

Enantioselective hydrogenation of olefins by chiral iridium phosphorothioite complex covalently anchored on mesoporous silica

Suman Sahoo^a, Pradeep Kumar^b, F. Lefebvre^c, S.B. Halligudi^{a,*}

^a *Inorganic Chemistry and Catalysis Division, National Chemical Laboratory, Pune 411008, India*

^b *Organic Chemistry Technology, National Chemical Laboratory, Pune 411 008, India*

^c *Laboratoire de Chimie Organometallique de Surface, CNRS-CPE, Villeurbanne Cedex, France*

Received 11 October 2007; revised 12 November 2007; accepted 2 December 2007

Available online 4 January 2008

Abstract

Chiral monodentate phosphorous-based ligands have proven effective for the enantioselective hydrogenation of olefins. Binol-derived monodentate phosphorothioite (PS) ligand was synthesized from binol and thiopropyltriethoxysilane, and its iridium complex was covalently anchored to mesoporous silica supports like SBA-15, MCM-41, and MCM-48. These catalysts were characterized by different physicochemical techniques and assessed for their catalytic performances in the heterogeneous asymmetric hydrogenation of itaconic acid and its derivatives. It was found that the catalytic activities and enantioselectivities of the heterogenized iridium complex (IrPSSBA-15) in the hydrogenation reactions were comparable to its homogeneous analogue. Binol-derived monodentate phosphorothioite ligand in heterogeneously anchored form (iridium complex) is a more effective catalyst than the reported monodentate phosphorous ligand systems in the hydrogenation reactions, possibly due to the changes in electronic properties around the iridium metal center. The effects of substrate-to-catalyst molar ratio, solvents, and temperature on substrate conversions and enantioselectivities of the products were investigated in hydrogenation reactions.

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Keywords: Binol; Monodentate ligand; Phosphorothioite ligand; Mesoporous silica SBA-15; Immobilization; Itaconic acid; Iridium complex; Enantioselective hydrogenation

1. Introduction

The pioneering work [1–4] at the start of this century brought about a renaissance in the use of monodentate phosphorus ligands in the asymmetric hydrogenation reactions. The development of binol-derived monodentate phosphorus ligands is a research topic of increasing interest because of their easy preparation methods, higher stabilities, and excellent activities and enantioselectivities in asymmetric catalysis [5]. Because of the high cost of chiral ligands and noble metals used in catalyst preparation, catalyst recovery becomes an important issue for the application of enantioselective catalyst in large-scale processes. In recent years, enormous progress has been made in interdisciplinary research on the development of stere-

oselective solid-phase catalysis for asymmetric synthesis [6]. The heterogenization of a homogeneous catalyst would provide many advantages, including easy separation, efficient recycling, minimization of metal traces in the product, and process control, which would finally reduce the overall process cost. It has been reported that heterogeneous catalysts are even more selective than their homogeneous analogues in some reactions [7,8]. Moreover, the potential of heterogeneous chiral catalysts has been reported in recent reviews [9–14]. Simons et al. have reported the successful immobilization of rhodium complex of the monodentate ligand on silica support [15,16] and used in the asymmetric hydrogenation reactions. The covalent anchoring of ligands suffers from the lengthy process involved in functionalization of ligand and effective covalent anchoring onto the support [17,18]. Although inorganic material-immobilized catalysts have some advantages, they have attracted little attention [19–21] compared with immobilized catalysts prepared from

* Corresponding author. Fax: +91 20 25902633.

E-mail address: sb.halligudi@ncl.res.in (S.B. Halligudi).

organic polymeric supports. The immobilized chiral transition metal catalysts prepared from inorganic materials can prevent intermolecular aggregations of the active species because of their rigid structures. These catalysts often exhibit superior thermal and mechanical stabilities, and they do not swell or dissolve in organic solvents.

Recently, an iridium complex of monodentate phosphoramidite ligand has been reported for asymmetric hydrogenation reactions in homogeneous conditions [22]. Hydrogenation products like chiral 2-substituted succinic acids have attracted much recent interest for their utility as chiral building blocks [23,24]. In this paper, we report synthesis of a binol-derived monodentate triethoxysilyl phosphorothioite PS ligand (hereafter PS) and its iridium complex covalently anchored onto high-surface area mesoporous silica supports, along with their applications in the asymmetric hydrogenation of itaconic acid and its derivatives. The effects of reaction parameters such as substrate-to-catalyst molar ratio, temperature, hydrogen pressure, catalyst concentration, and solvents on the optimum substrate conversions and product enantioselectivities in the hydrogenation of olefinic substrates are explored.

2. Experimental

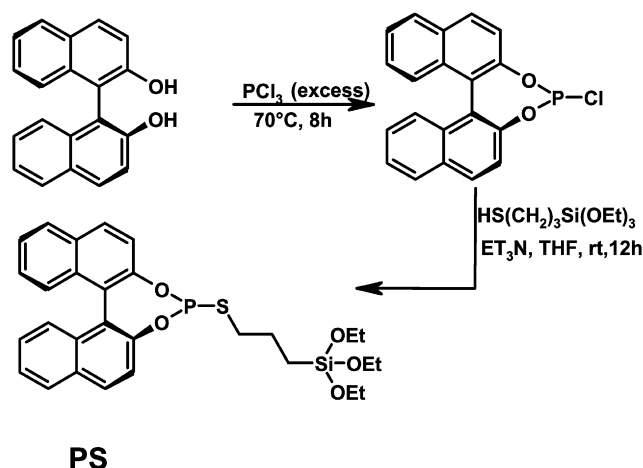
2.1. Chemicals

$[\text{Ir}(\text{COD})\text{Cl}]_2$, S-binol, 3-thiopropyltriethoxysilane, TEOS, pluronic-123, dimethylitaconate, itaconic acid, and triethylamine were purchased from Aldrich. Diethylitaconate was prepared from itaconic acid by esterification with ethanol. Phosphorous trichloride and cetyltrimethylammonium bromide (CTAB) were procured from Loba Chemie, India and were used as received without further purification. Dichloromethane, ethyl acetate, toluene, methanol, tetrahydrofuran, and diethyl ether were purchased from Ranbaxy, India and distilled before their use following the standard procedure. For the quantitative estimation of enantiomers, the racemic products were obtained by Pd-charcoal-catalyzed reduction.

2.2. Catalyst preparation

2.2.1. Synthesis of triethoxysilyl phosphorothioite ligand (PS)

Scheme 1 depicts the synthesis of the monodentate PS ligand. S-binol (0.5 g) in 3 ml of phosphorous chloride (PCl_3) was heated under reflux for 8 h. Then excess PCl_3 was removed by evaporation under vacuum. The resultant solid was subjected to azeotropic distillation with toluene and dried under vacuum. The resulting residue was dissolved in toluene (10 ml) and added to a solution of 0.38 g (1.8 mmol) of thiopropyltriethoxysilane and 0.6 ml triethylamine in 5 ml of dry tetrahydrofuran at 0°C . The resulting mixture was diluted with diethyl ether (12 ml), filtered over a plug of silica, and washed with 50 ml diethyl ether. The solvent was then removed under vacuum. Column chromatography on silica gave pure PS ligand. $[\alpha]_{\text{D}} = +57.53$ ($C = 2.01$, CHCl_3) $^1\text{H NMR}$ (CDCl_3): δ 0.64 (m, 2H), 1.25–1.33 (t, 12H), 1.65 (m, 2H), 1.93–1.97 (m,



Scheme 1. Synthesis of the monodentate triethoxysilylphosphorothioite ligand.

2H), 3.40–3.52 (m, 6H), 7.08 (1H), 7.27–7.40 (m, 7H), 7.84–7.95 (m, 4H) $^{31}\text{P NMR}$ (CDCl_3): δ 115. FTIR (cm^{-1}): 3059, 2942, 2839, 1460, 740, 809, 459.

2.2.2. Synthesis of homogeneous iridium complex of PS ligand (IrPS)

The homogeneous iridium phosphorothioite complex was synthesized as reported previously [22]. $[\text{Ir}(\text{COD})\text{Cl}]_2$ (65 mg, 0.096 mmol) was placed in a 10-ml Schlenk flask, and the entire apparatus was evacuated and backfilled with N_2 three times to establish an inert atmosphere. Dry, degassed dichloromethane (1 ml) and PS ligand (100 mg, 0.192 mmol) were added, and the reaction mixture was stirred at room temperature for 10 min. The solvent was removed under vacuum to give a homogeneous IrPS complex. $^1\text{H NMR}$ (300 MHz, CDCl_3): $^1\text{H NMR}$ (CDCl_3): δ 0.65 (m, 2H), 1.26–1.35 (t, 12H), 1.63 (m, 2H), 1.95–1.99 (m, 2H), 2.74–2.83 (m, 4H), 3.14–3.24 (m, 4H), 3.41–3.53 (m, 6H), 5.13–5.24 (m, 2H), 5.29–5.40 (m, 2H), 7.08 (1H), 7.27–7.40 (m, 7H), 7.84–7.95 (m, 4H) $^{31}\text{P NMR}$ (CDCl_3): δ 83.1. FTIR (cm^{-1}): 3059, 2942, 2839, 1460, 740, 809, 459.

2.2.3. Synthesis of siliceous support

The pure siliceous supports, such as MCM-41, MCM-48, and SBA-15, were prepared as described previously [25–27].

2.2.4. Synthesis of ligand functionalized SBA-15

3 g of SBA-15 and 0.5 g of the PS ligand were mixed in 50 ml of chloroform and refluxed for 18 h (Scheme 2). The resulting material was filtered and washed with chloroform for several times and dried under vacuum at 50°C to give ligand-functionalized SBA-15 (PSSBA-15). Ligand functionalization of MCM-41 and MCM-48 was carried out similarly to obtain PSMCM-41 and PSMCM-48, respectively.

2.2.5. Covalent anchoring of iridium complex onto ligand-modified SBA-15

$[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.05 g) dissolved in 50 ml of dichloromethane was slowly added to 3 g of the PSSBA-15, and the mixture was stirred at room temperature overnight. The resulting

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