Asymmetric hydroformylation of vinyl arenes catalyzed by furanoside diphosphinites-Rh(I) complexes

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Abstract

Diphosphinite ligands **2** and **3**, easily prepared from inexpensive D(+)-xylose in few steps, were tested in the Rh-catalyzed asymmetric hydroformylation of several vinyl arenes. High regio-selectivities in branched aldehyde (up to 99%) and moderate enantio-selectivity (up to 63%) were found (20–40 °C, 30–60 bar of syn gas). For the first time, the structure in solution of the species formed under hydroformylation conditions with diphosphinite ligands was determined.

Keywords: Furanoside ligands; Diphosphinite ligands; Asymmetric hydroformylation

1. Introduction

The metal-catalysed asymmetric hydroformylation of alkenes has attracted much attention as a potential tool for preparing enantiomerically pure aldehydes [1], which are important precursors for synthesizing biologically active compounds, biodegradable polymers and liquid crystals [1c]. Since the early 1970s, transition metal complexes based on rhodium and platinum have been used as catalysts in asymmetric hydroformylation. High enantio-selectivities have been obtained with Pt/diphosphine catalysts, but these suffer from low chemo- and low regio-selectivity [2]. In general, Rh/diphosphine catalysts have high catalytic activities and regio-selectivities in branched aldehydes, but the ee's do not exceed 60% [3]. In the last 10 years, two new types of ligands – diphosphite [4] and phosphine-phosphite [5] ligands – have emerged as suitable ligands for asymmetric hydroformylation, overcoming the limitations of the phosphine-based catalytic systems [6]. Most of the research published in the last decade has been dedicated to diphosphite ligands and less work has been done with diphosphinite ligands [4a,7].

Some of the best results with diphosphinite ligands have been obtained using a family of pyranoside diphosphinite ligands **1** described by RajanBabu and Ayers (Scheme 1) [7a–c]. Their Rh-hydroformylation results showed that there was a major electronic effect with these systems and a remarkable substrate effect on enantio-selectivity. Therefore, only the diphosphinite ligand **1a**, containing electron-withdrawing (3,5-CF_3)-C_6H_3 groups, provides good enantio-selectivities (Scheme 1) for 2-vinyl naphthalene and 6-methoxy-2-vinyl naphthalene as substrates. However, the difficult preparation of the ligand **1a** and the required high pressures (up to 108 bar) limit their application. On the other hand, ligand **1b** with commercially available diphenyl–phosphinite moieties provides only 8% ee. Hence, more research is needed to be done to study the scope that diphosphinite offer as a new class of ligand for this process.

Following our interest in carbohydrates as an inexpensive and highly modular chiral sources for preparing ligands, and

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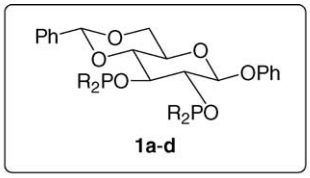

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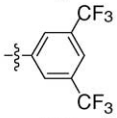
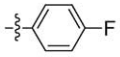
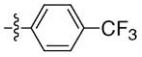
R =				
% ee	70%	8%	5%	15%
% regio	95%	94%	95%	95%

Scheme 1. Rh-catalyzed asymmetric hydroformylation of 6-methoxy-2-vinyl naphthalene using RajanBaBu ligands at 108 bar and room temperature.

encouraged by the excellent combination of regio- and enantio-selectivities obtained with diphosphite ligands with furanoside backbone in the asymmetric hydroformylation of olefins [4][4c-f], we report here the use of furanoside diphosphinite ligands **2** and **3** (Fig. 1) in the asymmetric Rh-catalysed hydroformylation of several vinyl arenes. We also discuss for the first time the structures in solution of the important intermediate species $[HRh(P–P)(CO)_2]$ formed under hydroformylation conditions using diphosphinite ligands.

2. Experimental

All experiments were carried out under argon atmosphere. All the solvents were dried using standard methods and distilled prior to use. Compounds **2–3** were prepared as previously described [11]. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer. Chemical shifts are relative to $SiMe_4$ (^1H) as internal standard or H_3PO_4 (^{31}P) as external standard. Gas chromatographic analyses were run on a Hewlett-Packard HP 5890A instrument (split/splitless injector, J&W Scientific, Ultra-225 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas: 150 kPa He, F.I.D. detector) equipped with a Hewlett-Packard HP 3396 series II integrator. Hydroformylation reactions were carried out in a home-made 100 mL stainless steel autoclave [12]. Enantiomeric excesses were measured after the aldehydes had been oxidised to their corresponding carboxylic acids [13] with a Hewlett-Packard HP 5890A gas chromatograph (split/splitless injector, J&W Scientific, FS-Cyclodex β-I/P 50 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas: 100 kPa He, F.I.D. detector).

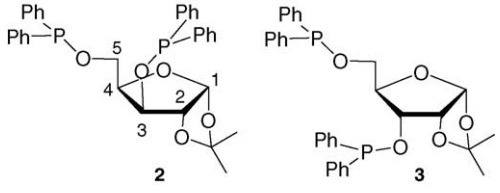


Fig. 1. Diphosphinite ligands **2** and **3**.

2.1. Hydroformylation of styrene

In a typical experiment, the autoclave was purged three times with CO. The solution was formed from $[Rh(acac)(CO)_2]$ (0.013 mmol), diphosphinite (0.014 mmol) and the corresponding substrate (9.1 mmol) in toluene (15 mL). The autoclave was then pressurized with *syn* gas and heated to the reaction temperature, and the reaction mixture was stirred. During the reaction, several samples were taken out of the autoclave. After the desired reaction time, the autoclave was cooled to room temperature and depressurized. The reaction mixture was analyzed by gas chromatography.

2.2. In situ HP-NMR hydroformylation experiments

In a typical experiment, a sapphire tube (ϕ = 10 mm) was filled under argon with a solution of $[Rh(acac)(CO)_2]$ (0.030 mmol) and ligand (molar ratio PP/Rh = 1.1) in toluene-d8 (1.5 mL). The HP-NMR tube was purged twice with CO and pressurized to the appropriate pressure of CO/H_2. After a reaction time of 1 h shaking at the desired temperature, the solution was analyzed.

2.3. High-pressure IR experiments

These experiments were performed in an SS 31,650 mL autoclave equipped with IRTRAN windows (ZnS, transparent up to 70 cm^{-1}, 10 mm i.d. optical path length 0.4 mm), a mechanical stirrer, a temperature controller, and a pressure device. In a typical experiment, a degassed solution of $[Rh(acac)(CO)_2]$ (0.013 mmol) and diphosphinite ligand (0.014 mmol) in methyltetrahydrofuran (15 mL) was introduced into the high-pressure IR autoclave. The autoclave was purged twice with CO, pressurized to 30 bar of CO/H_2 and heated to 40 °C. The autoclave was placed in the IR spectrometer and the spectra were recorded.

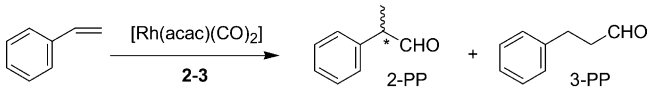
3. Results and discussion

3.1. Asymmetric hydroformylation of vinyl arenes

Diphosphinites **2–3**, derived from D-xylose, were tested in the rhodium-catalysed asymmetric hydroformylation of several vinyl arenes under several reaction conditions. In a first set of experiments, we used ligands **2–3** in the rhodium-catalysed asymmetric hydroformylation of styrene, which is widely used as a model substrate.

The catalysts were prepared in situ by adding the corresponding diphosphinite ligand to $[Rh(acac)(CO)_2]$ as a catalyst precursor. The conversion and selectivity results are

Table 1
Asymmetric hydroformylation of styrene catalysed by [Rh(acac)(CO)$_2$]/diphosphinite **2–3**[a]



Entry	Ligand	P (bar)	CO/H$_2$[b]	TOF[c]	%Conv (h)[d]	%2-PP[e]	%ee[f]
1	**2**	10	1	15	39 (24)	68	2 (R)
2	**2**	30	1	77	85 (8)	90	3 (R)
	2	60	1	434[g]	62 (1)	90	3 (R)
4[h]	**2**	30	1	78	86 (8)	90	3 (R)
5[i]	**2**	30	1	78	86 (8)	91	3 (R)
6	**2**	30	0.5	90	84 (5)	90	4 (R)
7[j]	**2**	30	0.5	30	73 (24)	90	5 (R)
8[k]	**2**	30	0.5	16	24 (8)	90	3 (R)
9[l]	**2**	30	0.5	18	54 (24)	90	8 (R)
10	**3**	30	0.5	67	85 (8)	90	10 (R)

[a] Reaction conditions: $T = 40$ °C, styrene (9.1 mmol), Rh(acac)(CO)$_2$ (0.013 mmol), ligand/Rh = 1.1, toluene (15 mL).
[b] pCO/pH$_2$ ratio.
[c] TOF in mol styrene × mol Rh^{-1} × h^{-1} determined after 5 h reaction time by GC.
[d] % Conversion of styrene.
[e] Regio-selectivity in 2-phenylpropanal.
[f] % Enantiomeric excess measured by GC.
[g] TOF measured after 1 h.
[h] Ligand/Rh = 2.
[i] Ligand/Rh = 4.
[j] THF as solvent.
[k] Et$_3$SiH as solvent.
[l] $T = 20$ °C.

summarized in Table 1. Hydrogenated or polymerized products of styrene were not observed.

The effects of several reaction parameters (i.e., CO/H$_2$ pressure, ligand-to-rhodium ratio, CO/H$_2$ pressure ratio, solvents and temperature) were investigated for the catalytic precursor containing ligand **2**.

Activity and selectivity to the branched aldehyde improved when the pressure was raised from 10 to 30 bar, while the enantio-selectivity remained the same (entry 1 versus 2). However, further increasing the *syn* gas pressure had a positive effect on the activity, while the regio- and enantio-selectivity were unaffected (entry 3).

Varying the ligand-to-rhodium ratio showed that this catalyst system is highly stable under hydroformylation conditions and no excess of ligand is needed (entries 2, 4 and 5). After identical catalyst preparation, we carried out a hydroformylation experiment under a lower CO/H$_2$ pressure ratio (entry 6). Our results clearly show that higher partial pressures of H$_2$ lead to higher initial turnover frequencies. Moreover, if we compare entries 2 and 6, we can see that both regio- and enantio-selectivity are hardly affected by changes in the H$_2$ partial pressure.

The type of solvent was important for the activity of the process but had little effect on regio- or enantio-selectivity (entries 7 and 8 versus 6). This contradicts with the results of RajanBabu and Ayers for the asymmetric hydroformylation of vinylarenes using diphosphinite ligands. These authors found a notable positive effect on enantio-selectivity when Et$_3$SiH was used as a solvent [7a–c]. Lowering the temperature to 20 °C led to an increase in enantio-selectivity (up to 8%) (entry 6 versus 9).

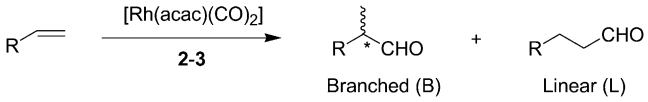
The use of ligand **3**, whose configuration of carbon atom C-3 is opposite, led to lower activity and slightly higher enantio-selectivity than catalyst system Rh/**2** (entry 6 versus 10). In both cases, the major enantiomer of the product was the same. This behaviour contrasts with that of related diphosphite ligands, for which the absolute configuration of the stereogenic carbon atom C-3 controlled the configuration of the hydroformylation product [4f].

We then applied these diphosphinite ligands **2** and **3** in the Rh-catalyzed asymmetric hydroformylation of other vinyl arenes (Table 2).

The presence of a fluoro substituent in the *para* position of the substrate hardly affected conversion, regio- and enantio-selectivity (Table 2 entries 1 and 7 versus 2 and 8). However, the presence of *para*-methoxy- (entries 3 and 9) and naphthyl (entries 4, 5, 10 and 11) substituents of the substrate had a clear positive effect on enantio-selectivities (up to 55%). In the hydroformylation of substrates 2-vinylnaphthalene and 6-methoxy-2-vinylnaphthalene, the positive effect was also in the regio-selectivity of the process (up to 99%).

Again, the use of ligand **3** hardly affected the conversion, regio- and enantio-selectivity of the process (entries 1–5 versus 7–11).

Table 2
Asymmetric hydroformylation of vinyl arenes catalysed by [Rh(acac)(CO)$_2$]/diphosphinite **2**–**3**[a]



Entry	Ligand	R	TOF[b]	%Conv (h)[c]	%Regio[d]	%ee[e]
1	**2**	C_6H_5	90	84 (5)	90	4 (R)
2	**2**	4-F-C_6H_4	78	100 (8)	92	2 (R)
3	**2**	4-OMe-C_6H_4	49	55 (8)	90	55 (S)
4	**2**	2-Naphthyl	67	48 (5)	97	53 (S)
5	**2**	6-OMe-2-Naphthyl	27	29 (8)	99	53 (+)
6[f]	**2**	2-Naphthyl	8.6	22 (18)	97	59 (S)
7	**3**	C_6H_5	67	85 (8)	90	10 (R)
8	**3**	4-F-C_6H_4	79	100 (8)	91	4 (R)
9	**3**	4-OMe-C_6H_4	56	56 (8)	90	54 (S)
10	**3**	2-Naphthyl	71	51 (5)	97	53 (S)
11	**3**	6-OMe-2-Naphthyl	28	31 (8)	99	53 (+)
12[g]	**2**	4-OMe-C_6H_4	118	42 (2.5)	95	57 (S)
13[g]	**2**	2-Naphthyl	274	98 (2.5)	99	58 (S)
14[g]	**2**	6-OMe-2-Naphthyl	154	55 (2.5)	99	59 (+)
15[f,g]	**2**	2-Naphthyl	91	32 (2.5)	99	63 (S)

[a] Reaction conditions: $T = 40$ °C, $P = 30$ bar, substrate (9.1 mmol), Rh(acac)(CO)$_2$ (0.013 mmol), ligand/Rh = 1.1, toluene (15 mL), $pCO/pH_2 = 0.5$.
[b] TOF in mol substrate × mol Rh^{-1} × h^{-1} determined after 5 h reaction time by GC.
[c] % Conversion of substrate.
[d] Regio-selectivity in branched aldehyde.
[e] % Enantiomeric excess measured by GC.
[f] $T = 20$ °C.
[g] $P = 60$ bar, TOF measured after 1 h.

Interestingly, in the hydroformylation of substrates *para*-methoxystyrene, 2-vinylnaphthalene and 6-methoxy-2-vinylnaphthalene, activity, regio- and enantio-selectivity improved when the *syn* gas pressure was raised from 30 to 60 bar (entries 12–14). Lowering the temperature to 20 °C led to an increase in enantio-selectivity (up to 63%) (entries 6 and 15).

To sum up, if we compare ligands **2** and **3** with ligand **1b**, which has the same substituent in the phosphinite moiety, we can see that the furanoside backbone is more effective in transferring the chirality than the pyranoside backbone. With readily available diphenyl diphosphinite ligands **2** and **3**, it therefore obtains, under milder conditions, similar enantiomeric excesses to the best one reported in the literature for the diphosphinite ligand system **1a**, which has electron deficient aryl groups at phosphorus [7a–c]. In addition, the regio-selectivity in the branched product obtained with the catalytic systems containing ligands **2** and **3** is higher than with ligands **1**.

3.2. Characterization of [HRh(P–P)(CO)$_2$] complexes

The [HRh(P–P)(CO)$_2$] (P–P = bidentate ligand) species are known to be the resting state in the hydroformylation reaction [1]. These complexes are generally assumed to have a trigonal bipyramidal structure. Two isomeric structures of these complexes, containing the bidentate ligand coordinated in a bis-equatorial (ee) or an equatorial–axial (ea) fashion (Fig. 2), are possible. The presence of only one active diastereoisomeric hydridorhodiumcarbonyl species with the Rh-diphosphites (ee) and Rh-phosphine-phosphite (ea) systems precursors is presumably the key to controlling efficient chirality transfer.

To obtain information about the structures in solution of [HRh(P–P)(CO)$_2$] species formed under hydroformylation conditions (PP = diphosphinite ligands **2** and **3**), we used high pressure NMR (HP-NMR) and high pressure IR (HP-IR).

These [HRh(P–P)(CO)$_2$] (PP = **2** and **3**) species were prepared in situ under hydroformylation conditions by adding 1.1 equiv. of diphosphinite ligand to the catalyst precursor [Rh(acac)(CO)$_2$] (Scheme 2). The spectroscopic data are summarized in Table 3.

At room temperature, the $^{31}P\{^1H\}$ NMR spectra of complexes **4** and **5** showed an eight sharp line spectrum due to the two non-equivalent coordinated phosphorus atoms and a rhodium atom (ABX system). The same NMR pattern was observed at low temperature (298–193 K). The simulation of these signals affords the two phosphorus atoms located at

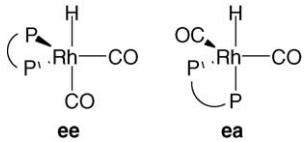
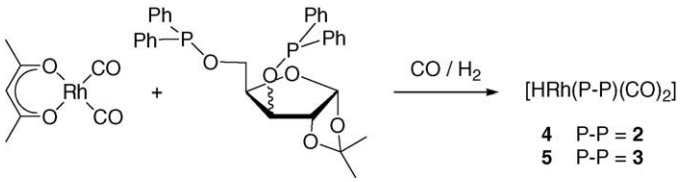


Fig. 2. Equatorial–equatorial (ee) and equatorial–axial (ea) [HRh(P–P)(CO)$_2$].



Scheme 2. Preparation of complexes **4**–**5**.

Table 3
Selected ^{1}H and ^{31}P NMR data for $[HRh(P–P)(CO)_2]$ complexes **4**–**5**[a]

Complex	δ_{P1}	δ_{P2}	$^{1}J_{Rh–P1}$	$^{1}J_{Rh–P2}$	$^{2}J_{P1–P2}$	δ H	$J_{H–X}$
4	126.0	126.7	155.4	160.9	72.8	−9.28 (bd)	3.9
5	125.5	126.3	155.3	160.9	72.5	−9.62 (bd)	4.5

[a] Prepared in toluene-d_8, δ in ppm. Coupling constants in Hz (bd = broad doublet), X = Rh, P.

126.0 ($^{1}J_{Rh–P1}$ = 155.4 Hz, $^{2}J_{P1–P2}$ = 72.8 Hz) and 126.7 ($^{1}J_{Rh–P2}$ = 160.9 Hz, $^{2}J_{P1–P2}$ = 72.8 Hz) for complex **4** and at 125.5 ($^{1}J_{Rh–P1}$ = 155.3 Hz, $^{2}J_{P1–P2}$ = 72.5 Hz) and 126.3 ($^{1}J_{Rh–P2}$ = 160.9 Hz, $^{2}J_{P1–P2}$ = 72.5 Hz) for complex **5**. The large values for the $^{1}J_{P–Rh}$ are characteristic of phosphinite ligands coordinated in an equatorial position [8].

For both complexes, the ^{1}H NMR spectra in the hydride region revealed a broad doublet. This indicates that both the $J_{Rh–H}$ and the $J_{P–H}$ coupling constants are small. No better resolution was found even at temperatures as low as 193 K. However, these small values of the phosphorus-hydride coupling constants ($^{2}J_{P–H} \leq 3.9$ Hz for complex **4** and $^{2}J_{P–H} \leq 4.5$ Hz for complex **5**) are typical of a trigonal bipyramidal (TBP) hydridorhodium dicarbonyl species with bis-equatorially (ee) coordinating phosphorus [9]. Small *cis* phosphorous-hydride coupling are characteristic of phosphinite ligands coordinated in an equatorial position [8a]. Large $J_{P–H}$ constants have already been reported for a phosphinite ligand in an axial position [8b].

We confirmed the presence of only equatorial–equatorial species by carrying out the HP-IR spectroscopy. For complex **4**, the spectrum showed two bands in the carbonyl region at 1972 m and 2040 s cm^{-1} that are characteristic of phosphorous ligands coordinated in an equatorial position [8]. If an equilibrium between equatorial–equatorial and equatorial–axial isomers occurs, two sets of carbonyl frequencies originating from the two isomers should be observed [10].

In summary, NMR data indicate trigonal bipyramidal (TBP) hydridorhodium dicarbonyl species with equatorial–equatorial coordinating diphosphinites. Further evidence is provided by IR in situ measurements. Moreover, the formation of only one diastereoisomer was confirmed by variable temperature NMR.

4. Conclusions

Diphosphinite ligands **2** and **3**, easily prepared from inexpensive D(+)-xylose in two and three steps, respectively were tested in the Rh-catalyzed asymmetric hydroformylation of several vinyl arenes. High regio-selectivities in branched aldehyde (up to 99%) and moderate enantio-selectivities (up to 63%) were obtained. The results showed a remarkable substrate effect on enantio-selectivity. Thus, the presence of *para*-methoxy and naphthyl substituents in the substrate had a positive effect on enantio-selectivities.

The characterization of the rhodium complexes formed under hydroformylation conditions by NMR techniques and in situ IR spectroscopy showed that the hydridorhodium dicarbonyl species exist in one diastereosiomeric equatorial–equatorial form. However, this strong coordination preference did not allow high enantio-selectivity.

Based on the encouraging results obtained with these new types of readily available furanoside diphosphinite ligands, further research of more active and stereo-selective catalysts is now in progress, exploiting the advantage that these sugar ligands can be so easily modified.

Acknowledgment

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[10] In general, the carbonyl bands of the equatorial–axial (ea) isomer are found at lower wavenumbers than those of the equatorial–equatorial isomer, see Ref. [4d].

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