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**Novel Titanocene-Tartrate complexes as catalysts for the asymmetric  
epoxidation of allylic alcohols**

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## **Abstract**

This communication presents the synthesis of novel titanocene-based chiral complexes and their application as catalysts for asymmetric oxidation reactions. These new complexes drive the catalytic asymmetric oxidation of allylic alcohols without the requirement of low temperature conditions, a usual drawback in asymmetric synthesis. Results from catalytic studies shows the enantioselectivity of these chiral complexes strongly depends on the steric hindrances caused by the chiral ligand and the alkyl hydroperoxide oxidant around the titanium centre.

## **1. Introduction**

Asymmetric oxidation is a powerful tool for the synthesis of enantiopure optically active compounds since unexpensive prochiral substances can be easily transformed into a large variety of enantiopure chiral chemicals [1, 2]. The Sharpless asymmetric epoxidation is one of the most powerful tools in this field [3] in spite of the requirement of low temperature conditions to achieve proper epoxide yields and high enantiomeric excess onto the final products, as many others in asymmetric oxidation. This requirement involves large operation costs restricting the application of asymmetric oxidation to a high scale production.

This work was initially focused on the preparation of new organometallic complexes able to catalyze the epoxidation of allylic alcohols at high temperatures, keeping high asymmetric activity to overcome this restriction. The new catalysts are based on titanocene dichloride instead of the usual titanium alkoxides, in an attempt to induce the asymmetric activity of the resultant complex through the presence of the bulky cyclopentadienyl rings around the metal centre and the important steric hindrances caused by. Chiral metallocene complexes have been applied before in the asymmetric catalysis of many types of reactions [4, 5], transferring enantioselectivity to the final product by means of the chirality located at the aromatic rings.

This function can also be developed by other compounds directly coordinated to the metallic centre, like the BINAP and BINOL ligands which have used together with titanocenes in asymmetric oxidation reactions [4-6].

The complexes reported in this work can be included in the group of the catalysts where the chiral ligand supports the asymmetric ability. Combining titanocene dichloride and dialkyltartrates leads to novel organometallic complexes being highly enantioselective in the oxidation of allylic alcohols.

## **2. Experimental**

### *2.1 General procedures*

All reactions were carried out under inert atmosphere using standard schlenck techniques. All reagents and solvents were distilled prior their use as follows:  $\text{CH}_2\text{Cl}_2$  (Scharlab) and  $\text{CHCl}_3$  (Scharlab) with  $\text{P}_2\text{O}_5$ , toluene (Aldrich) with Na, triethylamine (Aldrich) with  $\text{H}_2\text{Ca}$ . Titanocene dichloride was purified by recrystallization from dry toluene. Dialkyltartrates where distilled under vacuum prior their use in the synthesis of the complexes. Anhydrous TBHP solution in  $\text{CH}_2\text{Cl}_2$  was prepared accordingly to methods described in literature [7].

### *2.2 Synthesis of titanocene-tartrate complexes*

Titanocene-Tartrate complexes can be synthesized as follows: In a typical synthesis  $\text{Cp}_2\text{TiCl}_2$  (4 mmol), dialkyltartrate (4 mmol) and triethylamine (16 mmol) are dissolved in 50 mL of dry dichloromethane at room temperature. The resultant solution is then stirred for 72 hours under inert atmosphere before being concentrated in vacuo to give a light-brown solid. The solid thus obtained is suspended in dry toluene where the formed adduct (triethylamine hydrochloride;  $\text{NEt}_3\cdot\text{HCl}$ ) precipitates, allowing its separation, whereas the titanocene-tartrate complex remains dissolved. The clear solution obtained after filtration is concentrated in vacuo to give the corresponding chiral-titanocene complex which is used in the catalytic tests.

### *2.3 Catalyst characterization*

The titanocene-tartrate complexes have been characterized by means of different techniques.  $^1\text{H}$  and  $^{13}\text{C}$  NMR analysis were recorded in a Varian Mercury 400 MHz spectrometer. The carbon:titanium molar ratio was calculated by combination of ICP Atomic Emission Spectroscopy to determine the titanium and elemental analysis for the quantification of the carbon and hydrogen contents. FTIR analyses of solutions of titanocene-tartrate complex in methylene chloride were collected on a Mattson infinity series spectrometer.

### *2.4 Catalytic tests*

Several allylic alcohols were epoxidized with alkyl hydroperoxides in order to determine the catalytic activity of the titanocene tartrate complexes. Unless otherwise noticed, the reaction media was tuned by ageing the catalyst in presence of the oxidant for 1 hour before adding the substrate by dropping. The enantiomeric excess was determined by chiral-HPLC analysis using a (S,S)-Whelk-01 column operating in isocratic conditions of 89:11 v/v n-heptane:isopropyl alcohol, recording the chromatogram at 217 and 254 nm for quantification purposes.

## **3. Results and discussion**

### *3.1. Catalysts characterization*

$^1\text{H}$  and  $^{13}\text{C}$  chemical shifts obtained from the NMR analyses of the titanocene-tartrate complexes have been depicted in table 1. The comparison of the areas associated to different proton signals indicates the presence of one cyclopentadienyl ring for each tartrate ligand. Thus, these results reveal the loss of a Cp ring from the titanium coordination environment in the titanocene tartrate complexes. Unlike the presence of chloride atoms directly attached to the titanium centre that stabilizes the Cp ring in the titanocene complexes, the substitution of the halogen atoms by the tartrate ligand might destabilize the cyclopentadienyl functionalities, both by electronic and steric factors. Additionally it should be considered the

short alkyl chain used to create the titanate cycle with the tartrate ligand, only two carbons leading to a five membered ring, creates a considerable strain [8] that could be relaxed by the loss of a cp ring. Additionally, the stability of the resultant complex can be increased by the aggregation of the titanate complexes to form oligomeric species..

The atomic compositions achieved for the prepared complexes point to carbon:titanium atomic ratios corresponding to one Cp ring per tartrate ligand (Table 2), confirming the loss of a cyclopentadienyl ligand from the starting organometallic complexes. In the same way it is also interesting to note that chlorine was not detected, suggesting a complete conversion of the starting titanocene dichloride.

The lost of the cyclopentadienyl ligand from the titanium coordination sphere leads a coordination unsaturation which facilitates the entrance of the allyl alcohol as well as the alkyl hydroperoxide to catalyze the oxidation reaction.

FTIR analyses, recorded for the initial precursors and the titanocene-tartrate complexes are depicted in figure 1. These analyses confirm the removal of the hydroxyl functionalities located at the tartrate ligands, since the band located at  $3560\text{ cm}^{-1}$ , which is attributed to the bond stretching of the hydroxyl groups, is absent in the spectra recorded for the different titanocene-tartrate complexes. It is also noteworthy the decrease of the intensity of the signal centred at  $3100\text{ cm}^{-1}$  (stretching vibration of the C-H bond at the cyclopentadienyl ligands), as a consequence of the loss of the Cp ring in the titanocene-tartrate system, accordingly to the above discussed NMR and chemical analysis results. On the other hand, signals around  $1680\text{ cm}^{-1}$  shows up in the titanocene-tartrate spectra. These bands might be indicative of an interaction between the carbonyl functionalities of the ester groups at the tartrate ligands and the titanium centre in the titanocene tartrate complexes in a similar way to that described for carboxilate groups attached to metallocene species [9]. The result of this interaction is usually a higher stability of the resultant organometallic complexes.

From the characterization of the titanocene tartrate complexes it can be concluded the presence of one Cp ring per tartrate ligand and titanium centre. The starting titanocene dichloride is totally converted since no chlorine content has been detected at the resultant titanocene tartrate complex. Finally, these organometallics seems to be stabilized by the interaction of the carbonyl functionalities at the ester fragments of the tartrate ligands with the metallic centre. Further experiments are being developed in order to determine the complete structure of these organometallics.

### 3.2. *Catalytic activity*

The study on the catalytic activity of the titanocene-tartrate complexes was initially focused on determining the effect of the temperature in the range from -20 to 20°C. Likewise, different dialkyl-tartrates were used as chiral ligands in this initial investigation. The results obtained in this study are shown in Table 3.

Reference runs (Table 3, entry 1) have been performed using the  $\text{Ti}(\text{OiPr})_4$ -dimethyl tartrate Sharpless catalyst. As it is well known, the temperature affects the enantioselective behaviour of this catalyst achieving higher enantiomeric excess when lower temperature values are used. Thus, when increasing temperature from -20°C to 20°C (entry 1) a clear decrease on the enantiomeric excess is achieved. This reduction in enantioselectivity is accompanied by a decrease in the epoxide yield, because the Sharpless catalyst becomes less active when increasing temperature. This behaviour is usually attributed to the ligand acceleration effect caused by the coordination of the tartrate ligand to the titanium centre [10], which occurs in a higher extent at low temperatures because of a better assembly between the titanium centre and the chiral ligand.

Blank reactions (entry 2) have been performed in the presence of a mixture of commercial titanocene dichloride and dimethyl tartrate in order to determine the catalytic and enantioselective behaviour in absence of previous reaction both components. Unlike the case

of low temperature conditions where a negligible catalytic effect was noticed ( $-20^{\circ}\text{C}$ ), an increase of the temperature leads to a moderate epoxide yield (0 and  $20^{\circ}\text{C}$ ), although no enantioselective induction was detected. This fact shows that no coordination between the tartrate ligand and the titanium atom occurs under these conditions, and thus the asymmetric activity is not transferred to the catalytic centre. On the other hand, some epoxide yield is achieved at higher temperatures indicating that the TBHP acts as a ligand strong enough to displace the groups coordinated to the titanium atom, forming the peroxometallic cycle [11] which it is supposed to be the oxidant specie. These results confirm that the mixture of the titanocene and the tartrate does not induce enantioselectivity in epoxidation reactions.

Catalytic assays using different titanocene-tartrate have been carried out varying the temperature conditions (table 3; entries 3-5). Regarding the catalytic behaviour, the titanocene-tartrate complexes have been found to increase the epoxide yields at higher temperatures, the opposite situation found for the Sharpless catalyst. This difference could be related to the different interaction of the tartrate ligands and the titanium species in the Sharpless catalyst and in the titanocene-tartrate system. This assembly causes the ligand accelerated catalysis (LAC) effect on the Sharpless system [10] and since the coordination is closed when lower temperatures are used [7], it is supposed LAC is more important when decreasing temperature. On the other hand, unlike the Sharpless catalyst is formed accordingly to a ligand exchange equilibrium, the synthesis of the titanocene tartrate complexes are forced by the triethylamine and there is almost no reversibility. Moreover, the opposite relationship of the activity of these catalysts with temperature suggests these complexes are not influenced by the LAC effect.

In regards to the enantioselectivity, the experiments show that the titanocene tartrate complexes induce enantiomeric excess independently from temperature, confirming a completely different behaviour for the titanocene-tartrate complex compared to the Sharpless



catalyst [7]. Decreasing temperature reduces the fluxional nature of the Sharpless catalyst [12], and under those conditions the resultant stiffness around the metal centre leads to remarkable steric hindrances that are the origin of the enantioselectivity. The independence on temperature of the asymmetric activity from the titanocene-tartrate complexes indicates that the transitions between different conformations are clearly restricted, probably as a consequence of the presence of cyclopentadienyl ligands. Unlike the Sharpless catalyst where the dialkyl-tartrate chiral ligand is the only group that provides steric hindrances, the cyclopentadienyl groups at the titanocene-tartrate complexes induce additional steric restrictions around the metal centre, avoiding the fluxional phenomena. Thus, in this case there is no need to decrease temperature in order to achieve stiffness at the catalytic centre, leading to similar enantioselectivities independently from temperature.

Using different substituents at the tartrate chiral ligand indicates that bulkier tartrates steer higher epoxide yields. In this case, the catalytic behaviour is quite similar to that found for the Sharpless catalyst where an improvement of the catalytic activity has been also observed when using bulkier tartrate ligands [13]. In the same sense, increasing the size of the substituents at the ester groups of the tartrate ligands provides higher enantioselectivities, for the same reasons already mentioned.

Since the oxidant reagent has been proved to play a crucial role in the enantioselectivity of the Sharpless epoxidation catalyst [14], in the second part of this research work different variables related to the hydroperoxide have been investigated: the size of the alkyl chain and the oxidant:catalyst molar ratio.

The effect of the hydroperoxide alkyl chain size has to do with the creation of additional steric hindrances around the metal centre and it has been determined by comparison between cumyl (CHP) and *tert*-butyl (TBHP) hydroperoxides (table 4, entries 1 and 2). The size of the oxidant molecule seems to provide the same effect than the chiral tartrate does: the bulkier

oxidant the higher enantioselectivity is achieved, supporting the above mentioned conclusions. On the other hand, the epoxide yield decreases when CHP is used, probably because of the access of the reactants to the metal centre is partially hindered due to the same steric restrictions that result in an enantioselectivity improvement. This behaviour has also been observed for the Sharpless catalyst when epoxidising certain allylic alcohols [15].

The oxidant:catalyst molar ratio affects the stoichiometry of the complex, since the oxidant competes for the coordination to the titanium atom and therefore, the change in the ratio of the reactants would affect the activity and enantioselectivity of the titanocene-tartrate complex. This parameter has been varied in the range 10-40 (Table 4, entries 2, 3 and 4). A decrease in the concentration of this reactant leads, as expected, to a lower epoxide yield [16] whereas the enantioselectivity is clearly increased. This behaviour supports the hypothesis of a displacement of the chiral ligand from the metal coordination sphere by the hydroperoxide when this compound is used in high concentrations. Under this situation, the number of enantioselective catalytic species decreases in the reaction media achieving a lower enantiomeric excess.

Although tartrate is a bidentate ligand and it shows a much higher binding constant than a monodentate ligand [13], *t*-butyl hydroperoxide coordinates to the titanium centre through a bidentate bonding [11, 12] and in this way its binding constant could be high enough to displace the diol. In order to check this supposition, two experiments were carried out, ageing the catalyst in the presence either of the substrate or the oxidant respectively, adding the other reactant by dropping (Table 4 entries 4 and 5). The reaction carried out ageing the catalyst in the presence of the substrate leads to higher epoxide yield and enantioselectivity compared to the reaction aged in the presence of the hydroperoxide. This behaviour supports the idea of a competence for the coordination to the metal centre between the hydroperoxide and the tartrate ligand and thus, a high concentration of the oxidant could lead to a displacement of

the chiral ligand from the titanium coordination sphere resulting in a lower enantioselectivity of the epoxidation process.

The results have prompted us to check the dependency of the titanocene-based catalyst on the ageing time, the contact time between the catalyst and the reactants before the reaction is started. This parameter is crucial in the case of the Sharpless catalyst since it allows the assembly between all the compounds that forms the optically active oxidant species of the Sharpless catalyst [7]. For this purpose, an additional experiment, excluding the catalyst ageing step has been carried out (table 4, entry 6). The results for this reaction are quite similar to those obtained for the catalyst aged during 1 hour (table 4, entry 4). The similarity between both catalytic tests suggests the coordination rate of the oxidant alkyl hydroperoxide to the catalytic centre is fast enough to disregard the ageing step in the epoxidation process.

Finally, a final study has been tackled in order to evaluate the applicability range of these catalysts to the epoxidation of different allylic alcohols. Table 5 contains the results of the epoxidation of different substrates using TBHP as oxidant and titanocene-DIPT as catalyst. It is notheworthy, all of the substrates are epoxidised in a lower extent than that obtained for the cinnamyl alcohol (table 4, entry 4). The reason for this behaviour should be located at the substituents of the double bond in the allylic alcohol, leading a lower activation of the unsaturation. Thus, while allyl alcohol (table 5, entry 1) lead to the lower epoxide yield, the substrate conversion raises when increasing the inductive electronic effect over the activation of the double bond, as it occurs in substrate 5 and also in the cinnamyl alcohol. Additionally, cis-allylic alcohols are converted in a lower extension than their trans-analogues, in a similar way to that found for the Sharpless catalytic system. Regarding to the enantioselectivity of the process it is also interesting all the substrates tested in this study are epoxidized with notable asymmetric induction, confirming the versatility of the titanocene-tartrate complexes

as catalysts for asymmetric epoxidation, although enantiomeric excess should be improved in certain cases like the cis-allylic alcohols or the deactivated allyl alcohol

#### **4. Conclusions**

Titanocene-tartrate complexes show high catalytic activity in the asymmetric epoxidation of cinnamyl alcohol with alkyl hydroperoxides, being the chiral activity, unlike the Sharpless catalyst, non dependent on the temperature conditions. Moreover the catalytic activity of the titanocene tartrate catalysts follows the classical trend with temperature, the higher temperature the higher activity. Steric hindrances around the titanium centre, either caused by the tartrate ligand or the oxidant agent, seem to influence the enantioselectivity of the titanocene-tartrate catalyst. Finally, these new asymmetric complexes promote the asymmetric oxidation of different allylic alcohols with significant ee. Although the catalytic activity of the titanocene-tartrate catalysts is quite high, enantioselectivity is not still good enough and further experiments are being developed to improve this parameter.

#### **Acknowledgements**

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**Table 1**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR data for the different Titanocene Tartrate complexes.<sup>a</sup>

Tartrate ligand		-OR	-CH-O	$\text{C}_5\text{H}_5$ ring <sup>b</sup>	-COO-
Dimethyl	$^1\text{H}$	3.84 (6H)	3.12 (2H)	6.59 (5H)	---
	$^{13}\text{C}$	52.0	71.8	118.7	171.9
Diethyl	$^1\text{H}$	1.30 (6H); 4.39 (4H)	3.14 (2H)	6.65 (5H)	---
	$^{13}\text{C}$	14.1; 62.5	71.9	117.7	171.5
Diisopropyl	$^1\text{H}$	1.31 (12H); 5.14 (2H)	3.10 (2H)	6.50 (5H)	---
	$^{13}\text{C}$	21.7; 70.4	72.0	118.5	171.1

<sup>a</sup> In  $\text{CDCl}_3$ ;

g

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**Table 2** Chemical composition of the Titanocene Tartrate complexes.

<b>Tartrate ligand</b>	<b>% C</b>	<b>% H</b>	<b>% Ti</b>	<b>% Cl</b>	<b>C/Ti <sup>a</sup></b>	<b>C/Ti 1Cp <sup>b</sup></b>
Dimethyl	43,152	6,068	15,615	--- <sup>c</sup>	11,0	11.0
Diethyl	46,351	6,564	13,381	--- <sup>c</sup>	13,8	13.0
Diisopropyl	48,968	7,206	11,940	--- <sup>c</sup>	16,4	15.0

<sup>a</sup> Atomic ratio; <sup>b</sup> Atomic ratio C/Ti for a hypothetical complex formed by 1 Cp and 1 Tartrate ligand per titanium centre. <sup>c</sup> Not detected

**R. van Grieken *et Al.***

**Table 3** Epoxidation of cinnamyl alcohol using titanocene tartrate complexes

Entry <sup>a</sup>	Ligand <sup>b</sup>	Catalytic results <sup>c</sup>		
		-20°C	0°C	+20°C
1 <sup>d</sup>	DMT	95 (90)	87 (74)	83 (57)
2 <sup>e</sup>	DMT	0 (--)	4 (--)	17 (--)
3	DMT	29 (16)	41 (15)	68 (15)
4	DET	38 (28)	56 (29)	74 (28)
5	DIPT	50 (40)	66 (39)	83 (40)

<sup>a</sup> All reactions were performed using 10 mol% Ti to substrate and TBHP:Substrate molar ratio 3:1. <sup>b</sup> Chiral ligand: DMT:dimethyl-tartrate, DET:diethyl-tartrate, DIPT:diisopropyl-tartrate. <sup>c</sup> Epoxide yield determined by direct weight of the purified products and enantiomeric excess (in brackets) determined by chiral HPLC. <sup>d</sup> Reference runs carried out using the Sharpless catalyst (Ti(OiPr)<sub>4</sub>-DMT). <sup>e</sup> Blank reactions carried out in the presence of titanocene dichloride and dimethyl tartrate without previous reaction.

**R. van Grieken *et Al.***



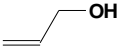
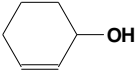
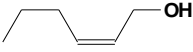
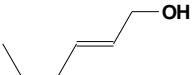
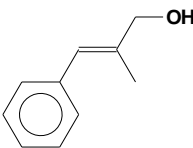
**Table 4** Effect of the oxidant on the catalytic behaviour.

Entry <sup>a</sup>	Oxidant	Oxidant:Catalyst molar ratio	Epoxide yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	CHP	40:1	45	63
2	TBHP	40:1	83	40
3	TBHP	20:1	78	70
4	TBHP	10:1	40	73
5 <sup>d</sup>	TBHP	10:1	55	80
6 <sup>e</sup>	TBHP	10:1	42	74

<sup>a</sup> Reactions performed in CH<sub>2</sub>Cl<sub>2</sub> using 10 mol% Ti, during 1 h in presence of titanocene-DIPT catalyst. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by chiral HPLC. <sup>d</sup> Catalyst aged in presence of the substrate - oxidant added by dropping. <sup>e</sup> Non-aged catalyst.

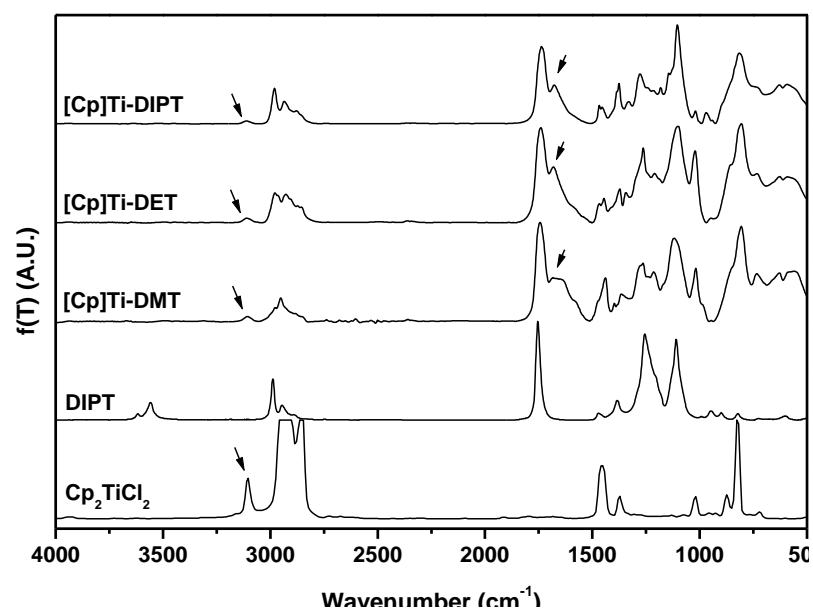
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**Table 5** Epoxidation of different allylic alcohols using titanocene-DIPT as catalyst.

Run <sup>a</sup> / Substrate	Epoxide Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1 	21	47
2 	29	60
3 	30	45
4 	34	67
5 	38	71

<sup>a</sup> Reactions performed in CH<sub>2</sub>Cl<sub>2</sub> during 1h at 20°C, using TBHP as oxidant and titanocene/DIPT as catalyst (10 mol%). <sup>b</sup> Isolated Yield. <sup>c</sup> Determined by chiral GC.

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**Figure 1** FTIR analysis of the titanocene-tartrate complexes and starting precursors

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