ChemPubSoc Europe

DOI: 10.1002/cplu.201402213

In Situ Synthesis of Neutral Dinuclear Rhodium Diphosphine Complexes [{Rh(diphosphine)(μ_2-X)}$_2$]: Systematic Investigations

Antje Meißner, Angelika Preetz, Hans-Joachim Drexler, Wolfgang Baumann, Anke Spannenberg, Anja König, and Detlef Heller*[a]

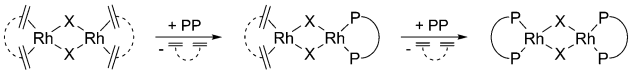
As the workhorses for many applications, neutral dimeric μ_2-X-bridged diphosphine rhodium complexes of the type [{Rh(diphosphine)(μ_2-X)}$_2$] (X = Cl, OH) are usually prepared in situ by the addition of diphosphine ligands to the rhodium complex [{Rh(diolefin)(μ_2-X)}$_2$] (diolefin = cyclooctadiene (cod) or norbornadiene (nbd)) or [{Rh(monoolefin)$_2$(μ_2-Cl)}$_2$] (monoolefin = cyclooctene (coe) or ethylene (C_2H_4)). The in situ procedure has been investigated for the diphosphines 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), 5,5′-bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole (SEGPHOS), 5,5′-bis[di(3,5-xylyl)-phosphino]-4,4′-bi-1,3-benzodioxole (DM-SEGPHOS), 5,5′-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4′-bi-1,3-benzodioxole (DTBM-SEGPHOS), 2,2′-bis(diphenylphosphino)-1,1′-dicyclopentane (BICP), 1-[2-(diphenylphosphino)ferrocenyl]ethyldi-*tert*-butylphosphine (PPF-P*t*Bu$_2$), 1,1′-bis(diisopropylphosphino)ferrocene (D*i*PPF), 1,2-bis(diphenylphosphino)-ethane (DPPE), 1,2-bis(*o*-methoxyphenylphosphino)ethane (DIPAMP), 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxalane (DIOP), 1,2-bis(2,5-dimethylphospholano)benzene (Me-DuPHOS), 1,4-bis(diphenylphosphino)butane (DPPB), and 1,3-bis(diphenylphosphino)propane (DPPP); the resulting complexes have been characterized by ^{31}P NMR spectroscopy and, in most cases, also by X-ray analysis. Depending on the diphosphine ligand, the solvent, the temperature, and the rhodium precursor, species other than the desired one [{Rh(diphosphine)(μ_2-X)}$_2$] are formed, for example, [(diolefin)Rh(μ_2-Cl)$_2$Rh(diphosphine)], [Rh(diphosphine)-(diolefin)]$^+$, [Rh(diphosphine)$_2$]$^+$, and [Rh(diphosphine)-(diolefin)(Cl)]. The results clearly show that the in situ method commonly applied for precatalyst preparation cannot be regarded as an optimal strategy for the formation of such neutral [{Rh(diphosphine)(μ_2-X)}$_2$] complexes.

Introduction

The choice of precatalyst in homogeneous catalysis has a crucial impact on the course of the reaction. This has been demonstrated in several cases, including asymmetric hydrogenation.[1]

Neutral μ_2-bridged dinuclear rhodium complexes of the type [{Rh(diphosphine)(μ_2-X)}$_2$] (X = Cl, or more rarely, OH) are known to promote (stereoselective) catalytic processes, for example, the hydrogenation of prochiral olefins,[2] ketones,[3] CO_2,[4] and polynuclear heteroaromatic compounds;[5] the ring opening of oxa- and azabicyclic alkenes,[6] the hydrogen-mediated formation of C–C bonds;[7] the addition of carboxylic acids to alkynes;[8] CO-gas-free hydroformylation[9] and carbonylations;[10] Pauson–Khand-type reactions;[11] olefin isomerization;[12] cycloadditions;[13] the coupling of aldehydes and allenes;[14] and 1,4-addition of organoboronic acids,[15] to mention only a few.

It is generally accepted that treatment of complexes [{Rh-(cod)(μ_2-Cl)}$_2$] (**1**; cod = cyclooctadiene), [{Rh(nbd)(μ_2-Cl)}$_2$] (**2**; nbd = norbornadiene), [{Rh(coe)$_2$(μ_2-Cl)}$_2$] (**3**; coe = cyclooctene), [{Rh(cod)(μ_2-OH)}$_2$] (**4**), and [{Rh(C_2H_4)$_2$(μ_2-Cl)}$_2$] (**5**) with diphosphine ligands smoothly affords neutral μ_2-bridged dinuclear rhodium complexes of the type [{Rh(diphosphine)(μ_2-X)}$_2$] (X = Cl or OH; Scheme 1). Hence, being considered straightforward, such in situ precatalyst preparation is applied almost exclusively in the catalyses mentioned above.



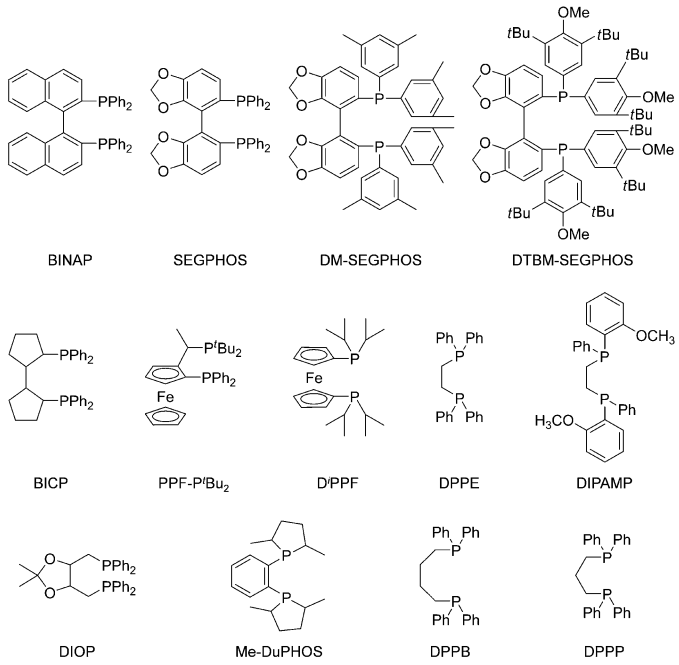
Scheme 1. Conventional synthesis of [{Rh(diphosphine)(μ_2-X)}$_2$] (PP = diphosphine, X = Cl or OH).

In the present study, systematic investigations into the synthesis of [{Rh(diphosphine)(μ_2-X)}$_2$] complexes according to Scheme 1 were carried out with precursors **1**–**5**. Diphosphine ligands such as 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), 5,5′-bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole (SEGPHOS), 5,5′-bis[di(3,5-xylyl)phosphino]-4,4′-bi-1,3-benzodioxole (DM-SEGPHOS), 5,5′-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4′-bi-1,3-benzodioxole (DTBM-SEGPHOS),

[a] *A. Meißner, Dr. A. Preetz, Dr. H.-J. Drexler, Priv.-Doz. Dr. W. Baumann, Dr. A. Spannenberg, A. König, Prof. Dr. D. Heller*
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-51183
E-mail: detlef.heller@catalysis.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cplu.201402213.

2,2′-bis(diphenylphosphino)-1,1′-dicyclopentane (BICP), 1-[2-(diphenylphosphino)ferrocenyl]ethyldi-*tert*-butylphosphine (PPF-P*t*Bu$_2$), 1,1′-bis(diisopropylphosphino)ferrocene (D*i*PPF), 1,2-bis(-diphenylphosphino)ethane (DPPE), 1,2-bis(*o*-methoxyphenylphosphino)ethane (DIPAMP), 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxalane (DIOP), 1,2-bis(2,5-dimethylphospholano)benzene (Me-DuPHOS), 1,4-bis(diphenylphosphino)butane (DPPB), and 1,3-bis(diphenylphosphino)propane (DPPP) were applied.



Special attention was devoted to assess, depending on solvent and temperature, the completeness of the conversion and the formation of intermediates and possible byproducts. In the case of BINAP, the rate of in situ precatalyst formation was also investigated.

Results and Discussion

^{31}P NMR spectroscopic data of the depicted complexes

The ^{31}P NMR spectroscopic data of the complexes described in the manuscript as a result of our investigations are summarized in Table 1. It is evident that the phosphorous signals of the neutral complexes of the type [{Rh(diphosphine)(μ_2-Cl)}$_2$] are quite low-field-shifted relative to those of the corresponding cationic complexes and of the pentacoordinated complexes. The typical *J*(P,Rh) coupling constants of such dinuclear neutral complexes range between 184 and 206 Hz. Similar chemical shifts and coupling constants were determined for the intermediate [(diolefin)Rh(μ_2-Cl)$_2$Rh(diphosphine)].

The values of the pentacoordinated neutral complexes [Rh(diphosphine)(diolefin)(Cl)] are similar to those of the corresponding cationic complexes [Rh(diphosphine)(diolefin)]BF$_4$, although the coupling constants *J*(P,Rh) of the neutral complexes are smaller than those of the cationic ones.

BINAP

The synthesis of [{Rh(BINAP)(μ_2-Cl)}$_2$] has been published recently;[15,16] however, it was included in this study only for comparison. At room temperature the in situ formation of the desired dinuclear rhodium complex [{Rh(BINAP)(μ_2-Cl)}$_2$] from the cod precursor **1** and two molar equivalents of BINAP (**1**/BINAP 1:2) in tetrahydrofuran (THF) as well as in toluene[16] is practically quantitative (>98% conversion) as proven by NMR spectroscopic measurements.[17,18] In dichloromethane (CH_2Cl_2), too, quantitative yields of [{Rh(BINAP)(μ_2-Cl)}$_2$] are observed at room temperature, with no oxidative addition of the solvent to rhodium taking place as a side reaction as previously described when using DPPE as the ligand.[19]

If BINAP is added in substoichiometric amounts to **1** (**1**/BINAP = 1:1) both in THF as well as in CH_2Cl_2 at room temperature, a mixture of two species is obtained as shown by the ^{31}P NMR spectrum. Surprisingly, the target compound [{Rh(BINAP)(μ_2-Cl)}$_2$] is detectable as a byproduct in addition to the main species; this is probably the intermediate [(cod)Rh(μ_2-Cl)$_2$Rh(BINAP)]. According to the ^{1}H NMR spectrum in CH_2Cl_2, traces of unreacted **1** are also present. Single crystals suitable for X-ray analysis were isolated from the reaction mixture. The corresponding molecular structure is reported in Figure 1.

Figure 1 shows the expected intermediate, [(cod)Rh(μ_2-Cl)$_2$Rh(BINAP)], that arises from the stepwise exchange of the diolefin ligands (see Scheme 1).[20] To the best of our knowledge, this is the first case in which the structure of this kind of complex has been unambiguously assigned by X-ray analysis.[21] If the crystals are redissolved in THF at room tempera-

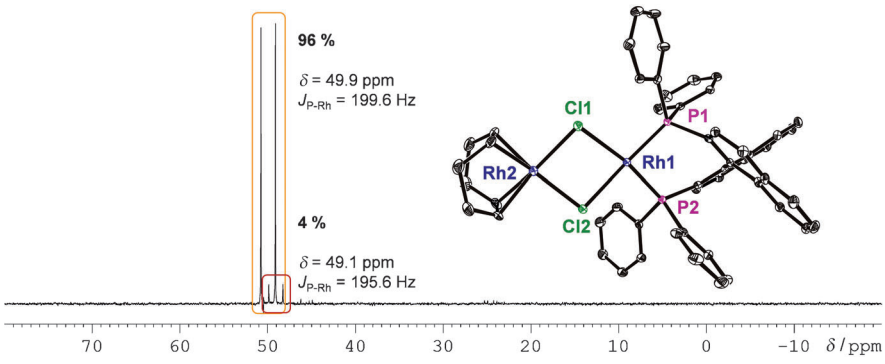


Figure 1. ^{31}P NMR spectrum of the solution obtained by dissolving single crystals of [(cod)Rh(μ_2-Cl)$_2$Rh(BINAP)] (yellow) in [D$_8$]THF at room temperature and the molecular structure of [(cod)Rh(μ_2-Cl)$_2$Rh(BINAP)]; ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. See below for a short discussion of the structural data. Selected bond lengths and angles are listed in Table S2 of the Supporting Information.

Table 1. ^{31}P NMR spectroscopic data relative to all complexes discussed in this study.

Ligand [PP]	Type of complex	Solvent	^{31}P NMR spectroscopic data δ [ppm]	J(P,Rh) [Hz]
BINAP	[{Rh(PP)(μ_2-Cl)}$_2$]	THF	49.1	194.8
	[(cod)Rh(μ_2-Cl)$_2$Rh(PP)]	THF	49.9	199.6
	[{Rh(PP)(μ_2-OH)}$_2$]	THF	54.5	185.5
	[Rh(PP)(nbd)]$^+$	MeOH	26.1	156.8
	[Rh(PP)(nbd)(Cl)]	CH_2Cl_2	25.0	141.2
SEGPHOS	[{Rh(PP)(μ_2-Cl)}$_2$]	THF	46.4	194.8
	[(cod)Rh(μ_2-Cl)$_2$Rh(PP)]	THF	47.6	199.6
	[Rh(PP)$_2$]$^+$	CH_2Cl_2	20.7	141.4
	[Rh(PP)(cod)]$^+$	MeOH	25.1	146.7
DM-SEGPHOS	[{Rh(PP)(μ_2-Cl)}$_2$]	THF	47.6	194.4
	[Rh(PP)(nbd)]$^+$	MeOH	25.6	155.5
BICP	[{Rh(PP)(μ_2-Cl)}$_2$]	THF	46.9	186.3
	[Rh(PP)(cod)]$^+$	MeOH	26.0	142.5
PPF-P*t*Bu$_2$ (**A**)	[{Rh(PP)(μ_2-Cl)}$_2$]	THF	41.2	199.1 (44.0)[a]
			111.9	206.0 (44.0)[a]
	[Rh(PP)(nbd)]$^+$	MeOH	23.9	155.5 (29.8)[a]
			74.6	151.6 (28.8)[a]
D*i*PPF	[{Rh(PP)(μ_2-Cl)}$_2$]	THF	63.1	205.2
DPPE	[{Rh(PP)(μ_2-Cl)}$_2$]	THF	72.9	198.3
	[(cod)Rh(μ_2-Cl)$_2$Rh(PP)]	THF	76.9	200.9
	[Rh(PP)$_2$]$^+$	CH_2Cl_2	57.9	133.5
DIPAMP	[{Rh(PP)(μ_2-Cl)}$_2$]	THF	74.3	199.6
	[(cod)Rh(μ_2-Cl)$_2$Rh(PP)]	THF	79.0	202.2
	[Rh(PP)$_2$]$^+$	CH_2Cl_2	54.9	137.4
	[Rh(PP)(cod)]$^+$	MeOH	51.2	150.3
DIOP	[{Rh(PP)(μ_2-Cl)}$_2$]	THF	33.5	190.5
	[(cod)Rh(μ_2-Cl)$_2$Rh(PP)]	THF	36.3	194.8
	[Rh(PP)(cod)]$^+$	MeOH	12.8	143.8
Me-DuPHOS	[{Rh(PP)(μ_2-Cl)}$_2$]	THF	96.5	199.1
	[(cod)Rh(μ_2-Cl)$_2$Rh(PP)]	THF	98.4	199.6
	[Rh(PP)$_2$]$^+$	THF	76.6	130.9
DPPB	[{Rh(PP)(μ_2-Cl)}$_2$]	THF	44.8	190.5
	[Rh(DPPB)(nbd)(Cl)]	THF	28.2	132.2
DPPP	[{Rh(PP)(μ_2-Cl)}$_2$]	THF	31.9	184.0
	[Rh(DPPP)(cod)(Cl)]	THF	13.0	116.6
	[Rh(DPPP)(nbd)(Cl)]	THF	18.7	128.3

[a] J (P,P) [Hz]

ture, [{Rh(BINAP)(μ_2-Cl)}$_2$] and [{Rh(cod)(μ_2-Cl)}$_2$] are formed, each of which accounts for approximately 4% of the rhodium content (according to ^{31}P NMR (Figure 1) and ^{1}H NMR spectroscopy).

This unexpected result clearly suggests that the equilibrium depicted in Scheme 2, undescribed thus far, is established in solution. A detailed discussion of such equilibrium and the rate constants are to be found in the literature.[22]

Exploratory UV/Vis spectroscopic investigations (stopped-flow/diode array)[23] in THF confirm that the diolefin ligand exchange is a stepwise process with the first diolefin being replaced very rapidly. The kinetically uniform reaction is in fact complete within seven seconds (Figure 2, left).

The exchange of the second diolefin ligand (reaction of crystals of the intermediate [(cod)Rh(μ_2-Cl)$_2$Rh-(BINAP)] with BINAP) is much slower under the chosen experimental conditions (Figure 2, right). The overall reaction time of approximately 30 minutes for the formation of [{Rh(BINAP)(μ_2-Cl)}$_2$] by in situ reaction of **1** with two equivalents of BINAP is thus due to the much slower second reaction step.[24]

If the nbd complex [{Rh(nbd)(μ_2-Cl)}$_2$] (**2**) is used instead of **1** under otherwise identical reaction conditions, the μ_2-Cl-bridged dimer complex is formed in only 80% yield. An unknown species and traces of the oxidized ligand are also detected (Figure 3a).[25] In CH_2Cl_2 the yield of the target compound [{Rh(BINAP)-(μ_2-Cl)}$_2$] drops to 22%, the main complex (78%) being an unexpected pentacoordinated neutral complex [Rh(BINAP)(nbd)(Cl)] as described in the literature[26] (Figure 3b).

Unexpectedly, in MeOH the ligand exchange provides no [{Rh(BINAP)(μ_2-Cl)}$_2$] but rather the cationic complex [Rh(BINAP)(nbd)]$^+$,[27] which, according to the ^{31}P NMR spectrum, is formed quantitatively, with chloride most likely being the counteranion (Figure 3c).[28]

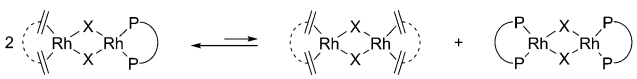
When the precursor [{Rh(coe)$_2$(μ_2-Cl)}$_2$] (**3**) is used, the desired dinuclear complex [{Rh(BINAP)(μ_2-Cl)}$_2$] is formed nearly quantitatively in THF at room temperature.

The yield drops to 45%, as shown by ^{31}P NMR spectroscopy, if the complex is prepared in situ at room temperature from [{Rh(cod)(μ_2-OH)}$_2$] (**4**) and BINAP either in THF or toluene.[29] Recently, it has been reported that rhodium–hydride species can be formed from **4**.[30]

SEGPHOS

Like BINAP, the cod precursor **1** and SEGPHOS (1:2) react in THF at room temperature to afford exclusively the desired complex [{Rh(SEGPHOS)(μ_2-Cl)}$_2$]. Its molecular structure is shown in Figure 4. If CH_2Cl_2 is used, surprisingly, only 68% of the target compound is formed. The byproduct is most likely [Rh-(SEGPHOS)$_2$]$^+$. This complex can also be formed through an excess amount of ligand (the ratio of **1** and SEGPHOS is 1:4).

Changing the ratio of **1** to SEGPHOS to 1:1 leads to 96% of the expected intermediate [(cod)Rh(μ_2-Cl)$_2$Rh(SEGPHOS)]. This



Scheme 2. Reaction sequence of the equilibrium between the intermediate [(diolefin)Rh(μ_2-X)$_2$Rh(diphosphine)] on one side and the precursor [{Rh-(diolefin)(μ_2-X)}$_2$] and the desired dinuclear complex [{Rh(diphosphine)(μ_2-X)}$_2$] on the other.

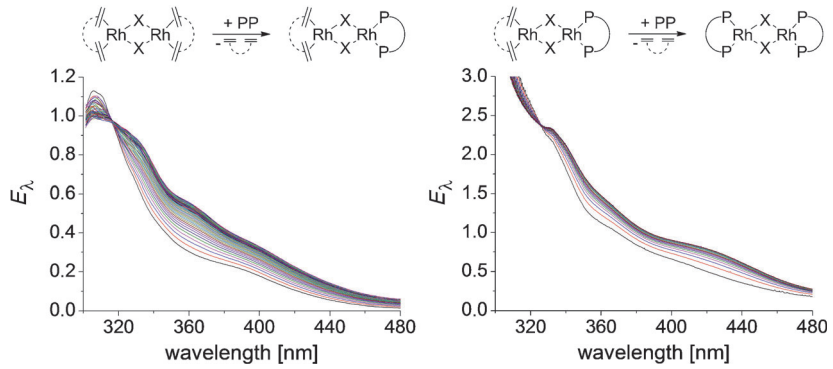


Figure 2. Left: UV/Vis reaction spectra of the first step, the reaction of 0.593 mmol L^{-1} [{Rh(cod)(μ_2-Cl)}$_2$] and 0.594 mmol L^{-1} BINAP in THF at 25 °C (spectra recorded every 7 ms, overall time 8 s, layer thickness 0.15 cm). Right: UV/Vis reaction spectra of the second step, the reaction of 0.310 mmol L^{-1} [(cod)Rh(μ_2-Cl)$_2$Rh(BINAP)] and 0.316 mmol L^{-1} BINAP in THF at 25 °C, cycle time 2.1 min, overall time 30 min, layer thickness 0.5 cm.

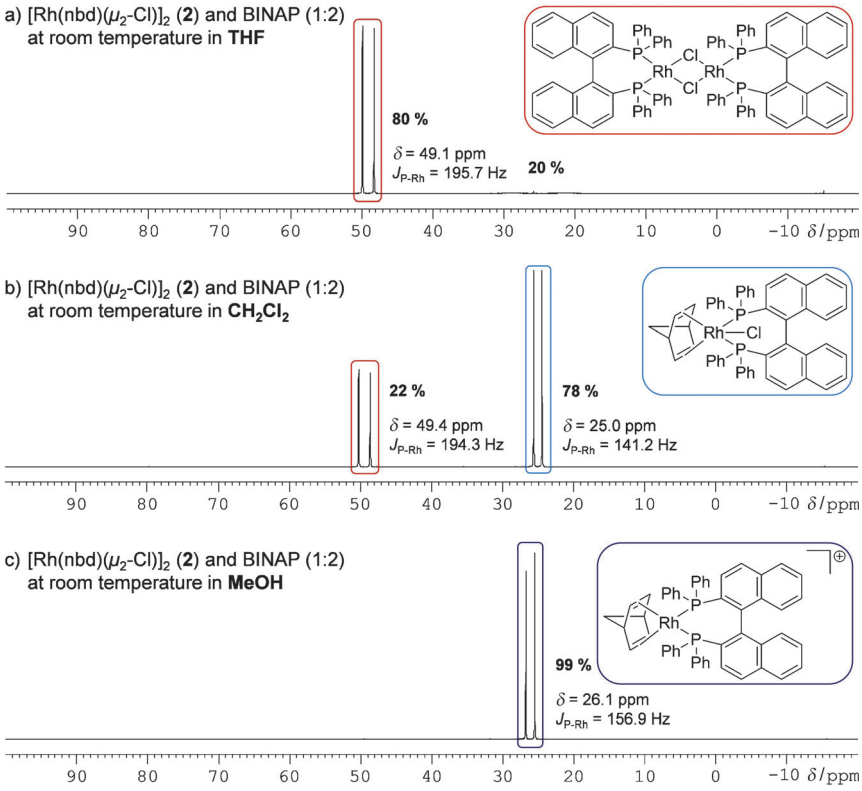


Figure 3. ^{31}P NMR spectra of the reaction solution of the in situ ligand exchange of [{Rh(nbd)(μ_2-Cl)}$_2$] (**2**) and BINAP (1:2) at room temperature in a) THF, b) CH_2Cl_2, and c) MeOH.

species can be safely assigned on the basis of the chemical shifts of the olefinic hydrogen atoms of cod, which are easily distinguished from the corresponding ones in the starting complex **1**. In addition, to about 4% of [{Rh(SEGPHOS)(μ_2-Cl)}$_2$] almost 6% of the starting complex **1** is present in solution (according to ^{1}H NMR spectroscopy), which is once again diagnostic of the presence of an equilibrium similar to the one already discussed for BINAP (Scheme 2).

Analogously to BINAP, a cationic complex is formed if MeOH is used instead of THF (the ratio of **1** to ligand is 1:2), although only in 76% yield. The remaining 26% rhodium content is shared between the target complex [{Rh(SEGPHOS)(μ_2-Cl)}$_2$] and the intermediate [(cod)Rh(μ_2-Cl)$_2$Rh(SEGPHOS)]. The molecular structure as well as the ^{31}P NMR spectrum of the cationic complex [Rh(SEGPHOS)(cod)]BF_4 are shown in Figure 5.

If the nbd precursor **2** is used, only 80% of the target compound of [{Rh(SEGPHOS)(μ_2-Cl)}$_2$] is formed in THF, together with 6% of the intermediate and a third unidentified species. In CH_2Cl_2 the yield drops to 35%. The main species (55%) as evidenced by ^{1}H NMR spectroscopy is probably a pentacoordinated monomeric rhodium complex [Rh(SEGPHOS)(nbd)(Cl)].

Starting with **4** and SEGPHOS in a ratio of 1:2 in toluene leads to only 52% of [{Rh(SEGPHOS)(μ_2-OH)}$_2$], the structure of which could be assigned by comparison with the ^{31}P NMR spectroscopic data of [{Rh(BINAP)(μ_2-OH)}$_2$].[15]

DM-SEGPHOS

As with BINAP and SEGPHOS, the addition of two equivalents of DM-SEGPHOS to **1** at room temperature quantitatively leads to the desired dinuclear complex [{Rh(DM-SEGPHOS)(μ_2-Cl)}$_2$] in THF.

If **2** is used as the rhodium source, [{Rh(DM-SEGPHOS)(μ_2-Cl)}$_2$] is formed in just 30% yield together with an as yet unidentified species. In CH_2Cl_2 the yield of the target compound is only 10%. Like for BINAP and SEGPHOS, the main product formed in situ is probably the pentacoordinated rhodium complex [Rh(DM-SEGPHOS)(nbd)(Cl)].[26] In MeOH, DM-SEGPHOS reacts with **2** to give the cationic rhodium species [Rh(DM-SEGPHOS)(nbd)]$^+$ in quantitative yield.

The above results show that at room temperature the dinuclear complexes of the general formula [{Rh(diphosphine)(μ_2-Cl)}$_2$] can be quantitatively prepared in situ starting from the cod complex **1** when using the three ligands BINAP, SEGPHOS, and DM-SEGPHOS either in CH_2Cl_2 or THF. Recently we reported comparable results for the structurally similar ligand 6,6′-

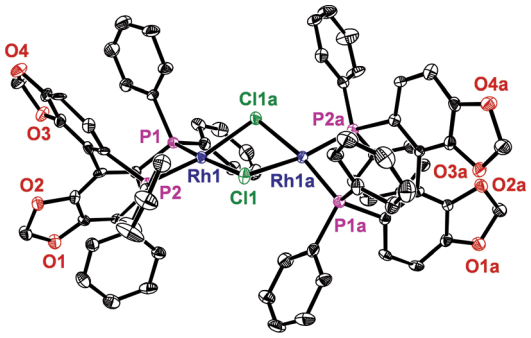


Figure 4. Molecular structure of [{Rh(SEGPHOS)(μ_2-Cl)}$_2$]; ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. See below for a short discussion of the structural data. Selected bond lengths and angles are listed in Table S1 of the Supporting Information.

bis(diphenylphosphino)-2,2′,3,3′-tetrahydro-5,5′-bi-1,4-benzodioxin (SYNPHOS).[31]

In contrast, in methanol and under otherwise identical conditions, the cationic complexes [Rh(diphosphine)(cod)]$^+$ are formed, with full conversion of **1** in the case of BINAP.

When using the nbd precursor **2**, the yield in the desired dinuclear complexes never exceeded 80%. Hence, **2** should not be considered the precursor of choice, and **4** is even less suitable.

DTBM-SEGPHOS

Preliminary experiments on the structurally related ligand DTBM-SEGPHOS show that in THF the reaction of **1** with two equivalents of the ligand only provides about 18% of [{Rh(DTBM-SEGPHOS)(μ_2-Cl)}$_2$]. The structure of this complex has been assigned based on the similarity of its spectroscopic features (chemical shifts and *J*(P,Rh) coupling constants) with those of the analogue complexes with SEGPHOS and DM-SEGPHOS. The yield of the target compound could not be improved by changing the solvent to CH_2Cl_2, although the cationic complex [Rh(DTBM-SEGPHOS)(cod)]$^+$ is formed in 50% yield. To confirm its structure, the BF_4^- analogue was independently prepared by the reaction of [Rh(diolefin)(acac)] (acac = acetylacetonate) and DTBM-SEGPHOS followed by the addition of HBF_4.[32]

No yield increase could be achieved by using **2**, which afforded a reactivity trend analogous to that observed with **1**. In CH_2Cl_2 the cationic complex [Rh(DTBM-SEGPHOS)(nbd)]$^+$ was formed in nearly quantitative yield (97%).

BICP

[{Rh(BICP)(μ_2-Cl)}$_2$] is quantitatively formed from **1** and two equivalents of BICP at room temperature in THF as the ^{31}P NMR spectrum of the reaction solution in Figure 6 shows. Figure 6 also shows the molecular structure of the target complex.

As reported in the literature,[33] such a precatalyst was used for enyne cyclizations in toluene. In this solvent, we observed that the in situ preparation effectively affords the catalyst in quantitative yield (>99%). However, if methanol is added to the toluene reaction mixture, the formation of the cationic species is observed (54%), as already noted for BINAP and SEGPHOS. If the reaction is carried out in methanol as the sole solvent, the yield in the cationic complex [Rh(BICP)(cod)]$^+$ is practically quantitative (98%). The molecular structure of this complex with BF_4 as counterion has been described previously.[34]

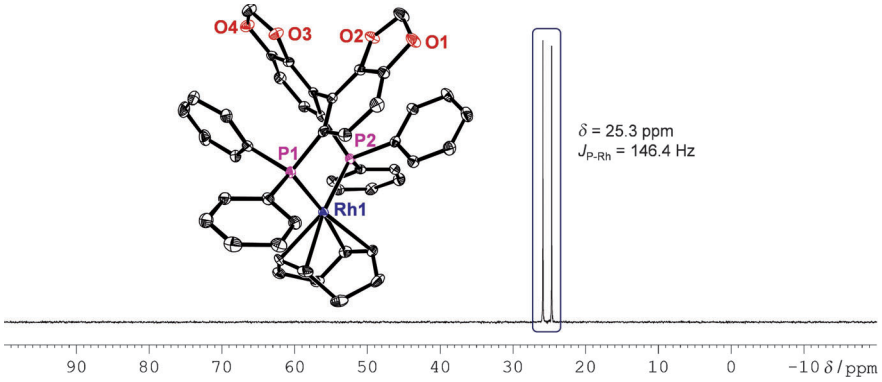


Figure 5. ^{31}P NMR spectrum in CD_2Cl_2 and molecular structure of the cation in [Rh(cod)(SEGPHOS)]BF_4; ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Rh–P 2.306–2.319(2), Rh–C 2.219–2.308(4); P-Rh-P 90.41–90.68(4).

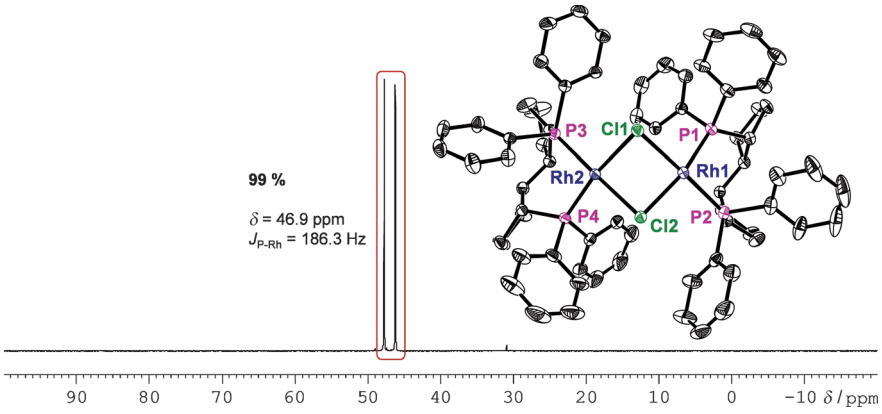


Figure 6. ^{31}P NMR spectrum of the solution resulting from the in situ conversion of [{Rh(cod)(μ_2-Cl)}$_2$] (**1**) in the presence of BICP (1:2) at room temperature in [D_8]THF and molecular structure of the product [{Rh(BICP)(μ_2-Cl)}$_2$]; ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. See below for a short discussion of the structural data. Selected bond lengths and angles are listed in Table S1 of the Supporting Information.

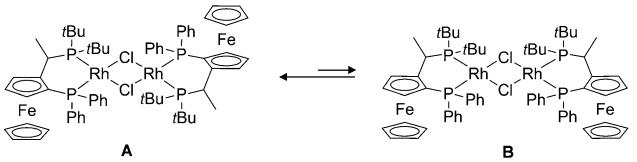
Although μ_2-Cl-bridged dinuclear rhodium complexes with either BINAP or SEGPHOS can be conveniently prepared in CH_2Cl_2, the latter is unsuitable for [{Rh(BICP)(μ_2-Cl)}$_2$] which, in this solvent, rearranges into an unidentified, unsymmetrical species.

Only very poor yields (ca. 5%) of [{Rh(BICP)(μ_2-Cl)}$_2$] are obtained if the nbd precursor **2** is used, whether in THF or toluene.

PPF-P*t*Bu$_2$

In situ prepared neutral complexes that contain the Josiphos derivative PPF-P*t*Bu$_2$ have been used in the ring-opening reaction of oxa- and azabicyclic alkenes.[6] The Merck Group applies this kind of in situ prepared complex in the industrial hydrogenation of an unprotected dehydro β-amino acid.[2c,35,36]

NMR spectroscopic analysis of a solution that contains **1** and two equivalents of PPF-P*t*Bu$_2$ in THF at room temperature revealed the presence of two species in a ratio of 73:27. The two species **A** and **B** (Scheme 3), in which the two diphosphine ligands have either the same or opposite orientation (*cis*/*trans*), such as has been described for a P,N ligand in the literature,[37] exhibit very similar NMR spectroscopic data in the ^{1}H, ^{31}P, as well as the ^{103}Rh NMR spectrum.



Scheme 3. Solution equilibrium between (**A**) *trans*- and (**B**) *cis*-[{Rh(PPF-P*t*Bu$_2$)(μ_2-Cl)}$_2$].

Recrystallization in THF/MeOH of the precipitate that resulted upon removal of the solvent from a solution of [{Rh(cod)(μ_2-Cl)}$_2$] and PPF-P*t*Bu$_2$ (1:2) in THF gave single crystals suitable for X-ray analysis. The molecular structure shown in Figure 7 indicates that the dimer **A** [{Rh(PPF-P*t*Bu$_2$)(μ_2-Cl)}$_2$], in which equivalent phosphorus are *trans* to each other, was isolated.

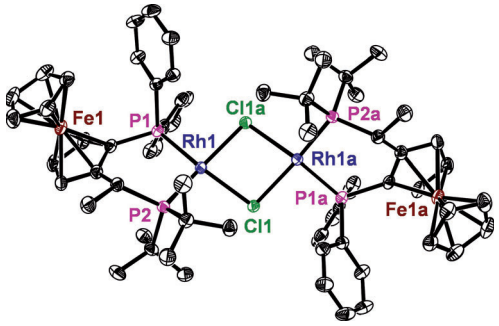


Figure 7. Molecular structure of [{Rh(PPF-P*t*Bu$_2$)(μ_2-Cl)}$_2$]; ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. See below for a short discussion of the structural data. Selected bond lengths and angles are listed in Table S1 of the Supporting Information.

When single crystals of **A** are dissolved in CH_2Cl_2, both species **A** and **B** are again detectable by ^{31}P NMR spectroscopy. Apparently, the isomers **A** and **B** are in equilibrium; NMR spectra recorded at variable low temperatures in THF can be found in the Supporting Information.

At variance with what has been observed with the ligands mentioned so far, which in no case led to a quantitative formation of the respective neutral dinuclear complexes when using the nbd precursor **2**, complex [{Rh(PPF-P*t*Bu$_2$)(μ_2-Cl)}$_2$] was formed quantitatively in THF at room temperature as a mixture of the two isomers **A** and **B** in a ratio of 73:27 (compare also Scheme 3).

Like the ligands discussed above, PPF-P*t*Bu$_2$ reacts with **2** in MeOH to give a cationic rhodium species [Rh(PPF-P*t*Bu$_2$)(nbd)]$^+$,[36] the molecular structure of which has been previously reported in the literature.[6b]

D*i*PPF

The molecular structure of the complex that contains the achiral ferrocene ligand D*i*PPF ([{Rh(D*i*PPF)(μ_2-Cl)}$_2$]), prepared in situ from **1** in THF as described above (97% yield), is shown in Figure 8.

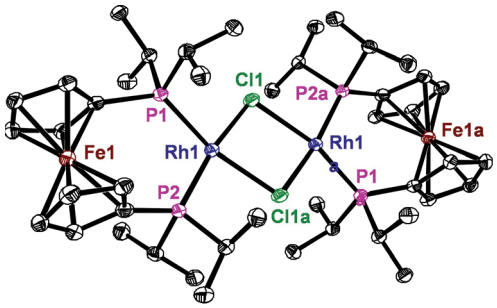


Figure 8. Molecular structure of [{Rh(D*i*PPF)(μ_2-Cl)}$_2$]; ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. See below for a short discussion of the structural data. Selected bond lengths and angles are listed in Table S1 of the Supporting Information.

DPPE

As reported by Bosnich et al., the in situ formation of [{Rh(DPPE)(μ_2-Cl)}$_2$] from **1** in toluene can only be achieved at elevated temperatures.[38] The hitherto unpublished molecular structure of [{Rh(DPPE)(μ_2-Cl)}$_2$], which is used as precatalyst for the aforementioned coupling of aldehydes and allenes,[14] is shown in Figure 9, right.

If the reaction is carried out at room temperature in THF, a precipitate is formed that accounts for more than 95% of the rhodium content. The precipitate could be identified as the known complex [Rh(DPPE)$_2$][Rh(cod)(Cl)$_2$].[39] Its molecular structure, in addition to the one reported in the literature,[39a] can be found in the Supporting Information. The ^{31}P NMR spectrum of the supernatant solution shows a doublet that could be assigned to the complex [(cod)Rh(μ_2-Cl)$_2$Rh(DPPE)]. The desired complex [{Rh(DPPE)(μ_2-Cl)}$_2$] was not formed at all.

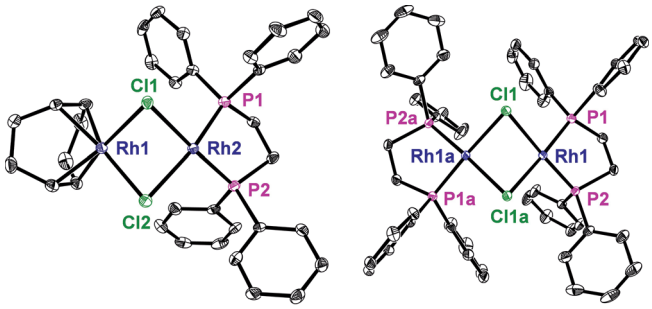


Figure 9. Molecular structure of [(cod)Rh(μ_2-Cl)$_2$Rh(DPPE)] (left); molecular structure of [{Rh(DPPE)(μ_2-Cl)}$_2$] (right); ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. See below for a short discussion of the structural data. Selected bond lengths and angles are listed in Table S1 and S2 of the Supporting Information).

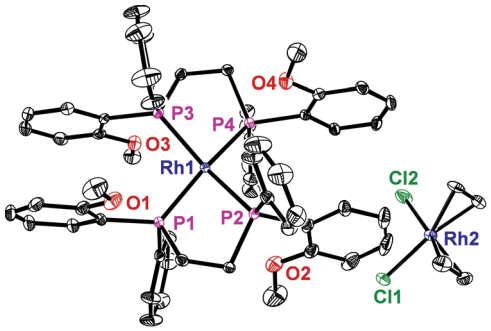


Figure 10. Molecular structure of [Rh(DIPAMP)$_2$][Rh(C_2H_4)$_2$(Cl)$_2$]; ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. See below for a short discussion of the structural data. Selected bond lengths and angles are listed in Table S3 of the Supporting Information.

Single crystals suitable for X-ray analysis could be isolated from the solution (Figure 9, left).

When the crystals are redissolved, an equilibrium analogous to the one described above for BINAP and SEGPHOS is established in solution (Scheme 2).

If the nbd precursor **2** is used instead of **1** under otherwise identical reaction conditions, a precipitate is formed as well, although in much lower amount, which was identified as the analogue complex [Rh(DPPE)$_2$][Rh(nbd)(Cl)$_2$] due to identical ^{31}P NMR spectrum and coordinated nbd found in the ^{1}H NMR. The hydrogen atoms of nbd are distinguisheable from the corresponding ones in the starting complex **2**.

The desired complex [{Rh(DPPE)(μ_2-Cl)}$_2$], which is soluble in THF, was obtained in approximately 89% yield according to the ^{31}P NMR spectrum of the homogeneous phase.[40] The in situ formation starting from **3** leads to 84% of the target complex [{Rh(DPPE)(μ_2-Cl)}$_2$] without the formation of a precipitate, which suggests that the coe complex **3** is a better precursor than the cod complex **1** and the nbd complex **2**, at least at room temperature.

The μ_2-OH-bridged precursor **4** seems to be unsuitable for the in situ preparation of [{Rh(DPPE)(μ_2-OH)}$_2$], which is formed in only 4% yield in THF at room temperature.[41]

DIPAMP

Upon addition of two equivalents of DIPAMP to **1** in THF at room temperature, a precipitate is formed that, analogously to DPPE, very likely is the ionic complex [Rh(DIPAMP)$_2$][Rh(cod)(Cl)$_2$]. The complex is much more soluble than the DPPE analogue. Two other species in addition to the ionic complex were detected in solution. As suggested by the comparison with the analogous complexes of DPPE, these are most probably the intermediate [(cod)Rh(μ_2-Cl)$_2$Rh(DIPAMP)] and the target compound [{Rh(DIPAMP)(μ_2-Cl)}$_2$], which, however, represents only 5% of the total rhodium content. The yield of [{Rh(DIPAMP)(μ_2-Cl)}$_2$] could be increased to 83% by very slow dropwise addition of the ligand to **1** at −90 °C.

As already observed with BINAP, SEGPHOS, BICP, and so forth, the ligand exchange with **1** in MeOH leads to the cationic complex [Rh(DIPAMP)(cod)]$^+$ as the main species (88%).

By the use of precursors **2**, **3**, and the μ_2-OH-bridged complex **4** and two equivalents of DIPAMP in THF, similar results were obtained. The target compound is formed in very poor yield (10% maximum), whereas, according to the ^{31}P NMR spectra, the main species obtained from the in situ synthesis (up to 94% yield) is the complex that contains the cation [Rh(DIPAMP)$_2$]$^+$.

Regardless of the solvent used (CH_2Cl_2, THF, *i*PrOH, MeOH, acetone), the ionic complex [Rh(DIPAMP)$_2$][Rh(C_2H_4)$_2$(Cl)$_2$] is mostly formed when using the ethylene complex [{Rh(C_2H_4)$_2$(μ_2-Cl)}$_2$] (**5**). Its molecular structure is shown in Figure 10.[42]

Although the cationic moiety of the complex is known, to the best of our knowledge the anion has not yet been reported. NMR spectra recorded at variable low temperatures in CH_2Cl_2 as well as ^{103}Rh NMR spectra of [Rh(DIPAMP)$_2$][Rh(C_2H_4)$_2$(Cl)$_2$] can be found in the Supporting Information.

Besides those with DPPE[39a] and 1,2-bis(dimethylphosphino)-ethane (DMPE),[43] the aforementioned complexes are the only examples reported so far that comprise a square-planar coordinated cation [Rh(PP)$_2$]$^+$ and anion [Rh(olefin)$_2$(Cl)$_2$]$^-$. A comparison of their structural features can be found in the Supporting Information.

DIOP

The in situ reaction of **1** with two equivalents of DIOP in THF at room temperature is not selective in affording the target compound [{Rh(DIOP)(μ_2-Cl)}$_2$] (36%). [(cod)Rh(μ_2-Cl)$_2$Rh(DIOP)] (2%) and other unidentified species are observed by NMR spectroscopic analysis of the resulting solution (see Figure 11). Neither CH_2Cl_2 nor acetone afforded better yields.[44]

However, we were able to show that by very slow addition of a solution of the ligand to **1** the yield of the target compound can be increased to about 80%. If the in situ synthesis is carried out in toluene at 125 °C, following the procedure described by Bosnich et al.,[38] the yield further improves to reach 90% (see the Supporting Information).[45]

In MeOH, the cationic complex [Rh(DIOP)(cod)]$^+$—probably with Cl$^-$ as the counterion—is formed in 87% yield, similarly to what observed with BINAP, SEGPHOS, BICP, and PPF-P*t*Bu$_2$. The identity of the compound could be established by com-

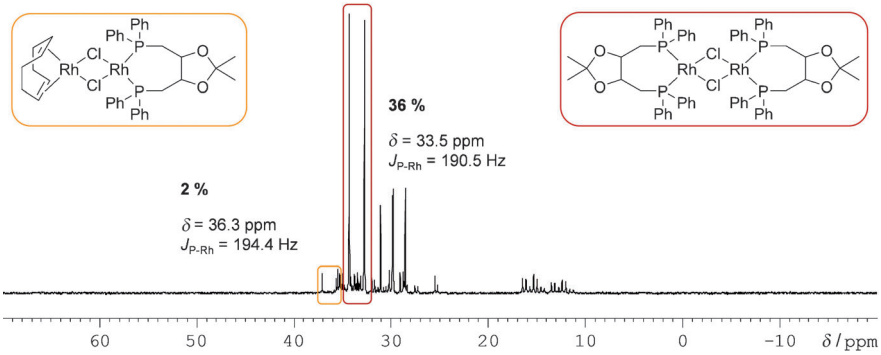


Figure 11. ^{31}P NMR spectrum of a solution of [{Rh(cod)(μ_2-Cl)}$_2$] (**1**) and two equivalents of DIOP in THF at room temperature.

parison of the spectroscopic data with those reported in several publications.[46]

With the nbd complex **2** and two equivalents of DIOP at room temperature in THF, only 1% of the target compound [{Rh(DIOP)(μ_2-Cl)}$_2$] is formed. The highest yield in THF at room temperature (74%) was obtained using the coe precursor **3**.

Me-DuPHOS

Addition of Me-DuPHOS to [{Rh(cod)(μ_2-Cl)}$_2$] (**1**) in a ratio of 2:1 in THF at room temperature similarly resulted in the formation of more than one species. These, however, could be identified as the target compound [{Rh(Me-DuPHOS)(μ_2-Cl)}$_2$] (62%),[47] the intermediate [(cod)Rh(μ_2-Cl)$_2$Rh(Me-DuPHOS)], and the cationic complex [Rh(Me-DuPHOS)$_2$]$^+$. Regardless of the use of precursor **1**, **2**, or **3**, the reaction with two equivalents of Me-DuPHOS always affords the cationic complex as suggested by ^{31}P NMR spectroscopy. The molecular structure of [{Rh(Me-DuPHOS)(μ_2-Cl)}$_2$] and the corresponding ^{31}P NMR spectrum are shown in Figure 12.

The formation of the cationic rhodium bis(diphosphine) complex [Rh(diphosphine)$_2$]$^+$ is an undesired side reaction in the in situ synthesis of [{Rh(diphosphine)(μ_2-Cl)}$_2$]. It can be suppressed, at least in this case, by lowering the reaction temperature and by adding the ligand very slowly. Indeed, when the synthesis was carried out at −78 °C, [{Rh(Me-DuPHOS)(μ_2-Cl)}$_2$] was obtained in quantitative yield.

A similar behavior was observed when using the nbd and coe precursors **2** and **3** at room temperature. They afford the desired product in 56 and 82% yield, respectively, together with the known cationic complex [Rh(Me-DuPHOS)$_2$]$^+$, in 41 and 12% yield, respectively.

If **4** is used as the rhodium source, the in situ procedure is less efficient. The yield of [{Rh(Me-DuPHOS)(μ_2-OH)}$_2$] is at best 40% and less selective. In fact, a number of unidentified species are formed.

DPPB

Only traces of the desired complex [{Rh(DPPB)(μ_2-Cl)}$_2$] are formed by treating the cod complex **1** with two equivalents of achiral DPPB, whether at room temperature in THF or at elevated temperature (125 °C) in toluene.[38] Several unidentified complexes were detected as shown in Figure 13a.

At room temperature in THF, precursor **2** quantitatively leads to the formation of just one species, which, however, was identified as the monomeric pentacoordinated neutral complex [Rh(DPPB)(nbd)(Cl)][26], Figure 13b.

The best precursor for the in situ synthesis of [{Rh(DPPB)(μ_2-Cl)}$_2$] is the coe complex **3**, which, under the same reaction conditions, provided quantitative yield (99%) of the desired complex, Figure 13c.

Equally unselective are the in situ procedures that rely on **4**. In THF at room temperature, the target compound accounts for only 13% of the rhodium content. In toluene, under otherwise identical conditions, the yield did not exceed 45%.

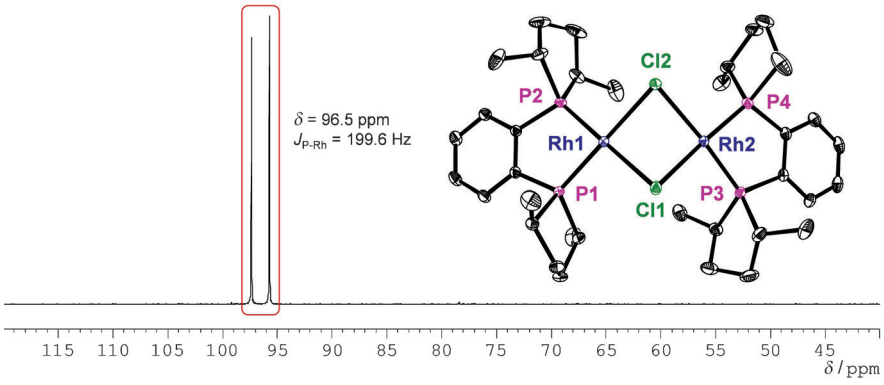


Figure 12. ^{31}P NMR spectrum of the solution obtained by dissolving crystals of [{Rh(Me-DuPHOS)(μ_2-Cl)}$_2$] in THF at room temperature and the X-ray structure of [Rh{(*S*,*S*)-Me-DuPHOS}(μ_2-Cl)}$_2$] (ORTEP, 30% probability ellipsoids). Hydrogen atoms are omitted for clarity. See below for a short discussion of the structural data. Selected bond lengths and angles are listed in Table S1 of the Supporting Information.

DPPP

The reaction of **1** with two equivalents of achiral DPPP in THF at room temperature, a procedure that is applied for the in situ formation of the catalyst precursor in, for example, the Pauson–Khand-type reaction of enynes,[11b] affords the target compound [{Rh(DPPP)(μ_2-Cl)}$_2$] (44%) and the monomeric pentacoordinated neutral complex [Rh(DPPP)(cod)(Cl)] (50%). Both complexes have been fully characterized by X-ray analysis and NMR spectroscopy.[26]

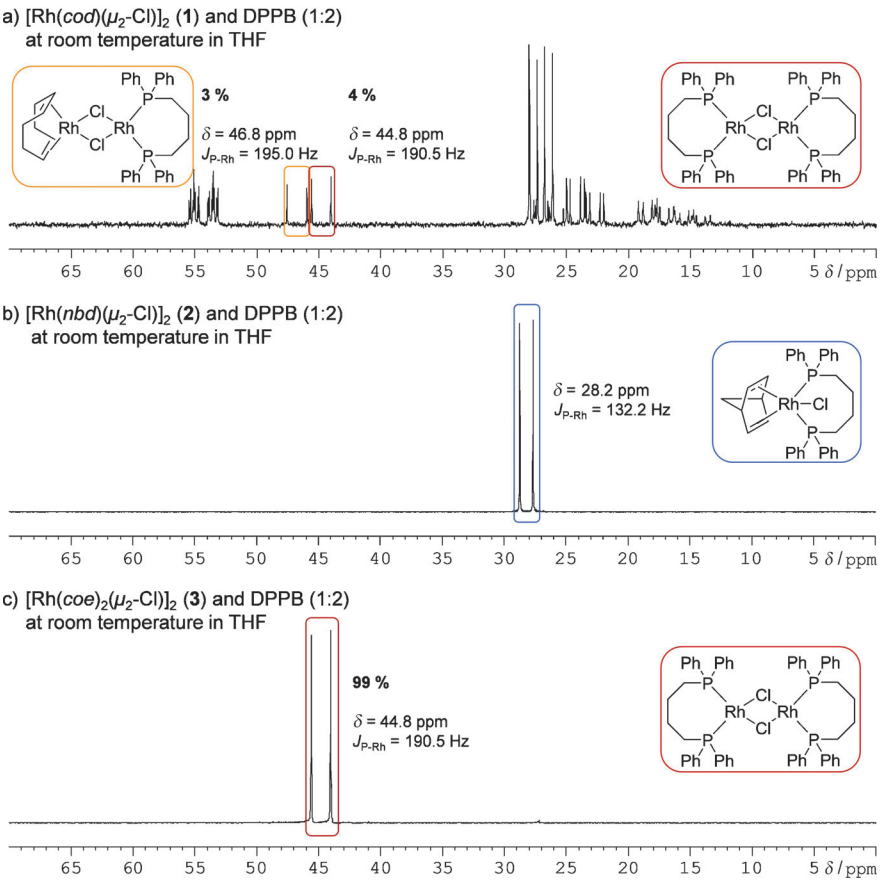


Figure 13. ^{31}P NMR spectra of the reaction solution of the in situ ligand exchange of a) [{Rh(cod)(μ_2-Cl)}$_2$] (**1**), b) [{Rh(nbd)(μ_2-Cl)}$_2$] (**2**), and c) [{Rh(coe)$_2$(μ_2-Cl)}$_2$] (**3**) with DPPB (1:2) in THF at room temperature.

Like the case of DPPB, the reaction of the nbd complex **2** with DPPP in THF quantitatively leads to a single complex, the corresponding monomeric pentacoordinated neutral complex [Rh(DPPP)(nbd)(Cl)].

Even in this case, however, the target compound [{Rh(DPPP)(μ_2-Cl)}$_2$] can be successfully synthesized in 98% yield starting from the coe complex **3** under otherwise identical conditions. When the DPPP ligand is used in substoichiometric amounts (**3**/DPPP 1:1) in THF at room temperature, the conversion apparently is not complete, as shown by the ^{31}P NMR spectrum. The formation of the target compound (3%), the presence of the precursor (3%), and the absence of free ligand in solution suggest that an equilibrium like the one already described for BINAP and SEGPHOS (Scheme 2) is actually established.

As already shown in the case of DPPB, the use of the μ_2-OH-bridged complex **4** affords [{Rh(DPPP)(μ_2-OH)}$_2$] in just 17% yield.

Structural details

Characteristic bond lengths and angles of six neutral complexes with the general formula [{Rh(diphosphine)(μ_2-Cl)}$_2$] described in this study are collected in Table S1 in the Supporting Information. Also included are the values that refer to six analogue neutral complexes that have been found in the Cambridge Structural Database.

The rhodium complexes display a distorted square-planar coordination geometry. The Rh–P bond lengths fall in the expected range between 2.176(1) and 2.241(1) Å. In the case of the C_1-symmetric ligand PPF-P*t*Bu$_2$, in which the two phosphorus donors possess different electronic properties, the two Rh–P distances are clearly different in the complex.

The bite angles (P-Rh-P) fall in the range between 75.23(10)° for the bidentate ligands in [{Rh(D*t*BPM)(μ_2-Cl)}$_2$] (YUWFEB; D*t*BPM = bis(di-*tert*-butylphosphino)methane)[48] and 100.29(4)° in [{Rh(D*i*PPF)(μ_2-Cl)}$_2$]. The bite angles in the seven-membered chelated complexes that contain BINAP, SEGPHOS, and BICP are around 90°. The Rh–Rh distances fall between 3.025(1) (DPPE) and 3.718(2) Å (D*i*PPF). The longest distance reported so far, 3.511 Å, was found in the analogous complex that contains the MeO-F$_{12}$-BIPHEP ligand.[49] The authors explain the weakening of the interaction between Rh···Rh as a consequence of the less σ-donating ability of the phosphorus donors, which is unfavorable for the d_{z^2} orbital of Rh.

Characteristic bond lengths and angles of the intermediates with the general formula [(diolefin)Rh(μ_2-Cl)$_2$Rh(diphosphine)] described in this study are collected in Table S2 of the Supporting Information. The Rh–P distances as well as the bite angles are comparable to those found in the complexes reported in Tables S1 and S2 of the Supporting Information. Quite impressive is the increase in the Rh–Rh distance from 3.287(1) Å in [{Rh(BINAP)(μ_2-Cl)}$_2$] to 3.581(1) Å in [(cod)Rh(μ_2-Cl)$_2$Rh(BINAP)]. This is clearly caused by an increase of the angle between the planes Cl-Rh1-Cl/Cl-Rh2-Cl from 126.18 to 168.40(4)°. The reason for this structural modification is not clear; in the case of the complexes [{Rh(DPPE)(μ_2-Cl)}$_2$]/[(cod)Rh(μ_2-Cl)$_2$Rh(DPPE)], the Rh–Rh distances are, on the contrary, very similar.

Conclusion

The results of the systematic investigations reported above show that the commonly applied in situ method for the preparation of neutral Rh complexes of the type [{Rh(PP)(μ_2-X)}$_2$] by addition of two equivalents of disphosphine ligand to precursors **1**–**5** might not be considered as straightforward and selective as generally thought. The outcome of the in situ proce-

dure, which is applied in a plethora of catalytic processes, is strongly affected by the nature of the diolefin present in the catalyst precursor used as the rhodium source, the ancillary (diphosphine) ligand, the solvent, and the temperature.

The results show that the expected neutral complexes are obtained quantitatively just with a couple of ligands under selected conditions. For example, in THF at room temperature the yield in the desired complex is practically quantitative with the ligands BINAP, SEGPHOS, DM-SEGPHOS, BICP, PPF-P*t*Bu$_2$, and D*i*PPF if the cod precursor **1** is used. Under otherwise identical conditions the best precursor is coe complex **3** for DPPB and DPPP as ligands.

However, our results show that, depending on the reaction conditions, either different rhodium species exist simultaneously (e.g., DIPAMP) or in some cases unexpected complexes are formed in quantitative yield (e.g., DPPB or DPPP). The general structures of such unexpected complexes, which were characterized by NMR spectroscopy and, where possible, also by X-ray analysis, are the following: [(diolefin)Rh(μ_2-Cl)$_2$Rh(diphosphine)], [Rh(diphosphine)(diolefin)]$^+$, [Rh(diphosphine)$_2$]$^+$, and [Rh(diphosphine)(diolefin)(Cl)].[50] They are depicted in Scheme 4.

Another important issue for catalysis is the temperature at which the reaction is performed, since the nature of the species that arises from the in situ synthesis of the catalyst precursor also depends on the temperature. This influence of temperature on the course of such in situ synthesis is strikingly evident in the case of ligands DPPE and Me-DuPHOS. The formation of [{Rh(Me-DuPHOS)(μ_2-Cl)}$_2$] from **1** in THF is quantitative only if the reaction is carried out at −78 °C, whereas that of [{Rh(DPPE)(μ_2-Cl)}$_2$] requires 125 °C.

Last but not least to affect the course of the in situ formation of the rhodium species is the solvent, as shown, for example, for BINAP (Figure 3). A large number of catalytic reactions are carried out in CH_2Cl_2. Based on our experience, mixtures of unknown species often resulted if CH_2Cl_2 was used. Instead the in situ procedure carried out in MeOH always led to cationic complexes, which were frequently formed in quantitative yield.

The result of the in situ formation of the active species mainly determines the outcome of the subsequent catalysis. If several metal species are formed, the activity as well as the selectivity of the catalytic process will be affected, since it cannot be assumed that different rhodium complexes all promote the same reaction mechanism.

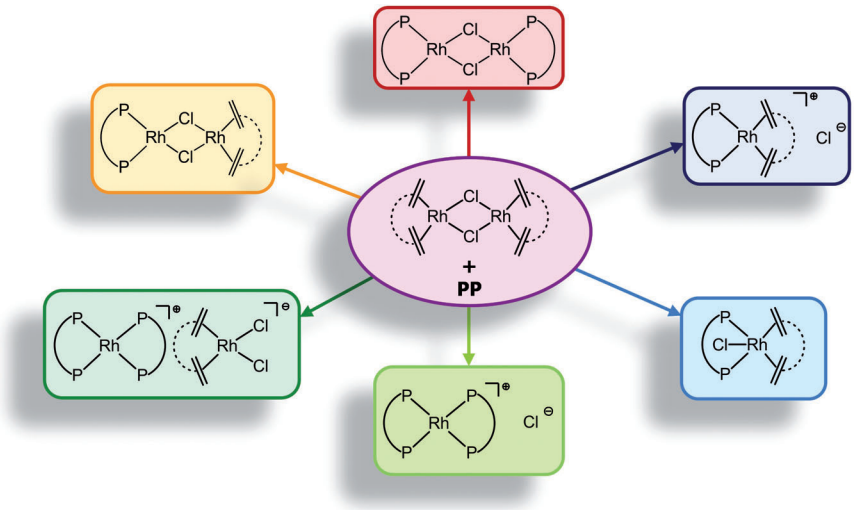
Although it is not possible to define a common behavior for the formation of the complexes described above, it is still possible to recognize some trends:

1) The exchange of the diolefins in the catalyst precursor proceeds stepwise and, as the results presented so far prove, the first diolefin is replaced considerably faster than the second one.
2) In MeOH such exchange unexpectedly affords complexes of the type [Rh(diphosphine)(diolefin)]$^+$.
3) An equilibrium exists, not yet described, between the intermediate product of such exchange on one side and the catalyst precursor and desired product on the other.

On the basis of the above results, it might be concluded that special care should be taken in the evaluation of catalyst performance in those processes that rely on the in situ technique for "catalyst" preparation. This is because the actual catalyst might either be only one of several species present in solution or, in the worst case, not the expected one.

Acknowledgements

We thank Dr. Elisabetta Alberico (Istituto di Chimica Biomolecolare, CNR, Italy) for helpful discussions and the DFG for financial support. We thank Takasago International Corporation for generously supplying us with the SEGPHOS, DM-SEGPHOS, and DTBM-SEGPHOS ligands.



Scheme 4. Observed rhodium complexes formed through the in situ synthesis of [{Rh(diphosphine)(μ_2-X)}$_2$] (PP = diphosphine).

Keywords: cations · ligand effects · P ligands · rhodium · solvent effects

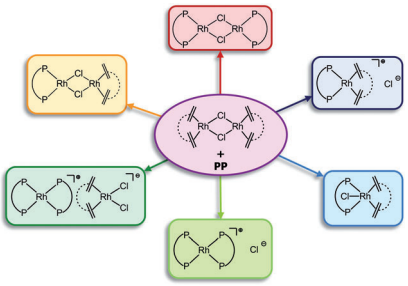
[1] D. Heller, A. H. M. de Vries, J. G. de Vries in *Homogeneous Hydrogenation* (Eds.: J. G. de Vries, C. Elsevier), Wiley-VCH, Weinheim, **2007**, Chapter 44, pp. 1483 – 1516.
[2] a) Y. Hsiao, N. R. Rivera, T. Rosner, S. W. Krska, E. Njolito, F. Wang, Y. K. Sun, J. D. Armstrong III, E. J. J. Grabowski, R. D. Tillyer, F. Spindler, C. Malan, *J. Am. Chem. Soc.* **2004**, *126*, 9918 – 9919; b) H. B. Kagan, T. P. Dang, *J. Am. Chem. Soc.* **1972**, *94*, 6429 – 6433; for industrial applications, see: c) C. S. Shultz, S. W. Krska, *Acc. Chem. Res.* **2007**, *40*, 1320 – 1326; d) G. Beck, *Synlett* **2002**, *6*, 837 – 850; e) H. Jendralla, B. Seuring, J. Herchen, B. Kulitzscher, J. Wunner, W. Stüber, R. Ko-

schinsky, *Tetrahedron* **1995**, *51*, 12047 – 12068.
[3] a) J.-F. Carpentier, A. Mortreux, *Tetrahedron: Asymmetry* **1997**, *8*, 1083 – 1099; b) A. Roucoux, L. Thieffry, J.-F. Carpentier, M. Devocelle, C. Meliet, F. Agbossou, A. Mortreux, *Organometallics* **1996**, *15*, 2440 – 2449.
[4] W. Leitner, E. Dinjus, F. Gaßner, *J. Organomet. Chem.* **1994**, *475*, 257 – 266.
[5] T. J. Kim, K. C. Lee, *Bull. Korean Chem. Soc.* **1989**, *10*, 279 – 282.
[6] a) G. C. Tsui, M. Lautens, *Angew. Chem.* **2012**, *124*, 5496 – 5500; *Angew. Chem. Int. Ed.* **2012**, *51*, 5400 – 5404; b) A. Preetz, C. Kohrt, H.-J. Drexler, A. Torrens, H. Buschmann, M. G. Lopez, D. Heller, *Adv. Synth. Catal.* **2010**, *352*, 2073 – 2080; c) K. Fagnou in *Modern Rhodium-Catalyzed Organic Reactions* (Ed.: P. A. Evans), Wiley-VCH, Weinheim **2005**, Chapter 9, pp. 173 – 190; d) M. Lautens, K. Fagnou, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5455 – 5460.
[7] a) C.-W. Cho, M. J. Krische in *Handbook of Homogeneous Hydrogenation* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim **2007**, Chapter 22, pp. 713 – 741; b) H.-Y. Jang, M. J. Krische, *Acc. Chem. Res.* **2004**, *37*, 653 – 661.
[8] a) U. Gellrich, A. Meißner, A. Steffani, M. Kähny, H.-J. Drexler, D. Heller, D. A. Plattner, B. Breit, *J. Am. Chem. Soc.* **2014**, *136*, 1097 – 1104; b) C. Li, B. Breit, *J. Am. Chem. Soc.* **2014**, *136*, 862 – 865; c) S. Wei, J. Pedroni, A. Meißner, A. Lumbroso, H.-J. Drexler, D. Heller, B. Breit, *Chem. Eur. J.* **2013**, *19*, 12067 – 12076; d) P. Koschker, A. Lumbroso, B. Breit, *J. Am. Chem. Soc.* **2011**, *133*, 20746 – 20749; e) A. Lumbroso, P. Koschker, N. R. Vautravers, B. Breit, *J. Am. Chem. Soc.* **2011**, *133*, 2386 – 2389; f) A. Lumbroso, N. R. Vautravers, B. Breit, *Org. Lett.* **2010**, *12*, 5498 – 5501.
[9] G. Makado, T. Morimoto, Y. Sugimoto, K. Tsutsumi, N. Kagawa, K. Kakiuchi, *Adv. Synth. Catal.* **2010**, *352*, 299 – 304.
[10] a) T. Morimoto, M. Fujioka, K. Fuji, K. Tsutsumi, K. Kakiuchi, *J. Organomet. Chem.* **2007**, *692*, 625 – 634; b) K. Fuji, T. Morimoto, K. Tsutsumi, K. Kakiuchi, *Chem. Commun.* **2005**, 3295 – 3297.
[11] a) K. Fuji, T. Morimoto, K. Tsutsumi, K. Kakiuchi, *Tetrahedron Lett.* **2004**, *45*, 9163 – 9166; b) K. Fuji, T. Morimoto, K. Tsutsumi, K. Kakiuchi, *Angew. Chem.* **2003**, *115*, 2511 – 2513; *Angew. Chem. Int. Ed.* **2003**, *42*, 2409 – 2411.
[12] D. M. Ohlmann, L. J. Gooßen, M. Dierker, *Chem. Eur. J.* **2011**, *17*, 9508 – 9519.
[13] F. Inagaki, K. Sugikubo, Y. Oura, C. Mukai, *Chem. Eur. J.* **2011**, *17*, 9062 – 9065.
[14] T. Toyoshima, T. Miura, M. Murakami, *Angew. Chem.* **2011**, *123*, 10620 – 10623; *Angew. Chem. Int. Ed.* **2011**, *50*, 10436 – 10439.
[15] T. Hayashi, M. Takahashi, Y. Takaya, M. Ogasawara, *J. Am. Chem. Soc.* **2002**, *124*, 5052 – 5058.
[16] K. A. Bunten, D. H. Farrar, A. J. Poë, A. Lough, *Organometallics* **2002**, *21*, 3344 – 3350.
[17] All spectra, further comments, and other information that support our conclusions are to be found in the Supporting Information.
[18] The molecular structure of [{Rh(BINAP)(μ_2-Cl)}$_2$]—single crystals were isolated from CH_2Cl_2—has already been reported in reference [16].
[19] G. E. Ball, W. R. Cullen, M. D. Fryzuk, B. R. James, S. J. Rettig, *Organometallics* **1991**, *10*, 3767 – 3769.
[20] T. Morimoto, K. Yamasaki, A. Hirano, K. Tsutsumi, N. Kagawa, K. Kakiuchi, Y. Harada, Y. Fukumoto, N. Chatani, T. Nishioka, *Org. Lett.* **2009**, *11*, 1777 – 1780. This complex was wrongly assigned as [{Rh(BINAP)(μ_2-Cl)}$_2$].
[21] C. Kunze, D. Selent, I. Neda, M. Freytag, P. G. Jones, R. Schmutzler, W. Baumann, A. Börner, *Z. Anorg. Allg. Chem.* **2002**, *628*, 779 – 787. An analogous complex that contains a phosphonite ligand is described.
[22] C. Fischer, A. König, A. Meißner, R. Thede, C. Selle, D. Heller, *Eur. J. Inorg. Chem.* **2014**, DOI: 10.1002/ejic.201402787
[23] C. Fischer, T. Beweries, A. Preetz, H.-J. Drexler, W. Baumann, S. Peitz, U. Rosenthal, D. Heller, *Catal. Today* **2010**, *155*, 282 – 288.
[24] As a result, the color change often observed during the in situ procedure (e.g., from orange to red for **1** as starting complex and BINAP as ligand) does not necessarily account for the formation of the desired target complex, but rather only for the formation of the intermediate [(diolefin)Rh(μ_2-Cl)$_2$Rh(diphosphine)].
[25] a) C. A. Busacca, R. Raju, N. Grinberg, N. Haddad, P. James-Jones, H. Lee, J. C. Lorenz, A. Saha, C. H. Senanayake, *J. Org. Chem.* **2008**, *73*, 1524 – 1531; b) T. Shimada, H. Kurushima, Y.-H. Cho, T. Hayashi, *J. Org. Chem.* **2001**, *66*, 8854 – 8858; For *Rh complexes* with oxidized BINAP see: c) A. Meissner, C. Selle, H.-J. Drexler, D. Heller, *Acta Crystallogr. Sect. E* **2012**, *68*, m259; d) S. Gladiali, S. Medici, T. Kegl, L. Kollar, *Monatsh. Chem.* **2000**, *131*, 1351 – 1361 and Ref. [16].
[26] A. Meissner, A. König, H.-J. Drexler, R. Thede, W. Baumann, D. Heller, *Chem. Eur. J.* **2014**, DOI: 10.1002/chem.201402816..
[27] a) A. Preetz, H.-J. Drexler, S. Schulz, D. Heller, *Tetrahedron: Asymmetry* **2010**, *21*, 1226 – 1231; b) A. Preetz, H.-J. Drexler, C. Fischer, Z. Dai, A. Börner, W. Baumann, A. Spannenberg, R. Thede, D. Heller, *Chem. Eur. J.* **2008**, *14*, 1445 – 1451.
[28] For monodentate phosphines this has been known for a long time: J. R. Shapley, R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1969**, *91*, 2816 – 2817.
[29] This value is approximated as the other species remains unknown and might be either a mono- or a multinuclear rhodium complex. Therefore each signal might account for one or more phosphorus nuclei depending on the nature of such species.
[30] K. Motokura, K. Nakayama, A. Miyaji, T. Baba, *ChemCatChem* **2011**, *3*, 1419 – 1421.
[31] A. Meißner, H.-J. Drexler, S. Keller, C. Selle, V. Ratovelomanana-Vidal, D. Heller, *Eur. J. Inorg. Chem.* **2014**, DOI: 10.1002/ejic.201402324.
[32] J. A. Osborn, R. R. Schrock, *J. Am. Chem. Soc.* **1971**, *93*, 2397 – 2407.
[33] P. Cao, X. Zhang, *Angew. Chem.* **2000**, *112*, 4270 – 4272; *Angew. Chem. Int. Ed.* **2000**, *39*, 4104 – 4106.
[34] A. Meissner, C. Pribbenow, H.-J. Drexler, D. Heller, *Acta Crystallogr. Sect. C* **2014**, DOI: 10.1107/S205322961401910X.
[35] H.-U. Blaser, B. Pugin, F. Spindler, *Organometallics as Catalysts in the Fine Chemical Industry* in Topics in Organometallic Chemistry (Eds.: M. Beller, H.-U. Blaser), Springer, Berlin, **2012**, *42*, 65 – 102.
[36] The solvent used for the industrial application is MeOH. As shown above for other ligands, no neutral but rather cationic species are built up in this solvent.
[37] N. Feiken, P. Pregosin, G. Trabesinger, *Organometallics* **1998**, *17*, 4510 – 4518.
[38] D. P. Fairlie, B. Bosnich, *Organometallics* **1988**, *7*, 936 – 945.
[39] a) S. I. Lee, S. Y. Park, J. H. Park, Y. K. Chung, J. W. Han, *Bull. Korean Chem. Soc.* **2007**, *28*, 1919 – 1920; other molecular structures of the cation can be found in: b) R. W. Bowen, E. M. Coyanis, M. Layh, R. Meijboom, C. B. Poole, *Acta Crystallogr. Sect. E* **2006**, *62*, m101 – m102; c) R. Dorta, L. Shimon, D. Milstein, *J. Organomet. Chem.* **2004**, *689*, 751 – 758; d) C. Pettinari, F. Marchetti, R. Pettinari, A. Pizzabiocca, A. Drozdov, S. I. Troyanov, *J. Organomet. Chem.* **2003**, *688*, 216 – 226; for the anion, see: e) A. P. Martínez, M. P. García, F. J. Lahoz, L. A. Oro, *Inorg. Chim. Acta* **2003**, *347*, 86 – 98; f) P. Imhoff, C. J. J. Elsevier, *J. Organomet. Chem.* **1989**, *361*, C61 – C65; g) M. A. Esteruelas, L. A. Oro, M. C. Apreda, C. Foces-Foces, F. H. Cano, R. M. Claramunt, C. Lopez, J. Elguero, M. Begtrup, *J. Organomet. Chem.* **1988**, *344*, 93 – 108.
[40] Owing to the small amounts handled in the experiment, it was very difficult to exactly determine the amount of precipitated solid.
[41] C. Krug, J. F. Hartwig, *Organometallics* **2004**, *23*, 4594 – 4607; [{Rh(DPPE)(μ_2-OH)}$_2$]: ^{31}P NMR (202.4 MHz, C_6D_6): $\delta = 74.4$ ppm (d, $J = 190$ Hz).
[42] The ethylene molecules coordinated to rhodium in the anion were only detectable in the ^{1}H NMR spectrum at low temperature. See the Supporting Information.
[43] M. Block, S. Gomez-Ruiz, D. Steinborn, *Acta Crystallogr. Sect. E* **2008**, *64*, m1405.
[44] D. Slack, I. Greveling, M. C. Baird, *Inorg. Chem.* **1979**, *18*, 3125 – 3132. (According to this reference, at room temperature in acetone only the neutral complex is present.)
[45] By simple recrystallization—that is, from *i*PrOH—[{Rh(DIOP)(μ_2-Cl)}$_2$] can be isolated as a pure compound.
[46] A. Fabrello, C. Dinoi, L. Perrin, P. Kalck, L. Maron, M. Urrutigoity, O. Dechy-Cabaret, *Magn. Reson. Chem.* **2010**, *48*, 848 – 856 and references cited therein.
[47] [{Rh(Me-DuPHOS)(μ_2-Cl)}$_2$], like other dinuclear complexes, is surprisingly air-sensitive. After just 10 min exposure of the solid to air, 24% of the ligand is oxidized. See also: A. Côté, A. A. Boezio, A. B. Charette, *Angew. Chem.* **2004**, *116*, 6687 – 6690; *Angew. Chem. Int. Ed.* **2004**, *43*, 6525 – 6528. (Literature: $\delta = 72.3$ ppm in MeOH; this study, $\delta = 69.6$ ppm in THF.)
[48] P. Hofmann, C. Meier, W. Hiller, M. Heckel, J. Riede, M. U. Schmidt, *J. Organomet. Chem.* **1995**, *490*, 51 – 70.

[49] T. Korenaga, K. Osaki, R. Maenishi, T. Sakai, *Org. Lett.* **2009**, *11*, 2325 – 2328.
[50] Similar observations were found for the ligand-exchange process with [Rh(cod)(acac)] as starting material and diphosphine ligands, which leads to five-membered chelate ring complexes (e.g., DPPE, DIPAMP, Me-DuPHOS). As described here, the formation of the cationic complex $[Rh(PP)_2]^+$ can be avoided by slow addition of the ligand at low temperature (−78 °C). See: K. Angermund, W. Baumann, E. Dinjus, R. Fornika, H. Görls, M. Kessler, C. Krüger, W. Leitner, F. Lutz, *Chem. Eur. J.* **1997**, *3*, 755 – 764.

Received: July 8, 2014
Revised: August 18, 2014
Published online on ■■ ■■, 0000

Rh revisited: The commonly applied in situ method for the preparation of neutral Rh complexes of the type $[\{Rh(PP)(\mu_2\text{-}X)\}_2]$ by addition of diphosphine ligand (2 equiv) to different rhodium precursors might not be as straightforward and selective as generally thought. The outcome is strongly affected by the nature of the diolefin present in the ancillary (diphosphine) ligand, the catalyst precursor, the solvent, and the temperature (see figure).



*A. Meißner, A. Preetz, H.-J. Drexler, W. Baumann, A. Spannenberg, A. König, D. Heller**

■■ – ■■

In Situ Synthesis of Neutral Dinuclear Rhodium Diphosphine Complexes $[\{Rh(diphosphine)(\mu_2\text{-}X)\}_2]$: Systematic Investigations