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 \([\text{Rh}_2(\mu-L)_n(\text{cod})_2]\) \((L = 1, n = 2; L = 2, n = 1; \text{cod} = 1,5\text{-cyclooctadiene})\). NMR and FAB⁺ mass spectrometry data are consistent with a binuclear structure for the species. These complexes, plus PPh₃ 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 systems/PH₃

Keywords: Thiolato ligands, sulphur ligands, binuclear complex, rhodium complex, homogeneous catalysis, 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 \((\text{rac/meso})-2,4\text{-pentanodiol diol} \text{2c}, \text{according to the synthetic pathway shown in Scheme 2. Treatment with tosyl chloride gave ditosyl derivative 2b. Nucleophilic substitution}\)

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 \([\text{Rh}_2(\mu-L)_n(\text{cod})_2]\) \((L = 1 n = 2; L = 2 n = 1; \text{cod} = 1,5\text{-cyclooctadiene})\) 3-4, and their use as catalytic precursors in styrene hydroformylation.

Keywords: PPh₃.

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 \([\text{Rh}_2(\mu-L)_n(\text{cod})_2]\) \((L = 1, n = 2; L = 2, n = 1; \text{cod} = 1,5\text{-cyclooctadiene})\). NMR and FAB⁺ mass spectrometry data are consistent with a binuclear structure for the species. These complexes, plus PPh₃, 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 systems/PH₃. So far, all the chiral ligands tested in this approach were clear, complex of rhodium, catalyst homogénea, hidroformilación.

Keywords: PPh₃.

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

Edgar Vargas-Malváez, Georgina Pimentel, Gustavo Trujillo, Erika Martin*
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) 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,AA'BB'MM'*X' 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 diastereomers. 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$_2$Cl$_2$ solutions of the corresponding diethiols 1-2 to solutions of [Rh(μ-O Me)(cod)$_2$]$_2$ 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(μ-L)(cod)$_2$]$_2$: 3: L = 1, n = 2, m/z = 696; 4: L = 2, n = 1, m/z = 556. Signals corresponding to higher molecular weight fragments were not 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$_6$D$_6$. 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 RR- or S,S-, the C$_3$ symmetry of the molecule makes the exo (a vs. b) or endo (c vs. d) carbons of the same cyclooctadiene ligand non-equivalent. Additionally, 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 methylenic 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 methylic 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 $J_{Rh-C}$ = 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 \textit{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:

\[ \text{Ph} \overset{\text{CO/H}_2}{\longrightarrow} \text{Ph} + \text{Ph} \overset{\text{CHO}}{\longrightarrow} \text{Ph} \]

Scheme 5. Hydroformylation reaction.

The catalytic species were generated \textit{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).

\[ [\text{Rh}_2(\mu-L)_2\text{(cod)}] \overset{\text{PPh}_3/\text{CO/H}_2}{\longrightarrow} [\text{Rh}_2(\mu-L)_2(\text{CO})_2(\text{PPh}_3)_2] \]

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

Scheme 6. Catalytic species \textit{in situ}

Previously it has been reported that complexes \([\text{Rh}_2(\mu-L)_2\text{(cod)}]\) are not active species for rhodium-catalysed hydroformylation reactions and it is necessary add phosphorous ligands to form active catalysts [9]. Kalck proposed that \([\text{Rh}_2(\mu-L)_2(\text{CO})_2(\text{P}φ_3)_2]\) 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 chemoselectivities 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 \textit{bis}(thiolato) complexes \([\text{Rh}_2(\mu-\text{SR})(\text{cod})]\) or dithiolato complexes with a more flexible backbone are very active even at 6 atm [6,13], while other rigid complexes such as \([\text{Rh}_2(\mu-L)(\text{cod})]\) \((L = 1,2\text{ethanedithiolato})\) 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 (diphenylphosphinopropane) 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>
<thead>
<tr>
<th>Entry</th>
<th>Precursor</th>
<th>L</th>
<th>T(°C)</th>
<th>Time(h)</th>
<th>Conv. (%)</th>
<th>Ald. (%)</th>
<th>Bran. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>PPh$_3$</td>
<td>80</td>
<td>1.6</td>
<td>97</td>
<td>100</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>PPh$_3$</td>
<td>60</td>
<td>2</td>
<td>97</td>
<td>&gt;99</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>PPh$_3$</td>
<td>40</td>
<td>4</td>
<td>88</td>
<td>&gt;99</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>PPh$_3$</td>
<td>80</td>
<td>2.7</td>
<td>87</td>
<td>100</td>
<td>36</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>PPh$_3$</td>
<td>60</td>
<td>2.7</td>
<td>88</td>
<td>100</td>
<td>55</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>PPh$_3$</td>
<td>40</td>
<td>4.5</td>
<td>31</td>
<td>100</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>dppp</td>
<td>60</td>
<td>4.5</td>
<td>82</td>
<td>100</td>
<td>88</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>dppb</td>
<td>60</td>
<td>4.0</td>
<td>15</td>
<td>100</td>
<td>69</td>
</tr>
</tbody>
</table>

* Reaction conditions: P = 5 atm, P$_{CO} = P_{H_2}$, 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. * Olefin converted with respect to the initial amount. * Aldehyde products with respect to the total of products. * Branched aldehyde with respect to the total of aldehyde formed.
3/PPh₃. 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 N₂ 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 without further purification. The complex [Rh(μ-OMe)(cod)]₂ [15] was prepared as previously reported. Infrared spectra were recorded on a Perkin-Elmer FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Perkin-Elmer spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes. Chemical shifts and coupling constants are given in ppm and Hz, respectively. MS was performed on a High-Resolution Jeol (JMS-DX 303). FTIR 1600 spectrometer. ¹H and ¹³C NMR were registered on a Varian 300 MHz spectrometer, using SiMe₄ as internal reference; CDCl₃ was used as solvent for the organic compounds and C₆D₆ for rhodium complexes.
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 LiAlH₄ 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 MgSO₄. The solution was evaporated to dryness to obtain a (3x15 mL). The combined organic layers were dried over.

Acknowledgement

We are grateful to CONACYT-3183P and CYTED-V.9 for financial support.

References