



# Oxidative addition of CH<sub>2</sub>Cl<sub>2</sub> to neutral dimeric rhodium diphosphine complexes

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## ABSTRACT

Neutral dimeric rhodium diphosphine complexes are often employed as catalytic precursors in the presence of the solvent CH<sub>2</sub>Cl<sub>2</sub>. The possibility of a collateral reaction between the solvent and the catalytic precursor is never considered as the activation of CH<sub>2</sub>Cl<sub>2</sub> by [Rh<sub>2</sub>(PP)<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>2</sub>] complexes is reputed difficult and uncommon. Herein we report the easy formation of three neutral dimeric Rh(III) complexes containing DPPP, DPPB and TangPhos through CH<sub>2</sub>Cl<sub>2</sub> activation as an extension of the few examples reported so far. The system [Rh<sub>2</sub>(DPPP)<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>2</sub>]/CH<sub>2</sub>Cl<sub>2</sub> has been selected for a detailed mechanistic investigation. Kinetic studies based on <sup>31</sup>P NMR monitoring combined with metathesis experiments reveal the fundamental role of a 14-electron intermediate [Rh(PP)Cl], which is involved in the CH<sub>2</sub>Cl<sub>2</sub> activation.

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## 1. Introduction

Dimeric rhodium(I) complexes of the type [Rh<sub>2</sub>(olefin)<sub>n</sub>(μ<sub>2</sub>-Cl)<sub>2</sub>] (olefin usually cod = 1,5-cyclooctadiene, nbd = 2,5-norbornadiene or coe = cyclooctene, n = 2 or 4) in combination with bidentate phosphorus ligands are often employed as catalytic precursors in homogeneous catalysis. Some recent applications of such systems include the hydrogenation of prochiral olefins [1], the ring opening of oxa- and azabicyclic alkenes [2], the hydrogen-mediated formation of C-C bonds [3], the addition of carboxylic acids to alkynes [4], the hydroamination of alkynes [5], the CO-gas-free hydroformylation [6] and carbonylations [7], the hydrothiolation of amines and imines [8], Pauson–Khand reactions [9], the olefin isomerization [10], cycloadditions [11], the coupling of aldehydes and allenes [12], and the 1,4-addition of organoboronic acids [13]. The employment of [Rh<sub>2</sub>(olefin)<sub>n</sub>(μ<sub>2</sub>-Cl)<sub>2</sub>] and diphosphine ligands in CH<sub>2</sub>Cl<sub>2</sub> is not uncommon, as for example in the hydrogenation of 1,2-dicyanoalkenes [14] and α,β-unsaturated

nitriles [15], or in the addition of carboxylic acids to terminal alkynes [4f].

Most of the times the active catalytic species are generated “*in situ*” and optimization of these systems is carried out on the basis of the catalytic outcome without any deep investigation of the real catalytic active species and of the possible activation and deactivation pathways [16].

The behavior of these systems in “*in situ*” conditions can be very complex. We previously reported the formation of different dimeric and monomeric complexes when [Rh<sub>2</sub>(diolefin)<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>2</sub>] precursors react with diphosphine ligands. In particular we found that the structure of these derivatives and their concentration in solution are strongly related to the diphosphine, to the diolefin (olefine), to the solvent, to the temperature and to the reaction time [17].

An adjunctive complication in this kind of systems could arise when halogenated solvents are employed; in fact C-X activation (X = halogen) by Rh(I) derivatives and oxidative addition are possible in that circumstances [18]. Also in the presence of halides, the formation of trinuclear complexes can represent an additional issue [19].

Activation of CH<sub>2</sub>Cl<sub>2</sub> by rhodium complexes of the type [Rh<sub>2</sub>(PP)<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>2</sub>] (PP = diphosphine ligand) is uncommon and

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restricted to the case of DPPE (DPPE = 1,2-bis(diphenylphosphino)ethane) [20].

Concerning monomeric Rh(I)/diphosphine complexes, oxidative addition of  $\text{CH}_2\text{Cl}_2$  on rhodium- $\beta$ -diketonate/diphosphine derivatives was described by Budzelaar and coworkers in the case of DPPM (DPPM = 1,1-bis(diphenylphosphino)methane), DPPE and DPPP (1,3-bis(diphenylphosphino)propane) [21], while Marder and coworkers have published a case of oxidative addition on the complex  $[\text{Rh}(\text{DMPE})_2\text{Cl}]$  (DMPE = 1,2-bis(dimethylphosphino)ethane) [22]. The activation of halo-benzenes by cationic monomeric bis(phosphane)rhodium complexes like  $[\text{Rh}(\text{DIPAMP})(\text{MeOH})_2]\text{BF}_4$  (DIPAMP = ethane-1,2-diylbis[(2-methoxyphenyl)phenylphosphine]) was recently reported by our research group [23]. The oxidative addition of aryl bromides and chlorides to the cationic rhodium complex  $[\text{Rh}(\text{P}^t\text{Bu}_3)_2\text{H}_2][\text{BAR}^F_4]$  was investigated by Weller and coworkers [24].

The mechanism of  $\text{CH}_2\text{Cl}_2$  activation by neutral dimeric rhodium complexes stabilized by diphosphine ligands is still unclear. In this regard Kempe and coworkers proposed a possible pathway for *P*-functionalized aminopyridine rhodium(I) complexes generated *in situ* by combining P-N ligands with  $[\text{Rh}_2(\text{cod})_2(\mu_2\text{-Cl})_2]$ . The authors suggested the *in situ* formation of a pentacoordinated complex  $[\text{Rh}(\text{PN})(\text{cod})\text{Cl}]$  which undergoes oxidative addition of  $\text{CH}_2\text{Cl}_2$ , and postulated the presence of a Rh(III) key intermediate of the type  $[\text{Rh}(\text{PN})(\text{CH}_2\text{Cl})\text{Cl}_2]$  [25].

A different mechanism involving a mixed valence intermediate dimer in a three-fragment four-electron oxidative addition was proposed by Oro and coworkers in the case of Rh/pyrazolate complexes [26].

In the present work the known oxidative addition of  $\text{CH}_2\text{Cl}_2$  to  $[\text{Rh}_2(\text{DPPE})_2(\mu_2\text{-Cl})_2]$  is extended to other Rh/diphosphine systems. In the case of the complex  $[\text{Rh}_2(\text{DPPP})_2(\mu_2\text{-Cl})_2]$  (DPPP = 1,2-bis(diphenylphosphino)propane) an extensive study has been conducted in order to clarify mechanistic aspects of this reaction.

## 2. Results and discussion

In a first experiment we added 1 mL of  $\text{CH}_2\text{Cl}_2$  to a solution of  $[\text{Rh}_2(\text{cod})_2(\mu_2\text{-Cl})_2]$  and DPPP (1:2 ratio) in 1 mL of THF. After about 36 h starting products were quantitatively consumed and only two species, **DPPP-Rh-1** and **DPPP-Rh-1A**, were observed in solution by  $^{31}\text{P}$  NMR (Fig. 1).

After some intensive 1D and 2D NMR studies and on the basis of the isolated crystals of **DPPP-Rh-1** (Fig. 2) it was possible to characterize **DPPP-Rh-1** and **DPPP-Rh-1A** respectively as the products of double and mono  $\text{CH}_2\text{Cl}_2$  activation, vide infra. A detailed discussion about all the molecular structures reported in the present paper can be found in the Supporting Information.

To the best of our knowledge this represents the first case of a simultaneous formation of bridging dimers with the core Rh- $\text{CH}_2$ -Rh and the fragment Rh- $\text{CH}_2\text{Cl}$ , in the presence of diphosphine

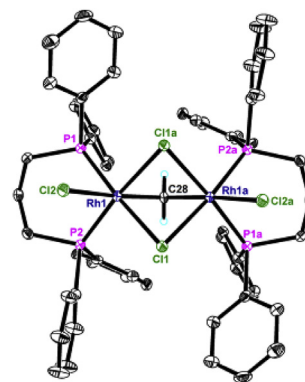


Fig. 2. Molecular structure of **DPPP-Rh-1**  $[\text{Rh}_2(\text{DPPP})_2(\mu_2\text{-Cl})_2(\mu_2\text{-CH}_2)\text{Cl}_2]$ . ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

ligands. To shed light on the mechanism of the reaction we performed further experiments: upon *in situ* combination of  $[\text{Rh}_2(\text{cod})_2(\mu_2\text{-Cl})_2]$  and DPPP in 1:2 ratio in THF (or other aprotic solvents), several species are generated depending on the rhodium precursor, solvent, temperature and reaction time. An overview of the species that can be observed in solution when  $[\text{Rh}_2(\text{cod})_2(\mu_2\text{-Cl})_2]$  is mixed *in situ* with DPPP is given in Scheme 1.

Cationic complex **DPPP-IS-II** (Scheme 1) has been briefly described by James et al. [27] and Claver et al. [28], while the pentacoordinated **DPPP-IS-III** has been recently studied by us extensively [29]. Finally, complex **DPPP-IS-IV** was reported by Slack et al. already in 1977 [30]. The equilibria involving the *in situ* formation of neutral  $(\mu_2\text{-Cl})$ -bridged dinuclear (diphosphine) rhodium complexes similar to **DPPP-I** and **DPPP-II** have been studied in the case of BINAP, SegPhos, DM-SegPhos and Di-FluorPhos [31].

The molecular structure of complex **DPPP-I**  $[\text{Rh}_2(\text{DPPP})(\text{cod})(\mu_2\text{-Cl})_2]$  was not reported to date (Fig. 3).

In order to avoid side reactions reported in Scheme 1 and so the formation of the well documented *in situ* species **DPPP-I**, **DPPP-IS-II**, **DPPP-IS-III** and **DPPP-IS-IV**, we considered starting from the preformed complex  $[\text{Rh}_2(\text{DPPP})_2(\mu_2\text{-Cl})_2]$  (**DPPP-II**). In this case a fast oxidative addition of  $\text{CH}_2\text{Cl}_2$  (1700 equivalents) to the preformed complex was observed, leading to complete conversion of the starting material in only 70 min (Supporting Information). As **DPPP-Rh-1** and **DPPP-Rh-1A** show low solubility in THF, the reaction was conducted in pure  $\text{CH}_2\text{Cl}_2$ . This protocol was extended to  $[\text{Rh}_2(\text{DPPB})_2(\mu_2\text{-Cl})_2]$ , and  $[\text{Rh}_2(\text{TangPhos})_2(\mu_2\text{-Cl})_2]$ , allowing for isolation of crystals suitable for X-ray analysis of complexes **DPPB-Rh-1** (DPPB = 1,4-bis(diphenylphosphino)buthane) and **TangPhos-Rh-1** (TangPhos = (1*S*,1'*S*,2*R*,2'*R*')-1,1-di-tert-butyl-(2,2')-diphospholane) (Fig. 4).

Analogous structures of complexes **DPPP-Rh-1\*CHCl<sub>3</sub>**, and **DPPE-Rh-1\*CH<sub>2</sub>Cl<sub>2</sub>** are reported in the Supporting Information.

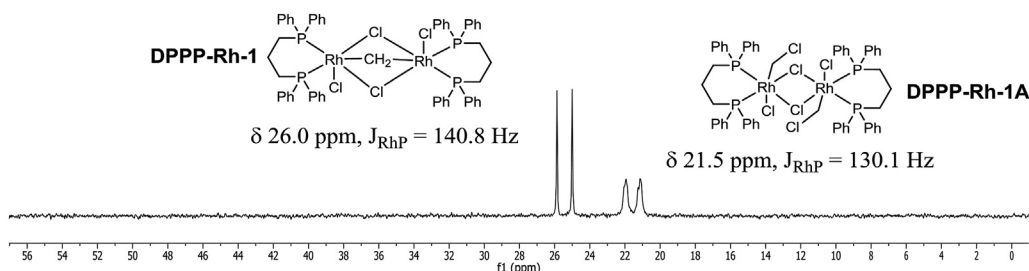
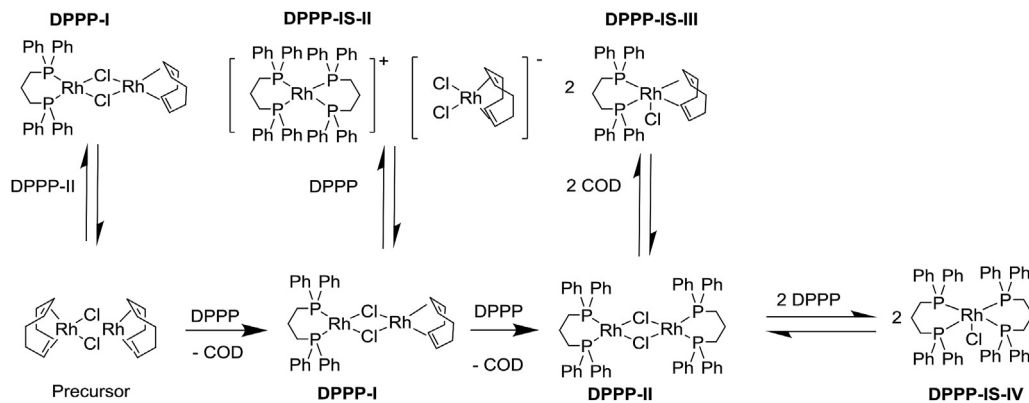


Fig. 1.  $^{31}\text{P}$  NMR of **DPPP-Rh-1** ( $\delta = 26$  ppm,  $J_{\text{PRh}} = 141$  Hz) and **DPPP-Rh-1A** ( $\delta = 22$  ppm,  $J_{\text{PRh}} = 130$  Hz) in THF-d<sub>8</sub>.



Scheme 1. Reactivity of  $[\text{Rh}_2(\text{cod})_2(\mu_2\text{-Cl})_2]$  and DPPP in aprotic solvents.

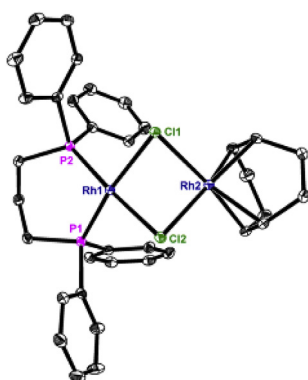


Fig. 3. Molecular structure of  $[\text{Rh}(\text{DPPP})(\mu_2\text{-Cl})_2\text{Rh}(\text{cod})]$  (DPPP-I). ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Kempe and coworkers reported a similar system where the formation of both  $-\text{CH}_2-$  bridged and  $-\text{CH}_2\text{Cl}$  terminal Rh(III) species arises from the oxidative addition of  $\text{CH}_2\text{Cl}_2$  to Rh(I) complexes containing PN ligands [25]. In that case a mechanism was depicted and the formation of a monomeric Rh(III) intermediate  $[\text{Rh}(\text{PN})(\text{CH}_2\text{Cl})\text{Cl}_2]$  which affords both products of oxidative addition by dimerization and coupling with the starting complex  $[\text{Rh}(\text{PN})(\text{cod})\text{Cl}]$  was proposed. Kempe's *in situ* system is formally simpler in comparison with that reported in Scheme 1. In fact from  $[\text{Rh}_2(\text{cod})_2(\mu_2\text{-Cl})_2]$  and the selected PN ligand only the pentacoordinate  $[\text{Rh}(\text{cod})(\text{PN})\text{Cl}]$  species and the salt  $[\text{Rh}(\text{PN})_2]^+[\text{Rh}(\text{Cl})_2]^-$  are formed. The authors excluded the

possibility of an oxidative addition on the ionic couple  $[\text{Rh}(\text{PN})_2]^+[\text{Rh}(\text{Cl})_2]^-$  and so they postulated the pentacoordinate complex as key intermediate. So far, it remains unclear when and how the oxidative step takes place.

Usually rationalization of oxidative addition reaction on transition metals involves a dissociative mechanism, which implies the generation of a vacant site at the metal complex [32]. In the case of our system it is reasonable to assume that cleavage of the dimer  $[\text{Rh}_2(\text{DPPP})_2(\mu_2\text{-Cl})_2]$  would afford the reactive intermediate monomer **III**  $[\text{Rh}(\text{DPPP})\text{Cl}]$ , which activates  $\text{CH}_2\text{Cl}_2$  (pathway A, Scheme 2).

In a previous work we proposed the formation of a highly reactive 14-electron intermediate species similar to **III** in the presence of DPE-Phos (DPE-Phos = Bis [2-(diphenylphosphino)phenyl]ether) [4d]. Also other authors reported similar intermediates in the case of DPPE [33], DPPB [33], MeO-BIPHEP (BIPHEP = 2,2'-bis(diphenylphosphanyl)-1,1'-biphenyl) [34] and  $\text{PPh}_3$  [35]. However such intermediates have been only postulated or even calculated but never observed directly.

An alternative *non-dissociative* pathway could involve the formation of a dimeric mixed valence intermediate, as in the three-fragment four-electron oxidative addition described by Oro and coworkers with pyrazolate ligands (pathway B, Scheme 2) [26]. In that case the authors postulated an intermediate Rh(I)-Rh(III) complex (analogue of **V** in Scheme 2) that would rapidly activate the Rh- $\text{CH}_2\text{Cl}$  fragment, giving the analogue of DPPP-Rh-1. It is important to note that in the case described with  $[\text{Rh}(\mu\text{-Pz})(\text{CNBut})_2]_2$  (Pz = pyrazolate) as starting complex, no addition of a second molecule of  $\text{CH}_2\text{Cl}_2$  was observed [36].

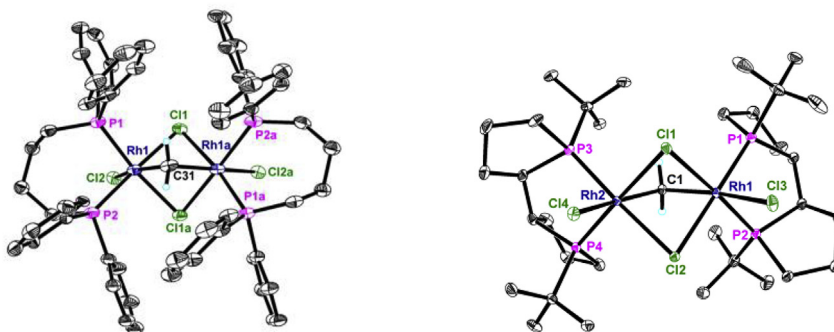
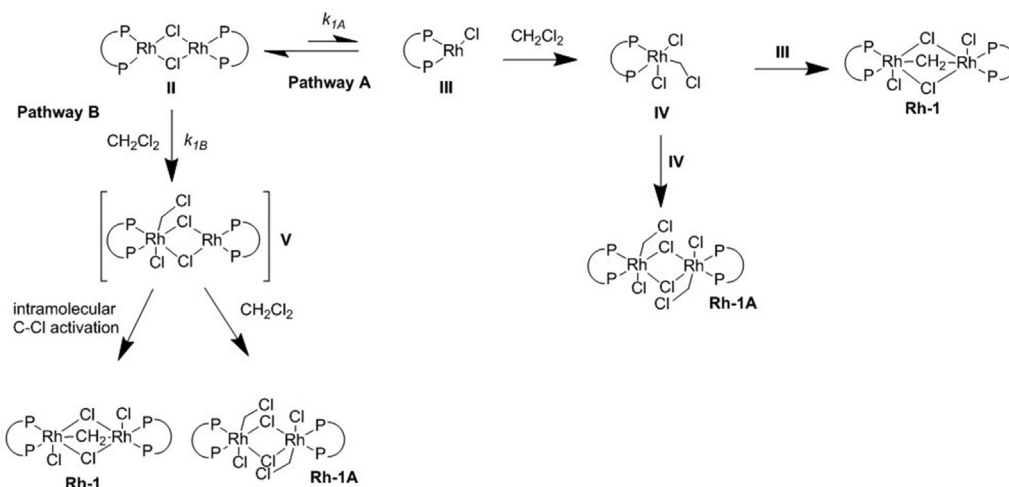


Fig. 4. Molecular structure of DPPB-Rh-1  $[\text{Rh}_2(\text{DPPB})_2(\mu_2\text{-Cl})_2(\mu_2\text{-CH}_2)_2\text{Cl}_2]$  (left) and TangPhos-Rh-1  $[\text{Rh}_2((1S,1'S,2R,2R')\text{-TangPhos})_2(\mu_2\text{-Cl})_2(\mu_2\text{-CH}_2)_2\text{Cl}_2]$  (right). ORTEP, 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.



**Scheme 2.** Possible pathways for the oxidative addition of  $\text{CH}_2\text{Cl}_2$  to preformed complex **II**.

### 3. Kinetics

In order to exclude one of the two pathways (A and B) reported in [Scheme 2](#), kinetic studies were conducted. Complex **DPPP-II**, that can be prepared according to our previously reported protocol<sup>[17]</sup> or following the procedure of Bosnich [\[37\]](#), was dissolved in a large excess of  $\text{CH}_2\text{Cl}_2$  (1700 equivalents), and the reaction was monitored by  $^{31}\text{P}$  NMR. Quantitative conversion (98%) of the starting complex was observed after only 70 min, giving a mixture of complexes **DPPP-Rh-1** and **DPPP-Rh-1A** [\[38\]](#).

The stability of complex **DPPP-Rh-1** was evaluated by dissolving some crystals in  $\text{CH}_2\text{Cl}_2\text{-d}_2$  and monitoring the solution by  $^{31}\text{P}$  NMR. No changes were observed even after a week [\[39\]](#).

Taking into consideration the two pathways postulated in [Scheme 2](#), two kinetic models can be deduced (more details are reported in the [Supporting Information](#)). Independently from the model the time-dependence of the concentration of starting complex **DPPP-II** should result in a first order reaction in agreement with the experimental data ([Supporting Information](#)).

The dependence of the product concentrations of **DPPP-Rh-1** and **DPPP-Rh-1A** on time is also determined by exponential functions but in a different form for the two models, the derivations can be found in the [Supporting Information](#). Consequently, discrimination between the models is quite difficult, when solely based on concentration-time data.

\*For pathway A, a simple integration is not possible, because the ratio of the concentrations  $[\text{III}]/[\text{IV}]$  is time dependent.

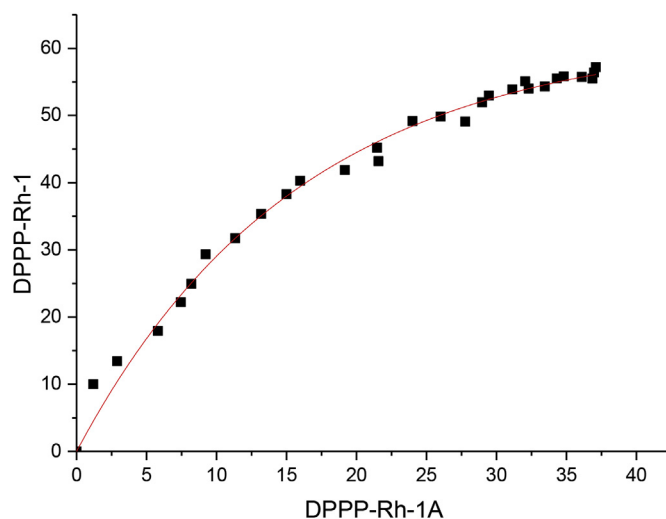
pathway A, equation 1	pathway B, equation 2
$[\text{II}] = [\text{II}]_0 e^{-k_{1A}t}$	$[\text{II}] = [\text{II}]_0 e^{-k_{1B}t} \quad (k_1, B = k_{1B}\text{CH}_2\text{Cl}_2)$
$d[\text{Rh-1}] = \left(\frac{k_3[\text{III}]}{k_4[\text{IV}]}\right) d[\text{Rh-1A}]^*$	$[\text{Rh-1}] = \left(\frac{k_2}{k_3}\right) [\text{Rh-1A}]$

(The complete numbering system for the rate constants can be found in the [Supporting Information](#)).

To distinguish between pathway A and B we used a so-called “concentration diagram” [\[40\]](#), specifically the plot of **DPPP-Rh-1** as function of **DPPP-Rh-1A**.

For *pathway B*, a zero point straight line should be expectable, while for *pathway A* nonlinear behavior should be observed.

In [Fig. 5](#) the variation of the concentrations of **DPPP-Rh-1** against **DPPP-Rh-1A** is reported (equation 1).

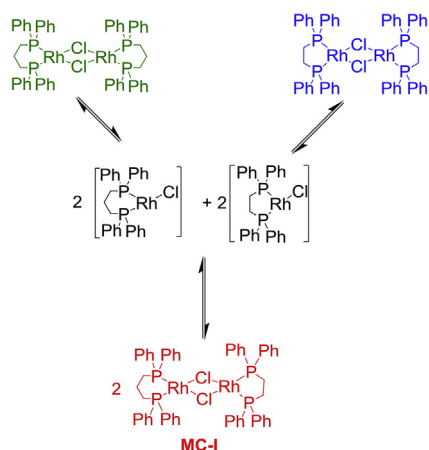


**Fig. 5.** Plot of the relative concentrations of **DPPP-Rh-1** against **DPPP-Rh-1A** in  $\text{CH}_2\text{Cl}_2\text{-d}_2$ . Conditions: 0.01 mmol of  $[\text{Rh}_2(\text{DPPP})_2(\mu_2\text{-Cl})_2]$  (**DPPP-II**) in 1.5 mL of  $\text{CH}_2\text{Cl}_2\text{-d}_2$  (1700 eq.).

The experimental results are in agreement with the kinetic calculations, pointing to an exclusion of the *pathway B* ([Scheme 2](#)) involving a dimeric intermediate species in a three-fragment four-electron oxidative addition. Indeed a dissociative mechanism fits with the equation 1 reported above. Considering that only from the kinetic calculations is not possible to prove that pathway A represents the real course of the reaction, we performed additional studies for reinforce the mechanism proposal.

An additional hint about the dimer-monomer equilibrium for complexes of the type  $[\text{Rh}_2(\text{PP})_2(\mu_2\text{-Cl})_2]$  has been obtained from the following metathesis experiment. **DPPP-II**  $[\text{Rh}_2(\text{DPPP})_2(\mu_2\text{-Cl})_2]$  and **DPPE-II**  $[\text{Rh}_2(\text{DPPE})_2(\mu_2\text{-Cl})_2]$  were mixed in 1:1 ratio and dissolved in THF. The solution was analyzed by  $^{31}\text{P}$  NMR, showing the formation of new signals which can be assigned to a metathesis complex of the type  $[\text{Rh}_2(\text{DPPP})(\text{DPPE})(\mu_2\text{-Cl})_2]$  ([Scheme 3](#) and [Fig. 6](#)).

In order to confirm that **MC-I** observed is the metathesis coupling product, it has been also prepared from a different independent route. One equivalent of DPPE was added to a solution of  $[\text{Rh}_2(\text{DPPP})(\text{cod})(\mu_2\text{-Cl})_2]$  (**DPPP-I**) and the mixture was analyzed



**Scheme 3.** Metathesis experiment between **DPPP-II** [ $\text{Rh}_2(\text{DPPP})_2(\mu_2\text{-Cl})_2$ ] and **DPPE-II** [ $\text{Rh}_2(\text{DPPE})_2(\mu_2\text{-Cl})_2$ ] in a 1:1 ratio in THF-d<sub>8</sub>.

by  $^{31}\text{P}$  NMR spectroscopy, confirming the same pattern of signals observed in the metathesis experiment (see [Supporting Information](#)).

Further investigations about these systems are object of our current research activity.

The insights about the formation of the 14-electron complex  $[\text{Rh}(\text{PP})\text{Cl}]$  collected in the present study grow in relevance if referred to the catalytic applications of the system  $[\text{Rh}_2(\text{diolefin})_2(\mu_2\text{-Cl})_2]/\text{diphosphine}$ . In fact the demonstration that  $[\text{Rh}(\text{PP})\text{Cl}]$  complexes fast activate the  $\text{CH}_2\text{Cl}_2$  suggests that active species can be consumed by an oxidative addition pathway when  $\text{CH}_2\text{Cl}_2$  is employed as solvent. This can lead to a wrong interpretation of the catalytic outcome.

#### 4. In situ experiments

In order to compare the outcome of the reaction on the preformed complex with the *in situ* conditions, and to get closer to the usual condition employed in several catalytic protocols, we monitored the reaction of  $[\text{Rh}_2(\text{cod})_2(\mu_2\text{-Cl})_2]$  and DPPP in a ratio 1:2 in  $\text{CH}_2\text{Cl}_2\text{-d}_2$  by  $^{31}\text{P}$  NMR (Fig. 7).

The  $^{31}\text{P}$  NMR monitoring of the reaction gave us some important information. The concentration of **DPPP-II** does not increase during the course of the reaction, indicating its fast consumption by oxidative addition and/or equilibria with the complexes **DPPP-IS-III** and **DPPP-IS-IV**. Another important aspect regards the conversion of all species present in the reaction mixture to give **DPPP-Rh-1** and **DPPP-Rh-1A** (see spectrum at 2940 min in Fig. 7). Considering that all the species formed are in equilibrium with **DPPP-II** (Scheme 1) (directly or indirectly), these equilibria would explain

the larger reaction time for the *in situ* system if compared to the reaction on the preformed neutral Rh dimer.

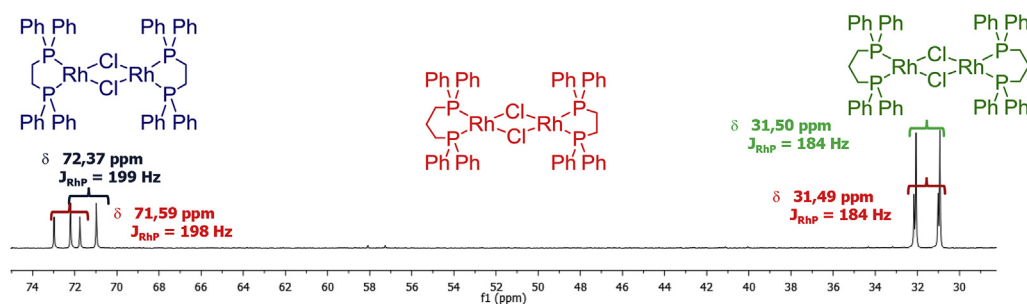
#### 5. Conclusions

We reported that oxidative addition of  $\text{CH}_2\text{Cl}_2$  on neutral, dimeric rhodium complexes stabilized by chelating diphosphines of general formula  $[\text{Rh}_2(\text{PP})_2(\mu_2\text{-Cl})_2]$  can be generalized to a series of diphosphine ligands. The crystal structures of the complexes  $[\text{Rh}_2(\text{DPPP})_2(\mu_2\text{-Cl})_2(\mu_2\text{-CH}_2\text{Cl}_2)]$  (**DPPP-Rh-1**),  $[\text{Rh}_2(\text{DPPP})_2(\mu_2\text{-Cl})_2(\mu_2\text{-CH}_2\text{Cl}_2)]^+\text{CHCl}_3^-$  (**DPPP-Rh-1\*CHCl<sub>3</sub>**),  $[\text{Rh}_2((1S,1S',2R,2R')\text{-TangPhos})_2(\mu_2\text{-Cl})_2(\mu_2\text{-CH}_2\text{Cl}_2)]$ , (**TangPhos-Rh-1**)  $[\text{Rh}_2(\text{DPPB})_2(\mu_2\text{-Cl})_2(\mu_2\text{-CH}_2\text{Cl}_2)]$  (**DPPB-Rh-1**),  $[\text{Rh}_2(\text{DPPE})_2(\mu_2\text{-Cl})_2(\mu_2\text{-CH}_2\text{Cl}_2)]^+\text{CH}_2\text{Cl}_2^-$  (**DPPE-Rh-1\*CH<sub>2</sub>Cl<sub>2</sub>**) arising from oxidative addition of  $\text{CH}_2\text{Cl}_2$  have been reported for the first time. In the case of the ligand DPPP, simultaneous formation of mono and double C-Cl activation was observed (**DPPP-Rh-1** and **DPPP-Rh-1A**) and thus a detailed investigation of the mechanism has been conducted. A mechanistic proposal has been presented on the basis of kinetics, NMR spectroscopic evidence, and metathesis experiments. In the suggested mechanism, highly reactive 14-electron rhodium intermediate species are directly involved in the  $\text{CH}_2\text{Cl}_2$  activation. Our conclusions support the mechanistic proposal of Kempe and co-workers in the case of *P*-functionalized aminopyridine rhodium(I) complexes. Finally we demonstrated that employing  $[\text{Rh}_2(\text{PP})_2(\mu_2\text{-Cl})_2]$  complexes (preformed or generated *in situ*) as catalytic precursors in the presence of  $\text{CH}_2\text{Cl}_2$ , as reported in several protocols, can lead to undesired oxidative addition with significant loss of catalytic active species, complete neglected in that cases.

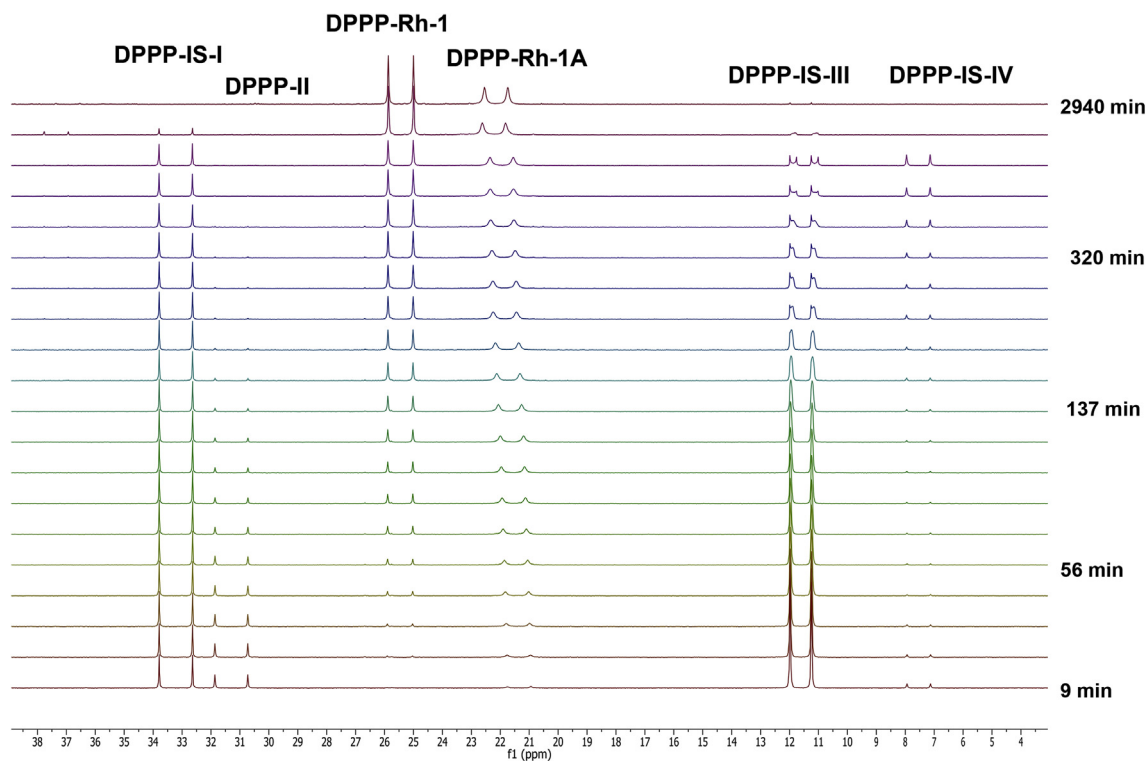
#### 6. Experimental section

All manipulations were carried out under argon using standard Schlenk techniques. THF, xylene, pentane and hexane were distilled from sodium, MeOH was distilled from magnesium, acetone was distilled from  $\text{CaH}_2$ . Subsequent removal of traces of oxygen from the deuterated solvents was carried out through the application of three freeze-thaw cycles. The rhodium precursors  $[\text{Rh}(\text{cod})_2(\mu_2\text{-Cl})_2]$  (98%) was purchased by STREM. The phosphines DPPE, DPPB, and TangPhos were purchased from STREM and employed as received. DPPP was purchased by Sigma Aldrich (98%) and recrystallized from MeOH.  $[\text{Rh}_2(\text{DPPE})_2(\mu_2\text{-Cl})_2]$ ,  $[\text{Rh}_2(\text{DPPP})_2(\mu_2\text{-Cl})_2]$ ,  $[\text{Rh}_2(\text{DPPB})_2(\mu_2\text{-Cl})_2]$  and  $[\text{Rh}_2(\text{TangPhos})_2(\mu_2\text{-Cl})_2]$  were prepared according to the reported procedures.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1585029 for **DPPP-Rh-1**, CCDC-1585030 for **DPPP-Rh-1\*CHCl<sub>3</sub>**, CCDC-1585033 for **TangPhos-Rh-1**, CCDC-1585034 for **DPPB-Rh-1**, CCDC-1585035 for **DPPE-Rh-1\*CH<sub>2</sub>Cl<sub>2</sub>**, and CCDC-



**Fig. 6.**  $^{31}\text{P}$  NMR of a mixture of **DPPP-II** [ $\text{Rh}_2(\text{DPPP})_2(\mu_2\text{-Cl})_2$ ] and **DPPE-II** [ $\text{Rh}_2(\text{DPPE})_2(\mu_2\text{-Cl})_2$ ] (1:1) in THF-d<sub>8</sub>.



**Fig. 7.**  $^{31}\text{P}$  NMR monitoring of the *in situ* reaction between  $[\text{Rh}_2(\text{cod})_2(\mu\text{-Cl})_2]$ , DPPPP and  $\text{CH}_2\text{Cl}_2$ . **DPPPP-I**  $[\text{Rh}_2(\text{DPPPP})(\text{cod})(\mu\text{-Cl})_2]$ , **DPPPP-II**  $[\text{Rh}_2(\text{DPPPP})_2(\mu\text{-Cl})_2]$ , **DPPPP-IS-I**  $[\text{Rh}(\text{DPPPP})_2]^+$ , **DPPPP-DPPPP-IS-III**  $[\text{Rh}(\text{DPPPP})(\text{cod})\text{Cl}]$ , and **DPPPP-IS-IV**  $[\text{Rh}(\text{DPPPP})_2\text{Cl}]$  in  $\text{CH}_2\text{Cl}_2\text{-d}_2$ . Conditions: 0.01 mmol of  $[\text{Rh}_2(\text{cod})_2(\mu\text{-Cl})_2]$  in 1.5 mL of  $\text{CH}_2\text{Cl}_2\text{-d}_2$  (1700 eq.).

1585032 for **DPPPP-IS-I**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: int. code + (1223) 336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

**NMR:**  $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR spectra were obtained on a Bruker AV-300 or AV-400 spectrometer at 297–298 K and were referenced internally to the deuterated solvent. For  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, 85%  $\text{H}_3\text{PO}_4$  was used as external standard. Data processing was performed by Topspin software (3.5 version) (Bruker). All the NMR spectra have been recorded at 297 K (24 °C) unless otherwise indicated.

**General synthesis of  $[\text{Rh}_2(\text{PP})_2(\mu\text{-Cl})_2(\mu\text{-CH}_2)\text{Cl}_2]$ , **[Rh-1]:** 10 mg of  $[\text{Rh}_2(\text{PP})_2(\mu\text{-Cl})_2]$  were dissolved in 1.0 mL of  $\text{CH}_2\text{Cl}_2$ . The resulting solution was stirred at room temperature overnight. After observing complete consuming of the starting product by  $^{31}\text{P}\{^1\text{H}\}$  NMR the solvent was removed under vacuum and the crude product crystallized as forward reported.**

**In situ synthesis of  $[\text{Rh}_2(\text{DPPPP})_2(\mu\text{-Cl})_2(\mu\text{-CH}_2)\text{Cl}_2]$ :** To a solution containing 32 mg of  $[\text{Rh}_2(\text{cod})_2(\mu\text{-Cl})_2]$  in THF (0.5 mL) a solution of DPPPP in 0.5 mL of THF was added dropwise. The resulting mixture was stirred at room temperature during 2 h and then 1 mL of  $\text{CH}_2\text{Cl}_2$  was added. The resulting yellow solution was stirred at room temperature during 36 h. After that the solution was stored under Ar and some small yellow crystals were formed in two days.

**$[\text{Rh}_2(\text{DPPPP})_2(\mu\text{-Cl})_2(\mu\text{-CH}_2)\text{Cl}_2]$ , **DPPPP-Rh-1:** isolated yield 45%. Crystallization: the crude mixture was dissolved in xylene/ $\text{CH}_2\text{Cl}_2$  1:1 and stored at room temperature during 24–48 h until small orange crystals were formed.**

**$^1\text{H}$  NMR** (300 MHz,  $\text{CH}_2\text{Cl}_2\text{-d}_2$ , 25 °C):  $\delta$  = 1.27–1.50 (m, 2H,  $\text{CH}_2$ ), 1.88–2.03 (m, 4H,  $\text{CH}_2$ ), 2.04–2.38 (m, 2H,  $\text{CH}_2$ ), 3.18–3.33 (m, 2H,  $\text{CH}_2$ ), 4.61 (bs, 2H,  $\text{CH}_2\text{-Rh}$ ), 6.78 (t,  $J_{\text{H-H}}$  = 7.8 Hz, 8H, CH-Ar), 6.97–7.11 (m, 16H, CH-Ar), 7.12–7.19 (m, 4H, CH-Ar), 7.28 (t,  $J_{\text{H-H}}$

$\text{H}$  = 7.5 Hz, 4H, CH-Ar), 7.65–7.78 (m, 8H, CH-Ar) ppm.  **$^{31}\text{P}\{^1\text{H}\}$  NMR** (300 MHz,  $\text{CH}_2\text{Cl}_2\text{-d}_2$ , 25 °C):  $\delta$  = 26.0 (d,  $J_{\text{P-Rh}}$  = 140.8 Hz) ppm. **MS (HR-ESI(+)):**  $m/z$  1194.6  $[(\text{M} - \text{Cl}) + \text{HCOOH}]^+$ .

**$[\text{Rh}_2(\text{DPPB})_2(\mu\text{-Cl})_2(\mu\text{-CH}_2)\text{Cl}_2]$ , **DPPB-Rh-1:** isolated yield 85%. Crystallization: the crude mixture was dissolved in xylene/ $\text{CH}_2\text{Cl}_2$  1:1 and the solution stored at room temperature during 24–48 h until small orange crystals were formed.**

**$^1\text{H}$  NMR** (400 MHz,  $\text{CH}_2\text{Cl}_2\text{-d}_2/\text{C}_6\text{H}_6\text{-d}_6$ , 25 °C):  $\delta$  = 1.18–1.31 (m, 2H,  $\text{CH}_2$ ), 1.41–1.57 (m, 4H,  $\text{CH}_2$ ), 2.11–2.26 (m, 6H,  $\text{CH}_2$ ), 3.56–3.70 (m, 4H,  $\text{CH}_2$ ), 4.89–4.97 (m, 2H,  $\text{CH}_2\text{-Rh}$ ), 7.32–7.53 (m, 24H, CH-Ar), 8.11–8.24 (m, 8H, CH-Ar) ppm.  **$^{31}\text{P}\{^1\text{H}\}$  NMR** (400 MHz,  $\text{CH}_2\text{Cl}_2\text{-d}_2/\text{C}_6\text{H}_6\text{-d}_6$ , 25 °C):  $\delta$  = 32.6 (d,  $J_{\text{P-Rh}}$  = 147.0 Hz) ppm. **MS (HR-ESI(+)):**  $m/z$  1236.6  $[(\text{M} - 2\text{Cl}) + 2 \text{HCOOH}]^+$ .

**$[\text{Rh}_2(\text{TangPhos})_2(\mu\text{-Cl})_2(\mu\text{-CH}_2)\text{Cl}_2]$ , **TangPhos-Rh-1:** the crude mixture was crystallized by dissolving it in  $\text{CH}_2\text{Cl}_2$  and layering with  $\text{Et}_2\text{O}$ , until small yellow needles were formed.**

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (300 MHz,  $\text{CH}_2\text{Cl}_2\text{-d}_2$ , 25 °C):  $\delta$  = 111.79 (dd,  $J_{\text{PRh}}$  = 143 Hz,  $J_{\text{PP}}$  = 8.7 Hz),  $\delta$  = 110.51 (dd,  $J_{\text{P-Rh}}$  = 151 Hz,  $J_{\text{PP}}$  = 8.3 Hz) ppm.

**$[\text{Rh}_2(\text{DPPPP})_2(\mu\text{-Cl})_2(\text{cod})]$ , **DPPPP-IS-1:** To a solution of 32 mg (0.063 mmol) of  $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$  in 1 mL of xylene at 75 °C, 13 mg of DPPPP in 1 mL of xylene were added dropwise and slowly (20 min). The resulting orange solution was stirred at 110 °C. After 3 h the solvent was removed under vacuum to give a red/orange powder in 95% of yield. Crystallization: the red/orange powder was dissolved in THF and layered with pentane. Orange crystals were formed overnight.**

**$^1\text{H}$  NMR** (300 MHz,  $\text{CH}_2\text{Cl}_2\text{-d}_2$ , 25 °C):  $\delta$  = 1.60–1.72 (m, 8H,  $\text{CH}_2(\text{cod})$ , 2H (DPPPP)), 2.10–2.18 (m, 4H,  $\text{CH}_2$  DPPPP), 2.25–2.40 (m, 8H,  $\text{CH}_2(\text{cod})$ ), 3.8 (s, 4H, CH (cod)), 7.16–7.23 (m, 12H, CH-Ar), 7.78–7.90 (m, 8H, CH-Ar) ppm.  **$^{31}\text{P}\{^1\text{H}\}$  NMR** (300 MHz,  $\text{CH}_2\text{Cl}_2\text{-d}_2$ , 25 °C):  $\delta$  = 33.8 (d,  $J_{\text{P-Rh}}$  = 187.7 Hz) ppm. **MS (HR-ESI(+)):**  $m/z$  445.0  $[(\text{M} + 2) \text{HCOOH}]^{2+}$ .

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jorganchem.2018.07.011>.

## References

- [1] (a) W. Gao, H. Lv, X. Zhang, *Org. Lett.* 19 (2017) 2877–2880; (b) C.S. Shultz, S.W. Krska, *Acc. Chem. Res.* 40 (2007) 1320–1326; (c) 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.* 126 (2004) 9918–9919; (d) H.B. Kagan, T.P. Dang, *J. Am. Chem. Soc.* 94 (1972) 6429–6433.
- [2] (a) G.C. Tsui, M. Lautens, *Angew. Chem. Int. Ed.* 51 (2012) 5400–5404; (b) *Angew. Chem.* 124 (2012) 5496–5500; (c) A. Preetz, C. Kohrt, H.-J. Drexler, A. Torrens, H. Buschmann, M.G. Lopez, D. Heller, *Adv. Synth. Catal.* 352 (2010) 2073–2080; (d) K. Fagnou, in: P.A. Evans (Ed.), *Modern Rhodium-Catalyzed Organic Reactions*, Wiley-VCH, Weinheim, 2005, pp. 173–190 (Chapter 9); (e) M. Lautens, K. Fagnou, *Proc. Natl. Acad. Sci. U. S. A.* 101 (2004) 5455–5460.
- [3] (a) G. Tran, K.D. Hesp, V. Mascitti, J.A. Ellman, *Angew. Chem. Int. Ed.* 56 (2017) 5899–5903; (b) *Angew. Chem.* 129 (2017) 5993; (c) T.M. Beck, B. Breit, *Angew. Chem. Int. Ed.* 56 (2017) 1903–1907; (d) *Angew. Chem.* 129 (2017) 1929–1933; (e) L.A. Schwartz, M.J. Krische, *Isr. J. Chem.* 57 (2017) 1–8.
- [4] (a) A.M. Haydl, B. Breit, T. Liang, M.J. Krische, *Angew. Chem. Int. Ed.* 56 (2017) 11312–11325; (b) *Angew. Chem.* 129 (2017) 11466–11480; (c) P. Koschker, M. Kähny, B. Breit, *J. Am. Chem. Soc.* 137 (2015) 3131–3137; (d) U. Gellrich, A. Meißner, A. Steffani, M. Kähny, H.-J. Drexler, D. Heller, D.A. Plattner, B. Breit, *J. Am. Chem. Soc.* 136 (2014) 1097–1104; (e) C. Li, B. Breit, *J. Am. Chem. Soc.* 136 (2014) 862–865; (f) S. Wei, J. Pedroni, A. Meißner, A. Lumbroso, H.-J. Drexler, D. Heller, B. Breit, *Chem. Eur. J.* 19 (2013) 12067–12076.
- [5] (a) A.M. Haydl, L.J. Hilpert, B. Breit, *Chem. Eur. J.* 22 (2016) 6547–6551; (b) Q.-A. Chen, Z. Chen, V.M. Dong, *J. Am. Chem. Soc.* 137 (2015) 8392–8395.
- [6] (a) T. Furusawa, T. Morimoto, Y. Nishiyama, H. Tanimoto, K. Kakiuchi, N. Chatani, T. Nishioka, *Chem. Asian J.* 11 (2016) 2312–2315; (b) G. Makado, T. Morimoto, Y. Sugimoto, K. Tsutsumi, N. Kagawa, K. Kakiuchi, *Adv. Synth. Catal.* 352 (2010) 299–304; (c) T. Morimoto, K. Yamasaki, A. Hirano, K. Tsutsumi, N. Kagawa, K. Kakiuchi, Y. Harada, Y. Fukumoto, *Org. Lett.* 11 (2009) 1777–1780.
- [7] (a) T. Furusawa, H. Tanimoto, Y. Nishiyama, T. Morimoto, K. Kakiuchi, *Adv. Synth. Catal.* 359 (2017) 240–245; (b) T. Furusawa, T. Morimoto, Y. Nishiyama, H. Tanimoto, K. Kakiuchi, *Chem. Asian J.* 11 (2016) 2312–2315.
- [8] (a) L. Han, Y. Li, T. Liu, *Dalton Trans.* 47 (2018) 150–158; (b) J.L. Kennemur, G.D. Kortman, K.L. Hull, *J. Am. Chem. Soc.* 138 (2016) 11914–11919; (c) A.K. Gupta, K.L. Hull, *Synlett* 26 (13) (2015) 1779–1784.
- [9] (a) L.C. Burrows, L.T. Jesikiewicz, G. Lu, S.J. Geib, P. Liu, K.M. Brummond, *J. Am. Chem. Soc.* 139 (2017) 15022–15032; (b) T. Furusawa, T. Morimoto, K. Ikeda, H. Tanimoto, Y. Nishiyama, K. Kakiuchi, N. Jeong, *Tetrahedron* 71 (2015) 875–881; (c) M. Ishida, Y. Shibata, K. Noguchi, K. Tanaka, *Chem. Eur. J.* 17 (2011) 12578–12581; (d) J. Park, Y. Cho, Y. Chung, *Angew. Chem. Int. Ed.* 49 (2010) 5138–5141; (e) *Angew. Chem.* 122 (2010) 5264–5267.
- [10] (a) D.M. Ohlmann, L.J. Gooßen, M. Dierker, *Chem. Eur. J.* 17 (2011) 9508–9519; (b) A. Behr, D. Obst, A. Westfechtel, *Eur. J. Lipid Sci. Technol.* 107 (2005) 213–219; (c) A. Seayad, M. Ahmed, H. Klein, R. Jackstell, T. Gross, M. Beller, *Science* 297 (2002) 1676–1678.
- [11] (a) P.A. Spreider, A.M. Haydl, M. Heinrich, B. Breit, *Angew. Chem. Int. Ed.* 55 (2016) 15569–15573; (b) *Angew. Chem.* 128 (2016) 15798–15802; (c) F. Inagaki, K. Sugikubo, Y. Oura, C. Mukai, *Chem. Eur. J.* 17 (2011) 9062–9065.
- [12] (a) T. Toyoshima, T. Miura, M. Murakami, *Angew. Chem. Int. Ed.* 50 (2011) 10436–10439; (b) *Angew. Chem.* 123 (2011) 10620–10623.
- [13] (a) T. Mühlhäuser, A. Savin, W. Frey, A. Baro, A.J. Schneider, H.-G. Döteberg, F. Bauer, A. Köhn, S. Laschat, *J. Org. Chem.* 82 (24) (2017) 13468–13480; (b) A. Lee, H. Kim, *J. Org. Chem.* 81 (9) (2016) 3520–3527; (c) T. Hayashi, M. Takahashi, Y. Takaya, M. Ogasawara, *J. Am. Chem. Soc.* 124 (2002) 5052–5058.
- [14] M. Li, D. Kong, G. Zi, G. Hou, *J. Org. Chem.* 82 (2017) 680–687.
- [15] (a) D. Kong, M. Li, G. Zi, G. Hou, *Org. Biomol. Chem.* 14 (2016) 4046–4053; (b) Q. Yan, D. Kong, M. Li, G. Hou, G. Zi, *J. Am. Chem. Soc.* 137 (2015) 10177–10181.
- [16] A. Meißner, E. Alberico, H.J. Drexler, W. Baumann, D. Heller, *Catal. Sci. Technol.* 4 (2014) 3409–3425.
- [17] A. Meißner, A. Preetz, H.-J. Drexler, W. Baumann, A. Spannenberg, A. König, D. Heller, *ChemPlusChem* 80 (2015) 169–180.
- [18] H.B. Friedrich, J.R. Moss, *Adv. Organomet. Chem.* 33 (1991) 235–290.
- [19] A. Preetz, C. Kohrt, A. Meißner, S. Wie, H.-J. Drexler, H. Buschmann, D. Heller, *Catal. Sci. Technol.* 3 (2013) 462–468.
- [20] G.E. Ball, W.R. Cullen, M.D. Fryzuk, B.R. James, S.J. Rettig, *Organometallics* 10 (1991) 3767–3769.
- [21] P.J. Fennis, P.H.M. Budzelaar, J.H.G. Frijns, *J. Organomet. Chem.* 393 (1990) 287–298.
- [22] T.B. Marder, W.C. Fultz, J.C. Calabrese, R.L. Harlow, D. Milstein, *J. Chem. Soc. Chem. Commun.* (1987) 1543–1545.
- [23] A. König, C. Fischer, E. Alberico, C. Selle, H.-J. Drexler, W. Baumann, D. Heller, *Eur. J. Inorg. Chem.* (2017) 2040–2047.
- [24] (a) S.D. Pike, A.S. Weller, *Dalton Trans.* 42 (2013) 12832–12835; (b) T.M. Douglas, A.B. Chaplin, A.S. Weller, *Organometallics* 27 (2008) 2918–2921.
- [25] B. Blank, G. Glatz, R. Kempe, *Chem. Asian J.* 4 (2009) 321–327.
- [26] M.A. Ciriano, M.A. Tena, L.A. Oro, *J. Chem. Soc. Dalton Trans.* (1992) 2123–2124.
- [27] B.R. James, D. Mahajan, *Can. J. Chem.* 57 (1979) 180–187.
- [28] A. Castellanos-Paez, J. Thayaparan, S. Castillon, C. Claver, *J. Organomet. Chem.* 551 (1998) 375–381.
- [29] A. Meißner, A. König, H.-J. Drexler, R. Thede, W. Baumann, D. Heller, *Chem. Eur. J.* 20 (2014) 14721–14728.
- [30] D.A. Slack, M.C. Baird, *J. Organomet. Chem.* 142 (1977) C69–C72.
- [31] C. Fischer, A. König, A. Meißner, R. Thede, C. Selle, C. Pribbenow, D. Heller, *Eur. J. Inorg. Chem.* (2014) 5849–5855.
- [32] (a) J.K. Stille, K.S.Y. Lau, *Acc. Chem. Res.* 10 (1977) 434–442; (b) J.P. Collman, W.R. Roper, *Adv. Organomet. Chem.* 7 (1969) 53–94.
- [33] S.M. Jackson, C.E. Hughes, S. Monfette, L. Rosenberg, *Inorg. Chim. Acta* 359 (2006) 2966–2972.
- [34] T. Korenaga, R. Sasaki, T. Takemoto, T. Yasuda, M. Watanabe, *Adv. Synth. Catal.* 360 (2018) 322–333.
- [35] J.M. Brown, P.L. Evans, A.R. Lucy, *J. Chem. Soc. Perkin Trans. I* (1987) 1589–1596.
- [36] C. Tejel, M.A. Ciriano, L.A. Oro, A. Tiripicchio, F. Ugozzoli, *Organometallics* 20 (2001) 1676–1682.
- [37] D.P. Fairlie, B. Bosnich, *Organometallics* 7 (1988) 936–945.
- [38] <sup>31</sup>P NMR monitoring with different ratios of [Rh(DPPP)(μ<sub>2</sub>-Cl)]<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> showed the same behavior, see Supporting Information.
- [39] While complex Rh-1 showed a high stability in a solution of THF, <sup>31</sup>P NMR monitoring of a THF solution of complex Rh-1A (in a mixture with Rh-1) revealed a slow degradation of the complex.
- [40] H. Mauser, *Formale Kinetik*, Bertelsmann Universitätsverlag, 1974.