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Investigations into the mechanism of the *in situ* formation of neutral dinuclear rhodium complexes

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ABSTRACT

The often applied *in situ* formation of neutral dinuclear rhodium precatalysts of the type [Rh(Diphosphine)(μ_2-Cl)]$_2$ with the ligands DPEPhos and DIOP has been mechanistically investigated by NMR spectroscopy. The structural characterization of reaction intermediates [Rh$_2$(μ_2-Diphosphine)(COD)$_2$(Cl)$_2$] and [Rh$_2$(Diphosphine)(COD)(μ_2-Cl)$_2$] was accomplished using X-ray crystallography. So a new and unexpected intermediate was found, which casts a new light on the mechanism of this ligand exchange. In addition, equilibria could be found which can at least influence the formation of neutral dinuclear rhodium precatalysts.

1. Introduction

Neutral dinuclear rhodium complexes of the type [Rh(Diphosphine)(μ_2-X)]$_2$ (X = Cl$^-$, OMe$^-$, OH$^-$…) are very often applied as catalyst precursors in homogeneous catalysis [1]. These coordination compounds are usually not commercially available and must therefore be synthetized. This is mostly done *in situ*. Previous work from our group has shown that, contrary to common belief, this procedure is far from being fast and selective in the formation of the desired neutral dinuclear rhodium species [Rh(Diphosphine)(μ_2-Cl)]$_2$ [2].

In almost 50% of the cases [3], depending on the rhodium precursor, the diphosphine ligand, the solvent, the reaction temperature and time, other unexpected coordination species are formed, either cationic and/or trinuclear [2], which can negatively affect the catalytic activity. A quantitative analysis by means of NMR and stopped-flow UV−Vis spectroscopy shows that the formation of the target complex [Rh(Diphosphine)(μ_2-Cl)]$_2$ according to Scheme 1 under standard conditions [4a] requires 22 min [4b]for the diphosphine ligand BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) and up to 28 min [4b] for DM-SEGPhos (5,5'−bis[di(3,5-xylyl)phosphino]-4,4′-bi-1,3- benzodioxol) [5].

Investigations into DPEPhos (Bis[(2-diphenylphosphino)phenyl] ether) and DIOP (*O*-Isopropyliden-2,3-dihydroxy-1,4-bis(diphenylphos-phino)-butan) point at a rather complex mechanism for the formation of the desired species [Rh(Diphosphine)(μ_2-Cl)]$_2$, where other reactions, beside those depicted in Scheme 1, are taking place. Both ligands are usually applied by Breit et al. in the atom-economic rhodium catalyzed redox-neutral propargylic CH activation [6].

Goal of the present work is the in-depth investigation into the mechanism of formation of the neutral dinuclear precatalyst [Rh(Diphosphine)(μ_2-Cl)]$_2$ for the ligands DPEPhos and DIOP (Fig. 1).

2. Results and discussion

When the *in situ* reaction of [Rh(COD)(μ_2-Cl)]$_2$ and DPEPhos in the ratio 1:2 in benzene at room temperature is monitored by NMR spectroscopy, beside the signals of the neutral complex [Rh(DPEPhos)(μ_2-Cl)]$_2$ (black) two additional doublets can be detected after 10 min (Fig. 2a). These signals, which disappear during the course of the reaction (Fig. 2b), can be ascribed to two likely intermediate rhodium species. Similar results can be observed with the chiral

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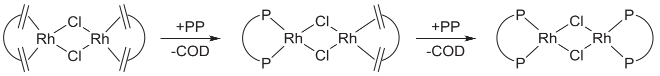


Scheme 1. Schematic representation of the two-step ligand substitution process in the rhodium-COD precursor with a diphosphine ligand in a stoichiometric ratio of 1:2 respectively.

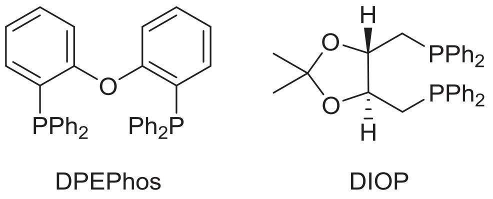


Fig. 1. Structures of ligands DPEPhos and DIOP.

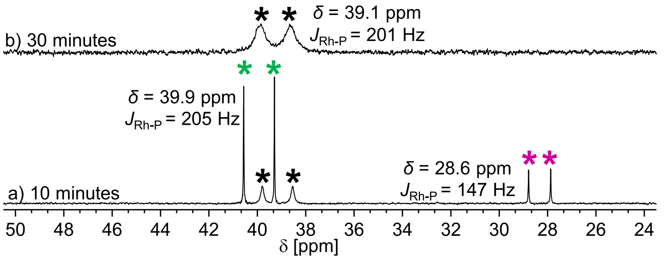


Fig. 2. ^{31}P NMR spectrum of the *in situ* reaction of [Rh(COD)(μ_2-Cl)]$_2$ and DPEPhos in the ratio 1:2 in benzene-d$_6$ at room temperature; a) after 10 min reaction time, neutral complex [Rh(DPEPhos)(μ_2-Cl)]$_2$: black; probable intermediate rhodium complexes, green and violet; b) after 30 min reaction time, neutral complex [Rh(DPEPhos)(μ_2-Cl)]$_2$: black [8]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

diphosphine ligand DIOP (see the supporting information Fig. S3) [7].

In order to disclose the nature of such intermediates, the *in situ* reaction of the COD precursor [Rh(COD)(μ_2-Cl)]$_2$ and the corresponding diphosphine ligand in a 1:1 ratio was investigated. The recorded ^{31}P NMR spectra show exclusively the two unassigned doublets (for ^{31}P NMR data see the supporting information Fig. S4 und S5). The signals of 1,5-cyclooctadiene (COD) in the corresponding ^{1}H NMR spectra allow to establish the stoichiometry of the two compounds. In one of the intermediates two molecules of COD are coordinated, which suggests a formula of the type „[Rh$_2$(Diphosphine)(COD)$_2$(Cl)$_2$]“. In the second one, only one COD acts as ligand, one is displaced, which leads to a formula of the type „[Rh$_2$(Diphosphine)(COD)(μ_2-Cl)$_2$]“ (for ^{1}H NMR data see the supporting information Fig. S6).

From the 1:1 reaction mixture of [Rh(COD)(μ_2-Cl)]$_2$ and DPEPhos, two different types of crystals could be isolated by means of fractional crystallization. The corresponding X-ray molecular structures are presented in Fig. 3. One corresponds to the μ_2-chloro bridged intermediate [Rh$_2$(DPEPhos)(COD)(μ_2-Cl)$_2$] (Fig. 3, left) whose structural motif is already known for other ligands [2a]. With DPEPhos a structural proof of this species could be provided for the first time. The other instead shows an unexpected structural motif (Fig. 3, right). The two rhodium centers are each bound to one COD and one chloro ligand. These two homoleptic fragments are connected by a DPEPhos molecule thus giving rise to a so far unknown diphosphine bridged intermediate with two COD ligands [Rh$_2$(μ_2-DPEPhos)(COD)$_2$(Cl)$_2$].

A perusal of the literature shows that such coordination compounds have been reported only for diphosphine ligands devoid of the Xanthen skeleton, among which ditbi [9], SPAN^{i}Pr [10] and chiral cyclophanes having very sterically demanding groups [9–11]. A similar structural motif has been recently described for a pincer ligand ^{iPr}PSCSP^{iPr} [12].

Also in the case of the chiral diphosphine ligand DIOP it was possible to isolate a diphosphine bridged complex [Rh$_2$(μ_2-DIOP)(COD)$_2$(Cl)$_2$] (for molecular structure see the supporting information Fig. S7).

NMR investigations suggest that the two intermediate rhodium species interconvert into each other. When a crystal of [Rh$_2$(μ_2-DPEPhos)(COD)$_2$(Cl)$_2$] (violet) is dissolved in benzene at 7 °C and the resulting solution warmed to room temperature (Fig. 4), the spectra unambiguously show that this species is directly converted into the μ_2-chloro bridged intermediate [Rh$_2$(DPEPhos)(COD)(μ_2-Cl)$_2$] (green) [13].

Between the intermediates in Scheme 2 an equilibrium exists, according to which the diphosphine bridged complex [Rh$_2$(μ_2-DPEPhos)(COD)$_2$(Cl)$_2$] (violet) can be formed from the μ_2-chloro bridged species [Rh$_2$(DPEPhos)(COD)(μ_2-Cl)$_2$] (green) only in the presence of added COD (Fig. 5). Therefore it should be possible to demonstrate a dependence on COD concentration in solution.

When the μ_2-chloro bridged intermediate [Rh$_2$(DPEPhos)(COD)(μ_2-Cl)$_2$] (green) is dissolved in solution, because of the lack

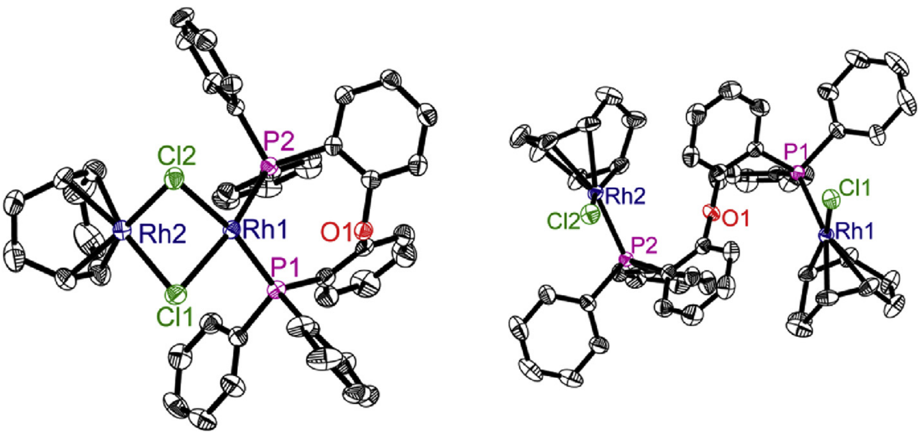


Fig. 3. Molecular structure of the two isolated intermediates, left [Rh$_2$(DPEPhos)(COD)(μ_2-Cl)$_2$], right [Rh$_2$(μ_2-DPEPhos)(COD)$_2$(Cl)$_2$]. The thermal ellipsoids are drawn at the 60% probability level, hydrogen atoms have been omitted for the sake of clarity.

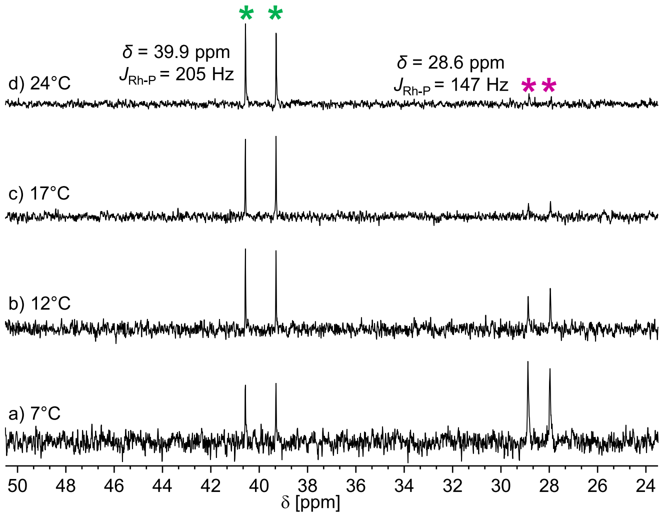
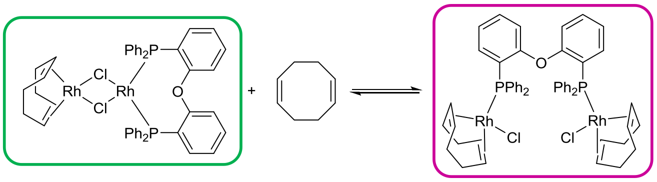


Fig. 4. Temperature dependence of the equilibrium between the two intermediates [$Rh_2(\mu_2$-DPEPhos)$(COD)_2(Cl)_2$] (violet) and [Rh_2(DPEPhos)(COD)(μ_2-$Cl)_2$] (green), ^{31}P NMR spectra of the solution obtained by dissolution of a single crystal of [$Rh_2(\mu_2$-DPEPhos)$(COD)_2(Cl)_2$] in benzene-d_6 measured at a) 7 °C; b) 12 °C; c) 17 °C and d) 24 °C. After the technical time required to reach the desired temperature, 30 min were elapsed at that temperature before recording the spectrum.



Scheme 2. Equilibrium between the μ_2-diphosphine bridged intermediate [$Rh_2(\mu_2$-DPEPhos)$(COD)_2(Cl)_2$] (violet) and the μ_2-chloro bridged intermediate [Rh_2(DPEPhos)(COD)(μ_2-$Cl)_2$] (green).

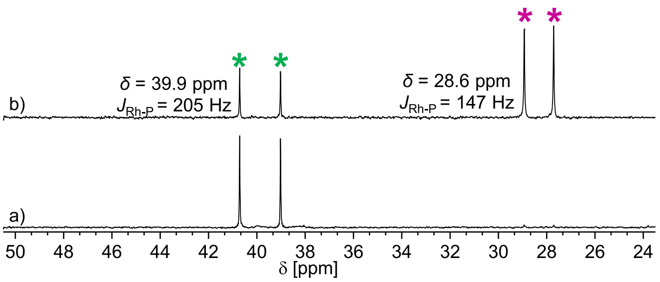


Fig. 5. Evidence of equilibrium onset between the μ_2-diphosphine bridged complex [$Rh_2(\mu_2$-DPEPhos)$(COD)_2(Cl)_2$] (violet) and the μ_2-chloro bridged complex [Rh_2(DPEPhos)(COD)(μ_2-$Cl)_2$] (green) upon addition of COD; a) ^{31}P NMR spectrum of the solution obtained by dissolution of a single crystal of the μ_2-chloro bridged complex [Rh_2(DPEPhos)(COD)(μ_2-$Cl)_2$] in benzene-d_6; b) ^{31}P NMR spectrum of the reaction mixture of the μ_2-chloro bridged complex [Rh_2(DPEPhos)(COD)(μ_2-$Cl)_2$] and an excess of COD.

of free COD, the formation of [$Rh_2(\mu_2$-DPEPhos)$(COD)_2(Cl)_2$] (violet) cannot be observed (Fig. 4a). As soon as COD is added to this solution, the formation of [$Rh_2(\mu_2$-DPEPhos)$(COD)_2(Cl)_2$] (violet) is unambiguously detected (Fig. 4b).

Also in the corresponding ^1H NMR spectrum it is possible to detect the formation of the diphosphine bridged complex [$Rh_2(\mu_2$-DPEPhos)$(COD)_2(Cl)_2$] (violet) following the addition of COD (see the supporting information Fig. S8). Worth noting are the signals relative to the different coordination modes of COD [14]. These experimental findings prove the equilibrium in Scheme 2 between the two intermediates.

A similar dependence on COD concentration is observed also for the equilibrium between the intermediates carrying the chiral ligand DIOP (for ^{31}P NMR data see the supporting information Fig. S9).

Concerning the influence of the solvent on the equilibrium, the more polar the solvent (a higher $E_\tau(30)$ value) [15] the bigger the relative amount of the diphosphine bridged complex [Rh_2(DPEPhos)$(COD)_2(Cl)_2$] (violet) in solution is (Fig. 6). On the other hand, in an apolar solvent like toluene the μ_2-chloro bridged complex [Rh_2(DPEPhos)(COD)(μ_2-$Cl)_2$] (green) is the prevailing species.

Interestingly, the chemical shift of the μ_2-chloro bridged intermediate [Rh_2(DPEPhos)(COD)(μ_2-$Cl)_2$] (green) is always the same, regardless of the solvent, while that of the diphosphine bridged complex [$Rh_2(\mu_2$-DPEPhos)$(COD)_2(Cl)_2$] (violet) slightly changes. This would suggest the build-up of a "solvent cage" around the latter in polar solvent which kinetically hampers its reaction to the μ_2-chloro bridged intermediate [Rh_2(DPEPhos)(COD)(μ_2-$Cl)_2$] (green).

Also the equilibrium between the intermediate rhodium species containing DIOP shows a similar solvent dependence (for ^{31}P NMR data see the supporting information Fig. S10).

A plausible mechanism for the formation of the two intermediate species is as follow: in the first step the dimeric COD precursor [Rh(COD)(μ_2-Cl)]$_2$ is cleaved, likely in a homolytic fashion [17]. A diphosphine ligand coordinates as monodentate to each rhodium center, thus acting as a bridging ligand between the two identical metal containing fragments. In the second step, an equilibrium is established through which one COD is released and at the same time a rhodium-phosphorus bond is broken. The diphosphine then coordinates as bidentate to only one of the two rhodium centers and this allows the formation of the μ_2-chloro bridged intermediate [Rh_2(diphosphine)(COD)-(μ_2-$Cl)_2$]. This step is unexpected as the rhodium-phosphorus bond is usually regarded as a strong one [18]. Indeed in the described examples such bond is broken in favor of chelation. The experimentally observed equilibrium between the

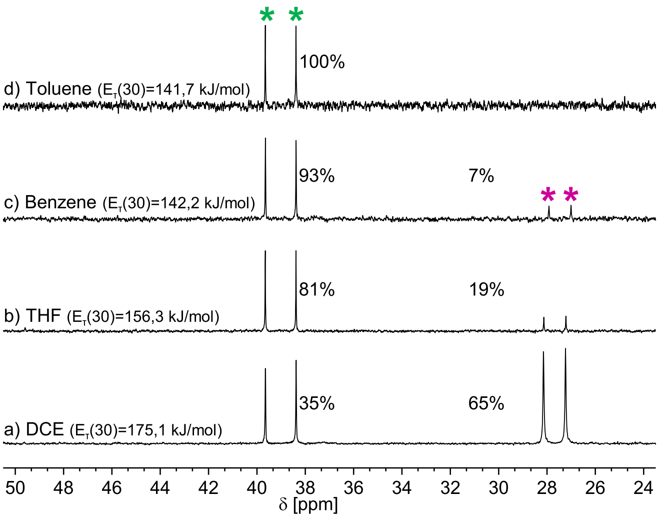
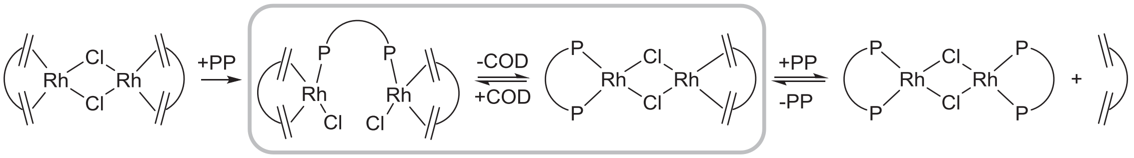


Fig. 6. Influence of the solvent on the equilibrium between the μ_2-chloro bridged intermediate [Rh_2(DPEPhos)(COD)(μ_2-$Cl)_2$] (green) and the diphosphine bridged complex [$Rh_2(\mu_2$-DPEPhos)$(COD)_2(Cl)_2$] (violet) (Scheme 2); ^{31}P NMR spectrum of the solution obtained by dissolution of a single crystal of the diphosphine bridged complex [$Rh_2(\mu_2$-DPEPhos)$(COD)_2(Cl)_2$] in a) 1,2-dichloroethane; b) tetrahydrofurane; c) benzene; d) toluene.



Scheme 3. Schematic representation of the modified mechanism of the classical *in situ* formation of the precatalyst [Rh(Diphosphine)(μ_2-Cl)]$_2$.[16]

intermediate species can be shifted by variation of reaction conditions (COD concentration, solvent, temperature).

In the final step, ligand exchange between COD and a second equivalent of the diphosphine ligand in the μ_2-chloro bridged intermediate [Rh$_2$(diphosphine)(COD)(μ_2-Cl)$_2$] affords the target precatalyst [Rh(diphosphine)(μ_2-Cl)]$_2$. Therefore the classical *in situ* synthesis of rhodium(I) precatalysts is clearly more complex than generally accepted.

In the case of DPEPhos, despite the complex equilibrium, the *in situ* procedure affords an almost quantitative conversion to the precatalyst within 30 min; this is not the case for DIOP, as the equilibria are shifted to the side of the intermediates. Should this *in situ* procedure be applied in a catalytic reaction, less rhodium precursor than expected would be converted into the proper DIOP-rhodium precatalyst from which the active species can form. As a consequence, the overall catalytic activity could be reduced. A negative impact might be observed also on selectivity. In fact, if the μ_2-chloro bridged intermediate [Rh$_2$(DIOP)(COD)(μ_2-Cl)$_2$] acts as the catalyst, then it might dissociate into its “mononuclear” fragments, one of which [Rh(COD)Cl] is devoid of the chiral ligand and can therefore not contribute to the overall selectivity, that would be then significantly reduced. A numerical simulation has been carried out which supports this conclusion (see supporting information).

3. Summary

A systematic investigation into the often applied *in situ* preparation of neutral dinuclear rhodium precatalysts has shown that the twofold COD substitution sequence in [Rh(COD)(μ_2-X)]$_2$ to afford [Rh(Diphosphine)(μ_2-X)]$_2$ is not straightforward but indeed proceeds through a so far undetected intermediate, the diphosphine bridged complex [Rh$_2$(μ_2-diphosphine)(COD)$_2$(Cl)$_2$], at least for the ligands DPEPhos and DIOP. The correct sequence of events, as experimentally proved in this work, is summarized in Scheme 3.

The solid state structure of these coordination compounds has been elucidated by single crystal X-ray diffraction. From the diphosphine bridged intermediate [Rh$_2$(μ_2-diphosphine)(-COD)$_2$(Cl)$_2$] the μ_2-chloro bridged intermediate [Rh$_2$(diphosphine)(COD)(μ_2-Cl)$_2$] is formed through an equilibrium the position of which is peculiar of the diphosphine under investigation and depends on the reaction conditions. The addition of a second equivalent of the diphosphine ligand reversibly leads to the precatalyst [Rh(diphosphine)(μ_2-Cl)]$_2$. It follows that all the species formed in the *in situ* synthesis are in equilibrium with each other. The equilibrium position for the diphosphine DPEPhos is almost entirely shifted to the side of the precatalyst, while for DIOP it lies to the side of the intermediate. This shows that the in-situ precatalyst formation is far less fast and selective than expected. Thus optimization of a catalytic process must include a detailed knowledge of the actual species generated during the *in situ* synthesis of the precatalyst.

Declaration of competing interest

The authors declare no competing financial interest.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.121002.

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[3] Detailed studies have been carried out by combining three different rhodium precursors ([Rh(COD)(μ_2-Cl)]$_2$, [Rh(NBD)(μ_2-Cl)]$_2$, [Rh(COE)$_2$(μ_2-Cl)]$_2$), six different solvents (THF, Methanol, DCM, Toluene, Benzene, Acetone) and 18 diphosphine ligands (DPPE, DIPAMP, Me-DuPhos, DPPP, DPPB, DIOP, BINAP, SEGPhos, DM-SEGPhos, DTBM-SEGPhos, Diflourphos, SYNPhos, BICP, Xanthphos, DPEPhos, DiPPF, PPF-P^{t}Bu$_2$ und DPPMP).[2a].

[4] a) $1{,}0\cdot10^{-2}$ mmol [Rh(diolefine)(μ_2-Cl)]$_2$ and $2{,}0\cdot10^{-2}$ mmol ligand in approx. 5 ml solvent.[6a], b) time required for 98% conversion under standard reaction conditions in literature.

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[13] The equilibrium between the intermediates is achieved so quickly that the μ_2-chloro bridged species [Rh_2(DPEPhos)(COD)(μ_2-Cl)$_2$] is formed directly on dissolving the diphosphine bridged complex [Rh_2(μ_2-DPEphos)(COD)$_2$(Cl)$_2$].

[14] At this point, it is not only possible to distinguish between the free and the coordinated COD, but, thanks to the corresponding characteristic chemical shifts, also between the different COD containing coordination compounds.

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[16] The reversibility of the last reaction step was experimentally verified for DIOP (foraNMR data see the supporting information Figure S11). For other ligands like DPEPHos (Figure 1b) and, for example, BINAP this step is irreversible.[5].

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