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Synthesis of titanium alkoxide complexes with alkyl lactate ligands. Asymmetric epoxidation of cinnamyl alcohol

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ABSTRACT

A family of titanium (IV) alkoxide compounds [{Ti(OPr^i)$_3$(OLact)}$_2$], and [Ti(OPr^i)$_2$(OLact)$_2$] (**1**–**6**) have been prepared by alcohol exchange of Ti(OPr^i)$_4$ and the corresponding alkyl-2-hydroxy-alkylpropionate or alkyl lactate (LactOH = Benzyl-(*S*)-lactate, methyl-(*S*)-3-phenyllactate and menthyl-(*S*)-lactate. These alkoxide titanium (IV) compounds have been characterized by spectroscopic and electrochemical techniques. In addition, these chiral Lewis acid titanium compounds have been studied in the asymmetric epoxidation of cynnamyl alcohol, the obtained results show that these complexes with dynamic behaviour in solution exert low control of the enantioselectivity. Electronic and sterical effects of the ligands in the catalytic results have been studied.

1. Introduction

Titanium compounds have been extensively investigated in the modern chemistry due to their presence in the environment, occurrence and effects on organisms, use in medicinal chemistry [1], important role as metallic precursors in the synthesis of new materials [2] and mainly due to their role as catalysts. Organotitanium derivatives offer a wide reactivity such as coordination of a carbon–carbon multiple bonds, oxidative addition, reductive elimination, β-hydride elimination, addition reaction or their use as carbanions source [3–5]; reactivity that justifies its versatility as catalysts. One of the current trends in the chemistry is the use of polydentate ligands for synthesis of titanium complexes which may be applied as catalysts for fine organic reactions [6,7] or processes of polymerization [8]. Within this field, ligands featuring anionic oxygen donors (alkoxides, aryloxides) and especially alkoxides with an additional intramolecular donor group attract the attention of scientists [9].The presence of such a bond in molecules allows control of the structural and electronic parameters of the titanium derivatives such as the coordination number of titanium atom, as well as, its coordination polyhedron and Lewis acidity and hence variation in the catalytic properties [10].

Previously, we have study the control over the assembly of titanium alkoxides using select ligands and their use as enantioselective catalysts in the epoxidation of cinnamyl alcohol [11]. Therefore, a series of unexplored chiral alkyl lactate ligands bearing different substituents on the backbone and with hydroxyl and ester functional groups have been evaluated for their potential utility controlling clustering effect and asymmetric induction in the catalytic process mentioned above.

2. Experimental

2.1. General

All reactions have been performed using standard Schlenk tube and dry box techniques under an atmosphere of dry nitrogen or argon. Solvents were distilled from appropriate drying agents and degassed before used. Benzyl (*S*)-(−)-lactate, methyl (*S*)-(−)-3-phenyllactate and menthyl (*S*)-(−)-lactate have been purchased from Aldrich and used as received. Ti(OPr^i)$_4$ has been purchased from Aldrich distilled and stored under an argon atmosphere prior to use. FTIR spectra were recorded on a Perkin–Elmer PE 883 IR spectrophotometer (4000–400 cm^{-1}) as nujol mulls between polyethylene pellets and KBr disks. ^{1}H, VT ^{1}H DOSY NMR and ^{13}C{^{1}H} NMR spectra were recorded on Varian FT-300 and Varian FT-400 spectrometers and chemical shifts were measured relative to residual ^{1}H and ^{13}C resonances in the deuterated solvents. Mass spectrometry analyses were performed on a ULTRAFLEX III Bruker instrument using ditranol as matrix. The electronic absorption UV–vis spectra were recorded in CH_2Cl_2 solution on a UV–Vis Analytik Jena Specord 200PC spectrophotometer.

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2.2. Cyclic voltammetry

The cyclic voltammograms were taken with a potentiostat/galvanostat Autolab PGSTAT302 Metrohm. All experiments were carried out using a conventional three electrode cell. Platinum was used as working and reference electrode. A Pt wire was also used as the auxiliary electrode. Electrochemical data were obtained using 0.2 mol L^{-1} solutions of hexafluorophospate tetrabutylammonium in THF as supporting electrolyte. All solutions were deaerated by bubbling high purity nitrogen. Ferrocene was employed as an internal standard in THF solution.

2.3. General synthesis

Due to the similarity of synthesis **1**–**6** a general description is supplied with specific details listed for each compound below. The desired alkyl lactate ligand was slowly added to a stirring solution of $Ti(OPr^i)_4$ in CH_2Cl_2 (≅25 mL), After 12 h, a clear reaction mixture was obtained and the solvent and free isopropyl alcohol were removed under vacuo to yield oils spectroscopically pure.

2.4. Synthesis of [{Ti(OPr^i)$_3$(OBzLact)}$_2$] (**1**)

Used benzyl (*S*)-(−)-lactate (1.00 mL, 6.21 mmol) and $Ti(OPr^i)_4$ (1.86 mL, 6.21 mmol). Colourless oil spectroscopically pure. Yield: 99%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.19 (bs, 18H, −OCH(CH_3)$_2$), 1.25 (bs, 3H, CH_3), 4.56 (bs, 1H, CHO−CH_3), 5.43 (bs, 2H, Ph−CH_2), 4.77, 4.93 and 5.10 (bs, 3H, −OCH(CH_3)$_2$), 7.27 (m, 5H, C_6H_5).

^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$, 25 °C): δ = 21.6 (CH_3), 26.2 (−CH(CH_3)$_2$), 72.0 (−CH_2Ph), 77.4 (−OCH(CH_3)$_2$), 126.0, 126.2 and 127.9 (C_6H_5), 186.1 CO(=O). FT−IR (Nujol−polyethylene, cm^{-1}): 612(br), 697(m), 730(m), 914(w), 950(w) 1025(m), 1054(m) 1105(s), 1134(s), 1262(m), 1329(w), 1376(s), 1455(s), 1494(w), 1670(s), 1741(w), 2854(m), 2924(s), 2965(s).

2.5. Synthesis of [{Ti(OPr^i)$_2$(OBzLact)$_2$}$_2$] (**2**)

Used benzyl (*S*)-(−)-lactate (1.00 mL, 6.21 mmol) and $Ti(OPr^i)_4$ (mL, 3.10 mmol). Colourless oil spectroscopically pure. Yield: 99%. ^{1}H NMR (300 MHz, $CDCl_3$), δ = 1.19 (bs, 12H, −OCH(CH_3)$_2$), 1.25 (bs, 6H, CH_3), 4.56 (bs, 2H, CHO−CH_3), 5.43 (bs, 4H, Ph−CH_2), 4.77, 4.93 and 5.10 (bs, 2H, −OCH(CH_3)$_2$), 7.27 (m, 10H, C_6H_5). ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$, 25 °C): δ = 21.9 (CH_3), 25.9 (−OCH(CH_3)$_2$), 72.4 (−CH_2Ph), 78.0 (−OCH(CH_3)$_2$), 126.2, 128.0 and 143.4 (C_6H_5), 186.6 CO(=O). FT−IR (Nujol−polyethylene, cm^{-1}): 606(br), 698(s), 733(s), 816(s), 910(w), 949(w) 1025(s), 1098(s) 1104(s), 1138(s), 1205(m), 1265(m), 1330(w), 1375(s), 1452(s), 1495(w), 1665(s), 1731(m), 2871(m), 2934(s), 2981(s), 3029(w).

2.6. Synthesis of [{Ti(OPr^i)$_3$(OMePhLact)}$_2$] (**3**)

Used methyl (*S*)-(−)-3-phenyl-lactate (1.00 g, 5.60 mmol) and $Ti(OPr^i)_4$ (1.66 mL, 5.60 mmol). Yellowish oil spectroscopically pure. Yield: 99%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.18 (bs, 18 H, −OCH(CH_3)$_2$), 3.02 (bs, 2H, CH_2Ph), 4.02 (s, 3H, CH_3), 4.51, 4.72 and 5.11 (bs, 3H, −OCH(CH_3)$_2$), 5.03 (s, 1H, CH(O)), 7.28 (m, 5H, C_6H_5). ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$, 25 °C): δ = 25.9 (−CH(CH_3)$_2$), 41.4 (CH_2Ph), 70.9 (OCH_3), 72.2 (CH(O)), 82.4 (−OCH(CH_3)$_2$), 126.2, 128.1, 130.0 and 138.5 (C_6H_5−CH_2), 184.7 CO(=O). FT-I.R. (Nujol, cm^{-1}): 523(s), 615(br), 687(s), 756(s), 796(s), 812(m), 854(s), 999(s), 1115(s), 1329(s), 1349(s), 1361(s), 1376(s), 1451(m), 1464(m), 1670(s), 1741(s), 2623(w), 2655(w). $Ti_2C_{38}O_8H_{72}$: Calc: C 60.63, H 9.64. Found: C 60.27, H 9.46%.

2.7. Synthesis of [{Ti(OPr^i)$_2$(OMePhLact)$_2$}$_2$] (**4**)

Used methyl-(*S*)-**(−)**-3-phenyl-lactate (1.00 g, 5.60 mmol) and $Ti(OPr^i)_4$ (0.84 mL, 2.8 mmol). δ = 1.18 (bs, 12 H, −OCH(CH_3)$_2$), 3.02 (bs, 4H, CH_2Ph), 4.02 (s, 6H, CH_3), 4.51, 4.72 and 5.11 (bs, 2H, −OCH(CH_3)$_2$), 5.03 (s, 2H, CH(O)), 7.28 (m, 10H, C_6H_5). ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$, 25 °C): δ = 21.9 (−OCH(CH_3)$_2$), 40.7 (CH_2Ph), 69.9 OCH_3, 71.4 (CH(O)), 77.5 (−OCH(CH_3)$_2$), 127.2, 128.4, 128.8 and 136.6 (C_6H_5−CH_2), 173.9 CO(=O). FT−IR (Nujol−polyethylene, cm^{-1}): 596(br), 699(s), 749(s), 814(m) 845(m), 907(w), 1012(s), 1104(s), 1195(s), 1282(s), 1330(m), 1375(s), 1454(m), 1496(w), 1669(s), 1740(s), 2927(s), 2976(s), 3028(m).

2.8. Synthesis of [{Ti(OPr^i)$_3$(OMentLact)}$_2$] (**5**)

Used (1*R*,2*S*,5*R*)-menthyl (*S*)-(−)-lactate solution (1 gmL, 4.38 mmol) and $Ti(OPr^i)_4$ (1.31 mL, 4.38 mmol). Colourless oil spectroscopically pure. Yield: 99%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.75 (d, 3H, CH_3), 1.20 (d, 18H, −OCH(CH_3)$_2$), 1.40 (d, 6H, CH_3), 1.00−2.00 (m, 9H, C_6H_9), 4.02 (m, 1H, C_6H_9) 4.45 (s, 3H, −OCH(CH_3)$_2$), 4.78 (m, 1H, CH−O). ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$, 25 °C): δ = 16.1 (CHO−CH_3), 21.9, (C_6H_8−(CH_3)), 22.9 (C_6H_8−CH(CH_3)$_2$), 26.7 (−OCH(CH_3)$_2$), 23.0, 31.9, 34.9, 46.6, 51.3 and 76.3 (C_6H_9), 83.5 (CH−O), 84.4 (−OCH(CH_3)$_2$), 185.1 CO(=O). FT−IR (Nujol−polyethylene, cm^{-1}): 607(br), 697(m), 768(m), 816(m), 852(m), 925(w), 952(s), 997(s), 1050(s) 1129(s), 1262(s), 1328(m), 1376(s), 1455(m), 1671(s), 1742(w), 2868(s), 2927(s), 2961(s).

2.9. Synthesis of [{Ti(OPr^i)$_2$(OMentLact)$_2$}$_2$] (**6**)

Used (1*R*,2*S*,5*R*)-Menthyl (*S*)-(−)-lactate solution (1 g, 4.38 mmol) and $Ti(OPr^i)_4$ (0.66 mL, 2.20 mmol). Colourless oil spectroscopically pure. Yield: 99%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.78 (d, 6H, CH_3), 1.20 (d, 12H, −OCH(CH_3)$_2$), 1.43 (d, 12H, CH_3), 1.00−2.00 (m, 18H, C_6H_9), 4.02 (m, 2H, C_6H_9) 4.45 (s, 2H, −OCH(CH_3)$_2$), 4.78 (m, 2H, CH−O). ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$, 25 °C): δ = 16.5 (CHO−CH_3), 21.5, (C_6H_8−(CH_3)), 21.7 (C_6H_8−CH(CH_3)$_2$), 26.2 (−OCH(CH_3)$_2$), 22.7, 31.86, 34.8, 46.6, 51.2 and 76.6 (C_6H_9), 83.4 (CH−O), 84.3 (−OCH(CH_3)$_2$), 185.9 CO(=O). FT−IR (Nujol−polyethylene, cm^{-1}): 617(br), 697(m), 717(m), 851(m), 925(w), 953(m), 1000(s), 1050(m) 1127(s), 1260(m), 1329(m), 1362(s), 1375(s), 1456(m), 1675(s), 1742(w), 2855(s), 2924(s), 2961(s).

2.10. General procedure for the catalytic asymmetric epoxidation (epoxycinnamyl alcohol)

A flame dried 250 ml two-necked flask was fitted dropping funnel and flushed with nitrogen, and charged with 2 g of activated, powdered 4A molecular sieves, 0.54 g (0.79 mmol) of titanium complex and 100 ml of dry CH_2Cl_2. After the mixture was cooled to −20 °C and 5.7 ml of a 5.5 M solution of TBHP in nonane (31.4 mmol) was added. The mixture was allowed to stir at −20 °C for 1 h and then treated with 3.2 ml of a 4.8 M solution of freshly distilled (E)-3-phenyl-2-propenol (cinnamyl alcohol) in CH_2Cl_2 (15.7 mmol), added dropwise over 1 h. The resulting homogeneous solution was stored 5 h to −20 °C. After the reaction mixture is quenched with 0.4 ml of a 10% aqueous solution of sodium hydroxide saturated with sodium chloride. After the cold bath is removed and stirred mixture is maintained 10 min. Then the mixture was treated with $MgSO_4$ and Celite, and after the solution is filtered, washing with Et_2O. The volatiles were removed in vacuo getting a yellow oil. Ee determined by HPLC with a chiralpack AD-H 250 × 4.6 μm column from VWR International Eurolab. ^{1}H NMR