

## Asymmetric Hydroformylation using Homogeneous and Polymer-bound Chiral Platinum Catalysts

Charles U. Pittman, Jr.,\* Yasuziro Kawabata, and Larry I. Flowers

Department of Chemistry, The University of Alabama, University, Alabama, U.S.A. 35486

The  $\text{PtCl}_2\text{-SnCl}_2$  complexes of the chiral ligands (4*R*, 5*R*)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolan [(–)-DIOP] and its bis(dibenzophosphole) analogue (–)-DBP-DIOP were employed as catalysts in homogeneous asymmetric hydroformylations of styrene, and high optical yields (*ca.* 94%) were obtained, the polymer-bound (–)-DIOP- $\text{PtCl}_2\text{-SnCl}_2$  giving optical yields of 25–30%; the rates, branched:normal isomer ratios, and optical yields were dependent on the gas pressure,  $\text{H}_2\text{:CO}$  ratio, and temperature.

Optical induction in asymmetric hydroformylation to date has resulted in only modest optical yields. The ligand (4*R*, 5*R*)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolan [(–)-DIOP]<sup>1</sup> and its dibenzophosphole analogue DBP-DIOP (**1**) have been well studied as ligands in rhodium-catalysed reactions. Optical yields in hydroformylations of styrene and its derivatives of *ca.* 40%,<sup>2</sup> and as high as 51% for vinyl acetate,<sup>3</sup> have been achieved using Rh-DBP-DIOP catalysts. Catalysts prepared from  $\text{PtCl}_2\text{-SnCl}_2$  and DIOP or DBP-DIOP gave moderate optical induction (22% for styrene at 100 °C) in preliminary studies.<sup>4,5</sup> Therefore, we prepared  $\text{PtCl}_2\text{-SnCl}_2\text{-(–)-DBP-DIOP}$  catalyst systems and found that under certain conditions they gave the highest optical yields ever reported for catalytic hydroformylations or, indeed, for any asymmetric catalytic carbon-carbon bond forming reaction (Table 1). For example, a 95% optical yield of (*S*)-(+)-2-

phenylpropanal was obtained at 50 °C in benzene using a  $\text{H}_2\text{:CO}$  ratio of 2.4:1 at 218 kg  $\text{cm}^{-2}$ .<sup>2</sup> These high optical yields were reproducible.

Optical rotations were measured in benzene using aldehyde samples purified by distillation and the aldehyde structures were confirmed by g.c.-m.s. and n.m.r. studies. 3-Phenylpropanal was produced and identified. The amount of each isomer was established by g.l.c. analysis for every sample used for optical rotation measurement. The optical rotation was linear with respect to 2-phenylpropanal concentration in the range 1.5–20 g in 100 ml of benzene. All optical yields were based on an absolute rotation  $[\alpha]_D^{25} + 238^\circ$ ,<sup>6</sup> rather than the often used value of  $[\alpha]_D^{25} + 160^\circ$ .<sup>4,7</sup>

Reaction with (–)-DIOP- $\text{PtCl}_2\text{-SnCl}_2$  (Table 2) showed that both optical yield and branched:normal (b:n) ratio increased with increased gas pressure. Higher  $\text{H}_2\text{:CO}$  ratios

Table 1. Asymmetric hydroformylation of styrene catalysed by<sup>a</sup> homogeneous (–)-DBP-DIOP- $\text{PtCl}_2$ .

Pressure/ $\text{kg cm}^{-2}$	$\text{H}_2\text{:CO}$	Time/h	Temp. $T/^\circ\text{C}$	Aldehyde <sup>b</sup> selectivity	b:n <sup>c</sup>	$[\alpha]^{21}$	Optical yield/% <sup>d</sup>
235	2.6	15	50	59	4.3	+216.7	91
125	1.3	20	50	78	3.6	+194.5	82
228	2.2	15	50	69	4.3	+224.6	94
218	2.4	36	40	70	4.1	+224.8	95
100	1.0	16	60	81	2.6	+161	68
90	1.0	13	60	78	2.5	+167	70

<sup>a</sup> Carried out in 50 ml glass-lined autoclaves (316 ss): preformed (–)-DBP-DIOP- $\text{PtCl}_2$ ,  $8 \times 10^{-6}$  mol; styrene, 1 ml; and benzene, 10 ml. Tin added as  $\text{SnCl}_2\cdot\text{H}_2\text{O}$ ,  $2 \times 10^{-5}$  mol. Styrene conversions >90% in each case. The amount of each isomer was determined by g.l.c. (SE 30 on AnaKrom, 110 → 200 °C at 8°  $\text{min}^{-1}$ ) with decane as the internal standard. <sup>b</sup> Aldehyde selectivity was based on amount of styrene reacted; ethylbenzene was also formed. <sup>c</sup> b:n is the branched:normal isomer ratio. <sup>d</sup> Specific rotation based on  $[\alpha]_D^{25} 238^\circ$ . <sup>e</sup> Results are reproducible to within  $\pm 1.5\%$ . Duplicate experiments were run for each entry.

**Table 2.** Asymmetric hydroformylation of styrene catalysed by homogeneous (–)-DIOP–PtCl<sub>2</sub>–SnCl<sub>2</sub>.<sup>a</sup>

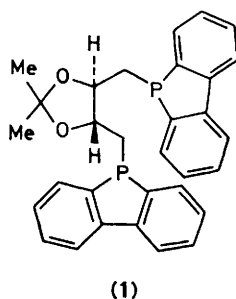
Pressure/ kg cm <sup>-2</sup>	H <sub>2</sub> :CO	Time/h	Temp. T/°C	Aldehyde selectivity/%	b:n	[α] <sub>D</sub> <sup>21</sup>	Optical <sup>b</sup> yield/%
93	1.0	10	50	90	0.30	+83.5	35
103	1.0	4	60	95	0.49	+83.8	35
48	1.0	4	80	86	0.68	+28	12
103	1.0	3	80	86	0.78	+63.3	27
169	1.1	3	80	84	0.85	+78.8	33
183	2.4	3.8	80	76	0.84	+85.3	36
103	2.3	3	80	74	0.95	+74.5	31
101	4	3	80	29	1.1	+70.6	30

<sup>a</sup> The conditions were the same as in Table 1 (footnote <sup>a</sup>) except that preformed (–)-DIOP–PtCl<sub>2</sub> was used. <sup>b</sup> Results of specific runs are given. They were reproduced to  $\pm 1.5\%$  in several cases.

**Table 3.** Asymmetric hydroformylation of styrene at 60 °C<sup>a</sup> catalysed by polymer-bound (–)-DIOP–PtCl<sub>2</sub>–SnCl<sub>2</sub>.

Reaction number	DIOP: Pt	SnCl <sub>2</sub> : Pt	Pressure/ kg cm <sup>-2</sup>	Time/h	Conversion/ %	Aldehyde selectivity/%	b:n	Optical yield/%
1	0.48	1.3	103	10	19	96	0.47	26
2	1.8	1.8	103	24	22	92	0.43	25
3	1.45	1.7	82	11	86	94	0.49	27
4	1	2.2	99	10	80	92	0.52	27
5	1	4.5	100	10	95	91	0.57	27
6	1	1.3	100	10	80	93	0.47	29
7	1	1.8	154	10	92	92	0.46	28
8	1	2.1	87	12	100	94	0.57	28
9	<sup>b</sup>		92	26	77	92	0.49	29
10	<sup>c</sup>		97	42	63	93	0.49	29

<sup>a</sup> Reactions 1–3 employed a styrene:Pt ratio of 1130, 1058, and 835:1 respectively. Reactions 4–10 employed styrene:Pt of 1058:1 with  $8 \times 10^{-6}$  mol of platinum. All other factors are the same as for Table 1. H<sub>2</sub>:CO = 1:1. <sup>b</sup> Resin was recycled from reaction 8. <sup>c</sup> Resin was recycled from reaction 9 with  $2.5 \times 10^{-2}$  mol of SnCl<sub>2</sub>·2H<sub>2</sub>O added.



gave larger b:n ratios and affected the optical yield. The best optical yields were obtained at a H<sub>2</sub>:CO ratio of 2.3:1. As expected, the optical yields increased as the temperature decreased. Changes in the concentrations of catalysts, styrene, or SnCl<sub>2</sub> induced only minor effects on the optical yields. Small changes in the (–)-DIOP:Pt ratio gave large rate changes and the maximum rate occurred at ratios of 1–1.5:1.

Previous attempts to use polymer-bound asymmetric rhodium complexes in hydroformylation have met with limited success.<sup>8</sup> We found that polymer-bound (–)-DIOP–Pt–Sn catalysts [polystyrene–divinylbenzene (1%), 10.5% ring substitution with (–)-DIOP] gave optical yields of 25–29% (Table 3). The maximum rates were obtained at DIOP:Pt of 1–1.5:1 as in the homogeneous reactions. Variation of the Sn:Pt ratio from 1.3 to 4.5:1 did not affect the optical purities, rates, or b:n ratios using the polymer-bound catalysts. Also, the optical purity was unchanged as the pressure was raised from 82 to 154 kg cm<sup>-2</sup> but the rate increased as the pressure increased. The polymer-bound catalysts could be recycled without changes in the optical purity of the products. However, rates decreased on recycling and no improvement could be achieved by subsequent addition of excess of SnCl<sub>2</sub>. Since

rates were so sensitive to variation of the (–)-DIOP:Pt ratio, the formation of phosphine oxide or metallic platinum could account for the rate decrease on recycling.

(–)-DBP–DIOP and (–)-DIOP led to aldehydes of opposite absolute configuration in styrene hydroformylations catalysed by rhodium. We found these ligands both give the same configuration, *S*, of 2-phenylpropanal in PtCl<sub>2</sub>–SnCl<sub>2</sub> catalysis. Kinetic studies showed styrene hydroformylation rates, using (–)-DIOP–PtCl<sub>2</sub>–SnCl<sub>2</sub> followed the expression: rate is proportional to [Pt]<sup>0.8</sup>[H<sub>2</sub>]<sup>1</sup>[CO]<sup>0</sup>[olefin]<sup>0.3</sup>. This low order in styrene and carbon monoxide pressure contrasts with that reported<sup>9</sup> for PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>–SnCl<sub>2</sub> (i.e.  $r \propto [\text{Pt}]^{1.5}[\text{olefin}]^1 p[\text{H}_2]^{1.5} p[\text{CO}]^{-0.5}$ ).

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