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Synthesis and catalytic activity of new supported rhodium(I) complexes for the enantioselective hydrogenation of methyl-(*Z*)-α-*N*-acetamidocinnamate

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Abstract

The polymerizable rhodium complex [(+)-diopRh(AAEMA)] (AAEMA$^-$: deprotonated form of the ligand 2-(acetoacetoxy)-ethylmethacrylate) was obtained by reaction of (cod)Rh(AAEMA) with (+)-diop at −80 °C. Supported chiral complexes have been obtained by copolymerization of [(+)-diopRh(AAEMA)] with *N*,*N*-dimethylacrylamide and *N*,*N*′-methylenebisacrylamide or by reaction of $[(+)\text{-diopRhCl}]_2$ with an opportunely prepared poly(β-ketoesterate). Catalytic tests carried out with the homogeneous catalyst or with both its heterogeneous analogues proved to be active in the enantioselective hydrogenation of methyl-(*Z*)-α-*N*-acetamidocinnamate yielding (*S*)-phenylalanine methylester with ee's up to 67%.

Keywords: Rhodium; Supported; Polymerizable complexes; Enantioselective catalysis

1. Introduction

Due to their potential recyclability, much effort has been focused on supporting a metal complex exhibiting catalytic activity onto insoluble organic or inorganic matrices [1,2]. Catalyst activity and selectivity have been optimized by changing the nature of the support, as well as that of the metal centre [3–5]. The materials obtained by suitably anchoring a soluble metal complex onto a polymeric material are often referred to as hybrid due to their halfway nature between homogeneous and heterogeneous, and have been developed with the aim of combining the advantages of homogeneous catalysis in terms of activity and selectivity with those of heterogeneous systems.

The synthetic strategies mostly used to synthesize a supported metal complex have been reported in Scheme 1.

Route 'a' envisages the polymerization of an opportunely prepared metal complex and has the advantage of the possibility to check the catalytic activity in the homogeneous and heterogeneous phases. Route 'b' is the "classical" synthesis of a macromolecular ligand followed by the anchoring of a metal salt or complex.

Among the most recent examples of supported rhodium catalysts are: (i) Rh complexes on Na^+–bentonite

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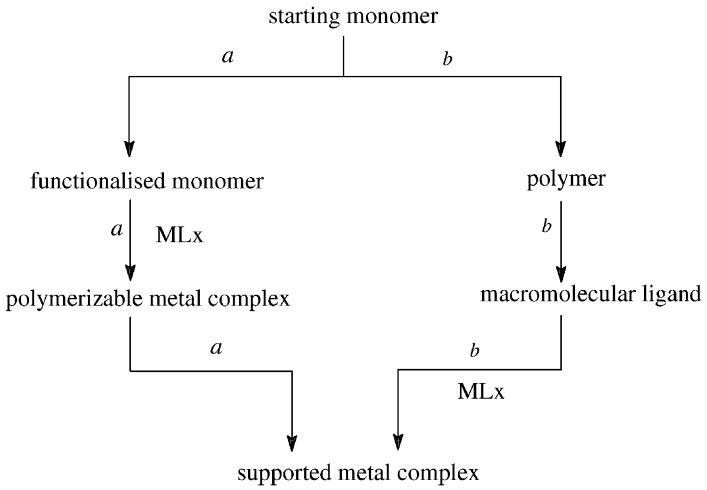

Scheme 1. Strategies for the synthesis of a supported metal complex.

[6] or on isonitrilic resins [7]; (ii) rhodium amine complexes tethered on silica supports [8–10], [Rh-$(CO)_2Cl]_2$ anchored on mesoporous silica MCM-41 [11,12]; (iii) rhodium acetate on a dendrimer-bound phosphine [13]; (iv) rhodium hydride complexes covalently bound on inorganic–organic matrices obtained by sol–gel polycondensation [14]; (v) supported catalysts obtained from polymerizable 1,2-bis-(diphenylphosphino)-ethane rhodium complexes [15]. Potentially enantioselective supported catalysts have naturally attracted a higher interest. Among the first examples of supported chiral rhodium(I) complexes are "classical" homogeneous precursors supported on silica [16–19] or on organic co-polymers of opportunely prepared derivatives of enantiopure diop or bppm [diop: 4,5-bis(diphenylphosphinomethyl)-2,2′-dimethyl-1,3-dioxolane; bppm: 1-*tert*-butoxycarbonyl-4-diphenylphosphino-2-(diphenylphosphinomethyl) pyrrolidine] [20–24]. Other papers describe supported chiral complexes obtained by the interaction of cationic rhodium compounds with ion exchange resins [25–30]. Entrapment of a soluble rhodium catalyst into an insoluble matrix has also been the goal of different recent investigations. To this purpose, sol–gel matrices [31], polydimethylsiloxane [32], $BaSO_4$, AgCl, cellulose, silica gel, aluminium oxide and charcoal [33] have been used as supports. Recent work on the topic dealt with rhodium catalysts anchored on cinchonine or ephedrine-modified divinylbenzene-crosslinked chloromethylated polystyrene [34]. Continuing previous studies by the authors on the synthesis, copolymerization and use in catalysis of group VIII–X metal complexes with the anion of 2-(acetoacetoxy)ethylmethacrylate ($AAEMA^-$) [35–41], the complex (cod) Rh(AAEMA) was synthesized. After its polymerization with suitable co-monomers and cross-linkers, its activity in the hydrogenation of several organic substrates was tested [42]. Since chiral rhodium β-diketonates exhibit enantioselectivity as hydrogenation catalysts [43], it was considered worthwhile to pursue the synthesis of the polymerizable [(+)-diopRh (AAEMA)] and of its heterogeneous analogues

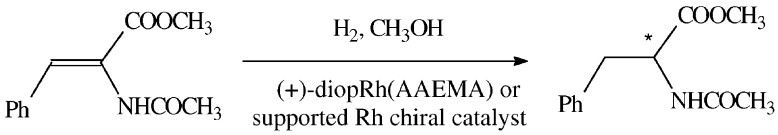

Fig. 1. Scope of the work.

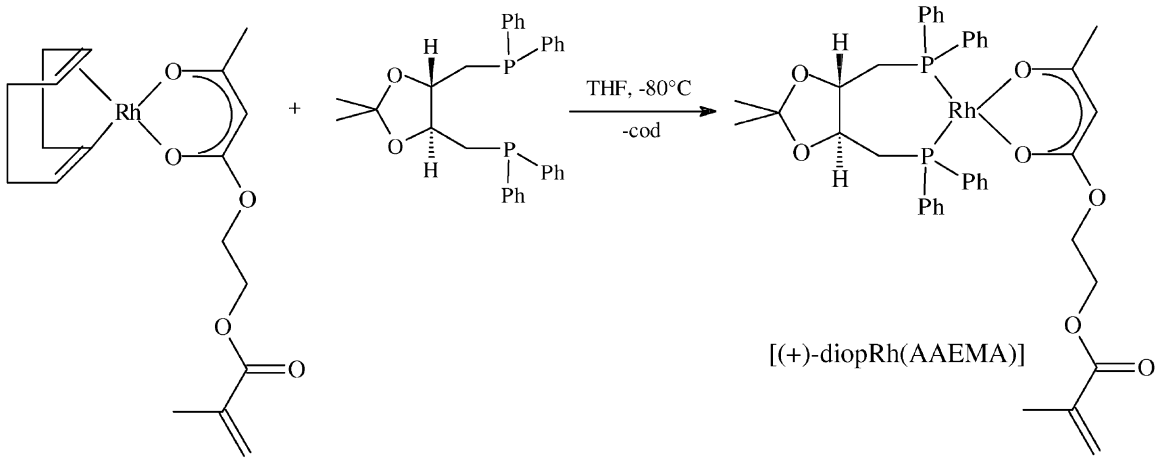

Fig. 2. Synthesis of [(+)-diopRh(AAEMA)].

obtained following route 'a' or 'b' (Scheme 1). Both resins proved to be active and enantioselective catalysts for the hydrogenation of methyl-(*Z*)-α-*N*-acetamidocinnamate (Fig. 1).

2. Results and discussion

2.1. Synthesis of [(+)-diopRh(AAEMA)] and of its heterogeneous analogues

The synthesis of the complex [(+)-diopRh (AAEMA)] was achieved by the direct reaction of (cod)Rh(AAEMA) with one equivalent of (+)-diop in THF at −80 °C as schematized in Fig. 2.

The complex was obtained as a light-orange powder and its IR spectrum shows the expected β-ketoesterate combination bands at 1605 and 1505 cm^{-1}. Moreover, typical medium bands for the coordinated phosphine appear at 723, 694 and 511 cm^{-1}.

The ^1H NMR spectrum shows the methacrylate olefinic protons at δ 5.13 and 6.12 ppm. Such signals are only slightly upfield shifted passing from (cod)Rh (AAEMA) (δ 5.19 and 6.15 ppm) to the [(+)-diopRh (AAEMA)] complex. The $AAEMA^-$ methylene protons in (+)-diopRh(AAEMA) are also shifted upfield (δ 3.06 and 3.80 ppm with respect to δ 3.84 and 4.0 ppm for (cod)Rh(AAEMA)). The methynic proton, on the other hand, shifts downfield (δ 5.07 ppm with respect to δ 4.89 ppm in (cod)Rh(AAEMA)). Very similar effects can be observed by comparing the ^1H NMR spectra of [(+)-diopRh(acac)] with those of (cod)Rh(acac) or (nbd)Rh(acac).[1] The $^{31}P\{^1H\}$ NMR spectrum of [(+)-diopRh(AAEMA)] shows only a doublet at δ 39.6 ppm that could be explained invoking a distorted square planar structure. A similar spectrum was observed for the unsymmetrical rhodium–phosphine complex $(PEt_3)_2Rh(tfac)$ (tfac: trifluoroacetylacetonate) [44]. The reported data were consistent with a chelating structure both for (+)-diop and for $AAEMA^-$.

[(+)-diopRh(AAEMA)] was co-polymerized with DMAA (*N*,*N*-dimethylacrylamide, comonomer) and MBAA (*N*,*N*-methylenebisacrylamide, cross-linker) in the presence of AIBN as radical initiator, with the aim of synthesizing a chiral-supported metal complex (Fig. 3) following the route 'a' in Scheme 1.

The IR spectrum of the obtained supported rhodium complex (in the following referred to as Rh-pol A*) shows the diagnostic bands for coordinated (+)-diop at 512, 696 and 742 cm^{-1}. The elemental analysis

[1] ^1H NMR recorded in benzene-d_6 shows a downfield shift for the methinic protons (the methinic proton in (+)-diopRh(acac) falls at 5.23 ppm [43] with respect to (nbd)Rh(acac) (5.16 ppm) and (cod)Rh(acac) (5.13 ppm)) and an upfield shift for the six acac methyl protons (the methyl protons in (+)-diopRh(acac) fall at 1.49 ppm [43] with respect to (nbd)Rh(acac) (1.79 ppm) and (cod)Rh(acac) (1.78 ppm)).

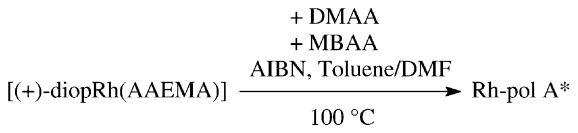

Fig. 3. Synthesis of the supported chiral complex Rh-pol A*.

showed a Rh content of 4.30% and a P/Rh ratio of 1.8. Alternatively, following route 'b' of Scheme 1, a macromolecular ligand was synthesized by a straightforward thermal polymerization carried out at 100 °C reacting HAAEMA with MBAA and DMAA in the presence of AIBN (Fig. 4). The IR spectrum of the matrix shows the two expected carbonyl bands of HAAEMA at 1722 cm^{-1} (ketone) and a shoulder at ca. 1745 ± 5 cm^{-1} (ester). The obtained resin was subsequently reacted with a slight excess of KOH to obtain a supported $AAEMA^-$ functionality. In order to determine the amount of base necessary for the deprotonation, it was assumed that the percentage of ligand HAAEMA incorporated in the polymer was equal to the calculated (14.9 wt.%). This assumption was based on the fact that the percent ratio of the isolated mass of the polymer with respect to the total reagent mass was 97%. The macromolecular ligand thus obtained was eventually reacted at room temperature with $[(+)\text{-diopRhCl}]_2$, yielding the supported rhodium chiral complex Rh-pol B* (Fig. 4). Elemental analyses revealed a P/Rh ratio of 2.0. Moreover, potassium and chlorine elemental analyses proved the absence of unreacted supported β-ketoesterate and of unreacted $[(+)\text{-diopRhCl}]_2$.

The IR spectrum of Rh-pol B* is very similar to that of Rh-pol A*, confirming the formation of a supported β-ketoesterate rhodium (+)-diop complex.

Table 1
Enantioselective hydrogenation of MAC (temperature: 22 °C; solvent: CH_3OH (8 ml); substrate/catalyst: 160 mol/mol; [MAC] = 0.125 mol/l; reaction time: 24 h if not otherwise specified). Substrate conversion is >99% except for entries 1 (70%), 9 (90%) and 13 (92%)

Entry	Catalyst	Pressure (bar)	ee (%)
1	[(+)-diopRh(acac)]	1	52
2	[(+)-diopRh(AAEMA)]	1	67
3	[(+)-diopRh(AAEMA)]	12	35
4	[(+)-diopRh(AAEMA)]	6	43
5	[(+)-diopRh(AAEMA)]	2	53
6	Rh-pol A*	12	24
7	Rh-pol A*	6	36
8	Rh-pol A*	2	53
9[a]	Rh-pol A*	2	30
10	Rh-pol B*	12	39
11	Rh-pol B*	6	42
12	Rh-pol B*	2	60
13[a]	Rh-pol B*	2	50

[a] Recycle of the previous run; reaction time: 48 h.

2.2. Catalytic activity of (+)diopRh(AAEMA) and of the supported chiral catalysts Rh-pol A* and Rh-pol B*

Both [(+)-diopRh(AAEMA)] and its heterogeneous analogues were used as catalysts for the hydrogenation of methyl-(*Z*)-α-*N*-acetamidocinnamate (in the following MAC). Table 1 shows the results of the above-mentioned study. The enantiomeric excess was in all cases directed towards the (*S*)-isomer, as pointed out by polarimetric measures [45].

Knowing that [(+)-diopRh(acac)] is an active catalyst for the hydrogenation of methyl-(*Z*)-α-*N*-acetamidocinnamic acid [43], first catalytic tests were aimed at comparing the activity and selectivity of β-dioxygenato complexes towards the hydrogenation

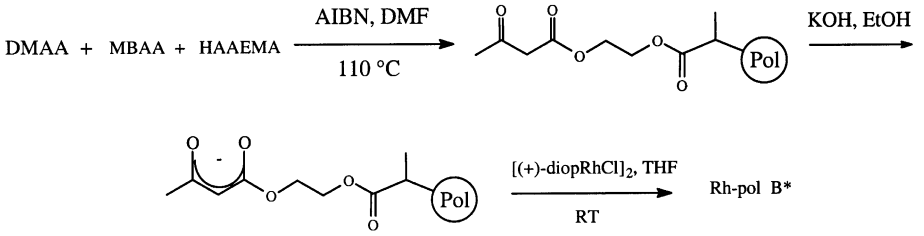

Fig. 4. Synthesis of the supported chiral complex Rh-pol B*.

of MAC at ambient temperature and pressure. A preliminary result was obtained by using [(+)-diopRh (acac)] in the hydrogenation of MAC under atmospheric H_2 pressure. An ee of 52% at 70% MAC conversion was obtained (entry 1). Carrying out the same reaction with [(+)-diopRh(AAEMA)] resulted in a marked enhancement of activity and selectivity (67% ee at quantitative MAC conversion, entry 2).

The effect of the pressure on the enantioselectivity [46] was studied by carrying out the hydrogenation with the polymerizable complex [(+)-diopRh(AAEMA)] at 12, 6 and 2 bar (entries 3–5). The enantiomeric excess shows a marked dependence on hydrogen pressure: an increased enantioselectivity was observed when the reaction was carried out at 12, 6 and 2 bar (35, 43 and 53% ee's, respectively; entries 3–5). The preliminary results obtained with the polymerizable complex [(+)-diopRh(AAEMA)] prompted us to use the supported chiral complexes Rh-pol A* and Rh-pol B* in the title hydrogenation. First tests carried out at ambient hydrogen pressure with Rh-pol A* and Rh-pol B* proved ineffective, giving MAC conversions ranging from 6 to 10% in each case. The ee was not determined under these conditions. The reaction was then carried out at 12, 6 and 2 bar (entries 6–8) and the enantiomeric excess rose again with the lowering of the pressure (24, 36 and 53%, respectively). This observation is in accordance with the assumption that the rate-determining step of the catalytic cycle is the hydrogen addition [47,48]. The recycle of this reaction exhibited a slightly lowered catalytic activity (90% conversion after 48 h) and selectivity (30% ee; entry 9). After the recycle of run 8, the rhodium content dropped to 2.15%. Rh-pol B* also proved active in the title hydrogenation giving complete conversion towards the corresponding phenylalanine methylester within 24 h when the reaction was carried out at pressures higher or equal to 2 bar. The expected increase in enantioselectivity occurred with the lowering of the pressure (entries 10–12) reaching an ee of 60% at 2 bar hydrogen (entry 12). A recycle of this reaction (entry 13) led to an ee of 50% at a substrate conversion of 92% after 48 h.

In order to gain further insights into the coordination mode of (+)-diop to rhodium in the obtained supported complexes, solid-state CP/MAS $^{31}P\{^1H\}$ NMR spectra of Rh-pol A* and Rh-pol B* was performed. In the case of Rh-pol B*, a broad signal at δ 39.9 ppm was found, in accordance with the signal observed for [(+)-diopRh(AAEMA)] in toluene-d_8 solution (δ $^{31}P\{^1H\}$ 39.6 ppm). It can be thus assumed that the coordination mode of (+)-diop is unchanged in the monomeric [(+)-diopRh(AAEMA)] complex and in its heterogeneous analogue Rh-pol B*.

Rh-pol A* exhibits in the solid-state $^{31}P\{^1H\}$ NMR spectrum a broad peak at δ 29.1 ppm. Such a signal can be attributed to the convolution of the signals due to a monoxidized (+)-diop ligand coordinated via the trivalent phosphorous to the rhodium(I). The resulting supported complex turned out still active in the hydrogenation of MAC, although its enantioselectivity, compared to that of Rh-pol B* was lower (comparison of entries 6–9 with entries 10–13 of Table 1).

IR spectroscopy was not useful to confirm the presence of monoxidized diop in Rh-pol A*, due to the crowding of bands attributable to the polyamidic support in the 1000–1200 cm^{-1} region. However, recording $^{31}P\{^1H\}$ NMR of a toluene-d_8 solution of [(+)-diopRh(AAEMA)] warmed at 80 °C for 45 min showed a sensible lowering of the δ 39.6 ppm signal, with the simultaneous appearance of two signals: a singlet (δ 25.3 ppm) and a doublet (δ 31.3 ppm, $^1J(Rh, P) = 150$ Hz). Such signals can be attributed to the monodentate ligand (+)-diop monoxide, coordinated to rhodium via the trivalent phosphorus atom.

It can therefore be concluded that a supported (+)-diop monoxide Rh(I) complex is formed during the co-polymerization of [(+)-diopRh(AAEMA)] carried out at 100 °C. A partial oxidation of the coordinated diop in Rh(I) acetylacetonato complexes was proposed by Brunner and Wagenhuber [43] to justify the lowered enantioselectivity exhibited in catalysis by isolated (+)-diopRh(acetylacetonato) complexes with respect to that exhibited in reactions carried out with catalysts prepared in situ.

In both Rh-pol A* and Rh-pol B* $^{31}P\{^1H\}$ NMR spectra, the broadening of the supported complex resonance with respect to that of [(+)-diopRh(AAEMA)] in solution is related to the substantial dispersion of ^{31}P chemical shift in amorphous systems such as surface-attached species. This feature due to environmental effects has been observed for other systems immobilized on silica gel or glass beads [49], and is responsible for the impossibility to resolve the two phosphorus signals for the coordinated (+)-diop monoxide in the solid-state $^{31}P\{^1H\}$ NMR.

3. Experimental

3.1. General procedures

All syntheses were carried out under nitrogen using standard Schlenk techniques. Catalytic procedures were carried out under a stream of dry nitrogen. HAAEMA was purchased from Polyscience, (+)-diop was purchased from Aldrich, DMAA and MBAA were purchased from Fluka. Reagents were used as-received. $[(cod)RhCl]_2$ [50], $[(+)\text{-diopRhCl}]_2$ [43] and (cod)Rh(AAEMA) [51] were prepared by literature methods. Methyl-(*Z*)-α-*N*-acetamidocinnamate was prepared by S_N2 reaction of (*Z*)-α-*N*-acetamidocinnamic acid with methyl iodide in the presence of K_2CO_3 in DMF [52] or by direct methylation with an equivalent of trimethylsilyldiazomethane solution [45]. UV–Vis spectra were recorded on a Uvikon 942 spectrophotometer. IR spectra were recorded on a Bruker Vector-22 instrument. NMR spectra were recorded on a Bruker AM 500 or on a Bruker Avance DRX500 spectrometer; frequencies were referenced to Me_4Si (^1H and ^{13}C), 85% H_3PO_4 (^{31}P). The high-resolution ^{31}P solid-state NMR spectra were performed on a Jeol GSE 270 (6.34 T) operating at 109.6 MHz under conditions of $^1H \rightarrow {}^{31}P$ cross-polarization, high-power proton decoupling and magic angle spinning. The 90° pulse was 6.0 μs and the contact pulse was 5 ms. The spectra of the complexes were collected after 1000 transients and a relaxation delay of 10 s. The line broadening was set to 100 Hz. H_3PO_4 85% was used as reference ($\delta = 0$ ppm). Cylindrical 6 mm o.d. zirconia rotors with sample volume of 120 μl were employed with spinning speed of 6.5 kHz. For all samples, the magic angle was adjusted from the ^{79}Br MAS spectrum of KBr by minimizing the linewidth of the spinning side band satellite transitions.

Atomic absorption analyses were performed on a Perkin Elmer 3110 instrument using a Rh hollow cathode lamp. C, H, N, elemental analyses were performed using a Carlo Erba 1108 analyser. Optical rotations were determined on a Perkin Elmer 241 MC polarimeter. Chromatographic analyses were carried out on a Hewlett Packard 6890 instrument using a 30 m HP-5 column. Conversions were calculated by GLC analysis. Isolated yields of (*S*)-phenylalanine methylester confirm the chromatographic determination within 5% error. Enantiomeric excess have been determined by HPLC on a HP 1050 instrument equipped with a Daicel® Chiralcel OD-H column and a UV diode array detector set at 220 nm.

3.2. Synthesis of (4S,5S)-(+)-4,5-bis-(diphenylphosphino-methyl)-2,2-dimethyl-1,3-dioxolaneRh (I)(AAEMA) [(+)-diopRh(AAEMA)]

A solution obtained dissolving 198.06 mg (0.467 mmol) of (cod)Rh(AAEMA) in 5 ml THF was cooled to −80 °C and kept under vigorous stirring. A solution obtained dissolving 231.86 mg (0.465 mmol) of (+)-diop in 11 ml THF was added dropwise over a 30 min time. A change in colour from yellow to light-orange was observed. After further 15 min at −80 °C, the solution volume was reduced to 5 ml in vacuo over a 60 min time, during which the reaction temperature was allowed to raise to −30 °C. To the obtained solution, 25 ml of petroleum ether (30–50 °C) at −30 °C was added, causing the immediate precipitation of a light-orange solid that was filtered at −30 °C, washed with 5 × 5 ml of petroleum ether and eventually dried in vacuo.

Yield: 339 mg (89.5%); analysis: calculated for $C_{41}H_{45}O_7P_2Rh$: C, 60.45%; H, 5.57%; Rh, 12.63%; P, 7.60%. Found: C, 59.79%; H, 5.63%; Rh, 12.81%; P, 7.40%; ^1H NMR (benzene-d_6, 500 MHz, 293 K): (ppm) δ = 1.15 (s, 3H, diop-CH_3), 1.16 (s, 3H, diop-CH_3), 1.45 (s, 3H, C(O)CH_3), 1.71 (m, 3H, methacrylate CH_3), 2.34–3.06 (m, 4H, diop-CH_2), 3.06 (m, 2H, O–CH_2), 3.80 (m, 2H, O–CH_2), 4.09 (br, 2H, diop-CH), 5.07 (s, 1H, C(O)CHC(O)), 5.13 (m, 1H, *cis*-vinyl proton), 6.12 (m, 1H, *trans*-vinyl proton), 6.90–7.15 (m, 12H, $Ph_{meta} + Ph_{para}$), 7.40–8.10 (m, 8H, Ph_{ortho}); $^{13}C\{^1H\}$ NMR (toluene-d_8, 126 MHz, 293 K): (ppm) δ = 18.3 (s, CH_3, methacrylate), 26.9 (s, CH_3, β-ketoesterate), 27.11 (s, CH_3, diop), 27.17 (s, CH_3, diop), 32.45 (pt, CH_2, diop), 33.50 (dd, CH_2, diop, $J_1 = 27.13$ Hz, $J_2 = 13.56$ Hz), 60.55 (s, *C*H_2–CH_2), 63.14 (s, CH_2–*C*H_2), 77.46 (d, $J(C, P) = 6.78$ Hz, CH, diop), 78.40 (d, $J(C, P) = 6.78$ Hz, CH, diop), 83.98 (s, O–C(O)*C*HC(O)CH_3), 107.96 (s, *C*$(CH_3)_2$, diop), 125.49 (m, O–C(O)C=*C*), 136.52 (m, O–C(O)*C*=C), 128–139 (C_{arom}), 166.52 (s, *C*=O, methacrylic), 170.2 (s, O–*C*(O)CHC(O)CH_3), 186.3 (s, O–C(O)CH*C*(O)CH_3).

$^{31}P\{^{1}H\}$ NMR (toluene-d_8, 202 MHz, 293 K); (ppm): $\delta = 39.6$ (d, $^{1}J(Rh, P) = 195$ Hz); IR (Nujol, cm^{-1}): $\nu = 1717$ (vs, C=O, methacrylate), 1605 (vs, β-ketoesterate combination band), 1505 (vs, β-ketoesterate combination band), 1263 (m), 1158 (m, β-ketoester C–O–C stretching), 1049 (w), 885 (w), 439 (m), 723 (m), 694 (m), 511 (m). $[\alpha]_{589\,nm} = -64^{\circ}$ ($c = 1.87$, toluene, $t = 23\,^{\circ}C$); UV–Vis (THF, mol/l): 281 nm ($\varepsilon = 7463\,l\,mol^{-1}\,cm^{-1}$), 249 nm ($\varepsilon = 13\,168\,l\,mol^{-1}\,cm^{-1}$), 236 nm ($\varepsilon = 16\,074\,l\,mol^{-1}\,cm^{-1}$). p.f.: 142 °C (decomposition).

3.3. Synthesis of Rh-pol A*

To a solution containing 171.08 mg (0.210 mmol) of [(+)-diopRh(AAEMA)] in 3 ml toluene and kept at −80 °C under vigorous stirring was added a solution obtained dissolving 318.90 μl (3.215 mmol) DMAA and 97.46 mg of MBAA (0.075 mmol) and 10 mg AIBN in 1 ml DMF.

The reaction mixture was heated under vigorous stirring at 100 °C for 10 min, after which the formation of a polymer that blocked the stirring was observed. After cooling the reaction mixture at room temperature, the solid was washed with 3 × 5 ml of toluene, 3 × 5 ml of diethylether and eventually dried in vacuo and stored at −30 °C.

Yield: 440 mg of polymer. Elemental analysis: Rh, 4.30%; P, 2.32%. IR (KBr) (cm^{-1}) $\nu = 3474$ (vs, vb), 2932 (s), 1635 (vs), 1507 (s), 1400 (s), 1261 (s), 1173 (s), 1054 (s), 742 (s), 696 (s), 512 (m). ^{31}P CP MAS-NMR (109.6 MHz, 293 K; $\delta = 29.1$ ppm.

3.4. Copolymerization of HAAEMA with DMAA and MBAA

A 25 ml Schlenk tube was added of 324.0 mg (1.5 mmol) HAAEMA, 1.703 g (17.2 mmol) DMAA, and 151.0 mg (1.0 mmol) MBAA in 6.5 ml DMF. The theoretical HAAEMA percentage is 14.87 wt.%. To this solution, 5 mg AIBN was added and the solution kept under vigorous stirring and warmed to 100 °C. After 10 min, the stirring was blocked by the formation of a gelatinous polymer that was treated with 50 ml diethylether, isolated by filtration, washed again with diethylether (4 × 20 ml) and dried in vacuo. Yield: 2.11 g; IR (KBr) (cm^{-1}): $\nu = 3468$ (vs), 2940 (vs), 1720 (s), 1630 (vs, vb), 1505 (s), 1405 (s), 1360 (s), 1260 (m), 1150 (m), 1060 (w).

3.5. Synthesis of Rh-pol B*

A 200 ml Schlenk tube was added of 715.4 mg of the macromolecular ligand obtained with the former preparation and was swollen in 12 ml EtOH. To this suspension, kept under vigorous stirring, 60.0 mg KOH (1.07 mmol) was added. After 1.5 h, 12 ml of petroleum ether was added, causing the immediate shrinking and precipitation of the polymer. The solution was removed with a syringe and the deprotonated polymer was washed with 3 × 20 ml of a 1:1 EtOH/Et_2O mixture. The macromolecular ligand was subsequently suspended in 10 ml THF under vigorous stirring and a solution of $[(+)\text{-diopRhCl}]_2$ (314.98 mg (0.247 mmol) in 50 ml THF) was added over a 30 min time. After 13 h reaction, 50 ml Et_2O was added to shrink the polymer and the solution removed with a syringe. The resin was washed with 3 × 35 ml water, 2 × 25 ml acetone and 2 × 25 ml Et_2O. The orange solid was eventually dried in vacuo. Elemental analysis revealed the absence of potassium and chlorine.

Yield: 500 mg of supported rhodium complex. Rh = 3.41%, $P = 2.0\%$. IR (KBr) (cm^{-1}): $\nu = 3468$ (vs), 2940 (vs), 1720 (s); 1630 (vs, vb), 1505 (s), 1405 (m), 1360 (m), 1260 (m), 1150 (m), 1060 (w), 746 (m, diop), 697 (m, diop), 510 (m, diop). ^{31}P CP MAS: NMR (109.6 MHz, 293 K): $\delta = 39.6$ ppm.

3.6. Hydrogenation of methyl-(Z)-α-N-acetamidocinnamate

In a typical run, a 50 ml stainless steel autoclave equipped with a transducer for online pressure monitoring was charged, under nitrogen stream, of the supported rhodium complex (6.25 μmol Rh), and of methyl-(*Z*)-α-*N*-acetamidocinnamate (219.24 mg, 1.0 mmol) in methanol (8 ml). The autoclave was then purged three times with hydrogen then pressurized and set on a magnetic stirrer. The reaction was stopped after 24 h (48 h for the recycles) and in any case, when no further hydrogen uptake was observed. After catalysis, the hydrogen was vented and the autoclave opened. The resin was recovered by centrifugation and the conversion determined by GLC. The solution was purified by silica gel percolation using ethyl acetate/*n*-hexane

(50:50) as eluant and subsequent solvent evaporation. An aliquot of the product was eventually dissolved in the HPLC eluant (isopropanol/*n*-hexane = 30:70) and analysed for ee. Retention times under the conditions previously reported are: (*R*)-enantiomer: t_R = 9.03 min; (*S*)-enantiomer: t_R = 10.19 min.

In the case of homogeneous catalysis runs with [(+)-diopRh(AAEMA)], the same procedure was followed except for the catalyst preparation, which was weighed in a separate Schlenk tube (5.09 mg, 6.25 μmol) and dissolved in methanol. The solution was transferred to the steel autoclave or to a Schlenk tube (for reactions carried out at ambient pressure) and stirred under the appropriate hydrogen pressure. The product isolation followed the previously described procedure.

For reactions carried out at ambient pressure, a Schlenk tube was added of the homogeneous or of the supported complex, the substrate and the solvent. The Schlenk tube was connected to a hydrogen balloon and the inert atmosphere was replaced by hydrogen. The tube was then stirred and the reaction course was monitored via GLC. The previously described procedure was then followed for product isolation.

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