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## Asymmetric Hydroformylation of Styrene Using Dithiolato Bridged Dirhodium Catalyst with BDPP as Chiral Ligand

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**Abstract:** Asymmetric hydroformylation of styrene is performed using dinuclear thiolato bridged rhodium complexes with BDPP as the chiral auxiliary ligand. The optical yields observed depend on the starting organometallic complex. When (+) and (-) dithiolato bridged complexes and (+) and (-) diphosphine are combined, there is one pair which enhances the enantioselectivity.

Transition metal complexes based on rhodium and platinum have been used as catalyst precursors in asymmetric hydroformylation. Platinum tin dichloride based catalytic systems had shown the highest level of enantioselectivity when modified with DIOP,<sup>1</sup> BPPM,<sup>2</sup> BCO,<sup>3</sup> and BDPP.<sup>4</sup> (Figure 1, 1-4) However, the regio and chemoselectivities were low.<sup>1-4</sup> In recent years, hydroformylation catalyst precursors based on [Rh(acac)(CO)<sub>2</sub>] modified with phosphine-phosphite<sup>5</sup> (BINAPHOS, 5) or diphosphites<sup>6</sup> (6) and [Rh(cod)(diphosphinites)]<sup>7</sup> (7) have provided an ee between 50 and 96 % in the hydroformylation of styrene and other olefins together with, in some cases, an excellent chemo and regioselectivity .

In practically all Pt or Rh chiral catalysts, chiral bidentate phosphorus ligands are present in the complex or are added to the catalytic solution. The dependence of the selectivity on the structure of different modified diphosphines and diphosphites has recently been proved.<sup>6,8,9</sup>

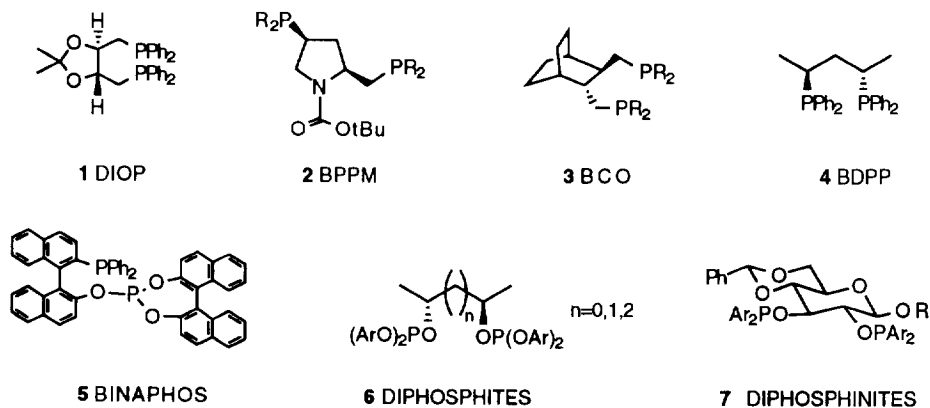


Figure 1

On the other hand, it has been established that dinuclear bridged dithiolate rhodium complexes behave as efficient catalyst precursors in the hydroformylation reaction. However, a phosphorus ligand, namely triphenylphosphine is required in most of the reported experiments to obtain high regioselectivities.<sup>10,11</sup> When C<sub>2</sub> symmetry rigid dithiolate ligands such as BINAS<sup>2-</sup> and DIOS<sup>2-</sup> were used in the hydroformylation of styrene, the reported enantioselectivities were low (ca. 15 %).<sup>10b,10c</sup> In this context we thought it would be interesting to combine the highly efficient dinuclear dithiolate rhodium complexes (Figure 2) with chiral diphosphines to be used as a catalytic precursor system.

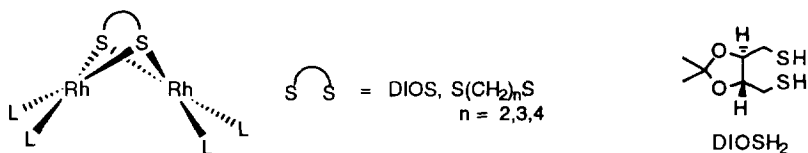


Figure 2

In order to study the influence of the dinuclear framework of the thiolate precursor we chose different thiolate and dithiolate bridge rhodium complexes together with a simple chiral diphosphine which had been reported to provide a high ee in enantioselective hydroformylation using platinum precursors. BDPP was used as chiral ligand in Pt/Sn catalysed enantioselective hydroformylation of styrene.<sup>4</sup> Although the best ee results with BDPP were 75 %<sup>4a</sup> and 88 %,<sup>4b</sup> the regioselectivity in 2-phenylpropanal was low, 40 % and 29 % respectively.<sup>4</sup> Using [PtCl<sub>2</sub>(BDPP)]/SnCl<sub>2</sub> in the presence of Ph<sub>2</sub>P<sub>2</sub>Y, an ee of 86 % was achieved, but the regioselectivity in 2-phenylpropanal was 32 %.<sup>4c</sup>

Initially we tested the addition of (+)-BDPP to the dinuclear thiolate rhodium complex [Rh( $\mu$ -S<sup>t</sup>But)(CO)<sub>2</sub>]<sub>2</sub> firstly prepared by Kalck and co-workers.<sup>12</sup> This system provides total conversion into aldehydes with a regioselectivity in 2-phenylpropanal of 90 %, but the ee was 10 % (R) (Table 1, entry 1).<sup>13</sup> Systems based on the dinuclear dithiolate complexes [Rh<sub>2</sub>( $\mu$ -S(CH<sub>2</sub>)<sub>n</sub>S)(COD)]<sub>2</sub> (n = 2, 3 and 4) were previously reported as active hydroformylation catalysts in the presence of PR<sub>3</sub>.<sup>10a</sup> The addition of BBDDP to these dithiolate systems produced an increase of the enantioselectivity. Enantiomeric excesses up to 43 % (S) (entries 2-4) were obtained at 30 bar and 65 °C, P/Rh ratio=2, with the dithiolate/BDPP systems which provided complete conversion into aldehydes and regioselectivity up to 94 % in 2-phenylpropanal. Unimportant differences in regio and enantioselectivity are observed when comparing the 1,2-, 1,3- and 1,4- dithiolates even if the [Rh<sub>2</sub>( $\mu$ -S(CH<sub>2</sub>)<sub>2</sub>S)(COD)]<sub>2</sub> /(+)-BDPP system is less active and the ee obtained is slightly lower 31 % (S) (entry 2). When (+) and (-)-BDPP are used the same ee of enantiomer S or R are obtained, as expected.

For comparison purposes, an achiral rhodium precursor system [Rh<sub>2</sub>( $\mu$ -OMe)(COD)]<sub>2</sub>, which is known to lead to the rhodium hydride carbonyl phosphorous species in hydroformylation conditions,<sup>14</sup> was used in the same conditions. At a ratio of P/Rh=2, [Rh<sub>2</sub>( $\mu$ -OMe)(COD)]<sub>2</sub>/(+)-BDPP system provides a lower ee (5 %) than the system based on dinuclear bridged dithiolate [Rh<sub>2</sub>( $\mu$ -S(CH<sub>2</sub>)<sub>n</sub>S)(COD)]<sub>2</sub> (n = 2, 3 and 4) complexes, (entry 5) showing that different species are involved in the catalytic cycle.

Despite providing a low ee, it has been recently shown that the dinuclear rhodium complex [Rh<sub>2</sub>( $\mu$ -DIOS)(COD)]<sub>2</sub> behaves as active catalyst precursor in the hydroformylation reaction with complete conversion

Table 1. Styrene Hydroformylation with  $[\text{Rh}_2(\mu\text{-dithiolate})(\text{COD})_2]/\text{BDPP}$  as Catalyst Precursor Systems.<sup>a</sup>

Entry	Catalyst precursor	Diphosphine	% Conv <sup>b</sup>	2-PP/3-PP (%) <sup>c</sup>	% ee <sup>d</sup>
1	$[\text{Rh}(\mu\text{-S}^t\text{But})(\text{CO})_2]_2$	(+)-BDPP	100	90/10	10 (R)
2	$[\text{Rh}_2(\mu\text{-S}(\text{CH}_2)_2\text{S})(\text{COD})_2]$	(+)-BDPP	38	94/6	31 (S)
3	$[\text{Rh}_2(\mu\text{-S}(\text{CH}_2)_3\text{S})(\text{COD})_2]$	(+)-BDPP	80	94/6	43 (S)
4	$[\text{Rh}_2(\mu\text{-S}(\text{CH}_2)_4\text{S})(\text{COD})_2]_2$	(+)-BDPP	86	94/6	42 (S)
5	$[\text{Rh}(\mu\text{-OMe})(\text{COD})]_2$	(+)-BDPP	98	91/9	5 (R)
6	$[\text{Rh}_2(\mu\text{-}(+)\text{-DIOS})(\text{COD})_2]^\text{e}$	$\text{PPh}_3$	91	90/10	4 (R)
7 <sup>10c</sup>	$[\text{Rh}_2(\mu\text{-}(-)\text{-DIOS})(\text{COD})_2]^\text{e}$	$\text{PPh}_3$	97	91/9	4 (S)
8	$[\text{Rh}_2(\mu\text{-}(+)\text{-DIOS})(\text{COD})_2]$	(+)-BDPP	100	90/10	4 (S)
9	$[\text{Rh}_2(\mu\text{-}(+)\text{-DIOS})(\text{COD})_2]$	(-)-BDPP	98	90/10	13 (R)
10	$[\text{Rh}_2(\mu\text{-}(-)\text{-DIOS})(\text{COD})_2]$	(+)-BDPP	50	93/7	34 (S)
11	$[\text{Rh}_2(\mu\text{-}(-)\text{-DIOS})(\text{COD})_2]$	(-)-BDPP	40	92/8	13 (R)

<sup>a</sup> Reaction conditions: Solvent = THF. Temperature = 65 °C, pressure 30 atm,  $\text{CO}/\text{H}_2 = 1/1$ ,  $\text{P}/\text{Rh} = 2$ , time = 24 h. <sup>b</sup> Conversion in aldehydes. <sup>c</sup> 2-PP = 2-phenylpropanal, 3-PP = 3-phenylpropanal. <sup>d</sup> absolute configuration in parenthesis. <sup>e</sup> time = 3h.

into aldehydes and regioselectivity up to 90 % in 2-phenylpropanal (entries 6, 7).<sup>10c</sup> The addition of (+)- or (-)-DIOF to the Rh(-)-DIOF complex produced different ee (17 % (S) and 3 % (R) respectively).<sup>10c</sup> Therefore we felt it would be interesting to study all possible combinations using two chiral ligands: (+)- and (-)-DIOF and (+)- and (-)-BDPP. Apart from our previous work the combination of anionic dithiolate ligands and chiral diphosphine in the hydroformylation reaction has not been explored.<sup>15</sup>

The results obtained with the four couples (+)- / (-)-DIOF and (+)- / (-)-BDPP at  $\text{P}/\text{Rh}=2$  (entries 8-11) show that (-)-BDPP gives a 13 % ee (R) with both (+)- or (-)-DIOF. Interestingly, the (+)-BDPP increases the enantioselectivity of the (-)-DIOF precursor up to 34 % (S) while (+)-DIOF / (+)-BDPP provides an ee of only 4 %.

In conclusion, in the hydroformylation of styrene, catalytic precursors based on dinuclear dithiolate bridge rhodium systems using BDPP as auxiliary phosphorus ligands provide a regioselectivity in 2-phenylpropanal of up to 94 %, together with ee of up to 43 %. This shows that the asymmetric induction of a given homochiral phosphorus ligand can be improved by changing the starting organometallic complex. Although no improvement in ee was observed when homochiral dithiolate ligands were used in combination with homochiral phosphines, it was proved that one ligand pair, namely (-)-DIOF / (+)-BDPP, provides better ee and it can be associated with a matched effect. This opens up new possibilities for the problem of asymmetric hydroformylation. Further studies concerning the effects of the combined use of chiral dithiolate and chiral diphosphine ligands are in progress.

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13. Typical procedure for hydroformylation reactions: Hydroformylation experiments were carried out in an autoclave with magnetic stirring. The catalytic solution was contained in a glass vessel. The inside of the autoclave cap is Teflon covered to avoid direct contact of the solution with the stainless steel. The temperature was maintained constant by circulating water through a double jacket. A solution of the substrate (20 mmol), the catalyst precursor (0.1 mmol) and the phosphorus compound in 15 ml of anhydrous tetrahydrofuran was introduced into the evacuated autoclave. The gas mixture was introduced and the system was heated. When thermal equilibrium was reached, the gas mixture was introduced until the desired pressure was reached. After the reaction time, the autoclave was cooled to room temperature and depressurized. Conversions and regioselectivities were determined by GC analysis of crude samples without the addition of any external standard. Enantiomeric excess was measured by GC with a chiral column with the alcohols obtained by reducing the resulting aldehydes<sup>10c</sup> and by <sup>1</sup>H NMR using Eu(hfc)<sub>3</sub> as a chiral shift reagent.<sup>16</sup>
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