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Hydrogenation of dienes by a recyclable poly(ethylene oxide)–rhodium phosphineless catalytic system

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Abstract

The monocationic complex $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$ in poly(ethylene oxide) (PEO) 3350/MeOH has proven to be a very efficient catalyst for 1,7-octadiene, 1,9-decadiene, and 1,5-cyclooctadiene hydrogenation. This system allows perfect product separation and catalyst phase recycling, resulting in thousands of catalytic cycles (TON $\approx$ 9000). Even at room temperature, turnover frequencies as high as 5000 h^{-1} are attained (50 bar), which makes this one of the most active catalytic systems for diene hydrogenation. Kinetic studies reveal that the reaction rate is second-order in H_2 pressure and first-order in both rhodium and diene concentrations. Typical tests suggest that, despite the reductive reaction conditions, which could lead to colloidal metal dispersion, the reduction of dienes is catalyzed by molecular species.

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1. Introduction

One of the most important challenges in organometallic catalysis is to develop an efficient and ecologically catalytic system that allows a facile product separation, catalyst recovery, and recycling [1]. The first studies of these systems used water as the polar phase and hydrosoluble phosphine as ligands [2]. More recently, fluorinated solvents [3] and ionic liquids [4–6] have replaced water. Other alternatives to address catalyst availability and recycling problems included using thermosensitive polymers [7] or poly(acrylamides) as homogeneous catalyst supports [8].

Our initial research on biphasic catalysis systems studied olefin hydrogenation [9] using a ternary system formed by two organic solvents with different polarities and poly(ethylene oxide) (PEO) 3350 [10–12]. Using the systems heptane/CH_2Cl_2 (or MeOH)/PEO 3350 + $RhCl(PPh_3)_3$ (or $[Rh(1,5\text{-COD})(dppe)]PF_6$, where 1,5-COD = 1,5-cyclooctadiene and dppe = diphenylphosphineethane), in the hydrogenation of hex-1-ene, we obtained excellent results in terms of phase separation, catalyst segregation to the polar phase, and catalytic performance. However, limits of four recyclings in the case of Wilkinson's complex and 10 recyclings for the cationic rhodium complex bearing a chelating diphosphine was observed. These limits were understood to be related to deactivation of the catalytic species due to phosphine leaching during the recycling process.

The literature contains many other applications of PEO or PEG (poly(ethylene glycol)) in catalysis. Important reactions include olefin hydrogenation using PEO/CO_2(sc) [13], olefin epoxidation [14], the Suzuki reaction [15–17], the Heck reaction [18], Sonogashira coupling using phosphines bound to MeOPEG [19], Sharpless asymmetric olefin dihydroxylation [20], and PEG-functionalized phosphines as ligands for rhodium-catalyzed olefin hydroformylation [21].

Considering our results for hex-1-ene hydrogenation and the ability of PEO to segregate the transition metal catalyst phase, we decided to study the rhodium-catalyzed hydrogenation of dienes. The hydrogenation of dienes is relevant to the fuel refining industry because the burning of a diene-containing fuel inside the engine can lead to undesirable heavy products that can damage the engine. We tested a phosphine-free

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cationic rhodium complex, $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$, where $Cp^* =$ pentamethylcyclopentadienyl, as a precatalyst to help overcome the phosphine leaching process. This complex contains a Cp^* ligand that could be an excellent substitute for the phosphine ligands, helping to stabilize the catalyst and allowing easy product separation and catalyst phase recycling. In this paper, we report our findings on the hydrogenation of 1,7-octadiene, 1,9-decadiene, and 1,5-cyclooctadiene catalyzed by $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$ in PEO 3350/MeOH polar phase.

2. Experimental

2.1. Materials

Dienes (Aldrich, 98%) were passed through a column of activated neutral alumina to eliminate peroxides and stocked over 3A activated molecular sieves under argon atmosphere. Heptane was distilled over Na/benzophenone, and MeOH was distilled over CaH_2. PEO (Alfa) 3350 was evacuated for 12 h under dynamic vacuum at room temperature and stocked under argon. Hydrogen (White Martins, 99.999%) was used as received. Argon (White Martins, 99.998%) was passed through two traps filled with 3A activated molecular sieves and one trap containing BASF catalyst R3-11 to remove traces of water and oxygen.

2.2. Characterizations

All NMR spectra were obtained using a Varian VXR Multinuclear spectrometer. ^1H NMR spectra were obtained at 200 MHz using C_3D_6O (d_6-acetone) or $CDCl_3$ as solvents and calibrated by the TMS signal. $^{31}P\{^1H\}$ NMR analysis were carried out at 121 MHz using a capillary tube filled with H_3PO_4 as reference and C_3D_6O as solvent. Elemental analyses were run in a Perkin–Elmer 2400 CHN Elemental Analyzer. UV spectra were performed between 300 and 800 nm in a Shimadzu (UV–1601 PC) spectrometer, using a quartz cell with an optical path length of 1 cm. IR spectra were collected in solid phase by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), 32 scans, in a Bomen MB102 spectrometer. GC/MS analyses were done using a Shimadzu 17A gas chromatograph equipped with a capillary column DB-5 (30.0 m × 0.25 mm), using He as carrier gas, coupled to a Shimadzu GCMS-QP5050 mass spectrometer operating at 70 eV (EI).

2.3. Catalyst precursor preparation

$[(\eta^5\text{-Cp}^*)Rh(\mu_2\text{-Cl})Cl]_2$ was prepared from $RhCl_3{\cdot}3H_2O$ and pentamethyl–cyclopentadiene (Aldrich, 99%) as stated in the literature, in almost quantitative yield [22]. The monocationic complex $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$ was prepared from $[(\eta^5\text{-Cp}^*)Rh(\mu_2\text{-Cl})Cl]_2$ as described previously, replacing NH_4PF_6 with KPF_6 [23]. The yield of the recrystallized product (orange-red crystals) was 60%. Its ^1H NMR spectrum demonstrating one singlet at 1.73 ppm related to the methyl groups of Cp^*. The spectrum of phosphorus resonance presented a heptuplet at −144 ppm related to the phosphorus atom coupled to six fluorine nuclei, confirming the presence of PF_6^- anion in the complex. The presence of chlorine was detected, with formation of a white precipitate of AgCl observed on the addition of an excess of aqueous $AgNO_3$ to a solution of the complex in MeCN. The weight of the AgCl obtained corresponded to 14.00% chlorine in the complex, very close to the expected value of 14.62%. The results of its elemental analysis (Perkin–Elmer 2400 CHN Elemental Analyzer) were C = 30.09%, H = 3.86%, N = 6.53% (Anal. calcd: C = 29.51%, H = 3.71%, N = 6.45%). These results lead us to conclude that the replacement of the cation NH_4^+ by K^+ on the hexafluorophosphate salt led to the same rhodium complex, as could be predicted.

2.4. Characterization of the complex $[(\eta^5\text{-Cp}^*)Rh(MeOH)_3](PF_6)_2$

IV (DRIFTS): $\nu_{O\text{–}H} = 3427\ cm^{-1}$, $\nu_{C\text{–}H_{aliphatic}} = 2960\ cm^{-1}$ and $2929\ cm^{-1}$, $\nu_{C=C} = 1469\ cm^{-1}$, $\nu_{C\text{–}C} = 1020\ cm^{-1}$, $\nu_{P\text{–}F} = 873\ cm^{-1}$, $862\ cm^{-1}$ and $559\ cm^{-1}$;

^1H *NMR* (CD_2Cl_2, 200 MHz, δ in ppm referred by TMS): δ 3.49 (CH_3–CH_3OH), δ 1.68 (CH_3–Cp^*);

C, H, N: observed: C = 25.24%, H = 4.20%. Anal. calcd: C = 25.01%, H = 4.36%; UV/vis (CH_3OH): 351 nm (sh), 394 nm and 505 nm.

2.5. Catalytic experiments

All catalytic systems were prepared under argon atmosphere. Reactions were performed under 40 bar hydrogen pressure in the MeOH/PEO polar phase, and the products were extracted at the end of the reaction using *n*-heptane. Samples for GC or GC/MS were withdrawn directly from the *n*-heptane phase. In a typical experiment, 1.4×10^{-2} mmol (10.2 mg) of $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$ was added to an argon-purged Schlenk tube, followed by 1.8 g of PEO 3350 (Sigma). These solids were dissolved by adding 7 ml of MeOH and 3.1 mmol (∼0.4 ml) of diene under magnetic stirring. This solution was then transferred by cannula to a stainless steel reactor that had been purged by vacuum/argon cycles. The reactor was closed, purged 3 times with H_2, and then pressurized to 40 bar. The products were analyzed by GC and GC/MS.

2.6. Filtration test for an active heterogeneous component in the catalysis

Maitlis and coworkers have developed a simple and very convenient test to verify whether small metal aggregates are involved in the catalytic activity of a homogeneously catalyzed reaction conducted under reducing conditions [24]. This method involves adding an inert filter aid, such as cellulose, to the reaction solution to adsorb small metal particles that could be very active catalysts in many processes. Then the mixture is filtered, and the catalytic activity of the filter aid and the filtered solution are evaluated. The catalytic experiments were done as described above using 1,7-octadiene (0.4 ml, 3 mmol) as a substrate and $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$ (1.4×10^{-2} mmol,

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