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Highly selective hydroformylation and dimerization reactions of 2-ferrocenylpropene

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Abstract

Selective dimerization and hydroformylation of 2-ferrocenylpropene has been shown to take place in the presence of platinum- and rhodium-catalysts, respectively. The cyclic dimerization proceeds selectively by a homoannular pathway. The hydroformylation gives the less-branched formyl isomer with more than 90% regioselectivity. Some optical induction is observed in both reactions.

Introduction

The importance of hydroformylation has given rise to many studies, aimed at extending the range of applicability and elucidating the mechanism [1]. In particular, a large number of simple and functionalized olefins have been investigated in the last few decades with the objective of obtaining compounds of practical interest [2]. A large variety of formyl derivatives have been used as important synthetic tools and so, it is surprising that there is only a single report of hydroformylation of unsaturated ferrocenyl derivatives [3]. Vinylferrocene showed high selectivity towards the formation of the branched aldehyde and the potential for asymmetric induction. To increase understanding of the role of structural factors, it seemed appropriate to investigate use of a substituted vinylferrocene and we report here results obtained with 2-ferrocenylpropene under hydroformylation conditions.

Results and discussion

2-Ferrocenylpropene (**1**) reacted with CO/H_2 (1:1) at 100°C, under a pressure of 80–160 bar, in the presence as *in situ* catalysts of either rhodium containing

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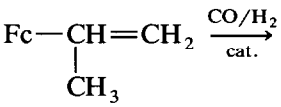
Table 1

Hydroformylation of 2-ferrocenylpropene (1) with rhodium–phosphine catalysts [a]

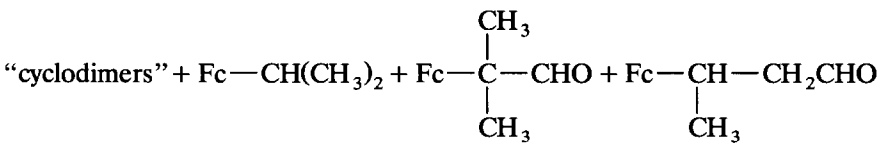
Catalyst	Temperature (°C)	p (bar)	Run time (h)	Conversion (%)	Product distribution [b]			
					2 [c]	3	4	5 [d]
$[Rh(nbd)Cl]_2 + 4PPh_3$	100	80	9	16	< 1	27	7	66
$[Rh(nbd)Cl]_2 + 4PPh_3$	100	160	7	82	< 1	32	6	62
$[Rh(nbd)Cl]_2$ + (−)-DIOP [g]	100	150	22	84	< 1	26	4	70 [e]
$[Rh(nbd)Cl]_2$ + (−)-CHIRAPH.	100	140	22	33	0	8	9	83
$[Rh(nbd)Cl]_2$ + (−)-CHIRAPH.	20	80	500	18	0	3	21	76 [f]

[a] Reaction conditions: 0.05 mmol of catalyst; 1 mmol of substrate; 20 ml of toluene; $p(CO) = p(H_2)$. [b] Determined by GC and ^1H NMR. [c] 2-*exo* + 2-*endo*. [d] e.e.s where determined by ^1H NMR using $Eu(dcm)_3$ and $Eu(hfc)_3$ [for CH_3 dublet: $\Delta\delta = 1.55$ ppm; $\Delta\Delta\delta = 0.01$ ppm; for CHO proton: $\Delta\delta = 5\,3$ ppm; $\Delta\Delta\delta = 0\,04$ ppm; $n(Eu)/n(substr.) = 0.55$) chiral shift reagents. [e] e.e. = 4% ($[\alpha]_{546}^{20} + 2.4$ (2.5, toluene). [f] e.e. < 2%. [g] For abbreviations see text.

precursor and a phosphine (Table 1) or platinum-containing precursor and tin(II) chloride (Table 2), as indicated in eq. 1.



(1)



(2) (3) (4) (5) (1)

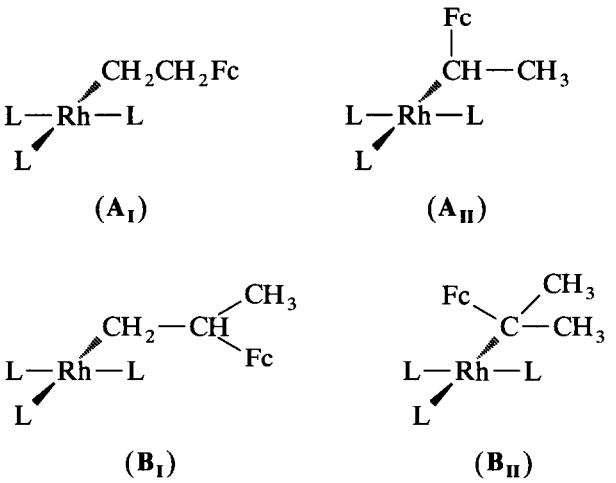
The two catalytic systems yielded strikingly different product distributions. Hydroformylation, accompained by hydrogenation, was the main process in the presence of rhodium-based catalysts, whereas the reaction was almost completely diverted toward dimerization in the presence of Pt^{II}/Sn^{II} systems.

Table 2

Reactions of 1 in the presence of platinum catalysts [a]

Catalyst	Temperature (°C)	p (bar)	Run time (h)	Conversion (%)	Product distribution [b]			
					2 [c]	3	4	5
$PtCl_2(BDPP) + 2SnCl_2$	60	80	20	100	98 [d]	2	< 0.5	< 0.5
$PtCl_2(BDPP)$ [e] $+ 2SnCl_2$	100	80	10	99	95	4	< 0.5	1
$SnCl_2$	100	90	10	96	100	0	0	0

[a] Reaction conditions: 0.5 mmol of catalyst; 1 mmol of substrate; 20 ml of toluene; $p(CO) = p(H_2)$. [b] Determined by GC and ^1H NMR. [c] 2-*exo* + 2-*endo*. [d] e.e. < 3% of 2-*exo* (determined by H NMR using $Eu(dcm)_3$ chiral shift reagent; $[\alpha]_{546}^{20} + 22.2$ (0 7, toluene)). [e] BDPP = = (2*S*, 4*S*)-bis(diphenylphosphino)pentane.



Scheme 1.

In the reaction catalyzed by the rhodium-phosphine catalyst (Table 1), the presence of an extra methyl group in the vinylferrocene system greatly changed the chemo- and regio-selectivity of the reaction. Thus 2-ferrocenylpropene underwent appreciable hydrogenation, depending on the diphosphine used in the catalyst, but no ethylferrocene was obtained from vinylferrocene [3]. Moreover, the regioselectivity was inverted, the terminal aldehyde from 2-ferrocenylpropene being greatly favoured, whereas the branched aldehyde was the main product of hydroformylation of vinylferrocene.

It is likely that a steric effect due to the methyl group in the α-position of vinylferrocene is responsible for the change in chemo-selectivity and in regio-selectivity. If we compare the structures of possible alkyl-intermediates (Scheme 1) from vinylferrocene (**A**) and 2-ferrocenylpropene (**B**), it is apparent that steric hindrance in **B** makes $\mathbf{B_I}$ favoured over $\mathbf{B_{II}}$. It is noteworthy that the preference of vinylferrocene toward the branched aldehyde is in contrast to the general behaviour of olefins with rhodium catalysts [1] and this may be attributed to the strong electron-donor ability of the ferrocenyl moiety [4]. It is known that electron-releasing substituents conjugated with the double bond favour the formyl-attack on the carbon atom α to the donor group [5].

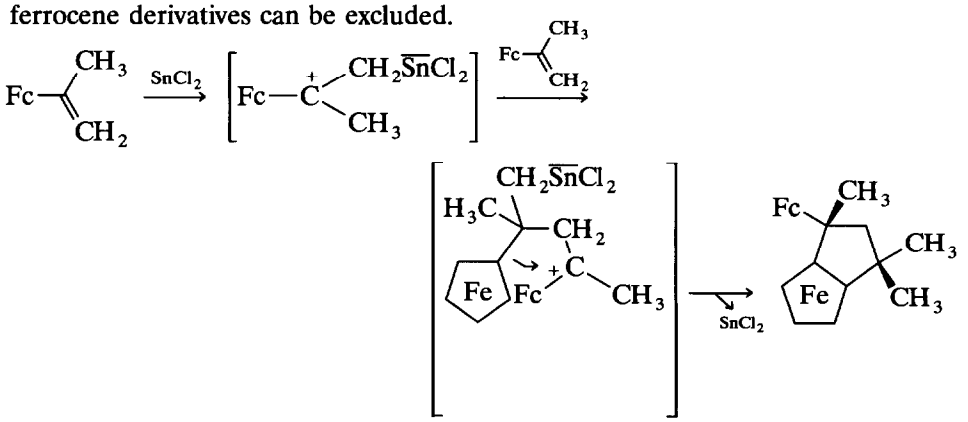
In the presence of rhodium-phosphine catalysts, the "linear" aldehyde (3-ferrocenylbutanal, **5**) was formed from 2-ferrocenylpropene (**1**) with moderate to excellent regioselectivity (Table 1). When a monodentate phosphine (PPh_3) was used, the regio-selectivity toward the less branched aldehyde was approximately 10:1. There was a sharp difference between chelating diphosphines, DIOP ((2*R*, 3*R*)-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane) and CHIRAPHOS ((2*S*, 3*S*)-bis(diphenylphosphino)butane). While the rhodium-DIOP system (7-membered chelate ring) showed excellent activity and regioselectivity, the CHIRAPHOS-containing catalyst (5-membered chelate ring) was less active and formation of the branched aldehyde **4** became more favoured, although **5** still predominated. The change in regio-selectivity is comparable with those reported

for styrene and 2-phenylpropene. The effects of different phosphine ligands in rhodium-catalyzed hydroformylation of **1** find a parallel in the results reported for the aforementioned olefins [6]. The favoured regio-selectivity was especially dominant at low temperature. The same phenomenon was observed in the hydroformylation of vinyl-aromatics [7].

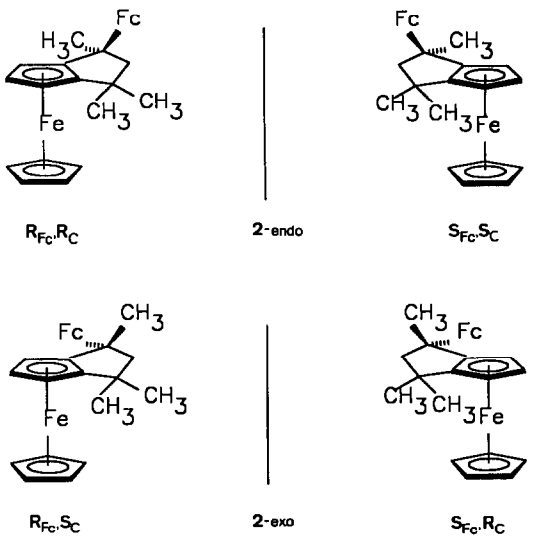
Surprisingly, very poor optical yields were obtained when chiral diphosphines were used. The e.es were $< 3\%$; they were checked by the NMR chiral shift technique using both $Eu(dcm)_3$ and $Eu(tfc)_3$ (see footnotes to Table 1). In the case of α-arylpropanals, with the formyl group attached directly to the asymmetric centre, the low optical induction was attributed to extensive racemization, especially at high temperature [8]. Racemization should be much less important with β-arylbutanals. A possible explanation for the low asymmetric induction may be found in steric hindrance; *e.g.*, between the phenyl-rings of the PPh_2 groups and the ferrocenyl-moiety. The bulk of the ferrocenyl-group might inhibit the selective formation of one of the diastereomeric transition states as a result of phenyl–ferrocenyl interaction.

The hydroformylation is practically always accompanied by competitive hydrogenation of the substrate. The chemo-selectivity of hydroformylation also depends on the type of the disphosphine used in the catalyst (Table 1).

A dimeric compound, **2** (found in traces (less than 1% by GLC) in the rhodium-catalyzed hydroformylation), was the main product obtained from 2-ferrocenylpropene in the presence of platinum-bisphosphine-tin(II) chloride catalysts. Two isomeric compounds (*exo* and *endo*) of homoannular cyclization were formed in an approximately 1 : 1 ratio, and were isolated by column chromatography. The structures were determined by NMR spectroscopy (^1H and ^{13}C NMR, ^1H-^1H-COSY, ^1H-^{13}C-HETCOR). The large difference between the chemical shifts of the methyl and methylene protons in **2**-*exo* and **2**-*endo* due to anisotropy of the ferrocenyl-moiety (shielding effect of iron) makes possible the identification of *exo* and *endo* isomers. The shielding effect of iron results in an upfield shift of the signals from the relevant protons. Structure **2** has been proposed for the minor product of acid-catalyzed dimerization of **1** [9–11]. The authors suggested that the heteroannular pathway is the more favoured in the cyclization of the dimeric carbonium ion. Our detailed NMR studies show that the presence of *ansa*-type ferrocene derivatives can be excluded.



Scheme 2



Scheme 3.

A possible route to the ring-closure product involves a simple dimerization followed by an alkylation at the adjacent position. The cyclization takes place even in the presence of tin(II) chloride alone, and may be attributed to the formation of a stable α-ferrocenyl carbocation [12] as a consequence of the interaction between the olefin and the Lewis acid $SnCl_2$ (Scheme 2). Nevertheless, the chiral platinum complex must play a role, since higher conversion and stereoselective dimerization were obtained. In fact, in the presence of optically active platinum catalysts some optical induction was detected (see footnotes to Table 2), related to the planar and central elements of chirality in the dimeric **2-*exo*** and **2-*endo*** (Scheme 3).

In conclusion, steric effects play a major role in the reaction of 2-ferrocenylpropene under "oxo"-conditions, determining the chemo-selectivity (the extent of hydrogenation) and the regio-selectivity (predominance of the less branched aldehyde). The high stability of the α-ferrocenyl-α-methyl carbocation is the driving force for the dimerization of the substrate in the presence of Lewis acids.

Experimental

Reagents

The catalytic precursors $[Rh(nbd)Cl]_2$ and $PtCl_2(BDPP)$ were prepared as described previously [13,14]. Toluene was distilled under argon from sodium in the presence of benzophenone. 2-Ferrocenylpropene was obtained by heating 2-ferrocenyl-2-propanol over neutral alumina and purified by column chromatography on silica gel with hexane as eluent [15].

The ^1H and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions containing TMS as internal standard on a Varian Unity 300 spectrometer. The samples were analyzed with a Hewlett Packard 5830A gas chromatograph fitted with an SPB-1 column. The MS spectra were recorded on a Hewlett Packard 5971A GC-MSD instrument. The optical rotation of the products was determined for $CHCl_3$ solutions with a Polamat A (Carl Zeiss Jena) automatic polarimeter.

Hydroformylation experiments

In a typical experiment a solution of 226 mg (1 mmol) of 2-ferrocenylpropene in 20 ml of toluene was transferred under argon into a 100 ml stainless steel autoclave containing 5.8 mg of $[Rh(nbd)Cl]_2$ and 0.0125 mmol of diphosphine. The autoclave was pressurized to the chosen pressure with a CO/H_2 (1:1) mixture, placed in a thermostated electric oven, and agitated with an arm shaker. After cooling and venting of the autoclave, the solution was analyzed by GLC and then evaporated to leave an oily residue. This was subjected to column chromatography on silica gel with hexane and hexane/benzene (1:1) as eluents. The hydroformylation product was isolated in 40–45% yield. (In the chromatography of the mixtures containing the dimeric compounds as major components, benzene was used after the elution of formylation and hydrogenation products.)

Characterization of the products

Spectroscopic data for **2**-*endo*: ^1H NMR ($CDCl_3$): δ 4.25 (s, 5H, unsubstituted Cp-ring); 4.13 (s, 5H, unsubstituted Cp-ring); 4.05 (m, 2H, Cp); 4.03 (m, 1H, Cp); 3.88 (m, 2H, Cp); 3.86 (m, 1H, Cp); 3.38 (m, 1H, Cp); 2.49 (d, 14 Hz, 1H, CH_aH_b); 1.93 (d, 14 Hz, 1H, CH_aH_b); 1.9 (s, 3H, CH_3); 1.36 (s, 3H, CH_3); 0.86 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 67.9 (Cp); 67.3 (Cp); 66.6; 66.3; 65.0; 56.6 (CH_2); 58.3; 57.0; 39.7 (C); 36.3 (C); 31.4 (CH_3); 30.8 (CH_3); 28.9 (CH_3); MS (*m/z* rel. int.): 452/1000 (M^+); 437/200 ($M^+ - CH_3$).

Spectroscopic data for **2**-*exo*: ^1H NMR ($CDCl_3$): δ 4.2 (m, 2H, Cp); 4.16 (s, 5H, unsubstituted Cp-ring); 4.13 (m, 2H, Cp); 3.9 (s, 5H, unsubstituted Cp-ring); 3.95 (m, 1H, Cp); 3.79 (m, 1H, Cp); 3.6 (m, 1H, Cp); 2.8 (d, 14 Hz, 1H, CH_aH_b); 2.07 (d, 14 Hz, 1H, CH_aH_b); 1.6 (s, 3H, CH_3); 1.50 (s, 3H, CH_3); 1.24 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 67.6 (Cp); 67.2 (Cp); 65.3; 65.2; 64.4; 62.6 (CH_2); 56.7; 56.5; 39.3 (C); 35.9 (C); 31.0 (CH_3); 30.9 (CH_3); 30.5 (CH_3).

Spectroscopic data for **3**: ^1H NMR ($CDCl_3$): δ 4.2 (s, 5H, Cp); 4.1 (brs, 4H, Cp); 2.55 (h, 7 Hz, 1H, $CH(CH_3)_2$); 1.15 (d, 7 Hz, 6H, $CH(CH_3)_2$).

Spectroscopic data for **4**: ^1H NMR ($CDCl_3$): δ 9.6 (s, 1H, CHO); 4.17 (s, 5H, Cp); 4.2 (m, 2H, Cp); 4.1 (m, 2H, Cp); 1.35 (s, 6H, $C(CH_3)_2$; MS (*m/z* rel. int.): 256/1000 (M^+); 227/730 ($M^+ - CHO$); 212/200 ($M^+ - CHO - CH_3$).

Spectroscopic data for **5**: ^1H NMR ($CDCl_3$): δ 9.8 (dd, 1.6 Hz, 2.2 Hz, 1H, CHO); 4.15 (s, 5H, Cp); 4.1 (m, 2H, Cp); 4.05 (m, 2H, Cp); 3.14 (ddq, 6.6 Hz, 5.5 Hz, 8 Hz, 1H, $CHCH_aH_b$); 2.69 (ddd, 1.6 Hz, 5.5 Hz, 16.0 Hz, 1H, CH_aH_b); 2.51 (ddd, 2.2 Hz, 8 Hz, 16.0 Hz, 1H, CH_aH_b). ^{13}C NMR ($CDCl_3$): δ 201.0 (CO); 67.4 (unsubstituted Cp-ring); 66.3; 66.2; 65.6; 64.9; 51.4 (CH); 26.9 (CH_2) 20.0 (CH_3). IR: ν(CO) 1714 cm^{-1} MS (*m/z* rel. int.): 256/1000 (M^+); 213/600 ($M^+ - CH_2CHO$).

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