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Binuclear and Polynuclear Rhodium Complexes Containing Chiral Dithiolate Ligands Derived from Lactic Acid

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Two precursors of the chiral dithiolato ligands, di-[(2*R*)-acetylmercaptopropyl] phthalate and isophthalate, 1 and 2 respectively, were synthesized from (*S*)-lactic acid. Reactions of 1 and 2 with $[Rh_2(\mu)\text{-}OMe)_2(cod)_2]$ (cod = 1,5-cyclo-octtadiene) yielded rhodium thiolato complexes of different nuclearities. The mixtures of complexes were analyzed by gel-permeation chromatography (GPC). The reaction with ligand 1 produced a mixture of oligomeric complexes, where the binuclear species was the main component. Higher-nuclearity complexes were the main products of the reaction with ligand 2. The rhodium complexes, in the presence of PPh_3, were tested as catalyst precursors for the asymmetric hydroformylation of styrene. Moderate activity and regioselectivity were achieved in most cases, but no enantioselective discrimination was observed. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

The study of asymmetric reactions catalyzed by transition-metal complexes containing homochiral sulfur ligands is an active research area.[1] Binuclear rhodium(I) complexes containing two bridging thiolato ligands and different ancillary ligands have been being investigated for some time,[2] but dithiolato complexes with the same binuclear structure have only more recently been characterized.[3] Studies with different dithiolato ligands have shown that the nuclearity of the rhodium(I) complexes depends on the structure of the bridging ligand. Thus, 1,2-dithiolates form binuclear species,[3] whereas 1,4-dithiolates may lead to dinuclear as well as to tetranuclear complexes, the nuclearity being mainly dependent on the ancillary ligands.[4]

Binuclear rhodium–thiolato complexes of formula $[Rh_2(\mu\text{-}SR)_2(CO)_2(PR'_3)_2]$ were reported to catalyze the hydroformylation of olefins at moderate pressure and temperature.[5] In principle, these species can be modified at both the phosphane and rhodium–thiolato backbones and this represents clear advantage over the classical phosphane catalytic systems. The true nature of the active species in the hydroformylation with binuclear rhodium–thiolato catalytic systems is, however, controversial and the original assumption of Kalck has been questioned.[6] Recently, it has been shown that these binuclear species dissociate under syngas pressure producing a variable amount of classical mononuclear catalysts such as $RhH(CO)_x(PR'_3)_y$, depending on the reaction conditions.[7] These results strongly suggest that the binuclear systems are not active themsleves, but are just precursors of mononuclear catalytic species which no longer contain the coordinated thiolato ligand. Although highly informative, these experiments cannot rule out the possibility that a partial contribution of the dithiolato species to the catalytic process may occur at low syngas pressure, even in the presence of the classical rhoduim–phosphane catalyst.

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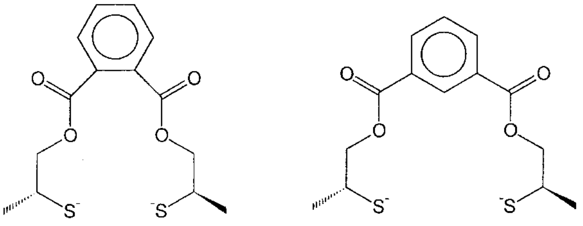


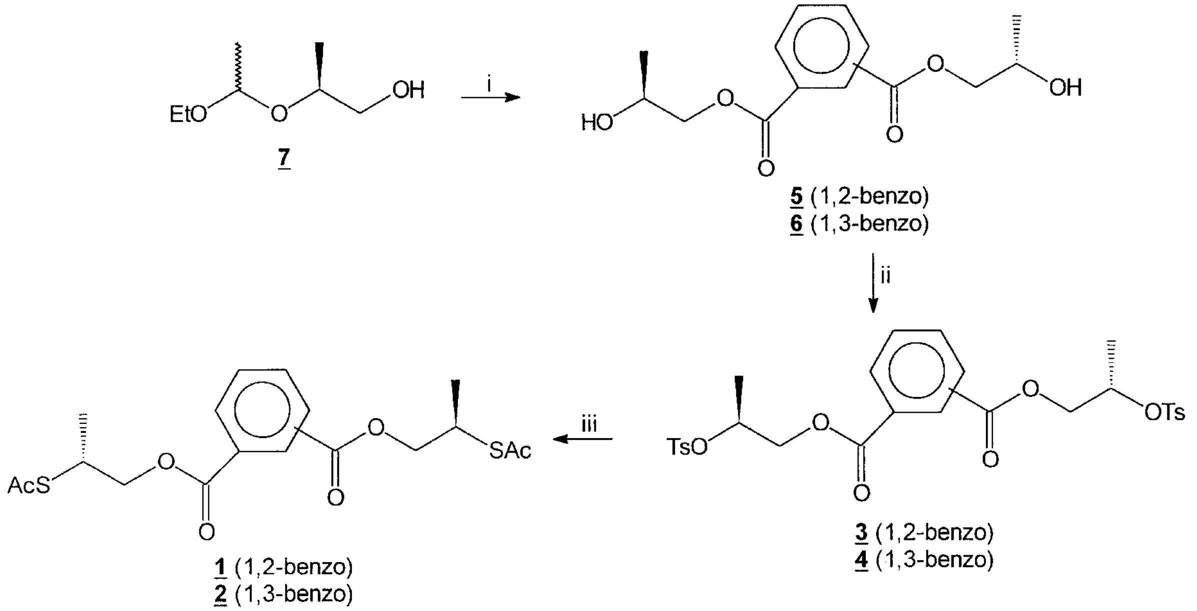
Scheme 1

The involvement of rhodium–thiolato species might be demonstrated by obtaining an enantiomeric excess (*ee*) in the reaction product when using chiral thiolates as ligands. This strategy has been successfully exploited in the asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid with the related complex $[Rh_2(\mu\text{-}Cl)(\mu\text{-}SR^*)(CO)_2P(tBu)_{32}]$ (SR^* = neomenthylthiolato). The presence of the chiral thiolato in the metal coordination sphere has been inferred from the mesurable *ee* displayed by the hydrogenation product.[8]

Several chiral dithiolato complexes have been tested in the hydroformylation reaction, but so far none of them has afforded an *ee* high enough to warrant the contribution of these species to the catalytic reaction. Chiral 1,2-dithiolato binuclear complexes require moderate pressures (30 bar) in order to give an active catalyst,[9] whereas 1,4-dithiolato complexes produce aldehydes at lower pressures. We would expect that, in order to prevent the dissociation of the dithiolato ligands, the use of low pressures is advisable.

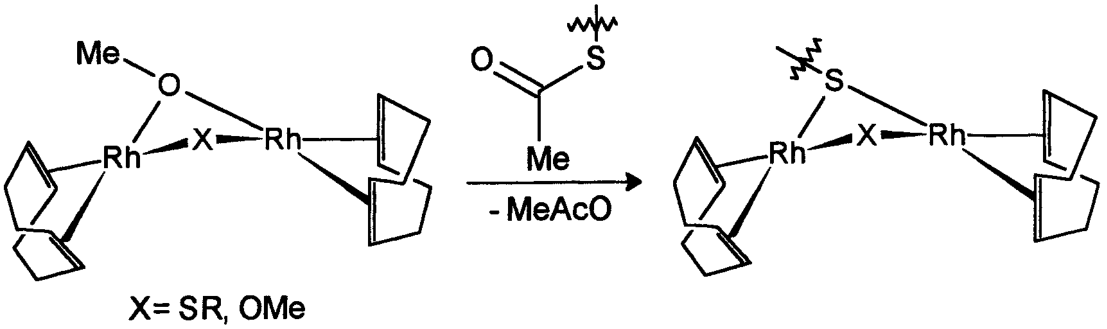
Here we report the synthesis of the two long-chain flexible chiral dithiolato ligands shown in scheme 1, the preparation of the corresponding rhodium complexes and their use as catalysts in the low-pressure hydroformylation of styrene.

This new type of ligands has been designed with the aim of filling the space above the open faces of the two metals in the folded binuclear structure, similarly to the well-known Trost long-chain diphosphine ligands. Upon coordination a palladium center, these last provide large chelate ring complexes, which have been successfully used in an enantioselective palladium-catalyzed allylic substitution.[10]



i: a) BuLi; b) *o*-$(ClOC)C_6H_4$ or *m*-$(ClOC)C_6H_4$; c) H^+/H_2O
ii: TsCl/py
iii: KAcS, 18-crown-6/DMF

Scheme 2



Scheme 3

RESULTS AND DISCUSSION

Ligands

The synthesis of the two dithioacetates **1** and **2** which are the precursors of the dithiolato ligands, is shown in Scheme 2.

(2*S*)-2-(1-Ethoxyethoxy)propan-1-ol **7** was obtained in two steps from (−)-(*S*)-ethyl lactate and was converted into the appropriate phthaloyl ester by treatment with the appropriate acyl chloride. When this reaction was performed in anhydrous pyridine, however, the expected hydroxyesters **5** and **6** could not be obtained in pure form. Phthaloyl chloride produced a mixture of esters containing only about 50% of **5**. The other products were the esters formed by reaction through the secondary alcohol, as well as the ethyl ester, which indicates partial hydrolysis of the starting ethyl acetal. Even in the stricter anhydrous conditions studied, the cleavage of the acetal could not be fully prevented. Under the same conditions, isophthaloyl chloride yielded less than 5% of product **6**.

The hydroxyesters **5** and **6** could be obtained successfully in fairly good yields by reaction of the protected diol **7** with n-butyllithium in THF–hexane, followed by addition of the corresponding acid chloride and by removal of the acetal with aqueous, hydrochloric acid. Compound **5** was isolated as an oil and was contaminated (less than 5%) by a product in which one of the two acyl groups had reacted with the secondary alcohol. This impurity could not be removed by flash chromatography and its formation could not be prevented, even when the reaction conditions were carefully controlled. Diol **6** was a solid, which was recrystallized to yield a pure microcrystalline product. Diols **5** and **6** were converted into the corresponding tosylates **3** and **4** by treatment with tosyl chloride in pyridine. By reaction with potassium thioacetate in the minimum volume of dimethylformamide(DMF) in the presence of a catalytic amount of 18-crown-6, the tosylates **3** and **4** afforded the dithioacetates **1** and **2** in moderate yields. ^{1}H NMR at 500 MHz did not show any evidence of the *meso*-diasteroisomer, which is consistent with a complete inversion of the configuration at the stereogenic carbon atoms in the substitution reaction.

Metal complexes

The rhodium–dithiolato complexes were obtained by reaction of the corresponding dithioacetates **1** and **2** with $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ (Scheme 3). The driving force for the hydrolysis of the dithioacetate groups is the subsequent coordination of the thiolate to the metal. Acyl removal was remarkably selective and the phthaloyl groups remained untouched.

The hydrolysis of the dithioacetate groups was monitored by IR spectroscopy Thus, the intensity of the COS absorption at 1694 cm^{-1} decreased steadily during the reaction, while the initial absorption of the ester group of the ligand at 1732 cm^{-1} increased due to the formation of methyl acetate. The reaction was run until the thiacetate absorption disappeared.

In addition to the desired binuclear complexes, the dithiolato ligands generated *in situ* give rise to rhodium complexes of higher nuclearity. In these species, each of the two sulfur atoms in the same ligand are coordinated to a different pair of rhodium atoms (Scheme 4).

In order to gain an insight into the nature of the rhodium complexes, we analyzed the nuclearity of the reaction products by GPC (gel-permeation chromatography). The column was previously

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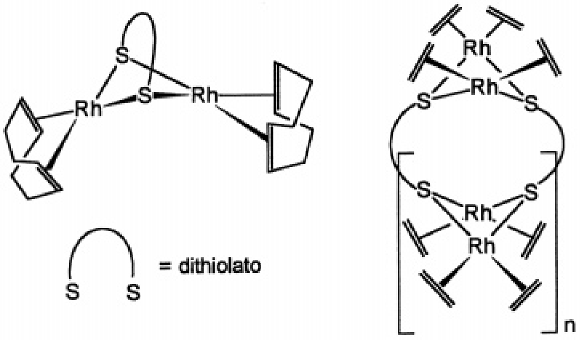

Scheme 4

calibrated with a series of polystyrene standards. Figure 1(a) represents the chromatogram of the solution obtained from the reaction of $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ with the ligand precursor **1** after all the dithioacetate had reacted. The Figure shows a number of peaks, which correspond to a mixture of reaction products of different nuclearity. It is clear that the main product of the mixture is the one with lowest nuclearity, since in GPC the smallest species is the last to be eluted. In the case of **2** (Figure 2a), the smallest species eluted at 10.4 min. Although this is not the main component of the mixture, this elution time compares well with the 10.2 min observed for the main component of the reaction mixture of **1**. These elution times correspond to polystyrene containing three to four units of the monomer. A visual inspection of molecular models revealed that both the binuclear species and the polystyrene polymer have about the same max-

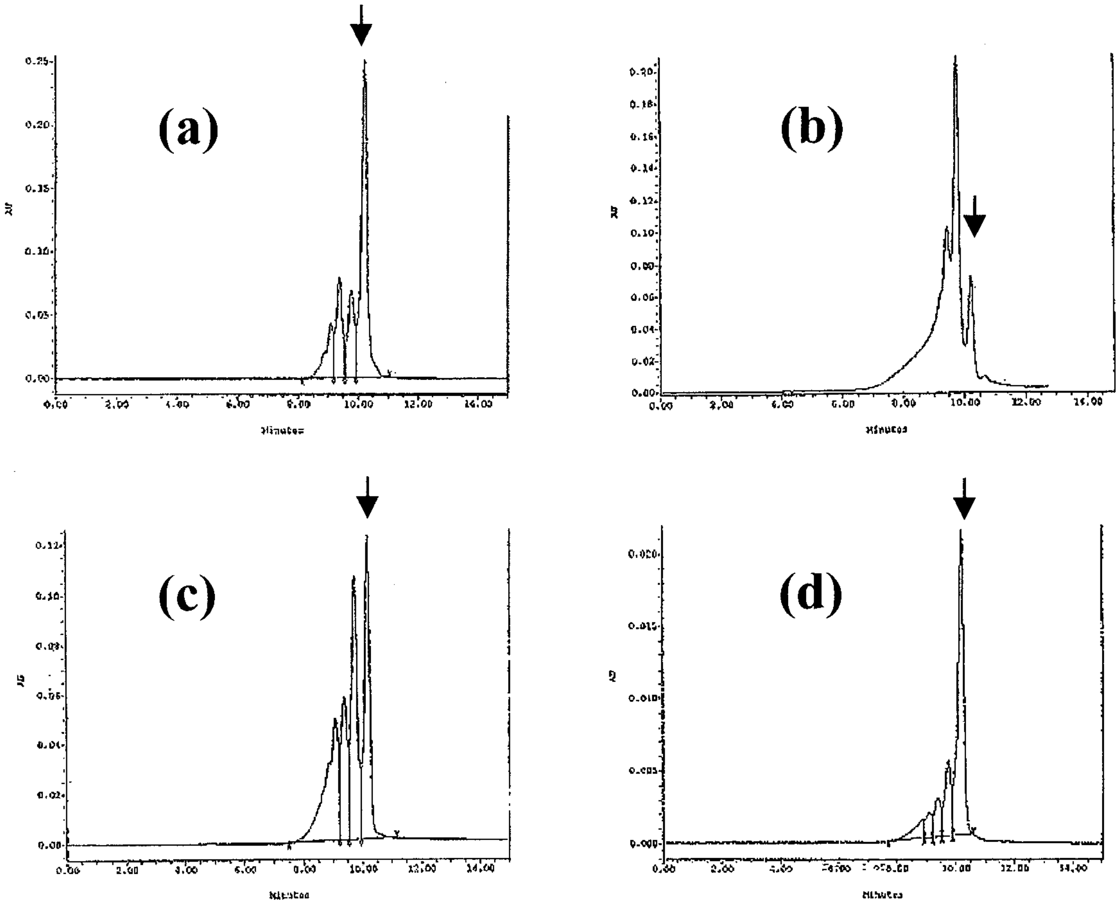

Figure 1 GPC chromatograms of the mixture of complexes obtained with **1** and $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ (all in CH_2Cl_2 solution): (a) solution before the precipitation of the products; (b) recrystallized in CH_2Cl_2/MeOH; (c) solid after precipitation and before recrystallization; (d) after purification by preparative chromatography. The arrow indicates the peak assigned to the binuclear rhodium species.

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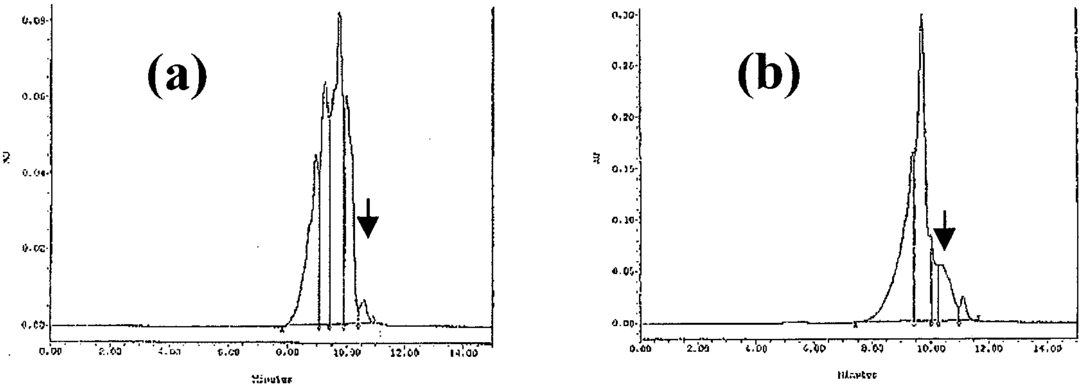

Figure 2 GPC chromatograms of the mixture of complexes obtained with **2** and [$Rh_2(\mu\text{-}OMe)_2(cod)_2$] (all in CH_2Cl_2 solution): (a) solution before the precipitation of the products; (b) recrystallized in CH_2Cl_2/MeOH. The arrow indicates the peak assigned to the binuclear rhodium species.

imum length (*ca* 15 Å). Furthermore, the elution time of the next-to-last peaks in the chromatograms of the metal complexes correspond to polystyrene 25 Å long which is far from the length of a rhodium binuclear complex. Thus, we assigned the last-eluted peaks to the expected binuclear rhodium species.

To corroborate this hypothesis, we analyzed by GPC a sample of [$Rh_2(\mu\text{-}SPr)_2(cod)_2$] taken as a model for an unequivocally binuclear species. As expected, this product gave a single peak with a elution time of 10.5 min. This again correlates well with the last-eluted dithiolato complexes for both the precursor ligands **1** and **2**. It is worth noting that the rhodium complexes derived from **2** show a greater tendency to form polynuclear species than the dithiolato derived from **1**. In the latter ligand, the *ortho* disposition of the ester groups seems to favor coordination to a single pair of rhodium atoms, yielding mainly the binuclear complex.

When methanol was added to solutions containing the mixture of the dithiolato complexes, yellow–orange precipitates were obtained in both cases. These solids were dissolved and analyzed by GPC. Figure 1(c) shows the chromatogram of the solid obtained from **1**. It is apparent that precipitation increases the degree of polymerization of the metal complexes. Both of the solids, derived from **1** and **2**, were recrystallized in dichloromethane/methanol (CH_2Cl_2/MeOH). Figure 1(b) and Figure 2(b) show that the amount of high-nuclearity species in the mixture increased even more.

In order to isolate the pure binuclear complex, preparative chromatography on silica was attempted in the case of the mixture of complexes derived from **1**. A sample somewhat richer in the binuclear species than the crude reaction solution (see Fig. 1d) was obtained, but in a very low yield (<5%) because the complexes seem to decompose on the stationary phase.

Catalytic experiments

The hydroformylation catalysts were generated *in situ* by adding the appropriate amount of PPh_3 to the corresponding cod complexes in the autoclave under syngas pressure, as previously described.[11] It is known that under these conditions a mixed carbonyl–phosphine species is formed (Eqn [1]; L = dithiolato)

$$[Rh_2(\mu\text{-}L)(cod)_2]_n + 2nPPh_3 + 2nCO \rightarrow [Rh_2(\mu\text{-}L)(CO)_2(PPh_3)_2]_n + 2n\text{cod} \qquad [1]$$

The experiments were run until the conversion was almost complete. In all the experiments, samples were withdrawn at about half-conversion to check the stability of the catalytic systems. Since the selectivity at this time was the same as at complete conversion, no variation in the nature of the catalytically active species seemed to take place over the entire process. Both the mixture of oligomeric complexes containing the dithiolato ligands derived from **1** and **2** as well as the purified binuclear complex of the former ligand, were tested in the hydroformylation of styrene. As is apparent from Table 1, under identical reaction conditions they produced nearly identical results. Entry 1 corresponds to a recrystallized sample (GPC chromatogram in Fig. 1b); in entry 2 the experiment

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Table 1 Hydroformylation[a] of styrene with **1 Rh** complexes (see text)

Entry	Conversion (%)[b]	*t*(min)	Regisselectivity (%)[c]	Stereoselectivity *ee* (%)[d]
1	97	245	87	<3
2	86	140	87	<3
3	96	120	84	<3
4	>99	305	86	<3

[a] Reaction conditions: 0.025 mmol of Rh, 0.050 mmol of PPh_3 and 5 mmol of styrene in 7.5 ml of toluene; $P = 6$ bar; $P(CO) = P(H_2)$; $T = 60$ °C.
[b] Styrene converted; chemoselectivity >99%.
[c] [Branched aldehyde]/[total aldehyde].
[d] Enantiomeric excess of 2-phenylpropanal.

was carried out with a sample precipitated without further recrystallization (GPC chromatogram in Fig. 1c); entry 3 refers to the mixture of complexes obtained directly from **1** and $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ without being isolated (GPC chromatogram in Fig. 1a), and finally, in the run of entry 4 a sample purified by chromatography was used (GPC chromatogram in Fig. 1d), which was a fairly pure sample of the binuclear species.

When the mixture of oligomers containing the dithiolato ligand derived from **2** was used in the reaction conditions described in Table 1, again the regioselectivity was 87% and the enantioselectivity was zero. When the reaction was run at a different pressure (30 bar) or temperature (80 °C), again no *ee* was observed. In all cases the results were very similar to those obtained under the same conditions when $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ was used instead of the bridged dithiolato complex as catalytic precursor. It is known that in the presence of PPh_3 and under syngas, this complex is converted into $RhH(CO)_x(PPh_3)_y$ species.

In summary, these results provide further support for the view that dithiolato ligands are easily displaced from rhodium centers under hydroformylation conditions and are not directly involved in the catalytic process.

EXPERIMENTAL

General methods

The metal complexes were handled under a nitrogen atmosphere using a vacuum line and standard Schlenk techniques. The complex $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ (cod = 1,5-cyclo-octadiene) was prepared as previously reported.[12] IR spectra were recorded on a Perkin-Elmer FT-1710. The H, C, N and S analyses were carried out with a Carlo Erba CHN EA-1108 microanalyzer. NMR spectra were acquired on Bruker AC-250 instruments at 250 MHz (^1H) and 63 MHz (^{13}C) and occasionally on a Varian 500 MHz, using $SiMe_4$ as standard. MS were recorded on a Hewlett–Packard G1800A GCD Series chromatograph using an HP-5 (5% phenylmethylsiloxane, 30 m × 0.25 mm i.d.) column, and a Hewlett–Packard 5989X instrument for the heaviest products. Optical activity of chiral products was measured with a PROPOL polarimeter. Catalytic reaction conversions and regioselectivities were analyzed by GC in a Hewlett–Packard 5890 Series II using an HP-5 (5% phenylmethylsiloxane) (30 m × 0.32 mm i.d.) column. Enantiomeric excesses were measured in a Konic HRGC-3000C instrument using a Supelco β-Dex. 120 (30 m × 0.25 mm i.d.) chiral column.

Catalytic hydroformylation

Hydroformylation experiments were carried out in a homemade stainless steel autoclave with magnetic stirring. To prevent direct contact with the stainless steel, the catalytic solution was contained in a glass vessel, and the autoclave cap was Teflon-covered. Temperature was kept constant by a preheated water bath circulating through an external autoclave jacket. Constant pressure was maintained by connecting the autoclave to a gas reservoir via a gas regulator. The drop in the pressure reservoir was measured with a precision manometer, which allowed the evolution of the reaction to be monitored.

In a typical experiment, the catalyst precursor (0.025 mmol of Rh), PPh_3 (0.050 mmol) and styrene (5 mmol) were dissolved in 7.5 ml of toluene. The solution was transferred into the evacuated autoclave, which was then pressurized with syngas to about 80% of the reaction pressure.

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The pre-heated water circuit was connected to the autoclave jacket, and when thermal equilibrium was reached (5–10 min) more gas mixture was introduced until the working pressure was achieved and stirring of the solution was begun. At the end of the reaction, the autoclave was cooled to room temperature and depressurized. The regioselectivity was analyzed directly from a sample of the reaction solution and 1 ml was reduced to the corresponding alcohols with $LiAlH_4$ to measure the enantiomeric excess in 2-phenylpropanol.

Synthesis of the products

Di[(2*S*)-hydroxypropyl] isophthalate 6

In a 500 ml flask, 10 g (67.6 mmol) of (2*S*)-(1-ethoxyethoxy)propan-1-o1[13] **7** was dissolved in 150 ml of dry THF. Commercial 2.5 M *n*-butyllithium in hexane (30 ml) was carefully added and the mixture was stirred for 4 h. The reaction mixture turned orange and a white precipitate formed. Then, 100 ml of a THF solution containing 7.54 g (37.2 mmol) of isophthaloyl chloride was added, and the reaction mixture was refluxed under nitrogen for 15 h, while a white precipitate of LiCl formed. This was filtered, the solution was cooled in an ice-bath and 100 ml of water was added. The mixture was acidified with concentrated HCl, stirred for 0.5 h at 60 °C and neutralized with an aqueous saturated solution of $NaHCO_3$. The organic solvent was evaporated and the residue was extracted with diethyl ether (3 × 75 ml). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under vacuum. The crude product, was dissolved in the minimum volume of ethylacetate, and precipitated by adding hexane at 0 °C, producing 7.19 g (75% yield) of **6** as a white microcrystalline solid. Analysis: Found: C, 59.41; H, 6.27; Calcd for $C_{14}H_{18}O_6$: C, 59.55; H, 6.43%. IR (KBr): 3367 cm^{-} (m) (st. O—H), 1717 cm^{-} (s) (st. C=O). ^1H NMR (250 MHz, $CDCl_3$): 1.28 (d, 6H, *J* = 5.8 Hz, C*H*$_3$); 2.31 (s, 2H, O*H*); 4.20 (m, 4H, C*H*(CH$_3$)C*H*H′); 4.35 (m, 2H, CH*H*′); 7.52 (t, 1H, *J* = 8.0 Hz, *H5* ring); 8.22 (dd, 2H, *J* = 8.0 Hz, J = 2.2 Hz, *H4,6* ring); 8.67 (s, 1H, *H2* ring). ^{13}C NMR (63 MHz, $CDCl_3$): 19.3 (*C*H$_3$); 66.2 (*C*HCH$_3$); 70.4 (O*C*H$_2$); 128.7 (*C5* ring); 130.4 (*Cl,3* ring); 130.8 (*C2* ring); 134.1 (*C4,6* ring); 165.8 (C=O). $[\alpha]_D^{20}$ +26.2 ° (*c* = 3.1, CH_2Cl_2). MS (*m/z*): 252 (*M* − 30), 0.3% 207, 100%; 149, 91%.

Di[(2*S*)-hydroxypropyl] phthalate 5

The procedure described above for **6** was also used here. The yellow residue obtained was purified by chromatography (ethyl acetate/hexane, 2,3 v/v) to give 6.4 g of a colorless liquid (yield 68%). Analysis: Found: C, 59.89; H, 6.60; Calcd for $C_{14}H_{18}O_6$: C, 59.55; H, 6.43%. IR (film): 3424 cm^{-1} (m) (st. O—H), 1724 cm^{-1} (s) (st. C=O). ^1H NMR (250 MHz, $CDCl_3$): 1.31 (d, 6H, *J* = 5.8 Hz, C*H*$_3$); 2.52 (s, 2H, O*H*); 4.13 (m, 4H, C*H*(CH$_3$)C*H*H′); 4.35 (m, 2H, CH*H*′); 7.55 (m, 2H, *H4,5* ring); 7.74 (dd, 2H, *J* = 5.8 Hz, *J* = 2.9 Hz, *H3,6* ring). ^{13}C NMR (63 MHz, $CDCl_3$): 18.9 (*C*H$_3$); 65.8 (*C*HCH$_3$); 71.0 (O*C*H$_2$); 129.2 (*C4,5* ring); 131.4 (*C3,6* ring); 131.7, (*C1,2* ring); 167.8 (C=O). $[\alpha]_D^{20}$ +43.5 ° (*c* 7.1, CH_2Cl_2). MS (*m/z*): 265 (*M*−17), 0.02%; 149, 100%.

Di[(2*S*)-tosyloxypropyl]) isophthalate 4

Under a nitrogen atmosphere, a solution of 1.93 g (10.1 mmol) of tosyl chloride was added to 1.3 g (4.6 mmol) of **6** dissolved in 10 ml of dichloromethane and 7 ml of pyridine cooled to 0 °C. The yellow solution was stirred for 24 h, while white pyridinium chloride precipitated. Then, a further 20 ml of dichloromethane was added and the organic layer was extracted with aqueous hydrochloric acid (10%) until all the pyridine was removed. The solution was washed in a saturated aqueous solution of sodium bicarbonate dried over magnesium sulfate and finally the solvent was evaporated under vacuum. The crude was recrystallized with ethyl acetate/hexane to obtain 1.76 g (yield 65%) of white solid. Analysis: Found: C, 56.86; H, 5.36; S, 10.80; Calcd for $C_{28}H_{30}O_{10}S_2$: C, 56.94; H, 5.12; S, 10.86%. IR (KBr): 1735 cm^{-1} (s) (st. C=O), 1356 cm^{-1} (m) (st. as. S=O). ^1H NMR (250 MHz, $CDCl_3$): 1.37 (d, 6H, *J* = 6.6 Hz, CHC*H*$_3$); 2.28 (s, 6H, C*H*$_3$ tosyl); 4.27 (dd, 2H, *J* = 12.0 Hz, *J* = 5.9 Hz, C*H*H′); 4.38 (dd, 2H, *J* = 12.0 Hz, *J* = 3.6 Hz, CH*H*′); 4.95 (d quintuplet, 2H, *J* = 6.7 Hz, *J* = 3.6 Hz, C*H*); 7.47 (t, 1H, ^3J = 7.6 Hz, *H5* ring); 8.10 (dd, 2H, *J* = 7.6 Hz, J = 1.9 Hz, *H4,6* ring); 8.50 (s, 1H, *H2* ring); 7.18, 7.75 (d, 4H, *J* = 8.0 Hz, *H* tosyl). ^{13}C NMR (63 MHz, $CDCl_3$): 17.5 (*C*H$_3$); 21.5 (*C*H$_3$ tosyl.); 66.6 (O*C*H$_2$); 76.4 (*C*HCH$_3$); 127.7 (*C5* tosyl); 128.5 (*C5* ring); 129.8 (*C2* ring); 129.9 (*C1,3* ring); 131.1 (*C3,5* tosyl); 133.9 (*C2,6* tosyl); 134.1 (*C4,6* ring); 144.7 (*C1* tosyl); 165.0 (C=O). $[\alpha]_D^{20}$ +8.0 ° (*c* = 7.7, CH_2Cl_2). MS (chemical impact, NH_3, *m/z*: 608 (*M* + 18), 8%; 377, 100%; 188, 21%.

Di[(2*S*)-tosyloxypropyl] phthalate 3

The procedure described above for **4** was also used here. The product was purified by chromatography (silica; ethyl acetate/hexane, 2:3 v/v) to produce 4.8 g (yield 70%) of a colorless viscous oil. Analysis: Found: C, 56.69; H, 5.17; S, 10.84; Calcd for $C_{28}H_{30}O_{10}S_2$: C, 56.94; H, 5.12; S, 10.86%. IR (film): 1732 cm^{-1} (s) (st. C=O), 1365 cm^{-1} (s) (st. S=O). ^1H NMR (250 MHz, $CDCl_3$): 1.32 (d, 6H, *J* = 6.6 Hz, CHC*H*$_3$); 2.32 (s, 2H, C*H*$_3$ tosyl); 4.21 (dd, 2H, *J* = 11.7 Hz, *J* = 6.6 Hz, C*H*H′); 4.31 (dd, 2H, *J* = 11.7 Hz, *J* = 3.6 Hz, CH*H*′); 4.85 (d quintuplet, 2H, *J* = 6.6 Hz, *J* = 3.6 Hz, C*H*(CH_3); 7.53 (m, 2H, *H3,6* ring); 7.60 (m, 2H, *H4,5* ring);7.16, 7.72 (d, 4H, *J* = 8 Hz, *H* tosyl). ^{13}C NMR (63 MHz, $CDCl_3$): 17.4 (*C*H$_3$); 21.5 (*C*H$_3$ tosyl); 76.4 (*C*HCH$_3$); 66.9 (O*C*H$_2$); 127.7 (*C4* tosyl); 129.0 (*C4,5* ring); 129.7 (*C3,6* ring); 129.7 (*C3,5* tosyl); 131.2 (*C1,2* ring); 133.9 (*C2,6* tosyl); 144.6 (*C1* tosyl); 166.6 (*C*=O). $[\alpha]_D^{20}$ +3.9 ° (*c* = 10.7, CH_2Cl_2). MS (chemical impact, NH_3, *m/z*): 608 ($M + 18$), 74%; 206, 100%.

Di[(2*R*)-acetylmercaptopropyl] isophthalate 2

Under a nitrogen atmosphere, 0.19 g (1.66 mmol) of potassium thioacetate (KAcS) and 30 mg of 18-crown-6 were dissolved in 1 ml of dimethylformamide. Once the reagent had dissolved and the solution turned green, 0.44 g (0.74 mmol) of **4** was added. The reaction was stirred for 10 days at room temperature. After this, 5 ml of water was added to the deep brown solution and the mixture was extracted with 4 × 10 ml of diethyl ether. The organic layer was dried over magnesium sulfate and the solvent was removed under vacuum. The crude was purified by chromatography (silica; ethyl acetate/hexane, 1:4 v/v) to yield 0.16 g (53%) of the product as a colorless liquid. Analysis: Found: C, 54.1; H, 5.63; S, 16.09; Cald for $C_{18}H_{22}O_6S_2$: C, 54.25; H, 5.56; S, 16.09%. IR (liquid film): 1726 cm^{-1} (s) (st. C=O ester), 1693cm^{-1} (s) (st. C=O thiacetate). ^1H NMR (250 MHz, $CDCl_3$): 1.41 (d, 6H, *J* = 7.3 Hz, CHC*H*$_3$); 2.32 (s, 6H, C*H*$_3$COS); 3.95 (sex., 2H, *J* = 6.5, C*H*(CH_3)); 4.38 (d, 4H, C*H*$_3$); 7.53 (t, 1H, *J* = 8.0 Hz, *H5* ring); 8.21 (dd, 2H, *J* = 8.0 Hz, *J* = 2.2 Hz, *H4,6* ring); 8.64 (s; 1H, *H2* ring). ^{13}C NMR (63 MHz, $CDCl_3$): 17.5 (*C*H$_3$); 30.6 (*C*H$_3$COS); 37.9 (*C*HCH$_3$); 67.9 (O*C*H$_2$); 128.8 (*C5* ring); 130.5 (*C1,3* ring); 130.9 (*C2* ring); 134.0 (*C4,6* ring); 165.8 (*C*OO); 194.8 (*C*OS). $[\alpha]_D^{20}$ +68.1 ° (*c* = 7.9, CH_2Cl_2). MS (*m/z*): 356 ($M-42$), 0.04%; 149, 100%; 117, 75%; 74, 42%; 43, 88%.

Di [(2*R*)-acetylmercaptopropyl] phthalate 1

The procedure described above for **2** was also used in this case, but starting from the tosylate **3**. The yield was 50%. Analysis: Found: C, 54.66; H, 5.75; S, 16.28; Calcd for $C_{18}H_{22}O_6S_2$: C, 54.25; H, 5.56; S, 16.09%. IR (liquid film): 1730 cm^{-1} (s) (st. C=O ester), 1695 cm^{-1} (s) (st. C=O thioacetate). ^1H NMR (250 MHz, $CDCl_3$): 1.35 (d, 6H, *J* = 7.3 Hz, CHC*H*$_3$); 2.29 (s, 6H, C*H*$_3$COS); 3.88 (sex., 2H, *J* = 6.6 Hz, C*H*(CH_3)); 4.33 (d, 4H, *J* = 5.8 Hz, *CH2*); 7.52 (m, 2H, *H4,5* ring); 7.70 (m, 2H, *H3,6* ring). ^{13}C NMR (63 MHz, $CDCl_3$): 17.5 (*C*H$_3$); 30.6 (*C*H$_3$COS); 37.7 (*C*HCH$_3$); 68.2 (O*C*H$_2$); 128.3 (*C4,5* ring); 131.2 (*C3,6* ring); 131.7 (*C1,2* ring); 167.0 (*C*OO); 194.7 (*C*OS). $[\alpha]_D^{20}$ +64.6 ° (*c* = 7.6, CH_2Cl_2). MS (*m/z*): 339 ($M-59$), 0.04%; 149, 70%; 117, 72%; 74, 100%; 43, 88%.

Rhodium complexes 1Rh and 2Rh

The same procedure was used for both complexes. Under a nitrogen atmosphere, 331 mg (0.68 mmol) of $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ was dissolved in 60 ml of dichloromethane. A solution of 300 mg (0.75 mmol) of ligand **1** or **2** dissolved in 20 ml of dichoromethane was added slowly, followed by a further 40 ml of the same solvent. The reaction was monitored by IR spectroscopy through the COS and COO absorptions. After 24 h the brown solution was concentrated under vacuum to 5–10 ml and methonol was added until an orange solid precipitated. The solid was filtered, rinsed with 3 × 10 ml of methonol at 0 °C and dried under vacuum. The solid was recrystallized by dissolving in the minimum volume of dicholoromethane and adding methanol dropwise. Both yields were in the range 30–40%. In the case of the ligand **1** the product could be further purified by preparative chromatography (silica; diethtl ether). Although the yield was only 5%, the sample allowed product characterization by NMR and elemental analysis. Analysis: Found: C, 48.85; H, 5.70; S, 8.69; Calcd for $Rh_2C_{30}H_{40}O_4S_2$: C, 49.05; H, 5.49; S, 8.73%. IR (in CH_2Cl_2): 1725 cm^{-1} (s) (st. C=O). ^1H NMR (250 MHz, CD_2Cl_2): 1.09–1.33 (m, C*H*$_3$); 1.92, 2.27 (s br, C*H*$_2$ cod); 3.8–4.0 (m, C*H*(CH_3)); 4.24 (m, CH(C*H*$_2$); 4.35 (m, *C*H cod); 7.50–7.80 (m, *H* ring). ^{13}C NMR (63 MHz, $CDCl_3$): 23.2 (*C*H$_3$), 32.2 (*C*H$_2$ cod); 39.0(*C*HCH$_3$); 72.2 (O*C*H$_2$); 81.0 (*C*H cod); 129.8 (*C4,5* ring); 131.9 (*C3,6* ring); 132.9 (*C1,2* ring); 167.7 (*C*OO).

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