Novel Asymmetric Michael Addition of α-Cyanopropionates to Acrolein by the Use of a Bis(oxazolinyl)phenylstannane-Derived Rhodium(III) Complex as a Chiral Lewis Acid Catalyst

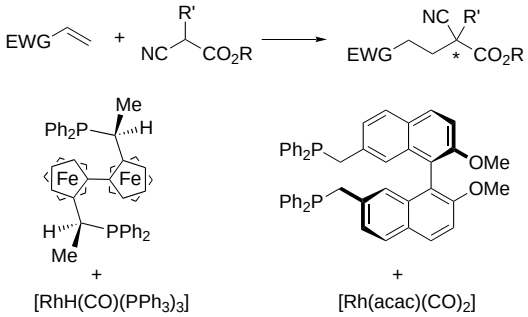
Yukihiro Motoyama,* Yoshiyuki Koga, Kouji Kobayashi, Katsuyuki Aoki, and Hisao Nishiyama[a]

Abstract: The rhodium complex prepared in situ by simply mixing [{RhCl(*c*-octene)$_2$}$_2$] and [(Phebox)SnMe$_3$] (**1**) (Phebox = 2,6-bis(oxazolinyl)phenyl) was found to serve as an efficient catalyst for the asymmetric Michael addition of α-cyanopropionates (**4**) to acrolein under mild and neutral conditions. In the present catalytic system, both the temperature of catalyst preparation and the order of the addition of the substrates were very important for the catalytic efficiency and enantioselectivity. Detailed mechanistic studies of this catalytic system revealed that the [(Phebox)Rh^{III}(SnMe$_3$)Cl] complex (**9**), generated by oxidative addition of [{RhCl(*c*-octene)$_2$}$_2$] to **1**, is an active catalyst and the turnover number (TON) of the present actual catalyst existing in a reaction mixture is greater than 10000. The obtained (*R*) stereochemistry of the Michael adducts **5** can be explained by N-bonded enol intermediates **C′**, which are formed by enolization of **4** bound to the Lewis acidic rhodium complex **9**. We also found that the active catalyst **9** gradually decomposed in the presence of the remaining [{RhCl(*c*-octene)$_2$}$_2$] in the reaction mixture to form the catalytically nonactive [(Phebox)RhCl$_2$] fragment **A**, whose structure was characterized by an X-ray crystallographic study after converting to the *t*BuNC complex **10**.

Keywords: asymmetric catalysis · α-cyanopropionates · Lewis acids · Michael addition · pincer ligands · rhodium

Introduction

The Michael addition of carbon nucleophiles to alkenes that contain an electron-withdrawing group (EWG) is widely recognized as one of the most important carbon–carbon bond-forming reactions in organic synthesis.[1] Although these reactions proceed by the use of Brønsted bases, such as tertiary amines, alkali metal alkoxides, or hydroxides, these basic conditions are often a limiting factor because there is a variety of side and subsequent reactions. To carry out the reactions under mild and neutral conditions, much attention has been recently focused on the transition-metal complexes as catalysts. Accordingly, numerous catalytic processes that use chiral transition-metal complexes have been reported.[2] Among various nucleophiles, α-cyanocarboxylates are useful substrates for this reaction in order to produce a quarternary carbon center with many different functional groups.[3] Nevertheless, there are only two reports of chiral catalysts, prepared from Rh^{I} precursors and *trans*-chelating ligands that have deep chiral surroundings, for the Michael addition with good-to-high enantioselectivities because the enantioselective carbon–carbon bond formation would be accomplished at the α-carbon atom very distant from the metal center (Scheme 1).[4]



Scheme 1. Chiral catalysts for asymmetric Michael addition of α-cyanopropionates to enals or enones.

Previously, we have designed a chiral anionic "N-C-N pincer" ligand,[5, 6] namely 2,6-bis(oxazolinyl)phenyl (abbreviated to Phebox),[7, 8] and synthesized the stannyl compounds **1** (Scheme 2) as stable aryl anion precursors since aryltri-

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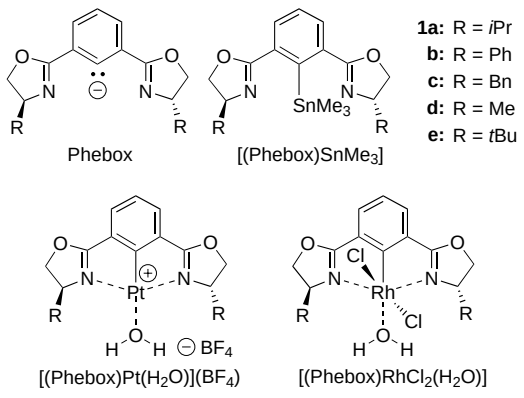
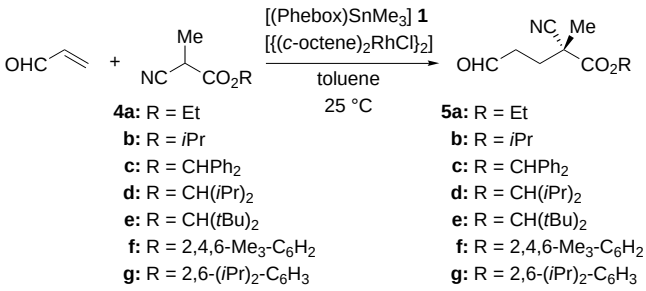


Scheme 2. Structures of [(Phebox)$SnMe_3$] (**1**), Phebox-Pt and Phebox-Rh aqua complexes **2** and **3**.

alkylstannanes are known to react with metal halides (by transmetalation) or low-valent transition metals (by oxidative addition).[9] Furthermore, we have also succeeded in the asymmetric alkylation of benzaldimine,[7b] enantioselective addition of allyl tins to aldehydes,[7c,d] and hetero-Diels–Alder reaction of Danishefsky's dienes[7e] by the use of Phebox-Pt and Phebox-Rh aqua complexes **2** and **3** as chiral Lewis acids (Scheme 2). In this context, we have been very interested in the application of Phebox ligands containing a deep chiral pocket to the asymmetric Michael addition of α-cyanocarboxylates and electrophiles as a further challenging subject. Although we examined the reaction of α-cyanopropionates **4** and acrolein with Phebox-derived Pt and Rh complexes, these aqua complexes **2** and **3** showed no catalytic activities without tertiary amines. In sharp contrast, we found that the rhodium catalyst generated in situ by simply mixing [{RhCl(*c*-octene)$_2$}$_2$] and [(Phebox)$SnMe_3$] (**1**) acts as an effective catalyst for the reaction of α-cyanopropionates **4** and acrolein (Scheme 3). We now report the novel asymmetric



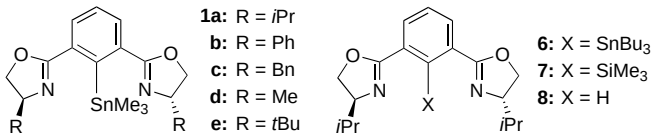
Scheme 3. Asymmetric Michael addition of α-cyanopropionates **4** to acrolein.

Michael addition of α-cyanopropionates to acrolein with a Phebox-derived Rh^{III} catalyst. We also describe X-ray crystallographic and NMR evidence for the basis of the reaction mechanism and transition-state assembly in this catalytic system.

Results and Discussion

Asymmetric Michael addition of α-cyanopropionates to acrolein: At first, several Phebox precursors (**1**, **6**–**8**) and Rh^I sources were examined in toluene for their catalytic activities and enantioselectivities in the asymmetric Michael addition of ethyl 2-cyanopropionate (**4a**) to acrolein. To a solution of the catalyst in toluene, prepared in situ from [(*i*Pr-Phebox)$SnMe_3$] (**1a**, 2 mol%) and [{RhCl(*c*-octene)$_2$}$_2$] (1 mol%), was added **4a** (0.5 mmol) and acrolein (0.75 mmol, 1.5 equiv) at 25 °C (Method A; see Experimental Section) for 2 h to produce the Michael adduct **5a** in quantitative yield with 64% *ee* (Table 1, entry 1). Depending on the temperature, the reactions were dramatically sluggish and the

Table 1. Asymmetric Michael addition of ethyl 2-cyanopropionate (**4a**) to acrolein with the Phebox-Rh^I system.[a]



Entry	Ligand	Rh^I	Solvent	Yield [%]	*ee* [%][b]
1	**1a**	[{RhCl(*c*-octene)$_2$}$_2$]	toluene	>99	64
2	**6**	[{RhCl(*c*-octene)$_2$}$_2$]	toluene	71	58
3[c]	**7**	[{RhCl(*c*-octene)$_2$}$_2$]	toluene	12	16
4[c]	**8**	[{RhCl(*c*-octene)$_2$}$_2$]	toluene	10	8
5	**1a**	[{RhCl(cod)}$_2$]	toluene	>99	49
6	**1a**	[{RhCl(CO)$_2$}$_2$]	toluene	>99	45
7	**1a**	[{RhCl(*c*-octene)$_2$}$_2$]	benzene	90	60
8	**1a**	[{RhCl(*c*-octene)$_2$}$_2$]	CH_2Cl_2	>99	17
9	**1a**	[{RhCl(*c*-octene)$_2$}$_2$]	THF	51	20
10[d]	**1a**	[{RhCl(*c*-octene)$_2$}$_2$]	Et_2O	>99	48
11	**1b**	[{RhCl(*c*-octene)$_2$}$_2$]	toluene	63	33
12	**1c**	[{RhCl(*c*-octene)$_2$}$_2$]	toluene	99	18
13	**1d**	[{RhCl(*c*-octene)$_2$}$_2$]	toluene	>99	30
14	**1e**	[{RhCl(*c*-octene)$_2$}$_2$]	toluene	70	69
15[d, e]	**1e**	[{RhCl(*c*-octene)$_2$}$_2$]	toluene	96	69

[a] All reactions were carried out with Phebox ligand (0.01 mmol; **1**, **6**–**8**), Rh^I dimer (0.005 mmol), ethyl 2-cyanopropionate (0.5 mmol; **4a**) and acrolein (0.75 mmol) in 1.5 mL of solvent at 25 °C for 2 h (Method A). [b] Determined by capillary GLC analysis using Astec Chiraldex G-TA (30M). [c] 8 h. [d] 1 h. [e] Ethyl 2-cyanopropionate (**4a**) was added to the catalyst/acrolein mixture (Method B).

enantiomeric excesses of **5a** decreased below 20 °C. A slightly lower catalytic activity and enantioselectivity for the reaction with catalyst derived from [(Phebox)$SnBu_3$] (**2**) were observed than those obtained with the catalyst derived from [(Phebox)$SnMe_3$] (entries 1 vs. 2 in Table 1). The rhodium catalyst prepared from other Phebox precursors **7** and **8** showed remarkably low catalytic activities and enantioselectivities (entries 3 and 4 in Table 1). The reactions that employed other Rh^I sources, such as [{RhCl(cod)}$_2$] (cod = 1,5-cyclooctadiene) or [{RhCl(CO)$_2$}$_2$], proceeded smoothly under the same conditions; however, the enantioselectivities of **5a** were both decreased (entries 5 and 6 in Table 1). Among the solvents tested, toluene proved to be effective for both chemical yield and enantioselectivity (entries 1 vs. 7–10 in Table 1). The substituent on the oxazoline rings had a great effect on the chemical yields and % *ee* values (entries 11–14 in Table 1). The activities of catalysts derived from both Ph-Phebox and *t*Bu-Phebox were lower than those of the others. The enantioselectivities obtained with Ph-, Bn-, and Me-Phebox-derived stannanes **1b**–**d** were remarkably decreased. Finally, an enantioselectivity of <69% *ee* was achieved by the use of the bulky *t*Bu-substituted **1e**. We also found that the addition order of the substrates was a significant factor governing the reaction rate: the reaction rate on adding **4a** to

the mixture of the catalyst and acrolein solution (Method B) was more than twice as fast as that found for the addition of acrolein to a mixture of catalyst and **4a** (Method A), without loss of the enantiomeric purity of the product **5a** (entries 14 vs. 15 in Table 1).

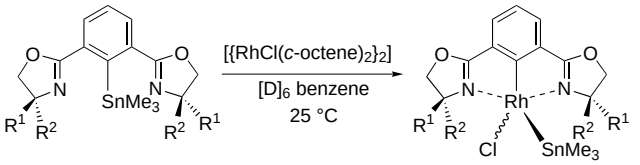
Next, the effects of the ester substituent on enantioselectivity and reactivity were investigated for both methods (Table 2). Remarkable improvement in the enantioselectivities was achieved by employing α-cyanopropionates with bulkier ester groups. The reaction with *i*Pr and diphenylmethyl esters **4b** and **4c** by Method A afforded the corresponding adducts **5b** and **5c** with 74% and 80% *ee*, respectively (entries 2 and 3 in Table 2). Although reactivities of both the bulky diisopropylmethyl and di(*tert*-butyl)methyl esters, **4d** and **4e**, were lower than those of the less hindered ones, extension of the reaction time to 24 h led to satisfactory yields with good enantioselectivities (entries 4 and 5 in Table 2). In spite of the steric bulkiness, the reactions of aryl esters **4f** and **4g** were much faster than those of the aliphatic esters (entries 6 and 7 in Table 2). The reaction rates were dramatically increased (within 2 h) by the use of Method B (entries 1–7 vs. 8–14 in Table 2). Although the enantiomeric excesses of **5a**–**e** derived from the aliphatic esters were not improved by Method B, the enantioselectivities of the reaction with aromatic esters **4f** and **4g** were higher than those obtained by Method A (entries 6–7 vs. 13–14 in Table 2). Finally, the enantioselectivities in the reaction were obtained with 85–86% *ee* for both bulky aliphatic and aromatic esters **4e** and **4g**. The absolute configuration of the isopropyl ester **5b** was determined as (*R*) by comparison of the optical rotation with the literature value ($[\alpha]_D^{20} = +3.1^\circ$ ($c = 5.0$–5.1, $CHCl_3$) for 87% *ee*, (*R*)).[4a,b]

Table 2. Asymmetric Michael addition of various α-cyanopropionates (**4**) to acrolein.[a]

Entry	Substrate/ Product (**4**/**5**)	Method	Time [h]	Yield [%]		*ee* [%][b]
1	**4a**/**5a**	A	2	70	69	
2	**4b**/**5b**	A	4	82	74	2 (*R*)[c]
3	**4c**/**5c**	A	4	80	80[d]	
4	**4d**/**5d**	A	24	81	82	
5	**4e**/**5e**	A	24	71	85	
6	**4f**/**5f**	A	2	93	70[d]	
7	**4g**/**5g**	A	2	94	80[e]	
8	**4a**/**5a**	B	1	96	69	
9	**4b**/**5b**	B	1	97	73	2 (*R*)[c]
10	**4c**/**5c**	B	1	97	79[d]	
11	**4d**/**5d**	B	2	82	80	
12	**4e**/**5e**	B	2	82	86	
13	**4f**/**5f**	B	0.5	93	75[d]	
14	**4g**/**5g**	B	0.5	95	85[e]	

[a] All reactions were carried out with [(*t*Bu-Phebox)$SnMe_3$] (0.01 mmol; **1e**), [{RhCl(*c*-octene)$_2$}$_2$] (0.005 mmol), α-cyanopropionate **4** (0.5 mmol), and acrolein (0.75 mmol) in toluene (1.5 mL) at 25 °C. [b] Determined by capillary GLC analysis (Astec Chiraldex G-TA). [c] Determined by comparison of the reported $[\alpha]_D$ data: see ref. [4a, b]. [d] Determined by HPLC analysis (Daicel CHIRALPAK AD) of the alcohol after reduction of **5** with $NaBH_4$. [e] Determined by HPLC analysis (Daicel CHIRALPAK AS) after conversion to the chiral acetal with (*S*,*S*)-2,4-pentandiol.

Reaction of [(Phebox)$SnMe_3$] with [{RhCl(*c*-octene)$_2$}$_2$]: To obtain information about catalytically active species, we first checked the reaction between [{RhCl(*c*-octene)$_2$}$_2$] and [(*i*Pr-Phebox)$SnMe_3$] (**1a**). On the basis of TLC studies and ^{1}H NMR spectroscopy, it was found that the reaction between the Rh^I complex and **1a** scarcely proceeded under 20 °C. However, the ^{1}H NMR spectrum of the reaction mixture in [D_6]benzene at 25 °C showed a small intensity of signals attributed to two nonsymmetrical complexes **9a** with an $SnMe_3$ group in a ratio of 5:1. These $SnMe_3$ signals appeared ($\delta = -4.97$ and -8.76) with $^{103}Rh-^{13}C$ couplings (2.0 Hz for both complexes) in the ^{13}C NMR spectrum. In addition, formation of Me_3SnCl ($\delta = 0.23$ ppm; satellite $J(Sn,H) = 58.2$, 55.6 Hz) by transmetalation of Rh^I with **1a** was not confirmed. Therefore, we concluded that the two [(*i*Pr-Phebox)Rh^{III}($SnMe_3$)Cl] complexes **9a**, which are conformational isomers with a five-coordinate structure, are formed by oxidative addition of [{RhCl(*c*-octene)$_2$}$_2$] to **1a** (Scheme 4). Similar results were obtained by the reaction of *t*Bu- and dMe-Phebox-derived stannanes **1e** and **1f** with [{RhCl(*c*-octene)$_2$}$_2$] (Table 3). In spite of an extension of the reaction time, the yields of the product [(Phebox)Rh^{III}($SnMe_3$)Cl] complexes **9** in the reaction mixture were not increased and only ≈3–9% of **9** were detected in ^{1}H NMR spectra. Therefore, most of the stannyl compound **1** could be recovered from the reaction media.



1a: R^1 = *i*Pr, R^2 = H
e: R^1 = *t*Bu, R^2 = H
f: R^1 = Me, R^2 = Me

9a: R^1 = *i*Pr, R^2 = H (6%)
e: R^1 = *t*Bu, R^2 = H (3%)
f: R^1 = Me, R^2 = Me (9%)

Scheme 4. Formation of [(Phebox)Rh^{III}($SnMe_3$)Cl] complexes **9** and yields detected by ^{1}H NMR spectroscopy.

[(Phebox)Rh^{III}($SnMe_3$)Cl] complex as an active catalyst: Next, we examined the differentiation between the Methods

Table 3. NMR data for the $SnMe_3$ signals of [(Phebox)Rh^{III}($SnMe_3$)Cl] complexes **9**.

Complex (major/minor)		^{1}H NMR[a] δ (ppm) (J(Sn,H)) [Hz]	^{13}C NMR[b] δ (ppm) (J(Rh,C)) [Hz] (J(Sn,C) [Hz]
9a	major	0.16	−4.97 (2.0)
(5:1)		(50.7, 47.8)	(266)
	minor	0.30	−8.76 (2.0)
		(42.6)	–[c]
9e	major	0.13	–[c]
(>98:2)		(48.5, 46.3)	
	minor	–[c]	–[c]
9f	major	0.14	−4.13 (2.2)
(3.5:1)		(50.2, 48.2)	(276, 262)
	minor	−0.05	−8.33 (1.5)
		(44.5)	–[c]

[a] Observed at 400 MHz in [D_6]benzene at room temperature. [b] Observed at 100 MHz in [D_6]benzene at room temperature. [c] Not detected.

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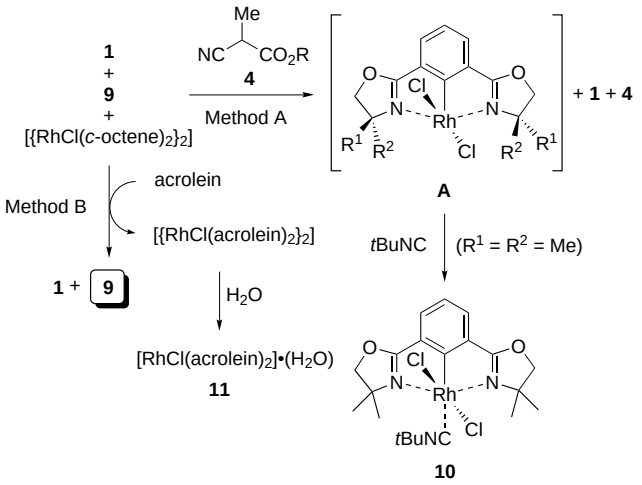
A and B in detail. When α-cyanoester **4a** was added to the catalyst solution (Method A), which includes the formed [(Phebox)Rh^{III}(SnMe$_3$)Cl] complex **9** and remaining (Phebox)SnMe$_3$ (**1**) and [{RhCl(*c*-octene)$_2$}$_2$], complex **9** gradually decomposed resulting in the formation of the catalytically nonactive dichloride fragments **A** (Scheme 5). Such a dichloride structure was characterized by a single-crystal X-ray structure study of an isonitrile complex **10** (Figure 1). On adding acrolein to the catalyst solution (Method B), the remaining [{RhCl(*c*-octene)$_2$}$_2$] complex was removed completely from the reaction media as an insoluble [RhCl(acrolein)$_2$] species, whose composition was determined to be



Scheme 5. Decomposition of [(Phebox)Rh^{III}(SnMe$_3$)Cl] complex **9** (Method A) and the formation of [{RhCl(acrolein)$_2$}$_2$] complex (Method B).

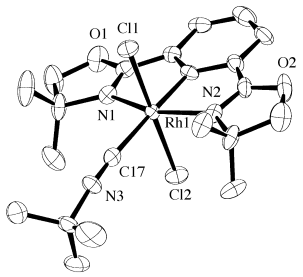


Figure 1. ORTEP drawing of [(dMe-Phebox)RhCl$_2$(CN*t*Bu)] complex **10**. Selected bond lengths [Å] and angles [°]: Rh1–Cl1 2.342(3), Rh1–Cl2 2.339(3), Rh1–N1 2.067(7), Rh1–N2 2.087(7), Rh1–C17 2.11(1), C17–N3 1.15(1), Rh1-C17-N3 174.4(9), N1-Rh1-N2 157.0(3), Cl1-Rh1-Cl2 179.7(1).

[RhCl(acrolein)$_2$]·(H$_2$O) (**11**) by elemental analysis after isolation. The [(Phebox)Rh^{III}(SnMe$_3$)Cl] complexes **9** still remained in the reaction mixture, and the ratio of the formed **9** and the starting stannyl compounds **1** were 1:16 for **9e** and 1:30 for **9e**, respectively (^{1}H NMR spectroscopy). As soon as the [(Phebox)Rh^{III}(SnMe$_3$)Cl] complex forms, the present Michael addition proceeds, even at 0 °C. For example, the reaction of **4g** and acrolein with *t*Bu-Phebox-derived catalyst **9e** at 0 °C for 18 h afforded the Michael adduct **5g** in 90% yield with 82% *ee* (c.f.: 25 °C, 0.5 h; 95% yield, 85% *ee*). These results indicate that the [(Phebox)Rh^{III}(SnMe$_3$)Cl] complex **9**, generated by the oxidative addition of [RhCl(*c*-octene)$_2$]$_2$ to **1**, is an active catalyst and the decomposition of the formed complex **9** may be inhibited by Method B because the Rh^I source was eliminated from the reaction mixture.

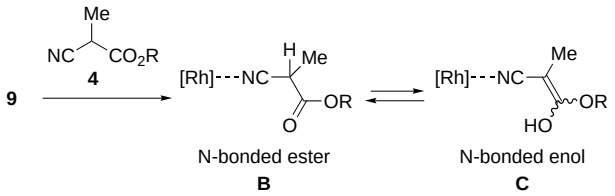
High catalytic efficiency of [(Phebox)Rh^{III}(SnMe$_3$)Cl] complex: Since the catalytically active (*t*Bu-Phebox)Rh^{III}(SnMe$_3$)Cl] complex **9e** was formed in only 3% by Method B (prepared from 2 mol% of **1e** and 1 mol% of [{RhCl(*c*-octene)$_2$}$_2$]), the calculated amount of the actual catalyst was $\approx 6.7 \times 10^{-2}$ mol%; S/C = 1500 (S/C = substrate/actual catalyst ratio) (entries 1 and 3 in Table 4). To confirm the high catalytic activity of the [(*t*Bu-Phebox)Rh^{III}(SnMe$_3$)Cl] complex **9e**, we also examined the reaction at very low catalyst loadings. The catalyst solution was prepared from [(*t*Bu-Phebox)SnMe$_3$] (**1e**) (5.0×10^{-3} mmol) and [{RhCl(*c*-octene)$_2$}$_2$] (2.5×10^{-3} mmol) in toluene (2.5 mL) at 25 °C for 15 min. In this mixture, therefore, 1.67×10^{-4} mmol of the active catalyst **9e** was thought to be present. When acrolein (3.0 mmol, 1.5 equiv) and α-cyanoesters **4a** or **4d** (2.0 mmol, S/C = 12000) were added to the catalyst solution, the corresponding Michael adducts **5a** or **5d** were obtained without loss of enantioselectivities (entries 2 and 4 in Table 4). The turnover numbers (TON) of the present catalytic system were thus found to be 10800 for **4a** and 10920 for **4d**, respectively.

Table 4. Experiments on the catalytic efficiency of complex **9e**.[a]

Entry	Substrate/product **4/5**	cat. [mol%]	S/C[b]	Time [h]	Yield [%]	TON	*ee*[c] [%]
1[d]	**4a/5a**	6.7×10^{-2}	1500	1	96	1440	69
2[e]	**4a/5a**	8.3×10^{-3}	12000	1	90	10800	66
3[d]	**4d/5d**	6.7×10^{-2}	1500	2	82	1230	80
4[e]	**4d/5d**	8.3×10^{-3}	12000	7	91	10920	81

[a] All reactions were carried out in toluene at 25 °C. [b] S/C = Ratio of substrate (**4**):catalyst (**9e**). [c] Determined by capillary GLC analysis (Astec Chiraldex G-TA). [d] α-Cyanopropionate **4** (0.5 mmol) and acrolein (0.75 mmol) in toluene (1.5 mL). [e] α-Cyanopropionate **4** (2.0 mmol) and acrolein (3.0 mmol) in toluene (2.5 mL).

Transition-state assembly: By the use of low-valent transition metal complexes as catalyst precursors, the active intermediates are known to be N-bonded enolate complexes which are formed by oxidative addition of low-valent transition metal complexes to α-cyanoesters.[10] Similar enolate intermediates are formed by the Lewis acid catalyzed reaction of α-nitroesters or β-ketoesters: Lewis acids initially coordinate to α-nitroesters or β-ketoesters at the carbonyl oxygen, then enolate complexes are generated.[11] In our catalytic system, the high-valent Rh^{III} complex **9** is formed and the nitrile group at the α-carbon atom is necessary for the Michael addition to proceed: no product was obtained in the reaction of β-ketoesters or α-nitro compounds with acrolein. Therefore, we assumed that complex **9** is coordinated to the N atom of α-cyanoesters **4** as a Lewis acid (Scheme 6**B**), then the bound esters **4** may enolize resulting in the formation of N-bonded enol **C**. This hypothesis can explain the higher reactivities of aromatic esters **4f** and **4g** than that of the aliphatic esters



Scheme 6. Hypothetical intermediate **C** for the present Michael addition.

4a–e: enolization of an aryl ester is easier than that of an aliphatic one because of the high electron-withdrawing ability of its aryloxy group.

The observed *R* stereochemistry of the Michael adducts **5** on using the (*S*,*S*)-[(*t*Bu-Phebox)Rh^{III}(SnMe$_3$)Cl] complex **9e** can be unambiguously explained by the intermediate **C′**. The enol plane bound to the Rh atom is parallel to the Phebox plane, and the *Si* face of the enol is masked by both one substituent on the oxazoline rings and the bulky SnMe$_3$ group. The acrolein attacked the exposed *re* face of the bound enol, so the *R* product was obtained (Figure 2).

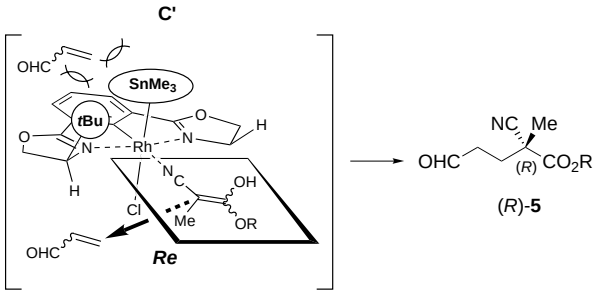


Figure 2. The transition state model **C′** for the present reaction.

Conclusion

We have found a novel catalytic system for the asymmetric Michael addition of α-cyanopropionates and acrolein by the use of a Phebox-derived rhodium(III) catalyst prepared in situ by simply mixing [{RhCl(*c*-octene)$_2$}$_2$] and [(Phebox)SnMe$_3$]. We have clarified that the chiral [(Phebox)Rh^{III}(SnMe$_3$)Cl] complex, generated by oxidative addition of [{RhCl(*c*-octene)$_2$}$_2$] to [(Phebox)SnMe$_3$], is an active catalyst and the turnover number of this catalytic system is $>10\,000$ within a few hours. We also deduced that the obtained *R* stereochemistry of the Michael adducts is attributed to the N-bonded enol intermediates formed by enolization of α-cyanopropionates bound to the Lewis acidic [(Phebox)-Rh^{III}(SnMe$_3$)Cl] complexes. To our knowledge, the [(Phebox)Rh^{III}(SnMe$_3$)Cl] complexes reported herein are the first examples of chiral Lewis acid catalysts for asymmetric Michael addition with extremely high catalytic efficiency.[12] Application of this catalytic system to other asymmetric reactions is currently under investigation.

Experimental Section

General methods: [{RhCl(CO)$_2$}$_2$], anhydrous dichloromethane, ether, benzene, toluene, and tetrahydrofuran were purchased from Kanto Chemical Co. Ethyl 2-cyanopropionate (**2a**), tributyltin chloride, and trimethylsilyl trifluoromethanesulfonate (TMSOTf) were purchased from Tokyo Chemical Industry Co., Ltd. ^{1}H and ^{13}C NMR spectra were measured on a VARIAN Inova-400 (400 MHz) spectrometer. Chemical shifts in ^{1}H NMR are given relative to tetramethylsilane as an internal standard ($\delta=0$) in CDCl$_3$, unless otherwise noted. Chemical shifts of ^{13}C NMR are given relative to CDCl$_3$ as an internal standard ($\delta=77.1$), unless otherwise noted. IR spectra were measured on a JASCO FT/IR-230 spectrometer. Melting points were measured on a Yanaco MP-J3. Elemental analyses were measured on a Yanaco CHN CORDER MT-6. Gas chromatography (GC) analyses were performed with a Shimadzu GC-14A gas chromatograph, and C-R5A chromatopac equipped with an ASTEC Chiraldex G-TA (30M) column. High-performance liquid chromatography (HPLC) analyses were carried out with a JASCO PU-980 HPLC pump, UV-975 and 980 UV/VIS detector, and CO-966 column thermostat (at 25 °C) with Daicel CHIRALPAK AD and AS columns. Optical rotations were measured on a JASCO P-1030 polarimeter. Column chromatography was performed with silica gel (Merck, Art. No. 7734). Analytical thin-layer chromatography (TLC) was performed on glass plates and aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F$_{254}$, layer thickness: 0.25 and 0.2 mm, respectively). Visualization was accomplished by UV light ($\lambda=254$ nm), anisaldehyde, and phosphomolybdic acid. All reactions were carried out under a nitrogen or argon atmosphere. [{RhCl(*c*-octene)$_2$}$_2$][13] and [{RhCl(cod)}$_2$][14] were prepared by the literature methods. [(Phebox)SnMe$_3$] (**1**) was prepared by our method.[7] (*i*Pr-Phebox)H (**8**) was prepared by the literature method.[15] α-Cyanopropionates (**4b** and **4d**) were prepared by the literature method.[4a,b]

[(*i*Pr-Phebox)SnBu$_3$] (6): Prepared from (*i*Pr-Phebox)Br and *n*Bu$_3$SnCl according to our method in 73% yield.[7] Colorless oil; IR (neat): $\tilde{\nu}=2956$, 1651, 1463, 1348, 1247, 1127, 1072, 982 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.86$ (t, $J=7.3$ Hz, 9H), 0.93 (d, $J=6.8$ Hz, 6H), 0.93–0.97 (m, 6H), 1.04 (d, $J=6.8$ Hz, 6H), 1.21–1.32 (m, 6H), 1.39–1.47 (m, 6H), 1.77–1.89 (m, 2H), 4.01–4.13 (m, 4H), 4.40–4.49 (m, 2H), 7.33 (t, $J=7.7$ Hz, 1H), 7.89 (d, $J=7.7$ Hz, satellite J(Sn,H) = 10.5 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=13.6$, 13.8 (satellite J(Sn,C) = 366, 352 Hz), 18.7, 19.2, 27.7 (satellite J(Sn,C) = 69, 65 Hz), 29.2 (satellite J(Sn,C) = 18 Hz), 33.2, 71.0, 73.4, 127.6 (satellite J(Sn,C) = 8 Hz), 131.0 (satellite J(Sn,C) = 27 Hz), 136.7 (satellite J(Sn,C) = 16 Hz), 146.4 (satellite J(Sn,C) = 369, 353 Hz), 165.6 (satellite J(Sn,C) = 12 Hz); elemental analysis calcd (%) for C$_{30}$H$_{50}$N$_2$O$_2$Sn: C 61.13, H 8.55, N 4.75; found: C 61.13, H 8.54, N 4.76.

(*i*Pr-Phebox)SiMe$_3$ (7): To a stirred solution of (*i*Pr-Phebox)Br (500 mg, 1.40 mmol) in tetrahydrofuran (3 mL) was added *n*BuLi in hexane (1.52 N, 1.20 mL, 1.82 mmol) at -78 °C. The mixture was stirred for 10 min, then TMSOTf (405 mL, 1.82 mmol) was added and the reaction mixture was warmed to -20 °C and stirred for 1 h. The mixture was diluted with ether (5 mL), washed twice with water (total of 10 mL), dried over Na$_2$SO$_4$, and concentrated under reduced pressure. Purification by silica gel chromatography (hexane/ethyl acetate = 3:1) gave **7** in 89% yield (466 mg, 1.25 mmol). Colorless oil; IR (neat): $\tilde{\nu}=2959$, 1655, 1467, 1347, 1118, 978 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.28$ (s, 9H), 0.95 (d, $J=6.8$ Hz, 6H), 1.07 (d, $J=6.8$ Hz, 6H), 1.85 (dsept, $J=6.8$, 6.8 Hz, 2H), 4.02 (td, $J=9.2$, 6.8 Hz, 2H), 4.09 (dd, $J=9.2$, 8.0 Hz, 2H), 4.44 (dd, $J=9.2$, 8.0 Hz, 2H), 7.36 (t, $J=7.6$ Hz, 1H), 7.79 (d, $J=7.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=1.5$, 18.8, 19.4, 33.1, 70.9, 73.6, 128.3, 131.5, 136.4, 141.4, 166.0; elemental analysis calcd (%) for C$_{21}$H$_{32}$N$_2$O$_2$Si: C 67.70, H 8.66, N 7.52; found: C 67.74, H 8.64, N 7.55.

Synthesis of α-cyanopropionates (4c, 4e, 4f, 4g): Prepared from corresponding alcohols and α-cyanopropionic acid according to a literature method.[4a,b]

Diphenylmethyl α-cyanopropionate (4c): Yield: 48%, white solid; m.p. 66–67 °C; IR (KBr): $\tilde{\nu}=3033$, 2924, 2252, 1748, 1496, 1456, 1181, 1107, 744, 697 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=1.61$ (d, $J=7.5$ Hz, 3H), 3.64 (q, $J=7.5$ Hz, 1H), 6.92 (s, 1H), 7.31–7.38 (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=15.2$, 31.8, 79.4, 117.2, 126.9, 127.2, 128.4, 128.5, 128.8 (2C), 139.02, 139.05, 165.6; elemental analysis calcd (%) for C$_{17}$H$_{15}$NO$_2$: C 76.96, H 5.70, N 5.28; found: C 76.99, H 5.73, N 5.29.

Di(*tert*-butyl)methyl α-cyanopropionate (4e): Yield: 43%; colorless oil; IR (neat): $\tilde{\nu}=2965$, 2251, 1741, 1480, 1455, 1400, 1371, 1335, 1259, 1198, 1110, 1038, 968, 934, 911, 876, 742 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=1.04$ (s, 9H), 1.05 (s, 9H), 1.63 (d, $J=7.5$ Hz, 3H), 3.58 (q, $J=7.5$ Hz, 1H), 4.66 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=15.6$, 28.6, 28.7, 31.8, 37.37, 37.43,

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89.3, 117.6, 166.2; elemental analysis calcd (%) for $C_{13}H_{23}NO_2$: C 69.29, H 10.29, N 6.22; found: C 69.31, H 10.32, N 6.20.

2,4,6-Trimethylphenyl α-cyanopropionate (4f): Yield: 68%; white solid; m.p. 45–46 °C; IR (KBr): $\tilde{\nu}$ = 2924, 1766, 1484, 1456, 1383, 1237, 1190, 1135, 859 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77 (d, J = 7.3 Hz, 3H), 2.13 (s, 6H), 2.28 (s, 3H), 3.83 (q, J = 7.3 Hz, 1H), 6.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.6, 16.2, 20.8, 31.5, 117.0, 129.4, 129.6, 136.3, 145.4, 164.7; elemental analysis calcd (%) for $C_{13}H_{15}NO_2$: C 71.87, H 6.96, N 6.45; found: C 71.72, H 6.95, N 6.48.

2,6-Diisopropylphenyl α-cyanopropionate (4g): Yield: 79%; white solid; m.p. 51–52 °C; IR (KBr): $\tilde{\nu}$ = 2967, 2872, 2252, 1767, 1710, 1456, 1232, 1166, 1100, 795, 736 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, J = 6.8 Hz, 12H), 1.78 (d, J = 7.3 Hz, 3H), 2.87 (sept, J = 6.8 Hz, 2H), 3.86 (q, J = 7.3 Hz, 1H), 7.18–7.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.5, 22.7, 23.9, 27.7, 31.5, 116.9, 124.3, 127.4, 140.0, 145.1, 165.4; elemental analysis calcd (%) for $C_{16}H_{21}NO_2$: C 74.10, H 8.16, N 5.40; found: C 73.94, H 8.07, N 5.53.

General procedure for the Michael addition of α-cyanopropionates to acrolein: To a stirred solution of [{RhCl(*c*-octene)$_2$}$_2$] (3.6 mg, 0.005 mmol) and [(*t*Bu-Phebox)SnMe$_3$] (**1e**, 4.9 mg, 0.01 mmol) in toluene (1.5 mL) was added freshly distilled acrolein (50 μL, 0.75 mmol) and the α-cyanopropionate **4** (0.5 mmol) at 25 °C under argon atmosphere. The reaction mixture was stirred for 0.5–2 h at that temperature, and was then poured into a mixture of ether and water. The mixture was extracted with ether and the extract was purified by silica gel chromatography (hexane/diethyl ether = 2:1) to afford **5**.

Ethyl 2-cyano-2-methyl-5-oxopentanoate (5a):[3a] Colorless oil; $[\alpha]_D^{26}$ = +2.19° (c = 1.14 in $CHCl_3$ for 69% *ee*); IR (neat): $\tilde{\nu}$ = 2988, 2245, 1741, 1458, 1387, 1254, 1134, 1018 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (t, J = 7.1 Hz, 3H), 1.62 (s, 3H), 2.10 (ddd, J = 14.3, 10.3, 5.5 Hz, 1H), 2.28 (ddd, J = 14.3, 10.1, 5.7 Hz, 1H), 2.65 (dddd, J = 18.5, 10.3, 5.7, 0.7 Hz, 1H), 2.75 (dddd, J = 18.5, 10.1, 5.5, 0.6 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 9.79 (dd, J = 0.7, 0.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 23.6, 30.1, 39.9, 43.1, 63.2, 119.4, 168.8, 199.2; ASTEC Chiraldex G-TA (30M), column temperature 125 °C, detection FID, t_R = 36.8 min (minor), 42.6 min (major).

Isopropyl 2-cyano-2-methyl-5-oxopentanoate (5b):[4a,b] Colorless oil; $[\alpha]_D^{26}$ = +2.50° (c = 1.24 in $CHCl_3$ for 74% *ee*, 2(*R*)); literature value:[4a,b] $[\alpha]_D^{20}$ = +3.1° (c = 5.0–5.1 in $CHCl_3$ for 87% *ee*, 2(*R*)); IR (neat): $\tilde{\nu}$ = 2985, 2247, 1734, 1459, 1383, 1257, 1103 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (d, J = 6.2 Hz, 3H), 1.31 (d, J = 6.4 Hz, 3H), 1.60 (s, 3H), 2.09 (ddd, J = 14.3, 10.4, 5.3 Hz, 1H), 2.26 (ddd, J = 14.3, 10.3, 5.3 Hz, 1H), 2.63 (dddd, J = 18.5, 10.4, 5.3, 0.9 Hz, 1H), 2.74 (dddd, J = 18.5, 10.3, 5.3, 0.7 Hz, 1H), 5.07 (qq, J = 6.4, 6.20 Hz, 1H), 9.79 (dd, J = 0.9, 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 21.6, 23.5, 30.0, 39.8, 43.2, 71.3, 119.5, 168.3, 199.2; ASTEC Chiraldex G-TA (30M), column temperature 130 °C, detection FID, t_R = 18.9 min (*S*), 22.6 min (*R*).

Diphenylmethyl 2-cyano-2-methyl-5-oxopentanoate (5c): Colorless oil; $[\alpha]_D^{26}$ = +3.63° (c = 0.93 in $CHCl_3$ for 80% *ee*); IR (neat): $\tilde{\nu}$ = 2939, 2250, 1744, 1496, 1455, 1385, 1247, 1130, 969, 745, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.63 (s, 3H), 2.11 (ddd, J = 14.3, 10.8, 5.0 Hz, 1H), 2.27 (ddd, J = 14.3, 10.6, 4.9 Hz, 1H), 2.40 (ddd, J = 18.5, 10.8, 4.9 Hz, 1H), 2.63 (ddd, J = 18.5, 10.6, 5.0 Hz, 1H), 6.90 (s, 1H), 7.32–7.38 (m, 10H), 9.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.5, 30.2, 39.6, 43.3, 79.5, 119.2, 126.9, 127.0, 128.52, 128.55, 128.8 (2C), 138.9, 139.0, 167.8, 198.9; elemental analysis calcd (%) for $C_{20}H_{19}NO_3$: C 74.75, H 5.96, N 4.36; found: C 74.66, H 5.89, N 4.41. The *ee* was determined by HPLC analysis of the alcohol after reduction of **5c** with $NaBH_4$: Daicel CHIRALPAK AD, UV detector 254 nm, 5:1 hexane/*i*PrOH, flow rate 0.5 mL min^{-1}: t_R = 13.5 min (major), 16.0 min (minor).

Diisopropylmethyl 2-cyano-2-methyl-5-oxopentanoate (5d):[4a,b] Colorless oil; $[\alpha]_D^{26}$ = +0.09° (c = 0.91 in $CHCl_3$ for 82% *ee*); IR (neat): $\tilde{\nu}$ = 2969, 2260, 1745, 1466, 1388, 1259, 1207, 1099 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87–0.94 (m, 12H), 1.64 (s, 3H), 1.91–2.05 (m, 2H), 2.09 (ddd, J = 14.3, 10.6, 5.3 Hz, 1H), 2.30 (ddd, J = 14.3, 10.8, 5.1 Hz, 1H), 2.66 (dddd, J = 15.9, 10.6, 5.1, 0.7 Hz, 1H), 2.75 (dddd, J = 15.9, 10.8, 5.3, 0.6 Hz, 1H), 4.64 (dd, J = 6.4, 6.0 Hz, 1H), 9.80 (dd, J = 0.7, 0.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.2, 17.4, 19.7, 19.8, 24.2, 29.5, 29.7, 29.9, 40.1, 43.6, 86.5, 119.6, 169.0, 199.4; ASTEC Chiraldex G-TA (30M), column temperature 140 °C, detection FID, t_R = 38.4 min (minor), 41.4 min (major).

Di(*tert*-butyl)methyl 2-cyano-2-methyl-5-oxopentanoate (5e): Colorless oil; $[\alpha]_D^{21}$ = −3.40° (c = 0.79 in $CHCl_3$ for 85% *ee*); IR (neat): $\tilde{\nu}$ 2963, 2727, 2242, 1732, 1699, 1652, 1456, 1372, 1334, 1253, 1038, 910, 783, 744, 519 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 9H), 1.04 (s,9H), 1.65 (s, 3H) 2.09 (ddd, J = 14.3, 10.1, 5.5 Hz, 1H), 2.32 (ddd, J = 14.3, 10.4, 5.3 Hz, 1H), 2.67 (dddd, J = 18.5, 10.1, 5.3, 0.7 Hz, 1H), 2.76 (dddd, J = 18.5, 10.4, 5.5, 0.6 Hz, 1H), 4.64 (s, 1H), 9.80 (dd, J = 0.7, 0.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.1, 28.6 (2C), 29.6, 37.3, 37.4, 40.0, 43.3, 89.6, 119.5, 168.4, 199.3; elemental analysis calcd (%) for $C_{16}H_{27}NO_3$: C 68.29, H 9.67, N 4.98; found: C 68.17, H 9.62, N 4.91; ASTEC Chiraldex G-TA (30M), column temperature 140 °C, detection FID, t_R = 69.1 min (minor), 72.7 min (major).

2,4,6-Trimethylphenyl 2-cyano-2-methyl-5-oxopentanoate (5f): Colorless oil; $[\alpha]_D^{25}$ = −12.5° (c = 1.19 in $CHCl_3$ for 75% *ee*); IR (neat): $\tilde{\nu}$ = 2922, 2853, 2732, 2245, 1760, 1725, 1485, 1456, 1386, 1189, 1134, 855 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.82 (s, 3H), 2.13 (s, 6H), 2.24 (ddd, J = 15.7, 10.3, 5.5 Hz, 1H), 2.27 (s, 3H), 2.46 (ddd, J = 15.7, 10.4, 5.5 Hz, 1H), 2.80 (dddd, J = 15.9, 10.4, 5.5, 0.6 Hz, 1H), 2.87 (dddd, J = 15.9, 10.3, 5.5, 0.7 Hz, 1H), 6.89 (m, 2H), 9.85 (dd, J = 0.7, 0.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.3, 20.8, 23.9, 29.7, 39.9, 43.1, 119.0, 129.2, 129.7, 136.4, 145.4, 166.9, 198.9; elemental analysis calcd (%) for $C_{16}H_{19}NO_3$: C 70.31, H 7.01, N 5.12; found: C 70.26, H 6.98, N 5.20. The *ee* was determined by HPLC analysis of the alcohol after reduction of **5f** with $NaBH_4$: Daicel CHIRALPAK AD, UV detector 254 nm, 9:1 hexane/*i*PrOH, flow rate 0.5 mL min^{-1}: t_R = 16.2 min (major), 18.7 min (minor).

2,6-Diisopropylphenyl 2-cyano-2-methyl-5-oxopentanoate (5g): Colorless oil; $[\alpha]_D^{23}$ = −8.70° (c = 0.28 in $CHCl_3$ for 80% *ee*); IR (neat): $\tilde{\nu}$ = 2968, 2872, 2244, 1759, 1726, 1460, 1220, 1165, 1122, 795, 737 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22–1.23 (m, 12H), 1.84 (s, 3H), 2.27 (ddd, J = 14.7, 10.3, 6.0 Hz, 1H), 2.48 (ddd, J = 14.7, 10.1, 5.7 Hz, 1H), 2.76–2.91 (m, 4H), 7.18–7.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.6, 22.7, 23.8, 27.6, 29.6, 39.8, 43.0, 119.0, 124.2, 127.4, 139.9, 145.1, 167.7, 198.9; elemental analysis calcd (%) for $C_{19}H_{25}NO_3$: C 72.35, H 7.99, N 4.44; found: C 72.32, H 8.01, N 4.42. The *ee* was determined by HPLC analysis after conversion to the chiral acetal with (*S*,*S*)-2,4-pentanediol: Daicel CHIRALPAK AS, UV detector 254 nm, 500:1 hexane/*i*PrOH, flow rate 0.5 mL min^{-1}: t_R = 17.4 min (minor), 20.1 min (major).

[(*i*Pr-Phebox)Rh^{III}(SnMe$_3$)Cl] (9a):

Major isomer: ^{1}H NMR (400 MHz, [D$_6$]benzene) δ = 0.16 (s, satellite J(Sn,H) = 50.7, 47.8 Hz, 9H; SnMe$_3$), 0.56 (d, J = 6.8 Hz, 3H; CH*Me*$_2$), 0.60 (d, J = 6.8 Hz, 3H; CH*Me*$_2$), 0.696 (d, J = 6.8 Hz, 3H; CH*Me*$_2$), 0.697 (d, J = 6.8 Hz, 3H; CH*Me*$_2$), 2.89–3.00 (m, 1H; C*H*Me$_2$), 3.48–3.60 (m, 1H; C*H*Me$_2$), 3.69–3.77 (m, 1H; OCH), 3.86–4.13 (m, 5H; OCH, NCH), 6.76 (t, J = 7.5 Hz, 1H; *p*-Ph), 7.32 (d, J = 7.5 Hz, 1H; *m*-Ph), 7.36 (d, J = 7.5 Hz, 1H; *m*-Ph); ^{13}C NMR (100 MHz, [D$_6$]benzene): δ = −4.97 (d, J(Rh,C) = 2.0 Hz, satellite J(Sn,C) = 266 Hz: SnMe$_3$), 14.1 (CH*Me*$_2$), 15.3 (CH*Me*$_2$), 18.9 (CH*Me*$_2$), 20.1 (CH*Me*$_2$), 28.8 (*C*HMe$_2$), 29.1 (*C*HMe$_2$), 67.6 (N*C*H), 68.8 (NCH), 71.0 (OCH$_2$), 71.1 (OCH$_2$), 126.6 (Ar), 126.9 (Ar), 127.2 (Ar), 132.3 (Ar), 133.9 (Ar), 174.5 (d, J(Rh,C) = 5.4 Hz: O-*C*=N), 174.7 (d, J(Rh,C) = 5.1 Hz: O-*C*=N), 188.8 (d, J(Rh,C) = 24.2 Hz: C_{ipso}).

Minor isomer: ^{1}H NMR (400 MHz, [D$_6$]benzene): δ = 0.30 (satellite J(Sn,H) = 42.6 Hz, 9H; SnMe$_3$); ^{13}C NMR (100 MHz, C_6D_6): δ = −8.76 (d, J(Rh,C) = 2.0 Hz).

[(*t*Bu-Phebox)Rh^{III}(SnMe$_3$)Cl] (9e): ^{1}H NMR (400 MHz, [D$_6$]benzene): δ = 0.13 (s, satellite J(Sn,H) = 48.5, 46.3 Hz, 9H), 1.08 (brs, 18H), 3.86–4.13 (m, 6H), 6.73 (dd, J = 8.0, 7.2 Hz, 1H), 7.32 (d, J = 7.2 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H).

[(dMe-Phebox)Rh^{III}(SnMe$_3$)Cl] (9f):

Major isomer: ^{1}H NMR (400 MHz, [D$_6$]benzene): δ = 0.14 (s, satellite J(Sn,H) = 50.2, 48.2 Hz, 9H), 1.42 (s, 6H), 1.53 (s, 6H), 3.75 (d, J = 8.6 Hz, 2H), 3.77 (d, J = 8.6 Hz, 2H), 6.78 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, [D$_6$]benzene): δ = −4.13 (d, J(Rh,C) = 2.2 Hz, satellite J(Sn,C) = 276, 262 Hz), 26.8, 29.3, 66.7, 83.6, 121.4, 126.9, 134.5, 173.9 (J(Rh,C) = 5.4 Hz), 189.0 (J(Rh,C) = 22.6 Hz).

Minor isomer: ^{1}H NMR (400 MHz, [D$_6$]benzene): δ = −0.05 (s, satellite J(Sn,H) = 44.5 Hz, 9H), 1.41 (s, 6H), 1.55 (s, 6H), 3.93 (d, J = 8.3 Hz, 2H), 4.00 (d, J = 8.3 Hz, 2H), 6.73 (t, J = 7.7 Hz, 1H), 7.38 (d, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, [D$_6$]benzene): δ = −8.33 (d, J(Rh,C) = 1.5 Hz: SnMe$_3$).

[(dMe-Phebox)RhCl$_2$(CN*t*Bu)] (10): Single crystals for the X-ray diffraction study were obtained from ethyl acetate/ether at room temperature; pale yellow solid, m.p. $>300\,^{\circ}$C; IR (KBr): $\tilde{\nu}=2975, 2926, 2191, 1621, 1404, 1384, 1208, 1151, 957, 742\ cm^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.52$ (s, 12H), 1.73 (brs, 9H), 4.53 (s, 4H), 7.25 (t, $J=8.0$ Hz, 1H), 7.60 (d, $J=8.0$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=27.8, 30.5, 57.2$ (J(N,C) = 5.3 Hz), 65.7, 81.8, 123.3, 127.7, 131.4, 144.0 (J(Rh,C) = 35.7, J(N,C) = 13.3 Hz), 171.6 (J(Rh,C) = 3.5 Hz), 194.6 (J(Rh,C) = 15.9 Hz); elemental analysis calcd (%) for $C_{21}H_{28}Cl_2N_3O_2Rh$: C 47.74, H 5.34, N 7.95; found: C 47.66, H 5.30, N 8.00.

[RhCl(acrolein)$_2$(H$_2$O)] (11): Pale yellow solid; m.p. 160 °C (decomp.); IR (KBr): $\tilde{\nu}=3339, 3061, 2822, 1665, 1553, 1472, 1361, 1162, 955\ cm^{-1}$; elemental analysis calcd (%) for $C_6H_{10}ClO_3Rh$: C 26.84, H 3.75; found: C 26.90, H 3.76.

X-ray structure determination and details of refinement: A crystal of **10** with X-ray quality was obtained directly from the preparations described above and mounted in a glass capillary. The diffraction measurements were performed on a Rigaku AFC-7R four-circle diffractometer equipped with graphite-monochromated $Mo_{K\alpha}$ radiation; $\lambda=0.71069$ Å. The lattice parameters and orientation matrices were obtained and refined from 24 machine-centered reflections with $29.56<2\theta<29.94^{\circ}$. Intensity data were collected with a $\omega-2\theta$ scan technique, and three standard reflections were recorded every 150 reflections. The data were corrected for Lorentz and polarization effects. Relevant crystal data are given in Table 5. The structure was solved by heavy-atom Patterson methods[16] and expanded with Fourier techniques.[17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2414 observed reflections ($I>3\sigma(I)$) and 262 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber.[18] All calculations were performed using the teXsan[19] crystallographic software package. Final refinement details are collected in Table 5, and the numbering scheme employed is shown in Figure 1, which was drawn with ORTEP with 30% probability ellipsoids. CCDC-178379 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (Japan).

[1] a) E. D. Bergmann, D. Ginsburg, R. Pappo, *Org. React.* **1959**, *10*, 179; b) D. A. Hunt, *Org. Prep. Proced. Int.* **1989**, *21*, 705; c) H.-G. Schmalz, *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, *Vol. 4*, Chapt. 1.5; d) P. Perlmutter, *Conjugate Addition Reactions in Organic Synthesis*, Pergamon, Oxford, 1992; e) B. E. Rossiter, N. M. Swingle, *Chem. Rev.* **1992**, *92*, 771; f) J. Christoffers, *Eur. J. Org. Chem.* **1998**, *63*, 1259.

[2] a) B. L. Feringa, A. H. M. de Vries, *Advances in Catalytic Process* (Ed.: M. D. Doyle), JAI Press, Connecticut, **1995**, *Vol. 1*, p. 151; b) K. Tomioka, Y. Nagaoka, *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, New York, **1999**, Chapt. 31.1; c) M. Yamaguchi, *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, New York, **1999**, Chapt. 31.2; d) M. Kanai, M. Shibasaki, *Catalytic Asymmetric Synthesis, 2nd ed.* (Ed.: I. Ojima), Wiley-VCH, New York, **2000**, Chapt. 8D; e) N. Krause, A. Hoffmann-Röder, *Synthesis* **2001**, 171. See also: f) M. Shibasaki, H. Sasai, T. Arai, *Angew. Chem.* **1997**, *109*, 1290; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1236; g) S.-I. Murahashi, H. Takaya, *Acc. Chem. Res.* **2000**, *33*, 225; h) T. Hayashi, *Synlett* **2001**, 879.

[3] Representative papers: a) T. Naota, H. Taki, M. Mizuno, S.-I. Murahashi, *J. Am. Chem. Soc.* **1989**, *111*, 5954; b) S. Paganelli, A. Schionato, C. Botteghi, *Tetrahedron Lett.* **1991**, *32*, 2807; c) S.-I. Murahashi, T. Naota, H. Taki, M. Mizuno, H. Takaya, S. Komiya, Y. Mizuho, N. Oyasato, M. Hiraoka, M. Hirano, A. Fukuoka, *J. Am. Chem. Soc.* **1995**, *117*, 12436; d) M. Hirano, M. Hirai, Y. Ito, T. Tsurumaki, A. Baba, A. Fukuoka, S. Komiya, *J. Organomet. Chem.* **1998**, *569*, 3; e) M. Hirano, A. Takenaka, Y. Mizuho, M. Hiraoka, S. Komiya, *J. Chem. Soc. Dalton Trans.* **1999**, 3209; f) M. Hirano, S. Kiyota, M. Imoto, S. Komiya, *Chem. Commun.* **2000**, 1679; g) V. Maraval, R. Laurent, A.-M. Caminade, J.-P. Majoral, *Organometallics* **2000**, *19*, 4025; h) S.-I. Murahashi, K. Take, T. Naota, H. Takaya, *Synlett* **2000**, 1016. See also ref. [2f].

[4] a) M. Sawamura, H. Hamashima, Y. Ito, *J. Am. Chem. Soc.* **1992**, *114*, 8295; b) M. Sawamura, H. Hashimoto, Y. Ito, *Tetrahedron* **1994**, *50*, 4439; c) K. Inagaki, K. Nozaki, H. Takaya, *Synlett* **1997**, 119. Other chiral catalysts were reported: Pt complexes (≈25% *ee*): d) A. J. Blacker, M. L. Clarke, M. S. Loft, M. F. Mahon, J. M. J. Williams, *Organometallics*, **1999**, *18*, 2867; Pd complexes (≈34% *ee*): e) M. A. Stark, G. Jones, C. J. Richards, *Organometallics* **2000**, *19*, 1282.

[5] Reviews: a) M. H. P. Rietveld, D. M. Grove, G. van Koten, *New J. Chem.* **1997**, *21*, 751; b) R. A. Gossage, L. A. van de Kuil, G. van Koten, *Acc. Chem. Res.* **1998**, *31*, 423; c) M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750, and references therein.

[6] Chiral N-C-N pincer complexes: for Ni complexes, see: a) L. A. van de Kuil, Y. S. J. Veldhuizen, D. M. Grove, J. W. Zwikker, L. W. Jenneskens, W. Drenth, W. J. J. Smeets, A. L. Spek, G. van Koten, *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 267; b) J. G. Donkervoort, J. L. Vicario, J. T. B. H. Jastrzebski, W. J. J. Smeets, A. L. Spek, G. van Koten, *J. Organomet. Chem.* **1998**, *551*, 1. For Pd complexes, see: c) S. E. Denmark, R. A. Stavenger, A.-M. Faucher, J. P. Edwards, *J. Org. Chem.* **1997**, *62*, 3375; d) M. A. Stark, C. J. Richards, *Tetrahedron Lett.* **1997**, *38*, 5881; e) M. Albrecht, B. M. Kocks, A. L. Spek, G. van Koten, *J. Organomet. Chem.* **2001**, *624*, 271, and Ref. [4e]. For Rh complexes, see: f) M. Gerisch, J. R. Krumper, R. G. Bergman, T. D. Tilley, *J. Am. Chem. Soc.* **2001**, *123*, 5818.

[7] a) Y. Motoyama, N. Makihara, Y. Mikami, K. Aoki, H. Nishiyama, *Chem. Lett.* **1997**, 951; b) Y. Motoyama, Y. Mikami, H. Kawakami, K. Aoki, H. Nishiyama, *Organometallics* **1999**, *18*, 3584; c) Y. Motoyama, H. Narusawa, H. Nishiyama, *Chem. Commun.* **1999**, 131; d) Y. Motoyama, M. Okano, H. Narusawa, N. Makihara, K. Aoki, H. Nishiyama, *Organometallics* **2001**, *20*, 1580; e) Y. Motoyama, Y. Koga, H. Nishiyama, *Tetrahedron* **2001**, *57*, 853.

[8] Phebox-coordinated palladium(II) complexes have been reported, see Refs. [4e, 6c, 6d].

[9] a) H. A. Brune, W.-D. Muller, *Chem. Ber.* **1986**, *119*, 759; b) J. T. B. H. Jastrzebski, G. van Koten, *Adv. Organomet. Chem.* **1993**, *35*, 241; c) P. Steenwinkel, J. T. B. H. Jastrzebski, B.-J. Deelman, D. M. Grove, H. Kooijman, N. Veldman, W. J. J. Smeets, A. L. Spek, G. van Koten, *Organometallics* **1997**, *16*, 5486; d) S. Oi, M. Moro, Y. Inoue, *Chem. Commun.* **1997**, 1621; e) R. R. Cesati, III, J. A. Katzenellenbogen, *J. Am. Chem. Soc.* **2001**, *123*, 4093; f) T. Huang, Y. Meng, S. Venkatraman, D. Wang, C.-J. Li, *J. Am. Chem. Soc.* **2001**, *123*, 7451.

[10] a) Y. Mizuho, N. Kasuga, S. Komiya, *Chem. Lett.* **1991**, 2127; b) S.-I. Murahashi, K. Take, T. Naota, H. Takaya, *Synlett* **2000**, 1016; c) T. Naota, A. Tannna, S.-I. Murahashi, *Chem. Commun.* **2001**, 63. Also see Refs. [3c, 3e].

[11] [Yb(OTf)$_3$]: a) E. Keller, B. L. Feringa, *Tetrahedron Lett.* **1996**, *37*, 1879; b) E. Keller, B. L. Feringa, *Synlett* **1997**, 842. $FeCl_3$: c) J. Christoffers, *Chem. Commun.* **1997**, 943; d) J. Christoffers, *J. Chem. Soc. Parkin Trans. 1* **1997**, 3141; e) J. Christoffers, *Synlett* **2001**, 723, and references cited therein. $CeCl_3$/NaI: f) G. Bartoli, M. Bosco, M. C. Bellucci, E. Marcantoni, L. Sambri, E. Torregiani, *Eur. J. Org. Chem.* **1999**, 617. Scandium tris(dodecyl sulfate) (STDS): g) Y. Mori, K. Kakumoto, K. Manabe, S. Kobayashi, *Tetrahedron Lett.* **2000**, *41*, 3107. Chiral catalysts; [Eu(hfc)$_3$]: h) F. Bonadies, A. Lattanzi, L. R. Orelli, S. Pesci, A. Scettri, *Tetrahedron Lett.* **1993**, *34*, 7649. [Sc(OTf)$_3$] chiral *N,N′*-dioxide: i) M. Nakajima, Y. Yamaguchi, S. Hashimoto, *Chem. Commun.* **2001**, 1596.

[12] Very recently, Ding et al. reported that the chiral titanium complex derived from H_4-BINOL and H_8-BINOL ligands showed high catalytic efficiency (TON = 12600/144 h) in the asymmetric hetero-Diels–Alder reaction of Danishefsky's diene and aldehydes, see: J. Long, J. Hu, X. Shen, B. Ji, K. Ding, *J. Am. Chem. Soc.* **2002**, *124*, 10.

  0947-6539/02/0813-2974 $ 17.50+.50/0

[13] A. van der Ent, A. C. Onderdelinden, *Inorg. Synth.* **1973**, *14*, 93.
[14] a) J. V. Kingston, *J. Chem. Soc. A* **1971**, 3399; b) H. Tayim, *J. Organomet. Chem.* **1975**, *92*, 107.
[15] C. Bolm, K. Weickhardt, M. Zehnder, T. Ranff, *Chem. Ber.* **1991**, *124*, 1173.
[16] *SAPI91*, Fan Hai-Fu (**1991**). Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan.
[17] DIRDIF92: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, *The DIRDIF program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen (The Netherlands), **1992**.
[18] D. T. Cromer, J. T. Waber, *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham (UK), **1974**, *Vol. 4*.
[19] teXane: Crystal Structure Analysis Package, Molecular Structure Corporation: The Woodlands, Texas (**1985** & **1992**).

Received: February 11, 2002 [F3867]

  0947-6539/02/0813-2975 $ 17.50+.50/0