Chiral bis(oxazolinyl)phenylrhodium(III) complexes as Lewis acid catalysts for enantioselective allylation of aldehydes

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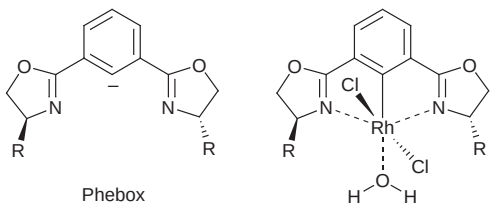
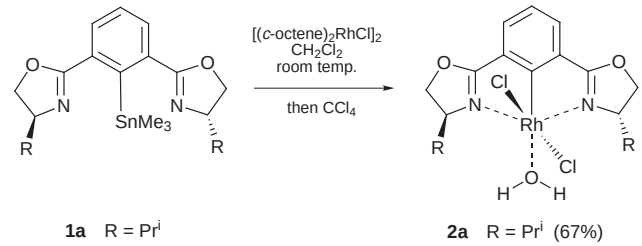
The reaction of (Phebox)$SnMe_3$ 1 [PheboxH = 2,6-bis(oxazolinyl)benzene] and [(*c*-octene)RhCl]$_2$ in the presence of CCl_4 provided air-stable and water-tolerant (Phebox)$RhCl_2(H_2O)$ complexes 2 which acted as asymmetric catalysts for the enantioselective allylation of aldehydes in up to 80% ee.

The development of chiral Lewis acid catalysts, particularly for carbon–carbon bond forming reactions, is one of the most challenging and formidable endeavors in organic synthesis.[1] Among various carbon–carbon bond forming reactions, asymmetric allylation of carbonyl compounds is a valuable means of constructing chiral functionalized structures, and therefore many chiral allylmetal reagents have been designed and synthesised.[2] Although numerous reactions using a stoichiometric amount of chiral allylmetal reagents have been reported,[3] there are only a few reports of catalytic processes using chiral Lewis acid complexes, including chiral (acyloxy)borane (CAB) complex and allylsilanes[4] or allylstannanes,[5] binaphthol-derived chiral titanium complexes and allylstannanes[6] or allylsilanes,[7] and BINAP-derived chiral silver complexes and allylstannanes.[8] The key to success in developing a new chiral Lewis acid catalyst is the choice of the central metal and the design of the chiral ligands. Traditional Lewis acids, such as boron, aluminium, titanium and tin, are extremely moisture-sensitive, and are known to form oligomers in solution. Furthermore, chiral complexes are almost always generated *in situ*, so there are a variety of species having different Lewis acid activity and enantioselectivity. On the other hand, transition metal complexes are generally insensitive to water and form a single well-defined species.[9,10] Here we report a catalytic enantioselective allylation reaction of aldehydes with allyltributylstannane catalyzed by new air-stable and water-tolerant rhodium(III) complexes **2** bearing a 2,6-bis(oxazolinyl)phenyl group (Phebox) as chiral ligands.[11] The Phebox ligand bonds *via* a central carbon–metal covalent bond and both of the oxazoline rings.

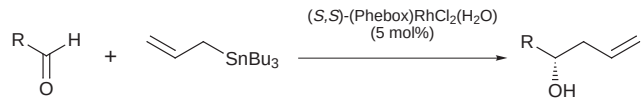


The (Phebox)$RhCl_2(H_2O)$ complexes **2**† were easily synthesized by the transmetalation reaction of [(*c*-octene)$_2$RhCl]$_2$ and (Phebox)$SnMe_3$ **1** in CH_2Cl_2 followed by treatment with CCl_4.‡ These complexes are air-stable enough to be purified by silica gel chromatography (Scheme 1).

The optimized allylation reaction conditions employed benzaldehyde and allyltributylstannane§ in the presence of 5 mol% of the (*S*,*S*)-(Phebox)$RhCl_2(H_2O)$ complex **2** as a chiral catalyst (Scheme 2). The absolute configuration of the allylated product was determined to be *S* by comparison of its optical rotation value with literature data.[3e] The rate of this allylation reaction was strongly dependent on the solvent: the allylation reaction proceeded smoothly in CH_2Cl_2, but when using THF or an aromatic solvent such as benzene or toluene, the reaction rates were remarkably slow although the enantioselectivities was almost the same (entries 1–4). In the presence of 4 Å molecular sieves this catalytic reaction was accelerated while the enantiomeric excess of the product **3** was not changed (Table 1, entries 4 *vs*. 5). The selectivity did not improve when the reaction temperature was lowered to 0 °C (entries 5 *vs*. 6). The substituent on the oxazoline rings had a significant effect on the chemical yields and ees (entries 5, 7–9). Notably, the enantioselectivity reaching 61% ee using Bn-Phebox-derived complex **2c**. It is worth noting that the complex **2** can be recovered almost quantitatively from the reaction medium by silica gel chromatography, and the recovered complex **2** catalyses the reaction with almost the same catalytic activity and enantioselectivity (entries 5 *vs*. 10).



Scheme 1



Scheme 2

Table 1 Asymmetric catalytic allylation of benzaldehyde catalyzed with Phebox–Rh^{III} complexes **2**[a]

Entry	Catalyst	Solvent	*T*/°C	*t*/h	Yield (%)	Ee (%)[b]
1	**2a**	toluene	room temp.	24	23	45
2	**2a**	benzene	room temp.	24	64	45
3	**2a**	THF	room temp.	24	66	52
4	**2a**	CH_2Cl_2	room temp.	7	79	52
5[c]	**2a**	CH_2Cl_2	room temp.	7	88	51
6[c]	**2a**	CH_2Cl_2	0	24	46	49
7[c]	**2b**	CH_2Cl_2	room temp.	7	42	6
8[c]	**2c**	CH_2Cl_2	room temp.	7	88	61
9[c]	**2d**	CH_2Cl_2	room temp.	7	43	46
10[c,d]	**2a**	CH_2Cl_2	room temp.	7	88	49

[a] All reactions were carried out using 0.5 mmol of benzaldehyde, 0.75 mmol of allyltin and 0.025 mmol of chiral catalyst **2** in 2 ml of solvent. [b] Determined by chiral HPLC analysis using Daicel CHIRALCEL OD. [c] In the presence of 4 Å molecular sieves (250 mg). [d] Recovered catalyst was used.

Table 2 Asymmetric catalytic allylation of aldehydes catalyzed with Phebox–Rh^{III} complex **2c**[a]

Entry	Aldehyde	Yield (%)	Ee (%)[b]	Configuration[c]	Ref
1	4-BrC_6H_4CHO	94	43[d]	*S*[e]	8(*a*)
2	PhCHO	88	61[f]	*S*	3(*e*)
3	4-MeOC_6H_4CHO	99	80	*S*	3(*n*)
4	2-MeC_6H_4CHO	98	53[g]	*S*[e]	8(*a*)
5	2-furyl-CHO	94	58[d]	*S*[e]	8(*a*)
6	PhCH_2CH_2CHO	84	63	*R*	3(*n*)
7	(*E*)-PhCH=CHCHO	98	77	*S*	3(*e*)

[a] All reactions were carried out using 0.5 mmol of aldehyde, 0.75 mmol of allyltributyltin and 0.025 mmol of chiral catalyst **2c** in 2 ml of CH_2Cl_2 in the presence of 4 Å molecular sieves (250 mg) at room temperature for 7 h. [b] Determined by chiral HPLC analysis using Daicel CHIRALCEL OD-H. [c] Assignment by comparison of the sign of optically rotation with reported value. [d] Determined by chiral HPLC analysis using Daicel CHIRALCEL OJ. [e] By analogy to the other case that is known unambiguously. [f] Determined by chiral HPLC analysis using Daicel CHIRALCEL OD. [g] Determined by chiral HPLC analysis using Daicel CHIRALPAK AD.

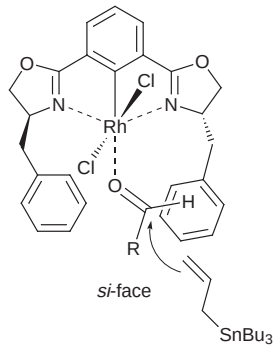


Fig. 1

Table 2 summarizes the results obtained for the allylation reaction of a variety of aldehydes catalysed with the complex **2c**. The characteristic features of the results are as follows: (i) an electron-donating substituents at the *para*-position of benzaldehyde increases the enantioselectivity; (ii) a methyl group at the *ortho*-position of benzaldehyde decreases the selectivity; (iii) all reactions result in high yields and comparable enantioselectivities with both aromatic and aliphatic aldehydes; (iv) in the reaction with enals, 1,2-addition reaction occurs exclusively; (v) in all of the cases, allyltributylstannane attacks to the *si*-face of the aldehyde's C=O plane.

A transition state that accounts for the observed stereoselectivities is shown in Fig. 1. The allylstannane approaches the carbonyl *si*-face because the *re*-face is shielded by the substituent on the oxazoline ring of the Phebox ligand.

In summary, we have demonstrated the effectiveness of Phebox–Rh^{III} complexes as chiral transition metal Lewis acid catalysts for the enantioselective addition of allyltributylstannane to aldehydes. Application of these complexes to other asymmetric reactions is now under investigation.

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Notes and references

† We previously reported the synthesis of **2a** by the transmetalation of $RhCl_3(H_2O)_3$ and **1a** in 47% yield (see ref 12). However, the chemical yield of Ph-Phebox-derived **2b** is very low (16%) by this method.

‡ We have already reported that the (dMe-Pybox)RhCl complex prepared from the dMe-Pybox and $[(c\text{-octene})_2RhCl]_2$ readily reacted with alkyl chlorides to form Rh^{III} species *via* an oxidative addition reaction, see ref. 13(*a*). And recently, Vrieze reported the same oxidative addition of carbon–chloride bonds to rhodium(I) complexes containing terdentate nitrogen ligands $[2,6\text{-}(CR^1{=}NR^2)_2C_2H_3N]$, see ref. 13(*b*).

§ Other substituted allylstannane reagents gave lower yields and enantioselectivities when catalyzed by **2a**: allyltrimethylstannane (48%, 35% ee), allyltriphenylstannane (7%, 27% ee).

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