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Rhodium cationic complexes using dithioethers as chiral ligands. Application in styrene hydroformylation

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Abstract

Addition of the dithioethers (−)-DIOSR$_2$ (R = Me, ^{i}Pr) (2,3-O-isopropylidene-1,4-dimethyl (and diisopropyl) thioether-L-threitol) to a dichloromethane solution of [Rh(COD)$_2$]ClO$_4$ (COD = 1,5-cyclooctadiene) yielded the mononuclear complexes [Rh(COD)(DIOSR$_2$)]ClO$_4$. X-ray diffraction methods showed that the [Rh(COD)(DIOS^{i}Pr$_2$)]ClO$_4$ complex had an square-planar coordination geometry at the rhodium atom with the ^{i}Pr groups in *anti* position. Cyclooctadiene complexes react with carbon monoxide to form dinuclear tetracarbonylated complexes [(CO)$_2$Rh(μ-DIOSR$_2$)$_2$(CO)$_2$](ClO$_4$)$_2$. [Rh(COD)(DIOSR$_2$)]ClO$_4$ are active catalyst precursors in styrene hydroformylation at 30 atm and 65°C which give conversions of up to 99% with a regioselectivity in 2-phenylpropanal as high as 74%. In all cases enantioselectivities are low. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium; Dithioether; Hydroformylation

1. Introduction

Cationic rhodium and iridium complexes with the general formula [M(diene)L$_n$]$^+$ $n = 2$ or 3 are homogeneous hydrogenation precursor catalysts since under hydrogen the diene is hydrogenated to generate the reactive ML$_2^+$ fragment [1]. This is an excellent catalyst and it has several unusual properties partly because of its ionic character. Interestingly, this cationic system is active for a large number of donor ligands L. The chemistry of cationic rhodium complexes has been extensively studied and the asymmetric induction of chiral bidentate phosphorus ligands has been discussed in depth [2].

Thioethers, R$_2$S, are considered to be relatively weak donors and poor acceptors, but binding is stronger with chelating or macrocyclic thioethers [3]. The two lone electron pairs allow the thioether to coordinate to the metal either in the terminal or the bridging position, providing in this case dinuclear complexes [3].

The first thioether rhodium(I) complexes of the type [Rh(diolefin)L$_2$]$^+$ were reported in 1978 using cycloocta-1,5-diene (COD) or norbornadiene (NBD) as the diolefinic ligand and 1,4-dithiacyclohexane as the sulphur ligand [4]. Another example of a [Rh(diolefin)L$_2$]$^+$ complex with tetrafluorobenzobarralene as the diolefin and tetrahydrothiophene (THT) as the sulphur ligand was reported in 1980 [5]. Since 1983, several works have appeared about the preparation and reactivity of this type of cationic complexes where the diolefin is COD or NBD and L is THT, trimethylene sulphide (TMS), SMe$_2$, SEt$_2$ or dithioethers such as 1,4-dithiacyclohexane (DT), MeS(CH$_2$)$_3$SMe and (^{t}BuS)(CH$_2$)$_3$(^{t}BuS) [6]. More recently, the atropoiso-

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meric dithioethers $BINASR_2$ and $BIPHESR_2$ (Fig. 1) have been used as ligands in the synthesis of cationic $[Rh(COD)(dithioether)]ClO_4$ complexes. These complexes have proved to be catalyst precursors in styrene hydroformylation which provide high catalytic activity and regioselectivity, although the stereoselectivity did not exceed 20% of enantiomeric excess [7].

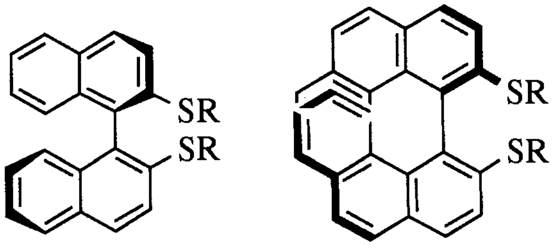
Using the well known chiral diphosphine (+)DIOP ((2S,3S)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis (diphenylphos phino)butane) as a model, related chiral chelating sulphoxide ligands have been used to prepare rhodium and ruthenium catalyst hydrogenation systems [8]. More recently dinuclear rhodium complexes have been prepared with the related dithiolate $(-)DIOS^{2-}$ (2,3-O-isopropylidene-1,4-dithio-L-threitol) as chiral bridging ligand and used in homogeneous styrene hydroformylation [9].

In order to investigate the chemistry and catalytic activities of cationic rhodium complexes containing related dithioether chiral ligands $DIOSR_2$, R = Me, ${}^iPr$, Ph (Fig. 2) we believed it would be of interest to study the preparation, characterization and reactivity of complexes of the type $[Rh(COD)(dithioether)]^+$ containing these ligands. The dithioether ligands were prepared during a project about metal complexes containing sulphur derivatives to be used in catalytic processes. The application of the cationic rhodium complexes as catalyst precursors in the styrene hydroformylation is also reported.

2. Results and discussion

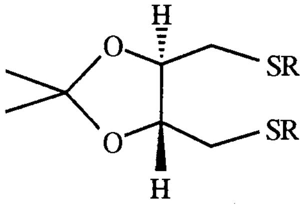
2.1. Preparation of [Rh(COD)(dithioether)]A ($A = ClO_4^-$) complexes

One way of preparing cationic complexes of the type $[M(diene)L_n]^+$ is to treat the dimer compounds $[M(\mu\text{-}Cl)(diene)]_2$ with an equimolecular amount of the silver salt and the corresponding ligand L [1]. An alternative and convenient method is to displace a COD molecule (1,5-cyclooctadiene) from the air stable, starting material $[M(COD)_2]A$ [10].



$BINASR_2$ $BIPHESR_2$

Fig. 1. Atropoisomeric dithioethers $BINASR_2$ and $BIPHESR_2$.



R = Me $DIOSMe_2$
${}^iPr$ $DIOS{}^iPr_2$
Ph $DIOSPh_2$

Fig. 2. Chiral ligands $DIOSR_2$.

In this work, the [Rh(COD)(dithioether)]A complexes were prepared by adding the corresponding dithioether ligand $DIOSR_2$ (R = Me, ${}^iPr$) to a dichloromethane solution of $[Rh(COD)_2]ClO_4$ (Eq. (1)). After stirring, the brown solution turned yellow and the addition of diethyl ether caused the precipitation of the moderately air-stable products for which the elemental analyses of C, H and S correspond to the stoichiometry $\{[Rh(COD)(dithioether)]ClO_4.1/2\ CH_2Cl_2\}_n$.

In the same conditions, $[Rh(COD)_2]ClO_4$ was not seen to react with the dithioether $DIOSPh_2$. In an attempt to favour COD substitution by hydrogenation, H_2 was bubbled through the reaction mixture but no reaction was observed.

$$[Rh(COD)_2ClO_4 + DIOSR_2 \rightarrow$$
$$\rightarrow [Rh(COD)(DIOSR_2)]ClO_4 + COD$$
$$\begin{array}{ll} R = Me & 1 \\ R = {}^iPr & 2 \end{array} \qquad (1)$$

The FAB mass spectrum shows the heaviest ion at $m/z = 433$ for complex **1** and at $m/z = 489$ for complex **2** which is indicative of mononuclear complexes where the anion ClO_4^- has been lost.

The IR spectrum shows two strong bands at 1096 and 625 cm^{-1} for complex **1** and at 1100 and 620 cm^{-1} for complex **2** which are characteristic of the non coordinated ClO_4^- anion in cationic rhodium complexes.

The ${}^1H$- and ${}^{13}C$-NMR data for both complexes **1** and **2** were assigned using HETCOR ${}^1H-{}^{13}C$ experiments and complex **2** also required COSY ${}^1H-{}^1H$ and DEPT experiments.

The ${}^1H$-NMR spectrum for complex **1** has one singlet signal at 1.45 and 2.38 ppm which shows the equivalence of the methylenic protons of the coordinated ligand CH_3-S and $O-C(CH_3)_2$ respectively. The olefinic –CH= protons of the coordinated COD appear as two multiplet signals at 4.65 and 4.55 ppm.

This distribution of signals is in agreement with a C_2 symmetry of the molecule caused by the chiral ligand, which can be seen in Fig. 3.

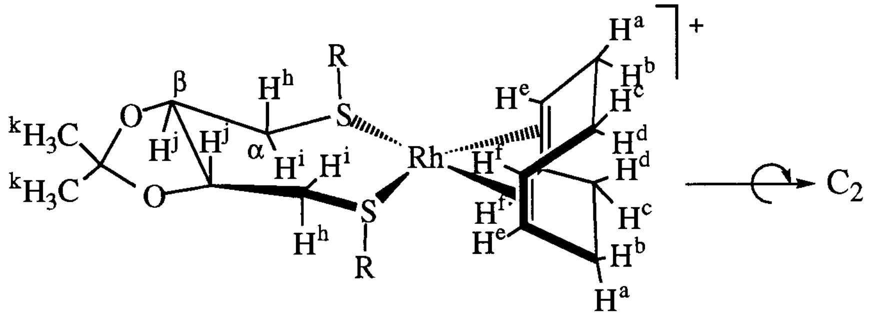


Fig. 3. Molecular symmetry of the catonic complexes $[Rh(COD)_2]^+$.

In accordance with this symmetry, the methylenic protons α and β to the dithioether group –CH^j–CH^{i}H^h–S are diastereotopic and appear as a complex second order ABX system at room temperature centred at 3 ppm. At 40°C this signal is resolved in two, at 3.12 and 3.27 ppm (Fig. 4). Both signals (corresponding to H^h and H^i) have a geminal coupling constant of 12 Hz. Taking into account that the coupling constants $^2J_{\mathrm{Hax-Hax}}$ are greater than $^2J_{\mathrm{Hax-Heq}}$, the signal at 3.12 ppm ($^2J_{\mathrm{H-H}} = 9$ Hz) was assigned to the H^h methylenic proton and the other signal at 3.27 ppm ($^2J_{\mathrm{H-H}} = 3$ Hz) was attributed to H^i protons coupled with H^j in an axial–equatorial manner.

As expected, two resonances were observed at 31.54 and 30.69 ppm in the ^{13}C-NMR spectra of complex **1** for the olefinic coordinated COD carbons. The rest of the ^{13}C-NMR signals were in accordance with a C_2 symmetry.

Dithioether ligands create two asymmetric centres when they coordinate to a metal atom. As DIOSR$_2$ are chiral ligands with a fixed SS configuration, there are three diastereoisomers possible for the new complexes with the configurations SSRR, SSSS and SSRS (Fig. 5) The diastereoisomers SSRR and SSSS correspond to the *anti* invertomer and the SSRS to the *syn* [11]. The *syn* invertomer will give two signals for the methyl protons of the DIOSMe$_2$ whereas a conformation can be found for the *anti* invertomer in which the methyl protons are related for a C$_2$-geometry and only one signal will appear in the ^{1}H-NMR spectra. As is shown by the ^{1}H-NMR spectra, either one of the two *anti* diastereoisomers is present in solution or there is a rapid exchange between them both which is not detected on the NMR time scale.

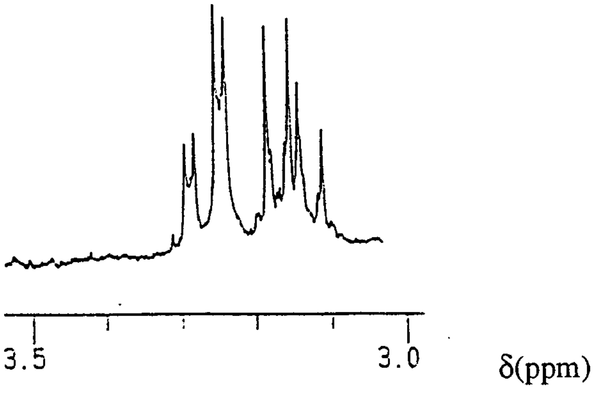


Fig. 4. ^{1}H-NMR spectra of complex **2** in the methylenic region of the coordinated DIOSMe$_2$ at 40°C.

In order to detect the presence in solution of other conformations of the seven membered dithiother ring or the formation of the *syn* invertomer, ^{1}H-NMR experiments were carried out in deuterated acetone at different temperatures. When the temperature decreased to − 40°C, poor signal resolution was observed and no other species could be detected.

For complex **2**, an H,H-COSY experiment was carried out because of the complexity of the ^{1}H-NMR spectra. The distribution of the signals of the coordinated COD and dithioether is similar to complex **1** which indicates that this complex has also a C$_2$ symmetry.

The structure of the complex **2** was confirmed by X-ray crystallography. An ORTEP drawing (thermal ellipsoids of 50% probability for the non-hydrogen atoms) is shown in Fig. 6. Selected bonds and angles are listed in Table 1. This compound crystallizes in the chiral space group $P2_12_12_1$, and it is optically active. In the crystal studied, the asymmetric unit was found to consist of two molecules of the chiral cation, with two counteranions. The rhodium atom has a slightly distorted square-planar environment. The metal atom is bonded to a cyclooctadiene molecule coordinated through both olefinic double bonds, and to the DIOS^{i}Pr$_2$ ligand coordinated via both sulphur atoms

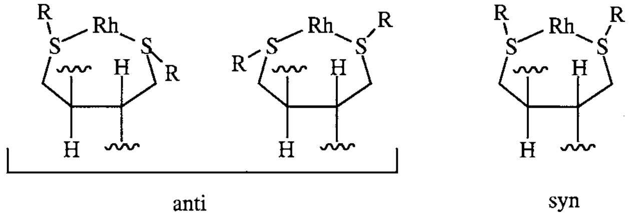


Fig. 5. Possible diastereoisomers for the new complexes.

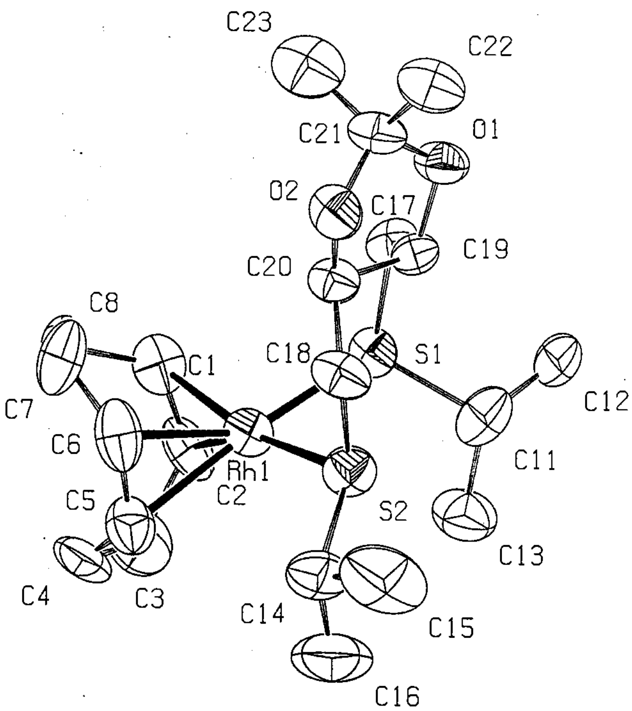


Fig. 6. ORTEP structure for complex **2** showing thermal ellipsoids at 50% probability.

The Rh–S and Rh–C distances (averages 2.360 and 2.178 Å respectively) are similar to other complexes with cyclooctadiene ligands *trans* to dithiolate bridged ligands. Thus, distances in the range 2.35–2.39 Å were found for the complexes $[Rh_2(\mu\text{-}S(CH_2)_nS)(COD)_2]$ ($n =$ 2 and 3) [12]. Related thioether complexes $[Rh(NBD)_2(SEt_2)]^+$ ([6]a,f) and $[Rh(CO)_2(^tBuSCH{=}CHS^tBu)]^+$ have Rh–S distances from 2.3643 to 2.500 Å.

The shortest intermolecular distance between two different molecules is 8.35 Å. This distance indicates that there is no interaction between the metal atoms of different molecules.

The relative configuration of the ^{i}Pr groups is *anti* as the NMR data showed.

Bubbling carbon monoxide at room temperature through dichloromethane solutions of $[Rh(COD)(DIOSR_2)]ClO_4$ (R = Me, ^{i}Pr) complexes gave the corresponding carbonylated species (Eq. (2)). The elemental analyses matched the stoichiometry $[Rh(CO)_2(dithioether)]_n(ClO_4)_n$.

$$2[Rh(COD)(DIOSR_2)]CPO_4 \xrightarrow{4CO}$$

$$\rightarrow [(CO)_2Rh(\mu\text{-}DIOSR_2)_2Rh(CO)_2](ClO_4)_2 + 2COD$$

$$\begin{array}{ll} R = Me & 3 \\ R = {}^iPr & 4 \end{array} \qquad (2)$$

The solid state and solution FT-IR spectra of these complexes show three ν(CO) stretching frequencies (1995 (s), 2019(s) and 2092(s) for $[Rh(CO)_2(DIOSMe_2)]_n(ClO_4)_n$ and 2017(s), 2052(s) and 2092(s) for $[Rh(CO)_2(DIOS^iPr_2)]_n(ClO_4)_n$) which are characteristic of tetracarbonylated dinuclear rhodium(I) complexes [13]. When equivalent conductivities of the tetracarbonylated complex **4** were measured in acetone solutions at various concentrations, the slopes for the Onsager's equation were characteristic of 2:1 electrolytes [14]. The conductivity study and the molecular weight of the carbonylated complex with the $DIOSMe_2$ ligand could not be determined because of its instability but, by comparison with complex **4**, we suggest it is a dinuclear species. In conclusion, the complexes can be formulated as $[(CO)_2Rh(\mu\text{-}DIOSR_2)_2Rh(CO)_2](ClO_4)_2$.

2.2. Styrene hydroformylation

It has been previously reported that cationic complexes containing dithioether chiral ligands $[Rh(COD)(BINASMe_2)]A$, $A = BF_4^-$, ClO_4^- behave as catalyst precursors in the hydroformylation of styrene without the addition of phosphorous ligands and provide regioselectivities as high as 86% and e.e. up to 15% ([7]a).

In this work, the mononuclear cationic rhodium complexes containing $DIOSR_2$, R = Me, ^{i}Pr, dithioether ligands have been used as catalyst precursor

Table 1
Selected bond distances (Å) and angles (°) for $[Rh(COD)(DIOS^iPr_2)]ClO_4$ (**2**) with e.s.d.s in parentheses

Rh–S(1)	2.363(4)	C(11)–C(11B)	1.55(3)
Rh–S(2)	2.361(4)	C(12)–C(12A)	1.28(5)
Rh–C(6)	2.140(13)	C(12)–C(12B)	1.56(3)
Rh–C(1)	2.168(14)	C(13)–C(15)	1.55(2)
Rh–C(2)	2.178(14)	C(14)–C(16)	1.53(2)
Rh–C(5)	2.19(2)	C(15)–O(1)	1.42(2)
S(1)–C(11)	1.84(2)	C(16)–O(2)	1.38(2)
S(1)–C(13)	1.81(2)	O(1)–C(17)	1.35(2)
S(2)–C(12)	1.85(2)	O(2)–C(17)	1.60(3)
S(2)–C(14)	1.81(2)	C(17)–C(18)	1.49(4)
C(11)–C(11A)	1.54(3)	C(17)–C(19)	1.79(6)
C(1)–C(2)	1.40(2)	C(5)–C(6)	1.43(2)
C(6)–Rh–C(1)	82.6(6)	C(6)–Rh–C(2)	99.0(6)
C(1)–Rh–C(2)	37.7(7)	C(6)–Rh–C(5)	38.4(6)
C(1)–Rh–C(5)	90.4(7)	C(2)–Rh–C(5)	82.7(6)
C(6)–Rh–S(2)	153.0(5)	C(1)–Rh–S(2)	86.5(5)
C(2)–Rh–S(2)	87.0(5)	C(5)–Rh–S(2)	166.6(5)
C(6)–Rh–S(1)	95.9(5)	C(1)–Rh–S(1)	167.8(5)
C(2)–Rh–S(1)	153.6(5)	C(5)–Rh–S(1)	96.0(5)
S(2)–Rh–S(1)	89.57(14)	C(13)–S(1)–Rh	107.0(5)
C(11)–S(1)–Rh	114.1(6)	C(14)–S(2)–Rh	110.5(6)
C(12)–S(2)–Rh	111.5(7)	M(1)–Rh–M(2)	94.51
C(14)–S(2)–C(12)	103.6(9)	C(13)–S(1)–C(11)	101.8(8)
S(1)–Rh–M(1)	97.23	S(1)–Rh–M(2)	167.89
S(2)–Rh–M(2)	80.29	S(2)–Rh–M(2)	173.96

M(1) and M(2) represent the midpoints of the C(5)–C(6) and C(1)–C(2) olefin double bonds.

Table 2
Styrene hydroformylation at 30 atm and 65°C[a]

Entry	Precursor	L	t (h)	$\%C^{b}_{ald}$	%2-PP/3-PP[c]	% e.e.[d]
1	**1**	—	14	57	69/31	3 (S)
2	**1**	3 (+)-DIOSMe$_2$	14	94	70/30	4 (S)
3	**2**	—	22	74	72/28	6 (S)
4	**2**	3 (−)-DIOS^{i}Pr$_2$	4	99	71/29	6 (S)
5	[Rh(acac)(CO)$_2$]	4 (−)-DIOS^{i}Pr$_2$	7	96	74/26	4 (S)
6	[Rh(acac)(CO)$_2$]	—	2	78	63/27	—

[a] Reaction conditions: styrene (10 mmol), complex (0.05 mmol), tetrahydrofuran (7.5 ml), CO/H$_2$ = 1.

[b] Aldehyde conversion measured by chromatography integral ratio with no addition of internal standard.

[c] 2-PP: 2-phenylpropanal, 3-PP: 3-phenylpropanal.

[d] % ee was mesured by chiral gas chromatography on the 2-phenylpropanol obtained by reducing the aldehydes with LiAlH$_4$.

in the hydroformylation of styrene in the form of isolated rhodium sulphur modified precursors. The conversion and selectivity results are shown in Table 2. When the [Rh(COD)(DIOS Me$_2$)]ClO$_4$ (**1**) and [Rh(COD)(DIOSiPr$_2$)]ClO$_4$ (**2**) are used as catalyst precursors at 30 bar and 65°C, the regioselectivity in 2-phenylpropanal is about 70% (entries 1 and 3).

The addition of a three-fold excess of free dithioether ligand, dithioether/Rh ratio = 4, (entries 2 and 4) increases the conversion into aldehydes. The conversion is practically total for the precursor **2** containing (−)-DIOS^{i}Pr$_2$ in 4 h. However, regioselectivities remain in the range of 70% in 2-phenylpropanal and are only slightly higher.

Although values of enantiomeric excess are very low, the precursor containing the (−)-DIOS^{i}Pr$_2$ provides higher e.e. than the corresponding methyl dithiother derivatives.

Experiment 5 was carried out in order to find out if the behaviour of the cationic isolated precursor system was the same as the species formed in situ by adding DIOSR$_2$ to the rhodium precursor [Rh(acac)(CO)$_2$]. When four mols of (−)-DIOS^{i}Pr$_2$ were added (dithioether/Rh ratio = 4) to the [Rh(acac)(CO)$_2$] complex, the conversion and regioselectivities were practically the same.

For comparison purposes, an experiment using [Rh(acac)(CO)$_2$] without dithiother ligand was carried out to give lower regioselectivity (entry 6). This indicates that the active species are modified by the dithioether ligand.

The activities and regioselectivities obtained using these dithioether-modified rhodium systems are in fact lower than using other Rh/diphosphine systems ([7]b). However, the regioselectivity obtained by these systems is higher than the regioselectivity obtained by the [Rh(μ-OMe)(COD)]$_2$/2DIOP system, in the same conditions, which provide 62% in 2-phenylpropanal [9]. It is also higher than the regioselectivity obtained with the [RhH(CO)(PPh$_3$)$_3$] system using DIOP as auxiliary ligand and which is about 60%.

In comparison with the results obtained using the precursor system based on the dithiolate bridged [Rh$_2$(μ-DIOS)(COD)$_2$] complex without phosphorous ligand, which in the same conditions achieves 64% of the regioselectivy in 2-phenylpropanal with the cationic dithioether precursor, conversions are lower but regioselectivities higher [9]. Although the introduction of the R substituents in the S-atom may favour chiral induction, the enatioselectivities are also low and only the regioselectivities are higher.

Although in the NMR studies were not observed different diastereoisomers, the low e.e. obtained in the hydroformylation of styrene could be attributed to the formation of an unfavourable mixture of diastereomeric rhodium complexes. This may be due to the configurational lability of the S-stereocenters under hydroformylation conditions.

3. Experimental

All the rhodium complexes were synthesized using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. The complexes [Rh(COD)$_2$]ClO$_4$ [10], [Rh(acac)(CO)$_2$] [15] and [Rh(μ-OMe)(COD)]$_2$ [16] and the dithioethers DIOSR$_2$ (R = Me, ^{i}Pr and Ph) ([8]b), [17], were prepared using literature methods. All other reagents were used as commercially supplied. Elemental analyses were performed on a Carlo-Erba microanalyzer. The IR spectra were obtained using a Nicolet 5ZDX-FT spectrophotometer and a Prospect spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian Gemini 300 MHz spectrophotometer, and the chemical shifts are quoted in ppm downfield from internal SiMe$_4$. FAB mass spectrometry was performed on a VG Autospect in a nitrobenzyl alcohol matrix. Gas chromatography analyses were performed on a

Hewlet Packard Model 5890, a gas chromatograph with a flame ionization detector using a 25 m × 0.2 mm of internal diameter in capillary column (Ultra 2). The enantiomeric excesses of the corresponding alcohols obtained as previously described [9] were measured on the same equipment using a 50 m × 0.25 mm of internal diameter in capillary column (FS-cyclodex β-I/P) The catalytic experiments were carried out according to a previously described standard procedure [9].

*3.1. Preparation of [Rh(COD)(DIOSMe$_2$)]ClO$_4$.1/2 CH$_2$Cl$_2$ (**1**)*

A slight excess of the DIOSMe$_2$ ligand (138 mg, 0.62 mmol) was added to a solution of [Rh(COD)$_2$]ClO$_4$ (200 mg, 0.48 mmol) in dichloromethane. The orange solution turned yellow. After stirring at room temperature for 10 min, diethyl ether was added to give a yellow precipitate of **1** which was filtered off and dried under vacuum (247 mg, 97% yield). (Found: C, 36.39; H,5.41; S, 11.65. Calc for $C_{35/2}H_{31}S_2O_6RhCl_2$: C, 36.50; H, 5.43; S, 11.14). ^{1}H-NMR (CDCl$_3$): δ 2.05 (m, 2H, –CH$_2$–, COD); 2.11 (m, 2H, –CH$_2$–, COD); 2.58 (m, 4H, –CH$_2$–, COD); 4.55 (m, 2H, –CH–, COD); 4.65 (m, 2H, –CH–, COD); 1.45 (s, 6H, CH$_3$–, DIOSMe$_2$); 2.38 (s, 6H, –S–CH$_3$, DIOSMe$_2$); 3.00 (m, 4H, –CH$_2$–, DIOSMe$_2$); 4.42 (m, 2H, –CH–, DIOSMe$_2$); 5.30 (s, 1H, CH$_2$Cl$_2$). ^{13}C-NMR (CD$_2$Cl$_2$): δ 17.34 (–S–CH$_3$, DIOSMe$_2$); 27.01 (CH$_3$–, DIOSMe$_2$); 30.69 (–CH$_2$–, COD); 31.54 (–CH$_2$–, COD); 41.43 (–CH$_2$–, DIOSMe$_2$); 79.04 (–CH–, DIOSMe$_2$); 91.17 (–CH–, COD); 92.03 (–CH–, COD); 111.18 (–*C*–CH$_3$, DIOSMe$_2$). F.A.B.: $m/z = 433$ [M–ClO$_4$].

*3.2. Preparation of [Rh(COD)(DIOS^{i}Pr$_2$)]ClO$_4$.1/2 CH$_2$Cl$_2$ (**2**)*

A slight excess of the DIOS^{i}Pr$_2$ ligand (43.2 mg, 0.15 mmol) was added to a solution of [Rh(COD)$_2$]ClO$_4$ (50 mg, 0.12 mmol) in dichloromethane. The orange solution turned yellow. After stirring at room temperature for 10 min, diethyl ether was added to give a yellow precipitate of **2** which was filtered off and dried under vacuum (64.7 mg, 92% yield). (Found: C, 40.20; H, 6.19; S, 10.00. Calc for $C_{43/2}H_{39}S_2O_6RhCl_2$: C, 40.68; H, 6.20; S, 10.09). ^{1}H-NMR (CDCl$_3$): δ 1.44 (s,12H, S–CH–C*H*$_3$, DIOS^{i}Pr$_2$); 1.48 (s, 6H, –C–CH$_3$, DIOS^{i}Pr$_2$); 2.05 (m, 2H, –CH$_2$–, COD); 2.40 (m, 4H, –CH$_2$–, COD); 2.65 (m, 2H, –CH$_2$–, COD); 2.88 (t, 2H, –CH$_2$–, DIOS^{i}Pr$_2$); 3.28 (bd, 2H, –CH$_2$–, DIOS^{i}Pr$_2$); 3.41 (m, 2H, S–C*H*–CH$_3$, DIOS^{i}Pr$_2$); 4.50 (m, 2H, –CH–, COD); 4.72 (m, 2H, –C*H*–CH$_2$–, DIOS^{i}Pr$_2$); 4.70 (m, 2H, –CH–, COD); 5.30 (s, 1H, CH$_2$Cl$_2$). ^{13}C-NMR (CDCl$_3$): δ 21.17 (S–CH–*C*H$_3$, DIOS^{i}Pr$_2$); 22.76 (S–CH–*C*H$_3$, DIOS^{i}Pr$_2$); 26.95 (–C–*C*H$_3$, DIOS^{i}Pr$_2$); 29.49 (–CH$_2$–, COD); 32.29 (–CH$_2$–, COD); 36.06 (S–*C*H–CH$_3$, DIOS^{i}Pr$_2$); 38.32 (CH$_2$, DIOS^{i}Pr$_2$); 78.51 (–CH–, DIOS^{i}Pr$_2$); 107.43 (–CH–, COD); 111.22 (–CH–, COD); 128.70 (–*C*–CH$_3$, DIOS^{i}Pr$_2$). F.A.B.: $m/z = 489$ [M–ClO$_4$].

*3.3. Preparation of [Rh(CO)$_2$(DIOSMe$_2$)]$_2$(ClO$_4$)$_2$ (**3**)*

Carbon monoxide was bubbled through a solution of [Rh(COD)(DIOSMe$_2$)]ClO$_4$ (50 mg, 0.094 mmol) in dichloromethane for 10 min. The initial yellow solution turned orange. Adding diethyl ether gave an orange precipitate which was filtered off under nitrogen, washed with diethyl ether and dried in vacuo (24.0 mg, 53.3% yield). (Found: C, 27.00; H, 4.50; S, 12.50. Calc. for $C_{22}H_{36}S_4O_{16}Rh_2Cl_2$: C, 27.50; H, 3.77; S, 13.34). IR (KBr): 2005, 2041, 2099; (CH$_2$Cl$_2$): 1995, 2019, 2092 cm^{-1}.

*3.4. Preparation of [Rh(CO)$_2$(DIOS^{i}Pr$_2$)]$_2$(ClO$_4$)$_2$ (**4**)*

Carbon monoxide was bubbled through a solution of [Rh(COD)(DIOS^{i}Pr$_2$)]ClO$_4$ (97 mg, 0.16 mmol) in tetrahydrofuran for 20 min. A yellow precipitate appeared inmediately which was filtered off, washed with diethyl ether and dried in vacuo (60.3 mg, 68% yield). (Found: C, 33.59; H, 5.08; S, 11.98. Calc. for $C_{30}H_{52}S_4O_{16}Rh_2Cl_2$: C, 33.56; H, 4.88; S, 11.94). IR (KBr): 2082, 2009, 1974; (CH$_2$Cl$_2$): 2105, 2052, 2017 cm^{-1}. ^{1}H-NMR (Aceton-D): δ 1.41 (s, 6H, –C–CH$_3$, DIOS^{i}Pr$_2$); 1.51 (m, 12H, S–CH–C*H*$_3$, DIOS^{i}Pr$_2$); 3.38 (t, 2H, –CH$_2$–, DIOS^{i}Pr$_2$); 3.67 (bd, 2H, –CH$_2$–, DIOS^{i}Pr$_2$); 3.86 (m, 2H, S–C*H*–CH$_3$, DIOS^{i}Pr$_2$); 4.62 (m, 2H, –C*H*–CH$_2$–, DIOS^{i}Pr$_2$). F.A.B.: $m/z = 687$ [M$^+$ – 4 ^{i}Pr$_2$ – 1 Me]; $m/z = 437$ [(M/2)H$^+$]; $m/z = 379$ [Rh + DIOS^{i}Pr$_2$ – H]. Conductivity in aceton $\Lambda_{eq} = 164.174–1207.511\ \sqrt{C_e}$; $r = -0.991$.

*3.5. Crystal structure determination for compound **2***

Suitable crystals of complex **2** were grown by slowly diffusing diethyl ether into a solution of the complex in CH$_2$Cl$_2$ and mounted on a glass fibre.

The data were collected and processed at room temperature on a Mar Research image plate scanner, and graphite-monochromated Mo K$_\alpha$ radiation was used to measure 95 2° frames, 360 s per frame.

2 × [RhS$_2$C$_{21}$H$_{34}$O$_2$.ClO$_4$.1/2CCl$_2$], $M = 1252.83$, orthorhombic, $a = 9.415(5)$, $b = 14.133(5)$, $c = 42.182(5)$ Å, $U = 5612.8$ Å^3, space group $P2_12_12_1$ (no. 19), $Z = 4$, $D_c = 1.483$ g cm^{-3}, $F(000) = 2576$. Orange, crystal dimensions 0.22 × 0.14 × 0.30 mm, μ(Mo K$_\alpha$) = 9.80 cm^{-1}.

The XDS package was used to give 3998 unique reflections [merging $R = 0.0992$]. The heavy atoms were found from the Patterson map using the SHELX86 program and refined subsequently from successive differ-

Table 3
Crystal Data for compound **2**

Empirical formula	$2\times[RhS_2C_{21}H_{34}O_2.ClO_4.1/2CCl_2]$
Formula weight	1252.83
Temperature	293 K
Wavelength	0.71069 A
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	$a=9.41(5)$ Å
	$b=14.13(5)$ Å
	$c=42.18(5)$ Å
Volume	5612.8 Å^3
Z	4
Density (calculated)	1.483 g/cm^3
Absorption coefficient	9.80 cm^{-1}
F(000)	2576
Crystal size	$0.22\times0.14\times0.30$ mm
θ range for data collection	2.04–22.61°
Index ranges	$0\leq h\leq10$, $0\leq k\leq14$, $-14\leq l\leq45$
Reflections collected	19 375
Independent reflections	3998 [R(int) = 0.0992]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3984/0/595
Goodness-of-fit on F^2	1.094
Final R indices $[I>2\sigma(I)]^a$	$R_1=0.0699$, $wR2=0.1712$
R indices (all data)^a	$R_2=0.0856$, $wR2=0.1927$
Absolute structure parameter	0.05(9)
Extinction coefficient	0.0043(6)
Largest diff. peak and hole	0.696 and -0.559 eÅ^{-3}

[a] $R_1=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$; $wR2=[\Sigma w(F_o^2-F_c^2)/\Sigma w(F_o^2)^2]^{1/2}$; $w=1/[\sigma^2(F_o^2)+(0.1025P)^2+21.43P]$ where $P=(\max(F_o^2,0)+2F_c^2)/3)$.

ence Fourier maps using SHELXL, by full-matrix least squares of 595 variables, to a final R-factor of 0.0699 for 3984 reflections with $[F_o]>4_\sigma(F_o)$. All atoms were revealed by the Fourier map difference. Non hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined with a fixed isotropic atomic displacement parameter. R values: R_1 ($[F_o]>4_\sigma(F_o)$, for 3984 reflections) = 0.0699; R_2 (all data) = 0.0856. The weighting scheme $w=1/[\sigma^2(F_o^2)+(0.1025P)^2+21.43P]$ where $P=(\max(F_o^2,0)+2F_c^2)/3)$ with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Large diff. peak and hole in the final difference map: 0.696 and $-$ 0.559 eÅ^{-3}. Data collection parameters including R_1 ($[I>2\sigma(I)]$) and R_2 (all data) values are summarized in Table 3.

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