Dalton Transactions

PERSPECTIVE

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Cite this: *Dalton Trans.*, 2018, **47**, 4755

Synthesis of platinum, palladium and rhodium complexes of α-aminophosphine ligands

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Received 15th January 2018,
Accepted 23rd February 2018

DOI: 10.1039/c8dt00178b

rsc.li/dalton

α-Aminophosphine-type ligands are of interest as building blocks of transition metal complexes. This review focuses on the utilization of α-aminophosphines as monodentate and bidentate ligands in platinum, palladium and rhodium complexes. Besides the linear derivatives, the applications of cyclic α-aminophosphines as ligands are also summarized. Various aspects, such as synthesis, structure and applications, as well as the catalytic activity of these complexes are discussed.

1. Introduction

Phosphorus(III) ligands, such as phosphines, phosphinines, phosphites and phosphinites, are a highly important class of ligands.[1,2] α-Aminophosphines form a significant group within the large family of phosphine ligands and play an important role in the synthesis of P(III)-transition metal complexes, which are widely applied catalysts in homogeneous catalytic reactions.[3–5]

Among the transition metal complexes, derivatives of the platinum group (such as platinum, palladium, rhodium and ruthenium) present special properties, as compared to other metals. From a catalytic point of view, complexes of platinum, palladium and rhodium are the most important. Industrially relevant examples of these species include Wilkinson's catalyst ($Rh(PPh_3)_3Cl$)[6] or tetrakis(triphenylphosphine)-palladium(0).[7] Complexes of ruthenium show unique coordination and medicinal properties, which can be considered as a separate research topic.[8–11] Besides the biologically active Ru derivatives, Pt complexes can also be used as anticancer agents.[12–14]

Phosphine ligands containing an amine group offer new functionalization possibilities of the transition metal complexes. Although a large amount of data has accumulated on α-aminophosphines (P–C–N), the related field has not been summarized. Reviews on similar compounds, such as phosphinoamines (P–N),[15] β-aminophosphines ($P–C_2–N$)[16] and miscellaneous aminophosphines ($P–C_n–N$), have been published previously.[17]

As the most common synthetic routes, α-aminophosphines may be prepared by the three-component condensation of an amine, an oxo-compound and a secondary phosphine,[18–23] by the reaction between amines and hydroxymethyl phosphines,[24–28] and by the deoxygenation of α-amino-

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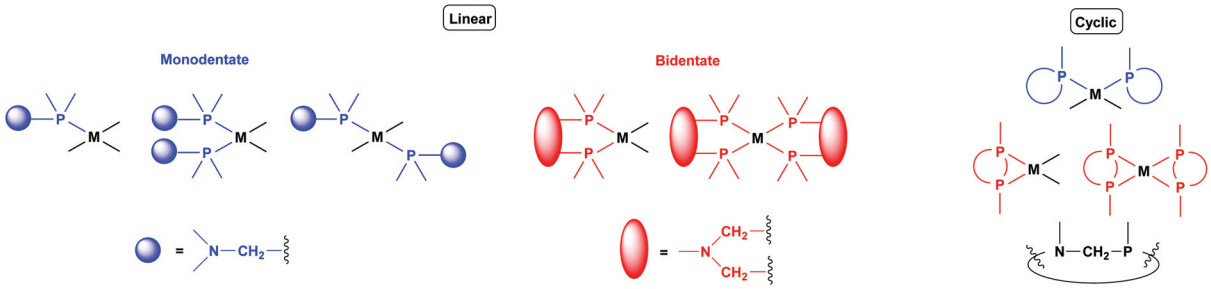

Scheme 1 General representation of transition metal complexes containing α-aminophosphine ligand.

phosphine oxides.[29,30] These derivatives can be functionalized further on the nitrogen atom, and they may be good starting materials for polymer-immobilized P-ligands.[31–33]

Synthetic methods for α-aminophosphines incorporating platinum, palladium and rhodium complexes have been developing since the 1980s. The purpose of this review is to summarize the most important results of this special field of organometallic chemistry. The utilization of the linear and cyclic α-aminophosphines as mono- and bidentate ligands in the synthesis of transition metal complexes comprising platinum-, palladium or rhodium is described. The general structures of the latter compounds are shown in Scheme 1. In addition, the application of several complexes as catalysts is also presented.

2. Utilization of α-aminophosphines as monodentate ligands

2.1. Synthesis of platinum and palladium complexes

Due to their similar valence structure and reactivity, the complexes of platinum and palladium are discussed together.

According to the literature, diphenylphosphinomethylamines are the most widely used monodentate α-aminophosphine ligands. A common procedure to prepare *cis*-oriented Pt^{II} and Pd^{II} complexes involves the reaction of the latter species with Pt^{II}- or $Pd^{II}(cod)Cl_2$ (cod = cycloocta-1,5-diene) at room temperature in DCM (dichloromethane) as the solvent (Table 1). This ligand family was utilized for the first time by Davis in 1993 (Table 1/entry 1). The corresponding *N*-^{t}Bu Pt^{II} complex was synthesized in a yield of 69%. The *cis* conformation of the product was proved by ^{31}P NMR spectroscopy based on the stereospecific Pt–P coupling (3710 Hz). Amino alcohol-functionalized α-aminophosphines were also proved to be efficient ligands in the synthesis of Pt^{II} complexes (Table 1/entry 2). The corresponding bis(phosphine)$PtCl_2$ compounds were obtained in yields of 58–74% after 15 min. The synthesis of both Pt^{II} and Pd^{II} complexes of *N*-4-pyridyl aminophosphines was also reported (Table 1/entry 3). It should be noted that in the case of $Pt^{II}(cod)Cl_2$, the reaction was carried out in DCM at the boiling point. The products obtained could be easily converted to water-soluble complexes by quaterniza-

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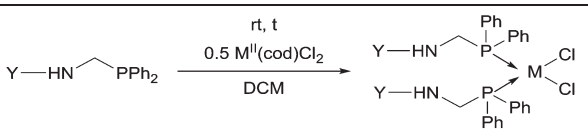
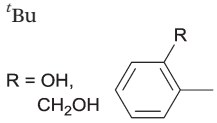
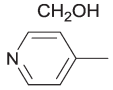
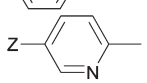
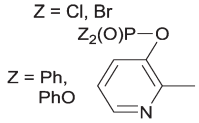
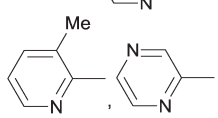
Anna Tripolszky was born in 1992. She graduated at the Budapest University of Technology and Economics in 2017 as a pharmaceutical engineer. She has been a member of the Organophosphorus Research Group since 2013. Since 2017, she has been a PhD student at the same university. Her interest lies in organophosphorus chemistry with a focus on the synthesis of aminophosphine oxide derivatives and their utilization in transition metal complexes.

Table 1 *cis*-Oriented complexes of Pt^{II} and Pd^{II} obtained by the reaction of diphenylphosphinomethylamines with $M^{II}(cod)Cl_2$ (M = Pt, Pd)



Entry	Y	M	*t*	Yield [%]	Ref.
1	^{t}Bu	Pt	30 min	69	34
2	 R = OH, CH_2OH	Pt	15 min	58–74	35
3		Pt[a], Pd	12 h	89–92	36
4	 Z = Cl, Br	Pt	15 min	70–89	34 and 37
5	 Z = Ph, PhO	Pt	15 min	67–79	38
6		Pd	30 min	63–86	39

[a] In case of Pt, the complexation was carried out in DCM at the boiling point.

tion of the N atom of the pyridine rings by HCl. α-Aminophosphines containing a halogenated pyridine moiety were coordinated to Pt^{II} in a reaction time of 15 min (Table 1/entry 4). X-Ray investigation of the 5-Cl-2-pyridyl derivative revealed dimers in the crystal structure, which were held together by two H-bonds between each N–H···Cl pair. Derivatives containing phosphate or phosphinate moieties on the hetaryl ring were also tried out as ligands in the complexation (Table 1/entry 5). In the X-ray structure of the products, there were two N–H···Cl–Pt intramolecular H-bonds, as well as P═O moieties oriented "away" to the central metal atom (Fig. 1). Other *N*-hetaryl (3-Me-pyridyl and 2-pyrazinyl) aminophosphines were also proved to be useful ligands in complexations (Table 1/entry 6). The Pd^{II} complexes synthesized were tested in the Heck reaction of styrene and aryl bromides (Scheme 2). The complexes (**A** and **B**) showed different catalytic activities, which was explained by the investigation of the reaction mechanism by DFT calculations.

α-Aminophosphines reacted easily with $Pt^{II}(cod)Cl_2$ or $Pd^{II}(cod)Cl_2$ at room temperature to furnish the Pt^{II} or Pd^{II} complexes in yields of *ca.* 60–90%. The reaction conditions required did not depend on the different (alkyl, aryl or hetaryl) substituents of the N atom.

In a few cases, both of the *cis* (major) and the *trans* (minor) complexes of bis(α-aminophosphine)$PdCl_2$ derivatives could be observed by NMR spectroscopy in solution, while the solid products showed only the *cis* conformation (Table 2). Starting from amino alcohol-functionalized α-aminophosphines, complexation afforded the products in yields of 68–93% after 15 min (Table 2/entry 1). IR spectroscopy revealed *cis* conformation in the solid phase, while in solution, the ratio of *cis* and *trans* complexes was 82 : 18 and 69 : 31 as determined by ^{31}P NMR. In the case of an *N*-quinolinyl derivative, the formation of the two isomers was also corroborated, but the composition was not reported (Table 2/entry 2). The complex was synthesized in a yield of 73%. In the reaction of halogenated diphenylphosphinomethylanilines with $Pt^{II}(cod)Cl_2$, the corresponding complexes were obtained in yields of 77–85% (Table 2/entry 3). The *cis* conformation in the solid phase was also confirmed by X-ray diffraction measurements besides IR spectroscopy. The *cis* : *trans* ratio (71 : 29) was only mentioned in the case of the 5-Cl-aniline derivative.

In the examples where the *cis* : *trans* ratio in the solution was given, the *cis* product was present as the major component. Furthermore, the *cis* : *trans* composition was similar starting from both aryl and hetaryl derivatives.

In the reaction of diphenylphosphinomethyl-4-methylaniline with $Pt^{II}(cod)Cl_2$, a mixture of two complexes was obtained based on ^{31}P NMR. According to the chemical shifts and the Pt–P couplings, a bis(phosphinomethyl)amine derivative was also formed as a by-product besides the expected Pt^{II} complex (Scheme 3).[41]

When an *N*-quinoline-α-aminophosphine was reacted with $Pt^{II}(cod)Cl_2$ at room temperature, the corresponding *cis* complex was obtained in a yield of 60% (Scheme 4).[40] Removing one of the chlorine atoms of the Pt^{II} complex with $AgBF_4$, the N atom of the hetaryl ring was coordinated to the Pt^{II}.

An α-aminophosphine containing a 2-pyridyl-piperazine moiety was also tested as a ligand for Pt^{II} (Scheme 5).[42] The product was obtained in a quantitative yield after a reaction time of 1 h. By reacting the product with $AgClO_4$, similarly to the previous example, the nitrogen atom of the hetero ring was coordinated to the Pt^{II} centre.

If an N atom is present at a suitable position of the Pt^{II} complexes, the parallel coordination of the N and cleavage of a Pt–Cl bond can be accomplished by adding silver salts.

The reaction of diphenylphosphinomethyldimethylamine with $Pt^{II}(nbd)Me_2$ (nbd = γ^4-2,5-norbornadiene) was performed at room temperature for 1 h in benzene as the solvent (Scheme 6).[43] The *cis* complex was obtained in a yield of 79%.

By applying different platinum(II) precursors, the conformation of Pt^{II} complexes of 2-(*N*-diphenylphosphinomethyl-*N*-benzyl)-aminopyridine could be fine-tuned. Complexation with $Pt^{II}(cod)Cl_2$ afforded the corresponding *cis* product, whereas by applying $Pt^{II}(cod)(C{\equiv}CPh)_2$, a complex with a *trans* conformation could be synthesized (Scheme 7).[44] The *trans* product could also be prepared by reaction of the *cis* derivative with sodium phenylacetilide; however, in this case the yield was only 46%. The related structures were proved by X-ray diffraction measurements (Fig. 2).

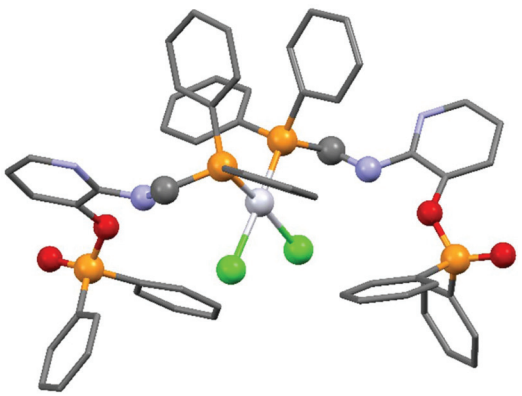
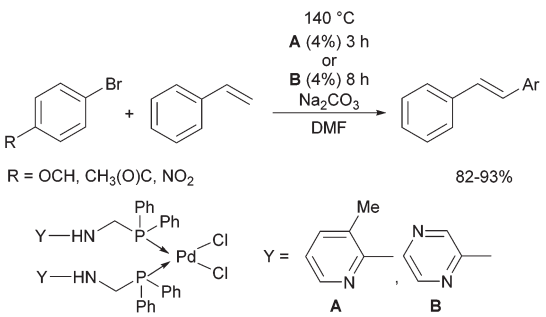
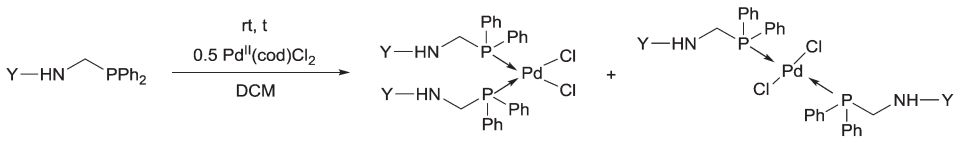


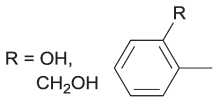
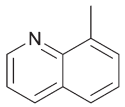
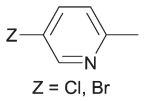
Fig. 1 X-Ray structure of *cis*-dichloro-bis(diphenyl(3-(diphenylphosphinato)-2-pyridylaminomethyl)phosphine)-platinum(II) [CCDC 150040].[38]



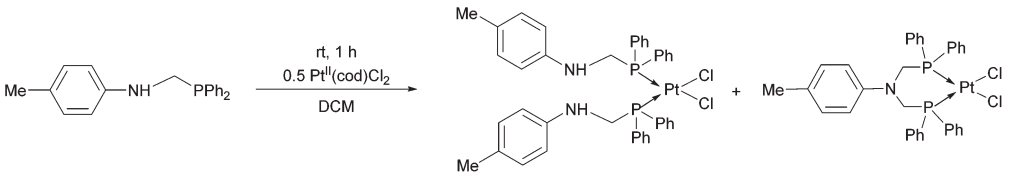
Scheme 2 Pd complexes of *N*-hetaryl α-aminophophines as catalysts in Heck reactions.

Table 2 *Cis* and *trans* Pd^{II} complexes of diphenylphosphinomethylamines

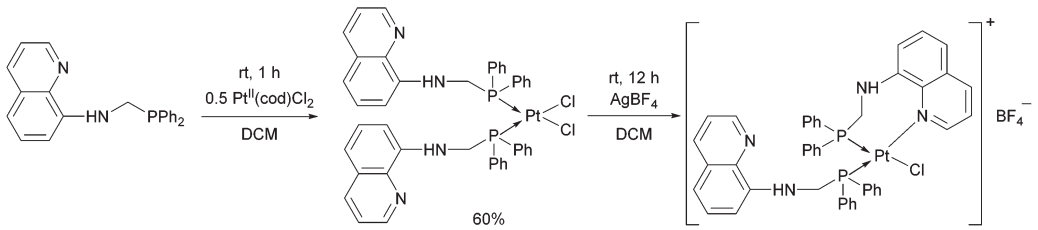


Entry	Y	*t* [min]	*cis* : *trans* ratio[a] [%]	Yield [%]	Ref.
1	 R = OH, CH_2OH	15	82 : 18 (R = HO) 69 : 31 (R = $HOCH_2$)	68–93	35
2		60	n.a.	73	40
3	 Z = Cl, Br	15	71 : 29 (X = Cl) n.a. (X = Br)	77–85	34 and 37

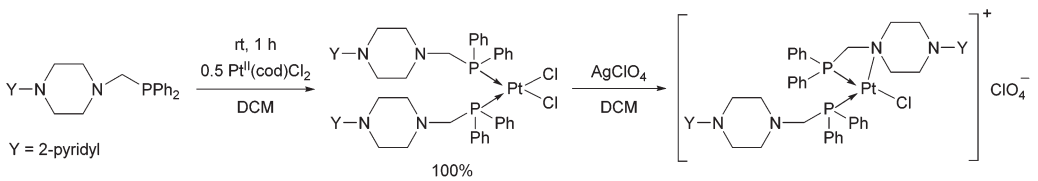
[a] In solution. n.a.: Not available.



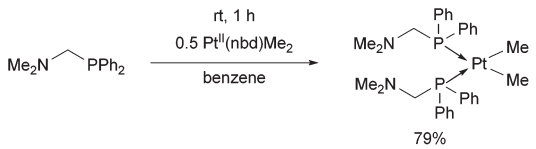
Scheme 3 The complexation of diphenylphosphinomethyl-4-methylaniline with $Pt^{II}(cod)Cl_2$.



Scheme 4 The reaction of an *N*-quinoline-α-aminophosphine with $Pt^{II}(cod)Cl_2$.



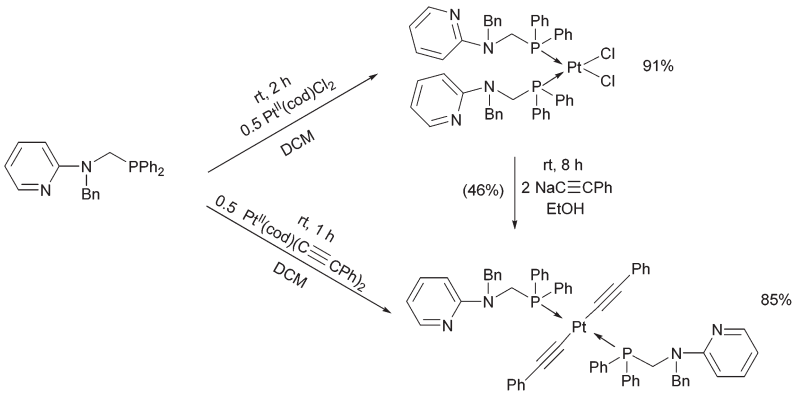
Scheme 5 Platinum(II) complexes of α-aminophosphine containing a 2-pyridyl-piperazine moiety.



Scheme 6 Synthesis of bis[(*N*,*N*-dimethylamino)-methyldiphenyl-phosphino]dimethyl-platinum(II).

In contrast to the previous cases, the *trans* Pd^{II} complex was obtained by the reaction of 2-(*N*-dicyclohexylphosphinomethyl-*N*-methyl)aminopyridine with $Pd^{II}(cod)Cl_2$ after 24 h (Scheme 8).[45] The different reactivity may be explained by the presence of two cyclohexyl groups on the phosphorus.

Another Pd^{II} complex containing a pyridyl moiety was synthesized from an *N*-4-pyridyl α-aminophosphine at room



Scheme 7 Fine-tuning the conformation of the P-ligands in the Pt^{II} complexes by varying the Pt^{II} precursors.

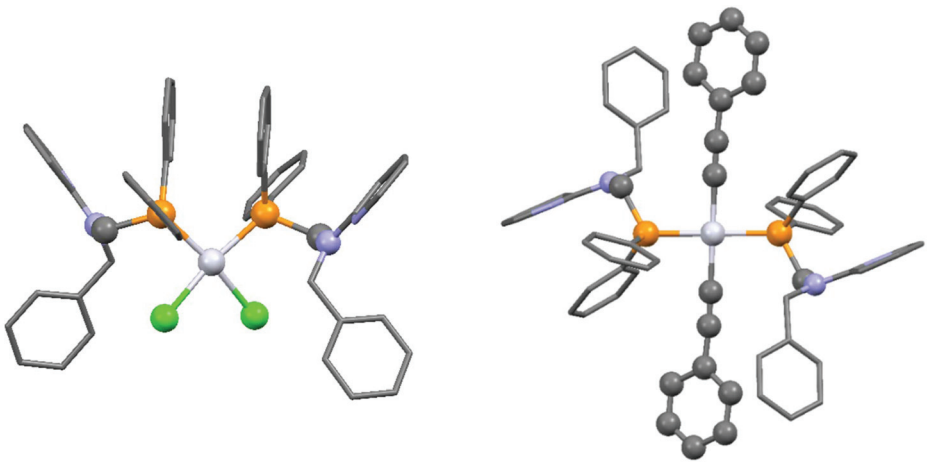
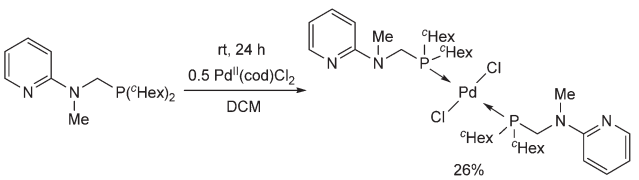
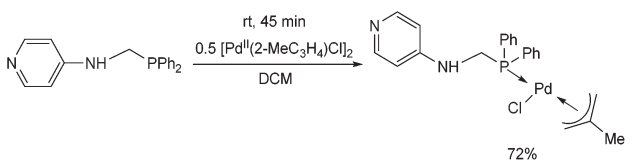


Fig. 2 X-Ray structures of Pt^{II} complexes incorporating 2-(*N*-diphenylphosphinomethyl-*N*-benzyl)aminopyridine [CCDC 197274, 197275].[44]



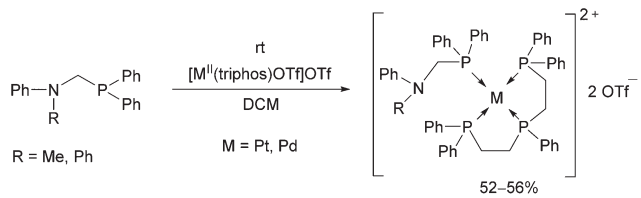
Scheme 8 The reaction of 2-(*N*-dicyclohexylphosphinomethyl-*N*-methyl)aminopyridine with $Pt^{II}(cod)Cl_2$.



Scheme 9 Complexation of an *N*-pyridyl α-aminophosphine with $[Pd^{II}(2\text{-}MeC_3H_4)Cl]_2$.

temperature after 45 min by applying $[Pd^{II}(2\text{-}MeC_3H_4)Cl]_2$ as the precursor (Scheme 9).[36]

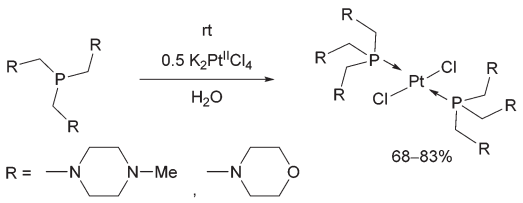
Reactions of diphenylphosphinomethylamines with $[M^{II}(triphos)OTf](OTf)$ (M = Pt, Pd) led to the corresponding



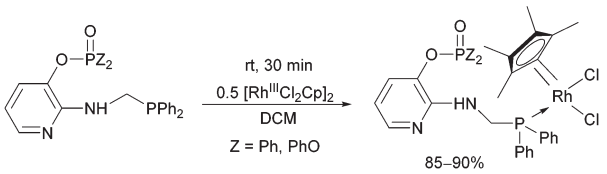
Scheme 10 Synthesis of $[Pt(triphos)P(Ph_2)CN(Ph)(R)](OTf)_2$ complexes.

tetracoordinated Pd^{II} complexes in yields of 52–56% at room temperature (Scheme 10).[46] The complexes were tested as catalysts in electrochemical proton reduction, and showed modest activities.

Tris(aminomethyl)phosphines were also efficient P-ligands in the synthesis of Pt^{II} complexes (Scheme 11).[47] The reactions were carried out by applying K_2PtCl_4 as the precursor in water. Due to the sterically demanding ligands, the *trans* isomers were the only products. The structure of the complexes was evaluated by X-ray measurements and DFT calculations. According to *in vitro* investigations, the complex containing morpholine moieties was able to induce apoptosis.



Scheme 11 Reaction of tris(aminomethyl)phosphines with $K_2Pt^{II}Cl_4$.



Scheme 15 The utilization of *N*-pyridyl-substituted aminophosphines as P-ligands.

2.2. Synthesis of rhodium complexes

In the case of monodentate α-aminophosphine ligands, $[Rh^{III}CpCl_2]_2$ was the most widely used precursor in the synthesis of rhodium(III) complexes. In most instances, the Rh^{III} complexes were prepared at room temperature using DCM as the solvent. Complexation of α-aminophosphines containing a hydroxy group led to full conversion after 15 minutes, furnishing the desired products in yields of 63–90% (Scheme 12).[35]

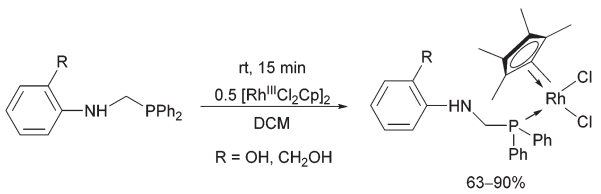
Complexation of *N*-diphenylphosphinomethyl(2-diphenylphosphino)aniline was investigated in THF (tetrahydrofuran) as the solvent (Scheme 13).[48] This special ligand was also able to act as a bidentate P-ligand *via* the coordination of the phosphine function to the Rh^{III} by reaction with $AgClO_4$.

The reaction of α-aminophosphines containing a 5-chloro- or 5-bromopyridyl moiety with $[Rh^{III}Cl_2Cp]_2$ was also studied (Scheme 14).[34,37] The N atom of the pyridine ring could also be coordinated to the metal centrum by a reaction of the resulting Rh^{III} complex with $AgBF_4$. The incorporation of a suitably disposed halogeno group offers the possibility for further functionalization of the products.

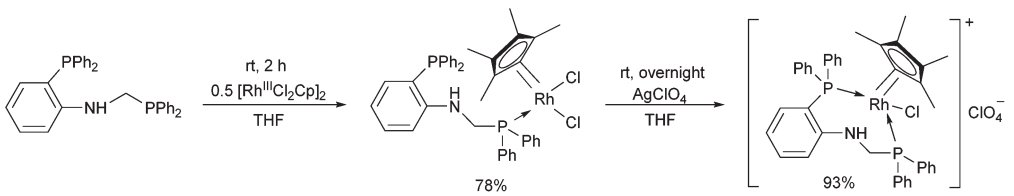
Due to their versatility, *N*-pyridyl-functionalized aminophosphines represent an important class among P-ligands.[49] Derivatives bearing a >P(O)O-function on the hetaryl ring (a pyridyl phosphate or phosphinate) were also used as P-ligands to obtain Rh^{III} complexes in good yields (85–90%) after a reaction time of 30 min (Scheme 15).[38]

8-(Diphenylphosphino)methylaminoquinoline (8-dppmaq) was also tried out in the complexation with $[Rh^{III}CpCl_2]_2$ as the metal precursor (Scheme 16).[40] An X-ray study of the product revealed an intramolecular H bond between the N atom of the quinoline and the H atom of the NH function (Fig. 3). When the resulting Rh^{III} complex was reacted with two equivalents of $AgBF_4$, the two N atoms of the aminoquinoline could also be coordinated to the metal centrum. The *in situ* formed Rh^{I} catalyst from the same ligand and $Rh(acac)CO_2$ as a Rh^{I} precursor was proved to be efficient in the hydroformylation of hex-1-ene.

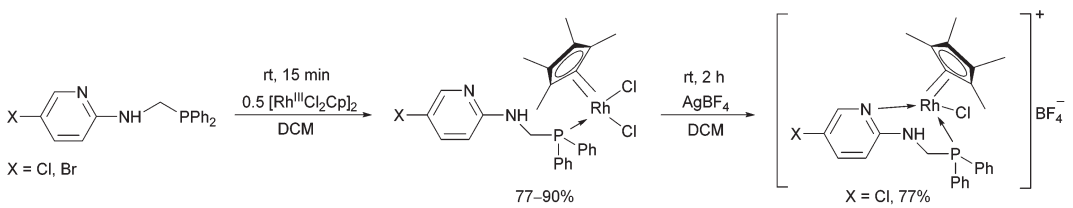
$[Rh^{III}Cl_2Cp]_2$ also served as a Rh^{III} precursor in the complexation of 9-(diphenylphosphinomethyl)adenine (Scheme 17).[50] After a reaction time of 1 h, the complex was prepared in a yield of 73%. It was found that the corresponding pincer-type complex, where the adenine ring is also a ligand, could not be



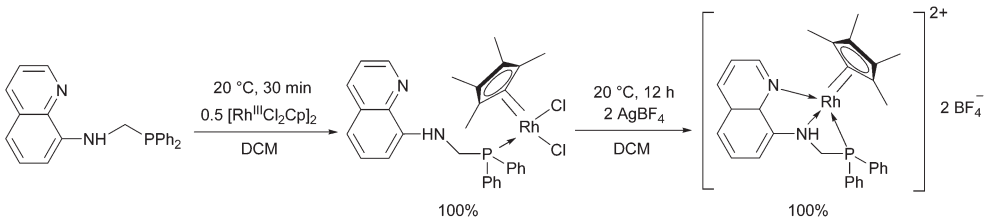
Scheme 12 The complexation of α-aminophosphines containing a hydroxy function.



Scheme 13 The use of *N*-diphenylphosphinomethyl(2-diphenylphosphino)aniline as a monodentate or a bidentate ligand.



Scheme 14 The reaction of α-aminophosphines containing a 5-halogeno-pyridyl moiety with $[Rh^{III}Cl_2Cp]_2$.



Scheme 16 The complexation of 8-(diphenylphosphino)methylaminoquinoline.

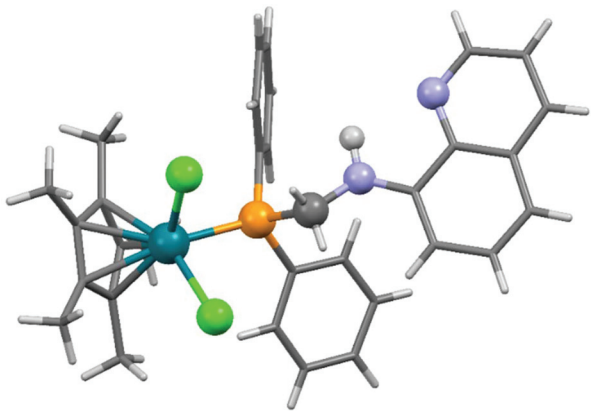


Fig. 3 X-Ray structure of [CpRhCl$_2$(8-dppmaq)] [CCDC 177446].[40]

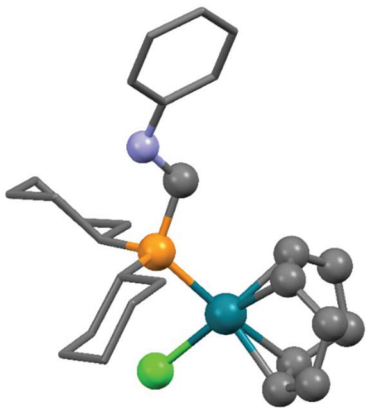
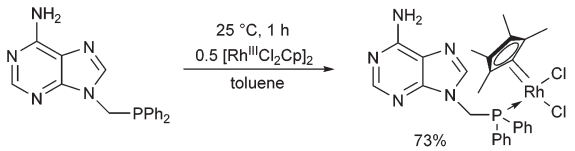
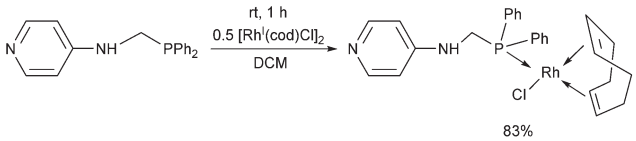


Fig. 4 X-Ray structure of (^{c}Hex$_2$PCH$_2$NHPh)Rh(cod)Cl [CCDC 748467].[51]



Scheme 17 The use of 9-(diphenylphosphinomethyl)adenine as a monodentate ligand.

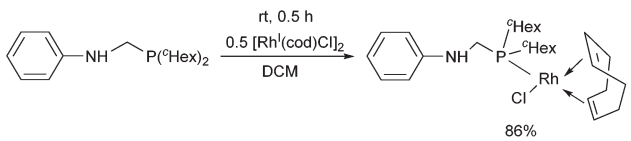


Scheme 19 The reaction of phosphinomethylamine ligands with [Rh^I(cod)Cl$_2$]$_2$.

obtained, because the complex was not electron-rich enough for the oxidative addition.

Dicyclohexylphosphinomethylaniline was also subjected to complexation (Scheme 18).[51] After a reaction time of 0.5 h, the corresponding Rh^I complex was obtained in a yield of 86%. An X-ray study of the product revealed a square planar geometry around the metal center (Fig. 4).

N-(Diphenylphosphinomethyl)-4-aminopyridine was also reacted with [Rh^I(cod)Cl$_2$]$_2$ as the rhodium(I) precursor (Scheme 19).[36] The Rh^I complex was prepared at room temperature using DCM as the solvent. Attempts to synthesize bimetallodendrimers from the corresponding Rh^I complex were not successful.

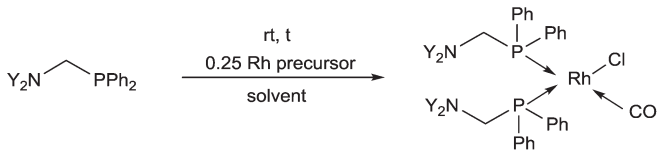


Scheme 18 Complexation of the dicyclohexylphosphinomethylaniline with [Rh^I(cod)Cl$_2$]$_2$.

Complexes containing two α-aminophosphine ligands could be obtained in the reactions of two equivalents of diphenylphosphinomethylamines with one equivalent of the Rh^I precursor (Table 3). Starting from diphenylphosphinomethyl-diethylamine and [Rh^I(CO)$_2$Cl]$_2$ or [Rh^I(CO)(CH$_2$=CH$_2$)Cl]$_2$, the complexations were carried out at room temperature for 2 h using DCM as the solvent (Table 3/entry 1). The products were characterized by NMR spectroscopy, but the yields were not reported. According to a recent study, the reaction of diphenylphosphinomethyldiphenylamine with [Rh^I(CO)$_2$Cl]$_2$ was complete after 0.5 h using toluene as the solvent (Table 3/entry 2). An X-ray study of the corresponding Rh^I complex confirmed the *trans* geometry (Fig. 5).

In a special case, tris[(arylamino)methyl]phosphines were used as monodentate P-ligands in the synthesis of Rh^I complexes by applying [Rh^I(CO)$_2$Cl]$_2$ as the metal precursor

Table 3 Rhodium complexes containing two diphenylphosphinomethylamine ligands



Entry	Y	Rh precursor	Solvent	*t* [h]	Yield [%]	Ref.
1	Et	$[Rh^{I}(CO)_2Cl]_2$, $[Rh^{I}(CO)(CH_2{=}CH_2)Cl]_2$	DCM	2	n.a.	52
2	Ph	$[Rh^{I}(CO)_2Cl]_2$	Toluene	0.5	67	53

n.a.: Not available.

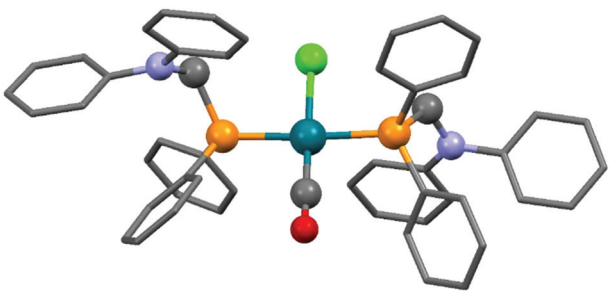


Fig. 5 X-Ray structure of $Rh(Ph_2PCH_2NPh_2)_2(CO)Cl$ [CCDC 1265045].[53]

(Scheme 20).[54] The reactions were performed in deuterated dichloromethane at room temperature to allow an NMR characterization study immediately after the reaction. As suggested by the IR spectra of the complexes, despite the rather long distance from the P-center, the effect of the different aryl substituents was significant on the C–O stretching frequencies.

2.3. General methods for the preparation of complexes containing monodentate α-aminophosphines as ligands

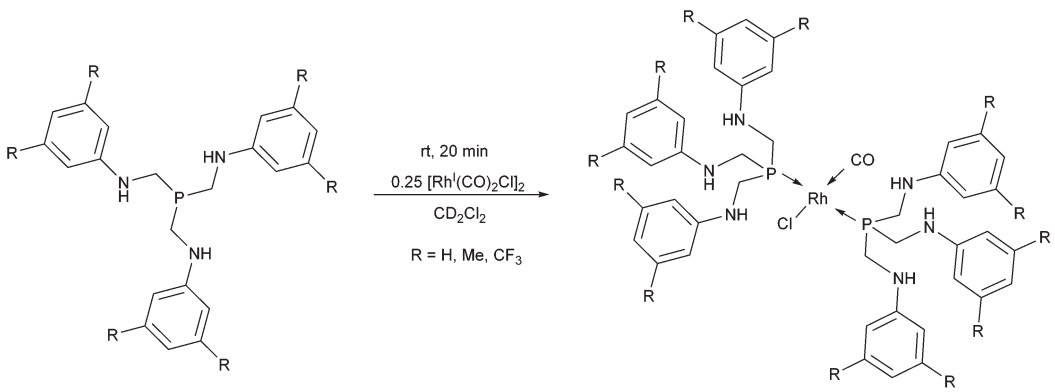
Based on the various synthetic methods reported, we wished to provide a brief summary of the preparation of Pt, Pd and Rh complexes incorporating α-aminophosphines as monodentate P-ligands (**I–III**) (Table 4). According to the literature data, most of the reactions can be carried out at room temperature using DCM as the solvent. Pt and Pd complexes with one monodentate P-ligand (**I**) may be prepared using $[M^{II}(triphos)OTf][OTf]$ (M = Pt, Pd) as the metal precursor to afford the complexes in yields of 52–56%. Similar Rh complexes may be synthesized by reaction of α-aminophosphines with 0.5 equivalents of $[Rh^{III}Cl_2Cp]_2$ in good to quantitative yields. Pt and Pd complexes bearing two α-aminophosphine ligands in *cis* conformation (**II**) may be obtained easily using 0.5 equivalents of $M^{II}(cod)Cl_2$ (M = Pt, Pd) to furnish the products in yields of 58–92%. The *trans* oriented Pt, Pd and Rh complexes (**III**) may be prepared by reaction of bulky α-aminophosphines with 0.5 equivalents of $Pt^{II}(cod)(C{\equiv}CPh)_2$, 0.5 equivalents of $Pd^{II}(cod)Cl_2$, or 0.25 equivalents of $[Rh^{I}(CO)_2Cl]_2$, respectively.

3. Utilization of α-aminophosphines as bidentate ligands

Among α-aminophosphines, bidentate derivatives are the most widely applied as ligands in the synthesis of platinum(II), palladium(II) or rhodium(II) complexes.

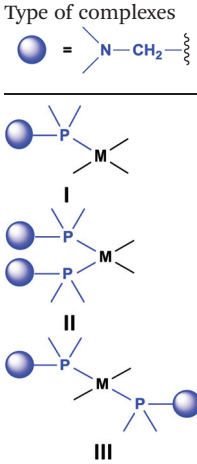
3.1. Synthesis of platinum and palladium complexes

Based on the literature data, one of the most important types of bidentate α-aminophosphine ligands is the family of bis(phosphinomethyl)amines. The synthesis of cyclic platinum complexes containing simple alkyl or aryl bis(phosphinomethyl)amine ligands at room temperature is summarized in Table 5. A series of *cis*-oriented [bis(diphenylphosphinomethyl)amine]dichloroplatinum(II) complexes was prepared by our group using dichlorodibenzonitrile platinum(II) (Table 5/entry 1). The complexation was extended by applying bis(aminophosphine) ligands bearing benzyl or 4-methylphenyl groups on the phosphorus atoms (Table 5/entry 2). The dependence of the energetics of the complexations on the substituents and the stereostructure of the complexes was evaluated by B3LYP/6-31G(d,p) calculations. The six-membered



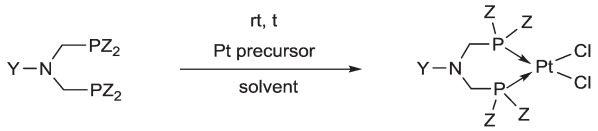
Scheme 20 Rhodium complexes incorporating two tris[(arylamino)methyl]phosphine derivatives as the ligands.

Table 4 General methods for the preparation of complexes containing monodentate α-aminophosphines as ligands

Type of complexes	M	Precursor	*t*	Average yield [%]
 I	Pt	$[Pt^{II}(triphos)OTf][OTf]$	n.a.	52–56
	Pd	$[Pd^{II}(triphos)OTf][OTf]$	n.a.	55–56
	Rh	0.5 $[Rh^{III}Cl_2Cp]_2$	15 min–2 h	63–100
II	Pt	0.5 $Pt^{II}(cod)Cl_2$	15–30 min	58–89
	Pd	0.5 $Pd^{II}(cod)Cl_2$	15–30 min	63–92
III	Pt	0.5 $Pt^{II}(cod)(CD{\equiv}CPh)_2$	1 h	85
	Pd	0.5 $Pd^{II}(cod)Cl_2$	24 h	26
	Rh	0.25 $[Rh^{I}(CO)_2Cl]_2$	0.5–2 h	67

n.a.: Not available.

Table 5 Synthesis of bidentate platinum(II) complexes containing bis(phosphinomethyl)amine ligands



Entry	Y	Z	Pt precursor	Solvent	*t* [h]	Yield [%]	Ref.
1	^{n}Pr, ^{n}Bu, ^{c}Hex, Bn, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$	Ph	$Pt^{II}(PhCN)_2Cl_2$	Benzene	24	38–60	29 and 55
2	^{n}Bu, ^{c}Hex, Bn	Bn, 4-MeC_6H_4	$Pt^{II}(PhCN)_2Cl_2$	Benzene	12	52–75	30
3	Ph	^{c}Hex, Ph	$Pt^{II}(cod)Cl_2$	THF, DCM	0.5–24	70–85	56
4	^{t}Bu, 4-MeC_6H_4	Ph	$Pt^{II}(cod)Cl_2$	DCM	1	74–79	41

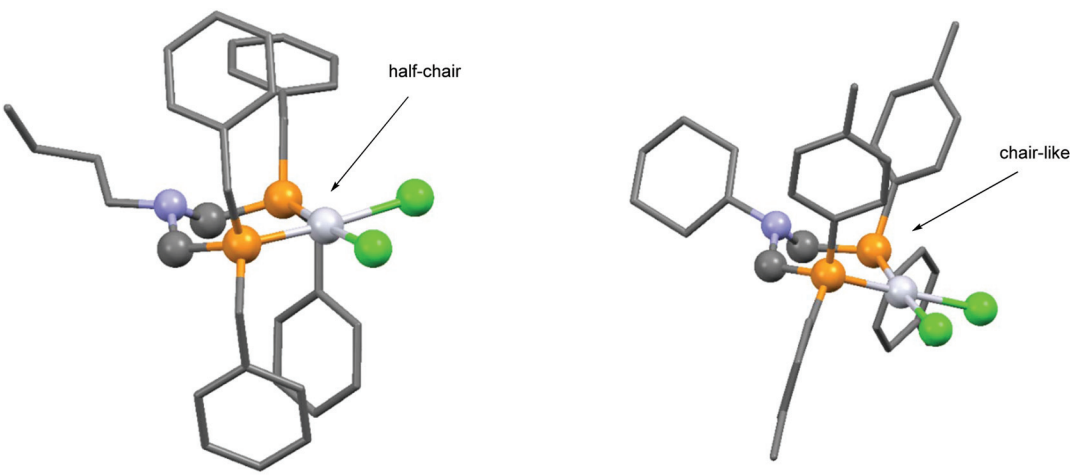
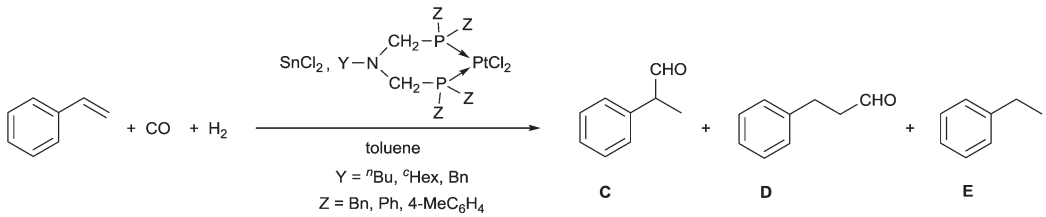


Fig. 6 X-Ray structures of *N,N*-[bis(dibenzylphosphinomethyl)butylamine]-dichloroplatinum(II) [CCDC 1414765] and *N,N*-[bis(ditolylphosphinomethyl)cyclohexylamine]-dichloroplatinum(II) [CCDC 1416216].[30]

metallocycle with two benzyl groups on each P atom adopts a half-chair conformation, while the P-aryl species take up a chair-like conformation. This was also confirmed by X-ray investigations (Fig. 6). $Pt^{II}(cod)Cl_2$ was also applied as a precursor for the synthesis of *cis* chelate Pt complexes (Table 5/entries 3 and 4). In these cases, the reactions were carried out in DCM or in THF, and the corresponding Pt^{II} complexes were obtained in yields of 70–85%.

Table 6 Hydroformylation of styrene in the presence of *in situ* formed catalysts from platinum(II) complexes and tin(II) chloride



Entry	Y	Z	Temperature [°C]	t [h]	Conversion [%]	R_c [%][a]	R_{br} [%][b]	Ref.
1[c]	^{c}Hex	Ph	60	20	~100	78	74	29
2[c]	Bn	Ph	60	5	87	76	77	
3[d]	^{n}Bu	Bn	100	3	32	72	65	30
4[d]	^{c}Hex	Bn	100	3	50	74	61	
5[d]	Bn	Bn	100	3	52	70	65	
6[d]	^{n}Bu	4-MeC$_6$H$_4$	100	8	98	75	63	30
7[d]	^{c}Hex	4-MeC$_6$H$_4$	100	6	98	74	63	
8[d]	Bn	4-MeC$_6$H$_4$	100	3	98	79	56	

[a] Chemoselectivity towards aldehydes (**C**, **D**). [(**C** + **D**)/(**C** + **D** + **E**) × 100]. [b] Regioselectivity towards branched aldehyde (**C**). [**C**/(**C** + **D**) × 100]. [c] Reaction conditions: Pt/SnCl$_2$/styrene = 1/1/100; p(CO) = p(H$_2$) = 40 bar. [d] Reaction conditions: Pt/SnCl$_2$/styrene = 1/2/200; p(CO) = p(H$_2$) = 40 bar.

On the above basis, the complexation of bis(phosphinomethyl)amines was efficient, independently of the substituents on the N and P atoms, with both types of Pt^{II} precursors affording cyclic *cis*-oriented complexes.

A few related Pt^{II} complexes were tested as catalysts in the hydroformylation of styrene, where tin(II) chloride was used as a cocatalyst, and toluene served as a solvent (Table 6). Comparing the effect of the substituents on the P atoms, it can be seen that the *P*-aryl complexes were more active than the *P*-benzyl derivatives (Table 6/entries 1, 2 and 6–8 *vs.* entries 3–5). Regarding the *N*-substituent, a benzyl group on the nitrogen atom increases the activity, as compared to the butyl and cyclohexyl groups (Table 6/entry 2 *vs.* entry 1, and entry 8 *vs.* entries 6, 7). As regards the chemoselectivity, the complexes had a similar effect; however, from the point of view of regioselectivity, the best precatalysts were the *P*-phenyl complexes giving the branched aldehyde (**C**) in regioselectivities of 74 and 77% (Table 6, entries 1 and 2).

The complexation of a chiral (*S*)-α-phenylethylamine functionalized α-aminophosphine with Pt^{II}(PhCN)$_2$Cl$_2$ has been described by our group (Scheme 21).[57] It was observed that besides the chiral bidentate Pt complex expected, a bicyclic derivative was also formed in a small amount as a by-product. Based on the ^{31}P NMR spectrum, the ratio of the two complexes was 85 : 15. The X-ray investigation of the bicyclic complex revealed a highly solvated complex salt structure, as

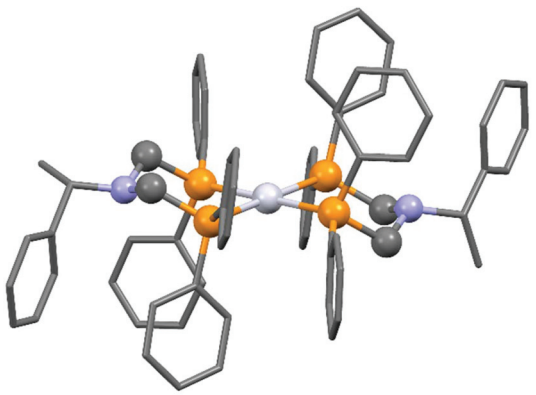
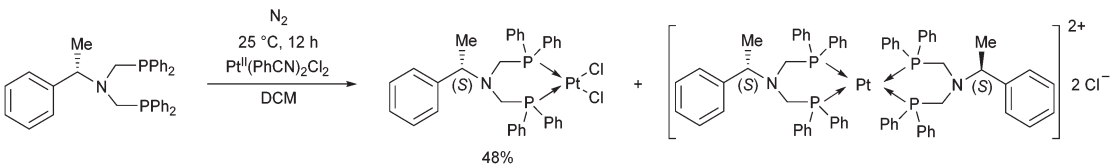


Fig. 7 X-Ray structure of the chiral bicyclic platinum(II) complex [CCDC 1547003].[57]

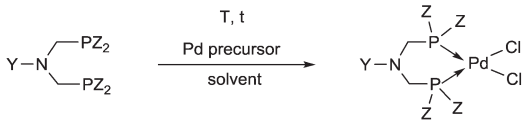
well as a pseudo-centrosymmetric disposition of most atoms of a chiral molecular complex in a chiral crystal lattice (Fig. 7).

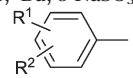
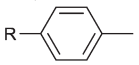
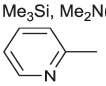
Bis(phosphinomethyl)amines were also proved to be efficient ligands in the synthesis of palladium(II) complexes (Table 7). The complexation of bis(diphenylphosphinomethyl) aniline with Pd^{II}(PhCN)$_2$Cl$_2$ in DCM afforded the corresponding complex in a yield of 79% after 5 min (Table 7/entry 1). According to the X-ray structure of the complex, a flattened boat conformation was observed. Similar Pd^{II} complexes con-



Scheme 21 Synthesis of a chiral platinum(II) complex.

Table 7 Synthesis of palladium(II) complexes of bidentate bis(phosphinomethyl)amine ligands

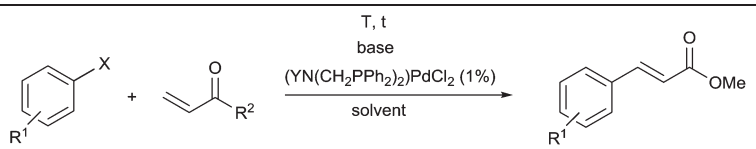


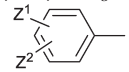
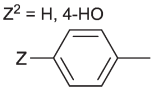
Entry	Y	Z	Pd precursor	Solvent	Temperature, *t*	Yield [%]	Ref.
1	Ph	Ph	$Pd^{II}(PhCN)_2Cl_2$	DCM	rt, 5 min	79	53
2	Ph	^{t}Bu, ^{c}Hex	$Pd^{II}(PhCN)_2Cl_2$	THF, toluene	65–80 °C, 18–20 h	85–99	56
3	Me, ^{t}Bu, 3-$NaSO_3$-C_6H_4	Ph	$Pd^{II}(cod)Cl_2$	DCM	rt, 1–2 h	81–88	58
4	 R^1 = 3-Me, 4-PhO, 2-PhS R^2 = H, 4-HO	Ph	$Pd^{II}(cod)Cl_2$	DCM	40 °C, 3–4 h	65–80	59
5	 R = HO, Br, Me_3SiO, Me_3Si, $Me_2N(CH_2)_2Me_2Si$	Ph	$Pd^{II}(cod)Cl_2$	DCM	rt, 3 h	75–87	60
6		Ph	$Pd^{II}Cl_2$	DCM : MeCN (1 : 1)	rt, 5 min	94	61 and 62

taining *tert*-butyl or cyclohexyl groups on the two P atoms were also prepared. In these cases, higher temperature (65–80 °C) and longer reaction time (18–20 h) were necessary (Table 7/entry 2). Starting from *N*-aliphatic or sulfonated phosphines and $Pd^{II}(cod)Cl_2$, the corresponding complexes were obtained at room temperature after 1–2 h in yields of 81–88% (Table 7/entry 3). By treatment of the same precursor with phosphines containing a substituted Ph-ring in boiling DCM, several new bidentate Pd^{II} chelate complexes were obtained, which were effective catalysts in the Heck reaction of olefins and aryl halides (Table 7/entry 4). Non-dendritic bisphosphines were also used as Pd ligands (Table 7/entry 5). The complexes synthesized were tested as catalysts in the Heck reaction of 4-iodotoluene and methyl acrylate. In the case of bis(diphenylphosphinomethyl) amino-2-pyridine as the ligand, $Pd^{II}Cl_2$ was applied as the precursor (Table 7/entry 6). The complexation performed at room temperature resulted in the formation of the Pd^{II} complex in a high yield (94%).

Starting from different types of Pd^{II} precursors, the palladium(II) complexes of bis(phosphinomethyl)amines could be prepared efficiently. Depending on the substituents of the P and N atoms of the ligand, the complexations required different reaction conditions. The catalytic activity of several Pd^{II} complexes was tested in the Heck reactions of aryl halides and alkyl acrylates (Table 8). In the reactions, potassium phosphate or triethylamine was used as the base in *N*-methylpyrrolidone (NMP) or in acetonitrile. It could be observed that the performance of the catalysts depended on

Table 8 Heck reaction of aryl halides and alkyl acrylate in the presence of bidentate Pd^{II} complexes



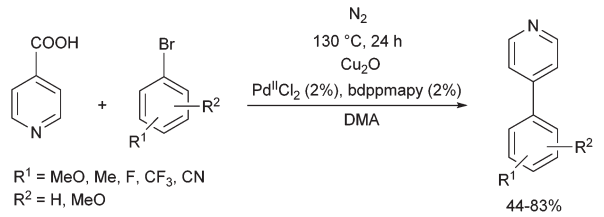
Entry	R^1	X	R^2	Y in catalyst	Base	Solvent	Temperature, *t*	Conversion [%]	Ref.
1	H	Cl, Br	Me	Me, ^{t}Bu, 3-$SO_3NaC_6H_4$	K_2PO_3	NMP	140 °C, 14 h	53–96	58
2	H, MeO	Cl, Br, I	Me, Bu	 Z^1 = 3-Me, 4-PhO, 2-PhS Z^2 = H, 4-HO	NEt_3	NMP	120 °C, 4–12 h	53–100	59
3	Me	I	Me	 Z = H, Me_3Si, Me_2N	NEt_3	MeCN	80 °C, 24 h	41–60	60

the *N*-substituents. The *N*-aliphatic or the *N*-(sodium benzenesulfonyl) complexes were less active than the Pd^{II} complexes bearing an aryl group on the nitrogen atom (Table 8/entry 1 *vs.* entry 2). Complexes of non-dendritic bisphosphines showed a modest activity and stability in the Heck reaction of 4-iodotoluene and methyl acrylate (Table 8/entry 3).

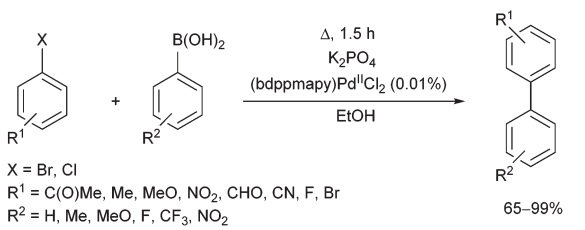
The Pd^{II} complex of bis(diphenylphosphinomethyl)amino-2-pyridine (bdppmapy) was applied as a catalyst in the decarboxylative C–C coupling of 4-picolinic acid with aromatic bromides, and showed a good catalytic performance (Scheme 22).[61] The reactions were carried out at 130 °C in *N*,*N*-dimethylacetamide (DMA) as the solvent. The catalytic activity of the bdppmapy-Pd complex was compared to that of other Pd^{II} complexes containing alkyl and aryl phosphines in cross-coupling of 4-picolinic acid and 2,4-dimethoxy bromobenzene. From the catalytic results, the bdppmapy-Pd complex was the most effective, as the yield of the product was 78%. In the case of other phosphine-Pd^{II} complexes, the yields were in the range of 15–48%.

The effect of different phosphine ligands on the Suzuki–Miyaura cross-coupling of 4-bromoacetophenone and 4-methoxyphenylboronic acid was also investigated, where the α-aminophosphine-based Pd^{II} complexes were also found to be more efficient than the alkyl and aryl phosphine complexes (yields of 99% *vs.* 79–85%, respectively).[62] The coupling reaction was extended to other aryl halides and arylboronic acids (Scheme 23). A wide range of biaryl compounds were obtained in yields of 65–99% under mild conditions.

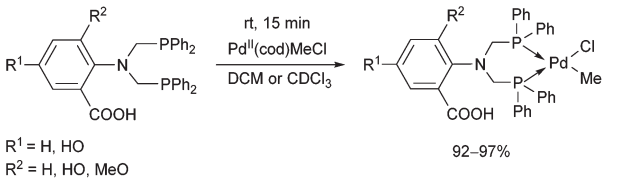
The complexation of α-aminophosphines bearing a benzoic acid moiety using Pd^{II}(cod)MeCl as the metal precursor was performed at room temperature for 15 min (Scheme 24).[63] The metathesis of one of the complexes (R^1 = H, R^2 = MeO) with sodium bromide and iodide was also elaborated, giving



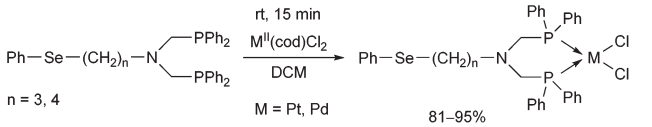
Scheme 22 Pd-Catalyzed cross-coupling of 4-picolinic acid and aryl bromides.



Scheme 23 Suzuki–Miyaura coupling of aryl halides with arylboronic acids.



Scheme 24 Preparation of mononuclear Pd^{II} complexes from α-aminophosphines bearing a benzoic acid moiety.



Scheme 25 Utilization of *N*-phenylselenoalkyl-bis(aminophosphines) as ligands in the synthesis of *cis* chelate transition metal complexes.

(methyl)bromopalladium(II) and (methyl)iodopalladium(II) derivatives.

N-Phenylselenoalkyl-bis(aminophosphines), a special family of ligands, were also utilized as bidentate P-ligands in the synthesis of Pt^{II} and Pd^{II} complexes (Scheme 25).[64] According to X-ray studies, the products were of *cis* configuration, and the metal centre was in a nearly square planar geometry.

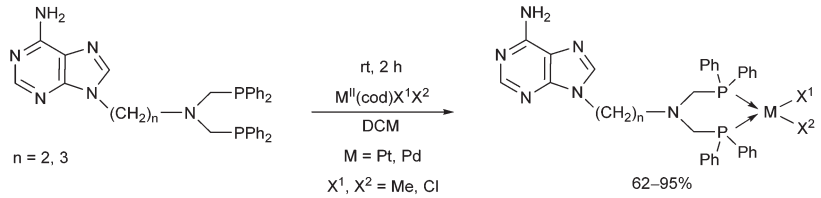
The coordination of bis(diphenylphosphinomethyl)amino derivatives of adenine to transition metals was also investigated (Scheme 26).[65] A series of bidentate chelate complexes was synthesized in good yields using various Pt^{II} and Pd^{II}(cod) precursors. It was observed that all complexes retained the free adenine moiety for complementary hydrogen bonding.

Crown ether-functionalized Pt^{II} and Pd^{II} complexes were synthesized by the reaction of bis(diphenylphosphinomethyl)-aminobenzo-15-crown-5 and $Pt^{II}(cod)Cl_2$ or $Pd^{II}(cod)Cl_2$ at room temperature using toluene–DCM as the solvent in a reaction time of 2 h (Scheme 27).[66]

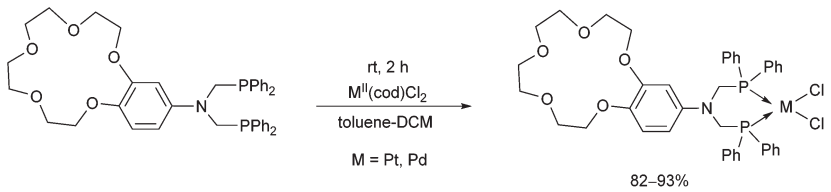
Water-soluble phosphine ligands incorporating an ethoxylated phosphonate chain were reacted with dihydrogen tetrachloropalladate(II) at the boiling point of butanol for 4 h (Scheme 28).[67] The corresponding Pd^{II} complexes obtained in yields of 70–78% showed good catalytic activity in the biphasic carbonylation of benzyl chloride.

Complexation of a (3-aminopropyl)triethoxysilane-functionalized bisphosphine ligand with $[Pd^{II}(\eta^3\text{-allyl})Cl]_2$ in THF afforded the desired Pd^{II} complex, which was co-immobilized with SiO_2, as well as with SiO_2-supported DABCO (1,4-diazabicyclo[2.2.2]octane) (Scheme 29).[68]

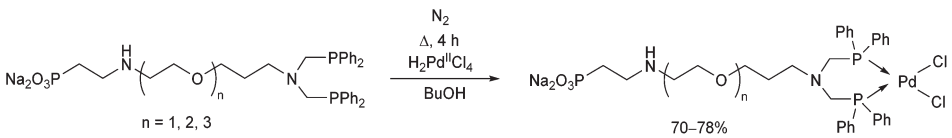
The complexes prepared were utilized as catalysts in the allylation of ethyl acetoacetate by (allyl)(methyl)carbonate (Table 9).[69] The reactions were carried out in the presence of K_2CO_3 in toluene at 70 °C for 60 min. It was observed that the catalytic activity of the homogeneous PP-Pd^{II} complex was similar to the SiO_2-supported heterogeneous PP-Pd^{II} catalyst



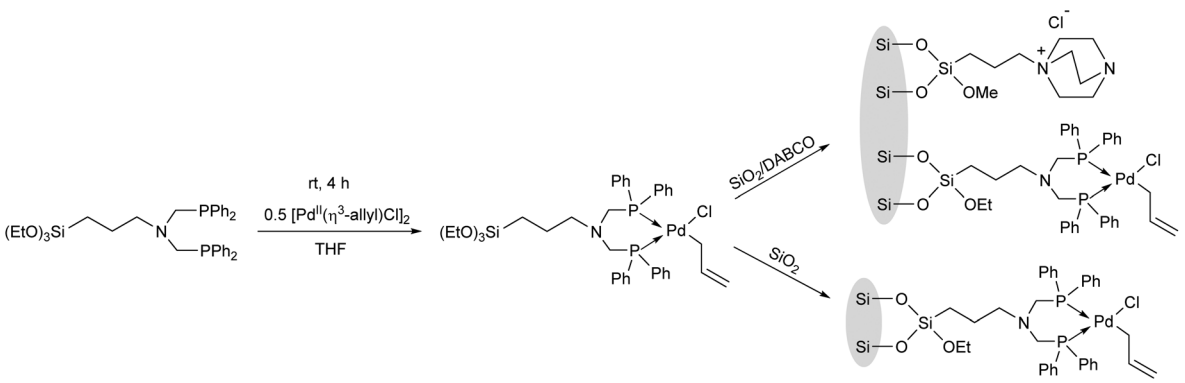
Scheme 26 Pt^{II} and Pd^{II} complexes of bis(α-aminophosphine) ligands containing an adenine moiety.



Scheme 27 Synthesis of crown ether-functionalized cyclic Pt^{II}/Pd^{II} complexes.

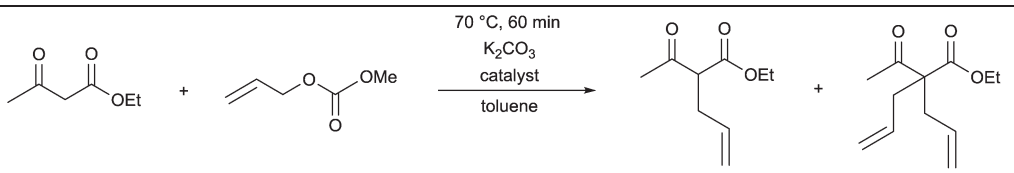


Scheme 28 Preparation of Pd^{II} complexes incorporating water-soluble bidentate α-aminophosphine ligands.



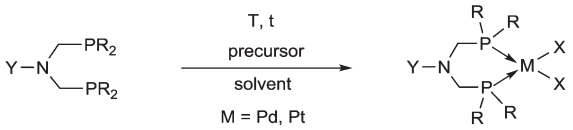
Scheme 29 Synthesis of SiO_2-supported palladium(II)-bisphosphine complexes.

Table 9 Allylation of ethyl acetoacetate in the presence of Pd^{II} complexes

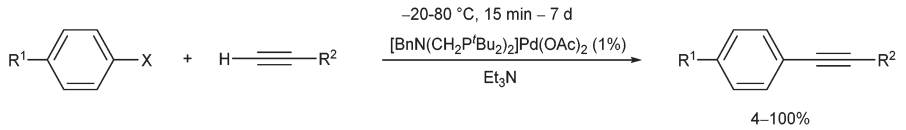


Entry	Catalyst	Conversion [%]	Yield (mono : di) [%]
1	PP-Pd^{II}	97	48 : 42
2	SiO_2/PP-Pd^{II}	98	40 : 49
3	SiO_2/DABCO/PP-Pd^{II}	99	18 : 81

Table 10 Bidentate palladium complexes of bis(dialkylphosphinomethyl)amine ligands



Entry	Y	R	Pd or Pt precursor	X	Solvent	Temperature, *t*	Yield [%]	Ref.
1	Bn	^{t}Bu	$Pd^{II}(OAc)_2$	OAc	DCM	rt, 1 h	95	70
2	Ph	^{t}Bu, ^{c}Hex	$Pd^{II}(PhCN)_2Cl_2$	Cl	THF or toluene	65–80 °C, 18–24 h	58–99	56
			$Pt^{II}(cod)_2Br_2$	Br				
		^{c}Hex	$Pt^{II}(cod)_2Cl_2$	Cl	THF	rt, 24 h		



Scheme 30 Pd-catalyzed cross-coupling of aryl halides and acetylenes.

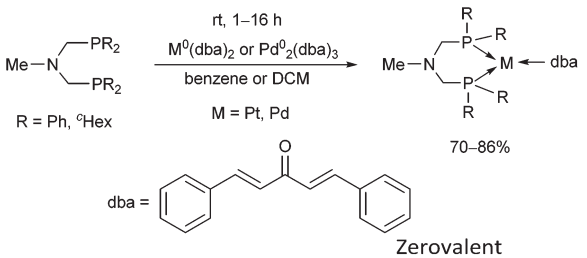
(Table 9/entry 1 *vs.* entry 2). The SiO_2/DABCO/PP-Pd^{II} catalyst exhibited the highest activity as shown by the complete conversion and the selectivity for the diallylated product (Table 9/entry 3). This allylation reaction was extended to other nucleophiles, such as nitriles, ketoesters, diketones or nitroethane, where the corresponding diallylated products were obtained selectively.

There are only a few examples of the synthesis of cyclic Pd^{II} and Pt^{II} complexes bearing alkyl groups on the phosphorus atoms (Table 10). In one case, the complexation of bis(*tert*-butylaminomethylphosphine) was performed using palladium acetate as the precursor (Table 10/entry 1). The complex synthesized was an efficient catalyst in the Sonogashira cross-coupling of aryl halides with acetylenes. In other instances, $Pd^{II}(PhCN)_2Cl_2$ or $Pt^{II}(cod)_2X_2$ (X = Cl, Br) was reacted with the bis(dialkylphosphinomethyl)anilines in THF or in toluene (Table 10/entry 2). In all cases, *cis* square planar complexes were formed.

The Pd^{II} complex of bis(di-*tert*-butylphosphinomethyl)-benzylamine is a useful catalyst in the Sonogashira cross-coupling of aryl halides and acetylenes (Scheme 30).[70] The advantage of this procedure is the possibility of avoiding the use of Cu^I co-catalysts.

The synthesis of zerovalent platinum and palladium complexes was also described, where $M^0(dba)_2$ (dba = dibenzylideneacetone) or $Pd^0{}_2(dba)_3$ was applied as the transition metal precursor (Scheme 31).[71] According to X-ray investigations, the transition metal was coordinated to the dba through one dative bond (Fig. 8). The six-membered metallocycle in the complexes is present in a flattened chair conformation.

A ferrocenyl-substituted ditertiary aminophosphine was applied as a novel ligand in the synthesis of Pt^{II} and Pd^{II} complexes (Scheme 32).[72] By a reaction with $M^{II}(cod)Cl_2$ (M = Pt, Pd), the *cis*-oriented chelate complexes were obtained in yields of 74–86%, whereas when using $Pd^{II}(cod)MeCl$, a complex with



Scheme 31 Zerovalent complexes of bis(phosphinomethyl) methylamines.

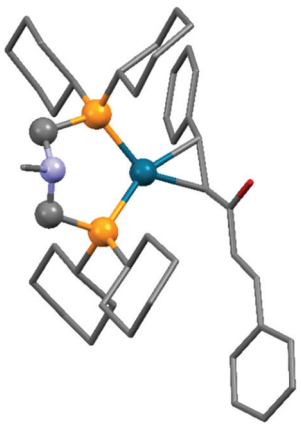
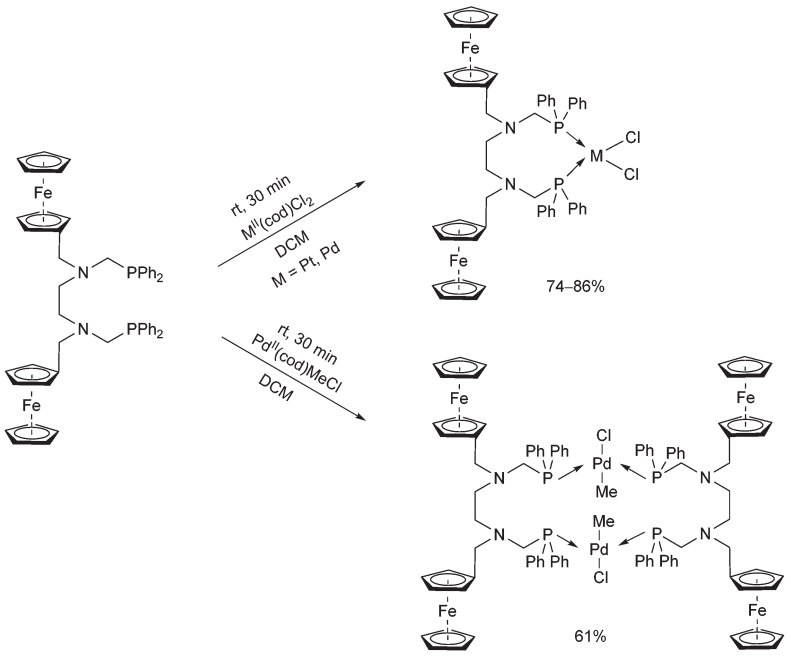


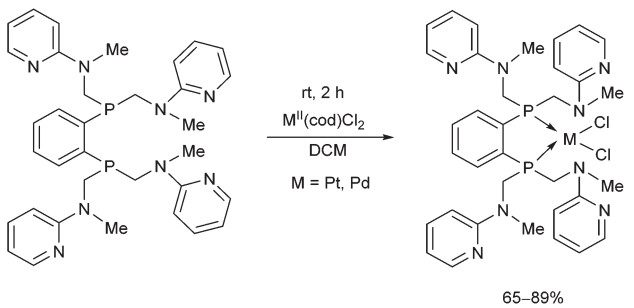
Fig. 8 X-Ray structure of Pd(dba)(^{c}Hex$_2$PCH$_2$)$_2$NMe [CCDC1304170].[71]

a *trans–trans* conformation could be prepared. The corresponding structures were proved by single crystal X-ray crystallography.

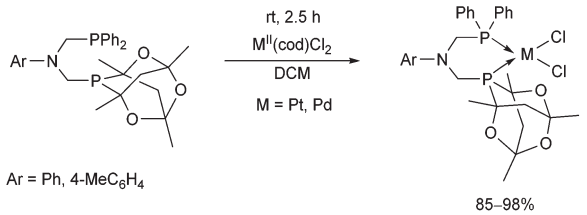
The synthesis of a new hexadentate P_2N_4 ligand system was also described (Scheme 33).[73] The complexation was carried out using $M^{II}(cod)Cl_2$ (M = Pt, Pd) in DCM at ambient tempera-



Scheme 32 Complexation of an aminophosphine ligand bearing two ferrocenyl groups.



Scheme 33 Platinum(II) and palladium(II) complexes of a hexadentate phosphine ligand.



Scheme 34 The complexation of nonsymmetrical bisaminophosphine ligands with $M^{II}(cod)Cl_2$ (M = Pt, Pd).

ture for 2 h. According to X-ray analysis, only the P atoms were coordinated to the corresponding transition metal, while the pyridyl groups remained non-bonding. The square planar Pt^{II} and Pd^{II} centers formed a 5-membered chelate ring with the bisphosphine in both complexes.

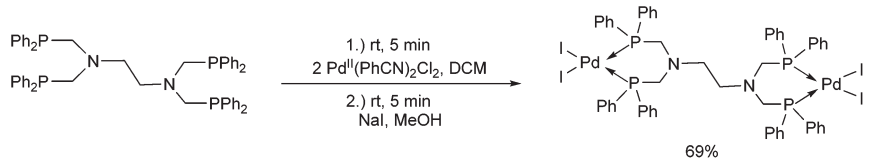
Nonsymmetrical ditertiary phosphines bearing an adamantanate moiety were also applied as efficient ligands (Scheme 34).[74] The corresponding Pt^{II} and Pd^{II} complexes were synthesized in high yields, and their conformation was determined by ^{31}P NMR spectroscopy and single crystal X-ray analysis. Due to the difference in stereoelectronic properties between the two phosphorus atoms, the $J_{(Pt-P)}$ coupling of the –P(Ad) group was twice as much as the coupling on the –PPh unit.

In the next part, the synthesis of palladium(II) and platinum(II) complexes containing two hetero rings is summarized. Two types of binuclear complexes are known; in one case the phosphine ligand contains a spacer between the donor atoms, which are coordinated to two transition metals. In the other instance, two aminophosphine ligands are coordinated to a single Pd^{II} or Pt^{II} atom.

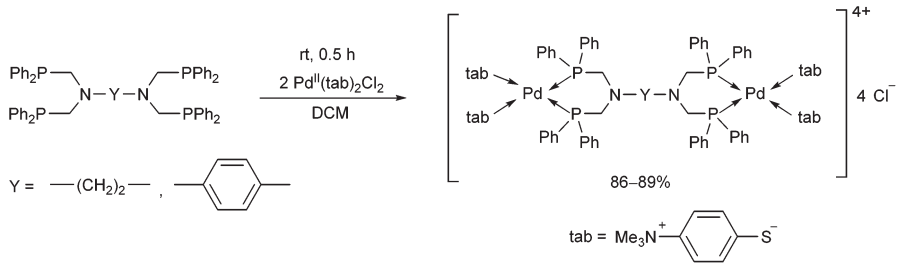
A polydentate phosphine ligand including an ethylene spacer was reacted with 2 equivalents of $Pd^{II}(PhCN)_2Cl_2$ in DCM (Scheme 35).[53] The tetrachloro-complex obtained was converted into the corresponding tetraiodo derivative, and its structure was elucidated by X-ray analysis. It was found that the coordination of the two Pd^{II} was distorted from planarity, leading to significantly bent *trans* P–Pd–I angles.

The reaction of tetra(diphenylphosphinomethyl)diamines with $Pd^{II}(tab)_2Cl_2$ (tab = 4-trimethylammonio-benzenethiolate) also led to binuclear compounds, but in this case in an ionic form (Scheme 36).[75] An X-ray analysis of the complexes revealed a square planar geometry (Fig. 9). Both of the Pd^{2+} ions were coordinated by two S atoms from the "tab" and two P atoms from the bis(phosphine ligand).

Besides the mononuclear Pd^{II} complexes of phosphine ligands containing an ethoxylated phosphonate chain (Scheme 28), binuclear-type derivatives were also synthesized by applying 0.5 equivalents of dihydrogen tetrachloropalladate(II) (Scheme 37).[67]



Scheme 35 Synthesis of binuclear Pd^{II} complexes containing an ethylene spacer.



Scheme 36 Binuclear Pd^{II} complexes bearing thiolate and aminophosphine ligands.

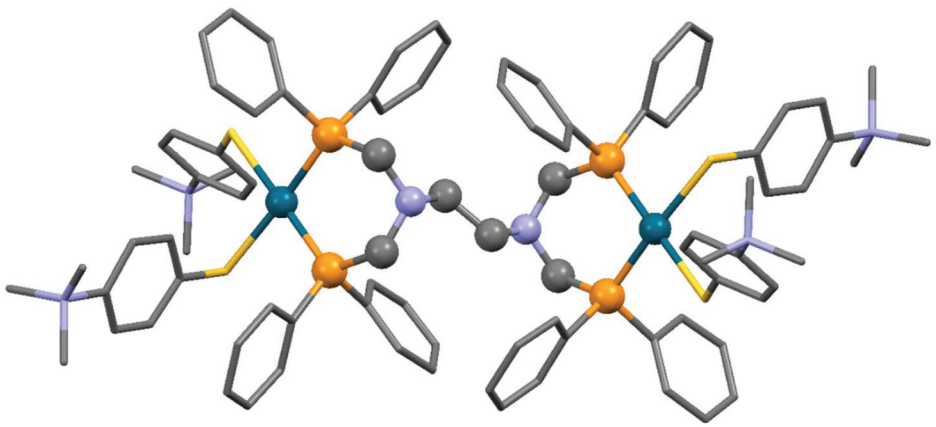
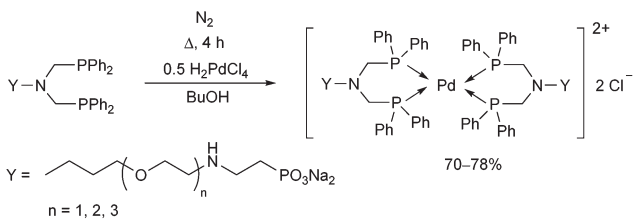
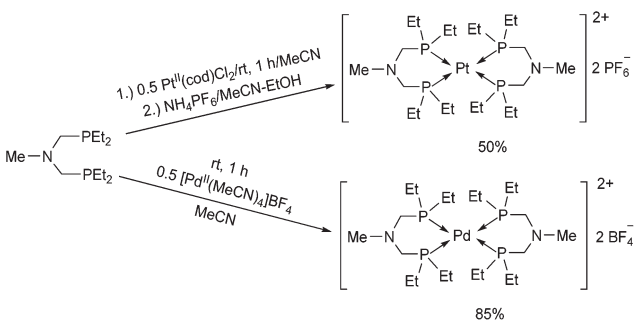


Fig. 9 X-Ray structure of $\{[Pd(tab)_2]_2(\mu\text{-dppeda})\}Cl_4$ [CCDC 800046].[75]



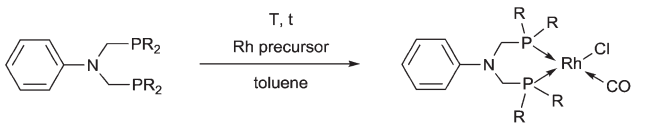
Scheme 37 Preparation of binuclear Pd^{II} complexes with water-soluble ligands.



Scheme 38 Synthesis of $Pt(PNP)_2(PF_6)_2$ and $Pd(PNP)_2(BF_4)_2$ complexes.

The synthesis of structurally similar Pt^{II} and Pd^{II} complexes incorporating ethyl groups on the P atoms was also described (Scheme 38).[76] When bis(diethylphosphinomethyl)-methylamine was reacted with $Pt^{II}(cod)Cl_2$ in acetonitrile, followed by treatment with ammonium hexafluorophosphate, the corresponding $Pt(PNP)_2(PF_6)_2$ (PNP = $Et_2PCH_2N(Me)CH_2PEt_2$) complex was obtained in a moderate yield. For the synthesis of the $Pd^{II}(PNP)_2(BF_4)_2$ derivative, $[Pd^{II}(MeCN)_4]BF_4$ was applied as the metal precursor. The hydride donor ability of the complexes was also investigated, and the Pd^{II} derivative proved to be a better reducing agent.

Table 11 Syntheses of Rh^{I} complexes including bis(phosphinomethyl) aniline ligands



Entry	R	Rh precursor	Temperature, *t*	Yield [%]	Ref.
1	^{t}Bu, ^{c}Hex	$Rh^{I}ClCO(PPh_3)_2$	80 °C, 20 h	59–84	56
2	Ph	0.5 $[Rh^{I}(CO)_2Cl]_2$,	rt, 10 min	88	53

3.2. Synthesis of rhodium complexes

Bis(phosphinomethyl)amines were also applied as efficient ligands in the synthesis of bidentate rhodium(I) complexes (Table 11). The complexation of bis(dialkylphosphinomethyl) aniline with chlorocarbonylbis(triphenylphosphine)rhodium(I) in toluene afforded the corresponding ring complexes in yields of 59–84% after 20 min (Table 11/entry 1). The same type of square planar Rh^{I} complex was synthesized by the reaction of $[Rh^{I}Cl(CO)_2Cl]_2$ with an excess of *N*,*N*-bis(diphenylphosphinomethyl)aniline under mild conditions (Table 11/entry 2).

The Rh^{I} complex of a bis(phosphinomethyl)amine derivative bearing a hydroxy functionality was synthesized by applying $[Rh^{I}(cod)Cl]_2$ as the rhodium precursor (Scheme 39).[77] The Rh^{I} complex obtained was bonded to the surface of activated carbon, and was tested as catalyst in the hydroformylation of 1-octene, where the formation of the linear aldehydes was predominant. The Rh^{I} complexes remained fully active in four consecutive catalytic cycles.

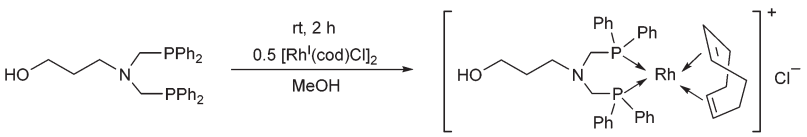
Bis(diphenylphosphinomethyl)amino acid derivatives were also utilized as bidentate P-ligands in the preparation of Rh^{I} complexes (Scheme 40).[78] The complexations were carried out with 0.5 equivalents of $[Rh^{I}(nbd)Cl]_2$ in methanol. The corresponding complexes obtained in yields of 74–81% were applied as catalysts in the enantioselective hydrogenation of α-acetamidocinnamic acid methyl ester.

The complexation of the sodium salt of bis(diphenylphosphinomethyl)amino acid was performed using 0.25 equivalents of $[Rh^{I}(nbd)Cl]_2$ (Scheme 41).[78] In this case, a binuclear Rh^{I} complex was obtained in a yield of 65%.

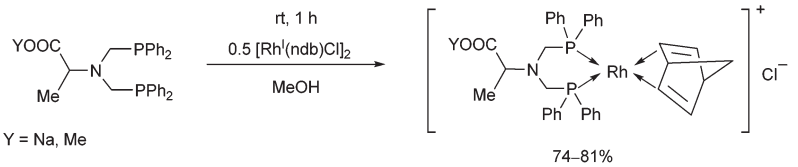
A ferrocenyl substituted bis(aminophosphine) ligand was utilized in the synthesis of a Rh^{I} complex (Scheme 42).[72] The complexation was performed with 0.5 equivalents of $[Rh^{I}(CO)_2Cl]_2$, furnishing the ring product with *trans–trans* conformation in a yield of 29%. The dimeric structure of the complex was confirmed by X-ray analysis (Fig. 10).

3.3. General methods for the preparation of complexes incorporating bidentate α-aminophosphines as ligands

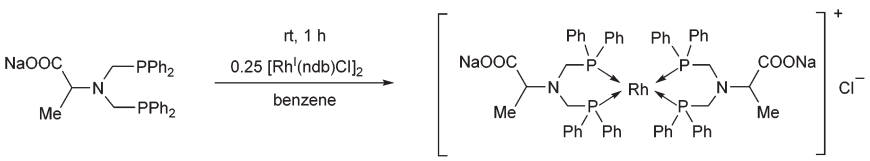
Similarly to the previous chapter, general methods for the preparation of complexes incorporating bidentate α-aminophosphines as P-ligands are summarized in Table 12. Pt and Pd complexes containing one bidentate α-aminophosphine ligand (**IV**) may be synthesized using $M^{II}(cod)Cl_2$ (M = Pt, Pd). In both cases, the products can be obtained in yields of *ca.* 70–85% using DCM as the solvent. A similar type of Rh complex can be prepared by applying 0.5



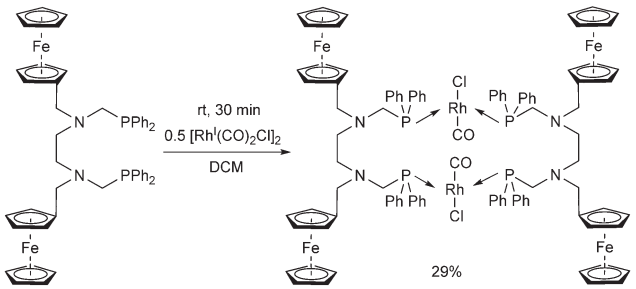
Scheme 39 Synthesis of a cyclic Rh^{I} complex containing a hydroxyl group.



Scheme 40 Rh^{I} complexes of bis(diphenylphosphinomethyl)amino acid derivatives.



Scheme 41 The binuclear Rh^{I} complex of the sodium salt of bis(diphenylphosphinomethyl)amino acid.



Scheme 42 Synthesis of a Rh^{I} complex bearing four ferrocenyl groups.

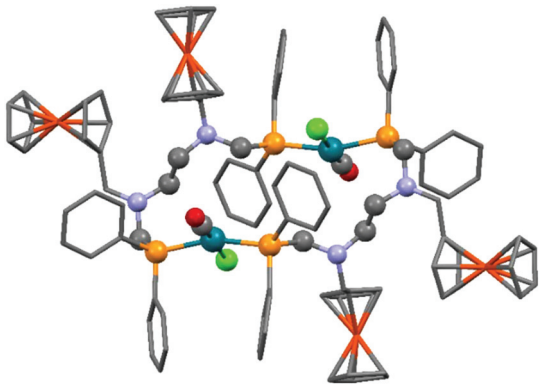


Fig. 10 X-Ray structure of $[Rh(CO)Cl\{FcCH_2N(CH_2PPh_2)CH_2\}_2]_2$ [CCDC 676683].[72]

equivalents of $[Rh^{I}(CO)_2Cl]_2$ or 1 equivalent of $Rh^{I}ClCO(PPh_3)_2$ in reaction times of 10 min or 20 h in toluene to afford the products in yields of 59–88%. Towards the synthesis of Pt, Pd and Rh complexes bearing two bidentate α-aminophosphine ligands (**V**), the starting phosphines should be reacted with 0.5 equivalents of $Pt^{II}(cod)Cl_2$ in toluene, 0.5 equivalents of $Pd^{II}(tab)Cl_2$ in DCM or 0.25 equivalents of $[Rh^{I}(ndb)Cl]_2$ in benzene.

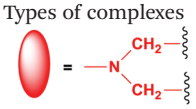
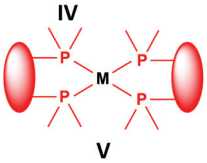
4. Utilization of cyclic α-aminophosphines as ligands

Cyclic α-aminophosphines form another prominent group of commonly used ligands in the synthesis of transition metal complexes. The application of 6-, 7- and 8-membered ring ligands comprising the α-aminophosphine scaffold is discussed in this chapter.

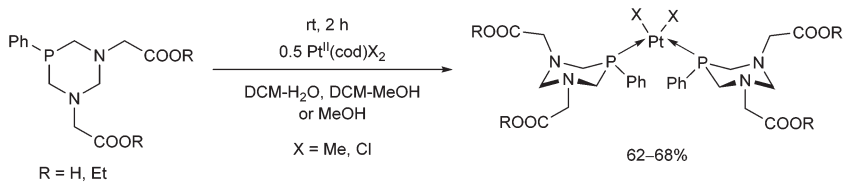
4.1. Complexation of 6-membered ring derivatives of α-aminophosphines

In the reaction of $Pt^{II}(cod)X_2$ precursors with 1,3-diaza-phosphacyclohexanes incorporating two glycine or glycinate moieties, the corresponding *cis* complexes were formed (Scheme 43).[79] Depending on the functionality (acid or ester), the complexes were soluble in water or in organic solvents, respectively. The structure of the free acid was confirmed by X-ray diffraction analysis.

Table 12 General methods for the preparation of complexes containing bidentate α-aminophosphines as ligands

Types of complexes	M	Precursor	*t*	Solvent	Average yield [%]
 IV	Pt	$Pt^{II}(cod)Cl_2$	0.5–24 h	DCM	70–85
	Pd	$Pd^{II}(cod)Cl_2$	5 min–4 h	DCM	68–85
	Rh	0.5 $[Rh^{I}(CO)_2Cl]_2$ or $Rh^{I}ClCO(PPh_3)_2$[a]	10 min or 20 h	Toluene	59–88
 V	Pt	0.5 $Pt^{II}(cod)Cl_2$	1 h	MeCN	50
	Pd	0.5 $Pd^{II}(tab)Cl_2$	0.5 h	DCM	86–89
	Rh	0.25 $[Rh^{I}(ndb)Cl]_2$	1 h	benzene	65

[a] At 80 °C.



Scheme 43 Pt^{II} complexes of 1,3-diaza-phosphacyclohexanes comprising amino acid or amino acid ester moieties.

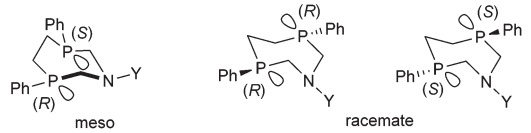
4.2. Complexation of 7-membered ring derivatives of α-aminophosphines

Stereochemistry plays an important role in the chemistry of 7-membered ring derivatives of α-aminophosphines. According to the literature data, derivatives of 1-aza-3,6-diphosphacycloheptanes were applied as ligands in the complexations. Isomers of these heterocycles differ from each other in respect of chelating abilities.[80] Only the *meso* (*RS*) form contains the two P atoms in the appropriate position suitable for complexation, while in the optically active derivatives (*RR* and *SS*), the lone pairs are present at different sides of the 7-membered ring (Scheme 44).

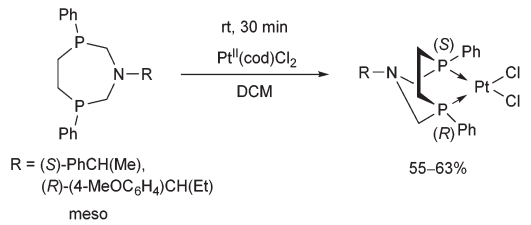
The *meso* form of chiral 1-aza-3,6-diphosphacycloheptanes was reacted with $Pt^{II}(cod)Cl_2$ at ambient temperature to afford the corresponding *cis* Pt^{II} complexes in yields of 55–63% (Scheme 45).[80]

In a similar reaction, by the use of a half equivalent of the Pt^{II} precursor, an ionic complex comprising two bidentate cyclic α-aminophosphines was formed (Scheme 46).[80] According to the previous explanation, starting from the pure *meso* isomer, or the mixture of the *meso* and the racemate, only the complexes incorporating the *meso* isomer were formed. This method was applicable to separate the racemate from the mixture.

A similar aminophosphine containing a benzhydryl substituent on the N atom acted similarly in the complexation (Scheme 47).[81] Starting from the mixture of the *meso* and the racemate forms, only the complexes of the *meso* form were obtained. The teracoordinated complex was formed in *cis* and *trans* forms in a ratio of 78 : 22.



Scheme 44 Isomers of 1-aza-3,6-diphosphacycloheptanes.



Scheme 45 The reaction of *meso* 1-aza-3,6-diphosphacycloheptanes with $Pt^{II}(cod)Cl_2$.

4.3. Complexation of 8-membered ring derivatives of α-aminophosphines

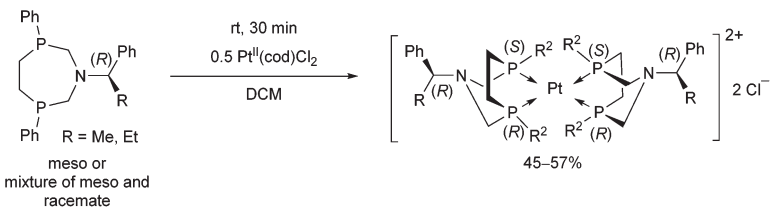
Novel Pt^{II} complexes were prepared by the reaction of 1-aza-3,7-diphosphacyclooctanes with $Pt^{II}(cod)Cl_2$ in DMF as the solvent (Scheme 48).[82] The structure of the products was confirmed by X-ray analysis.

Mostly $M^{II}(cod)Cl_2$ (M = Pt, Pd) served as the precursor in the complexation of P- and N-substituted 1,5-diaza-3,7-diphosphacyclooctanes (Table 13). The Ph- and Bn-substituted derivatives were obtained in yields of 79–90% after a reaction time of 4 h (Table 13/entry 1). Both the Pt^{II} and Pd^{II} complexes of *N*-4-MeC_6H_4- and *P*-menthyl 1,5-diaza-3,7-diphosphacyclooctanes were prepared in yields of 45–46% (Table 13/entry 2). The reaction was also performed starting from an optically active bidentate ligand. The corresponding Pd^{II} complex was synthesized in a yield of 50% (Table 13/entry 3). A cyclic aminophosphine bearing a 2-pyridyl substituent on the N atom was also tried out in the complexation (Table 13/entry 4).

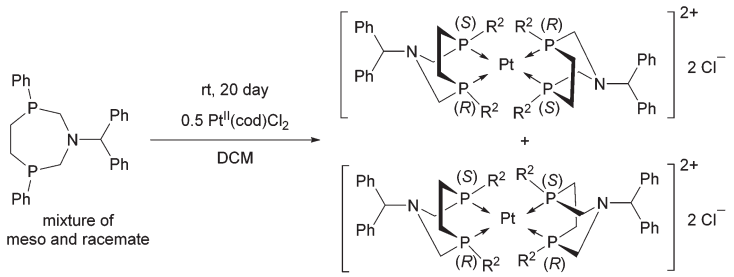
Based on X-ray diffraction measurements,[84,86] NMR studies[83,84] and quantum chemical calculations,[83] Pt^{II} and Pd^{II} complexes of 1,5-diaza-3,7-diphosphacyclooctanes contained two 6-membered metallocycles, one in chair, while the other in boat conformation. As a relevant example, the X-ray structure of [1,5-di(*p*-tolyl)-3,7-di(2-pyridyl)-1,5-diaza-3,7-diphosphacyclo-octane]$PdCl_2$ (Table 11/entry 4) can be seen in Fig. 11.

The 1,5-diphenyl-3,7-dicyclohexyl-1,5-diaza-3,7-diphosphacyclooctane Pd^{II} complex was synthesized by the reaction of the corresponding cyclic α-aminophosphine with $Pd(OAc)_2$ (Scheme 49).[87] The *in situ* prepared Pd^{II} complex was proved to be an efficient catalyst in the Suzuki–Miyaura coupling of aryl bromides and arylboronic acids (Scheme 50).

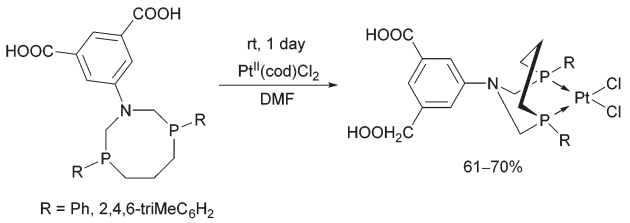
Tetracoordinated ionic Pt^{II} and Pd^{II} complexes were synthesized by the reaction of 1,5-diaza-3,7-diphosphacyclooctanes with a half equivalent of the metal precursors (Table 14). Bis[(1,3,5,7-tetrabenzyl-1,5-diaza-3,7-diphosphacyclooctane)]$PtCl_2$ was prepared from the 8-membered α-aminophosphine and $Pt^{II}(cod)Cl_2$ using DCM as the solvent (Table 14/entry 1). Alkyl- and aryl-substituted cyclic bidentate ligands were reacted with $Pd^{II}(PhCN)_2(BF_4)_2$ in acetonitrile to afford the corresponding complexes in yields of 66–81%



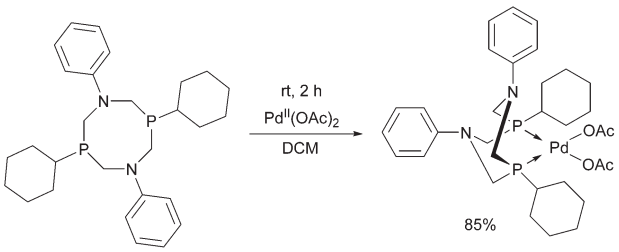
Scheme 46 Isolation of the *meso* isomer by complexation.



Scheme 47 Application of an *N*-benzhydryl cyclic aminophosphine as a bidentate ligand in Pt^{II} complexes.

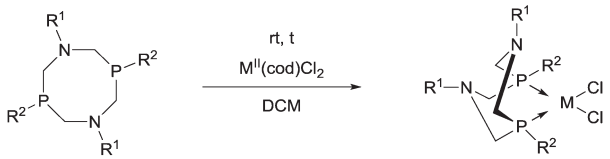


Scheme 48 Pt^{II} complexes formed from 1-aza-3,7-diphosphacyclo-octanes and $Pt^{II}(cod)Cl_2$.

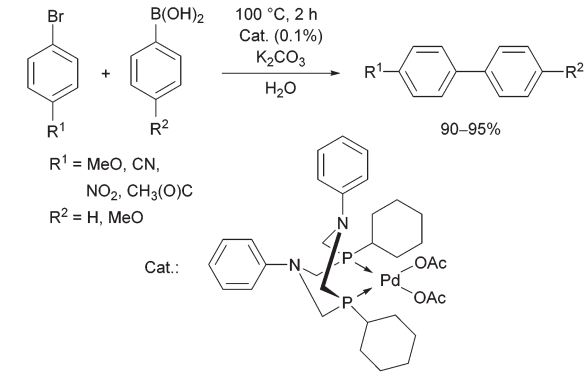


Scheme 49 Pd^{II} complex of 1,5-diphenyl-3,7-dicyclohexyl-1,5-diaza-3,7-diphosphacycylooctane.

Table 13 Bidentate complexes of 1,5-diaza-3,7-diphosphacyclooctanes



Entry	R^1	R^2	M	*t*	Yield [%]	Ref.
1	Bn, Ph	Bn, Ph	Pt	4 h	79–90	83
2	4-MeC_6H_4	Ment	Pt, Pd	4 h	45–46	84
3	(*S*)-PhCH(Me)	Ph	Pd	1 day	50	85
4	Bn, 4-MeC_6H_4	2-Pyridyl	Pt, Pd	30 min	62–92	86



Scheme 50 The Suzuki–Miyaura reaction of aryl bromides and aryl-boronic acids in the presence of the *in situ* formed complex (1,5-diphenyl-3,7-dicyclohexyl-1,5-diaza-3,7-diphosphacycylo-octane)$Pd(OAc)_2$.

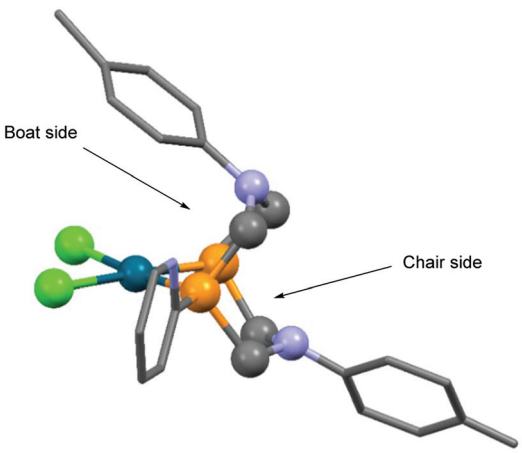


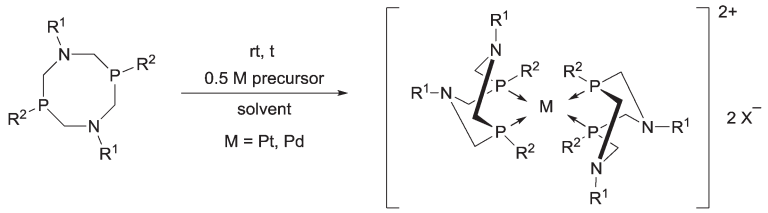
Fig. 11 X-Ray structure of [1,5-di(*p*-tolyl)-3,7-di(2-pyridyl)-1,5-diaza-3,7-diphosphacycylooctane]$PdCl_2$, [CCDC 932996].[86]

(Table 14/entry 2). The products were tested as catalysts in electrochemical proton reduction, but showed lower activity than the similar Ni^{II} complexes. Optically active 1,5-diaza-3,7-diphosphacyclooctanes were also utilized as ligands to afford Pt^{II} and Pd^{II} complexes in good yields (88–91%) (Table 14/entry 3).

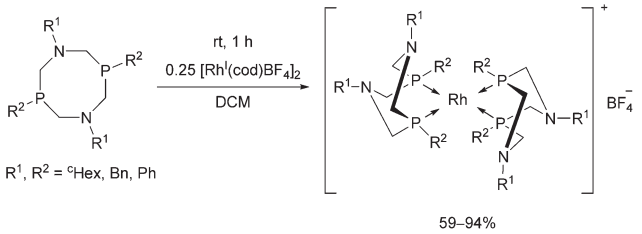
Starting from derivatives with 2-pyridyl substituents on the P atom, ionic tetracoordinated complexes comprising Pt^{II} or Pd^{II} were prepared using $M^{II}(cod)Cl_2$ (M = Pt, Pd) as the precursor. The reaction times were in the range of 30 min to 1 day (Table 14/entry 4). The structure of the products was proved by X-ray measurements.

Rhodium(I) complexes of alkyl- and aryl-substituted 1,5-diaza-3,7-diphosphacyclooctanes were also synthesized by reacting the corresponding bidentate α-aminophosphines with

Table 14 Tetracoordinated complexes of 1,5-diaza-3,7-diphosphacyclooctanes



Entry	R^1	R^2	M precursor	Solvent	t	Yield [%]	Ref.
1	Bn	Bn	$Pt^{II}(cod)Cl_2$	DCM	12 h	76	83
2	Bn, Ph	Me, ^{c}Hex, Ph	$Pd^{II}(PhCN)_2(BF_4)_2$	MeCN	12 h	66–81	88
3	(*S*)-PhCH(Me), (*R*)-PhCH(Me)	Ph	$M^{II}(cod)Cl_2$ (M = Pt, Pd)	DCM	1 day	88–91	85
4	PhCH(Me), 4-MeC_6H_4	2-Pyridyl	$M^{II}(cod)Cl_2$ (M = Pt, Pd)	DCM	30 min–1 day	55–92	86



Scheme 51 Rhodium(I) complexes of 1,5-diaza-3,7-diphosphacyclooctanes.

$[Rh^I(cod)BF_4]_2$ (Scheme 51).[89] The complexes were tested as catalysts in the reaction of CO_2 with hydrogen and showed moderate catalytic activities.

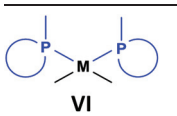
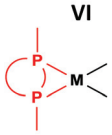
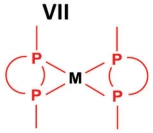
4.4. General methods for the preparation of complexes containing cyclic α-aminophosphines as ligands

General methods for the preparation of Pt, Pd and Rh complexes incorporating cyclic α-aminophosphines as the ligands are summarized in Table 15. The reactions may be carried out at ambient temperature using DCM as the solvent. Pt complexes of monodentate cyclic α-aminophosphines (**VI**) may be synthesized using 0.5 equivalents of $Pt^{II}(cod)X_2$ (X = Me, Cl) as the precursor. For the synthesis of Pt and Pd complexes of bidentate ligands (**VII**), $M^{II}(cod)Cl_2$ (M = Pt, Pd) was the most suitable reagent. The products (**VII**) were obtained in yields of 55–92% after a reaction time of 30 min–1 day. The complexes having two α-aminophosphines as the ligands (**VIII**) may be synthesized using 0.5 equivalents of $M^{II}(cod)Cl_2$ (M = Pt, Pd) or 0.25 equivalents of $[Rh^I(cod)BF_4]_2$ as the metal precursor in moderate to excellent yields.

5. Conclusions

The utilization of α-aminophosphine ligands in platinum, palladium and rhodium complexes came into the field of vision of organometallic chemists in the 1980s. Since then, this topic has been receiving growing attention; nearly half of the papers

Table 15 General methods for the preparation of complexes containing cyclic α-aminophosphines as ligands

Types of complexes	M	Precursor	t	Average yield [%]
 **VI**	Pt	0.5 $Pt^{II}(cod)X_2$, X = Me, Cl	2 h	62–68
 **VII**	Pt	$Pt^{II}(cod)Cl_2$	30 min–4 h	55–90
	Pd	$Pd^{II}(cod)Cl_2$	30 min–1 day	46–92
 **VIII**	Pt	0.5 $Pt^{II}(cod)Cl_2$	30 min–1 day	45–92
	Pd	0.5 $Pd^{II}(cod)Cl_2$	30 min–1 day	55–88
	Rh	0.25 $[Rh^I(cod)BF_4]_2$	1 h	59–94

have been published in the last five years. To make available α-aminophosphines with different properties, various linear and cyclic ligands were prepared. They were applied as monodentate and bidentate ligands in transition metal complexes. In this review, we have summarized the synthesis of platinum, palladium and rhodium complexes incorporating α-aminophosphines. Furthermore, the structure and utilization of a few relevant derivatives were also discussed. Several complexes described above revealed significant activities as catalysts in hydrogenation, cross-coupling, hydroformylation, allylation or carbonylation. In a few cases, the catalytic activity of α-aminophosphine-based complexes was compared to that of complexes of alkyl and aryl phosphines, where the α-aminophosphine derivatives were found to be more efficient. Besides discussing the literature data, the most commonly applied transition metal precursors and reaction conditions for the synthesis of the different types of α-aminophosphine-M (M = Pt, Pd or Rh) complexes were also summarized. Based on these tendencies, this field of organometallic chemistry will attract further attention in the future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Hungarian Research Development and Innovation Fund (FK123961 and K119202), and in part (E. B.) by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences (BO/00278/17/7). Ádám Tajti thanks Gedeon Richter Talentum Foundation and Pro Progressio Foundation for financial support.

Notes and references

1 M. M. Pereira, M. J. F. Calvete, R. M. B. Carrilho and A. R. Abreu, *Chem. Soc. Rev.*, 2013, **42**, 6990–7020.
2 P. W. N. M. van Leeuwen and P. C. J. Kamer, *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis*, John Wiley & Sons Ltd, Chichester, UK, 2012.
3 J. Tsuji, *Transition Metal Reagents and Catalysts*, John Wiley & Sons Ltd, Chichester, UK, 2002.
4 M. Beller and C. Bolm, *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*, John Wiley & Sons Ltd, Weinheim, 2004.
5 L. Kollár and G. Keglevich, *Chem. Rev.*, 2010, **110**, 4257–4302.
6 K. Burgess, W. A. van der Donk, C.-H. Jun and Y. J. Park, *Chlorotris(triphenylphosphine)-rhodium(I), e-EROS Encyclopedia of Reagents for Organic Synthesis*, John Wiley & Sons Ltd, Chichester, UK, 2006.
7 P. W. N. M. van Leeuwen, *Homogeneous Catalysis*, Springer, Dordrecht, Netherlands, 2004.
8 E. A. Sheddon and K. R. Sheddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, Oxford, New York, Tokyo, 1984.
9 W. P. Griffith, *Ruthenium Oxidation Complexes, Vol. 34*, Springer, Dordrecht, New York, Heidelberg, London, 2011.
10 S. Sabo-Etienne and M. Grellier, Ruthenium: Inorganic & Coordination Chemistry, in *Encyclopedia of Inorganic and Bioinorganic Chemistry*, John Wiley & Sons Ltd, 2006.
11 C. Bruneau and P. H. Dixneuf, *Ruthenium Catalysts and Fine Chemmistry*, Springer, Berlin, Heidelberg, New York, 2004.
12 S. J. Berners-Price and P. J. Sadler, Phosphines and metal phosphine complexes: Relationship of chemistry to anticancer and other biological activity, in *Bioinorg. Chem*, Springer, Berlin, 1988, vol. 70, pp. 27–102.
13 A. A. Nazarov and P. J. Dyson, in *Phosphorus Compounds, vol 37*, ed. G. Luca and M. Peruzzini, Springer, Dordrecht, 2011, pp. 445–461.
14 U. Ndagi, N. Mhlongo and M. E. Soliman, *Drug Des., Dev. Ther.*, 2017, **11**, 599–616.
15 V. A. Stepanova and I. P. Smoliakova, *Curr. Org. Chem.*, 2012, **16**, 2893–2920.
16 W. Li and J. Zhang, *Chem. Soc. Rev.*, 2016, **45**, 1657–1677.
17 J. Gopalakrishnan, *Appl. Organomet. Chem.*, 2009, **23**, 291–318.
18 L. A. Labios, C. J. Weiss, J. D. Egbert, S. Lense, R. M. Bullock, W. G. Dougherty, W. S. Kassel and M. T. Mock, *Z. Anorg. Allg. Chem.*, 2015, **641**, 105–117.
19 N. Priyadarshani, B. Ginovska, J. T. Bays, J. C. Linehan and W. J. Shaw, *Dalton Trans.*, 2015, **44**, 14854–14864.
20 J.-F. Zhang, W.-F. Fu, X. Gan and J.-H. Chen, *Dalton Trans.*, 2008, 3093–3100.
21 A. Hazari, J. A. Labiger and J. E. Bercaw, *Angew. Chem., Int. Ed.*, 2012, **51**, 8268–8271.
22 R. N. Naumov, E. I. Musina, K. B. Kanunnikov, T. I. Fesenko, D. B. Krivolapov, I. A. Litvinov, P. Lönnecke, E. Hey-Hawkins, A. A. Karasik and O. G. Sinyashin, *Dalton Trans.*, 2014, **43**, 12784–12789.
23 R. N. Naumov, A. A. Karasik, O. G. Sinyashin, P. Lönnecke and E. Hey-Hawkins, *Dalton Trans.*, 2004, 357–358.
24 A. Phanopoulos, N. J. Brown, A. J. P. White, N. J. Long and P. W. Miller, *Inorg. Chem.*, 2014, **53**, 3742–3752.
25 A. Phanopoulos, A. J. P. White, N. J. Long and P. W. Miller, *Dalton Trans.*, 2016, **45**, 5536–5548.
26 C. D. Swor, K. R. Hanson, L. N. Zakharov and D. R. Tyler, *Dalton Trans.*, 2011, **40**, 8604–8610.
27 M. Płotek, R. Starosta, U. K. Komarnicka, A. Skórska-Stania, M. Jeżowska-Bojczuk, G. Stochel and A. Kyzioł, *Dalton Trans.*, 2015, **44**, 13969–13978.
28 P. Das, M.-H. Ho, M. O'Hagan, W. J. Shaw, R. Morris Bullock, S. Raugei and M. L. Helm, *Dalton Trans.*, 2014, **43**, 2744–2754.
29 E. Bálint, E. Fazekas, P. Pongrácz, L. Kollár, L. Drahos, T. Holczbauer, M. Czugler and G. Keglevich, *J. Organomet. Chem.*, 2012, **717**, 75–82.

30 E. Bálint, A. Tripolszky, E. Jablonkai, K. Karaghiosoff, M. Czugler, Z. Mucsi, L. Kollár, P. Pongrácz and G. Keglevich, *J. Organomet. Chem.*, 2016, **801**, 111–121.
31 B. B.-N. Ben-Aroya and M. Portnoy, *J. Comb. Chem.*, 2001, **3**, 524–527.
32 B. B.-N. Ben-Aroya and M. Portnoy, *Tetrahedron*, 2002, **58**, 5147–5158.
33 A. Mansour and M. Portnoy, *Tetrahedron Lett.*, 2003, **44**, 2195–2198.
34 S. J. Coles, S. E. Durran, M. B. Hursthouse, A. M. Z. Slawin and M. B. Smith, *New J. Chem.*, 2001, **25**, 416–422.
35 S. E. Durran, M. B. Smith, A. M. Z. Slawin, T. Gelbrich, M. B. Hursthouse and M. E. Light, *Can. J. Chem.*, 2001, **79**, 780–791.
36 I. Angurell, E. Puig, O. Rossell, M. Seco, P. Gómez-Sal and A. Martín, *J. Organomet. Chem.*, 2012, **716**, 120–128.
37 S. E. Durran, M. B. Smith, S. H. Dale, S. J. Coles, M. B. Hursthouse and M. E. Light, *Inorg. Chim. Acta*, 2006, **359**, 2980–2988.
38 S. E. Durran, M. B. Smith, A. M. Z. Slawin and J. W. Steed, *J. Chem. Soc., Dalton Trans.*, 2000, 2771–2778.
39 O. Altan, O. Serindag, K. Sayın and D. Karakas, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2016, **191**, 993–999.
40 M. L. Clarke, D. J. Cole-Hamilton, D. F. Foster, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 2002, 1618–1624.
41 D. L. Davies, J. Neild, L. J. S. Prouse and D. R. Russell, *Polyhedron*, 1993, **12**, 2121–2124.
42 M. L. Clarke, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 2003, **22**, 19–26.
43 J. Pfeiffer, G. Kickelbick and U. Schubert, *Organometallics*, 2000, **19**, 62–71.
44 Q.-S. Li, F.-B. Xu, D.-J. Cui, K. Yu, X.-S. Zeng, X.-S. Leng, H.-B. Song and Z.-Z. Zhang, *Dalton Trans.*, 2003, 1551–1557.
45 D. A. Clarke, P. W. Miller, N. J. Long and A. J. P. White, *Dalton Trans.*, 2007, 4556–4564.
46 N. W. Waggoner, L. S. Spreer, B. J. Boro, D. L. DuBois and M. L. Helm, *Inorg. Chim. Acta*, 2012, **380**, 14–21.
47 R. Starosta, A. Bykowska, M. Barys, A. K. Wieliczko, Z. Staroniewicz and M. Jeżowska-Bojczuk, *Polyhedron*, 2011, **30**, 2914–2921.
48 Q. Zhang, S. M. Aucott, A. M. Z. Slawin and J. D. Woollins, *Eur. J. Inorg. Chem.*, 2002, 1635–1646.
49 P. Espinet and K. Soulantica, *Coord. Chem. Rev.*, 1999, **193–195**, 499–556.
50 D. Brackemeyer, C. Schulte to Brinke, F. Roelfes and F. E. Hahn, *Dalton Trans.*, 2017, **46**, 4510–4513.
51 E. Payet, A. Auffrant, X. F. Le Goff and P. Le Floch, *J. Organomet. Chem.*, 2010, **695**, 1499–1506.
52 R. Turpin, P. Dagnac and R. Poilblanc, *J. Organomet. Chem.*, 1987, **319**, 247–255.
53 A. L. Balch, M. M. Olmstead and S. P. Rowley, *Inorg. Chim. Acta*, 1990, **168**, 255–264.
54 H. Han, M. Elsmaili and S. A. Johnson, *Inorg. Chem.*, 2006, **45**, 7435–7445.
55 G. Keglevich, A. Szekrényi, Á. Szöllősy and L. Drahos, *Synth. Commun.*, 2011, **41**, 2265–2272.
56 M. Stickel, C. Maichle-Moessmer, L. Wesemann and H. A. Mayer, *Polyhedron*, 2013, **52**, 1471–1480.
57 E. Bálint, Á. Tajti, D. Kalocsai, B. Mátravölgyi, K. Karaghiosoff, M. Czugler and G. Keglevich, *Tetrahedron*, 2017, **73**, 5659–5667.
58 M. Keles, Z. Aydin and O. Serindag, *J. Organomet. Chem.*, 2007, **692**, 1951–1955.
59 M. Keles and M. K. Yilmaz, *Heteroat. Chem.*, 2012, **23**, 466–471.
60 S. Vigo, R. Andrés, P. Gómez-Sal, J. de la Mata and E. de Jesús, *J. Organomet. Chem.*, 2012, **717**, 88–98.
61 R.-T. He, J.-F. Wang, H.-F. Wang, Z.-G. Ren and J.-P. Lang, *Dalton Trans.*, 2014, **43**, 9786–9794.
62 J.-J. Ning, J.-F. Wang, Z.-G. Ren, D. J. Young and J.-P. Lang, *Tetrahedron*, 2015, **71**, 4000–4006.
63 M. R. J. Elsegood, M. B. Smith and P. M. Staniland, *Inorg. Chem.*, 2006, **45**, 6761–6770.
64 S. E. Durran, M. R. J. Elsegood and M. B. Smith, *New J. Chem.*, 2002, **26**, 1402–1408.
65 Q. Z. Zhang, G. X. Hua, P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *Eur. J. Inorg. Chem.*, 2003, 2426–2437.
66 O. Serindag, *Synth. React. Inorg. Met.-Org. Chem.*, 1995, **25**, 327–335.
67 X. Ma and X. Fu, *J. Mol. Catal. A: Chem.*, 2003, **195**, 47–53.
68 K. Motokura, K. Saitoh, H. Noda, Y. Uemura, W.-J. Chun, A. Miyaji, S. Yamaguchi and T. Baba, *ChemCatChem*, 2016, **8**, 331–335.
69 K. Motokura, K. Saitoh, H. Noda, W.-J. Chun, A. Miyaji, S. Yamaguchi and T. Baba, *Catal. Sci. Technol.*, 2016, **6**, 5380–5388.
70 D. Méry, K. Heuzé and D. Astruc, *Chem. Commun.*, 2003, 1934–1935.
71 J. Fawcett, R. D. W. Kemmitt, D. R. Russell and O. Serindag, *J. Organomet. Chem.*, 1995, **486**, 171–176.
72 M. R. J. Elsegood, A. J. Lake, R. J. Mortimer, M. B. Smith and G. W. Weaver, *J. Organomet. Chem.*, 2008, **693**, 2317–2326.
73 P. W. Miller, N. J. Long and A. J. P. White, *Dalton Trans.*, 2009, 5284–5286.
74 G. M. Brown, M. R. J. Elsegood, A. J. Lake, N. M. Sanchez-Ballester, M. B. Smith, T. S. Varley and K. Blann, *Eur. J. Inorg. Chem.*, 2007, 1405–1414.
75 A.-X. Zheng, Z.-G. Ren, H.-F. Wang, H.-X. Li and J.-P. Lang, *Inorg. Chim. Acta*, 2012, **382**, 43–51.
76 C. J. Curtis, A. Miedaner, J. W. Raebiger and D. L. Dubois, *Organometallics*, 2004, **23**, 511–516.
77 M. C. Román-Martínez, J. A. Díaz-Auñón, C. Salinas-Martínez de Lecea and H. Alper, *J. Mol. Catal. A: Chem.*, 2004, **213**, 177–182.
78 K. Kellner, W. Hanke, A. Tzschach, Z. Nagy-Magos and L. Markó, *J. Organomet. Chem.*, 1984, **268**, 175–183.
79 A. Jain, M. L. Helm, J. C. Linehan, D. L. DuBois and W. J. Shaw, *Inorg. Chem. Commun.*, 2012, **22**, 65–67.

80 E. I. Musina, A. A. Karasik, A. S. Balueva, I. D. Strelnik, T. I. Fesenko, A. B. Dobrynin, T. P. Gerasimova, S. A. Katsyuba, O. N. Kataeva, P. Lönnecke, E. Hey-Hawkins and O. G. Sinyashin, *Eur. J. Inorg. Chem.*, 2012, 1857–1866.
81 A. Plikhta, A. Pöthig, E. Herdtweck and B. Rieger, *Inorg. Chem.*, 2015, **54**, 9517–9528.
82 A. A. Karasik, R. N. Naumov, Y. S. Spiridonova, O. G. Sinyashin, P. Lönnecke and E. Hey-Hawkins, *Z. Anorg. Allg. Chem.*, 2007, **633**, 205–210.
83 S. Latypov, A. Strelnik, A. Balueva, Y. Spiridonova, A. Karasik and O. Sinyashin, *Eur. J. Inorg. Chem.*, 2016, 1068–1084.
84 S. N. Ignatieva, A. S. Balueva, A. A. Karasik, S. K. Latypov, A. G. Nikonova, O. E. Naumova, P. Lönnecke, E. Hey-Hawkins and O. G. Sinyashin, *Inorg. Chem.*, 2010, **49**, 5407–5412.
85 A. A. Karasik, R. N. Naumov, O. G. Sinyashin, G. P. Belov, H. V. Novikova, P. Lönnecke and E. Hey-Hawkins, *Dalton Trans.*, 2003, 2209–2214.
86 E. I. Musina, V. V. Khrizanforova, I. D. Strelnik, M. I. Valitov, Y. S. Spiridonova, D. M. Krivolapov, I. A. Litvinov, M. K. Kadirov, P. Lönnecke, E. Hey-Hawkins, Y. H. Budnikova, A. A. Karasik and O. G. Sinyashin, *Chem. – Eur. J.*, 2014, **20**, 3169–3182.
87 A. Fihri, D. Luart, C. Len, A. Solhy, C. Chevrin and V. Polshettiwar, *Dalton Trans.*, 2011, **40**, 3116–3121.
88 C. S. Seu, D. Ung, M. D. Doud, C. E. Moore, A. L. Rheingold and C. P. Kubiak, *Organometallics*, 2013, **32**, 4556–4563.
89 A. M. Lilio, M. H. Reineke, C. E. Moore, A. L. Rheingold, M. K. Takase and C. P. Kubiak, *J. Am. Chem. Soc.*, 2015, **137**, 8251–8260.