

# Bis(hydroxyphenyloxazolinato)-titanium(IV) and -zirconium(IV) triflates as novel transition metal-based Lewis acids

Pier Giorgio Cozzi and Carlo Floriani\*

Institut de Chimie Minérale et Analytique, BCH, Université de Lausanne, CH-1015 Lausanne, Switzerland

The preparation of novel titanium, **3**, and zirconium, **4**, organometallic Lewis acids by treatment of the readily available  $[M(L)_2(Cl)_2]$  complexes ( $M = Ti, Zr$ ;  $L =$  hydroxyphenyl-4,5-dihydrooxazole) with  $AgOSO_2CF_3$  are described. The new homogeneous organometallic Lewis acids, prepared *in situ*, are active in promoting aldol reactions, additions to imines and catalytic allylations. In addition, some examples of the use of **3** and **4** in other reactions (*i.e.* Mukaiyama–Michael reaction, addition of  $Me_3SiCN$ , Diels–Alder, and hetero Diels–Alder reaction) are presented. Some mechanistic studies on the aldol reaction and on the catalytic allylation have been performed in order to show some of the characteristics of the present Lewis acid system.

## Introduction

In Lewis acid-promoted reactions the ubiquity of which in current stereoselective organic synthesis is well-documented,<sup>1</sup> complexation of a Lewis acid with a substrate such as an aldehyde or ketone can have a dramatic effect upon subsequent paths of attack. Herein lies the origin of the high selectivities sometimes observed with chiral Lewis acids.<sup>2</sup>

Traditionally, the most powerful Lewis acids have been the halides of  $B^{III}$ ,  $Al^{III}$  and  $Ti^{IV}$ , although derivatives of  $Sn^{IV}$ ,  $Fe^{III}$ ,  $Si^{IV}$  and the lanthanions have found use when less active agents are required.<sup>3</sup> All these species rely on their oxophilicity to promote reactions and, consequently, they are highly sensitive to moisture. When the Lewis acid environment is modified by incorporating ligands<sup>4</sup> at the metal centre the sensitivity to hydrolysis is usually enhanced. In order to function catalytically, these Lewis acids demand strictly anhydrous conditions. To alleviate this problem they are often used in stoichiometric quantities, a technique which is obviously inappropriate if the Lewis acid bears expensive, difficult to prepare, ligands.

Modified Lewis acids are usually prepared and used *in situ*. Consequently, a mixture of products can result based on the rapid equilibration of the ligand with the parent halide (or other precursors). It is therefore difficult to identify with certainty the species responsible for catalysis. Although excellent results have been reported for enantioselective traditional Lewis acids,<sup>4</sup> the lack of structural information on the key intermediates obviously hampers rapid future development.

One approach to this problem is the use of well-defined, isolable organometallic species where a single catalytic site on the molecule promotes the reaction with high turnover. The incorporation of a chiral ligand into the metal co-ordination sphere should ideally exert a fixed, stable geometry and be readily modifiable in order to fine tune the Lewis acidity.<sup>5</sup> More importantly, the binding of the substrate to the catalyst should be rapid and reversible with a binding constant greater than that of the product.

Studies into such systems have already been reported, and indeed, efficient Lewis acids with cyclopentadienyl (cp) substituents have been developed.<sup>6</sup> However, those systems featuring chiral cp ligands usually display low enantiomeric excesses in organic-promoted reactions.<sup>7</sup> In those cases where promising ees have been obtained the syntheses of the chiral cp-based Lewis acid are complicated.<sup>8</sup>

We have therefore sought to replace the cp ligand with easily prepared hydroxyphenyloxazolines<sup>†</sup><sup>9,10</sup> as ancillary ligands

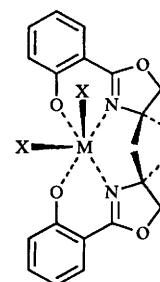
for early transition metal Lewis acids (see compounds 1–4). The stereoelectronic properties of this class of ligands serve to give a spatial arrangement at the acidic metal centre comparable to that obtained with cp-based ligands.<sup>11</sup>

Here we report our results on the homogeneous catalysis reactions of bis(hydroxyphenyloxazolinato)-titanium(IV) and -zirconium(IV) triflates.

## Results and discussion

### (i) Mukaiyama cross-aldol reaction

The organometallic acid reagents to be studied, **3** and **4**, were prepared *via* the metathetical reaction of  $Ag(OSO_2CF_3)$  with the fully characterized Ti and Zr complexes, **1** and **2**, respectively (Scheme 1).<sup>11</sup> Although we have demonstrated that it is possible to isolate and characterize **4**, both **3** and **4** were generated *in situ* in methylene dichloride.



- 1  $M = Ti, X = Cl$   
 2  $M = Zr, X = Cl$   
 $2AgOTf \downarrow$   
 3  $M = Ti, X = OTf$   
 4  $M = Zr, X = OTf$

Scheme 1

Despite the strong reducing ability of enol silanes,<sup>12</sup> in no reaction promoted by complexes **3** and **4** have we observed evidence which supports reduction of the catalysts.

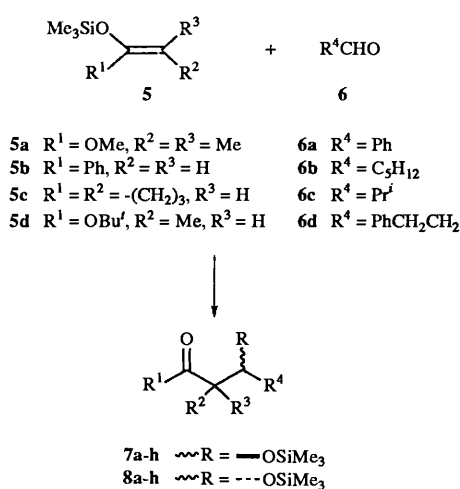
Solutions of complexes **3** and **4** are stable for several weeks and show no loss of reactivity. The results obtained with a variety of non-stereogenic and stereogenic enol silanes<sup>5a-d</sup> and aldehydes<sup>6a-d</sup> (Scheme 2) promoted by 3–4 mol% of **4** are collected in Table 1.

† For convenience, the compounds are referred to as oxazolines rather than 4,5-dihydrooxazoles as required by IUPAC rules of nomenclature.

**Table 1** Aldol reactions catalysed by complexes **3** and **4**

Entry <sup>a</sup>	Enol silane	Aldehyde	Temp. (T/°C)	Time (t/h)	Product	Yield (%) <sup>b</sup>	7:8 <sup>c</sup>
1	<b>5a</b>	<b>6a</b>	25	1	<b>7, 8a</b>	95	
2	<b>5a</b>	<b>6a</b>	-78	2	<b>7, 8a</b>	93	
3	<b>5a</b>	<b>6b</b>	-78	3	<b>7, 8b</b>	78	
4	<b>5a</b>	<b>6c</b>	-78	3	<b>7, 8c</b>	49	
5	<b>5a</b>	<b>6c</b>	-78	6	<b>7, 8c</b>	52	
6	<b>5b</b>	<b>6a</b>	-78	2	<b>7, 8d</b>	0	
7	<b>5b</b>	<b>6c</b>	-78	3	<b>7, 8e</b>	0	
8	<b>5b</b>	<b>6a</b>	25	2	<b>7, 8d</b>	78	
9	<b>5b</b>	<b>6c</b>	25	2	<b>7, 8e</b>	63	
10	<b>5c</b>	<b>6a</b>	-78	4 <sup>e,f</sup>	<b>7, 8f</b>	0	
11	<b>5c</b>	<b>6a</b>	-30	5	<b>7, 8f</b>	62	70:30
12	<b>5c</b>	<b>6a</b>	-78-25 <sup>d</sup>	12 <sup>e,f</sup>	<b>7, 8f</b>	86	70:30
13	<b>5c</b>	<b>6a</b>	25	2	<b>7, 8f</b>	85	66:34
14	<b>5c</b>	<b>6a</b>	25	4 <sup>e</sup>	<b>7, 8f</b>	80	80:20
15	<b>5c</b>	<b>6d</b>	25	4	<b>7, 8g</b>	40	60:40
16	<b>5d</b>	<b>6a</b>	25	3 <sup>f</sup>	<b>7, 8h</b>	85	50:50

<sup>a</sup> All the reactions were carried out in CH<sub>2</sub>Cl<sub>2</sub> solution using 1.0–1.2 mmol of enol silane, 1.0 mmol of aldehyde, and 0.03 mmol of the catalyst **4**, unless otherwise stated. <sup>b</sup> Isolated yields. <sup>c</sup> Ratios determined by <sup>1</sup>H NMR are specified only when stereogenic enol silane **5c** and **5d** were used: assignments are based on deprotection of the *o*-silyl products and comparison with the <sup>1</sup>H NMR spectra of known β-hydroxy ketones (**7g**, **8g**) and β-hydroxy esters (**7h**, **8h**). <sup>d</sup> The reaction was slowly warmed to room temperature. <sup>e</sup> The titanium catalyst was used. <sup>f</sup> 0.04 mmol of catalyst were used.

**Scheme 2**

Several differences are apparent between the results obtained with **3** and **4** and with [Ti(cp)<sub>2</sub>(OTf)<sub>2</sub>] and [Zr(cp)<sub>2</sub>(OTf)<sub>2</sub>].<sup>6</sup> First, our catalysts require no particular solvent in order to promote the aldol reaction {[M(cp)<sub>2</sub>(OTf)<sub>2</sub>]-promoted reactions are performed in MeNO<sub>2</sub>}. Further, the extremely active metallocene zirconium and titanium bis(triflate)<sup>6</sup> catalysts react rapidly with both silyl enol ethers and silyl ketene acetals, even though the latter class of compounds are the more reactive Mukaiyama partners. With our systems, however, the silyl ketene acetal can be consumed at low (-78 °C) temperature, whilst the silyl enol ether require higher temperatures in order to react. The selectivity exhibited by **3** and **4** can therefore be used to transform a silyl ketene acetal in the presence of a less reactive enol silane. The mild nature of **3** and **4** is further demonstrated by entries 3 and 4 which clearly show the marked reactivity of aromatic substrates over aliphatic ones. Finally, it is worth noting that unbranched aliphatic aldehydes are more reactive than their branched analogues. We believe that this order reflects the ease of co-ordination of the carbonyl substrate to the metal centre.

The co-ordination of the carbonyl was investigated using low-temperature NMR spectroscopy. A solution of **4** was prepared in CD<sub>2</sub>Cl<sub>2</sub> (40 mg in 2.0 cm<sup>3</sup>): its <sup>1</sup>H NMR showed no

difference from the stock solution used above. Both the <sup>1</sup>H and <sup>19</sup>F NMR spectra of **4** are highly complex, possibly owing to the formation of aggregate species *via* co-ordination of the triflate oxygen atoms to neighbouring oxophilic zirconium centres. The <sup>1</sup>H NMR spectra point to the presence of two major components, but show no significant change at low temperature. Inspection of the <sup>19</sup>F NMR spectra failed to show the presence of free triflate, again due to their complicated nature.

Upon addition of benzaldehyde (1.9 equiv., 90% excess) to the mixture no evidence for the presence of complexed aldehyde was observed in the <sup>1</sup>H and <sup>19</sup>F NMR spectra at room temperature. Moreover, the aldehydic proton signal is sharp indicating that exchange is rapid on the NMR time scale. However, at 213 K the <sup>1</sup>H NMR spectra clearly show well resolved signals corresponding to complexed PhCHO, including the aldehyde methine proton as a sharp singlet at 11.8 ppm.

The diastereoselective influence of our two catalysts was investigated with stereogenic silyl enol ethers (Table 1, entries 11–16); moderate preference for the *syn* diastereoisomer was observed. The assignment of this configuration was made by comparison with the known product.<sup>13</sup> Although the titanium-based complex **3** shows increased selectivity (entry 14), entry 16 in Table 1 suggests that this methodology will have little practical value. The increase of the catalyst amount (from 3–4% to 15%) does not affect the low stereoselection. The diastereoisomeric ratio was not temperature-dependent (entries 11–13). When Scott, Collins and co-workers investigated the diastereoselection displayed by [Zr(cp)<sub>2</sub>(OBu<sup>t</sup>)]<sup>+</sup> catalyst,<sup>14</sup> they too noted that the reaction had limited preparative scope.

According to the observed reactivities and the experiments carried out at low temperature, we propose for the reaction an acyclic transition state (Fig. 1). A similar model was presented for cationic zirconocene catalysts.<sup>14</sup>

The low *syn* preference exhibited by **5c** in the aldolic reaction can derive from avoided steric interactions between the aldehyde substituent and the enol silane in an acyclic transition state (Fig. 2). The interaction between enol silane and the zirconium ligands are, in this case, less important.

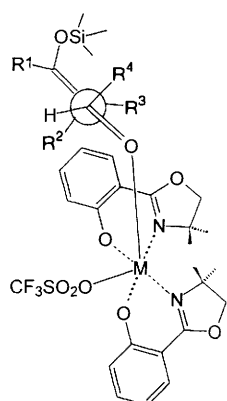
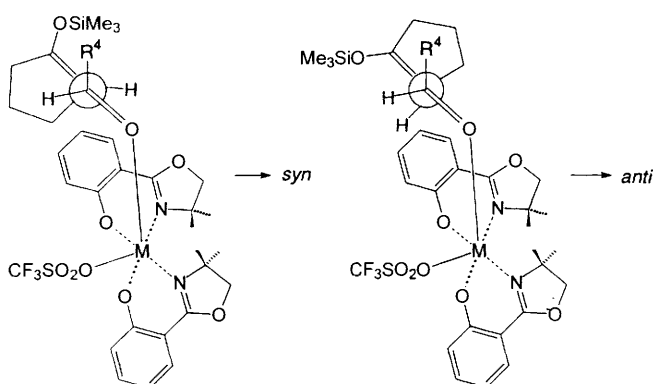
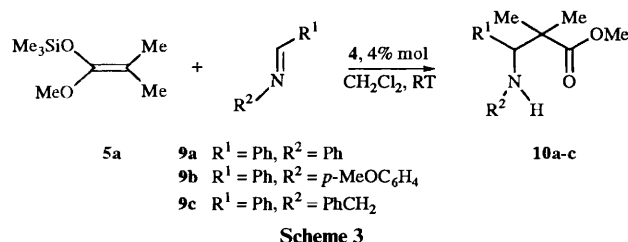
#### (ii) Mukaiyama reaction with imines

Silyl ketene acetals also react with imines (Scheme 3),<sup>15</sup> but only recently has this class of reaction been studied with catalytic

**Table 2** Reaction of enol silanes with imines

Entry <sup>a</sup>	Silyl ketene	Imine	Temp ( <i>T</i> /°C)	Time ( <i>t</i> /h)	Product	Yield (%) <sup>b</sup>
1	<b>5a</b>	<b>9a</b>	25	10	<b>10a</b>	73
2	<b>5a</b>	<b>9b</b>	25	10	<b>10b</b>	85
3	<b>5a</b>	<b>9c</b>	25	10	<b>10c</b>	65
4	<b>5a</b>	<b>9b</b>	25	10	<b>10b</b>	86 <sup>c</sup>

<sup>a</sup> All the reactions were carried out in CH<sub>2</sub>Cl<sub>2</sub> solution using 1.2 mmol of enol silane, 1 mmol of imine, and 0.04 mmol of the catalyst **4**, unless otherwise stated. <sup>b</sup> Isolated yields. <sup>c</sup> Catalyst **3** was used.

**Fig. 1****Fig. 2**

amounts of Lewis acid. Although a report has appeared detailing an enantioselective stoichiometric variant of this reaction,<sup>16</sup> an enantioselective catalyst for the parent reaction is still to be discovered.

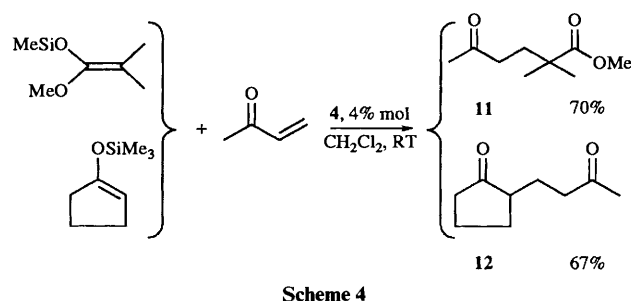
Furthermore, to the best of our knowledge no organo transition metal complex has been reported to promote efficiently the Mukaiyama imine reaction. This is probably related to the ability of imines to co-ordinate strongly to the acidic metal centre, thus deactivating the catalytic cycle. However, **3** and **4** successfully promote the clean reaction of imines with silyl enols as summarized in Table 2. The reaction proceeds at a satisfactory turnover rate, and judicious choice of

imine protecting group yields products of use for further transformations, *e.g.* for  $\beta$ -lactam synthesis.

However, this interesting reaction cannot be extended to stereogenic or non-substituted silyl enol ethers; these compounds are totally inert under the reaction conditions employed. However, the failure of these reactions simply reflects insufficient activation (or excessive deactivation) of the catalysts studied. This problem may therefore be overcome by modifying the electronic properties of the two oxazoline ligands.

### (iii) Mukaiyama–Michael reaction

A significant test for our Lewis acid systems was the Mukaiyama–Michael reaction<sup>17</sup> (Scheme 4), which has never

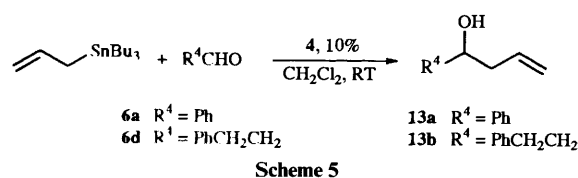


been explored with transition metal Lewis acid catalysts. Complexes **3** and **4** do, however, efficiently promote this reaction. After non-acidic work-up a mixture of silyl enol ethers can be isolated; hydrolysis affords the corresponding dicarbonyls in good yield.

As with our experiences of the Mukaiyama cross-aldol reactions catalysed by **3** and **4**, these reactions proceed without obvious reduction of the metal centre.

### (iv) Catalytic allylation

Lewis acid-promoted allylation of carbonyls has recently been reported in a catalytic, enantioselective manner.<sup>18</sup> The bis(oxazoline) catalysts studied here also promote catalytic allylation with allyltributylstannane, although no reaction was observed with allyltrimethylsilane (Scheme 5). Results are summarized in Table 3.



With the titanium complex **3** the allylstannane was added to the Lewis acid prior to the carbonyl substrates. However, since aromatic aldehydes require 2 days at room temperature to react completely, we considered the order of addition to

**Table 3** Catalytic allylation

Entry <sup>a</sup>	Aldehyde	Time (t/h)	Product	Yield (%) <sup>b</sup>
1	<b>6a</b>	24	<b>13a</b>	74 <sup>c</sup>
2	<b>6a</b>	24	<b>13a</b>	84
3	<b>6d</b>	24	<b>13b</b>	68
4	<b>6a</b>	48	<b>13a</b>	82
5	<b>6a</b>	24	<b>13a</b>	0 <sup>d</sup>
6	<b>6d</b>	48	<b>13b</b>	0

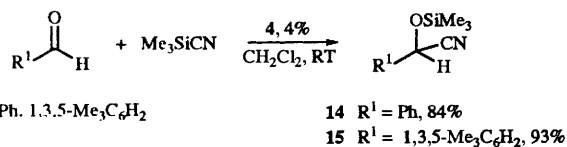
<sup>a</sup> All the reactions were carried out at room temperature using 1.0 cm<sup>3</sup> of allyltributylstannane, 1.0 mmol of aldehyde, and 0.10 mmol of the catalyst **4**, unless otherwise stated. <sup>b</sup> Isolated yields. <sup>c</sup> 1.5 mmol of allyltributylstannane were employed. <sup>d</sup> Allyltrimethylsilane was used.

be unimportant. After 20 min the titanium complex changes colour, suggesting the formation of a new species. For **4** addition of allylstannane at room temperature in CH<sub>2</sub>Cl<sub>2</sub> gives an immediate fine grey-black precipitate whilst the solution becomes light yellow. The reaction was repeated in CD<sub>2</sub>Cl<sub>2</sub> and monitored by <sup>1</sup>H NMR spectroscopy. After 1 h, a maroon solid settles leaving a clear solution. <sup>1</sup>H NMR showed a broadening of the allyl region of the allyltributylstannane.

Stoichiometric addition of allylstannane to compound **4** on a large scale followed by stirring of the reaction mixture for 24 h allowed the maroon solid to be isolated. Although insoluble in CD<sub>2</sub>Cl<sub>2</sub>, IR spectroscopy revealed an absorption characteristic of the presence of an oxazoline along with other unassigned stretching modes. A small quantity of the solid was suspended in CH<sub>2</sub>Cl<sub>2</sub> and benzaldehyde and the allylstannane reagent were added; the solid does indeed function as an active catalyst for the allylation. The solution upon filtration and evaporation gave a white solid which was shown to be Bu<sub>3</sub>SnOTf (by <sup>19</sup>F NMR). As reported previously, the reaction of allyltributylstannane with [TiCl<sub>2</sub>(binol)<sub>2</sub>] gave tributylstannyl chloride.<sup>18</sup> The exact nature of the solid isolated here and the mechanism will be addressed in the future.

#### (v) Catalytic hydrocyanation

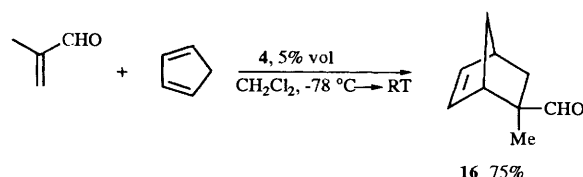
The catalytic asymmetric addition of Me<sub>3</sub>SiCN to carbonyl groups affords versatile synthetic species bearing two easily manipulated functional groups which have been used to prepare a wide range of homochiral products, such as α-hydroxy acids, α-hydroxy aldehydes, α-hydroxy ketones and α-amino acid derivatives<sup>19</sup> (Scheme 6). The ability of compounds **3** and **4** to catalyse the addition of Me<sub>3</sub>SiCN to two aromatic aldehydes is one of the reported uses of early transition metal Lewis acids in this field. Addition of the silyl nucleophile to the catalyst in a NMR tube does not lead to the formation of trimethylsilyl triflate. This marked difference from observations recorded above with the tin nucleophile leads us to suggest a simple activation of the carbonyl substrate as the operative reaction mechanism in the latter series of experiments.

**Scheme 6**

#### (vi) Diels–Alder and hetero–Diels–Alder reactions

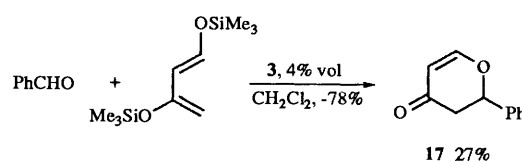
Although a number of chiral catalysts have been claimed to promote the Diels–Alder cycloaddition<sup>20</sup> of a carbonyl and a diene, high enantiomeric excesses have been observed only with highly reactive α,β-unsaturated oxazoline dienophiles<sup>21</sup> or with α-β unsaturated aldehydes.<sup>20</sup>

[M(cp)<sub>2</sub>(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] (M = Ti, Zr) promote the Diels–Alder reaction catalytically in low yield.<sup>6</sup> However, with intrinsically slow dienophiles, diene polymerisation can compete. Catalysts **3** and **4** are less active Lewis acids than their metallocene relatives and, consequently, diene polymerization is not promoted. However, they only show Diels–Alder catalytic activity with two very reactive cycloaddition partners. With other substrates, or with milder conditions than those shown (Scheme 7), no product is obtained.

**Scheme 7**

Studies into the cycloaddition chemistry of the extremely reactive Danishefsky diene<sup>22</sup> revealed an instantaneous reaction on mixing with **3** and **4** at room temperature to form decomposition products.

At low temperature the Danishefsky diene reacts with benzaldehyde to give the expected product, but only in low yield (Scheme 8). Attempts to increase the yields by changing the

**Scheme 8**

reaction conditions were unsuccessful. We therefore feel that it is reasonable to suppose that in this example the product strongly inhibits further reaction.

In conclusion, bis(oxazoline) ligated transition metal Lewis acids display activity for almost all commonly encountered Lewis acid-promoted reactions. The high degree of certainty concerning the structure of the active catalytic site and the possibility of making fine adjustments to the stereoelectronic properties of the oxazoline ancillaries should allow us to improve systematically the reactivity and selectivity of the reactions described herein. ‡

## Experimental

### General

All manipulations of air- and/or moisture-sensitive materials were performed on a vacuum/nitrogen atmosphere line using Schlenk and cannular techniques, or in a nitrogen-filled glove box. IR spectra were recorded using KBr windows. NMR spectra, <sup>1</sup>H (200.13 MHz) and <sup>13</sup>C (50.32 MHz), were recorded on a Bruker AC200-instrument. The following abbreviations have been used for band multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Chemical shifts are quoted as δ in ppm with respect to the following references: <sup>13</sup>C (C<sub>6</sub>D<sub>6</sub>, 128.7 ppm); <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 7.15 ppm, C<sub>7</sub>D<sub>8</sub> 2.35 ppm). Complexes **1** and **2** were prepared as reported.<sup>11</sup> Silver triflate, 1-methoxy-1-trimethylsiloxy-2-methylpropene, trimethylsilyloxycyclopentene,

‡ We have obtained low enantiomeric excesses in catalytic allylation using optically active oxazoline complexes. This fact implies that the weak Lewis acid Me<sub>3</sub>SiOTf, presumed to form in the catalytic cycle, is not the catalyst of these reactions.

allyltributylstannane, allyltrimethylsilane, and Danishefsky diene are commercially available. Imines were prepared as described.<sup>23</sup> 1-*tert*-Butoxy-(*E*)-1-dimethyl-*tert*-butylsiloxy-2-methylpropene and 1-phenyl-1-trimethylsiloxyethene were prepared by standard procedures.<sup>24</sup> Selected examples of the use of compounds **3** and **4** are described for Lewis acid-promoted reactions. All of the chiral products were obtained in the racemic form; **7a**, **8a**;<sup>14</sup> **7b**, **8b**;<sup>25</sup> **7c**, **8c**;<sup>26</sup> **7d**, **8d**;<sup>27</sup> **7e**, **8e**;<sup>28</sup> **7g**, **8g**;<sup>29</sup> **7h**, **8h**;<sup>30</sup> **13a**,<sup>31</sup> **14**;<sup>32</sup> **16**;<sup>33</sup> and **17**<sup>34</sup> are known compounds.

#### Preparation of complex **4**

AgOSO<sub>2</sub>CF<sub>3</sub> (1.42 g, 5.52 mmol) was added to a solution of complex **2**<sup>11</sup> (1.45 g, 2.02 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (80 cm<sup>3</sup>), and the mixture was stirred in the dark for 6 h at room temperature. AgCl was filtered off and the filtrate was evaporated. Et<sub>2</sub>O (40 cm<sup>3</sup>) was added to the white residue and the resulting solid was collected and dried *in vacuo* (1.2 g, 68%); δ<sub>H</sub>(CD<sub>2</sub>Cl<sub>2</sub>) 7.94 (dd, *J* 8.1, 1.1, more intense), 7.7 (d, *J* 7, less intense), 7.59 (dt, *J* 7.2, 1.1, more intense), 7.48 (t, *J* 7.4, less intense), 7.1–6.6 (m), 4.69 (s), 4.37 (AB, *J* 8.75) and 2–0.5 (m). The complexity of the NMR spectra, owing to the probable aggregation of the compound, does not allow clear-cut assignments; ν<sub>max</sub>/cm<sup>-1</sup> 1604.9, 1582.4 and 1580.5 (Found: C, 37.3; H, 3.25; N, 3.6. Calc. for C<sub>24</sub>H<sub>24</sub>F<sub>6</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub>Zr: C, 37.44; H, 3.12; N, 3.64 %).

#### Preparation of complex **3 in situ**

AgOSO<sub>2</sub>CF<sub>3</sub> (0.15 g, 0.57 mmol) was added to a dark red solution of complex **1**<sup>11</sup> (0.12 g, 0.285 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 cm<sup>3</sup>), and the mixture was stirred in the dark for 2 h. AgCl was filtered off and the filtrate was evaporated and the residue dried and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (80 cm<sup>3</sup>). The resulting red solution was considered 3.56 × 10<sup>-3</sup> mol dm<sup>-3</sup> in the catalyst.

#### Preparation of complex **4 in situ**

AgOSO<sub>2</sub>CF<sub>3</sub> (0.146 g, 0.57 mmol) was added to a colourless solution of complex **2**<sup>11</sup> (0.36 g, 0.66 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 cm<sup>3</sup>), and the mixture was stirred in the dark at room temperature over 3 h. AgCl was filtered off and the filtrate was evaporated to afford a white solid which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (120 cm<sup>3</sup>). The resulting colourless solution was considered 3.658 × 10<sup>-3</sup> mol dm<sup>-3</sup> in the catalyst **4**.

#### NMR study in CD<sub>2</sub>Cl<sub>2</sub>

A standard solution of complex **4** was prepared in a dry box with **4** (0.036 g) and CD<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>). PhCHO (0.016 cm<sup>3</sup>, 0.15 mmol) was added to this solution (0.6 cm<sup>3</sup>, 0.015 mmol) in a NMR tube, which was then sealed; the NMR spectrum was recorded at 293, 253 and 213 K: δ<sub>H</sub>(CD<sub>2</sub>Cl<sub>2</sub>, 213 K): δ 11.8 (s, 1 H, CHO), 9.1–8.6 (m, 5 H, Ph) (complexed PHCHO). For the other temperatures the complexed PHCHO was not visible.

#### Preparation of compounds **7a** and **8a** (Table 1, entry 2)

PhCHO **6a** (0.113 cm<sup>3</sup>, 1.12 mmol) and 1-methoxy-2-methyl-1-trimethylsiloxypropene **5a** (0.25 cm<sup>3</sup>, 1.24 mmol) were added to a solution of complex **4** (10 cm<sup>3</sup>, 0.036 mmol) at -78 °C, and the solution was stirred for 2 h. The reaction was quenched with saturated aqueous NaHCO<sub>3</sub> (15 cm<sup>3</sup>), and the organic phase was separated. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 5 cm<sup>3</sup>) and the combined organic phases were dried and evaporated under reduced pressure to give an oil which was purified by flash chromatography (hexane–Et<sub>2</sub>O, 8:2) (93%); δ<sub>H</sub>(CHCl<sub>3</sub>) 7.30 (m, 5 H, Ph), 4.98 (s, 1 H, CHOSi), 3.70 (s, 3 H, OMe), 1.15 (s, 3 H, Me), 1.02 (s, 3 H, Me) and 0.09 (s, 9 H, SiMe<sub>3</sub>); ν<sub>max</sub>(liquid film)/cm<sup>-1</sup> 3030 and 1738 (Found: C, 64.5; H, 8.55. Calc. for C<sub>15</sub>H<sub>24</sub>O<sub>3</sub>Si: C, 64.25; H, 8.63%).

#### Preparation of compounds **7f** and **8f** (Table 1, entry 14)

PhCHO **6a** (0.126 cm<sup>3</sup>, 1.24 mmol) and 1-(trimethylsilyloxy)-cyclopentene **5c** (0.22 cm<sup>3</sup>, 1.24 mmol) were added to a solution of complex **4** (10 cm<sup>3</sup>, 0.038 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature and the solution was stirred over 4 h. The reaction was quenched with saturated aqueous NaHCO<sub>3</sub> (10 cm<sup>3</sup>) and the mixture worked up as described earlier. The silylated crude product was dissolved in THF (1 cm<sup>3</sup>) and hydrochloric acid (1 mol dm<sup>-3</sup>; 1 cm<sup>3</sup>) was added to the solution. The mixture was stirred at room temperature until the desilylation was completed (checked by TLC) after which it was diluted with water (4 cm<sup>3</sup>) and extracted with Et<sub>2</sub>O (2 × 10 cm<sup>3</sup>). The combined extracts were washed with brine, dried and evaporated under reduced pressure to give a clear oil which was purified by flash chromatography (hexane–Et<sub>2</sub>O, 1:1) (80%) (*syn*: *anti* 80:20); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.4–7.2 (m, 5 H, Ph), 5.28 (d, 1 H, *J* 2.6, CHO), 2.6–1.4 (m, 7 H), *syn* **7f**: 7.4–7.2 (m, 5 H, Ph), 4.70 (d, 1 H, *J* 9.1, CHO) and 2.6–1.4 (m, 7 H), *anti* **8f**; ν<sub>max</sub>(liquid film)/cm<sup>-1</sup> 3500 and 1735 (Found: C, 75.8; H, 7.3. Calc. for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>: C, 75.78; H, 7.36%).

#### Preparation of compound **10b** (Table 2, entry 2)

The imine **9b** (0.211 g, 1 mmol) and 1-methoxy-2-methyl-1-trimethylsiloxypropene **5a** (0.25 cm<sup>3</sup>, 1.24 mmol) were added to a solution of **4** (10 cm<sup>3</sup>, 0.004 mmol) in CH<sub>2</sub>Cl<sub>2</sub> and the yellow solution was stirred for 3 h at room temperature. EtOH (4 cm<sup>3</sup>) and HCl (2 mol dm<sup>-3</sup>) were added to the solution and the mixture was stirred at room temperature for 1 h; it was then diluted with water and the EtOH removed by evaporation. The mixture was basified with saturated aqueous NaHCO<sub>3</sub> and extracted with Et<sub>2</sub>O (2 × 10 cm<sup>3</sup>). The combined extracts were washed with brine, dried and evaporated under reduced pressure to afford a white solid purified by flash chromatography (hexane–acetone, 8:2) (85%); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.32 (m, 5 H), 6.58 (AA', BB' system, 4 H, *J* 8.7, *p*-MeOC<sub>6</sub>H<sub>4</sub>), 4.5 (br s, 1 H, CHPh), 3.71 (s, 6 H, OCH<sub>3</sub> and *p*-MeOC<sub>6</sub>H<sub>4</sub>), 1.30 (s, 3 H, Me) and 1.21 (s, 3 H, Me); ν<sub>max</sub>(Nujol)/cm<sup>-1</sup> 1730, 1493 and 1455 (Found: C, 72.1; H, 7.3; N, 4.4. Calc. for C<sub>19</sub>H<sub>23</sub>NO<sub>3</sub>: C, 72.82; H, 7.40; N, 4.47%).

#### Preparation of compound **13a** (Table 3, entry 4)

PhCHO (0.037 cm<sup>3</sup>, 0.373 mmol) and allyltributylstannane (0.114 cm<sup>3</sup>, 0.373 mmol) were added to a solution of complex **4** (10 cm<sup>3</sup>, 0.0373 mmol) in CH<sub>2</sub>Cl<sub>2</sub> and the mixture was stirred for 2 days at room temperature then quenched by the addition of saturated aqueous NaHCO<sub>3</sub>. The organic phase was separated and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 cm<sup>3</sup>). The combined organic phases were washed with brine, dried and evaporated under reduced pressure to afford an oil which was purified by flash chromatography (hexane–Et<sub>2</sub>O, 7:3) (82%); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.37–7.27 (m, 5 H, Ph), 5.9–5.7 (m, 1 H, C=CH), 5.19–5.1 (m, 2 H, CH<sub>2</sub>=), 4.71 (m, 1 H, CHO), 2.53–2.48 (m, 2 H, CH<sub>2</sub>) and 2.24 (d, 1 H, *J* 7.4, OH); ν<sub>max</sub>(liquid film)/cm<sup>-1</sup> 3400, 1640 and 1500 (Found: C, 81.1; H, 8.05. Calc. for C<sub>10</sub>H<sub>12</sub>O: C, 81.04; H, 8.16%).

#### Stoichiometric addition of allyltributylstannane to complex **4**

Allyltributylstannane (0.543 cm<sup>3</sup>, 1.769 mmol) was added to a stirred suspension of complex **4** (0.8 g, 1.479 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>). Immediately a maroon solid started to precipitate. The mixture was stirred at room temperature for 1 day after which the precipitate was filtered off and dried *in vacuo*. The filtrate was evaporated under reduced pressure and the white residue was analysed by <sup>19</sup>F NMR spectroscopy and shown to be tributyltin triflate; ν<sub>max</sub>/cm<sup>-1</sup> (collected insoluble solid) 1604 and 1530. A portion of isolated solid (0.053 g) was suspended in CH<sub>2</sub>Cl<sub>2</sub> and allyltributylstannane (0.6 cm<sup>3</sup>, 1.8 mmol) and PhCHO (0.15 cm<sup>3</sup>, 1.48 mmol) were added. The solution was

stirred at room temperature for 2 days and worked up as previously described to give 1-phenyl-but-3-en-1-ol.

#### Preparation of compound 13b (Table 3, entry 3)

The 3-phenylpropionaldehyde **6d** (0.05 cm<sup>3</sup>, 0.373 mmol) and allyltributylstannane (0.125 cm<sup>3</sup>, 0.4102 mmol) were added to a solution of complex **4** (10 cm<sup>3</sup>, 0.0373 mmol) in CH<sub>2</sub>Cl<sub>2</sub> and the solution was stirred at room temperature for 2 days. The reaction was quenched with saturated aqueous NaHCO<sub>3</sub> and the organic phase was separated. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 cm<sup>3</sup>) and the combined organic phases were washed with brine, dried and evaporated under reduced pressure to afford an oil which was purified by flash chromatography (hexane–Et<sub>2</sub>O, 6:4) (68%); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.38–7.23 (m, 5 H, Ph), 5.88–5.29 (m, 1 H, =CH), 5.24–5.15 (m, 2 H, CH<sub>2</sub>=), 3.73–3.71 (m, 1 H, CH<sub>2</sub>CH=), 2.6–2.3 (m, 2 H, CH<sub>2</sub>Ph) and 2.0–1.7 (m, 2 H, CH<sub>2</sub>CHOH); ν<sub>max</sub>(liquid film)/cm<sup>-1</sup> 3350, 2940 and 1650 (Found: C, 81.75; H, 9.0. Calc. for C<sub>12</sub>H<sub>16</sub>O: C, 81.77; H, 9.15%).

#### Preparation of compound 11 (Scheme 4)

Methyl vinyl ketone (0.100 cm<sup>3</sup>, 1.246 mmol) and 1-methoxy-1-trimethylsiloxy-2-methylpropene **5a** (0.253 cm<sup>3</sup>, 1.246 mmol) were added to a solution of complex **4** (10 cm<sup>3</sup>, 0.0373 mmol), and the mixture was stirred for 6 h at room temperature. The reaction was quenched with saturated aqueous NaHCO<sub>3</sub> and worked up as described earlier. The crude product was dissolved in THF (5 cm<sup>3</sup>) and hydrochloric acid (3 mol dm<sup>-3</sup>; 5 cm<sup>3</sup>) was added to the solution. After the mixture had been stirred at room temperature for 1 h it was diluted with water and the THF removed by evaporation. The residue was extracted with Et<sub>2</sub>O (2 × 15 cm<sup>3</sup>) and the combined extracts were washed with brine, dried and evaporated under reduced pressure to give an oil purified by flash chromatography (hexane–Et<sub>2</sub>O, 7:3) (60%); δ<sub>H</sub>(CDCl<sub>3</sub>) 3.68 (s, 3 H, OMe), 2.46–2.39 (m, 2 H, CH<sub>2</sub>CO), 2.17 (s, 3 H, CH<sub>3</sub>CO), 1.87–1.78 (m, 2 H, CH<sub>2</sub>) and 1.20 (s, 6 H, Me); for **11** ν<sub>max</sub>(liquid film)/cm<sup>-1</sup> 2980, 1740 and 1720 (Found: C, 62.8; H, 9.3. Calc. for C<sub>9</sub>H<sub>16</sub>O<sub>3</sub>: C, 62.77; H, 9.36%).

#### Preparation of compound 15 (Scheme 6)

AgOSO<sub>2</sub>CF<sub>3</sub> (0.1 g, 0.394 mmol) was added to a solution of complex **4** (0.129 g, 0.197 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>), and the mixture was stirred in the dark for 2 h. AgCl was filtered off and mesitylaldehyde (0.57 cm<sup>3</sup>, 3.945 mmol) and trimethylsilyl cyanide (0.49 cm<sup>3</sup>, 3.94 mmol) were added to the filtrate. The mixture was stirred for 1 h at room temperature after which the reaction was quenched with saturated aqueous NaHCO<sub>3</sub>. The organic phase was separated and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 cm<sup>3</sup>). The combined organic phases were washed with brine, dried and evaporated under reduced pressure to afford an oil which was purified by flash chromatography (hexane–Et<sub>2</sub>O, 9:1) (93%); δ<sub>H</sub>(CDCl<sub>3</sub>) 6.95 (s, 2 H, Ph), 5.9 (s, 1 H, CHOSi), 2.52 (s, 6 H, Me), 2.44 (s, 3 H, Me) and 0.28 (s, 9 H, SiMe<sub>3</sub>); ν<sub>max</sub>(liquid film)/cm<sup>-1</sup> 2980, 2880 and 2250 (Found: C, 67.7; H, 8.45; N, 5.6. Calc. for C<sub>14</sub>H<sub>21</sub>NOSi: C, 67.97; H, 8.56; N, 5.66%).

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