Diastereoisomeric bisphosphite ligands in the hydroformylation of octenes: rhodium catalysis and HP-NMR investigations†

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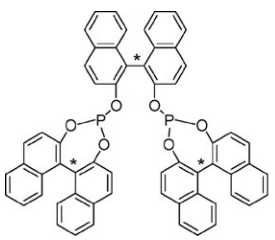
Diastereoisomeric hydroformylation catalysts show differences for the catalyst preformation pathway and a strongly reduced *n*-octene hydroformylation activity for the (*S*,*S*,*R*)-isomer.

Rhodium-catalyzed hydroformylation of olefins affording aldehydes, is one of the most important homogeneously catalyzed reactions.[1] It is used for the production of commodities as well as for the synthesis of fine chemicals. In dependence on the catalyst used either linear or branched aldehydes are formed predominantly. Regioselectivity can be adjusted with the assistance of ancillary ligands, mainly trivalent phosphorus compounds. In most cases branched aldehydes are chiral, therefore the goal of the asymmetric hydroformylation is the achievement of high isoregioselectivity and stereoselectivity.[2] In contrast, only high regioselectivity counts for the production of *n*-aldehydes. Also for *n*-regioselective reactions, frequently ligands have been employed which possess elements of chirality. Of particular importance are biaryl-based bidentate ligands, which have seen widespread application. Without appropriate substitution, free rotation around the biaryl axis is not restricted under reaction conditions and *atropo* isomers can not be differentiated. However, the incorporation of additional chirality elements in the molecule, like stereogenic P-atoms, may lead to diastereomers, which are configurationally stable.[3] The performance of diastereomeric catalysts is hardly to be predicted, though they are expected to influence differently the outcome of the hydroformylation reaction. Successful concepts describing ligand properties include the bite angle for the achiral Xanthphos ligand type, with shows correlation with regioselectivity in rhodium catalyzed hydroformylation.[4] Based on MM3 calculations, recently Briggs and Whiteker suggested that coordination of rotationally hindered diastereomeric biphenyldiphosphites of the Biphephos ligand type to the Rh-center may result in different, configuration-dependent structures of the catalysts resting state $[HRh(CO)_2(bisphosphite)]$.[5] Differences in both, bite angles and probably more important the cone angles at each phosphorus atom were discussed as a reason for variations in both, *n*-regioselectivity and catalytic activity found in the hydroformylation of the standard olefin 1-octene. For bidentate ligands exhibiting flexible backbones and a tendency for epimerization, the overall steric demand can vary. The transition metal ligand complex, when travelling through the catalytic cycle, experiences structural changes with the ligand adopting energetically favourable conformations, and configurations. Consequently, also the appropriate set of ligand cone angle profiles would be informative to describe steric demands.[6] In a parallel paper we show that the ratio of diastereomeric ligands bearing a stereogenic P-center and a rotationally flexible biaryl axis can be affected by achiral counter ligands in the precatalyst or resting state (*e.g.* anionic ligands as are allyl, acetylacetonate, hydride).[7] A further change of this ratio during the formation of catalytic intermediates discussed as are alkyl and acyl complexes, is likely to be expected.

Herein we will give evidence that regioselectivity in 1-octene hydroformylation does not necessarily change due to application of a distinct diastereomeric bisphosphite (**1**) based on 2,2′-dihydroxybinaphthyl. However, significant ligand-dependent differences are observed for precatalyst formation and catalyst activity, respectively. A pronounced change in regioselectivity is noted for internal olefins applied as substrates, where kinetic control of consecutive isomerization-hydroformylation reaction is one of the requirements for predominant *n*-regioselectivity.

1-(*R*,*R*,*R*)- and **1**-(*S*,*R*,*S*) (Scheme 1) were synthesized by employment of enantiopure starting material according to literature.[8] **1**-(*S*,*S*,*R*) was obtained by subsequent reaction of (*S*)-2,2′-dihydroxybinaphthyl with the BINOL-phosphochloridites of (*S*)-2,2′-dihydroxybinaphthyl and (*R*)-2,2′-dihydroxybinaphthyl in the presence of NEt_3. Prior to the final esterification step, it was necessary to purify intermediate 2′-((*S*)-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-yloxy)-1,1′-(*S*)-binaphthyl-2-ol by column chromatography. ^{31}P NMR spectroscopy proved the presence of configurationally different phosphorus atoms absorbing at 144.8 (d) and 146.5 (d) ppm exhibiting a 20.8 Hz 'through space' coupling, and the presence of 5% of **1**-(*S*,*S*,*S*) as an impurity.[9]

To study the impact of a distinct ligand configuration on the electron donating properties of compounds **1**, diselenides were prepared.[10] Reaction with six equivalents of selenium in boiling toluene gave quantitative conversion to **1**-Se_2 within 17 h. Interestingly, under these conditions, a selenium mediated



1-(*R*,*R*,*R*) middle descriptor given
1-(*S*,*R*,*S*) claims configuration
1-(*S*,*S*,*R*) of bridging binaphthyl unit

^{31}P-NMR data of diselenides
($CDCl_3$, δ [ppm] / $^1J(^{31}P\text{-}^{77}Se)$ [Hz])
1-(*R*,*R*,*R*)Se_2, 71.19/ 1045.3
1-(*S*,*R*,*S*)Se_2, 71.26/ 1045.8
1-(*S*,*S*,*R*)Se_2, 71.86/ 1048.8 + 70.41/ 1045.3

Scheme 1 Diastereomeric binaphthol based bisphosphites.

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transesterification occurred for **1**-(*S*,*R*,*S*) resulting in 39% of **1**-(*S*,*S*,*R*)Se_2 in the final product.[11] Chemical shifts as well as ^{31}P–^{77}Se couplings obtained from ^{31}P NMR showed only minor differences (Scheme 1). Thus, for the diselenides a comparable donor behaviour of phosphorus is proved for the isomers of **1**.

In preliminary trials a mixture of diastereomeric ligands **1** as obtained from racemic 2,2′-dihydroxybinaphthyl, consisting of 55.9% (*R*,*R*,*R*)-, 38.7% (*S*,*S*,*R*)- and 5.4% (*S*,*R*,*S*)-diphosphite isomer after workup, was tested in the hydroformylation of 1-octene. Aldehyde yields ranging from 84 to 89%, containing a 0.959 *n*-nonanal molar fraction (ratio **1** : Rh = 5) were determined after reaction at 100 °C/50 bar (see Table 1). For a technical mixture of less reactive internal octenes applied as an substrate at 120 °C/20 bar, the ligand : rhodium ratio showed a remarkable effect with almost complete inhibition of hydroformylation reaction at L : Rh = 5 : 1.

Further experiments verified the contribution of each diastereomer. In 1-octene hydroformylation, **1**-(*R*,*R*,*R*) and **1**-(*S*,*R*,*S*) showed almost identical modifying properties to the catalyst. The (*S*,*S*,*R*)-diphosphite gave poor yields of 11–17% at L/Rh = 5, but a convenient result with less equivalents of ligand applied. For L/Rh = 2, 89% of aldehyde yield were paired with a regioselectivity of 95.6%. The regioselectivities obtained prove only a minor contribution of unmodified catalysis, if present at all. From the internal octene mixture, only traces of aldehyde again are found with the (*S*,*S*,*R*)-ligand applied at a concentration of 3.75×10^{-3} mol l^{-1} (ligand/Rh = 5). Interestingly, **1**-(*S*,*R*,*S*) gave a low yield, too. The catalyst derived from **1**-(*R*,*R*,*R*) showed superior performance. This is surprising, because results from 1-octene hydroformylation did not reveal enhanced capability for olefin isomerization. From this substrate containing 3.3% 1-octene regioselectivity reached a value of 71.9% at L/Rh = 2. For all catalysts, incomplete precursor to catalyst transformation can be excluded as a factor altering results. Because batches performed with a prolonged catalyst preformation time of 4 h gave almost identical catalytic performance, the routine heating methodology (30 min for 100 and 120 °C) seems to be sufficient. From the results it is obvious that **1**-(*S*,*S*,*R*) is dominating in modifying catalytic activity, if the diastereomeric mixture of diphosphites is applied. Depending on the substrates used, yield-based performance can be evaluated as follows: 1-octene, **1**-(*R*,*R*,*R*) ~ **1**-(*S*,*R*,*S*) > **1**-(*S*,*S*,*R*); internal octenes, **1**-(*R*,*R*,*R*) > **1**-(*S*,*R*,*S*) ~ **1**-(*S*,*S*,*R*).

Table 1 Hydroformylation of 1-octene[a] and isomeric *n*-octenes[b]

	1-Octene		*n*-Octenes	
	L/Rh = 5 Yield/ *n*-nonanal (%)	L/Rh = 2 Yield/ *n*-nonanal (%)	L/Rh = 5 Yield/ *n*-nonanal (%)	L/Rh = 2 Yield/ *n*-nonanal (%)
mixture	84/95.9	89/94.8	2/n.d.	41/67.0
1-(*R*,*R*,*R*)	87/94.4	86/93.5 88/92.8[c]	20/76.1	68/71.9 71/71.4[c]
1-(*S*,*R*,*S*)	87/94.8 87/94.9[c]	92/94.8	4/85.4 4/86.1[c]	34/63.4
1-(*S*,*S*,*R*)	11/96.2 17/95.8[c]	89/95.6	0.5/n.d. 0.3/n.d.[c]	40/64.3

[a] T = 100 °C, p = 50 bar, [Rh] = 0.3×10^{-3} mol l^{-1}, substrate/catalyst = 5410, toluene, t = 4 h. [b] 120 °C, 20 bar, [Rh] = 0.75×10^{-3} mol l^{-1}, substrate/catalyst = 2160), toluene, 4 h. A technical substrate mixture was applied: 3.3% 1-octene; 48.4% *Z*/*E*-2-octene; 29.2% *Z*/*E*-3-octene; 16.4% *Z*/*E*-4-octene; 2.1% skeletal C_8-olefinic isomers; 0.6% *n*-octane. [c] Additional catalyst preformation time applied at reaction temperature: 4 h.

It has to be noted that regioselectivities for *n*-nonanal obtained from 1-octene differ only within a range of 1.8% for the three diastereomers. This may point toward similar geometries of the catalysts formed. Indeed, PM3 semi-empirical calculations performed for the catalyst's resting state [$HRh(CO)_2$(**1**)] gave relatively small deviations for the P–Rh–P bite angle only, ranging from 118.6 to 121.8° for the energetically favoured bisequatorial diphosphite coordination identified for all the three diastereomeric complexes (ESI†)[12] In order to get more information on the catalytically active species formed from ligands **1**, hydride complex formation under an atmosphere of syngas was studied by means of HP-NMR spectroscopy in a modified sapphire cell equipped with a gas circulation device ensuring full control of pressure and gas saturation.[7] Already at the stage of dissolving precursors under argon for sample preparation remarkable differences in reactivity were found.

If one equivalent of **1**-(*S*,*R*,*S*) was reacted with [acacRh-(COD-1.5)] under argon in toluene-d_8, the ^{31}P NMR spectrum obtained at room temperature showed that the diphosphite is not able to replace entirely the diolefin from the metal centre. The spectrum is characterized by a broadened doublet at 144.6 ppm, (J_{PRh} = 301 Hz) for [acacRh(**1**-(*S*,*R*,*S*))] covering 60% of overall signal intensity, accompanied by the signal of free ligand at 146.1 ppm. However, when a stream of syngas was passed through the solution at 20 bar pressure, CO accelerated the substitution of diolefin and a pure complex formed immediately. Spectroscopic data obtained for the rhodium compound observed did not change, compared to that measured under argon, therefore the intermediate formation of [acacRh(CO)(**1**-(*S*,*R*,*S*))] is unlikely. Already after 10 min of syngas treatment at 25 °C, [$HRh(CO)_2$(**1**-(*S*,*R*,*S*))] is detectable. After increasing the temperature to 70 °C, complete precursor to rhodium hydride transformation was achieved within 3 h without the reaction system passing through a detectable intermediate. Only one phosphorus signal is observed for the complex which is centered at 167.5 ppm (d, J_{PRh} = 237.5 Hz). The hydride signal is found at −10.57 ppm (d, J_{HRh} = 2.9 Hz). The hydride complex solution remained unchanged for several hours after cooling to room temperature and depressurization to one bar of CO/H_2. This allowed IR spectroscopic measurement at the same gas-saturated sample, resulting in stretching frequencies ν(CO) = 2020, 2070 cm^{-1}. Further details, as is the absence of detectable H–P coupling, verified a bisequatorial coordination of the bisphosphite.[13]

Analogous measurements were performed with **1**-(*R*,*R*,*R*). The corresponding enantiomer, **1**-(*S*,*S*,*S*), combined with [acacRh$(CO)_2$] and cationic rhodium precursors was already subject to an HP-NMR investigation for asymmetric hydroformylation.[14] Hydride complex formation was described to take 16 h at 40 °C. With [acacRh(COD-1.5)], **1**-(*R*,*R*,*R*) under argon reacts promptly to [acacRh(**1**-(*R*,*R*,*R*))] (δ = 140.0 ppm, J_{PRh} = 309.7 Hz). The latter complex immediately disappears upon syngas treatment of the solution. First, only

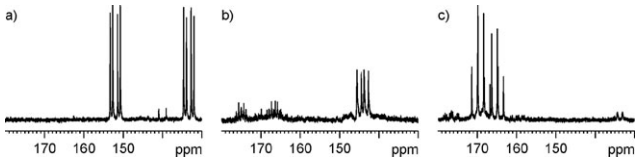

Fig. 1 ^{31}P NMR spectra of the reaction of [acacRh(COD-1.5)] with **1**-(*S*,*S*,*R*) (0.1 mmol each) in toluene-d_8 (2.2 ml). (a) 30 min after mixing at 25 °C, argon. (b) 15 min after supplying 20 bar CO/H_2 at 25 °C. (c) After cumulative heating at 52 °C, 30 min, and 74 °C, 1.5 h. For (b) and (c), syngas flow was adjusted at 1 ml min^{-1}. Saturation of solution with syngas was proved by following the signal intensity of dissolved H_2, δ = 4.44 ppm.

the low field shifted signal of [acacRh(CO)(**1**-(*R*,*R*,*R*))] at 143.5 ppm (J_{PRh} = 273.7 Hz) is observed. Within 45 min an additional set of multiplets in the range of 158 and 172 ppm acquiring 10% of signal intensity, together with a broad hydride signal at −10.65 ppm in the proton spectrum is formed. We were not able to identify these latter compounds. They are of intermediate character holding a maximum of 70% of the phosphorus signal intensity after 2.5 h at 25 °C. At this stage, still 18% of the acetylacetonate educt is present. Further cumulative heating at 40 °C/1.0 h, 55 °C/1.5 h and 80 °C/3 h brings the reaction to equilibrium with the formation of [HRh(CO)$_2$(**1**-(*R*,*R*,*R*))], resonating at 167.0 ppm (J_{PRh} = 232.8 Hz). As expected, NMR spectroscopic data obtained are almost identical to [HRh(CO)$_2$(**1**-(*S*,*S*,*S*))], however, for the latter complex a chemical shift for phosphorus of 162.0 ppm (J_{PRh} = 233 Hz) was reported in the literature. IR spectroscopy verified vibrations ν(CO) at 2067, 2013, 2023 (split asymmetric band) and ν(RhH) = 1991 cm^{-1}.

Comparable to **1**-(*R*,*R*,*R*) and in contrast to **1**-(*S*,*R*,*S*) the *S*,*S*,*R*-diastereomer at 25 °C under argon spontaneously reacted to give [acacRh(**1**-(*S*,*S*,*R*))]. The ^{31}P NMR spectrum (see Fig. 1(a)) is characterized by two double doublets at 133.4 ($^1J_{PRh}$ = 307 Hz) and 152.0 ($^1J_{PRh}$ = 311 Hz) ppm, each exhibiting a $^2J_{PP}$ coupling constant of 111 Hz between the configurationally different phosphorus atoms. The minor component seen at 140.0 ppm ($^1J_{PRh}$ = 309 Hz) is assigned to [acacRh(**1**-(*S*,*S*,*S*))] derived from the diastereomeric impurity present in the ligand used. Addition of syngas (20 bar) at 25 °C resulted in the formation of [acacRh(CO)(**1**-(*S*,*S*,*R*))] showing a multiplet centered at 144.1 ppm, accounting for 67% of signal intensity after 15 min (Fig. 1(b)). The formation of intermediate hydride complexes is deduced from a signal set in the range of 163 to 177 ppm, accompanied by a sharp signal at −10.56 ppm ($^1J_{HRh}$ = 4.1 Hz) and additional very broad signals at −10.1 and −10.4 ppm in the proton NMR spectrum. Further heating and holding the solution at 74 °C for 1.5 h led to equilibrium of reaction, where [HRh(CO)$_2$(**1**-(*S*,*S*,*R*))] is the major component. This rhodium complex exhibits a hydride signal at −10.37 ppm ($^1J_{HRh}$ = 3.8 Hz, $^2J_{HP}$ not resolved). In ^{31}P NMR it is characterized by two phosphorus signals at 169.4 ppm (dd, $^1J_{PRh}$ = 240 Hz, $^2J_{PP}$ = 254 Hz), and 164.6 ppm (dd, $^1J_{PRh}$ = 234 Hz, $^2J_{PP}$ = 255 Hz). These data, together with the observed IR stretching vibrations ν(CO) located at 2018, 2078 cm^{-1} point toward a favoured bisequatorial coordination of the bisphosphite at the metal centre, similar to the other diastereomers. It must be noted that a clean formation of a single hydride was not achieved. About 10% of signal intensity is calculated for a badly resolved, virtual triplet of quintets shaped phosphorus signal at 176.6 ppm corresponding to a broad hydride resonance at −11.1 ppm. Thus, the formation of the two possible isomeric hydride complexes with an *ax*,*eq* ligand coordination may be seen here also. An investigation to the real nature of these hydrides and to their contributions to catalysis is underway.

In conclusion, the formation pathway and the composition of the hydroformylation catalysts is dependent on the configuration of the diastereomeric ligand applied. The results from catalysis with different substrates, especially internal octenes, reveal that the bisphosphite isomers form intrinsically different catalysts. These differences will be overseen if interpretation of performance is based only on a linkage between the comparable regioselectivities obtained for 1-octene hydroformylation, and spectroscopic data pointing toward similar geometries around the rhodium centers in the hydride complexes.

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