Cr(salen)-catalyzed Asymmetric Addition of Allylstannane to Aldehydes

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Cr(salen) complex **3** was found to be an efficient catalyst for asymmetric addition of allyltributylstannane to non-branched aliphatic aldehydes, giving the corresponding homoallylic alcohols in a highly enantioselective manner. For example, its addition to 3-phenylpropanal and 6-phenoxyhexanal proceeded with 92 and 94% ees, respectively, under atmospheric pressure.

The nucleophilic addition of allylic organometallics to aldehydes or ketones such as the Hosomi–Sakurai reaction is a conventional method for synthesis of homoallylic alcohols and its asymmetric version has been extensively studied by using chiral Lewis acid as catalyst.[1,2] In 1991, Yamamoto and co-workers reported a seminal study of this type of reaction, addition of allyltrimethylsilane catalyzed by a chiral acyloxy borane derived from tartaric acid.[3] Since then, many efficient methods for the enantioselective addition of allylstannane and allylsilane derivatives have been developed and good to high enantioselectivities have been achieved in the reactions of both aromatic and aliphatic aldehydes.[4] Although many chiral Lewis acids have been used as catalysts, chiral Ti(IV)–BINOL,[5] Zr(IV)–BINOL,[6] Ag(I)–BINAP,[7] In(III)–PYBOX[8] and Rh(III)–BOX complexes[9] are among the most efficient ones. Especially, a bimetallic Ti-BINOL complex served as excellent catalyst.[10] In 2004, Cr(salen) complex **1** (Figure 1) was found to catalyze enantioselective addition of allyltributylstannane to alkyl glyoxylates.[11] Recently, **1** was further reported to catalyze addition of allyltributylstannane to simple aldehydes with good enantioselectivity (up to 79% ee) under high-pressure (10 kbar).[12] We recently found that readily available and manageable chiral Cr(salen) complexes **2** serve as efficient Lewis acid catalysts for hetero-Diels–Alder[13] and Mukaiyama-aldol reactions.[14,15] Moreover, the salen ligand bearing a binaphthyl unit has been disclosed to attractively interact with substrates through a weak bond interaction such as CH–π interaction.[16] Thus, we expected that complexes **2** would also catalyze addition of allyltributylstannane to simple aldehydes under milder pressure in an enantioselective manner.

We first examined addition of allyltributylstannane to 3-phenylpropanal under atmospheric pressure in the presence of **2a** bearing the same counter anion, BF_4^-, as **1** and found that it catalyzed the addition even at $-20\,^\circ$C, albeit with modest yield. In addition, complex **2b** bearing SbF_6^- as the anion was found to show better catalytic activity. Thus, we examined the addition using **3**–**7** bearing SbF_6^- anion as catalyst and found that complex **3** bearing (*R*,*R*)-1,2-diphenylethylenediamine as the diamine unit was the most effective catalyst for this reaction in terms of enantioselectivity and chemical yield (Entry 3). Complex **4** showed somewhat lower enantioselectivity (Entry 4). Complex **5** was less catalytically active and induced modest enantioselectivity. However, the sense of asymmetric induction by **5** was opposite to that by **3** or **4**, indicating that the C2″-aryl substituent plays an important role in the asymmetric induction and the expected ligand acceleration[16] (Entry 5).

The effect of the solvent on enantioselectivity was examined by using complex **3** as catalyst (Table 2) and the best enantioselectivity was attained albeit with only modest yield, when the reaction was carried out in *tert*-butyl methyl ether (TBME) (Entry 7). Fortunately, the chemical yield was improved and the selectivity maintained, when the reaction was carried out in a 1:1 mixture of TBME and CH_2Cl_2 (Entry 8). Lowering the reaction

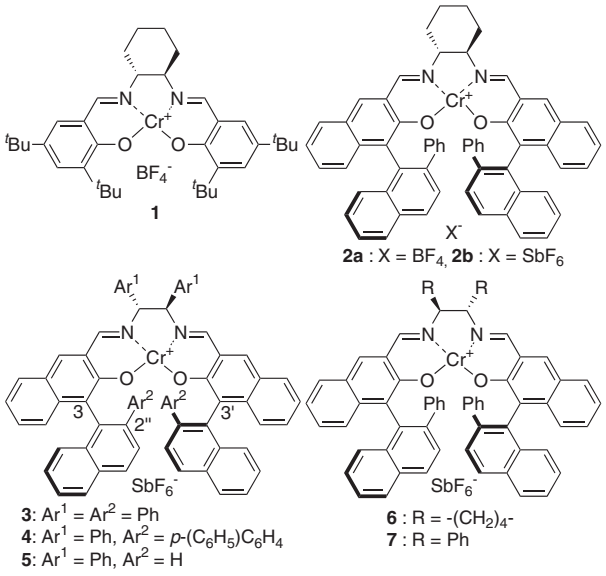
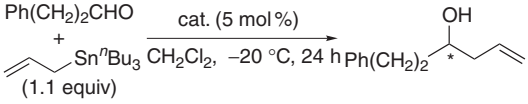


Figure 1.

Table 1. Asymmetric addition of allyltributylstannane using various Cr(salen) complexes as catalysts



Entry	cat.	Yield/%[a]	ee/%[b]	Config.[c]
1	**2a**	16	80	*S*
2	**2b**	39	80	*S*
3	**3**	59	90	*S*
4	**4**	56	88	*S*
5	**5**	28	45	*R*
6	**6**	40	24	*S*
7	**7**	45	50	*S*

[a]Isolated yield. [b]Determined by HPLC analysis using chiral stationary phase column (Daicel Chiralcel OD-H, Ref. 7). [c]Absolute configuration was determined by chiroptical comparison (Ref. 7).

Table 2. Optimization of asymmetric addition of allyltributylstannane to 3-phenylpropanal using **3** as catalyst

Entry	Solvent	Temp/°C	Time/h	Yield/%[a]	ee/%[b]
1	CH_2Cl_2	−20	24	59	90
2	$CHCl_3$	−20	24	37	87
3	$(CH_2Cl_2)_2$	−20	24	41	85
4	*i*-Pr_2O	−20	24	36	88
5	Et_2O	−20	24	30	77
6	THF	−20	24	39	50
7	TBME	−20	24	33	93
8	TBME/CH_2Cl_2	−20	24	59	92
9	TBME/CH_2Cl_2	−30	24	43	92

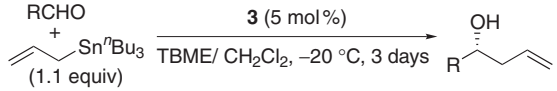
[a]Isolated yield. [b]Determined by HPLC analysis using chiral stationary phase column (Daicel Chiralcel OD-H, Ref. 7).

temperature did not affect the selectivity.

Under the optimized conditions, the reactions of other aldehydes were examined (Table 3). The reactions of nonbranched aliphatic aldehydes such as octanal and 6-phenoxyhexanal also proceeded with high enantioselectivity (>90% ee, Entries 1–5). However, the reactions of bulky aldehyde and conjugated aldehyde were sluggish, though the reason is unclear. Even at 23 °C, the reactions were considerably slow and modestly enantioselective (Entries 6 and 7). A similar trend has been observed in the reaction using Rh(III)-tetraaza complex as catalyst.[17]

Typical experimental procedure was exemplified by the reaction of 3-phenypropanal and allyltributylstannane: Complex **3** (6.1 mg, 5 mol %) was dissolved in a mixture of CH_2Cl_2 (125 μL) and TBME (125 μL) under nitrogen. To the solution was added 3-phenypropanal (13 μL, 0.10 mmol), and the mixture was cooled to −20 °C. Allyltributylstannane (34 μL, 0.11 mmol) was added to the mixture and stirred for 3 days at the temperature. The reaction mixture was treated with sat. $NaHCO_3$, stirred for 30 minutes, dried (Na_2SO_4), and filtered. The filtrate was chromatographed on silica gel (hexane/AcOEt = 9:1) to give the corresponding product in 80% yield. The enantiomeric excess of the product was determined by HPLC analysis, as described in the footnote to Table 1.

Table 3. Asymmetric allylation of various aldehydes using **3** as catalyst



Entry	R	Yield/%[a]	ee/%[b]	Config.[c]
1	$Ph(CH_2)_2$	80	92	*S*
2[d]	*n*-C_7H_{15}	77	92[e]	—
3	$PhO(CH_2)_5$	84	94	—
4	$PhO(CH_2)_2$	67	94	—
5	$(CH_3)_3CCOO(CH_2)_5$	72	94[e]	—
6[f]	*c*-C_6H_{11}	18	40[e]	*R*
7[f]	Ph	40	53	*R*

[a]Isolated yield. [b]Determined by HPLC analysis using chiral stationary phase column (Daicel Chiralcel OD-H, Ref. 7), unless otherwise mentioned. [c]Absolute configuration was determined by chiroptical comparison (Ref. 7). [d]10 mol % of **3** was used. When 5 mol % of **3** was used, the yield and the ee of the product were 56% and 92% ee, respectively. [e]Determined by HPLC analysis using chiral stationary phase column (Daicel Chiralpak AS-H), after the product was converted into the corresponding 3,5-dinitrobenzoate (3,5-dinitrobenzoyl chloride, triethylamine/dichloromethane). [f]Reaction was carried out at 23 °C.

In conclusion, we were able to demonstrate that complex **3** catalyzes asymmetric addition of allyltributylstannane to simple aldehydes under atmospheric pressure, though good substrates were limited to nonbranched aldehydes.

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References and Notes

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