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Synthesis of Rhodium (I) Complexes with Mono and Dithiolato Ligands: Application in Catalytic Hydroformylation of Olefins

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Abstract. The thiols,1-phenylethanothiol **1** and 2,4-pentanodithiol **2** were synthesised and used to prepare binuclear rhodium species **3**, **4** of the type $[Rh_2(\mu\text{–}L)_n(cod)_2]$ (L = **1**, n = 2; L = **2**, n = 1; cod = 1,5cyclooctadiene). NMR and FAB^+ mass spectrometry data are consistent with a binuclear structure for the species. These complexes, plus PPh_3 or diphosphines (dppp, dppb), were used as catalytic precursors for the hydroformylation of styrene under mild conditions. Fairly good activities and regioselectivities were achieved for catalytic system **3**/ PPh_3
Keywords: Thiolato ligands, sulphur ligands, binuclear complex, rhodium complex, homogeneous catalysis, hydroformylation.

Resumen. Los tioles,1-feniletanotiol **1** and 2,4-pentanoditiol **2** fueron sintetizados y empleados para preparar especies binucleares de rodio **3**, **4** de formulación $[Rh_2(\mu\text{–}L)_n(cod)_2]$ (L = **1**, n = 2; L = **2**, n = 1; cod = 1,5-ciclooctadieno). Los espectros de RMN y espectrometría de masas FAB^+ son consistentes con una estructura binuclear para estas especies. Estos complejos junto con $P\phi_3$ o difosfinas (dppp, dppb), fueron usados como precursores catalíticos en la hidroformilación de estireno en condiciones suaves de reacción. Con el sistema catalítico **3**/$P\phi_3$ se alcanzaron buenas actividades y selectividades.
Palabras Clave: Ligantes tiolato, ligantes azufrados, complejo binuclear, complejo de rodio, catálisis homogénea, hidroformilación.

Introduction

The use of binucleating ligands in the synthesis of homo- and heterodinuclear transition-metal complexes, and in particular the study of the catalytic activity of bimetallic complexes has attracted considerable interest in recent years [1]. Co-operative effects of two or more metal centres in heterogeneous catalytic reactions are well established [2]; however bi- or polymetallic co-operativity in homogeneous catalysis is unusual and far less well understood [3].

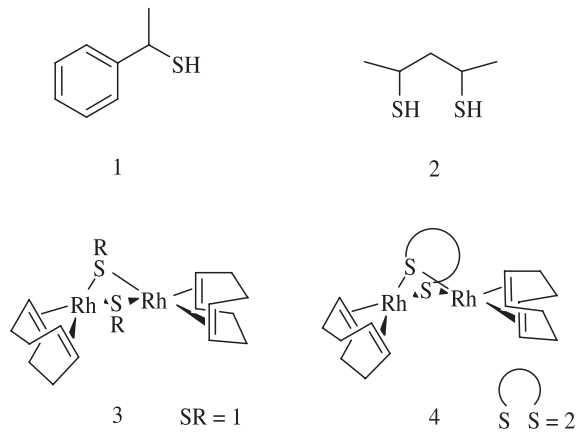
In fact, a number of binuclear complexes has been synthesised with the goal to find evidences for a co-operative effect in catalytic processes [4]. Most of them use ligands containing phosphorous donors, but several efforts have been made to prepare binuclear complexes with sulphur ligands [5-8]. Kalck reported that binuclear complexes of type $[Rh_2(\mu\text{-}SR)_2(CO)_2(PR'_3)_2]$ are active catalysts in the hydroformylation of alkenes in mild conditions [9]. These systems are attractive since they allow chemical modifications in both, the thiolato and the P-donor ligands. Thus, chiral dithiolato ligands have been used to develop the asymmetric version of the reaction. However, although good catalytic activities and regioselectivities were obtained, the enantiomeric excesses were always low [10]. So far, all the chiral ligands tested in this approach were 1,4-dithiols, which produce relatively flexible seven-membered metallocycles. Binuclear complexes containing 1,3-dithiolato ligands will generate a more rigid structure. This should decrease the conformational mobility of the intermediate species during the catalytic cycle, therefore allowing a better stereochemical control of the reaction. Additionally, the molecular flexibility can be modulated by using mono- or diphospines as auxiliary ligands in the binuclear complexes.

We describe here the synthesis of the thiols **1-2** in order to investigate the flexibility/rigidity properties of catalytic metal precursors containing mono- **1** and di-thiolato **2** ligands. For this, we also report the synthesis and spectral characterisation of the rhodium binuclear complexes $[Rh_2(\mu\text{–}L)_n(cod)_2]$ (L = **1** n = 2; L = **2** n = 1; cod = 1,5-cyclooctadiene) **3-4**, and their use as catalytic precursors in styrene hydroformylation.

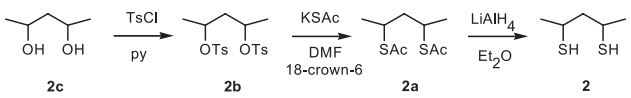
Results and Discussion

*Synthesis of thiol ligand **1***. Reaction of 1-phenylethanol (racemic mixture) with Lawesson reagent during 80 min afforded the thiol **1** in high yield (94 %).

*Synthesis of dithiol ligand **2***. The dithiol 2 was prepared from the (*rac*)/*meso*-2,4-pentanodiol diol **2c**, according to the synthetic pathway shown in Scheme 2. Treatment with tosyl chloride gave ditosyl derivative **2b**. Nucleophilic substitution



Scheme 1. Synthesised compounds.



Scheme 2. Synthetic route to obtain **2**.

of tosylate groups by thioacetate groups afforded the compound **2a**. The reduction of **2a** produced the dithiol **2** in moderate yield.

The ^{1}H NMR spectrum of **1** shows the expected first order signals for the aliphatic moiety (AMX_3) and a multiplet for the aromatic protons. In the case of the ^{13}C NMR spectrum, the five lines observed are unambiguously assigned. However, the ^{1}H NMR spectra of **2** and the organic intermediates **2a-b** show complex patterns, since the products contain two stereogenic centres generating two NMR-observable isomers, (*R,S*) and *meso*. In the case of ditosyl **2b** and dithioacetate **2c** derivatives, their spectra were resolved using sub-spectral analysis and subsequent simulation [11]. Their spectral data are reported in the experimental part without further details.

As expected, the ^{1}H NMR spectrum of **2** shows two sets of signals, each set assignable for each diastereoisomer. Each set contains four groups of signals corresponding to CH_3, CH, CH_2 and SH protons and were analysed as $X_3AA'BB'MM'X'_3$ magnetic system for *meso* isomer or for (*R,S*) racemic mixture. The shifts and constants obtained are reported in the experimental part.

The ^{13}C NMR spectrum shows also two sets of signals, corroborating the presence of two diasteromers. Similar analyses were carried out for the organic intermediates **2a-b**.

*Synthesis of rhodium complexes **3,4**.* The rhodium *bis*-thiolato and dithiolato bridged complexes, **3** and **4** respectively, were prepared by addition of CH_2Cl_2 solutions of the corresponding dithiols **1-2** to solutions of $[Rh_2(\mu - OMe)_2(cod)_2]$ in the presence of two equivalents of NEt_3. The role of the amine is not well understood [12], since the methoxy groups in the rhodium complex are basic enough to deprotonate the thiol groups. However, the reactions carried out in the absence of the amine yielded a mixture of complexes. Although these mixtures were not thoroughly investigated, they seem to contain oligomers of the binuclear species, as the ones reported in related systems [5,7,8].

The moderate air-stable orange-red solids **3** and **4** were isolated in good yields. FAB$^+$ mass spectra showed peaks corresponding to a binuclear formulation $[Rh_2(\mu\text{-}L)_n(cod)_2]$ **3**: *L* = **1**, *n* = 2, *m/z* = 696; **4**: *L* = **2**, *n* = 1, *m/z* = 556. Signals corresponding to higher molecular weight fragments were no detected.

In solution, complex **3** may exist as mixture of isomers depending on both, the relative position of sulphur substituents in the molecule (*syn* and *anti* isomers) and the stereochemistry of both stereogenic carbons (*R,R*, *S,S* and *R,S* isomers). As is shown in scheme 3, the isomers *anti* and *syn* are involved in a temperature-dependent equilibrium, meanwhile the isomers *R,R*, *S,S* and *R,S* are configurationally stable.

The ^{1}H NMR spectrum of **3** at room temperature shows six broad signals assigned to protons of the molecule (see experimental part). The reason for the spectrum broadening is the presence of four NMR-observable isomers (taking into account that it is not possible to distinguish between *R,R* and *S,S* isomers by NMR) as well as by the slow interconversion of the isomers *anti* and *syn* at room temperature. Therefore, we studied the dynamic behaviour of **3** as a function of temperature, recording ^{1}H NMR experiments at 30, 40 50 60, 70 and 75 °C in C_6D_6. As temperature increases the signals become well-defined, because the equilibrium between *syn* and *anti* isomers is faster. In fact, in the methyl protons region (1.2-2.6 ppm), it is only possible to observe a broad signal at low temperature, which is well-defined at 75 °C as two doublets (Fig 1).

This behaviour is consistent with the presence of the four NMR-observable isomers at low temperature (*anti-RR/SS*, *syn-RR/SS*, *anti-R,S* and *syn-R/S*) and as the temperature increases, a faster interconversion *syn/anti* is carried out. At 75 °C it is possible to observe one doublet due to **p**-*RR/SS* and another one assignable to **p**-R/S (**p** is an average structure of the *syn* and *anti* isomers).

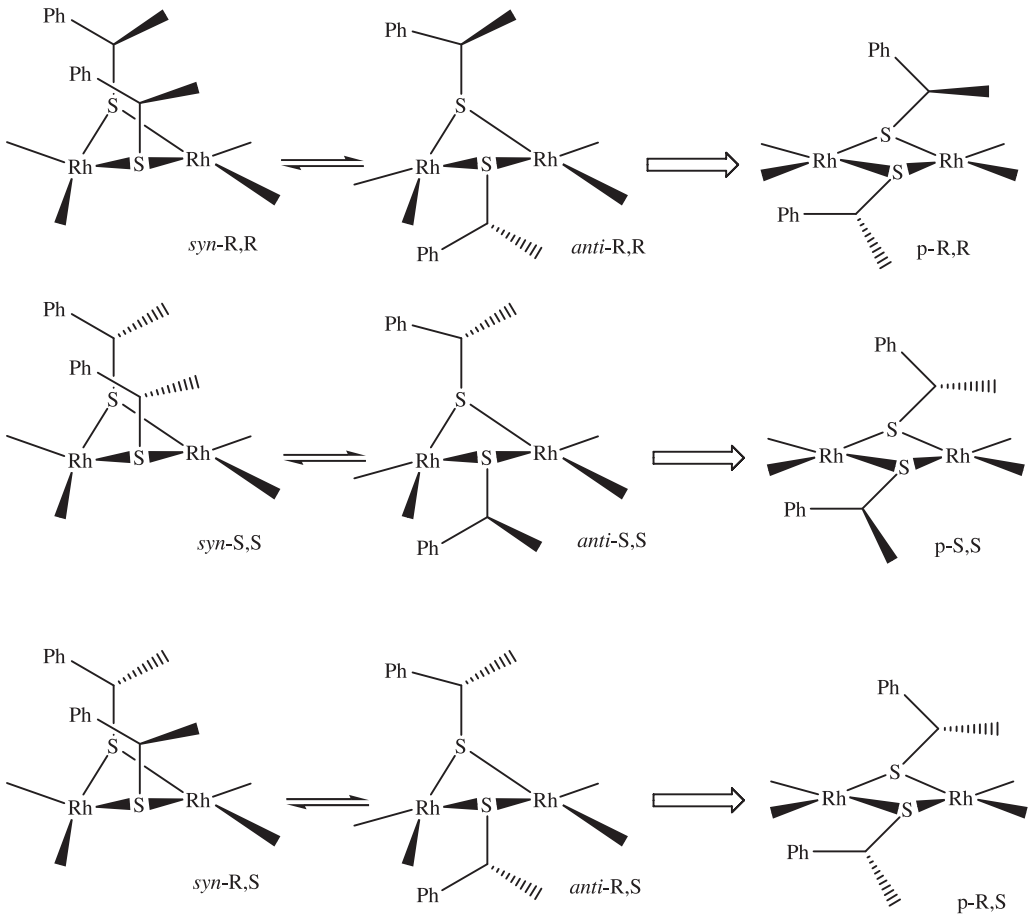
The ^{13}C NMR spectrum at 21 °C shows again broad signals for each carbon type of the molecule (for assignment see the experimental part).

In complex **4**, the rigid frame of the ligand prevents the inversion of the butterfly structure. Therefore, only the *RR/SS* and *RS* isomers are possible and where the *exo* (a,b/a',b') and *endo* (c,d/c',d') carbons of the diene ligand do not interconvert (Scheme 4). Furthermore, in the case of isomer *R,R*- or *S,S*-, the C_2 symmetry of the molecule makes the *exo* (a *vs.* b) or *endo* (c *vs.* d) carbons of the same cyclooctadiene ligand non-equivalent. Addtionally, the *meso* complex shows non-equivalent cyclooctadiene groups, each one bearing equivalent *exo* (a' or b') and *endo* (c' or d') carbons.

The ^{1}H NMR spectrum of **4** is very complex due to the presence of the two NMR-observable isomers and the magnetic non-equivalences caused by the interaction of methyl groups of the bridge ligand with the methynic groups of the cyclooctadiene ligands. However, it is possible to identify two doublets assignable to *RR/SS* and *R/S* isomers in the methylic region.

The ^{13}C NMR spectrum is clearer and consistent with the presence of the *RR/SS* and *RS* isomers and their molecular symmetry. For methyl, methylenic and methynic carbons of the dithiolato ligand two signals were observed for each one, which are assignable to *RR/SS* and *RS* isomers. For the diene ligand, the ^{13}C NMR spectrum displays eight doublets for the vinylic carbons (range of $J_{Rh\text{-}C}$= 14-20 Hz) and eight singlets for the CH_2 carbons. It is noteworthy that the doublet at 73.45 is far away from the other doublets of vinylic carbons (80.12-84.66), which could be related to the close interaction between both methyl carbons of dithiolato-bridged and vinylic carbons of COD in the *R/S* isomer.

All these spectroscopic features strongly support the binuclear structure of the complexes. Moreover, they also would suggest a remarkable influence of the chiral fragment of the



Scheme 3. Configurational and conformational isomers of complex **3**. The scheme also shows the *syn/anti* interconversion by S-inversion and the planar average structure (diene ligands are omitted for clarity).

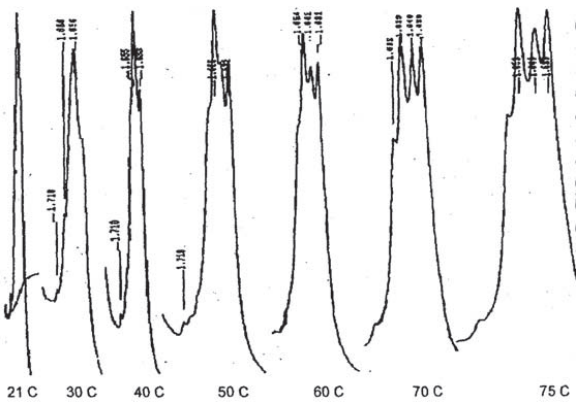
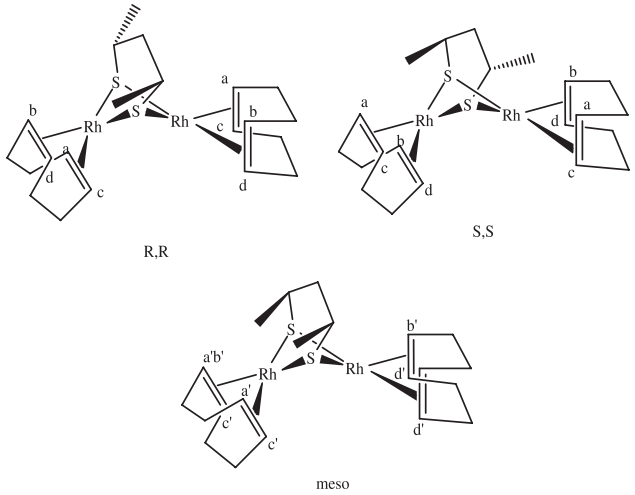


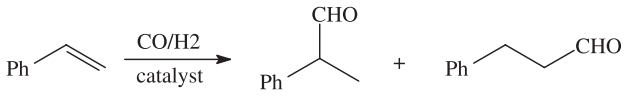
Fig. 1. Methylic region of dynamic ^{1}H NMR of compound **3**.



Scheme 4. Isomers of compound **4**.

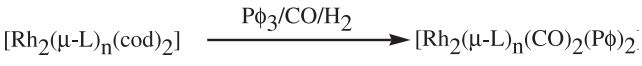
molecule on the environment of the olefin co-ordinated to the rhodium. Due to the different dynamic behaviour, related to their different molecular flexibility, we explored the activity and selectivity of these binuclear species in the styrene hydroformylation reaction.

Catalytic experiments. The binuclear complexes **3-4** were used as catalytic precursors in the hydroformylation of styrene:



Scheme 5. Hydroformylation reaction.

The catalytic species were generated *in situ* by mixing the complexes **3-4** with the appropriate amount of the PPh_3 or diphosphine as co-catalyst, under syn-gas (Scheme 6).



3: n=2, L= 1
4: n=1, L= 2

Scheme 6. Catalytic species *in situ*

Previously it has been reported that complexes $[Rh_2(\mu\text{-}L)_2(cod)]$ are not active species for rhodium-catalysed hydroformylation reactions and it is necessary add phosphorous ligands to form active catalysts [9]. Kalck proposed that $[Rh_2(\mu\text{-}L)_2(CO)_2(P\phi_3)_2]$ is responsible of the catalytic behaviour however, depending of the thiolato ligand, also it has been reported that this kind of complexes produce active monomeric species under catalytic conditions [13].

In this work, we carried out the catalytic reactions under soft conditions to prevent the bridge rupture. The catalytic results are collected in Table 1, and in all cases excellent chemioselectivities towards the aldehydes formation were achieved. The catalytic systems with monothiol **1** were very active also at low temperatures (entries 1-3). In contrast, the catalytic systems with dithiol **2** were less active (entries 4-6), probably because of the rigidity imposed by the six-membered metallocycle in comparison with the flexibility of catalytic systems **3**/PPh_3. It should be noticed that analogous *bis*(thiolato) complexes $[Rh_2(\mu - SR)_2(cod)_2]$ or dithiolato complexes with a more flexible backbone are very active even at 6 atm [6,13], while other rigid complexes such as $[Rh_2(\mu - L)(cod)_2]$ (L = 1,2ethanedithiolato) are not active at this pressure [14].

Additionally, the **3**/PPh_3 systems are more selective towards the branched aldehyde, providing up to 93 % of regioselectivity. In the case of the more rigid **4**/PPh_3 catalytic systems the regioselectivities obtained (entries 4,5) may be related to the higher steric hindrance of the binuclear complexes with dithiolato ligand, thus unfavouring the branched alkyl –complex intermediate formation.

In an effort to improve the selectivity of **3**, we use as co-catalyst dppp (diphenylphosphinepropane) or dppb (diphenylphosphinebutane) and tested these systems at optimised reaction conditions (60 °C and 5 atm). However, the activities were lower than for the system 3/PPh_3 (entries 7,8 *versus* 2). With respect to selectivity, the **3**//PPh_3 as well as 3/dppp provided the same regioselectivity, which means both catalytic systems share similar catalytic active species, while the **3**/dppb system, which give 69% of branched aldehyde, has to generate active species of a different nature.

In summary, only dimeric species of rhodium were synthesised and the fragments in the bridging ligands produce different dynamic behaviour in solution. The complex containing the dithiolato ligand, seems to strongly interact with the ancillary olefin ligands. The rigidity/flexibility of the rhodium complexes is connected to the activity and regioselectivity of the catalysts in the styrene hydroformylation. The best results were obtained with the more flexible catalytic system

Table 1. Catalytic hydroformylation of styrene with organometallic rhodium precursors **3-4**[a].

Entry	Precursor	*L*	T(°C)	Time(h)	Conv.(%)[b]	Ald. (%)[c]	Bran. (%)[d]
1	3	PPh_3	80	1.6	97	100	68
2	3	PPh_3	60	2	97	>99	86
3	3	PPh_3	40	4	88	>99	93
4	4	PPh_3	80	2.7	87	100	36
5	4	PPh_3	60	2.7	88	100	55
6	4	PPh_3	40	4.5	31	100	90
7	3	dppp	60	4.5	82	100	88
8	3	dppb	60	4.0	15	100	69

[a] Reaction conditions: P = 5 atm, $P_{co} = P_{H2}$, 5 mmols of styrene, 0.0125 mmol of rhodium precursor, and 0.05 mmol of PPh_3 or 0.025 mmol of diphosphine in 7.5 mL of toluene. [b]Olefin converted with respect to the initial amount. [c] Aldehyde products with respect to the total of products. [d]Branched aldehyde with respect to the total of aldehyde formed.

3/PPh_3. In order to identify which is the nature of the active catalyst species is necessary to carry out a HP-NMR study of complexes **3** and **4** in presence of the phosphine ligands under syn-gas.

Experimental

Chemical reagents were used as commercially supplied. Solvents were dried and distilled by standard procedures under N_2 atmosphere. The synthesis of the rhodium complexes was carried out using Schlenk techniques under nitrogen atmosphere and with deoxygenated solvents.

1-phenylethanol and 2,3-pentanodiol were purchased to Aldrich and were used withouth further purification. The complex $[Rh(\mu\text{-}OMe)(cod)]_2$ [15] was prepared as previously reported. Infrared spectra were recorded on a Perkin-Elmer FTIR 1600 spectrometer. ^1H and ^{13}C NMR were registered on a Varian 300 MHz spectrometer, using $SiMe_4$ as internal reference; $CDCl_3$ was used as solvent for the organic compounds and C_6D_6 for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-5x102A) instrument using EI^+, CI^+ and FAB^+ (nitrobenzyl alcohol matrix) techniques. The C, H and S microanalysis were determined by Galbraith Laboratories, USA. The course of catalytic and synthesis reaction was followed with a GC Varian 3800 using a column Supelco β–Dex (120, 30 m x 0.25 mm).

Catalysis

Hydroformylation experiments were carried out in a Trallero autoclave with magnetic stirring. The catalytic solution was contained in a glass vessel, and the autoclave cap was Teflon-covered. Constant temperature was controlled with a FUJI equipment that contained an internal thermocouple sensor.

The catalyst precursor $[Rh_2(\mu - L)_n(cod)_2]$ (0.0125 mmols), PPh_3 (0.05 mmols)/diphosphine (0.025 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 syn-gas to about 80% of the reaction pressure. The temperature controller was connected to the autoclave. When the programmed temperature was reached (5-10 min), more gas mixture was introduced until the working pressure was achieved. Samples was taken during and at the end of the reaction. When the reaction was complete the autoclave was cooled to room temperature and depressurized. Analysis of samples was performed by gas chromatography.

Synthesis of thiol 1. 1 was prepared by the following modified procedure to previously reported [16]. A solution of 1.525 g (12.483 mmol) of 1-phenylethanol and 5.0976 g (12.603 mmol) of Lawesson reagent in 70 mL of anhydrous toluene was refluxed under N_2 atmosphere. The pale reaction mixture changed slowly to yellow colour. The course of the reaction was followed by GC and after 80 min. 94% of conversion to 1-phenylethanothiol was reached. Subsequently, the system was cooled, the solvent was evaporated to 30 mL, the residue was filtered off and the solution was totally evaporated in a vacuum line. The white oil obtained was purified by reduced pressure [0.05 mmHg, 95 °C].Yield of **1** 0.725.2 g (43%). Analysis found for **1**: C, 69.45; H, 7.34; S, 23.10. Calculated for $C_8H_{10}S$: C, 69.54; H, 7.30; S, 23.16. ^1H NMR: AMX_3 ,1.67 (d, 3, X, J = 6.89, 0.60), 1.99 (q_td 1, A, J = 5.09), 4.23 (dq_t,1, M, J = 6.89), 7.29 (m, 5, Ph). ^{13}C NMR: 20.03 (CH_3), 38.68 (CH), 126.33 (C_{orto}), 127.11 (C_{para}), 128.59 (C_{meta}), 145.8 (C_{ipso}). EI: 138 m/z [M^+].

Synthesis of ditosyl derivative 2b. A solution of 13.34 g (70 mmol) of tosyl chloride in 20 mL of pyridine was added dropwise to a solution of 3 g (29.07 mmol) of **2c** in 10 mL of pyridine at 0°C. The mixture was stirred 24 h at room temperature, then 40 mL of 15% HCl solution was added. The organic layer was extracted with 40 mL of dichloromethane and washed with 15% HCl solution (4 × 40 ml), water (40 mL) and a saturated solution of $KHCO_3$ (40 mL). Finally, the solution was dried over Na_2SO_4 and evaporated under reduced pressure to obtain a white solid which was recrystallised in dichloromethane/hexane. Yield of **2b** 8.27g (70%). Analysis found for **2b**: C, 55.35; H, 5.82; S, 15.38. Calculated for $C_{19}H_{24}O_6S_2$: C, 55.32; H, 5.87; S, 15.54. ^1H NMR: $X_3AA'BB'X_3'$,1.172 (d, X/X'$_{meso}$, J = 6.29), 1.23 (d, XX'$_{R,S}$, J = 6.29) 1.69, 2.03 (q_tt, BB'$_{meso}$, J = 14.31, 6.35, 6.99), 1.87 (t, BB'$_{R,S}$, J = 6.29), 2.42 (s, CH_3-Tos), 4.56 (sx, AA'$_{meso}$), 4.69 (sx, AA'$_{R,S}$), 7.34 (d, H_m, J = 8.09), 7.75 (d, $H_{o\ meso}$), 7.8 (d, $H_{o\ R,S}$). ^{13}C NMR: 20.48 ($CH_{3\ meso}$), 21.27 ($CH_{3\ R,S}$), 21.59 (CH_3-Ts), 43.11 ($CH_{2\ meso}$), 43.85 ($CH_{2\ R,S}$), 76.03 (CH_{meso}), 76.72 ($CH_{R,S}$),127.61 ($C_{o\ meso}$), 127.66 ($C_{o\ R,S}$), 129.77($C_{m\ meso}$), 129.81 ($C_{m\ R,S}$), 133.9 ($C_{i\text{-}SO3\ meso}$), 134.21 ($C_{i\text{-}SO3\ R,S}$), 144.67 ($C_{i\text{-}CH3\ meso}$), 144.76 ($C_{i\text{-}CH3\ R,S}$). EI: 412 m/z [M^+].

Synthesis of dithioacetate 2a. A solution of 3g (7.26 mmol) of **4b**, 2.015 g (17.64 mmol) of KAcS and 1 mg of 18-crown-6 in 7 mL of anhydrous DMF was stirred under N_2 atmosphere for 72 h. Afterwards, 25 mL of water were added and the mixture was extracted with diethyl ether (4x15 mL). The combined ether solutions were dried over $MgSO_4$ and evaporated to obtain a dark orange oil. The oil was purified by column chromatography (silica gel; hexane-ethyl acetate 10:1) to obtain 0.936 g of **2a** as a pale yellow oil (59%). Analysis found for **2a**: C, 49.15; H, 7.25; S, 29.13. Calculated for $C_9H_{16}O_2S_2$: C, 49.05; H, 7.33; S, 29.1. ^1H NMR: $X_3AA'BB'X_3'$,1.3 (d, X/X'$_{meso}$, J = 7.21), 1.36 (d, XX'$_{R,S}$, J = 6.91) 1.7,1.87 (q_tt, BB'$_{meso}$, J = 14.26, 7.44, 8.02), 1.78 (t, BB'$_{R,S}$, J = 7.51), 2.3 (s, CH_3-CO $_{R,S}$), 2.32 (s, CH_3-CO $_{meso}$), 3.63 (sx, AA'$_{meso}$), 3.64 (sx, AA'$_{R,S}$). ^{13}C NMR: 21.26 ($CH_{3\ meso}$), 21.35 ($CH_{3\ R,S}$), 30.65 (CH_3-CO $_{R,S}$), 30.67 (CH_3-CO $_{meso}$), 37.1 ($CH_{2\ meso}$), 37.24 ($CH_{2\ R,S}$), 42.67 ($CH_{R,S}$), 42.73 (CH_{meso}), 195.36 ($CO_{R,S}$), 195.52 (CO_{meso}). EIMS: 220 *m/z* [M^+].

Synthesis of dithiol 2. A solution of 0.679 g (3.09 mmol) of **2a** in 5 mL of dry diethyl ether was added dropwise to a suspension of 0.2872 g (7.416 mmol) of $LiAlH_4$ in 5 mL of diethyl ether cooled in an ice-bath. The mixture was stirred for 48 h. at room temperature, then methanol was slowly added until hydrogen no longer evolved and later, water was added to form a white cake. Then, 15 % HCl solution was dropped into the suspension until pH = 1, the ether layer was extracted and the aqueous layer was washed further with ethyl ether (3x15 mL). The combined organic layers were dried over $MgSO_4$. The solution was evaporated to dryness to obtain a pale yellow liquid which was purified by column chromatography using hexane:ethyl acetate 10:1 as eluent. Yield of **2**: 0.291 g (69%). Analysis found for **2**: C, 44.5; H, 9.01; S, 46.8. Calculated for $C_5H_{12}S_2$: C, 44.06; H, 8.88; S, 47.05. ^{1}H NMR: $X_3AA'BB'MM'X_3'$,1.35 (d, X/X'$_{R,S}$, J = 6.91), 1.38 (d, XX'$_{meso}$, J = 6.6) 1.45 (dd, SH $_{meso}$ J = 7.21,1.2), 1.5 (d, SH $_{R,S}$ J = 7.21), 1.68 ($q_t$dd, BB'$_{meso}$, J = 14.83, 7.81, 6.6), 1.78 (t, BB'$_{R,S}$, J = 7.34), 3.08 (h, AA'$_{meso}$), 3.17 (dsx, AA'$_{R,S}$). ^{13}C NMR: 21.35($CH_{3\ R,S}$), 26.22 ($CH_{3\ meso}$), 33.22 ($CH_{2\ R,S}$), 33.97 ($CH_{2\ meso}$), 51.49 (CH $_{meso}$), 52.06 (CH $_{R,S}$). EIMS: 136 *m*/*z* [M$^+$].

Synthesis of [Rh_2(μ – *L*)$_n$(cod)$_2$] complexes 3,4. *General procedure*. A solution of 0.413 mmol of [Rh(μ-OMe)(cod)] in 30 mL of CH_2Cl_2 was added under nitrogen 0.826 mmol of NEt_3. Then, a solution of 0.826 of **1** or 0.413 mmol of **2** dissolved in 10 mL de CH_2Cl_2 was slowly added, while vigorous stirring was maintained. After 30 min, the clear orange or red solution was evaporated to dryness and washed several times with 3 × 5 mL of cold ethanol and water. Finally, the orange-red solids were dried in vacuum for 12 h. Yields: **3** = 78%, **4** = 96%.

Analysis found for **3**: C, 55.57; H, 6.15; S, 8.93. Calculated for $C_{32}H_{42}Rh_2S_2$: C, 55.17; H, 6.08; S, 9.19. ^{1}H NMR: 1.65 (b, 6, CH_3), 1.8 (m, 8, $CH_{2\ COD}$), 2.21 (m, 8, $CH_{2\ COD}$), 4.3 (b,10, $CH_{COD+ligand}$) 7.12 (m, 8, $H_{m,p}$), 7.52 (m, 4, H_o). ^{13}C NMR: 29.73 (b, CH_3), 31-33 (b,$CH_{2\ COD}$) 44 (b,CH), 79-90 (b, CH_{COD}), 126.5-129 ($C_{orto,para,meta}$), 148.08(C_{ipso}). MSFAB: 696 *m*/*z* [M$^+$].

Analysis found for **4**: C, 45.74; H, 6.11; S, 10.76. Calculated for $C_{21}H_{34}Rh_2S_2$: C, 45.33; H, 6.17; S, 11.52. ^{1}H NMR:1.35 (d, $CH_{3\ meso}$, J = 6.9), 1.33 (d, $CH_{3\ R,S}$, J = 8.7) 1.43 (m, $CH_{2\ meso}$), 1.59 (m, $CH_{2\ R,S}$), 1.65-2.7 (m, 8 $CH_{2\ COD}$) 2.94 (m, 1, CH), 3.56, 4.31, 4.47, 4.76 (m, 4, CH_{COD}). ^{13}C NMR: 27.55 ($CH_{3\ R,S}$), 27.91 ($CH_{3\ meso}$), 30.64, 31.27,31.54,31.79,31.97,32.04,31.18,32.3 (s,$CH_{2\ COD}$), 41.62 ($CH_{2\ R,S}$), 41.72 ($CH_{2\ meso}$), 52.22 (CH $_{R,S}$) 57.516 (CH $_{meso}$), 73.44 (d, CH_{COD}, J = 19.9), 80.5 (d, CH_{COD}, J = 14), 80.66 (d, CH_{COD}, J = 14.5), 81.21 (d, CH_{COD}, J = 15.8), 81.52 (d, CH_{COD}, J = 17.3), 82.93 (d, CH_{COD}, J = 17.95), 84.54 (d, CH_{COD}, J = 17.1), 85.13 (d, CH_{COD}, J = 16). MSFAB: 556 *m*/*z* [M$^+$].

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