

FLUORINATED POLYMERIC BINAP LIGAND FOR ASYMMETRIC HYDROGENATION IN SC CO₂

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The chiral polymeric BINAP ligand was synthesized by condensation of the 6,6'-diaminoethyl-perfluoroBINAP with terephthalaldehyde. The synthesized polymeric ligand was characterized ¹H, ¹⁹F and ³¹P NMR. Rhodium complex of ligand gives 55-85% conversion for the hydrogenation of styrene. Hydrogenation was carried out in 0.050 mmol of ligand solution of scCO₂ under following reaction conditions: Substrate/catalyst= 200 (molar ratio); H₂ pressure 10 bar, CO₂ pressure 1800 psi 323.15-352.15 K, and determined by chiral GC analysis.

INTRODUCTION

Hydrogenation is one of the most versatile methods for the functionalization of C=C bonds [1]. Chiral rhodium BINAP complexes have found important applications as catalysts in hydrogenation reactions. Numerous chiral BINAP and modified BINAP have been synthesized to be used as ligands for transition-metal-catalyzed homogeneous asymmetric synthesis [2–5]. A major problem associated with most homogeneous catalyst systems is separation and recycling of the expensive chiral catalyst. One way to solve this problem would be to employ a heterogeneous catalysis, particularly soluble polymeric or polymer supported homogeneous catalysis. Unfortunately, despite the advantage of easy separation, the use of insoluble polymer-supported catalyst suffered from lowered catalytic and stereo selectivity due to the restriction of the polymer matrix which resulted in limited mobility and accessibility of the active sites. In the past decades, the attachment of homogeneous catalysts to soluble polymer supports has been attracting considerable attention owing to its potential combination of the advantages, and minimization of the disadvantages, of homogeneous and heterogeneous catalysis [6].

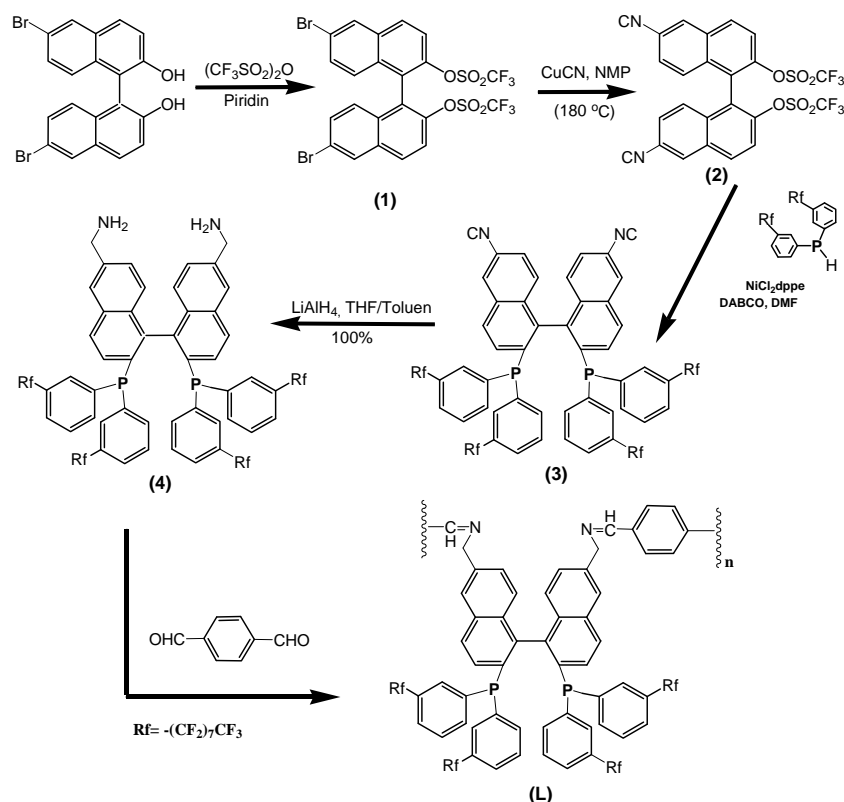
One of the current frontiers in homogeneous catalysis concern the use as reaction media of nontraditional solvents such as ionic liquids, water, fluorine solvents and supercritical carbon dioxide (scCO₂) [7]. The use of scCO₂ has found increasing interest as a nontoxic and environmentally benign solvent for catalytic processes. Most homogeneous catalysts, however, are not soluble in scCO₂ without modification. It is well known that long perfluoroalkyl chains groups attached to conventional ligands increase their solubility in scCO₂ [8-11].

Here, we report use of chiral polymeric BINAP ligands for asymmetric hydrogenation. BINAP was chosen as a model ligand for this study, since it is probably the most versatile and effective ligand among all the chiral phosphine ligands which have been studied for asymmetric catalysis [1,2]. The chiral polymeric BINAP ligand was synthesized by condensation of the 6,6'-diaminoethyl-perfluoroBINAP with terephthalaldehyde. The synthesized ligands were characterized ¹H, ¹⁹F and ³¹P NMR. Solubility studies in scCO₂ were performed at the conditions of 323.15 K, 1800 psi pressure. Rhodium complex of ligand it gives 55-85% conversion for the hydrogenation of styrene. Hydrogenation was carried out in 0.050 mmol of ligand solution of scCO₂ under following reaction conditions: Substrate/catalyst= 200 (molar ratio); H₂ pressure 10 bar, CO₂ pressure 1800 psi and 323.15-353.15 K. Conversion was determined by GC analysis.

RESULT AND DISCUSSION

Characterization of the ligand and the complex

The perfluoro alkyl-containing polymeric BINAP (**L**) was obtained according to a modified literature methods (scheme 1). The structure of fluorinated diphenylphosphine was confirmed by elemental analysis and IR and NMR spectroscopy. The orange color polymeric catalyst is stable in solid state at room temperature.



Scheme 1.

The IR spectra of the perfluoroalkylated ligand shows a absorption bands in the range $1657\text{--}870\text{ cm}^{-1}$ assigned to different vibration modes of the naphthyl, phenyl and perfluoroalkyl groups. Characteristic IR absorption bands of imin stretching and C–F stretching vibrations can be observed around 1650 and 1150 cm^{-1} , respectively. The ^{13}C NMR spectrum exhibited the expected absorption peaks for every carbon-13 atom of ML. The clear quartet centered at about 129.8 ppm was peculiar to the $-\text{CF}_3$ carbons. The ^1H NMR spectroscopic data of the aromatic protons of (**ML**) are in the range of $6.74\text{--}7.28\text{ ppm}$, and the resonance signal of imin HC=N protons is observed at 8.30 ppm . Rhodium-phosphorus NMR coupling has been reviewed by several authors. The values are normally in the range of $81\text{--}150\text{ Hz}$ [11]. The peak at 69.7 ppm (d , $J_{\text{Rh-P}}=147\text{ Hz}$) in the ^{31}P NMR spectra (in CDCl_3) is, therefore, consistent with the literature. The ^{19}F NMR spectra (in CDCl_3) show a singlet at -63.3 ppm . All the peaks obtained by ^1H NMR spectra were consistent with the literature [12].

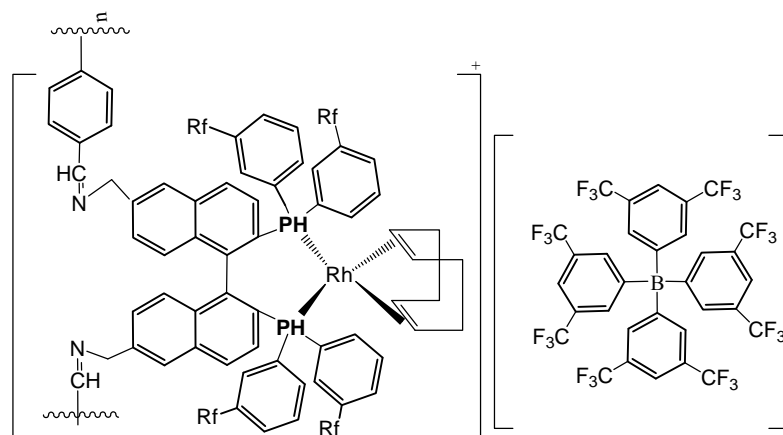


Figure 1. Polymeric catalyst (**ML**)

Solubility of ligand and polymeric catalyst

The solubility of the synthesized polybinaphthyl was determined qualitatively in $scCO_2$. The solubility of ligand and catalyst in $scCO_2$ and H_2 mixture can be estimated by visual observation through window. Different amount of catalyst were added in to the view cell and it was heated until desired temperature (323 K). After that, the cell was introduced with CO_2 (1800 psi) and observed visually solubility behavior of the catalyst. The experiment was repeated as above in that case after heating process the cell was introduced with H_2 first, followed by introduction of CO_2 up to different pressures by syringe pump. Under the reaction conditions, no undissolved solid could be observed.

Hydrogenation

The complex **ML** was tested in the catalytic hydrogenation of styrene (Table 1) in $scCO_2$. This complex showed a good activity and an appreciable selectivity for the hydrogenation of styrene double bond. Complex **ML** was catalytically active even at 50°C with a TOF of 3 h. However, increasing the reaction temperature up to 60°C resulted in a significant enhancement of the activity of **ML** giving TOF values of 64.1 and 98.2, respectively. The catalyst having the higher activity at 80 °C.

Table 1. Catalytic hydrogenation of styrene in presence of **ML**

T (°C)	Yield (%) ^a	TOF ^b (h ⁻¹)
50	55	>16.2
60	76	>51.7
70	81	>86.5
80	85	>98.2

Reaction conditions: PH_2 : 10 bar, P_{total} : 1800 psi, time: 3 h, Substrate/catalyst = 200.

^b % conversion of styrene after 3 h.; ^d TOF after 3 h.

EXPERIMENTAL

All synthetic procedures were carried out under an inert argon or nitrogen atmosphere using standard Schlenk techniques and glove box, and using flame-dried glassware. Diethyl ether (Et_2O), hexane, and tetrahydrofuran (THF) were distilled from sodium benzophenone kettle under nitrogen. Methylene chloride (CH_2Cl_2) was distilled from CaH_2 . The 1H NMR spectra were obtained on a Bruker-Advance DPX 400 spectrometer in $CDCl_3$. IR spectra were recorded

on a Perkin Elmer Mattson 1000 FT-IR spectrometer as KBr pellets in range 4000-400 cm^{-1} . Elemental analyses were recorded on a LECO CHNS-932 analyzer. Melting point was determined on a Gallenkamp apparatus in a sealed capillary and is uncorrected. Styrene was obtained from Sigma-Aldrich with a minimum purity of 99% and was used without further purification. Hydrogen and carbon dioxide were obtained from, BOSS Company (Adana, Turkey) each with a minimum purity of 99.9 and 99.5%. The solubility and catalytic studies were performed with stainless steel batch reactor (PARR, 50 ml, windowed and autoclave engineering stirred reactor 100 mL) and syringe pump (ISCO, series D) in scCO_2 .

6,6'-Dibromo-2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (1): The compound was synthesized as described in the Ref.12. Anal. Calcd for $\text{C}_{22}\text{H}_{11}\text{O}_6\text{BrF}_6\text{S}_2$: C, 41.99; H, 1.76. Found: C, 40.74; H, 1.85. IR (KBr, $\nu = \text{cm}^{-1}$): 3073, 1585, 1495, 1421, 1218, 1139, 938, 823, 675, 500 cm^{-1} . ^1H NMR (CDCl_3): δ 7.51 (d, $J_{3,4} = 9$ Hz, H_3), 8.09 (d, $J_{3,4} = 9$ Hz, H_4), 8.21 (d, $J_{5,7} = 2$ Hz, H_5), 7.69 (d, $J_{7,8} = 9$ Hz, H_7), 7.10 (d, $J_{7,8} = 9$ Hz, H_8).

6,6'-Dicyano-2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (2): The compound was synthesized as described in the Ref.12 and 13. Anal. Calcd for $\text{C}_{23}\text{H}_{11}\text{NO}_6\text{F}_6\text{S}_2$: C, 48.01; H, 1.93; N, 2.43. Found: C, 48.21; H, 2.20; N, 2.43. IR (KBr, $\nu = \text{cm}^{-1}$): 3083, 2923, 2231 (-CN), 1595, 1498, 1425, 1220, 1136, 951, 806 cm^{-1} . ^1H NMR (CDCl_3): 7.16 (d, $J = 8.6$ Hz, 1H), 7.37 (d, $J = 8.9$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 1H), 7.55 (dd, $J = 8.9, 1.5$ Hz, 1H), 7.62 (t, $J = 7.2$ Hz, 1H), 7.62 (d, $J = 9.2$ Hz, 1H), 7.77 (d, $J = 9.2$ Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 1H), 8.19 (d, $J = 9.0$ Hz, 1H), 8.23 (d, $J = 9.2$ Hz, 1H), 8.42 (s, 1H). ^{19}F NMR (CDCl_3): δ -74.24 ppm.

Rf-BINAP from (R)-1,1'-binaphth-2,2'-diyl ditriflate (3): To preactivated zinc powder (1.34 g, 21 mmol), in 5 ml tetrahydrofuran and a crystal of iodine, was added (R)-1,1'-binaphth-2,2'-diyl ditriflate (3.82 g, 6.9 mmol) in DMF dropwise over 30 minutes at 45 °C. The reaction mixture was cooled to room temperature and $\text{NiCl}_2(\text{dppe})$ (362 mg, 0.68 mmol) was added at once, followed by the dropwise addition of $\text{HP}(3\text{-Rf-Ph})_2$ (14.5 g, 13.8 mmol) in 8 ml DMF over 15 minutes at 4 °C -7 °C, and the mixture was heated with stirring at 100 °C. for 19 hours. The reaction was monitored by gas chromatography until starting material was depleted. The dark reddish mixture was filtered while hot. A solid precipitated upon cooling which was collected by filtration and washed with two 5 ml portions of methanol to give 1.72 g of (R)-BINAP. The filtrate was allowed to stand overnight at 5 °C, yield 0.81 g (m.p. 41 °C) Anal. Calcd for $\text{C}_{78}\text{H}_{26}\text{F}_{68}\text{N}_2\text{P}_2$: C, 39.95; H, 1.12; N, 1.19; Found: C, 39.81; H, 1.14; N, 1.13; ^1H NMR (CDCl_3): 6.65 (d, $J = 8.6$ Hz, 1H), 6.74 (d, $J = 8.8$ Hz, 1H), 6.85-6.90 (m, 2H), 6.96-7.03 (m, 4H), 7.06-7.12 (m, 6H), 7.15-7.25 (m, 10H), 7.33 (t, $J = 8.1$ Hz, 1H), 7.42 (dd, $J = 8.6, 2.6$ Hz, 1H), 7.57 (dd, $J = 8.5, 2.3$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.90 (d, $J = 8.6$ Hz, 2H), 8.17 (s, 1H). ^{31}P NMR (CDCl_3): -13.8 (d, $J_{\text{p-p}} = 17.4$ Hz, 1P), -13.9 (d, $J_{\text{p-p}} = 17.4$ Hz, 1P).

6,6'-bis(aminomethyl)-2,2'-bis(perfluorodiphenylphosphino)-1,1'-binaphthyl (4): The compound was synthesized as described in the Ref.13. Anal. Calcd for $\text{C}_{78}\text{H}_{34}\text{F}_{68}\text{N}_2\text{P}_2$: C, 39.82; H, 1.46; N, 1.19 found: C, 38.14; H, 1.44; N, 1.13. ^1H NMR (CDCl_3) δ (ppm): 1.72 (s, 4H, NH_2); 3.69 (s, 4H, CH_2); 6.84 (s, 4H, CH); 6.92-7.27 (m, 20H, CH); 7.33 (d, 2H, CH); 7.64 (s, 2H, CH); 7.76 (d, 2H, CH). ^{31}P NMR (CDCl_3 , 81 MHz) δ (ppm): -16.14.

6,6'-bis(phenylimino)-2,2'-bis(perfluorodiphenylphosphino)-1,1'-binaphthyl (L): To a solution of 500 mg of (4) in dichloromethane and 5 mL glacial acetic acid was added a warm solution of ...mg of 1,4-fenildialdehyde in glacial acetic acid. Then the temperature was slowly raised to 60°C and the mixture was stirred 2 hours. After cooling to room temperature precipitate was filtered, washed with water, alcohol and THF, and dried to give polymeric-perfluoro BINAP. ^1H NMR (CDCl_3) δ (ppm): 3.69 (s, 4H, CH_2); 6.84 (s, 4H, CH); 6.92-7.27 (m, 20H, CH); 7.33 (d, 2H, CH); 7.64 (s, 2H, CH); 7.76 (d, 2H, CH). ^{31}P NMR (CDCl_3 , 81 MHz) δ (ppm): -16.14.

Synthesis of catalyst (ML): A solution of [(COD)₂Rh]BARF (250 mg, 0.21 mmol) in 15 ml of THF at 25 °C was added dropwise to a solution of (**L**) (500 mg, 0.2 mmol) in 8 ml of THF. The color of the solution turned from yellow to orange upon phosphine addition. The reaction was stirred for 15 min and after that the THF was removed under reduced pressure precipitating an orange product: yield 524 mg (79%). ³¹P NMR (300 MHz, CDCl₃) 68.6 ppm (*J*_{Rh-P}=141 Hz).

Hydrogenation: The reactions were carried out in a 100 ml stainless steel autoclave. The air was evacuated prior to the introduction of catalyst and substrate. Hydrogen was then added up to 10 bar. The reactor was pressurised with CO₂ to a predetermined set point. The stirrer was switched on during the addition of CO₂ to ensure that equilibrium was attained between the liquid and vapour phases at the desired operating temperature. Small quantities of the reaction mixture were repeatedly taken out and analyzed by gas chromatograph with flame ionization detector.

CONCLUSIONS

In summary, a practical improved method for the synthesis of polymeric-fluorinated BINAP via three steps by using BINAPO as starting material has been described. Polymer was slightly soluble in scCO₂ and could be cast into amorphous and tough films. Their catalytic activity was examined for Rh-catalyzed asymmetric hydrogenation of styrene. It was found that these modified BINAP ligands showed good catalytic properties.

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