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Synthesis, reactivity and catalytic properties of rhodium complexes of (*R*,*R*)-1-benzyl-3,4-dithioetherpyrrolidines

M. Diéguez [a], A. Ruiz [a,*], C. Claver [a], M.M. Pereira [b,1], M.T. Flor [b], J.C. Bayón [b], M.E.S. Serra [c], A.M. d'A. Rocha Gonsalves [c]

[a] *Departament de Química Física i Inorgànica, Facultat de Química, Universitat Rovira I Virgili, 43005 Tarragona, Spain*
[b] *Departamento de Química, Universitat Autonoma de Barcelona, Bellaterra, 08193 Barcelona, Spain*
[c] *Departamento de Química, Rua Larga, Universidade de Coimbra, 3049 Coimbra, Portugal*

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Abstract

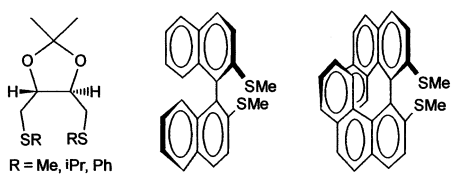
Complexes [Rh(cod)(degusR)]ClO_4, where cod is 1,5-cyclooctadiene and degusR represents the homochiral dithioethers (*R*,*R*)-1-benzyl-3,4-bis(methylsulfanyl)pyrrolidine, (*R*,*R*)-1-benzyl-3,4-bis(isopropylsulfanyl)pyrrolidine and (*R*,*R*)-1-benzyl-3,4-bis(phenylsulfanyl)pyrrolidine were prepared and characterized. Their reactivity with CO and PPh_3 was investigated. The complexes were assayed as catalysts in hydroformylation of styrene, hydrogenation of acrylic acids and hydroboration of styrene. Although these complexes containing dithioethers behave as catalytic precursors in hydroformylation reaction, the results suggest that mononuclear hydride rhodium carbonyl species is responsible for the catalytic activity. The cationic complexes are not active in the hydrogenation of acrylic acids in the conditions tested. These complexes are moderately active in the hydroboration of styrene with catecholborane, but their selectivities are not satisfactory. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium complexes; Dithioether ligands; Hydroformylation; Hydrogenation; Hydroboration

1. Introduction

In previous years, sulfur ligands have been attracting an increasing interest in transition metal catalyzed reactions [1]. In particular, metal complexes containing chiral thioethers have been used as catalysts in different enantioselective reactions [2].

Chiral dithioethers $DIOSR_2$ (**1**), $BINASMe_2$ (**2**) and $BIPHESMe_2$ (**3**) (Scheme 1) have been used to form cationic complexes $[M(diolefin)L]^+$ (M = Rh, Ir; L = dithioether). These species are related to well-known diphosphine complexes (L = diphosphine), which are the most widely used Rh(I) and Ir(I) catalysts in asymmetric hydrogenation. Early work, regarding the use of rhodium–thioether complexes in catalytic hydrogenation, was reported a long time ago [3]. However, the dithioether complexes, such as $[Rh(cod)L](PF_6)$ (L = 1,4-dithiane) are only scarcely active even at 50 bar in the hydrogenation of cyclohexene [4]. Furthermore, in the case of complexes $[PtCl_2(PR_3)(SR'_2)]$, which are active in the hydrogenation of styrene at 50 bar, it has been stated that the thioether acts as a labile ligand, creating the required vacant coordination site when it dissociates [5]. However, it has been recently reported that iridium dithioether complexes $[Ir(cod)(DIOSR_2)]BF_4$ (cod = 1,5-cyclooctadiene) hydrogenate acrylic acid derivatives at 1 bar H_2 and 20°C, rendering



1 **2** **3**

Scheme 1.

* Corresponding author. Tel.: +34-977-559 572; fax: +34-977-559 563.
E-mail addresses: aruiz@quimica.urv.es (A. Ruiz), iqibayon@cc.uab.es (J.C. Bayón)
[1] Permanent address: Departamento de Química, Rua Larga, Universidade de Coimbra, 3049 Coimbra, Portugal.

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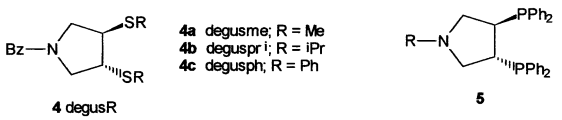
fair enantioselectivity (< 50%) [6]. Clearly, in this case, the chiral dithioether ligand remains coordinated at least during the stereoselective step of the catalytic process. Also, rhodium complexes of homochiral dithioethers $DIOSR_2$ (R = Me, ^{i}Pr), $BINASMe_2$ and $BIPHESMe_2$ are reported to be active catalysts in styrene hydroformylation providing good regioselectivity, although the stereoselectivity did not exceed 20% ee [7].

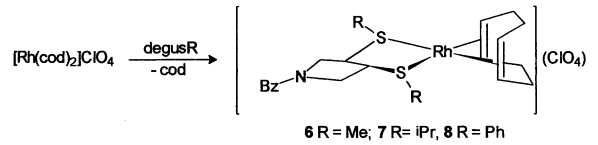
Asymmetric hydroboration with catecholborane is an attractive strategy for the functionalization of prochiral olefins, constituting a favorable alternative to the use of chiral boranes in stoichiometric reactions [8]. Rhodium complexes $[Rh(diolefin)L]^+$, where L are diphosphines [9] or heterobidentate *P*,*N*-ligands [10], have been used as catalysts for this reaction with excellent results. To our knowledge, dithioether ligands have not been essayed in catalytic hydroboration.

The synthesis of a new family of chiral dithioethers degusR **4** with a rigid backbone has been recently reported [11]. These ligands are structurally related to 3,4-bis(diphenylphosphino)pyrrolidine type ligands **5** [12] (Scheme 2), which are efficient chiral auxiliaries in the rhodium catalyzed enantioselective hydrogenation of acrylic acids [13] and hydrogen transfer from formic acid to the same type of substrates [14]. It is well known that the ligand backbone and the size of the metal chelate ring are determining factors in the efficiency and stereoselectivity of catalytic reactions. Thus, the iridium complexes $[Ir(cod)(degusR)]BF_4$ are shown to be more active in the asymmetric hydrogenation of acrylic acids, than the related seven-membered chelate-ring iridium dithioether $DIOSR_2$ (R = Me, ^{i}Pr, Ph) systems previously reported [6]. Results were best with ligand degusph **4c**. In the hydrogenation of itaconic acid (substrate/catalyst = 40), complete conversion was reached in 2 h, at 1 bar H_2 and 20°C, with an enantiomeric excess of 68% [11]. To the best of our knowledge this is the highest ee reported in asymmetric hydrogenation using metal chiral dithioether complexes.

We report here the synthesis and characterization of the new cationic rhodium dithioether complexes $[Rh(cod)(degusR)]ClO_4$. Exploratory tests in the hydrogenation of acrylic acids, as well as in the hydroformylation and hydroboration of styrene, are also reported.



Scheme 2.



Scheme 3.

2. Results and discussion

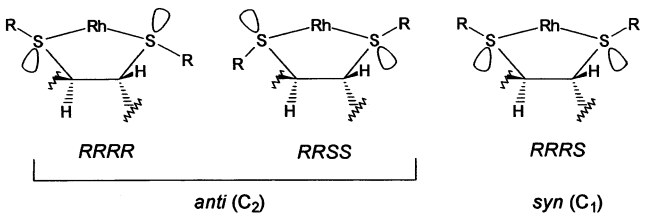
2.1. Synthesis of the cyclooctadiene complexes

The diene complexes $[Rh(cod)(degusme)]ClO_4$ (**6**), $[Rh(cod)(degusprⁱ)]ClO_4 \cdot 1/2CH_2Cl_2$ (**7**) and $[Rh(cod)(degusph)]ClO_4$ (**8**) were prepared by adding the corresponding chiral dithioether degusR (R = Me, ^{i}Pr, Ph) to a dichloromethane solution of $[Rh(cod)_2]ClO_4$. The yellow solids were precipitated with ether (Scheme 3).

The complexes are moderately stable in air. The FAB MS of the solids show peaks corresponding to the cations at *m*/*z* 464 for **6**, *m*/*z* 520 for **7** and *m*/*z* 588 for **8**. In the case of complex **6** peaks at + 16 (*m*/*z* 480) and + 32 (*m*/*z* 496) are also observed, corresponding to the addition of one and two oxygen atoms from the matrix [15]. The IR spectra show a strong band around 1100 cm^{-1} and a medium one around 620 cm^{-1} for all complexes, which are characteristic of the non coordinated perchlorate anion [16].

A feature of dithioether ligands is that, upon coordination to the metal, a new stereogenic center is generated on each of the sulfur atoms, producing different stereoisomers. Because the chiral dithioether ligands degusR have a 3*R*,4*R* configuration at the carbon atoms, there are three possible diastereoisomers for each complex, namely *RRSS*, *RRRR* and *RRRS*, where the first two configurations refer to the carbons and the last two to the sulfurs. The diastereomers *RRSS* and *RRRR* correspond to *anti* invertomers and the *RRRS* to the *syn* [17] (Scheme 4). If the *N*-benzyl bond rotates freely, the diastereoisomers *RRSS* and *RRRR* have a C_2 symmetry, while *RRRS* is C_1.

Complex **6** shows a broad ^{1}H NMR spectrum, which cannot be resolved even at − 70°C. This result can indicate a fast dissociation of the ligand or a rapid interconversion between different diastereoisomers in the NMR time scale. Similar behavior has been ob-



Scheme 4.

served for the related complex [Rh(cod)(BINAS-Me)]ClO_4 [7c]. The signals in the ^1H NMR spectra of complexes **7** and **8** were assigned using COSY spectra. These spectra are consistent with pseudo C_2 symmetry. Thus, the signals of the olefinic cyclooctadiene protons appear as two multiplets for complex **7** and a broad signal for **8**. For the *endo*- and *exo*-methylenic protons of cyclooctadiene, four signals of equal intensity were observed for complex **8** and three (intensity 2:1:1) for complex **7**. For both **7** and **8**, the four diastereotopic methylenic protons CH_2N appear as two multiplets corresponding to an AB system. The two methinic protons CH are observed as one multiplet in both spectra. In complex **7**, the signals of the two diastereotopic methylic protons of the ^{i}PrS groups are very close and their assignment could not be achieved. The aromatic proton signals of PhS and $PhCH_2N$ groups of complex **8** show a complex pattern which could not be resolved. The NMR data for complexes **7** and **8** indicate the existence of a single *anti* diastereoisomer or a fast exchange among different isomers, such as the average signal is observed. Thus, a variable temperature study was undertaken. When the temperature was changed from -70 to $+70$°C, no other signals were observed for **7** and **8** in this temperature range. Similar results were reported for complexes [M(cod)-(DIOSR$_2$)]X (M = Rh, R = Me, ^{i}Pr, X = ClO_4; M = Ir, R = Me, ^{i}Pr, Ph, X = BF_4) [6,7a], as well as for complexes [Ir(cod)(degusR)]BF_4 (R = Me, ^{i}Pr, Ph) [11].

Molecular mechanics calculations were carried out for each one of the three diastereoisomers of complexes **6–8** and the relative strain energies for the three possible diastereoisomers of these cations were obtained. Since the force field used (UFF) in these calculations is not properly parameterized for transition metal systems, the results can only be analyzed qualitatively. However, recent studies by our group with Rh–dithiolate complexes [18] indicate that the relative energies calculated by molecular mechanics and those computed by methods based on density functional theory (DFT) [19] agree strongly for different conformers. From this point of view, the results are quite consistent with the NMR spectra. Thus, the differences in energy between at least two of the diastereoisomers of **6** are relatively small (about 3 kcal mol^{-1}), which could explain its fluxional behavior in solution. In the case of **7**, one *RRSS anti* invertomer seems to be significantly more stable than the other two isomers (>20 kcal mol^{-1}). This is consistent with the observation of a single set of signals with C_2 symmetry. Finally, in the case of **8**, the molecular mechanics calculations show that the two *anti* isomers are relatively close in energy (about 7 kcal mol^{-1}), although again the *RRSS* isomer is the most stable. Therefore, from the NMR spectra and MM calculations a *RRSS anti* configuration could be proposed for the complex cations **7** and **8** in solution. The recently reported X-ray structure of the complex [Rh(cod)(DIOSPr^i)]ClO_4 also shows an *anti* configuration for the sulfur atoms [7a].

2.2. Reactivity of the cyclooctadiene complexes with CO

When CO was bubbled through dichloromethane solutions of the diene complexes [Rh(cod)(degusR)]-ClO_4, the carbonyl complexes [Rh(degusR)$(CO)_2]_n$-$(ClO_4)_n$ (R = Me **9**, ^{i}Pr **10**, Ph **11**) formed by displacing the cyclooctadiene ligand. The elemental analysis for **11** matches the stoichiometry proposed. Complexes **9** and **10** were detected in solution, but they could not be isolated pure in the solid state.

The nuclearity of complex **11** was established by measuring its equivalent conductivity in acetone solutions at different concentrations. The plot of the Onsager equation ($\Lambda_e = \Lambda_o - A \times c^{1/2}$) gives an A value of 717 ohm^{-1} l$^{1/2}$ equiv$^{-1/2}$, which is characteristic of a 2:1 electrolyte [20]. The IR spectra in solution of the three complexes agree with a binuclear structure [Rh_2(μ-degusR)$_2$$(CO)_4$][$(ClO_4)_2$ for these carbonyl complexes, as they show three stretching frequencies ν(CO) in the 2100–1990 cm^{-1} region, with the characteristic pattern of binuclear tetracarbonyl Rh(I) and Ir(I) complexes [7a,20c,d,21].

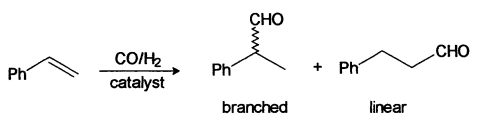
2.3. Reactivity of the cyclooctadiene complexes with PPh_3

The reactivity of the diene complexes [Rh(cod)(degusR)]ClO_4 with PPh_3 in a P:Rh molar ratio of 2:1 displaces the dithioether ligands, yielding the perchlorate salt of the previously reported cationic complex [Rh(cod)$(PPh_3)_2$]ClO_4 [22].

2.4. Hydroformylation of styrene

Rhodium complexes were tested in the hydroformylation of styrene (Scheme 5). Table 1 collects selected results from these experiments.

In all the catalytic experiments, the enantiomeric excess was 0 within the experimental error. Furthermore, regardless of the pressure and temperature of the reaction, the regioselectivity yielded by the cationic rhodium complexes **6–8**, as well as a mixture of [Rh_2(μ-OMe)$_2$$(cod)_2$] and dithioethers ligands **4a–4c**, was



Scheme 5.

Table 1
Hydroformylation of styrene [a]

Entry	L	[L]/[Rh]	*P* (bar)	Con. (%) [b]	*t* (h)	Reg. (%) [c]
1		0	15	>99	7	44
2	**4c**	2	15	86	7	41
3	**4c**	10	15	64	7	43
4	**4a**	10	15	52	7	49
5	**4b**	10	15	36	7	46
6		0	30	>99	2	51
7	**4c**	4	30	>99	2	51

[a] Reaction conditions: 5 mmol of styrene and 0.025 mmol of rhodium as $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ in 7.5 ml of toluene. $T = 80$°C. In all experiments, chemoselectivity was 97% and ee was <3%.
[b] [styrene converted] × 100/[styrene].
[c] [branched aldehyde]/[total aldehyde].

nearly identical to the value obtained when $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ was used as catalytic precursor without dithioether ligand. As the $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ complex is known to give the mononuclear species $RhH(CO)_4$ under hydroformylation conditions, these results suggest that in all cases $RhH(CO)_4$ species is responsible for the catalytic activity. We assume that conditions being the same, the selectivity observed is indicative of the nature of the active species in catalytic process.

Interestingly, the conversions obtained at a fixed time depend on the dithioether:rhodium molar ratio. Thus, the highest conversion was observed in the absence of dithioether ligand, and lower conversions were obtained when the concentration of the dithioether ligand was increased. This observation suggest an equilibrium between $RhH(CO)_4$ and catalytically inactive species containing the dithioether ligands.

Assuming this proposal, a fraction of the rhodium present in the solution would not be available for the catalytic reaction, since it would be blocked as an inactive dithioether complex. The nature of these complexes could not be elucidated. As it is expected, the equilibrium can be shifted to the hydride rhodium carbonyl complex if the pressure is raised, with the subsequent increase in the conversion.

The drop in the conversion caused by the presence of the dithioether ligands is also sensitive to the substituent on the sulfur atom. By comparing the conversions produced by catalytic mixtures which contain ligands **4a**–**4c** in identical conditions, the order of stability for the Rh dithioether complexes can be established: **4b** > **4a** > **4c**.

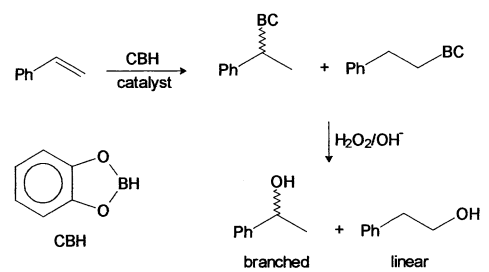
2.5. Hydrogenation of acrylic acids

Complexes **6**–**8** were tested as catalysts in the hydrogenation of *Z*-α-acetamidocinnamic acid and itaconic acid at 1 bar of H_2 and 25°C. Conversions were meaningless (<2%) in these conditions and did not improve even when the pressure was raised to 5 bar and the temperature to 65°C. Both ethanol and CH_2Cl_2 were used as solvents, with identical results. Thus, contrary to the homologous iridium dithioether complexes [11], the rhodium species are not active in the hydrogenation of this type of substrates.

2.6. Hydroboration of styrene

Rhodium complexes **6**–**8** were tested in the hydroboration of styrene with catecholborane (Scheme 6).

The catalysts show moderate activity at 25°C (<86%), but in some cases conversions are significantly lower at −14°C (<50%). Furthermore, at low temperatures the chemoselectivity is worse than at 25°C, ethylbenzene being the major product of the reaction. The regioselectivity was very poor (ca. 50%), as well as the enantioselectivity (ee < 6%). In summary, dithioethers do not provide any advantages as chiral auxiliaries in the hydroboration reaction over diphosphines or *P*,*N*-donor ligands. In order to compare the dithioether with a structurally related diphosphine, the hydroboration of styrene with the complex $[Rh(cod)L]BF_4$, L = **5** (R = Bz), was assayed. Nearly complete conversions (>90%) were achieved in 2 h, both at 25 and −14°C, with chemoselectivity > 95% and regioselectivity of 90% in the branched product. However, the best enantiomeric excess was only 14% (at −14°C).



Scheme 6.

3. Experimental

3.1. General comments

All the rhodium complexes were synthesized using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. The complex $[Rh(cod)_2]ClO_4$ [23], and the dithioether ligands degusR [11] were prepared using reported 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. ^1H 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 were performed on a VG Autospec in a nitrobenzyl alcohol matrix. Gas chromatography analyses were performed on a Hewlett–Packard Model 5890, with a flame ionization detector using a 25 m × 0.2 mm capillary column (Ultra 2). The enantiomeric excesses were measured with the same equipment using a 50 m × 0.25 mm FS-cyclodex β-I/P capillary column.

3.2. Computational details

Molecular mechanics calculations were carried out by using the program CERIUS2 developed by Molecular Simulations (MSI) with the force field UFF developed by Rappe and co-workers [24]. Electrostatic interactions were taken into account from atomic charges generated by the Qeq method [25].

3.3. Synthesis of the complexes

Caution: All the perchlorate salts reported in this study are potentially explosive and therefore, should be handled with care.

3.3.1. $[Rh(cod)(degusme)]ClO_4$ (6)

The compound was prepared by adding degusme (24 mg, 0.1 mmol) to a dichloromethane solution of $[Rh(cod)_2]ClO_4$ (40 mg, 0.08 mmol). The addition produced an immediate color change from brown to yellow. Subsequent addition of ether precipitated out the complex, which was filtered off, washed with cold ether and vacuum dried. The yield was 49 mg (91%). *Anal.* Found: C, 43.90; H, 5.46; N, 2.57; S, 11.70. Calc. for $RhC_{21}H_3S_2NClO_4$: C, 44.70; H, 5.54; N, 2.48; S, 11.37%. MS: m/z, 464 (M^+).

3.3.2. $[Rh(cod)(degusprⁱ)]ClO_4 \cdot 1/2CH_2Cl_2$ (7)

The procedure described for the previous compound was used. Yield 46 mg (76%). *Anal.* Found: C, 46.08; H, 6.26; N, 2.15; S, 10.22. Calc. for $RhC_{25}H_3S_2NClO_4$: C, 46.23; H, 6.08; N, 2.12; S, 9.67%. MS: m/z, 520 (M^+). ^1H NMR (300 MHz, $CDCl_3$): 1.32 (12H, m, Me), 1.85 (2H, m, CH_2, cod), 2.10 (2H, m, CH_2N), 2.50 (4H, m, CH_2, cod), 2.70 (2H, m, CH_2N), 2.71 (2H, m, CH_2, cod), 3.22 (2H, m, CH), 3.45 (2H, m, SCH), 3.60 (1H, m, CH_2Ph), 4.35 (1H, m, CH_2Ph), 4.50 (2H, m, CH, cod), 4.60 (2H, m, CH, cod), 5.32 (1H, s, CH_2Cl_2), 7.40 (5H, m, Ph).

3.3.3. $[Rh(cod)(degusph)]ClO_4$ (8)

The procedure described for **5** and **6** was used, yielding 56 mg (85%). *Anal.* Found: C, 53.45; H, 5.00; N, 1.96; S, 9.29. Calc. for $RhC_{31}H_{35}S_2NClO_4$: C, 54.11; H, 5.00; N, 2.03; S, 9.30%. MS: m/z, 588 (M^+). ^1H NMR (300 MHz, $CDCl_3$): 1.80 (2H, m, CH_2, cod), 2.20 (2H, m, CH_2, cod), 2.40 (2H, m, CH_2, cod), 2.70 (2H, m, CH_2N), 2.90 (2H, m, CH_2, cod), 3.20 (2H, m, CH_2N), 3.65 (2H, m, CH), 3.95 (1H, m, CH_2Ph), 4.25 (1H, m, CH_2Ph), 4.60 (4H, b, CH, cod), 7.30, 7.50 and 8.00 (15H, m, Ph).

3.3.4. $[Rh_2(\mu\text{-}degusme)_2(CO)_4](ClO_4)_2$ (9)

Carbon monoxide was bubbled through a CH_2Cl_2 solution of the complex $[Rh(cod)(degusme)]ClO_4$ (40 mg, 0.070 mmol). After 5 min, the solution lightened. The solid compound could not be isolated. The IR spectrum was registered in the reaction solution. ν(CO, cm^{-1}): 2044(s), 2020(m) and 1994(m).

3.3.5. $[Rh_2(\mu\text{-}deguspr^i)_2(CO)_4](ClO_4)_2$ (10)

This complex was prepared as for **8**. As it could not be isolated as a pure solid, it was characterized in solution by IR spectroscopy. ν(CO, cm^{-1}): 2040(s), 2021(m), 1995(m).

3.3.6. $[Rh_2(\mu\text{-}degusph)_2(CO)_4](ClO_4)_2$ (11)

Carbon monoxide was bubbled through a CH_2Cl_2 solution of 40 mg (0.058 mmol) of **7**. The solution became paler. By addition of ether, the solid precipitated; then it was filtered off, washed with cold ether and vacuum dried. (14.8 mg, 40%). *Anal.* Found: C, 56.02; H, 4.40; N, 2.71; S, 12.10. Calc. for $Rh_2C_{50}H_{46}O_4S_4N_2B_2F_8$: C, 55.97; H, 4.32; N, 2.61; S, 11.95%. ν(CO, cm^{-1}): 2044(m), 2020(s), 1996(s).

3.4. Hydroformylation procedure

The catalyst precursor $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ (0.025 mmol), the ligand in the desired molar ratio and styrene (5 mmol) were dissolved in 7.5 ml of toluene. After transferring the solution into the evacuated autoclave, it was pressurized with syn-gas to about 80% of the reaction pressure. The preheated water circuit was connected to the autoclave jacket and when thermal equilibrium was reached (5–10 min) more gas mixture was introduced until the required pressure was achieved. At

the end of the reaction, the autoclave was cooled to room temperature and depressurized. Samples were analyzed by GC. Enantiomeric excesses were measured by converting the aldehydes in the corresponding acids or alcohols with $KMnO_4$ in acetone or $LiAlH_4$ in THF, respectively. These products were analyzed by GC using a chiral column.

3.5. Hydrogenation procedure

The hydrogenation experiments were carried out as previously described [11]. In a typical run, 0.25 mmol of substrate and 5 μmol of the rhodium complex were dissolved in 6 ml of solvent (CH_2Cl_2 or EtOH). The solution was shaken under the required H_2 pressure and temperature for 6 h. A glass vessel was used for the experiments at 1 bar and the tests at 6 bar were carried out in a small home-made autoclave. The conversion was measured by ^1H NMR.

3.6. Hydroboration procedure

The cationic complex (20 μmol), freshly distilled catecholborane (2.2 mmol) and styrene (2 mmol), previously passed through a small alumina column, were dissolved in 3 ml of THF under an inert atmosphere. The reaction was stirred at the required temperature for 2 h. After this time, the mixture was cooled in an ice bath and methanol (4 ml), NaOH, 3 M (4.8 ml) and hydrogen peroxide 30% (0.48 ml) were added. After stirring at room temperature for 3 h, the mixture was extracted with ether, and the joint organic phases were washed with 1 M NaOH, 1 M NH_4Cl, and finally dried with $MgSO_4$. Chemo- and regioselectivity were determined by GC analysis. Enantiomeric excesses were measured by GC using a chiral column.

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