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Chiral Ti(IV) complexes of hexadentate Schiff bases as precatalysts for aldehyde allylation: unusual additive effect of trimethylsilyl chloride

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Abstract—Chiral dinuclear titanium(IV) complexes have been found to be more effective catalysts for the asymmetric allylation of *p*-nitrobenzaldehyde than their mononuclear analogues. The addition of trimethylsilyl chloride to the reaction mixture decreases the rate of the background reaction and increases the yield of the reaction catalysed by the dinuclear complex.

1. Introduction

Asymmetric allylation of aldehydes constitutes as a very important, enantioselective C–C bond forming reaction in a series of total syntheses.[1a,b] This explains why the asymmetric allylation of aldehydes remains one of the most important and fundamental carbonyl addition reactions in organic synthesis. Naturally, catalytic versions of the reaction remain the most useful.[2] Unfortunately, these reactions are usually conducted at low temperatures and take several days to obtain reasonable chemical yields and enantiomeric purities with some substrates. Thus, an improvement to the asymmetric catalytic systems is still required.

The development of chiral polynuclear complexes of metals as precatalysts for asymmetric conversions is a rapidly growing and promising field of catalyst research.[1c,d] The potential advantages of their use are the expected enthalpy and entropy gains in the transition state of binuclear catalysed reactions, compared to the corresponding mononuclear catalysts. Recently, a series of chiral dinuclear catalysts for the allylation of aldehydes were elaborated by Maruoka and co-workers[3] Previously, we described the use of chiral bis-(salen)Ti-μ-O complexes as highly efficient catalysts for aldehyde cyanation.[4a] The kinetics of this reaction clearly indicated the presence of two titanium ions in the transition state of the reaction.[4b] The important feature, responsible for the catalytic activity of the complexes, was the presence of an oxygen bridge in the complex.[4c] The importance of oxygen bridges for the activity of (*S*)-binaphthoxytitanium complexes in the catalytic allylation of aldehydes was also established by Maruoka and co-workers[3c] Recently, we described the synthesis of new hexadentate Schiff bases, their chiral binuclear complexes with titanium(IV), and their use as precatalysts for the asymmetric addition of trimethylsilylcyanide to aldehydes.[5] An important feature of this system was a cooperative interaction of the two oxygen-atom-bridged titanium ions. Amongst other details, the system differed from the previously studied titanium(salen) complexes by the additional rigidity imposed by the hexadentate framework of its ligand.

Herein, we report the asymmetric allylation of aldehydes promoted by hexadentate Schiff base derived binuclear titanium complexes and show that the addition of trimethylsilyl chloride to the reaction mixture increases the yield of the reaction product and its enantiomeric purity. We postulate that the dissociation of the product from the

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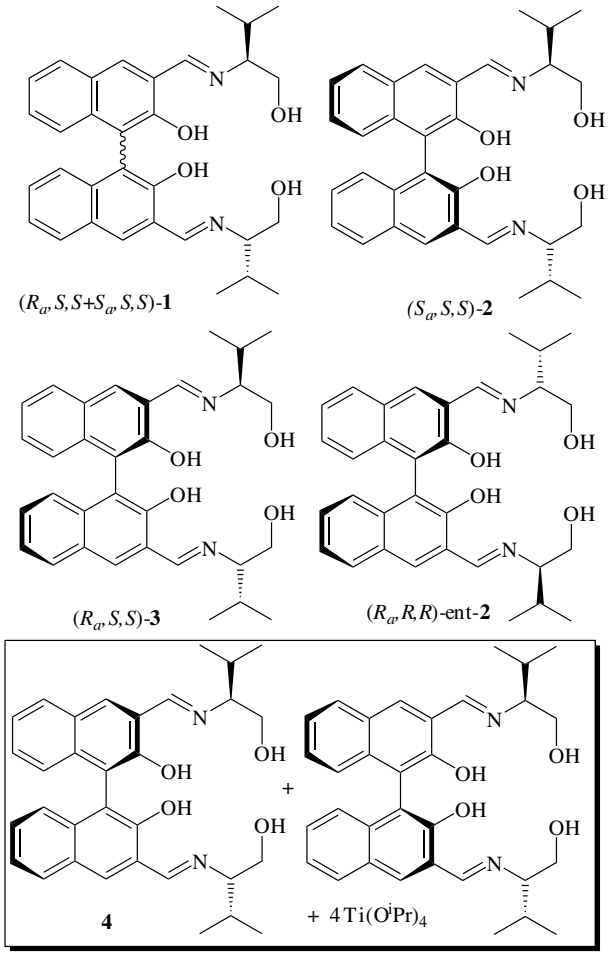
catalytic entity may be the rate limiting step of the catalysed reactions.

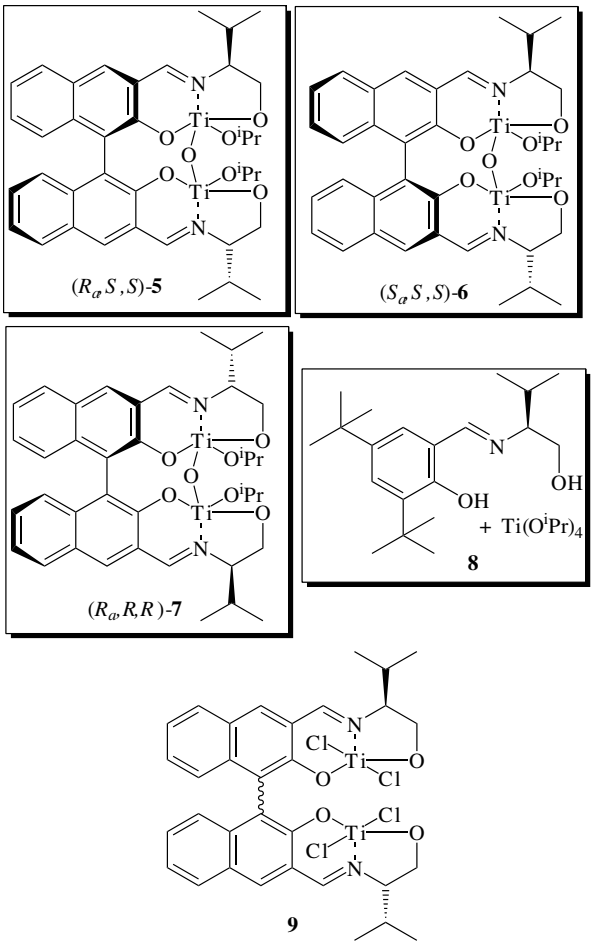
2. Results and discussion

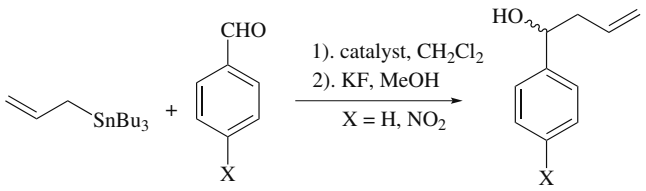
Ligands **1**–**3** were prepared as described earlier from the corresponding racemic and enantiomerically pure binaphthols.[5,6] Precatalysts **4**–**8** were prepared in situ by mixing the corresponding ligands with 2 equiv of titanium isopropoxide. The ^{1}H NMR spectra of the resulting mixtures after solvent removal indicated the presence of two isopropoxyl groups for each ligand, which in turn implied the existence of one oxygen atom bridge linking two titanium atoms.

The addition of allyltributyltin to benzaldehyde and *p*-nitrobenzaldehyde in CH_2Cl_2 at ambient temperature (Scheme 1) was studied as a model reaction. Precatalysts **4** (20 mol % of $Ti(O^iPr)_4$ with respect to the carbonyl compound) produced the final product in a low yield (47%) and ee (8%) after 24 h (Table 1, entry 1). Clearly, under the experimental conditions, they did not show any significant catalytic activity, as a blank control reaction produced almost the same yield of product (45%) after 24 h (Table 1, entry 2).

The catalytic activity of the mixture of diastereoisomeric complexes **4** was greatly promoted by the addition of trimethylsilyl chloride (Table 1, entries 4–10). Increasing the amount of trimethylsilyl chloride up to a fivefold ratio relative to the aldehyde increased both the chemical yield of the product and its enantiomeric excess (Table 1, entries 1, 4–9). The further addition of trimethylsilyl chloride up to 10 equiv had a negative effect on the enantioselectivity of the reaction (Table 1, entry 10).







Scheme 1. Addition of tributylallyltin to aldehydes.

A comparison of entries 11 and 12 in Table 1 indicates that both the catalytic activity and the asymmetry inducing ability of complex **6** were much greater than those of complex **5**. Thus, it was complex **6** which was responsible for the overall catalytic activity of the mixture of precatalysts **5** and **6**.

Under the optimal conditions, the use of precatalyst **7** led to the formation of (*R*)-product, as expected, with 96% chemical yield and 70% ee after 1.5 h (Table 1, entry 20).

Table 1. Addition of allyltributyltin to aldehydes catalysed by the titanium complexes **4**–**9**[a]

Entry	Catalyst	R	TMSCl[b]	Temperature	Time (h)	Yield[c] (%)	ee[d] (%)
1	**4**	*p*-NO_2	0	20	24	47	8 (*S*)
2	—	*p*-NO_2	0	20	24	45	0
3	—	*p*-NO_2	2.1	20	24	22	0
4	**4**	*p*-NO_2	2.1	20	2.5	79	50 (*S*)
5	**4**	*p*-NO_2	0.8	20	24	53	50 (*S*)
6	**4**	*p*-NO_2	1.0	20	24	61	43 (*S*)
7	**4**	*p*-NO_2	1.5	20	4.5	78	38 (*S*)
8	**4**	*p*-NO_2	3.0	20	1.5	87	63 (*S*)
9	**4**	*p*-NO_2	5.0	20	1.5	88	65 (*S*)
10	**4**	*p*-NO_2	10.0	20	1.5	82	55 (*S*)
11	**5**	*p*-NO_2	5.0	20	24	65	3 (*S*)
12	**6**	*p*-NO_2	5.0	20	2.5	94	70 (*S*)
13[e]	**4**	*p*-NO_2	0	20	2.5	30	2 (*S*)
14[e]	**4**	*p*-NO_2	5.0	20	2.5	36	7 (*S*)
15[f]	**4**	*p*-NO_2	5.0	20	2	87	40 (*S*)
16[g]	**4**	*p*-NO_2	5.0	20	1	90	56 (*S*)
17[h]	**8**	*p*-NO_2	5.0	20	18	91	11 (*R*)
18	**7**	*p*-NO_2	2.1	−20	24	87	43 (*R*)
19	**7**	*p*-NO_2	2.1	0	5	81	57 (*R*)
20	**7**	*p*-NO_2	2.1	20	1.5	96	70 (*R*)
21	**7**	*p*-NO_2	2.1	40	1.5	85	58 (*R*)
22[i]	**6**	*p*-NO_2	5.0	20	1	94	74 (*S*)
23	**6**	H	5.0	20	8	84	67 (*S*)
24[j]	**9**	*p*-NO_2	0	20	24	33	8 (*S*)
25[j]	**9**	*p*-NO_2	2.0	20	24	57	2 (*S*)

[a] To a solution of the catalyst (0.025 mmol, 20 mol % of titanium with respect to aldehyde) were added 1 equiv of *p*-nitrobenzaldehyde (0.250 mmol) and 1.5 equiv of tributylallyltin (0.333 mmol) and additive.
[b] The number of equivalents of trimethylsilyl chloride with respect to the aldehyde.
[c] Isolated yield after removing tin and purification by chromatography.
[d] The enantiomeric excess was determined by HPLC.
[e] 1.2 equiv of Hünigs base was added.
[f] The amount of ligand used was 5 mol % and titanium isopropoxide was 10 mol %.
[g] The amount of ligand used was 20 mol % and titanium isopropoxide was 40 mol %.
[h] The amount of ligand **8** was 20 mol % and titanium isopropoxide was 20 mol %.
[i] 3 Å molecular sieves were added to the reaction mixture.
[j] To a solution of the ligand (10 mol % with respect to aldehyde) were added 4 equiv of potassium *tert*-butoxide and 2 equiv of titanium tetrachloride. The precipitate was removed and washed with dichloromethane. The solvent was removed on a rotary evaporator and the catalyst was redissolved in dry dichloromethane.

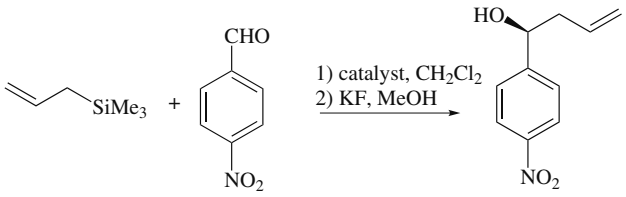
The use of 1.2 equiv of Hünigs base as an additive instead of trimethylsilyl chloride, or with trimethylsilyl chloride, had a harmful effect on the performance of the catalytic system, as the chemical yield was only 30% after 2.5 h and the product was virtually racemic (Table 1, entries 13 and 14). A twofold decrease or increase of the precatalyst concentration led to some reduction in the enantiomeric purity of the product (Table 1, entries 15 and 16).

Under the optimal conditions, complex **8**, a monomeric analogue of bimetallic complexes **5** and **6**, had a low catalytic activity and asymmetry inducing ability, forming the (*R*)-allylic alcohol with only 11% ee (Table 1, entry 17). Significantly, the configuration of the alcohol was the opposite of that generated with either complex **5** or **6**.

The temperature dependence of the asymmetric induction was at its optimum at 20 °C (Table 1, entries 18–21). The asymmetric induction was almost insensitive to the presence or absence of a nitro-group in the benzaldehyde molecule, as entries 23 and 12 testified. The addition of molecular sieves to the reaction mixture led to an increase in the asymmetric induction to 74% (Table 1, entry 22).

Another possible source of the allyl group was trimethylallylsilane (Scheme 2). In this case, the background reaction between *p*-nitrobenzaldehyde and trimethylallylsilane was not detected (Table 2, entry 1) even in the presence of trimethylsilyl chloride (Table 2, entry 2). Precatalyst **4** (mixture of complexes **5** and **6**) was not active at a loading of 10 mol % at room temperature (Table 2, entry 3), but the addition of 1.2 equiv of trimethylsilyl chloride to complex **4** facilitated the reaction and the final product was obtained in 91% chemical yield and 51% ee after 24 h (Table 2, entry 4).

The dependence of the ee of the product on the ratio of trimethylsilyl chloride to benzaldehyde was the opposite to that observed in the tributylallyltin reaction (Table 2). In this case, the optimal amount was 1.2 equiv of trimethylsilyl chloride with respect to the aldehyde (Table 2, entry 4). Further increase in the amount of the additive led to the ee values falling steadily (Table 2, entries 4–7), though the relative reactivity of precatalysts **5** and **6** stayed the same. Thus, precatalyst **5** was less catalytically active than complex **6** and produced only racemic product even under optimal conditions (Table 2, entry 8), whilst precatalyst **6**



Scheme 2. Addition of trimethylallylsilane to *p*-nitrobenzaldehyde.

produced the product with a chemical yield of 87% and with 60% ee after 24 h (Table 2, entry 9).

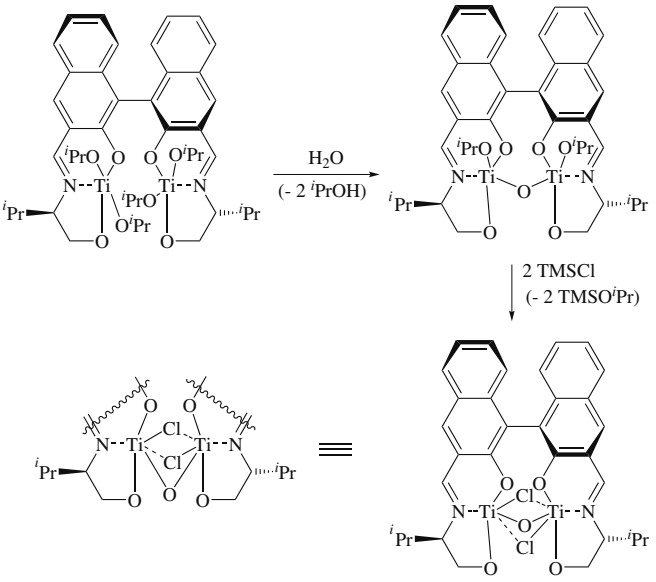
Table 2. Addition of allyltrimethylsilane to *p*-nitrobenzaldehyde catalysed by the titanium complexes **4**–**6**[a]

Entry	Catalyst	TMSCl[b]	Time (h)	Yield[c] (%)	ee[d] (%)
1	—	—	24	0	0
2	—	1.2	24	0	0
3	**4**	—	24	0	0
4	**4**	1.2	24	91	51 (*S*)
5	**4**	3.0	24	81	37 (*S*)
6	**4**	5.0	24	87	30 (*S*)
7	**4**	10.0	24	88	27 (*S*)
8	**5**	1.2	24	33	0
9	**6**	1.2	24	87	60 (*S*)

[a] To a solution of the catalyst (0.025 mmol, 20 mol % of titanium with respect to aldehyde) were added 1 equiv of *p*-nitrobenzaldehyde (0.250 mmol) and 1.5 equiv of tributylallyltin (0.333 mmol) and additive.
[b] The number of equivalents of trimethylsilyl chloride with respect to the aldehyde.
[c] Isolated yield after purification by chromatography.
[d] The enantiomeric excess was determined by HPLC.

Precatalyst **9** generated from titanium tetrachloride and ligand **4** had a low catalytic activity (Table 1, entries 24 and 25). The addition of 2 equiv of trimethylsilyl chloride to precatalyst **9** after 24 h gave only a 57% yield of the racemic alcohol. Thus, clearly, the function of trimethylsilyl chloride was not to convert complexes **5** or **6** into their corresponding chloride forms with the complete elimination of any remaining Ti–O bonds. Most likely, the real catalytically active species is an oxygen-bridged bimetallic titanium complex, where isopropoxy-groups were substituted with chloride anions (Scheme 3). The increase in the reaction enantioselectivity as the amount of trimethylsilyl chloride was increased may be rationalised by the accompanied increase of the number of chloride ions at the Ti-centres.

However, the most important function of the trimethylsilyl chloride seems to be increasing the reaction rate in both catalytic versions of allylation (see Table 1, entries 1 vs 4 and Table 2, entries 3 vs 4). This phenomenon can be rationalised by assuming that in the case of both allylating agents, the catalytic species formed in solution were similar and that the decomposition of a highly stable intermediate complex formed from allyl alcoholate and two titanium ions represents the rate limiting step of the catalytic cycle. Thus, the silylation step, regenerating the initial catalytic species, will be the rate limiting one in the whole catalytic sequence (Scheme 4).



Scheme 3. Generation of probable catalytic species.

In spite of all the progress in the field of dinuclear catalysis, particularly as applied to Lewis acid catalysis, there seems to be an inherent obstacle to catalyst turnover. For example, nucleophilic addition to aldehydes should be greatly accelerated by simultaneous coordination of their carbonyl group to both metal ions. However, the alkoxide product of the nucleophilic addition will also be stabilised in the same way. As a result, the rate of product dissociation from the dinuclear centre may become the rate limiting step of the whole process and even cause the formation of the final product to be slowed down, relative to catalysis by the corresponding mononuclear catalyst.

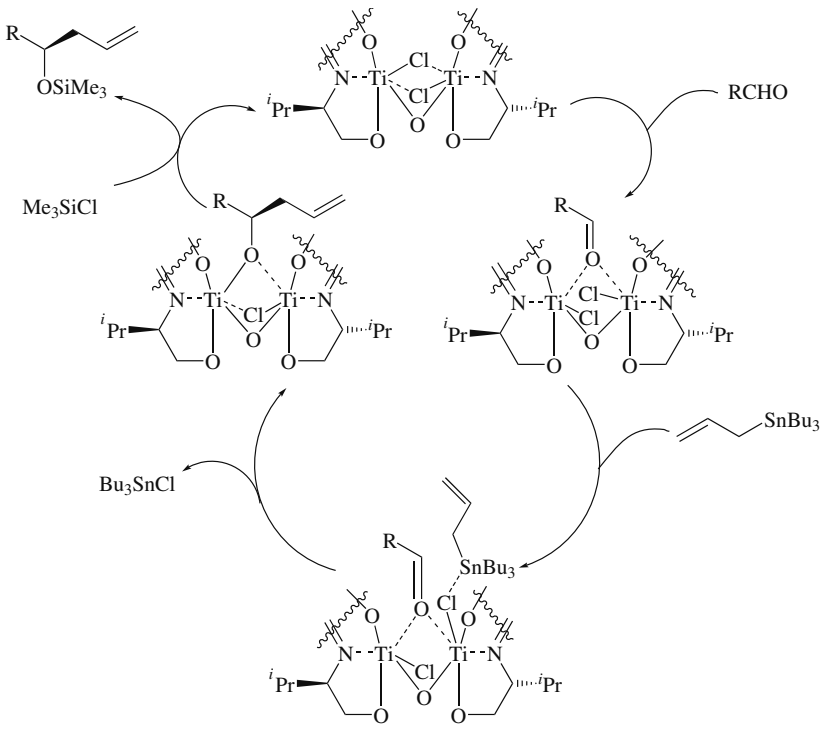
3. Conclusions

In conclusion, we have shown that binuclear catalysts are much more active than mononuclear ones in the allylation of aldehydes. In addition, we found an unusual effect of trimethylsilyl chloride addition on the effectiveness of the allylation of aldehydes with both allyltributyltin and trimethylallylsilane. Despite its modest enantioselectivity, the reaction can be brought to completion (94% isolated yield) after 1 h at a room temperature. Ongoing work is aimed at modifying the structure of the chiral ligand to provide higher enantioselectivities with the same reaction rate at room temperature.

4. Experimental

4.1. General

Specific rotations were measured on a Perkin–Elmer 241 polarimeter and are reported as follows: $[\alpha]_{\lambda}^{T}$ (concentration in g/100 mL, solvent). Enantiomeric excesses were determined by HPLC analysis using a Kromasil column (0.25 m × 46 mm) with UV detection at 254 nm.



Scheme 4. Probable mechanism of aldehyde allylation.

^{1}H NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer and are reported in parts per million using the solvent as internal standard. Data are reported as s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hertz, integration. Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker Avance 300 (75.5 MHz) spectrometer and are reported in parts per million using the solvent as an internal standard. Melting points were determined in open capillary tubes and are uncorrected. Elemental analyses were carried out by the laboratory of Microanalysis of INEOS RAS.

THF was freshly distilled from sodium/benzophenone under argon. Dichloromethane was distilled under argon from P_2O_5 and dried over 3 Å molecular sieves (1 g sieves for 1 mL dichloromethane). Benzaldehyde was distilled in vacuo under argon prior to use. All reagents were purchased from Aldrich or Acros, and used without purification unless otherwise stated.

4.2. Synthesis of methoxymethyl protected binaphthols

4.2.1. (*R*)-2,2′-Bis-(methoxymethoxy)-1,1′-binaphthalene.[6b] A solution of (*R*)-BINOL (2.40 g, 8.4 mmol) in DMF (20 mL) was added to a stirred suspension of sodium hydride (60% suspension in mineral oil, 2.36 g, 59 mmol) in DMF (20 mL) at 0 °C. After stirring for 10 min, methoxymethyl chloride (2.5 mL, 33.3 mmol) was added, and the reaction was then stirred for 50 min at 0 °C and 3 h at room temperature. The reaction mixture was quenched with water (250 mL) and extracted with diethyl ether (3 × 40 mL). The combined extracts were washed with water (×4), satd $NaHCO_3$, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure at room temperature and the residue was purified by short column chromatography on silica gel, eluting first with hexane and then with ethyl acetate to give the title compound as colourless crystals. Isolated yield 85%. $R_f = 0.39$ (hexane/ethyl acetate 3:1); $[\alpha]_D^{25} = +98$ (*c* 1, THF); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.15 (s, 6H), 4.98 (d, *J* 6.6 Hz, 2H), 5.09 (d, *J* 6.6 Hz, 2H), 7.40–7.26 (m, 6H), 7.35 (d, *J* 8.9 Hz, 2H), 7.58 (d, *J* 9.0 Hz, 2H), 7.88 (d, *J* 8.1 Hz, 2H), 7.96 (d, *J* 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.8, 95.1, 117.2, 121.2, 124.0, 125.5, 126.3, 127.8, 129.4, 129.8, 134.0, 152.6.

4.2.2. (*S*)-2,2′-Bis-(methoxymethoxy)-1,1′-binaphthalene. The title compound was prepared in the same way as the corresponding (*R*)-enantiomer, using (*S*)-BINOL as the starting material.

4.2.3. *rac*-2,2′-Bis-(methoxymethoxy)-1,1′-binaphthalene. The title compound was prepared in the same way as the corresponding (*R*)-enantiomer, using *rac*-BINOL as the starting material.

4.3. Synthesis of dialdehydes

4.3.1. (*R*)-3,3′-Diformyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene. *n*-Butyllithium (2.5 M in hexane, 9.0 mL, 22 mmol) was added to a solution of (*R*)-2,2′-bis(methoxymethyl)-1,1′-binaphthalene (2.46 g, 6.6 mmol) in ether (100 mL) under an argon atmosphere at −78 °C. The mixture was stirred for 2 h at room temperature, which produced a grey suspension, after which the reaction was

cooled to 0 °C and DMF (1.85 mL, 24 mmol) was added. The reaction was allowed to warm to room temperature and stirred for 16 h. Saturated NH_4Cl (50 mL) was then added to quench the reaction. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water and brine and dried over Na_2SO_4. The solvent was removed in vacuo and the residue purified by column chromatography on silica gel eluting with hexane/ethyl acetate (4:1) to give (*R*)-3,3′-diformyl-2,2′-bis (methoxymethyl)-1,1′-binaphthalene as white crystals. Isolated yield, 57% (lit.[6a] sticky yellow oil). $R_f = 0.17$ (hexane/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.87 (s, 6H), 4.69 (d, *J* 6.6 Hz, 2H), 4.73 (d, *J* 6.3 Hz, 2H), 7.22 (d, *J* 8.7 Hz, 2H), 7.42–7.50 (m, 2H), 7.52–7.60 (m, 2H), 8.08 (d, *J* 8.1 Hz, 2H), 8.62 (s, 2H), 10.55 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 57.0, 100.6, 125.9, 126.1, 126.3, 128.8, 129.6, 130.1, 130.3, 132.29, 136.7, 154.0, 190.6.

4.3.2. (*S*)-3,3′-Diformyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene. The title compound was prepared in the same way as the corresponding (*R*)-enantiomer using (*S*)-2,2′-bis(methoxymethyl)-1,1′-binaphthalene as the starting material.

4.3.3. *rac*-3,3′-Diformyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene. The title compound was prepared in the same way as the corresponding (*R*)-enantiomer using *rac*-2,2′-bis(methoxymethyl)-1,1′-binaphthalene as the starting material.

4.4. Deprotection of MOM-groups

4.4.1. (*R*)-3,3′-Diformyl-2,2′-dihydroxy-1,1′-binaphthalene.[6c] (*R*)-3,3′-diformyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene (1.17 g, 2.72 mmol) was dissolved in THF (20 mL). The solution was cooled in an ice bath, and then 12 M hydrochloric acid (10 mL) was added over 5 min. The ice bath was removed and the reaction mixture was stirred for 3 h at room temperature. The solution was extracted with ethyl acetate (7 × 20 mL), the combined extracts were washed with water, satd $NaHCO_3$, brine and dried over Na_2SO_4. The solvent was evaporated to give the title compound (0.93 g, 100%) as yellow crystals. To produce dialdehyde with good elemental analysis, the product was purified by chromatography on Sephadex LH-20 (eluent THF). $R_f = 0.35$ (hexane/ethyl acetate 4:1); mp 285 °C; $[\alpha]_D^{25} = +249.5$ (*c* 0.8, CH_2C_2) {lit.[7] $[\alpha]_D^{20} = +248$ (*c* 0.5, CH_2Cl_2)}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10–7.15 (m, 2H), 7.30–7.37 (m, 4H), 7.90–7.95 (m, 2H), 8.30 (s, 2H), 10.12 (s, 2H), 10.52 (s, 2H). ee >99.9% determined by HPLC analysis (Kromasil 0.46 cm × 25 cm, eluent hexane/iso-propyl alcohol 100/4, 1 mL/min, UV detector 254 nm) R_t (major) = 22.79 min, R_t (minor) = 20.81 min.

4.4.2. (*S*)-3,3′-Diformyl-2,2′-dihydroxy-1,1′-binaphthalene. The title compound was prepared in the same way as the corresponding (*R*)-enantiomer using (*S*)-3,3′-diformyl-2,2′-bis-(methoxymethoxy)-1,1′-binaphthalene as the starting material. $[\alpha]_D^{25} = -267.0$ (*c* 0.5, CH_2Cl_2) {lit.[6b] $[\alpha]_D^{20} = -254$ (*c* 0.3, CH_2Cl_2)}. ee >99.9% determined by HPLC analysis (Kromasil 0.46 cm × 25 cm, eluent hexane/iso-propyl alcohol 100/4, 1 mL/min, UV detector 254 nm) R_t (major)= 20.81 min, R_t (minor)= 22.79 min.

4.4.3. *rac*-3,3′-Diformyl-2,2′-dihydroxy-1,1′-binaphthalene. The title compound was prepared in the same way as the corresponding (*R*)-enantiomer using *rac*-3,3′-diformyl-2,2′-bis-(methoxymethoxy)-1,1′-binaphthalene as the starting material.

4.5. Synthesis of aminoalcohols

4.5.1. (*S*)-2-Amino-3-methyl-1-butanol. To a suspension of lithium aluminium hydride (5 g, 0.131 mol) under an argon atmosphere in dry THF (100 mL) at room temperature was carefully added L-valine (10 g, 0.085 mol) in 20 portions. The reaction mixture was refluxed for 16 h and after cooling was poured into diethyl ether (or methyl-*tert*-butyl ether) (100 mL). To the ether layer was slowly added water (15 mL), followed by 15% aqueous sodium hydroxide solution (15 mL) and water (45 mL). The solution was filtered, and the precipitate was washed twice with ether (50 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. After distillation in vacuo, the title compound (6.6 g, 0.064 mol, 75%) was obtained. It is best to switch off the water in the condenser of the distillation apparatus when (*S*)-2-amino-3-methyl-1-butanol begins to distil. $[\alpha]_D^{25} = +17$ (*c* 11.5, ethanol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (d, *J* 4.9 Hz, 3H), 0.93 (d, *J* 4.9 Hz, 3H), 1.60–1.73 (m, 1H), 1.90–2.50 (br s, 3H), 2.83–2.92 (m, 1H), 3.21 (dd, *J* 10.6, 8.0 Hz, 1H), 3.53 (dd, *J* 10.6, 3.7 Hz, 1H).

4.5.2. (*R*)-2-Amino-3-methyl-1-butanol. The title compound was prepared in the same way as the corresponding (*S*)-enantiomer using (*R*)-valine as the starting material.

4.6. Synthesis of ligands

4.6.1. Compound 3. A solution of (*S*)-2-amino-3-methyl-1-butanol (0.19 g, 1.8 mmol) in ethanol (5 mL) and benzene (5 mL) was added to (*R*)-3,3′-diformyl-2,2′-dihydroxy-1,1′-binaphthyl (0.31 g, 0.91 mmol). The reaction mixture was heated in a Dean–Stark apparatus for 10 h. The solution was concentrated and the residue purified by short column chromatography on aluminium oxide eluting with hexane/dichloromethane/ethanol (20:5:1), then the eluent was further purified by chromatography on Sephadex LH-20 eluting with dry benzene to give compound **2** (0.44 g, 95%) as a red solid. $[\alpha]_D^{25} = -139.8$ (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.92 (d, *J* 7.0 Hz, 3H), 0.95 (d, *J* 7.2 Hz, 3H), 1.80–1.90 (m, 2H), 2.30–2.80 (br m, 2H), 3.00–3.15 (m, 2H), 3.65–3.75 (m, 4H), 7.10–7.19 (m, 2H), 7.27–7.33 (m, 4H), 7.86–7.89 (m, 2H), 7.99 (s, 2H), 8.64 (s, 2H), 13.19 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.9, 19.6, 30.0, 64.1, 77.8, 116.5, 120.7, 123.2, 124.9, 127.5, 128.2, 128.8, 133.4, 135.1, 154.6, 165.9. Anal. Calcd for $C_{32}H_{36}N_2O_4$: C, 74.97; H, 7.08; N, 5.46. Found: C, 75.03; H, 7.40; N, 5.27.

4.6.2. Compound 2. The title compound was prepared as described in Section 4.6.1 for compound **3**, using (*S*)-3,3′-diformyl-2,2′-dihydroxy-1,1′-binaphthyl as the starting

material. Yield 95%. $[\alpha]_D^{25} = -163$ (*c* 1, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.92 (d, *J* 7.0 Hz, 3H), 0.95 (d, *J* 7.2 Hz, 3H), 1.56 (br m, 2H), 1.89–1.91 (m, 2H), 3.09–3.14 (m, 2H), 3.70–3.86 (m, 4H), 7.19–7.22 (m, 2H), 7.29–7.36 (m, 4H), 7.87–7.90 (m, 2H), 8.00 (s, 2H), 8.64 (s, 2H), 12.95 (s, 2H). Anal. Calcd for $C_{32}H_{36}N_2O_4$: C, 74.97; H, 7.08; N, 5.46. Found: C, 74.91; H, 6.99; N, 5.28.

4.6.3. Compound *ent*-2. The title compound was prepared as described in Section 4.6.1 for compound **3**, using (*R*)-3,3′-diformyl-2,2′-dihydroxy-1,1′-binaphthyl and (*R*)-2-amino-3-methyl-1-butanol as the starting material. Yield 94%. $[\alpha]_D^{25} = +163$ (*c* 1, $CHCl_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.9, 19.7, 30.2, 64.4, 78.3, 116.5, 120.8, 123.4, 124.8, 127.6, 128.4, 129.0, 133.8, 135.2, 154.7, 166.1. Anal. Calcd for $C_{32}H_{36}N_2O_4$: C, 74.97; H, 7.08; N, 5.46. Found: C, 75.01; H, 7.15; N, 5.50.

4.6.4. Compound 1. The title compound was prepared as described in Section 4.6.1 for compound **3**, using *rac*-3,3′-diformyl-2,2′-dihydroxy-1,1′-binaphthyl as the starting material. $[\alpha]_D^{25} = -14.6$ (*c* 1, $CHCl_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.7, 18.8, 19.5, 19.6, 29.9, 30.0, 64.1, 64.2, 77.9, 78.1, 116.4, 116.5, 120.7, 120.8, 123.2, 123.3, 124.7, 124.8, 127.5, 128.2, 128.4, 128.8, 128.9, 133.4, 133.7, 135.1, 154.6, 165.9, 166.0. Anal. Calcd for $C_{32}H_{36}N_2O_4$: C, 74.97; H, 7.08; N, 5.46. Found: C, 75.04; H, 7.41; N, 5.26.

4.6.5. (*S*)-2-(*N*-3′,5′-Di-*tert*-butylsalicylideneamino)-3-methylbutan-1-ol. A solution of (*S*)-2-amino-3-methyl-1-butanol (0.10 g, 0.97 mmol) in ethanol (5 mL) and benzene (5 mL) was added to 2,4-di-*tert*-butylsalicylaldehyde (0.23 g, 0.97 mmol). The reaction mixture heated in a Dean–Stark apparatus for 10 h. The solution was concentrated and the residue purified by column chromatography on aluminium oxide eluting with hexane/dichloromethane/ethanol (20:5:1) to give the title compound (0.30 g, 86%) as yellow crystals. $[\alpha]_D^{25} = -33.3$ (*c* 0.78, MeOH); ^1H NMR (300 MHz, $CDCl_3$) δ 1.02 (d, *J* 4.1 Hz, 3H), 1.04 (d, *J* 4.1 Hz, 3H), 1.32 (s, 9H), 1.45 (s, 9H), 1.85–2.05 (m, 1H), 2.99–3.07 (m, 1H), 3.70–3.90 (m, 2H), 7.13 (d, *J* 2.4 Hz, 1H), 7.40 (d, *J* 2.4 Hz, 1H), 8.38 (s, 1H), 13.40–13.70 (br s, 1H); Anal. Calcd for $C_{20}H_{33}NO_2$: C, 75.19; H, 10.41; N, 4.38. Found: C, 75.04; H, 10.41; N, 4.37.

4.7. Catalytic reactions

4.7.1. Asymmetric allylation reactions

4.7.1.1. Typical procedure with allyltributyltin. $Ti(O^iPr)_4$ (15 μL, 0.05 mmol) was added to a solution of ligand (0.025 mmol) in dichloromethane (0.125 mL). The solution changed colour from yellow to orange. After stirring for 20 min, the solvent was evaporated. A solution of *p*-nitrobenzaldehyde (38 mg, 0.25 mmol) in dry dichloromethane (0.125 mL) was added to the reaction mixture. Allyltributyltin (0.117 mL, 0.375 mmol) was then added followed (optionally) by the appropriate additive. The solution colour changed to deep red. The reaction mixture was stirred for the required time. The reaction could be monitored by TLC (SiO_2 on aluminium plates, CH_2Cl_2). When the reaction was complete, solvent was evaporated and to the residue was added a saturated solution of potassium fluoride in methanol (5 mL). After 20 min, dichloromethane (20 mL) was added. The resulting precipitate was filtered off, the solution was evaporated and the product was purified by preparative-scale chromatography ($R_f = 0.3$, CH_2Cl_2).

4.7.2. (*S*)-(−)-1-(4-Nitrophenyl)-but-3-en-1-ol. ^1H NMR ($CDCl_3$) δ 2.19 (br s, 1H), 2.42–2.49 (m, 1H), 2.54–2.60 (m, 1H), 4.86 (dd, *J* 8.0, 4.6 Hz, 1H), 5.17–5.22 (m, 2H), 5.74–5.84 (m, 1H), 7.54 (d, *J* 8.6, 2H), 8.21 (d, *J* 8.6, 2H). HPLC Daicel AS-H, hexane/iso-propanol 98:2 (R_t[(*R*)-enantiomer] = 44.5 min, R_t[(*S*)-enantiomer] = 47 min); $[\alpha]_D^{25} = -35.7$ (*c* 0.5, $CHCl_3$) for 74% ee {lit.[8] $[\alpha]_D^{25} = -33.2$ (*c* 0.5, $CHCl_3$) for 65% ee}.

4.7.3. (*S*)-(−)-1-Phenyl-but-3-en-1-ol. ^1H NMR ($CDCl_3$) δ 2.06 (br s, 1H), 2.48–2.56 (m, 2H), 4.77 (dd, *J* 7.7, 5.2 Hz, 1H), 5.15–5.22 (m, 2H), 5.79–5.89 (m, 1H), 7.28–7.39 (m, 5H). HPLC Daicel OD-H, hexane/iso-propanol 98:2 (R_t[(*R*)-enantiomer] = 15.7 min, R_t[(*S*)-enantiomer] = 19.9 min); $[\alpha]_D^{25} = -44.6$ (*c* 1.05, $CHCl_3$) for 67% ee {lit.[8] $[\alpha]_D^{25} = -61.2$ (*c* 1.05, $CHCl_3$) for 92% ee}.

4.7.4. Typical procedure with allyltrimethylsilane. $Ti(O^iPr)_4$ (15 μL, 0.05 mmol) was added to a solution of ligand (0.025 mmol) in dichloromethane (0.125 mL). The solution changed colour from yellow to orange. After stirring for 20 min, the solvent was evaporated. A solution of *p*-nitrobenzaldehyde (38 mg, 0.25 mmol) in dry dichloromethane (0.125 mL) was added to the reaction mixture. Subsequently, allyltrimethylsilane (59.6 μL, 0.375 mmol) was added followed (optionally) by the appropriate additive. The solution colour changed to deep red. The reaction mixture was stirred for 24 h. The reaction could be monitored by TLC (SiO_2 on aluminium plates, CH_2Cl_2). When the reaction was complete, solvent was evaporated and a saturated solution of potassium fluoride in methanol (5 mL) was added. After 20 min, dichloromethane (20 mL) was added. The resulting precipitate was filtered off, the solution was evaporated and the product was purified by preparative-scale chromatography ($R_f = 0.3$, CH_2Cl_2).

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