suspension. The soluble portion of this mixture could be used as a catalyst for the Michael addition of β-keto esters to unsaturated ketones.

When a mixture of methyl 1-oxo-2-indanecarboxylate **1a**, methyl vinyl ketone **2**, and the in situ prepared Rh catalyst (**1a**:**2**:Rh = 100:350:1 mol ratio) was stirred at −30°C for 10 hours, (*S*)-methyl 1-oxo-2-(3′-oxobutyl)-2-indanecarboxylate [(*S*)-**3a**] was obtained in >99% yield with 75% e.e. The catalyst system generated from (*R*,*R*)-**5b** and KOH in the absence of **4a** gave the adduct **3a** in good yield but with very low e.e. of <5%, showing that the **4a**/(*R*,*R*)-**5b**/KOH catalyst system is essential to achieve high enantioselectivity in the reaction.

Table 1 shows some examples of the asymmetric Michael addition of β-keto esters **1** to methyl vinyl ketone **2** using (*R*,*R*)-**5**/Rh[10] and other metal catalysts. Compared to other metal complexes, the Rh catalyst

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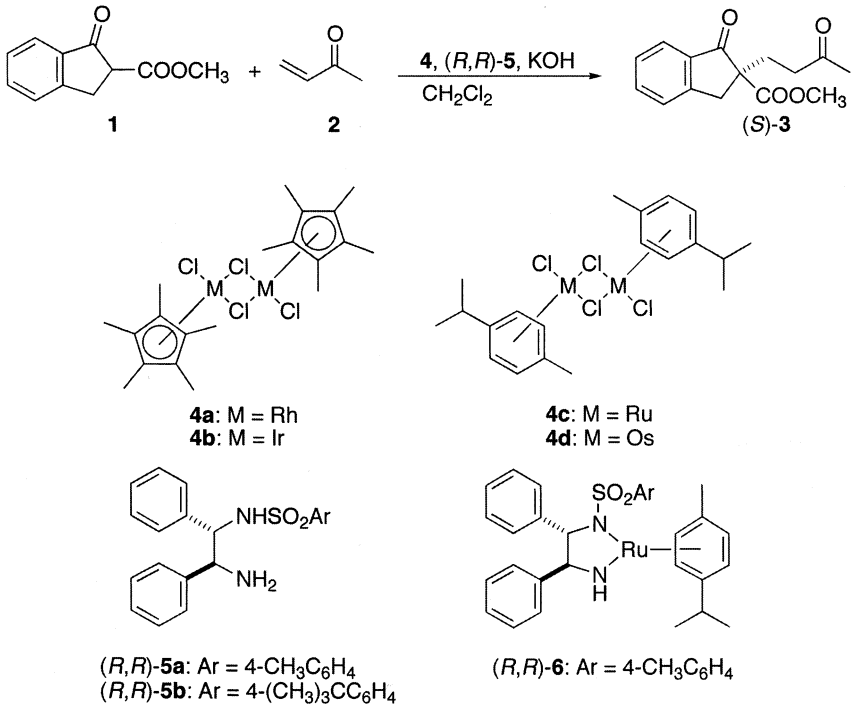


Scheme 1. Asymmetric Michael reaction of 2-methoxycarbonyl-1-indanone **1a** and 3-buten-2-one **2**.

had the highest enantioselectivity and reactivity (entries 2–4 and 6). Although the known 16-electron Ru complex **6**[11e] gave better results than the in situ prepared Ru complex (entries 4 and 5), isolation of the corresponding Rh complex was not possible due to the instability of the catalyst.[10b]

The nitrogen substituent of the (1*R*,2*R*)-1,2-diphenylethylendiamine affects the enantioselectivity of the reaction markedly. Whilst 4-alkylated benzenesulfonyl groups gave excellent yields (>99%) of products and e.e.s of 67–75% (entries 1 and 2), other sulfonylated derivatives gave the widely different results: CH_3SO_2, >99% yield, 57% e.e.; 4-$CH_3OC_6H_4SO_2$, 90% yield, 46% e.e.; 4-$NO_2C_6H_4SO_2$, 13% yield, 23% e.e.

The cyclopentanone derivative **1b** also gave the Michael adduct quantitatively in similarly good e.e. of 67% (entry 7). Facial selection for the β-keto esters examined in this study is the same, although the absolute configurations are different due to a change in the priority order of the substituents (entries 2 and 7). The reactivity of the Rh catalyst for the reaction of a five-membered system is several times higher than that of the known catalyst systems (entries 1 and 2).[2–7] As anticipated from the literature, the reactivity and selectivity differed depending on the ring size. For example, the less acidic cyclohexanone derivative **1c** had lower reactivity with low e.e. (entry 8). Acyclic β-keto ester **1d** could also be used as a donor, although the enantioselectivity of the reaction was lower (entry 9).

Table 1. Asymmetric Michael addition of β-keto esters to methyl vinyl ketone catalyzed by a chiral Rh(III) complex[a]

Entry	β-Keto ester	Catalyst		Time (h)	Michael adduct			
		Metal	Diamine		No.	% Yield[b]	% e.e.[c]	Config.[d]
1	Methyl 1-oxo-2-indanecarboxylate **1a**	**4a**	(*R*,*R*)-**5b**	10	**3a**	>99	75	*S*
2	**1a**	**4a**	(*R*,*R*)-**5a**	8	**3a**	>99	67	*S*
3	**1a**	**4b**	(*R*,*R*)-**5a**	15	**3a**	53	47	*S*
4	**1a**	**4c**	(*R*,*R*)-**5a**	15	**3a**	69	39	*S*
5	**1a**	(*R*,*R*)-**6**[e]	(*R*,*R*)-**6**[e]	15	**3a**	>99	48	*S*
6	**1a**	**4d**	(*R*,*R*)-**5a**	15	**3a**	64	26	*S*
7	Ethyl 1-oxo-2-cyclopentanecarboxylate **1b**	**4a**	(*R*,*R*)-**5a**	3	**3b**	>99	67	*R*
8	Ethyl 1-oxo-2-cyclohexanecarboxylate **1c**	**4a**	(*R*,*R*)-**5a**	72	**3c**	30	34	*R*
9	Ethyl 3-oxo-2-methylbutanoate **1d**	**4a**	(*R*,*R*)-**5a**	72	**3d**	73	10	*S*

[a] Unless otherwise stated, the reaction was conducted at −30°C using β-keto ester (0.50 mmol) and methyl vinyl ketone (1.80 mmol) in CH_2Cl_2 containing the catalyst (1 mol%).
[b] Isolated yield.
[c] The e.e. of **3a** was determined by chiral HPLC. The e.e. of **3b** was determined by chiral HPLC after conversion to the 3′,3′-dimethyl acetal. The e.e. of **3c** and **3d** were determined by optical rotation.
[d] The absolute configurations were determined by the sign of the optical rotation of the products.
[e] Isolable 16-electron Ru complex (*R*,*R*)-**6** was used without treatment with KOH, instead of in situ prepared complex.

Although the detailed reaction mechanism remains unclear, a possible mechanism is presented in Scheme 2. As observed in the transfer hydrogenation promoted by chiral diamine-based transition metal complexes,[10,11] treatment of a CH_2Cl_2 solution of **4** and **5** with KOH generates a deep blue 16-electron species, which may be the active catalytic species. Treatment of the catalyst solution with the β-keto ester afforded a yellow solution. After addition of **2** and stirring, the color of the reaction mixture changed to deep blue, indicating completion of the reaction.

In summary, the diamine-based Rh complexes have been found to catalyze the asymmetric Michael reaction of β-keto esters and methyl vinyl ketone. This is the first example of a C–C bond-forming reaction using these types of complexes. Investigation of the use of other catalyst systems and a mechanistic study of the reaction are currently in progress.

3. Experimental

3.1. Materials and methods

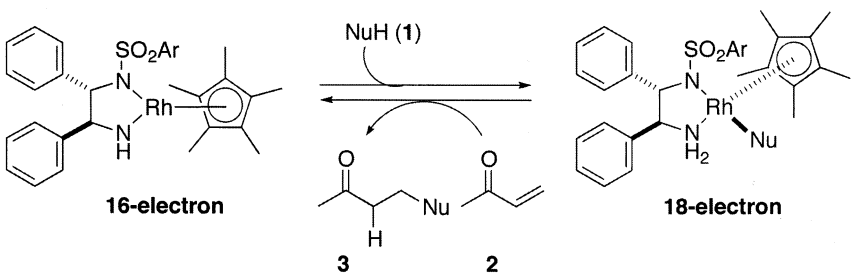
^{1}H NMR spectra were recorded on a JEOL GSX-270 (270 MHz) spectrometer. Chemical shifts are reported in ppm on the δ scale downfield from tetramethylsilane used as an internal standard, and signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak. ^{13}C NMR spectra were measured on a JEOL JNM-LA-500 spectrometer at 125 MHz. Chemical shifts are reported in ppm with chloroform-*d* (77.00 ppm) as an internal standard. Infrared (IR) spectra were recorded on a Perkin–Elmer PARAGON 1000 spectrometer. High-performance liquid chromatographic (HPLC) analyses were performed on a JASCO PU-980 pump, with a JASCO UV-970 UV detector. The analytical column was a Daicel Chiralpak AD or Chiralcel OD (4.6 mm i.d.×250 mm). Optical rotation measurements of chiral compounds were performed on a JASCO DIP-181 polarimeter. Analytical thin-layer chromatography was performed using Merck 5715 indicating plates precoated with silica gel 60 F254 (layer thickness 0.25 mm). The product spots were visualized with either iodine or a solution of *o*-anisaldehyde. Liquid chromatographic purification was performed by flash column chromatography using a glass column packed with Kanto chemical silica gel 60 (spherical) (40–50 μm). CH_2Cl_2 was distilled from CaH_2. (*R*,*R*)-1,2-Diphenylethylenediamine was purchased from the Kankyo-Kagaku Center. Ethyl 1-oxo-2-cyclopentanecarboxylate **1b** was purchased from Nacalai Tesque, Inc. Ethyl 1-oxo-2-cyclohexanecarboxylate **1c** was purchased from Merck. Ethyl 3-oxo-2-methylbutanoate **1d** was purchased from Wako Chemicals. β-Keto esters **1b**, **1c**, and **1d** were distilled over 4 Å molecular sieves. Methyl vinyl ketone **2** was purchased from Tokyo Kasei and distilled under reduced pressure. KOH was purchased from Nacalai Tesque, Inc. and was broken up in a mortar before use. The following compounds were prepared according to previously reported methods: methyl 1-oxo-2-indanecarboxylate (**1a**),[12] $[Cp^*RhCl_2]_2$ **4a**,[13] $[Cp^*IrCl_2]_2$ **4b**,[14] $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ **4c**,[14] $[\{OsCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ **4d**,[15] (*R*,*R*)-**5a**[16] and **6**.[11e] (*R*,*R*)-*N*-(4-*tert*-Butylbenzenesulfonyl)-1,2-diphenylethylenediamine (*R*,*R*)-**5b** was prepared from 4-*tert*-butylbenzenesulfonyl chloride and (*R*,*R*)-1,2-diphenylethylenediamine. **5b**: ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.27$ (s, 9H), 4.13 (d, $J = 5.4$ Hz, 1H), 4.38 (d, $J = 5.4$ Hz, 1H), 6.05 (br, 1H), 7.00–7.35 (m, 14H).

3.2. Typical procedure for the catalytic asymmetric Michael reaction

A typical procedure for a 0.5 mmol scale Michael addition of β-keto ester to methyl vinyl ketone is as follows.

A mixture of **4a** (4.6 mg, 7.5 μmol), (*R*,*R*)-**5b** (6.1 mg, 15 μmol), and KOH (4.2 mg, 75 μmol) in CH_2Cl_2 (1.5 mL) was stirred for 2 h at room temperature. During this period, the reaction mixture changed color from an orange to a deep blue suspension. The supernatant solution was used as a catalyst stock solution (10 mM). The same catalyst stock solution was prepared by mixing the reagents in an ultrasonic cleaning bath for 10 min.

The catalyst solution (0.5 mL, 5 μmol, 1 mol%) and methyl vinyl ketone **2** (0.15 mL, 1.75 mmol) was added to a solution of **1a** (95.1 mg, 0.5 mmol) in CH_2Cl_2 (1.5 mL) at −30°C and the mixture was stirred for 10 h. Then aqueous HCl (1 M) was added. The mixture was extracted with ether and washed with brine. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure, and the residue was subjected to silica gel column chromatography (2:1 hexane–ethyl acetate) to give (*S*)-**3a** (130 mg, >99% yield, 75% e.e.) as a white solid.



Scheme 2. Possible mechanism of asymmetric Michael reaction of **1** and **2**.

3.2.1. (*S*)-(−)-Methyl 1-oxo-2-(3′-oxobutyl)-2-indanecarboxylate 3a[17]. IR (KBr) 1734, 1710 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) $\delta = 2.13$ (s, 3H), 2.15–2.30 (m, 2H), 2.40–2.70 (m, 2H), 3.04 (d, $J = 16.0$ Hz, 1H), 3.66 (d, $J = 16.0$ Hz, 1H), 3.70 (s, 3H), 7.41–7.80 (m, 4H); $[\alpha]_D^{24} = -45.2$ (*c* 1.0, benzene, 75% e.e.). Lit. (*S*)-enantiomer[2b] $[\alpha]_{578}^{rt} = -77$ (*c* 2, benzene, 100% e.e.).

The e.e. was determined using chiral HPLC analysis: column, Daicel Chiralpak AD (4.6 mm i.d.×250 mm); eluent, propan-2-ol:hexane 5:95; flow rate, 1.0 mL/min; detection, 254 nm light; t_R of (*S*)-**3a**, 20 min; t_R of (*R*)-enantiomer, 23 min.

3.2.2. (*R*)-(−)-Ethyl 2-oxo-1-(3′-oxobutyl)cyclopentanecarboxylate 3b[18]. IR (neat) 1718, 1166 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) $\delta = 1.25$ (t, $J = 7.4$ Hz, 3H), 1.80–2.20 (m, 5H), 2.14 (s, 3H), 2.30–2.60 (m, 4H), 2.60–2.80 (m, 1H), 4.17 (q, $J = 7.4$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 14.1$, 19.5, 27.0, 29.9, 34.4, 38.0, 38.9, 58.9, 61.4, 171.4, 207.8, 214.8; $[\alpha]_D^{24} = -5.5$ (*c* 1.66, $CHCl_3$, 67% e.e.). Lit. (*R*)-enantiomer[19] $[\alpha]_D^{23} = -6.9$ (*c* 5.3, $CHCl_3$, 40% e.e.).

The e.e. of **3b** was determined using chiral HPLC analysis after conversion to the 3′,3′-dimethyl acetal:[7] IR (KBr) 1734, 1710 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) $\delta = 1.25$ (t, $J = 7.4$ Hz, 3H), 1.27 (s, 3H), 1.40–2.60 (m, 5H), 3.16 (s, 3H), 3.18 (s, 3H), 4.16 (q, $J = 7.4$ Hz, 2H); column, Daicel Chiralcel OD (4.6 mm i.d.× 250 mm); eluent, propan-2-ol:hexane 1:100; flow rate, 0.3 mL/min; detection, RI light; t_R of (*R*)-enantiomer, 36 min; t_R of (*S*)-isomer, 39 min.

3.2.3. (*R*)-(+)-Ethyl 2-oxo-1-(3′-oxobutyl)cyclohexanecarboxylate 3c[18]. IR (neat) 1718, 1244 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) $\delta = 1.29$ (t, $J = 7.4$ Hz, 3H), 1.40–2.20 (m, 7H), 2.13 (s, 3H), 2.30–2.70 (m, 5H), 4.20 (q, $J = 7.4$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 14.1$, 22.5, 27.5, 28.4, 29.9, 36.6, 38.8, 41.0, 59.9, 61.3, 172.0, 207.7, 207.9; $[\alpha]_{578}^{22} = +28.5$ (*c* 1.03, CCl_4, 34% e.e.). Lit. (*R*)-enantiomer[20] $[\alpha]_{578}^{22} = +85.0$ (*c* 1.03, CCl_4, 100% e.e.).

3.2.4. (*S*)-(−)-Ethyl 2-acetyl-2-methyl-5-oxohexanoate 3d[18]. IR (neat) 1717, 1254 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) $\delta = 1.26$ (t, $J = 7.4$ Hz, 3H), 1.33 (s, 3H), 2.00–2.30 (m, 2H), 2.14 (s, 3H), 2.15 (s, 3H), 2.30–2.50 (m, 2H), 4.19 (q, $J = 7.4$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 14.0$, 19.3, 26.1, 28.3, 29.9, 38.6, 58.6, 61.4, 172.6, 205.4, 207.3; $[\alpha]_D^{20} = -0.93$ (*c* 1.57, $CHCl_3$, 34% e.e.). Lit. (*S*)-enantiomer[21] $[\alpha]_D^{22} = -8.32$ (*c* 1.3, $CHCl_3$, 100% e.e.).

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