Hydroformylation of Vinylferrocene with Rhodium and Platinum Catalysts**

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Abstract: 2- and 3-ferrocenylpropionaldehydes (**2** and **3**) have been prepared by highly regioselective hydroformylation of vinylferrocene (**1**) using rhodium and platinum catalysts. In the asymmetric hydroformylation with a Rh/(R,R)-DIOP catalytic system a low enantiomeric excess has been achieved.

The synthesis of ferrocenyl aldehydes has been relatively little investigated; 2- and 3-ferrocenylpropionaldehydes (**2** and **3**) have been obtained from acetylferrocene and dimethylsulfonium methylide (8% yield) or iodoferrocene and allyl alcohol (40% yield), respectively[1,2]. The relatively easy availability of vinylferrocene (**1**)[3] prompted us to investigate the stability of the ferrocenyl group under hydroformylation conditions and the synthetic potential of hydroformylation as a synthetic tool in the field of ferrocenyl derivatives.

Scheme 1

$$\underset{\mathbf{1}}{\text{Fc–CH=CH}_2} \xrightarrow{\text{CO/H}_2(1:1)} \underset{\mathbf{2}}{\text{Fc–CH(CH}_3\text{)–CHO}} + \underset{\mathbf{3}}{\text{Fc–(CH}_2\text{)}_2\text{–CHO}} + \underset{\mathbf{4}}{\text{Fc–CH}_2\text{CH}_3}$$

Using $Rh_4(CO)_{12}$ as a catalyst precursor, vinylferrocene **1** was easily hydroformylated at 100 °C under a pressure of 80 bar of $CO/H_2(1:1)$. After 4.5 h an almost complete conversion has been observed with a very high selectivity ($\approx 100\%$) toward aldehydes (Table 1). The mixture of the reaction products has been analyzed and quantitatively determined as reported in Table 1 immediately after the evaporation of the solvent, using mesitylene as internal standard; the aldehydes **2** and **3** and ethylferrocene **4** have been identified by ^{1}H-NMR. The 2-ferrocenylpropionaldehyde largely prevails (80% of the aldehydic products) over the 3-ferrocenylpropionaldehyde; the observed regioselectivity is higher than that observed for styrene under similar conditions (2-phenylpropionaldehyde:3-phenylpropionaldehyde = 70:30).

This very promising result and particularly the large prevalence of the chiral **2** prompted us to continue our investigation using a Rh/(R,R)-DIOP catalytic system obtained from $Rh_4(CO)_{12}$ and (R,R)-DIOP and a Pt/(R,R)-DIOP system obtained

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from the precursor [PtCl($SnCl_3$){(*R*,*R*)-DIOP}]. In both cases a high conversion of the substrate has been obtained (Table 1). In the case of the rhodium catalyst the chemoselectivity and regioselectivity are not affected by the presence of DIOP [2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis (diphenylphosphino)butane]. In the case of the platinum catalyst the chemoselectivity is lower than in the case of the Rh/(*R*,*R*)-DIOP catalytic system and about 20% of the converted substrate is hydrogenated even if a low hydroformylation temperature (50 °C) has been used. Furthermore, as in the case of styrene hydroformylation[4], the extent of regioselectivity is about the same as with the rodium catalyst but in this case **3** prevails. The enantiomeric composition of **2** has been investigated by ^{1}H-NMR chiral shift technique using Eu(dcm)$_3$ [tris(dicampholylmethanato)-europium(III)] as chiral shift reagent. The determination of the optical purity has been carried out using the ^{1}H signal of the formyl group. The NMR analysis shows that the products obtained were racemic within the range of the experimental errors ($\leq$ 5%). This result is surprising in view of the mentioned similarities of the hydroformylation of styrene and **1** and of the fact that 2-phenylpropionaldehyde with an optical purity of 18.3% and 28.6% were obtained with styrene under the above hydroformylation conditions with the rhodium[5] and the platinum[6] catalytic systems, respectively. As in the asymmetric hydroformylation of olefins the enantiomeric excess increases operating at low temperature and atmospheric pressure[7], the hydroformylation of **1** was further investigated under mild conditions (1 bar CO/H_2(1:1), room temperature) using the [RhH(CO)(PPh_3)$_3$]/(*R*,*R*)-DIOP (1:4) catalytic system which was prepared «in situ». A conversion of 58% was obtained in 240 h and no hydrogenation product has been found in the reaction mixture. The ratio of the two isomeric aldehydes is 71:29, and the isomer **2** prevails. The enantiomeric excess of the chiral aldehyde determined by ^{1}H-NMR spectroscopy is 11.9%, the optical activity has negative sign. At higher substrate/Rh ratio the chiral aldehyde **2** was succesfully separated and $[\alpha]_D^{20} = -1.9°$ ($CHCl_3$, $c = 8$) has been measured. The determination of the absolute configuration of (−)-**2** is in progress. The very low enantiomeric excess (if any) obtained under the usual hydroformylation conditions with both Rh/DIOP and Pt/DIOP catalytic systems might be connected with a very rapid racemization of **2** during the reaction[8].

Table 1. Hydroformylation of **1** with different catalytic systems[a].

Catalytic system	Conversion[b] [%]	Reaction time [h]	Yield[c] [%] **2**	**3**	**4**
$Rh_4(CO)_{12}$	98	4.5	80	20	0
$Rh_4(CO)_{12}$ + 8 (*R*, *R*)-DIOP	100	[g]	80.5	19.5	0
HRh (CO) (PPh_3)$_3$ + 4 (*R*, *R*)-DIOP[d]	58	240	71[h]	29	0
HRh (CO) (PPh_3)$_3$ + 4 (*R*, *R*)-DIOP[d,e]	93	310	83[i]	17	0
PtCl ($SnCl_3$) { (*R*, *R*)-DIOP }[f]	100	[g]	17.5	64	18.5

[a] Reaction conditions (unless otherwise stated: $p_{CO} = p_{H_2} = 40$ bar; $T = 100$ °C; 30 mL hexane; Rh(Pt)/substrate = 1:40. [b] (mol reacted substrate)/(mol initial substrate) × 100. [c] (mol product)/(mol reacted substrate) × 100. [d] $p_{CO} = p_{H_2} = 0.5$ bar; room temperature; 30mL toluene. [e] Rh/substrate = 1:350. [f] 50 °C; 30 mL toluene. [g] Not determined. [h] *ee* = 11.9%. [i] $[\alpha]_D^{20} = -1.9°$ ($CHCl_3$, $c = 8$); *ee* = 7%.

Experimental

Carbon monoxide was prepared by decomposition of formic acid; its purity was higher than 99.5% by GC analysis. Hydrogen was a product of Sauerstoff- und Wasserstoffwerke AG, Luzern, with a purity $\geq$ 99.5%. Hexane and toluene (Fluka products) were purified through distillation over Na-K-alloy under nitrogen. [HRh(CO)(PPh_3)$_3$] and $SnCl_2$ were Fluka products (purum) and were used without further purification. (*R*,*R*)-DIOP[9] and [PtCl($SnCl_3$){(*R*,*R*)-DIOP}][10] were prepared according to known literature methods.

The NMR analyses were recorded on a Bruker AM 300 WB spectrometer using tetramethylsilane as the internal standard. The conversion was determined using mesitylene as the internal standard compared its CH singlet ($\delta = 6.8$) with the CH_3 doublet (1.29) of **2**, the (CH_2)$_2$ signal (2.68) of **3**, and CH_3 triplet (1.16) of **4**.

In a typical experiment the solution of 4.7 mg (0.00625 mmol) $Rh_4(CO)_{12}$ – or 23.8 mg (0.025 mmol) [PtCl($SnCl_3$){(*R*,*R*)-DIOP}] – and 212 mg (1 mmol) **1** in 30 mL hexane (toluene) was transferred under nitrogen into a 150 mL stainless steel autoclave. The autoclave was pressurized to 80 bar total pressure ($CO:H_2 = 1:1$) and put into an oil bath with continual agitation by an arm shaker. After the reaction it was cooled to room temperature and vented, then the solution was removed. The solvent was evaporated at room temperature and the residue immediately analyzed by ^{1}H-NMR spectroscopy.

The atmospheric hydroformylation was carried out in a reaction vessel connected to a gas-burette containing $CO:H_2 = 1:1$ mixture. The progress of the reaction was followed by measuring the gas consumption. Removal of the solvent gave the mixture of ferrocenyl aldehydes, the components of which were separated under nitrogen by chromatography on silica gel with benzene as eluent.

Analytical data of the reaction products: For **2**: IR (in hexane): 1725 cm^{-1}; ^{1}H-NMR (in $CDCl_3$): 9.65 (d, 1 H, CHO, $J = 2.0$ Hz), 4.0–4.15 (m, 9 H, Fc), 3.18 (dq, 1 H, CH, $J_1 = 2.0$ Hz, $J_2 = 6.7$ Hz), 1.29 (d, 3 H, CH_3, $J = 6.7$ Hz). – For **3**: IR (in hexane): 1725 cm^{-1}; ^{1}H-NMR (in $CDCl_3$): 9.74 (s, 1 H, CHO), 4.0–4.15 (m, 9 H, Fc), 2.6 (s, 4 H, (CH_2)$_2$). – For **4**: ^{1}H-NMR (in $CDCl_3$): 4.0–4.15 (m, 9 H, Fc), 2.34 (q, 2 H, CH_2, $J = 7.6$ Hz), 1.16 (t, 3 H, CH_3, $J = 7.6$ Hz).

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[1] J. P. Sevenair, D. H. Lewis, B. W. Ponder, *J. Org. Chem. 37* (1972) 4061.

[2] A. Kasahara, T. Izumi, M. Maemura, *Bull. Chem. Soc. Jpn. 50* (1977) 1021.

[3] B. Floris, G. Illuminati, *J. Organomet. Chem. 168* (1979) 203.

[4] G. Consiglio, F. Morandini, M. Scalone, P. Pino, *J. Organomet. Chem. 279* (1985) 193.

[5] T. Hayashi, M. Tanaka, Y. Ikeda, I. Ogata, *Bull. Chem. Soc. Jpn. 52* (1979) 2605.

[6] G. Consiglio, P. Pino, *Top. Curr. Chem. 105* (1982) 77.

[7] C. Salomon, G. Consiglio, C. Botteghi, P. Pino, *Chimia 27* (1973) 215.

[8] A. McKenzie, E. M. Luis, A. G. Mitchell, *Ber. Dtsch. Chem. Ges. 65* (1932) 798.

[9] B. A. Murrer, J. M. Brown, P. A. Chaloner, P. N. Nicholson, D. Parker, *Synthesis* (1979) 350.

[10] P. Haelg, G. Consiglio, P. Pino, *J. Organomet. Chem. 296* (1985) 281.