Asymmetric Hydroformylation of Styrene by Rhodium(I) Catalysts with Chiral Ligands containing Sulfur Donors†

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Rhodium(I) complexes containing the atropisomeric sulfur ligands 1,1'-binaphthalene-2,2'-dithiol **1** (binas) or the relevant dimethyl sulfide **2** (Me_2binas) are efficient catalysts for the highly regioselective hydroformylation of styrene.

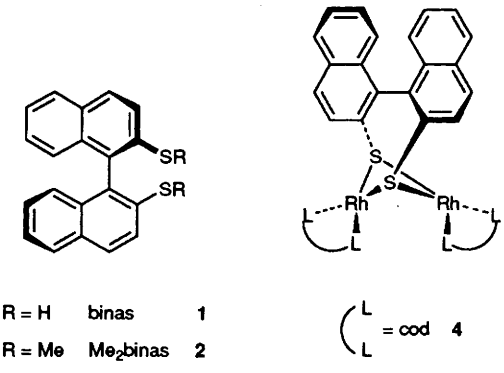
The high catalytic activity displayed in hydroformylation by dinuclear thiolato bridged rhodium complexes containing phosphine or phosphite ligands has been documented for many years.[1] More recently some of us have published that dinuclear dithiolato rhodium complexes are readily available from dithiol ligands[2] and are active hydroformylation catalysts.[3] Apart from a preliminary account,[4] the use of aracemic thiols to induce asymmetry in this reaction has no precedent so far.

In the past decade a lot of atropisomeric C_2 symmetry binaphthyl derivatives were prepared and used as chiral modifiers in metal-mediated asymmetric reactions.[5] Recently a practical synthesis of enantiomerically pure 1,1'-binaphthalene-2,2'-dithiol **1** (binas) has been accomplished.[6] This prompted us to exploit the potential of binas and of the relevant dimethyl thioether (Me_2binas, **2**) in the enantioselective hydroformylation of styrene. This reaction is of interest since it provides a straightforward synthetic route to α-arylpropanoic acids, an important class of anti-inflammatory agents.

Addition of a stoichiometric amount of binas to a dichloromethane solution of $[Rh(\mu\text{-}OMe)(cod)]_2$ (cod = cycloocta-1,5-diene) **3** led to the isolation of the dinuclear neutral complex **4** in moderate yield.‡ In the presence of triphenylphosphine, **4** is able to promote the hydroformylation of styrene under mild conditions with excellent yield and regioselectivity, but with low enantiomeric excess (e.e.).

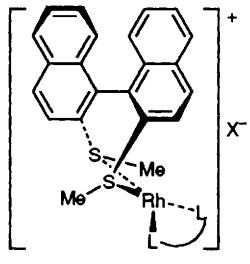
Surprisingly, complex **4** is an active catalyst also in the absence of additional phosphorus ligand. In this case, a small increase in e.e is observed, but this is contrasted by a decrease in regioselectivity (Table 1). To the best of our knowledge, this is the first time that the hydroformylation is catalysed by a complex which contains only sulfur derivatives as the heterodonor ligands.

This observation prompted us to exploit also the potential of the neutral ligand **2** which can be viewed as a sulfur-analogue of the well known binap. Reaction of **2** with $[Rh(cod)_2]^+X^-$ afforded the cationic complex $[Rh(cod)(Me_2binas)]^+X^-$ (**5a**, X = BF_4; **5b**, X = ClO_4) in good yield.§ This complex displayed a high catalytic activity in hydroformylation: styrene was quantitatively converted into 2- and 3-phenylpropanal in mild conditions (30 bars and 80 °C) with complete chemoselectivity.¶ At 80 °C, increase of pressure (80 bars) and



R = H binas **1**
R = Me Me_2binas **2**

L, L = cod **4**



X = BF_4 **5a**
X = ClO_4 **5b**

Table 1 Hydroformylation of styrene catalysed by rhodium complexes **4** and **5**[a]

Catalyst	*t*/°C	Conversion (%)	Branched (%)	e.e. (%)
4	80	77	56	11
4 + $2PPh_3$[b]	60	100	92	7
5	80	98	51	6
5 + **2** (3 equiv.)[c]	80	100	84	15
5 + **2** (3 equiv.)[c]	40	100	94	6
5 + **2** (3 equiv.)[c]	25	81	96	2

[a] *Reaction conditions*: Styrene (20 mmol) in tetrahydrofuran or toluene (7.5 ml); pressure 30 bar; CO:H_2 = 1; Rh:substrate = 1:400; *t* = 24 h. [b] *t* = 4 h. [c] Pressure = 80 bar.

† Presented in part at the 8th International Symposium of Homogeneous Catalysis, Amsterdam, August 1992.

‡ *Selected data* for **4**: ^{1}H NMR ($CDCl_3$) δ 7.96 (d, *J* 8.7 Hz, Ar, 2H), 7.80 (d, *J* 9.0 Hz, Ar, 2H), 7.71 (d, *J* 9.0 Hz, Ar, 2H), 7.26 (t, *J* 8.6 Hz, Ar, 2H), 7.01 (t, *J* 8.7 Hz, Ar, 2H), 6.52 (d, *J* 9.0 Hz, Ar, 2H), 4.42 (bs, 4H, CH), 4.09 (bs, 4H, CH), 2.21 (m, 8H, CH_2), 1.70 (m, 8H, CH_2); ^{13}C NMR ($CDCl_3$) δ 132.1, 128.0, 127.9, 126.0, 125.4, 124.3, 79.1 (CH), 79.0 (CH), 33.3 (CH_2), 29.1 (CH_2); *m/z* 738 (M^+), 629.9 (M-cod), 519.8 (M-2cod), 341.8; satisfactory elemental analyses were obtained. M_r 738 g mol^{-1} (found by osmometry: 784.2 g mol^{-1}, CH_2Cl_2 at 25 °C).

§ *Selected data* for **5b**: (94% yield); ^{1}H NMR ($CDCl_3$) δ 8.21 (d, *J* 9.0 Hz, Ar, 2H), 8.04 (d, *J* 8.2 Hz, Ar, 2H), 7.76 (d, *J* 8.5 Hz, Ar, 2H), 7.58 (t, *J* 7.6 Hz, Ar, 2H), 7.34 (t, *J* 8.2 Hz, Ar, 2H), 7.00 (d, *J* 9.0 Hz, Ar, 2H), 4.76 (bs, CH, 2H), 4.36 (bs, CH, 2H), 2.47 (bs, CH_2, 4H), 2.42 (s, Me, 6H), 2.10 (d, *J* 9.3 Hz, CH_2, 4H); ^{13}C NMR ($CDCl_3$) δ 134.4, 133.9, 132.6, 130.2, 129.7, 129.0, 127.0, 124.6, 82.0 (CH), 79.9 (CH), 34.2 (CH_2), 32.3 (Me); IR ν_{max} (KBr)/cm^{-1}: 1096s; 625m. Satisfactory elemental analyses were obtained.

¶ Reaction mixtures were analysed by gas chromatography. Enantiomeric excesses were determined on the alcohols obtained by $LiAlH_4$ reduction through GC analysis with 30 m cyclodex-β column (J & W Scientific). The prevailing enantiomer had always the (*S*) configuration.

addition of a threefold excess of ligand improved the amount of the branched aldehyde from 51 to 84%. An even higher proportion of this product (96%) could be obtained when the reaction was carried out at room temperature (Table 1). This value did not change upon increasing the excess of additional ligand (**2**: Rh = 15). This is one of the most favourable regioselectivities so far obtained in the hydroformylation of styrene with a rhodium catalyst containing a chiral ligand.[7]

Using (*R*)-Me_2binas as the ligand, the reaction leads to (*S*)-2-phenylpropanal in up to 15% e.e. Albeit low, this value is comparable with the enantioselectivities usually obtained in the rhodium-catalysed hydroformylation of styrene with chiral biphosphine ligands (maximum e.e. 30%[8]) and is the highest so far recorded with ligands containing donor atoms different from phosphorus.

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