



Asymmetric transfer hydrogenation of carbonyl compounds catalyzed by rhodium nanoparticles



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ABSTRACT

Transfer hydrogenation of acetophenone and methyl benzoylformate with 2-propanol has been studied on rhodium nanoparticles obtained by the reduction of rhodium(I) complexes in the presence of optically active compounds, including chiral diamine *S,S*-DIODMA, (4*S*,5*S*)-*N*⁴,*N*⁵,*N*⁵,2,2-hexamethyl-4,5-bis-(aminomethylene)-1,3-dioxolane, quaternary diammonium salt (4*S*,5*S*)-(-)-*N*¹,*N*⁴-dibenzyl-2,3-dihydroxy-*N*¹,*N*¹,*N*⁴,*N*⁴-tetramethylbutane-1,4-diammonium dichloride, and (8*S*,9*R*)-(-)-cinchonidine. Increasing the modifier to Rh ratio leads to an increase in the enantiomeric excess (*ee*) of the reaction products. The greatest *ee* values (43.8% for (*R*)-1-phenylethanol and 58.2% for the methyl ester of (*R*)-mandelic acid) were achieved at (8*S*,9*R*)-(-)-cinchonidine/Rh ratios of 9:1 and 3:1, respectively.

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1. Introduction

Transition metal nanoparticles are currently in the focus of researchers' attention [1–6] because the shape- and size-dependent physical and chemical properties of nanocrystals, including catalytic activity and selectivity, are of great interest. Identification of the mechanisms of their formation [5,7–9], stabilization, and prevention of their agglomeration [1,2,10,11] could help to regulate the activity and selectivity of catalysts based on these metal nanoparticles. Many studies have focused on controlling the shape and size [3,6,12–15] of metal nanoparticles using different synthetic routes. Owing to their unique catalytic activity and selectivity, metal nanoparticles with controlled shape, size, chemical composition, and surface structure are employed for applications in a wide range of heterogeneous reactions [3,4,9,13,14,16–19].

Significant efforts of many researchers in the area of catalysis are focused on stabilization methods for transition metal nanoparticles on the surfaces of supports or dispersed in media. The efficiency of stabilizers, whose role is to prevent agglomeration, depends in a complex way on the nature of the precursor, reducing agent, and solvent, and on the ratio between these components [1]. Small neutral molecules and ions, as well as macromolecules, are used as stabilizers, which, as a rule, coordinate to the surface atoms of

metals via donor atoms and provide electrostatic, steric, and “electrosteric” stabilization [1,4,5,20,21].

If organic compounds with stereogenic centers are used as stabilizers, it is possible to affect the stereoselective direction of reactions catalyzed by the nanoparticles [18–22] because the optically active compounds (ligands) modify the surface of the nanoparticles and induce chirality. Nanoparticle-catalyzed asymmetric processes are widely reported in the scientific literature; for example, one of the most thoroughly studied reactions is the hydrogenation of ethyl pyruvate (Orito reaction) supported on Pt, Ir, or Pd particles modified by cinchona alkaloids [20,22–31]. However, the reduction of other prochiral substrates has been less studied [24,29–33].

Cinchona alkaloids, which are found in the bark of cinchona trees, are relatively cheap reagents and have shown great promise for the promotion of enantioselectivity in heterogeneous catalysis [34,35]. The natural cinchona alkaloid is widely used as a unique modifier for transition metal nanoparticles that catalyze the asymmetric hydrogenation of keto esters [23–35]. For this reaction, the Pt/Al₂O₃ catalysts achieved the highest enantiomeric excess (*ee*) of up to 78–83% [23,24]. In addition, Kagan's diphosphine (*R,R*)- and (*S,S*)-DIOP have been used as modifiers for Pt nanoclusters in the Orito reaction (80% yield, 4.4% *ee*) [24,33]. When using a Pd-chitosan/SiO₂ catalyst for the hydrogen transfer from formates to acetophenone, a 68.9% *ee* of (*R*)-1-phenylethanol was achieved [36], whereas using 2-propanol as the hydrogen donor with a Fe(III)-(chitosan)/SBA-15 catalyst led to 87.4% *ee* of the product [37].

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Metal nanoparticles (Rh, Ir) dispersed in the reaction medium with various stabilizers are most commonly used for the catalytic hydrogenation of arenes [12–15] and alkenes [38]. Jansat et al. [39] reported the synthesis of Ru colloids obtained by reduction of ruthenium(I) cyclooctadiene complexes with molecular H₂ in the presence of a family of chiral oxazolines and amino alcohols. These systems were tested for catalytic hydrogen transfer to acetophenone, but no significant *ee* was achieved (10% *ee*), as well as in the hydrogenation of *ortho*- and *para*-methylanisole and dimethyl itaconate (up to 18% *ee*). Blaser et al. [40] obtained up to 68% *ee* of ethyl lactate from the hydrogenation of ethyl pyruvate in the presence of cinchona-modified Pt colloids. In the enantioselective hydrogenation of ethyl 2-oxopropionate on Pt colloids (“quasi-homogeneous”), Bonnemant and Braun [41] achieved an *ee* of 81.3%. Moreover, the turnover frequency of the “quasi-homogeneous” colloidal platinum exceeded that of the heterogeneous system by a factor of 3. PVP–Pt colloidal clusters also were highly effective, with up to 97.6% *ee* obtained for the hydrogenation of alkylpyruvates.

The first example of highly active asymmetric catalysis not based on precious metals is the use of colloidal iron(0) nanoparticles in numerous hydrogen transfer reactions [42], in which *ee* of approximately 64% is achieved in the product.

Although there are successful examples of the application of transition metal nanoparticles in hydrogenation with molecular H₂ and in transfer hydrogenation, the latter reaction has not been studied on colloidal Rh nanoparticles. There are rare examples of the use of Rh nanoparticles in other reactions in the scientific literature. For example, one of the earliest examples of chiral Rh nanoparticles was developed by Han et al. for the catalytic asymmetric hydroformylation of styrene [43] catalyzed by (*R*)-BINAP–Rh/SiO₂ (*ee* for product *ca.* 30%). Interestingly, the activity and the enantioselectivity were affected by the ligand/metal molar ratio in the supported catalyst. The same reaction was performed using rhodium colloids obtained by H₂ reduction of Rh precursors in THF in the presence of chiral xylo-furanoside diphosphite ligands [44]. Compared with the corresponding BINAP–Rh molecular catalyst under the same reaction conditions (up to 36% *ee*), the activity of the colloids was lower, although a slightly higher enantioselectivity was observed (max. 45% *ee*).

Previously, we showed that enantioselective transfer hydrogenation (TH) of acetophenone with 2-propanol on soluble cationic diamine complex [Rh(*S,S*-DIODMA)₂]⁺TfO[−], where *S,S*-DIODMA is (4*S*,5*S*)-*N*⁴,*N*⁴,*N*⁵,*N*⁵,2,2-hexamethyl-4,5-bis-(aminomethylene)-1,3-dioxolane (*S,S*-I) and TfO[−] is the trifluoromethanesulfonate anion, resulted in the formation of rhodium nanoparticles [45]. According to X-ray diffraction analysis, these nanoparticles had a cubic crystalline structure with an average particle size of ~45 Å. The question arises whether this reaction is catalyzed by the soluble [Rh(*S,S*-DIODMA)₂]⁺TfO[−] transition metal complex or if catalysis occurs on the formed rhodium nanoparticles.

The present study was undertaken to test rhodium nanoparticles derived from rhodium complexes [Rh(1,5-cod)Cl]₂ and [Rh(1,5-cod)₂]⁺TfO[−] for the TH reaction in the presence of optically active modifiers. Rhodium cyclooctadiene complexes were chosen because they have been used as precursors of soluble transition metal complexes in previous studies [45].

2. Experimental

2.1. Reactants and catalysts

The purchased reagents and solvents were purified and distilled before use. Acetophenone (Acros Organics, 99%), methyl benzoylformate (Aldrich, 95%), and solvents (methanol, 2-propanol,

toluene, chloroform, and hexane) were thoroughly cleaned, dehydrated, and stored in an argon atmosphere after distillation. Diamine *S,S*-DIODMA (*S,S*-I) [46], complexes [Rh(*S,S*-I)₂]⁺TfO[−], [Rh(1,5-cod)(μ-Cl)₂] (IIa), and [Rh(1,5-cod)₂]⁺TfO[−] (IIb) [47] were synthesized following known procedures. All procedures were performed under an argon atmosphere.

2.1.1. Synthesis of (4*S*,5*S*)-(-)-*N*¹,*N*⁴-dibenzyl-2,3-dihydroxy-*N*¹,*N*¹,*N*⁴,*N*⁴-tetramethylbutane-1,4-diammonium dichloride (*S,S*-III)

Benzyl chloride (5.5 mL; 46.6 mmol) in 20 mL anhydrous CHCl₃ was added dropwise to a stirred solution of *S,S*-I (4.6 g; 21.2 mmol) in CHCl₃ (50 mL). The reaction mixture was boiled for 2 h, concentrated under reduced pressure, and left at 6 °C overnight. The obtained beige precipitate was recrystallized from a mixture of acetone and 2-propanol (2:1), and a white solid (8.1 g) was obtained. Yield: 89 wt%. mp: 194–197 °C; [α]_D −29.0° (c 1, MeOH); ¹H NMR (CD₃OD): δ (ppm) 3.15 (s, 6H, N(Me)₂), 3.19 (s, 6H, N(Me)₂), 3.51–3.66 (m, 4H, CH₂N), 3.66 (br, 2H, OH), 4.39–4.42 (m, 2H, OCH), 4.64–4.72 (m, 4H, CH₂Ph), 7.53–7.67 (m, 10H, Ph); ¹³C NMR (CD₃OD): δ (ppm) 51.41 (NMe), 51.72 (NMe), 66.99 (CH₂N), 68.77 (CH₂Ph), 70.70 (OCH), 128.89 (Ph⁴), 130.34 (Ph^{5,3}), 131.97 (Ph¹), 134.53 (Ph^{6,2}).

Commercially available (8*S*,9*R*)-(-)-cinchonidine (IV) (Merck, 97%), recrystallized from methanol, was used.

2.2. Materials characterization

The ¹H and ¹³C NMR spectra were recorded on a Bruker DPX-400 spectrometer, using hexamethyldisilane as an internal reference.

2.2.1. GC analysis

The catalytic reaction products were analyzed and identified using a Shimadzu QP2010 Plus GC–MS. Electronic impact ionization at 70 eV was used and *m/z* was scanned in the range from 40 to 350. An Equity 5 capillary column (30 mm × 0.25 mm i.d., 95% dimethylpolysiloxane, 5% diphenylpolysiloxane, carrier gas: helium) was used.

2.3. Optical rotation

The optical rotations of the pure samples or solutions were determined using an ADP410 automatic digital polarimeter at 589 nm (*l* = 50 mm, *C* = 1–5 g/100 mL). The *ee* values of the reaction products were determined using an Agilent 7890A GC equipped with a Dean switch, CYCLODEX-B chiral capillary column (30 m × 0.25 mm i.d.), and a flame ionization detector.

2.3.1. X-ray diffraction analysis (XRD)

XRD analysis of the solid samples was carried out with a Shimadzu XRD 7000 diffractometer operating at the Cu-K_α radiation line (λ = 0.15418 nm) in the angle range of 3.000°–80.000° with a scanning step of 0.05°. Phase identification was carried out using the Match! 1.1. software and PDF-2 international database. The average diameter of the rhodium nanoparticles was estimated from the broadening of the (111) X-ray diffraction line by means of the Debye–Scherrer equation.

2.3.2. Surface area

The surface areas were determined by BET measurements using nitrogen on a Sorbtometer-M instrument.

2.3.3. Thermal analysis

Thermal gravimetric analysis (TG), differential gravimetric analysis (DTG) and differential scanning calorimetry (DSC) scans were

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