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# Synthesis of rhodium(I) complexes with the new dithiol chiral ligand (+)-*trans*-2,3-bis(mercaptomethyl)-bicyclo[2.2.2]octane ($H_2$BCOS). Their application as catalysts precursors in the styrene hydroformylation

A. Castellanos-Páez, S. Castillón, C. Claver *

*Departament de Química, Facultat de Química, Universitat Rovira i Virgili. Pça. Imperial Tàrraco 1, 43005 Tarragona, Spain*

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**Abstract**

The new dithiol ligand (+)-$H_2$BCOS ((+)-**1**) has been synthesized. The tetranuclear rhodium complex $[Rh_2(\mu\text{-BCOS})(cod)_2]_2$ (**8**) (cod = cycloocta-1,5-diene) was prepared by starting with the dinuclear complex $[Rh(\mu\text{-OMe})(cod)]_2$ (**7**) through an exchange reaction with the dithiol ligand. The reactivity of **8** towards CO and phosphorus-donor ligands was studied; the mixed CO/P complex $[Rh_2(\mu\text{-BCOS})(CO)_2(PPh_3)_2]$ (**10**) was prepared and studied by IR and $^{31}$P NMR. The $[Rh_2(\mu\text{-(+)-BCOS})(cod)_2]_2$ complex was tested as a catalyst precursor in the enantioselective hydroformylation of styrene. The influence of P-donor as modifying ligand, temperature and pressure on the catalytic activity and selectivity was explored, achieving *ee* up to 55% with total conversion into aldehydes in the presence of BDPP. These results revealed a slight cooperative effect between the dithiolate and the diphosphine ligands. © 1997 Elsevier Science S.A.

*Keywords:* Enantioselective catalysis; Asymmetric hydroformylation; Rhodium complexes; Chiral thiolate

## 1. Introduction

The asymmetric hydroformylation reaction represents a powerful tool for the preparation of large number of different chiral products to be used as precursors of several organic compounds endowed with therapeutic activity [1–3].

From many years, transition-metal complexes based on rhodium and platinum have been used as catalysts in asymmetric hydroformylation [2,3]. Platinum tin dichloride catalytic systems had shown high enantioselectivity when modified with DIOP [4], BPPM [5], BCO [6,7], and BDPP [8], although the regio- and chemoselectivity were in general low [4–8]. In recent years, different rhodium complexes modified with chiral phosphorus ligands such as BINAPHOS [9], diphosphites [10] and diphosphinites [11] had also provided high asymmetric induction in hydroformylation of styrene and other olefins, showing in some cases excellent regio- and chemoselectivity (Fig. 1).

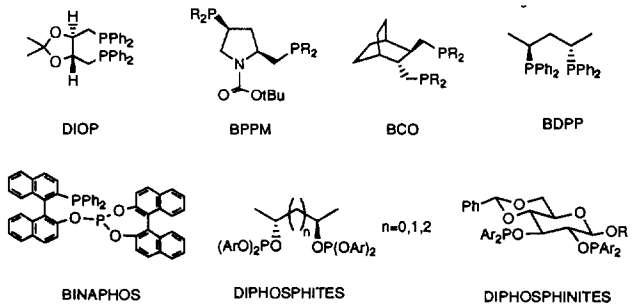


Fig. 1.

In contrast, dinuclear thiolate-bridged rhodium complexes have been shown to be efficient catalysts in the hydroformylation of olefins and other substrates under mild conditions [12]. An advantage of using these types of dinuclear complex is that subtle changes can be

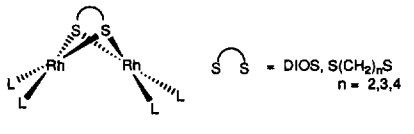


Fig. 2.

* Corresponding author.


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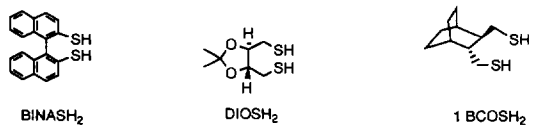



Fig. 3.

introduced into the bridging ligands. With the aim of exploring the use of these complexes in asymmetric hydroformylation we speculate that the presence of dithiolato bridge would be more suitable, since it would avoid different possible conformations of the monothiolato ligand.

Firstly, we synthesized simple dinuclear complexes with dithiolate bridge ligands such as $[\{Rh_2[\mu\text{-}S(CH_2)_nS](cod)_2\}_x]$ ($n = 2$–4, $x = 1$ or 2) (Fig. 2), for which X-ray diffraction studies when $n = 2$ or 3 showed a bent dinuclear structure [13]. Then we studied the reactivity of these diolefinic complexes towards carbon monoxide and towards carbon monoxide together with phosphorus ligands [14]. These complexes turned out to be active in hydroformylation of 1-hexene in the presence of phosphorous ligands [14].

Taking as model chiral those phosphorous ligands that had successfully been used in asymmetric hydroformylation with platinum and rhodium catalysts, we synthesized the $C_2$ symmetry chiral dithiol ligands $BINASH_2$ and $DIOSH_2$ (Fig. 3), and the corresponding dithiolato bridge rhodium complexes which incorporated these ligands [15,16]. We have demonstrated that these complexes provide asymmetric induction in the hydroformylation of styrene in the absence of phosphines (the case of $[Rh(BINAS)(cod)]_n$) [17], and that the presence of chiral diphosphines improve the *ee* obtained, depending on the dithiol/diphosphine ratio used and on the starting rhodium complex [18].

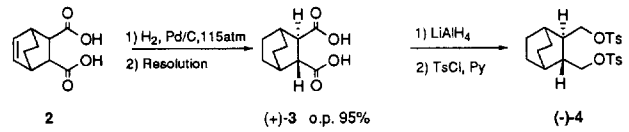
Here we report the synthesis of the new dithiol ligand *trans*-2,3-bis(mercaptomethyl)-bicyclo[2.2.2]octane ($H_2BCOS$) (**1**) (racemic) and the corresponding pure enantiomer (+)-$H_2BCOS$ ((+)-**1**) (Fig. 3), which are structurally related with the BCO ligand (Fig. 1). This diphosphine ligand, when used in $Pt\text{–}SnCl_2$ systems, provided a regioselectivity in 2-phenylpropanal up to 80% together with an *ee* of 86% [6,7].

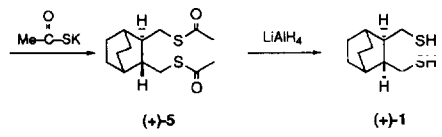
The ligand **1** has been used in to prepare of dithiolate bridge dinuclear rhodium(I) complexes which were subsequently tested as catalysts in the asymmetric hydroformylation of styrene.

## 2. Results and discussion

### 2.1. Synthesis of the dithiol ligand

The new ligand (+)-$H_2BCOS$ ((+)-**1**) was prepared from the diacid **2** [19] according to the pathways of




Scheme 1.

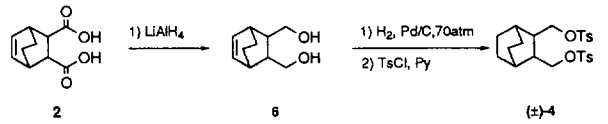
synthesis shown in Scheme 1. Diacid **2** was initially reduced using Pd/C 10% as catalyst and hydrogen at a pressure of 115 bar to obtain the diacid **3** (racemic) which was resolved using a reported procedure [20]. The resulting enantiomer (+)-**3** had an optical purity of 95% [7]. The acid functions were reduced in (+)-**3** with $LiAlH_4$, and subsequent treatment of the diol obtained with tosyl chloride gave the ditosyl derivative (−)-**4**. Nucleophilic substitution of tosyl groups by reaction with potassium thioacetate in 2-butanone gave compound (+)-**5** in 81% yield. Reduction of (+)-**5** with $LiAlH_4$ provides compound (+)-**1** in 89% yield.

Racemic ligand **1** was synthesized in a similar to the chiral ligand, omitting the resolution step. However, if **2** was first reduced to the unsaturated diol **6** [21], the double bond could be hydrogenated at lower pressure (ca. 70 bar) (Scheme 2).

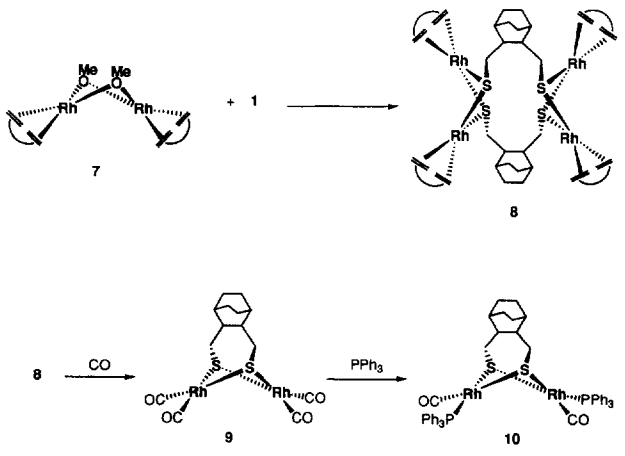
### 2.2. Synthesis of the dithiolate complexes

The $[Rh_2(\mu\text{-}(\pm)\text{-BCOS})(cod)_2]_2$ complex (**8**, cod = 1,5-cyclooctadiene) (Scheme 3) was obtained by adding racemic $H_2BCOS$ (**1**) to a dichloromethane solution of $[Rh(\mu\text{-OMe})(cod)]_2$ (**7**). Adding methanol caused the precipitation of a yellow-orange solid (**8**), the microanalytical data of which match the $[\{Rh_2(\mu\text{-}(\pm)\text{-BCOS})(cod)_2\}_n]$ stoichiometry. The molecular weight was determined osmometrically in $CHCl_3$ at 25 °C ($M_r$ = 1585), indicating that **8** is tetranuclear. The molecular ion $m/z = 1136$ is the heaviest ion in the mass FAB spectrum, which suggests that **8** undergoes fragmentation $[M_r - cod]^+$.

The $^1H$ NMR spectrum at −40 °C of complex **8** in $CDCl_3$ solution shows the olefinic proton signals of the coordinated cyclooctadiene as two multiplets at $\delta$ 4.1 and 4.4 ppm. Owing to the bent structure [13,15] and to




Scheme 2.




Scheme 3.

the nature of the dithiolate ligand, four non-equivalent sites are expected. However, not all non-equivalences were resolved, as has been reported in previous work on similar subjects [15]. The *endo*- and *exo*-methylene protons of the cod ligand show three multiplet signals at $\delta$ 3.9, 4.2 and 4.35. The different signals corresponding to the protons of the dithiolate ligand are observed in the range $\delta$ 1.0–1.5 (m, –CH– and $-CH_2-$) and at $\delta$ 2.0 (m, $-CH_2-S$).

Bubbling carbon monoxide through a dichloromethane solution of the diene complex yields a carbonyl complex which is formed by displacing the diene. The elemental analysis matches the stoichiometry $[\{Rh_2(\mu\text{-}(\pm)\text{-BCOS})(CO)_4\}_n]$ (**9**, Scheme 3). The FT-IR spectrum in solution of this compound shows three $\nu$(CO) stretching frequencies (2003s, 2059s and 2075s $cm^{-1}$) which have been observed to be characteristic for dinuclear tetracarbonylrhodium complexes [22–24]. The molecular weight could not be determined by osmometric measurements due to the compound's instability. However, related dinuclear tetracarbonyl-rhodium complexes containing dithiolate bridge ligands have been previously reported [13,15], and the osmometrically determined molecular weight for this type of complex suggests the formation of dinuclear compounds [15].

The dinuclear tetracarbonyl $[Rh_2(\mu\text{-}(\pm)\text{-BCOS})(CO)_4]$ (**9**) reacts with $PPh_3$, displacing the CO, giving rise to a mixed $PPh_3/CO$ complex which, according to the elemental analysis, matches the stoichiometry $[\{Rh_2(\mu\text{-}(\pm)\text{-BCOS})(CO)_2(PPh_3)_2\}_n]$ (**10**, Scheme 3).

The FT-IR spectrum of complex **10** in dichloromethane solution shows a very strong $\nu$(CO) signal at 1963s $cm^{-1}$ which could be attributed to the *trans* isomer in the case of the dinuclear complex. The $^{31}P\{^1H\}$ NMR spectrum in $CD_2Cl_2$ shows two doublets at $\delta$ 38.9 ($^1J_{Rh-P}$ = 159.1 Hz) and $\delta$ 41.0 ($^1J_{Rh-P}$ = 164.5 Hz), ratio 1:1, which suggests the co-existence in solution of the two isomers, *cis* and *trans* [14]. The fact that only one $\nu$(CO) signal is observed in the FT-IR spectrum could suggest that both frequencies accidentally coincide, or that the absorbance of the *cis* isomer is too low. The molecular weight could not be determined by osmometric measurements due to the poor solubility of the compound in the usual solvents. The FAB spectrum is not indicative because the $m/z$ of the first observed fragment is lower than that expected for the dinuclear complex.

### 2.3. Catalytic activity

To explore the behaviour of the Rh–BCOS complex as catalyst precursor, we initially studied the hydroformylation of styrene using the racemic $[Rh_2(\mu\text{-}(\pm)\text{-BCOS})(cod)_2]$ complex as catalyst precursor. When there was no phosphorus ligand at 5 and 10 bar of syn gas, no catalytic activity was observed. At 30 bar and 65 °C there was only a 2% conversion into aldehyde in 24 h. However, when the temperature was increased to 80 °C, the conversion into aldehydes was complete in 24 h (Table 1, entry 1). No side reactions were observed but the selectivity was practically null, ratio $n/iso \sim 1$.

When $PPh_3$ was added at P/Rh = 2, the system showed catalytic activity at 5 bar and 80 °C, and a 47% conversion into aldehydes was obtained in 24 h, but the regioselectivity was low, 66% in 2-phenylpropanal (entry 2). When pressure was increased to 10 bar, there was an 86% conversion into aldehydes in 12 h with a better regioselectivity, 86% in 2-phenylpropanal (entry 3). When the P/Rh ratio was increased to 4 or 8, no improvement in yield and selectivity were observed (entries 4 and 5). By decreasing the temperature to 65 °C a slightly better regioselectivity was obtained, but it took 24 h to achieve considerable conversions (entry 6).

Using the homochiral complex $[Rh_2(\mu\text{-}(+)\text{-BCOS})(cod)_2]$ as catalyst precursor in the hydroformylation of styrene, with no phosphorus ligand (Table 2,

Table 1
Styrene hydroformylation using $[Rh_2(\mu\text{-BCOS})(cod)_2]_2 / nPPh_3$ system as catalyst precursor [a]

| Entry | $P$ (bar) | $t$ (h) | $n$ | P/Rh | $C_{ald}$ (%) [c] | 2-PP/3-PP (%) |
|---|---|---|---|---|---|---|
| 1 | 30 | 24 | — | — | 99 | 54/46 |
| 2 | 5 | 24 | 8 | 2 | 47 | 66/34 |
| 3 | 10 | 12 | 8 | 2 | 86 | 86/14 |
| 4 | 10 | 8 | 16 | 4 | 86 | 86/14 |
| 5 | 10 | 8 | 32 | 8 | 81 | 85/15 |
| 6 [b] | 10 | 24 | 32 | 8 | 81 | 90/10 |

[a] Reaction conditions: substrate/precursor = 200 (molar); THF (15 ml), $CO/H_2 = 1$; $T$ = 80 °C. [b] 65 °C. [c] $C_{ald}(\%) = 100([2\text{-PP} + 3\text{-PP}]/[2\text{-PP} + 3\text{-PP} + \text{styrene}])$, 2-PP = 2-phenylpropanal, 3-PP = 3-phenylpropanal; hydrogenation and isomerization were < 1%.

Table 2
Styrene hydoformylation using $[Rh_2(\mu\text{-}(+)\text{-BCOS})(cod)_2]_2$/L as catalyst precursor [a]

| Entry | P (bar) | t (h) | L/Rh | P/Rh | $C_{ald}$ (%) [b] | 2-PP/3-PP (%) | ee (%) |
|---|---|---|---|---|---|---|---|
| 7 | 30 | 24 | — | — | 81 | 49/51 | 8(S) [c], 8(S) [d] |
| 8 [e] | 5 | 24 | $4PPh_3$ | 4 | 50 | 73/27 | 7(S) [d] |
| 9 | 10 | 24 | $4PPh_3$ | 4 | 93 | 90/10 | 5(S) [d] |
| 10 | 10 | 12 | 1dppp | 2 | 88 | 92/8 | 10(S) [c,d] |
| 11 | 10 | 23 | 2(+)-DIOP | 4 | 98 | 60/40 | 16(S) [c] |
| 12 | 10 | 23 | 2(−)-DIOP | 4 | 98 | 57/43 | 8 (R) [c] |
| 13 | 10 | 23 | 2(+)-BDPP | 4 | 99 | 95/5 | 55(S) [c] |
| 14 | 10 | 23 | 2(−)-BDPP | 4 | 99 | 94/6 | 43(R) [c] |
| 15 | 10 | 12 | 1(+)-BDPP | 2 | 94 | 94/6 | 52(S) [c], 47(S) [d] |
| 16 | 10 | 12 | 1(−)-BDPP | 2 | 96 | 94/6 | 48(R) [c], 50(R) [d] |

[a] Reaction conditions: substrate/precursor = 200 (molar); THF (15 ml), $CO/H_2 = 1$; $T = 65$ °C. $e.e.(\%) = 100([R - S])/(R + S)$. [b] $C_{ald}(\%) = 100([2\text{-PP} + 3\text{-PP}]/[2\text{-PP} + 3\text{-PP} + \text{styrene}])$, 2-PP = 2-phenylpropanal, 3-PP = 3-phenylpropanal; hydrogenation and isomerization were < 1%. [c] Determined by GC; [d] Determined by $^1H$ NMR using $Eu(hfc)_3$; [e] 80 °C.

entry 7), yield and regioselectivity were similar to those obtained with the racemic complex, as expected, (Table 1, entry 1). The enantiomeric excess was very low (8%). When $PPh_3$ was added to reaction mixture in a P/Rh ratio of 4, the catalytic system was active at 5 bar, giving a better regioselectivity, although the *ee* was still low (entry 8). At 10 bar, a regioselectivity of 90% in the branched aldehyde was obtained (entry 9). The results were similar when an achiral diphosphine was used, with a slightly improved *ee* (entry 10).

We have recently reported that the combined use of dithiolate and diphosphine chiral ligands gave moderate enantiomeric excess, and observing a cooperative effect for a given pair of ligands [18]. We choose the diphosphines DIOP and BDPP (Fig. 1) which had provided good results in previous enantioselective catalysis studies [1–3,18]. The hydroformylations were performed at 10 bar and 65 °C, because these reaction conditions were the most appropriate in our case. When (+)-DIOP was used as phosphorus ligand, with a P/Rh ratio of 4, the conversion was complete in 24 h, with 60% of the branched aldehyde and 16% of *ee* (entry 11). The (−)-DIOP isomer gave similar yield and regioselectivity, but only 8% of *ee* was obtained, and in this case the isomer *R* was the major one (entry 12). The use of (+)-BDPP and (−)-BDPP with the same P/Rh ratio gave complete conversion in 24 h together with excellent regioselectivity in the branched isomer, with *ee* of 55% for (+)-BDPP (entry 13) and 43% for (−)-BDPP (entry 14).

To observe the effect of the excess of diphosphine, some experiments were performed with a P/Rh ratio of 2, and similar results in yield and selectivity were obtained (entries 15 and 16).

These results reveal a slight cooperative effect between the dithiolate and the diphosphine ligands. This cooperative effect was more clearly observed in other related cases [18]. Different studies under hydroformylation conditions are at the moment in course in order to determinate which are the catalytic species when BDPP is used in the presence of different rhodium complexes.

## 3. Experimental procedure

The organic reagents were of commercial origin and they were used as-purchased. All rhodium complexes were synthesized using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. The $[Rh(\mu\text{-OMe})(cod)]_2$ (**7**) complex was prepared using standard methods [25]. Triphenylphosphine, dppp and BDPP were of commercial origin and used without further purification.

Proton and $^{13}C$ NMR spectra were measured on a Varian 300 MHz spectrophotometer, and chemical shifts are quoted in parts per million downfield with $SiMe_4$ as the internal standard. $^{31}P\{^1H\}$ NMR spectra were recorded on the same equipment, using 85% $H_3PO_4$ as the external reference. Optical rotations were measured on a Perkin–Elmer 241 MC polarimeter.

Gas chromatographic analyses were carried out on a Hewlett-Packard Model 5890 A gas chromatograph with flame ionization detector using a 25 m capillary column (Ultra 2). Enantiomeric excess was measured by GC on the same equipment using a 50 m capillary column (FS-Cyclodex β-I/P) with the alcohols or acids obtained respectively by reducing or oxidizing the product aldehydes [16].

Microanalyses were carried out on a Carbo Erba microanalyser. Infrared spectra were performed using a Nicolet 5ZDX spectrophotometer.

Hydroformylation experiments were carried out in an autoclave with magnetic stirring. The catalytic solution was contained in a glass vessel. The inside of the autoclave cap was Teflon-covered to avoid direct contact of the solution with stainless steel. Constant temperature was maintained by circulation of water through a double jacket.

### 3.1. Preparations

#### 3.1.1. Synthesis of (+)-bicyclo[2.2.2]octane-2,3-trans-dicarboxylic acid ((+)-3). Resolution [20]

In a representative experiment 6.8 g (0.034 mol) of racemic bicyclo[2.2.2]octane-2,3-*trans*-dicarboxylic acid (**3**) [19,21] was dissolved in 200 ml of absolute ethanol and then heated until it boiled. (−)-(*S*)-benzylmethylamine, 8.34 g (69 mmol), was added and the heating was continued for another 3 h to reduced the solution volume to 50% of the original. The solution was allowed to stand at room temperature for 24 h and the flask was then scratched. White crystals formed during the second standing period of 24 h. The crystals were removed by filtration to give 4.31 g of the corresponding salt. The filtrate was allowed to stand to obtain additional portions of crystals. The salt was treated with 100 ml of absolute ethanol and heated to reflux. White crystals formed when the solution was cooled to room temperature. The crystals were filtered and dried to give 2.64 g of the (+)-(−) diastereomer of the salt. These crystals were then treated with 30% $H_2SO_4$ to afford the diacid compound. Yield 1.0 g of the optically active (+)-bicyclo[2.2.2]octane-2,3-*trans*-dicarboxylic acid ((+)-**3**). $[\alpha]_D = +71.0°$ ($c = 0.5$, acetone) (95% optical purity). Anal. Found: C, 60.3; H, 7.1. $C_{10}H_{14}O_4$. Calc.: C, 60.6; H, 7.1%. NMR (DMSO-$d_6$): $^1$H, $\delta$ 1.40 (m, 8H, $-CH_2-C$); 1.95 (s, 2H, $-CH-C$); 2.60 (s, 2H, $-CH-C=O$); 14.0 (broad signal, OH acid). $^{13}$C (DMSO-$d_6$), $\delta$ 21.4; 25.1; 26.5; 44.4; 176.1.

Through analogous experiments, other fractions of (+)-bicyclo[2.2.2]octane-2,3-*trans*-dicarboxylic acid ((+)-**3**) were obtained, which were combined for further reactions.

#### 3.1.2. (−)-trans-2,3-Bis((tosyloxy)methyl)bicyclo-[2.2.2]octane ((−)-4) [7]

A solution of 1.82 g (9.2 mmol) of (+)-bicyclo[2.2.2]octane-2,3-*trans*-dicarboxylic acid ((+)-**3**) in 15 ml of dry THF was added dropwise to a suspension of 1.1 g (29 mmol) of $LiAlH_4$ in 5 ml of dry THF heated to reflux. The mixture was stirred overnight at room temperature and then the excess hydride was destroyed by the addition of 10 ml of water. Then 10 ml of 4 M NaOH and 10 ml of water were quickly added. The mixture was filtered off and the organic fraction was dried over $MgSO_4$, filtered and concentrated to give 1.2 g of *trans*-2,3-bis(hydroxymethyl)bicyclo[2.2.2]octane [7,21] as white crystals. Afterwards, a solution of 1.2 g (7.2 mmol) of this compound in 5 ml of pyridine was added dropwise to a solution of 3 g (15.6 mmol) of tosyl chloride in 5 ml of pyridine, during which time the temperature was kept at 0 °C. This solution was stirred overnight at room temperature, 10 g of ice was added, and the mixture was extracted with benzene. The combined benzene fractions were washed with a 1 M NaOH solution (2 × 10 ml), water (10 ml), a 2.5 M HCl solution (40 ml), water (10 ml), a 10% $NaHCO_3$ solution (10 ml), and water (2 × 10 ml). The organic fraction was dried over $MgSO_4$ and filtered, after which the solvent was removed under reduced pressure obtaining 3.0 g (89%) of (−)-*trans*-2,3-bis((tosyloxy)methyl) bicyclo[2.2.2]octane ((−)-**4**). $[\alpha]_D = -9.26°$ ($c = 0.6$, acetone) ($[\alpha]_{365} = -25.5°$ [7]). Anal. Found: C, 60.9; H, 6.4; S, 13.1. $C_{24}H_{30}O_6S_2$. Calc.: C, 60.2; H, 6.3; S, 13.3%. NMR ($CDCl_3$): $^1$H, $\delta$ 1.35 (m, 12H, $-CH_2-C$, $-CH-C$); 2.45 (s, 6H, $-CH_3$); 7.35 and 7.75 (8H, aromatic). $^{13}$C ($CDCl_3$), $\delta$ 19.9 ($-CH_2-C$); 21.7 ($-CH_3$); 24.8 ($-CH-C$); 25.9 ($-CH_2-C$); 39.1 ($-CH-C$); 71.6 ($-CH_2-OH$); 127.9 and 129.9 (aromatic).

#### 3.1.3. trans-2,3-Bis((tosyloxy)methyl)bicyclo[2.2.2]octane ((±)-4)

This was prepared in the same way as (−)-**4**, using (±)-**3**.

#### 3.1.4. (+)-trans-2,3-Bis((thiolacetyl)methyl)bicyclo-[2.2.2]octane ((+)-5)

A solution of 2.5 g (5.2 mmol) of (−)-*trans*-2,3-bis((tosyloxy)methyl)bicyclo[2.2.2]octane ((−)-**4**) and 1.81 g (16 mmol) of potassium thioacetate in 50 ml of 2-butanone was refluxed for 8 h. Then the solution was cooled to room temperature, filtered through Celite and concentrated. Adding 20 ml of diethylic ether caused the precipitation of more potasic tosylate which was filtered through Celite and the solution was concentrated again to obtain a dark brown oil. The residue was purified by CC (Silicagel; hexane–ethyl acetate 15:1) obtaining 1.17 g (81%) of (+)-*trans*-2,3-bis((thiolacethyl)methyl)bicyclo[2.2.2]octane ((+)-**5**). $[\alpha]_D = +8.4°$ ($c = 0.5$, $CH_2Cl_2$). NMR ($CDCl_3$): $^1$H, $\delta$ 1.50 (m, 12H, $-CH_2-C$, $-CH-C$); 2.30 (s, 6H, $-CH_3-C=O$); 2.80 (dd, 2H, $-CH_2-S$); 3.15 (dd, 2H, $-CH_2-S$). $^{13}$C ($CDCl_3$), $\delta$ 19.8; 26.6; 27.7; 30.7; 32.7; 44.0; 195.8.

#### 3.1.5. trans-2,3-Bis((thiolacetyl)methyl)bicyclo[2.2.2]-octane ((±)-5)

This was prepared in a similar way to (+)-**5**, using (±)-**4**.

#### 3.1.6. (+)-trans-2,3-Bis(mercaptomethyl)bicyclo-[2.2.2]octane ((+)-1)

A solution of 1.14 g (4 mmol) of *trans*-2,3-bis((thiolacethyl)methyl)bicyclo[2.2.2]octane ((+)-**5**) in 25 ml of dry diethylic ether was added dropwise to a cooled suspension of 0.5 g (13 mmol) of $LiAlH_4$ in 20 ml of dry diethyl ether. The mixture was stirred 3 h at room temperature. The excess of hydride was carefully destroyed by adding water dropwise until hydrogen was no longer evolved (about 5 ml). Then 10%

$H_2SO_4$ (about 20 ml) followed by 10 ml of water were quickly added. This combination dissolved all the inorganic salts formed and resulted in the formation of two clear layers. The ether layer was washed with water (3 × 10 ml) and dried over anhydrous $MgSO_4$ obtaining 0.72 g of (+)-*trans*-2,3-bis(mercaptomethyl)bicyclo-[2.2.2]octane ((+)-**1**) (89%). $[\alpha]_D = +30.0°$ ($c = 0.5$, $CH_2Cl_2$). NMR ($CDCl_3$): $^1H$, $\delta$ 1.23 (m, 2H, –CH–C); 1.34 (t, 2H, –SH, $J = 7.95$ Hz); 1.38 (m, 4H, $-CH_2-C$); 1.57 (m, 4H, $-CH_2-C$); 1.75 (m, 2H, CH–C); 2.6 (m, 4H, $CH_2$–SH). $^{13}C$ ($CDCl_3$), $\delta$ 19.7 ($-CH_2-C$); 26.6 and 26.7 ($-CH_2-C$); 29.0 ($-CH_2-S$); 47.8 (–CH–C). IR (NaCl) $cm^{-1}$: 2540 (SH st).

### 3.1.7. *trans-2,3-Bis(mercaptomethyl)bicyclo[2.2.2]octane ((±)-1)*

This was prepared similarly to (+)-**1**, using (±)-**5**.

### 3.1.8. *$[Rh_2(\mu\text{-BCOS})(cod)_2]_2$ (8)*

The ligand $H_2$BCOS (44 mg, 0.22 mmol) was added to a solution of $[Rh(\mu\text{-OMe})(cod)]_2$ in dichloromethane. The yellow solution became red, and after stirring 1 h at room temperature the solution turned orange. Then methanol was added to give a yellow-orange precipitate which was filtered off and dried in vacuo obtaining 126 mg (98% yield). Anal. Found: C, 50.5; H, 6.7; S, 10.5. $Rh_2C_{26}H_{40}S_2$: Calc.: C, 50.1; H, 6.4; S, 10.3%. NMR ($CDCl_3$): $^1H$, $\delta$ 1.0–1.75 (m, 12H, BCOS); 2.0 (m, 12H, $-CH_2-$[cod] and $-CH_2-$S[BCOS]); 2.4 (m, 8H, $-CH_2-$[cod]); 3.9–4.4 (m, 8H, –CH=[cod]). FAB: $m/z$ 1136 $[M - cod]^+$. $M_r$ 1244 g $mol^{-1}$ (found by osmometry: 1585 g $mol^{-1}$, $CDCl_3$ at 25 °C).

### 3.1.9. *$[Rh_2(\mu\text{-BCOS})(CO)_4]$ (9)*

Carbon monoxide was bubbled through a solution of $[Rh_2(\mu\text{-BCOS})(cod)_2]_2$ (50 mg, 0.08 mmol) in dichloromethane for 30 min. The initial orange solution became dark red. Adding methanol gave a dark red precipitate which was collected by filtration, washed with methanol and dried in vacuo (28 mg, 68% yield). Anal. Found: C, 34.4; H, 3.3; S, 12.4. $Rh_2C_{14}H_{16}O_4S_2$. Calc.: C, 34.4; H, 3.1; S, 12.4%. IR ($CH_2Cl_2$) $cm^{-1}$: 2075 (s), 2059 (s), 2003 (s).

### 3.1.10. *$[Rh_2(\mu\text{-BCOS})(CO)_2(P(C_6H_5)_3)_2]$ (10)*

A stoichiometric amount of triphenylphosphine (45 mg, 0.17 mmol) was added to a solution of $[Rh_2(\mu\text{-BCOS})(CO)_4]$ (50 mg, 0.08 mmol) in dichloromethane (5 ml). The resulting solution was stirred for 30 min and reduced to 0.5 ml under vacuum. Adding 5 ml of methanol caused the precipitation of a brown solid which was collected by filtration, washed with cold methanol and dried in vacuo obtaining 61 mg (77% yield). Anal. Found: C, 57.2; H, 4.7; S, 6.6. $Rh_2C_{48}H_{46}O_2P_2S_2$. Calc.: C,58.4; H, 4.7; S, 6.5%. NMR ($CD_2Cl_2$): $^{31}P\{^1H\}$ $\delta$ 38.9 (d, $J_{P-Rh} = 159.1$ Hz), 41.0 (d, $J_{P-Rh} = 164.5$ Hz). IR ($CD_2Cl_2$) $cm^{-1}$: 1963 (s).

### 3.2. *Standard catalysis experiment*

A solution of the substrate (20 mmol), the catalyst precursor (0.1 mmol) and the phosphorus compound in 15 ml of the solvent was introduced into the evacuated autoclave. The gas mixture was introduced and the system was heated. When thermal equilibrium had been reached, the gas mixture was introduced until the desired pressure. After the given reaction time, the autoclave was cooled to room temperature and depressurised. Analyses of samples were performed by gas chromatography.

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