Coordination Chemistry Reviews 255 (2011) 473–483

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

N-Heterocyclic carbene–rhodium complexes as catalysts for hydroformylation and related reactions

W. Gil, A.M. Trzeciak*

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

Contents

ARTICLE INFO

Article history:
Received 24 July 2010
Accepted 1 November 2010
Available online 10 November 2010

Key words:
Hydroformylation
Rhodium catalyst
N-heterocyclic carbene
Supported Rh–carbene complex

ABSTRACT

Rhodium(I) complexes with N-heterocyclic carbenes (Rh–NHC) can be considered as important candidates for catalysts of hydroformylation of olefins. The high stability of Rh-C(NHC) bonding under reaction conditions allow to expect that NHC ligand will be present in coordination sphere of the catalytically active rhodium complex and therefore influences the reaction yield and regioselectivity. The potential applicability of Rh–NHC complexes containing chiral carbene ligand in asymmetric hydroformylation can be also considered. The excellent review articles relevant to application of Rh–NHC in hydroformylation have been published recently [1–3]. After that, important contributions to this subject, concerning theoretical and experimental studies, both structural and catalytic, have been reported. Therefore, the reactivity of Rh–NHC complexes can be discussed now in term of these new data. The up to now reported results indicate that the most promising and selective systems for hydroformylation can be composed from Rh–NHC complex and stoichiometric amount of electron-withdrawing phosphorus ligand.

1. Introduction

Hydroformylation, the catalytic formation of aldehydes from olefins, carbon monoxide, and dihydrogen, is a reaction with 100% atom economy and one of the most important industrial processes employing a homogeneous catalyst [4–9]. Hydroformylation accounts for an annual production of almost eight million tons of aldehydes and alcohols. Therefore, it is not surprising that improvement in the rate and selectivity of hydroformylation, mainly through ligand design, has been receiving a lot of attention (Fig. 1).

The first generation of hydroformylation catalysts consisted of cobalt carbonyl derivatives, unmodified or containing phosphorus ligands [4]. The results obtained by Wilkinson redirected interest to rhodium complexes, which appeared to be about a thousand times more active compared with cobalt [10–12]. Rhodium complexes bearing phosphorus ligands made it possible to perform hydroformylation under relatively mild conditions, with high selectivity to linear aldehydes (*l*), more desired than branched (*b*) ones when aliphatic olefins are used as substrates. In the case of styrene and related vinylarenes, high regioselectivity in branched aldehydes is always obtained. Regioselectivity of the hydroformylation reaction is strongly dependent on the kind of phosphorus ligand present in the reaction mixture, and, consequently, the choice of ligand is a key point in the design of new catalytic systems [13–17]. Despite their different steric properties, N-heterocyclic carbenes (NHCs)

---

* Corresponding author. Tel.: +48 71 3757253; fax: +48 71 3757356.
E-mail address: ania@wchuwr.chem.uni.wroc.pl (A.M. Trzeciak).

0010-8545/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2010.11.005

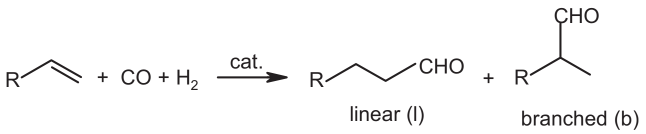


Fig. 1. Scheme of hydroformylation reaction.

have often been treated as phosphine mimics, so it seems reasonable to consider them as components of hydroformylation catalytic systems [1–3,18–22]. Intensive studies in the field of NHC ligands in recent years have resulted in the collection of many physicochemical data that make it possible to discuss and predict the role of NHC–rhodium complexes as hydroformylation catalysts.

The influence of the modifying phosphorus ligands in the hydroformylation reaction is usually considered in terms of two main parameters describing electronic and steric properties of ligands, according to the well accepted Tolman scale [23]. Before presenting the reported applications of NHC–rhodium complexes as catalysts for hydroformylation, it would be useful to analyze their electronic and steric properties in comparison to those of phosphorus ligands.

2. Electronic effect of ligands

The up-to-date results relevant to the influence of phosphorus ligands on the hydroformylation reaction show increasing selectivity for the linear aldehyde as the electron withdrawing properties of the ligand increase. According to the well-accepted mechanism of hydroformylation, *l*/*b* selectivity can be determined by the migration–insertion step, i.e., olefin insertion into the Rh–H bond of a hydrido complex [14,16,24]. When olefin insertion obeys an anti-Markovnikoff route, an alkyl complex with a straight-chain alkyl ligand is formed which is next transformed to linear aldehyde as a final product of olefin hydroformylation. An alternative explanation of the high regioselectivity to l-aldehyde is based on the differences in the rates of β-hydrogen elimination between the respective rhodium-alkyl species containing straight and branched chains. Such a mechanism has been confirmed by deuterioformylation experiments performed for rhodium complexes phosphacyclic xanthene type ligands [25,26]. As shown in Fig. 2, deuterium is incorporated in the β-position and in the aldehyde group of the main product. It has also been concluded that in all the cases studied, over 92% of the linear alkyl intermediate reverts directly to the aldehyde.

Experimental observations, correlating electron withdrawing properties with a high *l*/*b* ratio, have recently supported theoretical DFT calculations performed for $[RhH(CO)_3L]$ model catalysts [27]. When L represents a more electron-donating ligand (i.e., alkyl phosphine, aryl phosphine), the rate-determining reaction is the migration–insertion of olefin, leading to the formation of an alkyl intermediate. In contrast, for more electron-withdrawing ligands, the last step of the catalytic process, namely hydrogenolysis, was the rate-determining one [27]. This conclusion, based on theoretical calculations, is in agreement with some experimental observations [6,28–31], but it cannot be generalized [32]. Rhodium catalysts with more electron acceptor ligands also have very low barriers to β-hydrogen elimination from the rhodium-alkyl intermediate and could show improved activity for the formation of linear aldehydes starting from internal olefins. However, in the hydroformylation of 1-hexene catalyzed by $[Rh(acac)(CO)_2]/P(OPh)_3$ ($[P(OPh)_3]$:[Rh] = 1.2), the *l*/*b* ratio was only 1.1 at a 39% yield of aldehydes [33]. Similarly, a very low *l*/*b* value, close to 0.2, was found in the hydroformylation of 1-hexene and 2-hexene catalyzed by $[RhH(CO)(P(OPh)_3)_3]$ [34].

The reason was the strong ability of 1-hexene to isomerize to 2-hexene and at the same time a high rate of hydroformylation of the internal olefin, mainly to 2-methylhexanal.

In general, an increase in the electron-withdrawing character of the phosphorus ligand in the rhodium catalyst led to significant improvement in catalytic activity facilitating higher rates and selectivities than electron donating ones [13]. Pruett and Smith first showed that phosphito ligands offer a higher *l*/*b* ratio of aldehydes than stronger donor phosphines [35–37]. Catalytic systems with different phosphito ligands are active in the hydroformylation of olefins, dienes, and unsaturated alcohols [38–42]. The only industrial application of phosphites is the hydroformylation of 3-methylbut-3-en-1-ol, for production of 3-methyl pentane-1,5-diol, known as the Kuraray process [43]. An increase in the *l*/*b* ratio was also noted for strongly π-acceptor pyrrolylphosphines [17].

NHC ligands derived from imidazoles are stronger electron donors than most basic phosphines, such as PMe_3 and PCy_3 [44]. As electronegative substituents decrease the HOMO energy, reduction of the number of nitrogen atoms attached to the ylidene carbon should enhance the NHC donor strength. To check such a hypothesis, the electron properties of NHCs bearing one or two nitrogen atoms at the ylidene carbon have recently been analyzed [27]. The donor properties of NHCs have been estimated according to the Tolman electron parameter [23], by comparing the calculated values of $\nu(CO)$ (cm^{-1}) in $[(NHC)Rh(CO)_2Cl]$ complexes. It was concluded that the electronic character of an NHC can be altered by changing the nature of the azole ring [27]. The values of the $\nu(CO)$ (cm^{-1}) decrease in the order of increasing of donor properties [45] (Fig. 3):

For comparison, the $\nu(CO)$ value calculated by the same method for $[Rh(PPh_3)(CO)_2Cl]$ was 2048 cm^{-1}. Thus, all NHCs are stronger donors than PPh_3. A similar estimation of donor properties has also been shown for a series of three NHCs in $[RhH(CO)_3L]$ complexes

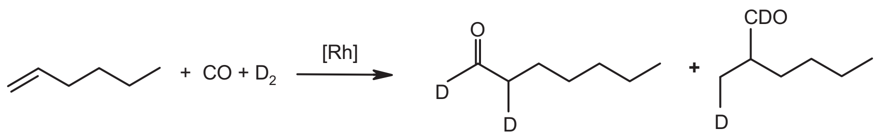


Fig. 2. Results of deuterioformylation experiments.

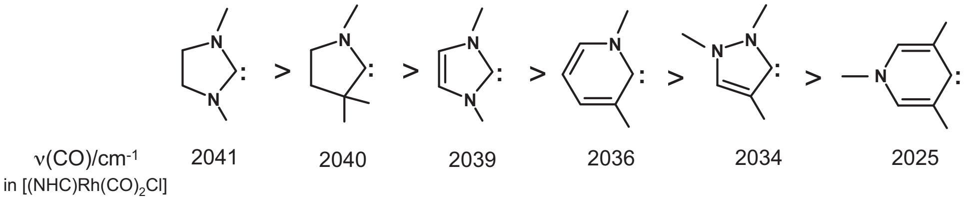


Fig. 3. The order of $\nu(CO)$ (cm^{-1}) decrease in $[(NHC)Rh(CO)_2Cl]$ complexes coinciding with the order of increasing donor properties [45].

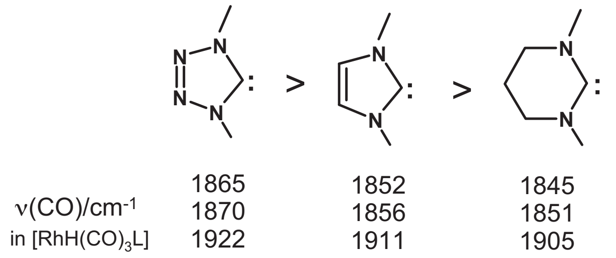


Fig. 4. The order of ν(CO) (cm^{-1}) decrease in [RhH(CO)$_3$L] complexes with different ligands L [27].

that exhibited stronger donor properties than all phosphines and phosphites considered in calculations [27] (Fig. 4).

The general order of L donor strength increase established on the basis of ν(CO) in [RhH(CO)$_3$L] complexes is as follows: CO < strongly electron-withdrawing phosphites < standard phosphites < aryl phosphines < alkyl phosphines < N-heterocyclic carbenes.

Remarkably, the electron-withdrawing ability of an NHC can increase when electron-withdrawing substituents, such as CF_3 or 2,4,6-trinitro phenyl, are bonded to the N-atoms of the tetrazole ring [27]. Similarly, NHCs possessing electron-withdrawing substituents (NO_2, CN) at the C4 and C5 carbon atoms of the imidazole ring show lower electron donor ability [46].

3. Steric effect of NHC ligands

Although it is impossible to fully separate electronic from steric influence, a tendency observed for phosphorus ligands is that those with stronger steric hindrance facilitate an increase in the hydroformylation reaction rate [47].

Selectivity to the linear aldehyde in rhodium-catalyzed hydroformylation of 1-alkenes increases upon changing from a bulky monophosphite to a bulky diphosphite ligand based on a bisphenol linker [48,49]. The bite angle of the diphosphine and diphosphite ligands is probably an important parameter determining the selectivity of the hydroformylation reaction [50,51]. A linear correlation has been found between the amount of l-aldehyde and the bite angle. In general, bis-equatorial coordination of the chelating phosphorus ligand facilitates the increase of yield of linear aldehyde [50,51]. However, the bite angle induces not only a steric effect but also an electronic effect because the structure of the intermediate rhodium species is influenced by the kind of diphosphine used [16].

The shape of the NHC ligand is quite different from the shape of phosphine, and consequently the application of the Tolman cone angle is not useful for the estimation of the steric demand of carbenes. The R substituents on the nitrogen atoms have a strong influence on the ligand shape as defined by $\%V_{\text{bur}}$, the volume buried by the overlap between a sphere with a radius of 3 Å centered around the metal with the atoms of the ligand within this sphere. The bulkier a specific ligand, the larger the amount of the sphere ($\%V_{\text{bur}}$) occupied by the ligand [52].

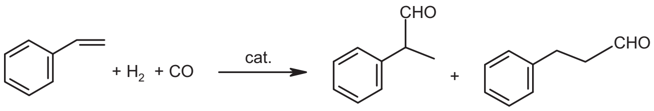


Fig. 5. Scheme of styrene hydroformylation.

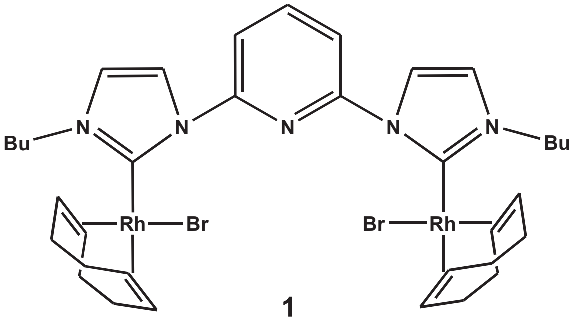


Fig. 6. Rhodium complex with 2,6-bis(1-butylimidazolium-3-yl)pyridine ligand [53].

4. Hydroformylation of styrene catalyzed by Rh–NHC complexes

The hydroformylation of styrene catalyzed by rhodium complexes with N-heterocyclic carbene ligands, Rh–NHC, has been studied intensively by many research groups. In most cases the reaction performed at 30–80 atm pressure led to branched aldehyde (b) as the main product (Fig. 5).

Fernandez and Peris investigated the dimeric rhodium(I) complex **1** with a carbene ligand derivative of 2,6-bis(1-butylimidazolium-3-yl)pyridine (Fig. 6) as a catalyst for the hydroformylation of aliphatic and aromatic olefins [53].

Complex **1** turned out to be an active catalyst for styrene hydroformylation, producing up to 100% of branched aldehydes after 24 h. Results obtained at a [styrene]/[Rh] ratio of 400 are presented in Table 1.

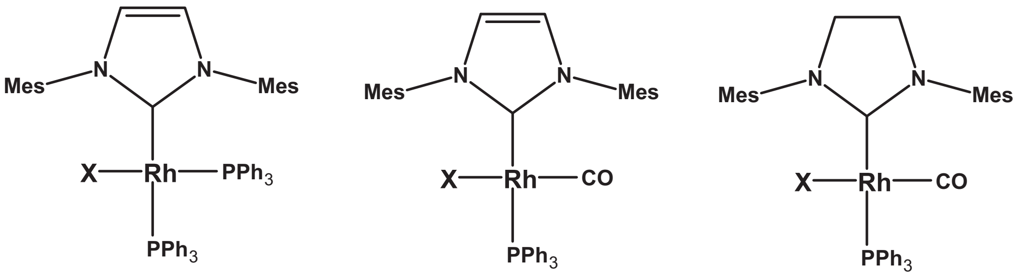
At 30 atm, the conversion of styrene was quite low, whereas at 80 atm, a 99% yield of aldehydes was achieved. Complex **1** was employed in the hydroformylation of substituted styrenes, and also in these reactions a high selectivity to branched aldehydes, close to 96%, was noted. Non-aromatic substrates were also tested. 1-Octene produced similar amounts of linear and branched aldehydes, and in the hydroformylation of 2,5-dihydrofuran, 63% of 3-formyl-tetrahydrofuran and 37% of 2-formyl-tetrahydrofuran were obtained (Table 1).

Crudden and co-workers successfully applied [Rh(IMes)(PPh$_3$)$_2$Cl] (Fig. 7) as a catalyst for styrene hydroformylation. Despite the presence of phosphine, a relatively high

Table 1
Results of hydroformylation with **1** [53].

Substrate	*T* [°C]	*p* [atm]	Conversion [%]	Aldehydes [%]	Branched [%]
Styrene[a]	40	80	30	98	98
Styrene[a]	80	80	100	99	86
p-(MeO)-styrene[b]	40	50	74	100	96
p-(F)-styrene[b]	40	50	69	100	96
1-Octene[b]	40	50	70	92	43
2,5-Dihydrofuran	40	50	90	98	63[c]

[a] [Substrate]/[Rh] = 700, 24 h.
[b] [Substrate]/[Rh] = 400.
[c] 3-Formyl-terahydrofuran.



[RhCl(IMes)(PPh$_3$)$_2$] [RhCl(IMes)(CO)(PPh$_3$)] [RhCl(SIMes)(CO)(PPh$_3$)]

Fig. 7. Rh–NHC complexes used in styrene hydroformylation.

pressure (68 atm) and a long time (19 h) were needed to get reasonable conversion of the substrate. Under such conditions an *l*/*b* ratio of 96:4 was achieved, and the catalytic results were better than with the application of the Wilkinson complex under the same reaction conditions (Table 2) [54].

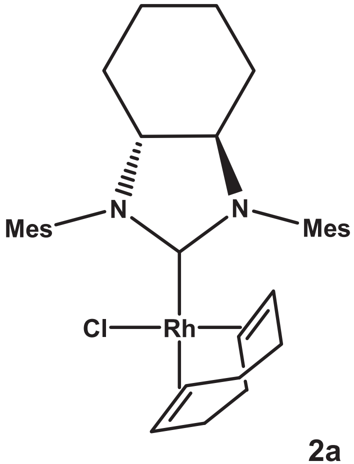
The complex [RhCl(IMes)(PPh$_3$)(CO)] (Fig. 7), formed from [Rh(IMes)(PPh$_3$)$_2$Cl] in the presence of CO, presents high selectivity also in the hydroformylation of differently substituted styrenes (Table 2).

When a similar complex with a saturated NHC ligand, [RhCl(SIMes)(CO)P] (P = phosphorus ligand) (Fig. 7), was used in styrene hydroformylation, an influence of the kind similar to that of the added phosphorus ligand on TOF and the *b*/*l* ratio was observed [1]. Interestingly, in this system the addition of NEt$_3$ caused an approximately ten-time increase in the TOF value. It was explained that the elimination of HX promoted by NEt$_3$ made an important contribution to catalytic activity, and therefore TOF/h^{-1} increased from *ca.* 10–30 to *ca.* 100–125 upon the addition of NEt$_3$ [1].

During the hydroformylation of aliphatic olefins, selectivity often decreased as a result of hydrogen β-elimination from the intermediate alkyl complex leading to internal olefins. Many rhodium catalysts with NHCs also showed a strong ability to form internal olefins *via* β-hydrogen elimination even when high selectivity to aldehydes was observed [55–58]. The catalyst obtained by Crudden's group, [Rh(OAc)(CO)$_2$(IPr)] containing NHC and unidentate acetate, was not active in the isomerization of double bonds, whether terminal or internal [59]. It was demonstrated for the hydroformylation of 1-decene, when only aldehydes were formed without isomerization or hydrogenation of the double bond with *l*/*b* = 3. Similarly, isomerization and hydrogenation were not observed during the hydroformylation of 2-octene and 4-phenyl-1-butene [59].

4.1. Asymmetric hydroformylation

Asymmetric hydroformylation is a very promising catalytic reaction that makes it possible to obtain chiral aldehydes from inexpensive substrates in one-step synthesis [60]. The high catalytic potential of rhodium complexes containing chiral phosphorus ligands in this process has been confirmed by many studies, recently reviewed in detail [60]. The highest enantioselectivities in asymmetric hydroformylation have been obtained using rhodium catalysts containing two types of chelating ligands of the diphosphite or phosphine–phosphite type [60]. For both ligands, complexes with the formula [RhH(L–L)(CO)$_2$] have been characterized as the resting state of the catalyst. Applying a phosphine–phosphite ligand (R,S) BINAPHOS, Takaya obtained 96% ee with total substrate conversion [61,62]. The advantages of C$_1$-symmetric BINAPHOS compared with bisphosphine ligands of C$_2$ symmetry have been discussed using a theoretical approach [63]. The application of chiral ligands derived from bisnaphtol or bisphenol configuration have made it possible to achieve high ee values [62,64–66]. Recently, it has been shown that, besides diphosphites and phosphine–phosphites, diphosphines also induce high enantioselectivity of hydroformylation [67,68].



2a

Fig. 8. Lai catalyst [69].

There are very few reports on asymmetric hydroformylation catalyzed by Rh–NHC complexes with monodentate NHC ligands. Laï and co-workers used an Rh(I) complex with a chiral N-heterocyclic carbene **2a** (Fig. 8) in the hydroformylation of styrene [69]. Surprisingly, the enantioselectivity and regioselectivity of this reaction

Table 2
Hydroformylation of styrene [54].

Substrate	Catalyst	Co-catalyst	Conversion [%]	*b*/*l*
Styrene	ClRh(PPh$_3$)$_3$	–	35	87:13
Styrene	ClRh(PPh$_3$)$_2$(CO)	PPh$_3$ (2 eq.)	27	88:12
p-Me-styrene	ClRh(IMes)(PPh$_3$)(CO).	PPh$_3$ (2 eq.)	96	96:4
p-Cl-styrene	ClRh(IMes)(PPh$_3$)(CO).	PPh$_3$ (2 eq.)	94	97:3
p-OMe-styrene	ClRh(IMes)(PPh$_3$)(CO).	PPh$_3$ (2 eq.)	98	95:5
p-^{i}Pr-styrene	ClRh(IMes)(PPh$_3$)(CO).	PPh$_3$ (2 eq.)	93	96:4

0.5 mol % of catalyst, 19 h, 60 °C, 68 atm (1000 psi) H$_2$/CO (1:1). b, yield of linear aldehydes (%); l, yield of branched aldehydes (%).

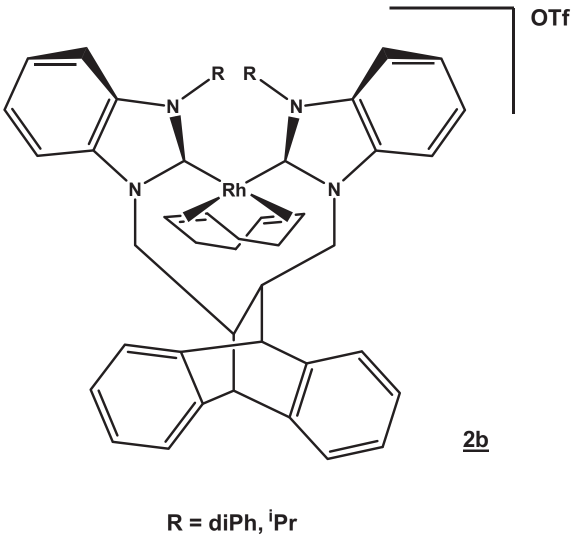


Fig. 9. Veige catalyst [70].

were rather low, and similar amounts of l- and b-aldehydes were formed. An increase in enantioselectivity to ee = 12.5 was observed in the presence of a small excess of free PPh_3 (3 equivalents), whereas when a higher amount of PPh_3 (10 equivalents) was added, enantioselectivity decreased to ee = 7 although the *b*/*l* ratio increased from 42:58 to 91:9.

Enantioselective hydroformylation of styrene was also studied by the Veige group using dicarbene rhodium complexes **2b** (Fig. 9) [70]. Reactions were performed at 50 °C for 24 h, at catalyst concentrations ranging from 0.1 to 5 mol% and H_2/CO pressure over 80 atm. Under such conditions, conversion from 75 to 100% was reached, whereas *b*/*l* selectivity ranged from 94:6 to 97:3. It was suggested that the active form of the catalyst was the hydrido–carbonyl complex $[Rh(CO)_4H]$, formed after the elimination of the NHC ligand. The low enantioselectivity of the hydroformylation of styrene and the hydrogenation of methyl-2-acetamidoacrylate and methyl ketone could be explained by the decomposition of the catalyst or the reductive elimination of the NHC ligand. Chiral Rh–NHC complexes not applied yet in catalytic reactions have also been reported [71,72].

5. Hydroformylation of aliphatic olefins

The first patent claiming the application of an Rh–NHC complex, [RhCl(cod)(NHC)] (NHC = 1,3-dimethylimidazolin-2-ylidene), in the hydroformylation of 1-hexene was presented by Herrmann et al. in 1997 [73]. Various other Rh–NHC complexes, bearing ligands originating not only from imidazoles but also from other N-heterocyclic rings, have been tested in the hydroformylation of aliphatic olefins since. The effect of the kind of carbene ring on 1-octene hydroformylation is illustrated by the data presented in Fig. 10 [74].

Complex **10**, with a carbene ligand derived from tetrazole, appeared the most active, with a TOF value of 3540 h^{-1} [74]. The increasing order of TOF values and conversion follows the order of decreasing electron-donor properties of the NHC ligand. Thus, the best results were obtained for the weakest donor, tetrazole. The use of different halogens did not reveal any significant changes in reactivity. However; the use of 1,3-dimesityl (**6**) instead of 1,3-bis(2-propyl) (**4**) resulted in a dramatic increase in reactivity despite similar donor properties of both ligands, as proved by ν(CO) data [27]. Interestingly, application of bulky substituents to the NHC ligand has no influence on the *l*/*b* ratio, which was rather low (*ca.* 0.5) with all studied catalysts [27]. It can suggest formation of $[RhH(CO)_4]$ as the active species, however, using ^{13}C NMR results, authors proposed that Rh–NHC bond remained stable and Rh–NHC carbonyl hydrido species was responsible for the catalytic activity [27].

Rhodium complexes with annulated diaminocarbene ligands (Fig. 11) have been tested for the hydroformylation of 1-octene. The highest yields of aldehydes (96–99%) were obtained at pressures higher than 20 atm, and the *l*/*b* ratio ranged from 0.85 to 1.72 [75].

The rhodium complexes **12**–**16** (Fig. 12) with less sterically demanding NHC ligands, [Rh(bmim-y)(1,5-cod)X] (X = Cl, Br, I, SCN) and [Rh(demim-y)(1,5-cod)Cl] (bmim-y = 1-butyl-3-methylimidazolin-2-ylidene, demim-y = 1,3-diethoxymethylimidazolin-2-ylidene), modified by

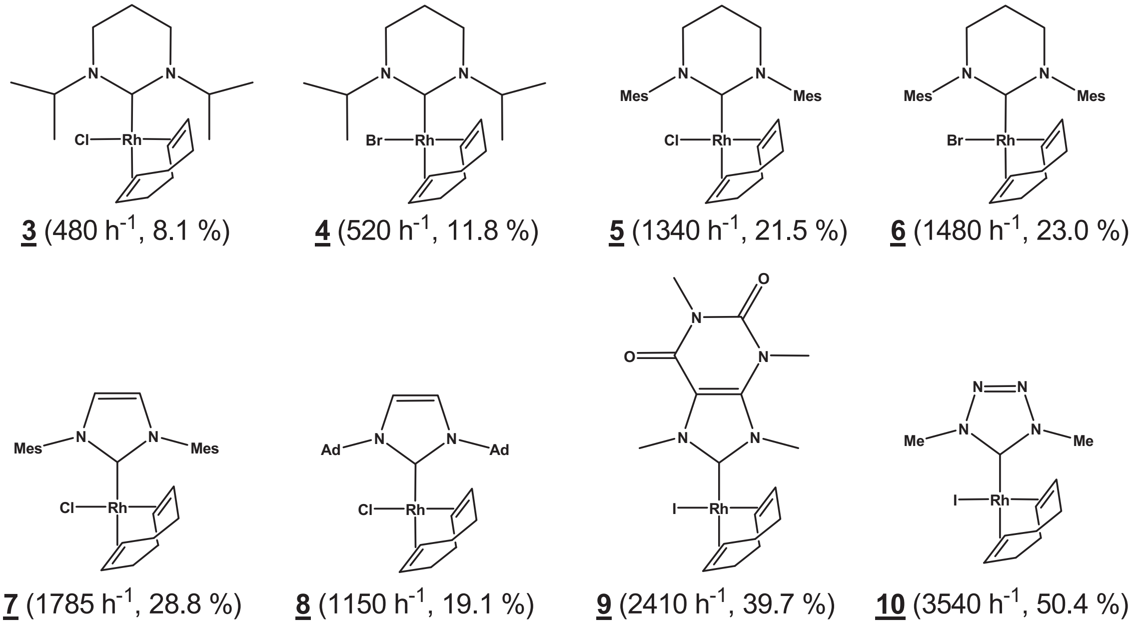


Fig. 10. TOF (h^{-1}) values and conversion of 1-octene (%) obtained in reactions catalyzed by Rh–NHC complexes [74].

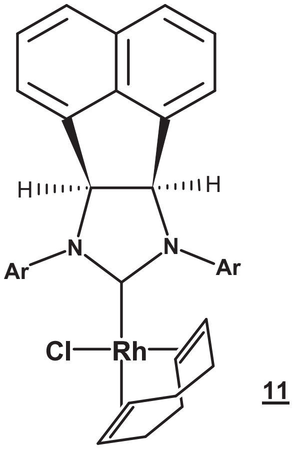


Fig. 11. Rhodium complex with annulated diaminocarbene ligand [75].

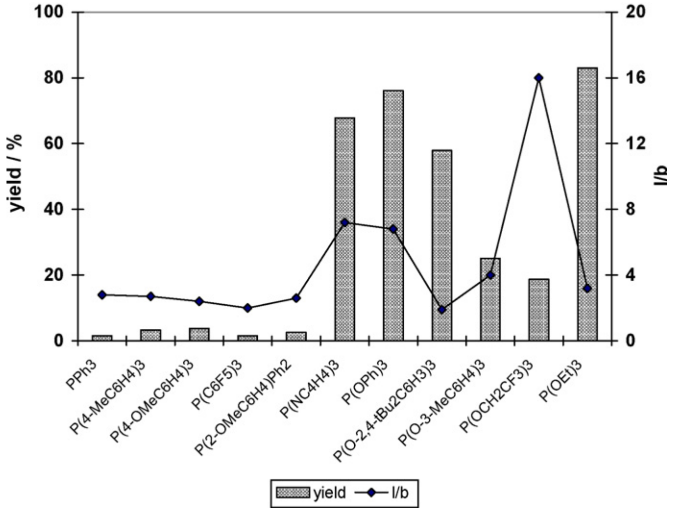


Fig. 13. Results of hydroformylation of 1-hexene catalyzed by [Rh(bmim-y)(cod)Br] and different phosphorus ligands ([P]/[Rh] = 2, 10 atm, 80 °C) [76].

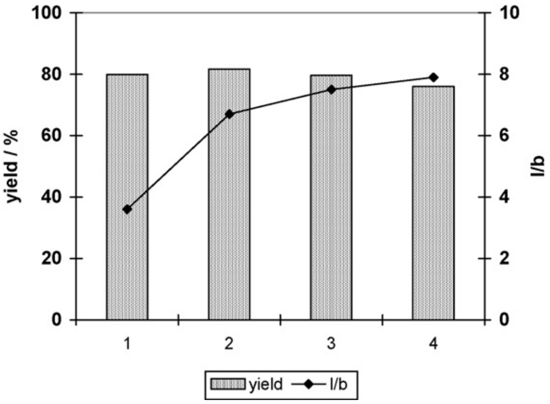


Fig. 14. Effect of [P(OPh)$_3$]/[Rh] ratio on the results of hydroformylation of 1-hexene catalyzed by [Rh(bmim-y)(cod)Br] [76].

different phosphorus ligands, were used as catalysts for the hydroformylation of 1-hexene [76].

Particularly good activity and selectivity were noted when P(OPh)$_3$ was used as a modifying ligand, as illustrated by the data shown in Fig. 12. The *ca.* 80% yield of aldehydes with an *l*/*b* ratio of *ca.* 7, achieved in 4 h at 10 atm H_2/CO, can be considered a very promising result. In a similar rhodium system containing P(OPh)$_3$ but without an NHC ligand, the highest *l*/*b* ratio was below 3 [34] (Fig. 13).

Under the same conditions, high *l*/*b* selectivity was also found for electron-withdrawing P(OCH$_2$CF$_3$)$_3$ and P(NC$_4$H$_4$)$_3$ as modifying ligands. The application of P(OCH$_2$CF$_3$)$_3$ resulted in the achievement of the highest *l*/*b* value, 16.6, but simultaneously aldehyde yield decreased to just 18.7%. Prolongation of the reaction time from 4 h to 8 h increased the yield to 69.1%, but the *l*/*b* ratio decreased to 7.8. Enhancement of the [P]/[Rh] ratio to 3 resulted in the highest *l*/*b* value rising to 27.7 at a total aldehyde yield of 26.2%. Very good results, presenting a compromise between high yield and selectivity, 66.5% of aldehydes with *l*/*b* = 4.6, were obtained with P(NC$_4$H$_4$)$_3$. Remarkably, increasing the amount of P(NC$_4$H$_4$)$_3$ caused an increase in selectivity to *l*/*b* = 7.1 and only a small increase in yield. Generally, aryl phosphites provided higher yields of aldehydes, and with P(O–C$_6$H$_3$–2,4-*t*Bu$_2$)$_3$, P(OC$_6$H$_4$–*m*–CH$_3$)$_3$, and P(OCH$_2$CH$_3$)$_3$, aldehyde yield ranged from 25.1 to 83% with the *l*/*b* ratio ranging from 1.9 to 4.0. The maximum yield of 2-hexene, the only side product formed in these reactions, was equal *ca.* 30%. In contrast, the application of phosphines such as PPh$_3$, P(*p*-CH$_3$–C$_6$H$_4$)$_3$, P(*p*-CH$_3$O–C$_6$H$_4$)$_3$, P(C$_6$F$_5$)$_3$, or P(2-CH$_3$O–C$_6$H$_4$)(Ph)$_2$ resulted in rather low yields (from 1.5 to 3.7%) and *l*/*b* selectivity of from 2.2 to 2.7. In the same time the amount of 2-hexene ranged from 0.5% to 5% [76]. A threefold excess of the phosphorus ligand in relation to rhodium was an optimal one for both high aldehyde yields and high *l*/*b* ratios (Fig. 14).

In the hydroformylation of 1-hexene, comparable amounts of linear and branched aldehydes were obtained with the application of neutral and cationic rhodium complexes containing mono- and bis-carbene ligands of rather low steric hindrance. Under 80 atm *l*/*b* ratio *ca.* 1:0.6 was noted after 16 h and a decrease in reaction selectivity over time was observed [77]. Rhodium complexes with NHC ligands functionalized with indenyl group, characterized by a very high electron density on Rh, showed some activity for the hydro-

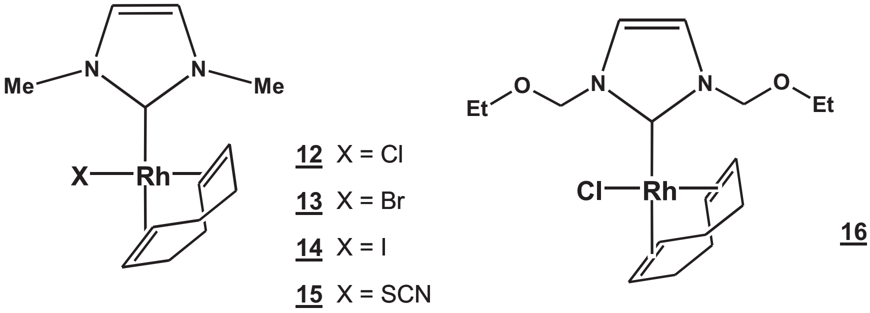
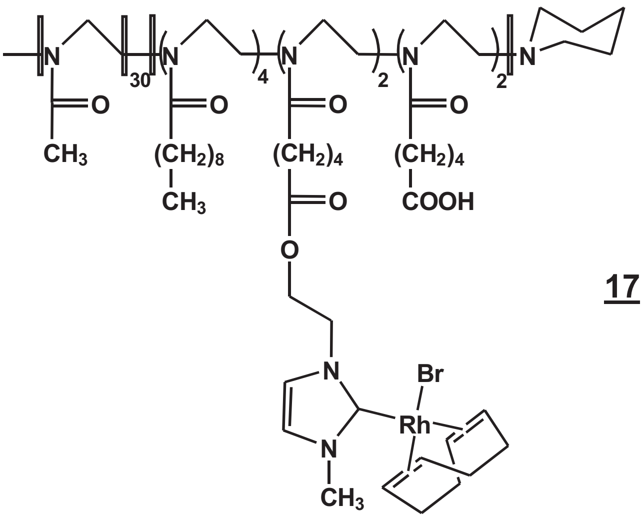


Fig. 12. Rh–NHC complexes used in hydroformylation of 1-hexene [76].



17

Fig. 15. The first immobilized Rh–NHC complex used in hydroformylation.

formylation of 1-octene. An intensive isomerization of substrate led to final *l*/*b* ratio only 1.25 [78].

6. Immobilized Rh–NHC catalysts

The first immobilized Rh–NHC catalyst for hydroformylation was reported by Weberskirch, who applied a water-soluble polymer as a carrier for rhodium. The advantage of such a catalyst is that it can be applied in biphasic water-organic systems [55]. An immobilized catalyst was obtained from a Rh(I) precursor containing an N-heterocyclic carbene ligand with an –OH group. Complex **17** (Fig. 15) showed a high activity in the hydroformylation of 1-octene represented by a TOF value of 2360 h^{-1}, although the unsupported starting complex was even more active. The immobilized complex **17** was separated and used in four consecutive reactions producing from 22.0% to 43.2% of aldehydes with *l*/*b* value decreasing from 72:28 to 57:43 (Table 3).

Rh(I) carbene complexes immobilized on Merrifield resin were used as heterogeneous catalysts in the hydroformylation of 1-hexene without solvent. Complexes **18** and **19** (Fig. 16) modified with phosphites ($P(OPh)_3$, $P(OCH_2CF_3)_3$) catalyze hydroformylation with *l*/*b* over 7 and TOF up to 1400 h^{-1} [79].

Catalysts immobilized on Merrifield resin can be easily separated from the reaction mixture. Moreover, they are very stable under the reaction conditions and can be re-used eight times (**18**) or four times (**19**) without a marked decrease in activity or selectivity (Fig. 17). However, to keep a high activity it was necessary to add a new portion of $P(OPh)_3$ to each reaction. When $P(OCH_2CF_3)_3$ was used as the modifying ligand, selectivity was higher and an *l*/*b* value of 49 was achieved; however, the stability of the catalyst decreased. Consequently, it was possible to perform only three cycles and already in the third one the yield of hydroformylation was very low. Similarly, low stability was characteristic for systems containing PPh_3 as the modifying ligand, which additionally gave low *l*/*b*, *ca.* 3.2.

Table 3
Hydroformylation of 1-octene catalyzed by **17** [55].

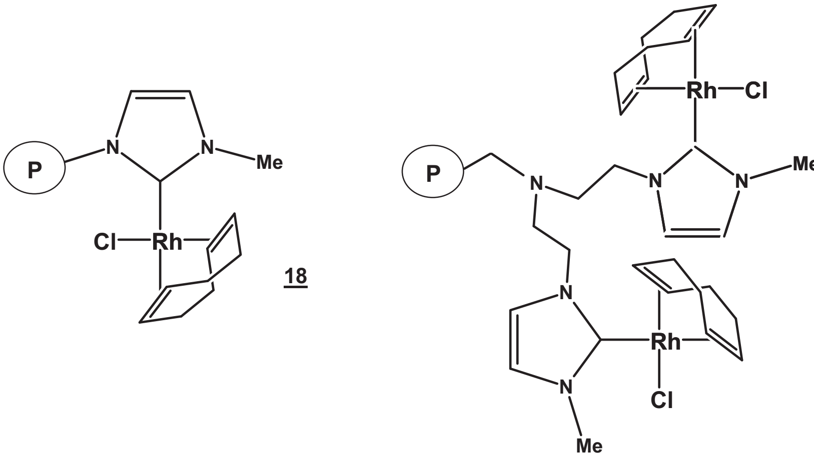
Cycle	Yield [%]	TOF [h^{-1}]	*l*/*b*
1	22.0	1100	72:28
2	34.7	1790	66:34
3	43.7	2320	55:45
4	43.2	2360	57:43

100 °C, 50 atm H_2/CO (1:1), 17.9 mg of **17** in 50 cm^3 of water, pH = 6, [1-octene]/[Rh] = 10,000). b, yield of linear aldehydes (%); l, yield of branched aldehydes (%).

Immobilized catalysts **18** and **19** were also tested in the hydroformylation of 1-octene, and the activity was slightly lower than in the case of 1-hexene; however, selectivity was similar in both systems [57].

7. Studies of catalytic resting states

According to the well accepted mechanism of hydroformylation, the hydrido carbonyl pentacoordinated rhodium complex $[RhH(CO)(PPh_3)_3]$, transformed under hydroformylation reaction conditions to $[RhH(CO)_2(PPh_3)_2]$, should be considered as the resting state of the catalyst in reactions performed in the presence of PPh_3 [6,10,24]. For both complexes, as well for their phosphite analogues, $[RhH(CO)(P(OPh)_3)_3]$ and $[RhH(CO)_2(P(OPh)_3)_2]$, trigonal bipyramidal structures have been confirmed in solution and in solid state [10,33,80]. Similarly, the complex $[RhH(CO)(P(NC_4H_4)_3)_3]$ formed a distorted trigonal bipyramid with the rhodium atom placed out of the plane of the $P(NC_4H_4)_3$ ligands [81]. Complexes of the hydrido carbonyl type, namely $[RhH(CO)_2(\text{diphosphine})]$, have been characterized for phosphacyclic diphosphines based on the xanthene backbone [82]. The formation of hydrido rhodium complexes with amphiphilic phosphines was evidenced by the NMR method and IR spectroscopy under hydroformylation reaction conditions [83]. Monodentate phosphorus amidite and phosphinite ligands formed mixtures of $[RhH(CO)_2L_2]$ and $[RhH(CO)L_3]$ complexes, whereas their bidentate analogues formed mixtures



18

19

Fig. 16. Rh–NHC complexes immobilized on Merrifield resin.

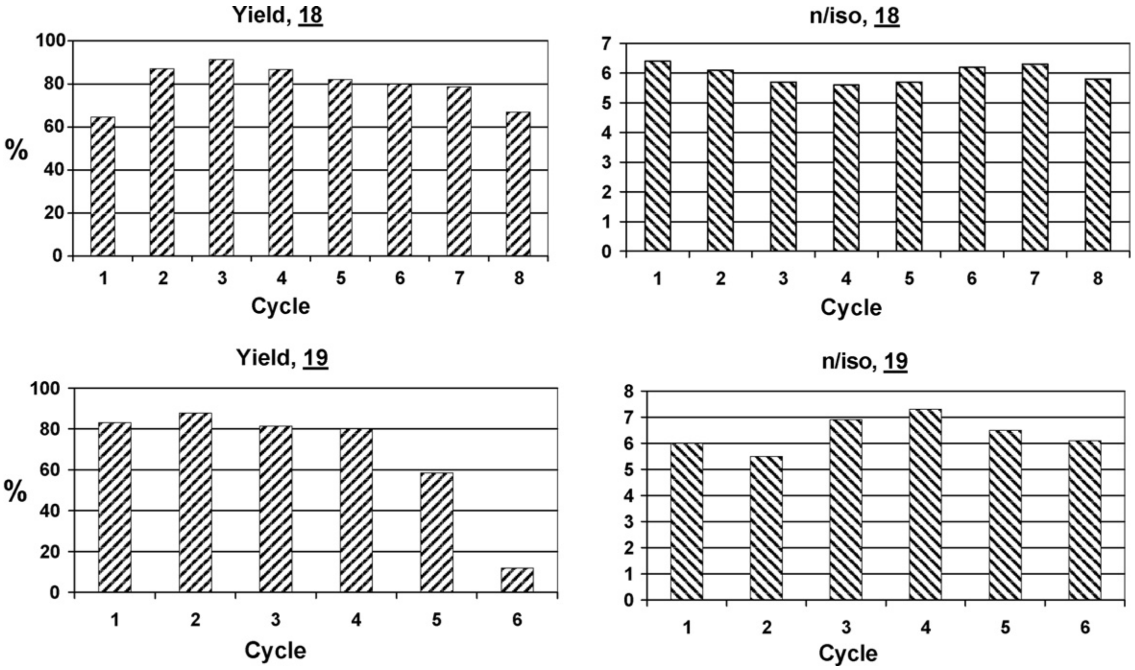


Fig. 17. Yield and *l*/*b* ratio obtained in hydroformylation of 1-hexene catalyzed by **18** and **19** (80 °C, 10 atm. H_2/CO, [1-hexene]/[Rh] = 1000, [$P(OPh)_3$]/[Rh] = 2).

of [$RhH(CO)_2$(L–L)] and [RhH(CO)(L–L)(L–L′)] complexes, where L–L′ acted as a monodentate [84]. Monodentate and bidentate phosphorus diamide ligands derived from a 1,3,5-trisubstituted biuret structure formed complexes [$RhH(CO)_2L_2$], [$RhH(CO)_3L$], and [$RhH(CO)_2$(L–L)] under hydroformylation reaction conditions [85]. A phosphorus diamide ligand formed a hydride rhodium complex with phosphorus ligands coordinated in di-equatorial mode under hydroformylation reaction conditions [86]. In contrast, BINAPHOS coordinates to rhodium in equatorial–axial fashion [61,62].

In the case of Rh–NHC catalysts, the most important question is that of the stability of the Rh–NHC bonding. Studies by Crudden and Fernandez and Peris showed that during hydroformylation the NHC ligand remained in the coordination sphere of rhodium [18,53]. A similar conclusion about the high stability of the Rh–NHC bond was also formulated by Bortenschlager for another type of carbene on the basis of MS measurements [74].

The formation of an Rh–NHC complex during the hydroformylation of 1-octene was demonstrated by means of labeling experiments performed with [$Rh(acac)(CO)_2$] and Xantphos-type phosphine dissolved in ionic liquid (1-n-butyl-3-methylimidazolium-d_3 NTf_2) and followed by ^{1}H NMR. It was concluded that Rh–NHC complexes were probably present even in typical hydroformylation reactions in ionic liquids promoted by metal complexes without strong σ-donor ligands [87].

It can be expected that a hydrido complex with an NHC ligand presents the active form of a hydroformylation catalyst formed *in situ* from a Rh–NHC precursor. However, what is a problem is the tendency for reductive elimination of the NHC ligand in the form of imidazolium salt (H–NHC$^+$), which is plausible in the presence of H_2. Whittlesey and coworkers synthesized hydrido-NHC compounds starting from [$RhH(PPh_3)_4$] and [$RhH(CO)(PPh_3)_3$] and free carbene [88]. [$RhH(PPh_3)_4$] reacted with ICy or other alkyl-carbenes forming a mixture of mono- and di-carbene species with *cis* and *trans* structures. Under the same conditions, IMes did not form any product. When [$RhH(CO)(PPh_3)_3$] was used, hydrido–dicarbene complexes were obtained for both carbenes, IMes and Icy [88].

In studies of Rh–NHC complexes bearing bulky substituents in positions 1 and 3 of the imidazole ring, like mesityl or adamantyl, hydrido complexes were formed in reaction with gaseous dihydrogen [89,90]. Dimeric complexes [$RhCl(COE)(NHC)]_2$ (COE = cyclooctene, NHC = IMes, IPr) reacted with dihydrogen forming dimeric a hydrido–carbene Rh(III) complex (Fig. 18). The same reaction performed in the presence of free carbene led to a monomeric dihydrido complex with two NHC ligands (Fig. 18).

Interestingly, in reaction of IMes carbene with [$RhCl(COE)_2]_2$, an orthometallated rhodium complex was formed in high yield. X-ray studies of this compound confirmed the presence of intramolecular

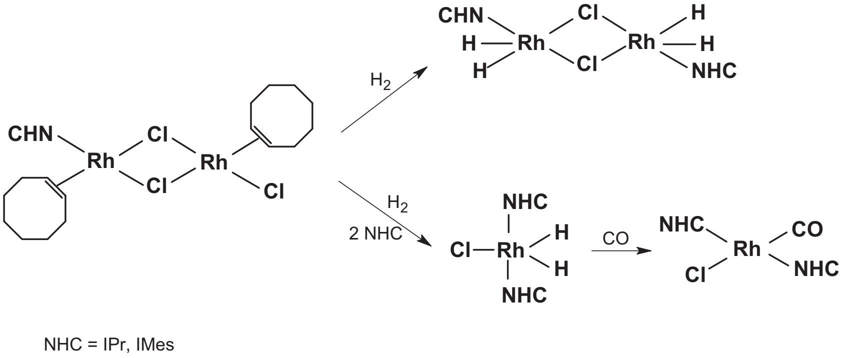


Fig. 18. Formation of hydrido dimeric and monomeric Rh–NHC complexes.

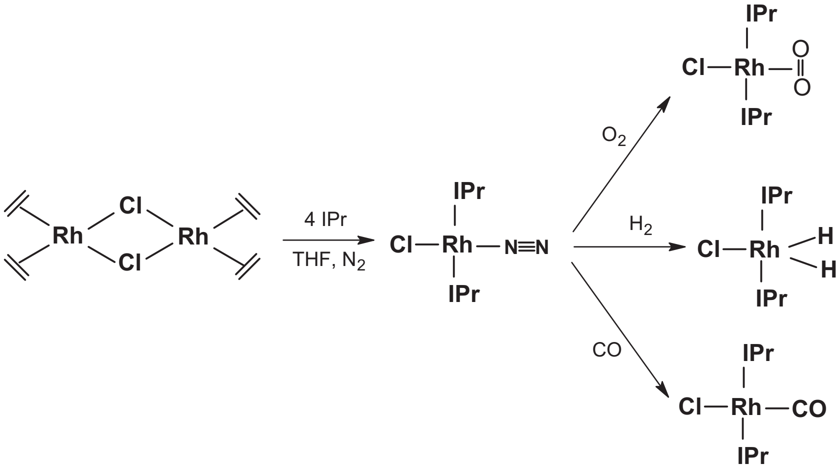


Fig. 19. Reactivity of dinitrogen Rh–dicarbene (IPr, IMes) complexes [90].

C–H activation of one ortho methyl group, leading to Rh–H and Rh–C bond formation [91].

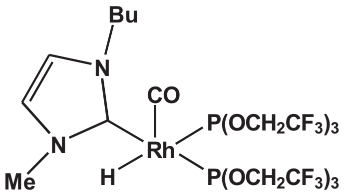
The results reported by the Crudden group also shown a high activity of dicarbene complexes towards dihydrogen. In the first step, a dinitrogen rhodium complex was obtained in reaction of rhodium ethylene dimer with IMes or IPr carbenes under a dinitrogen atmosphere (Fig. 19) [90]. A coordinated dinitrogen ligand can be easily substituted by H_2, CO, or O_2 with formation of respective rhodium species.

Rh–NHC complexes with smaller substituents in the imidazole ring, such as methyl or butyl, do not react with H_2, even at 10 atm pressure. According to ^{1}H NMR analysis of the reaction solution, hydrido ligands were not present, and the relevant signals were also absent after the introduction of phosphorus ligands [76]. However, NMR studies of the [RhX(bmim-y)(CO)(P(OCH$_2$CF$_3$)$_3$)] catalyst under hydroformylation conditions (80 °C, 10 atm H_2/CO) resulted in the identification of a new [RhH(bmim-y)(CO)(P(OCH$_2$CF$_3$)$_3$)$_2$] complex [76]. What is unique is that this new hydrido complex **20** has a square pyramidal structure with the hydrido ligand located in a plane and two phosphito ligands occupying *cis* positions (Fig. 20).

Such symmetry was evidenced by the ^{1}H NMR and ^{1}H{^{31}P} NMR spectra shown in Fig. 21. In ^{1}H NMR, eight lines were observed as a result of the hydrido signal being split by two non-equivalent phosphorus and one rhodium atoms, but the multiplet was partially overlapped by a second intensive multiplet originating from [HRh(P(OCH$_2$CF$_3$)$_3$)$_4$] (Fig. 21). A clearer spectrum, containing only three doublets assigned to three different rhodium–hydrides was obtained with ^{31}P decoupling.

8. Hydrogenation of olefins catalyzed by Rh–NHC complexes

Here we would like to discuss shortly the reactivity of Rh–NHC complexes under hydrogenation reaction conditions. These data are useful for understanding of reactivity of Rh–NHC towards H_2 and olefin, which are also reactants in hydroformylation. Interestingly, despite the efficient formation of hydrido complexes, Rh–NHC species are rather poor catalysts for olefins hydrogenation. For example, the pre-formed hydrido complexes [Rh(H)$_2$Cl(NHC)$_2$] (NHC = IPr, IMes) appeared not to be useful catalysts for hydrogenation, with just 15% of cyclooctane formed from cyclooctane after 24 h at 45 °C [89]. Moreover, decomposition of the complexes to colloidal metal was mentioned. Similar observations were reported by Herrmann et al., who studied [RhCl(COD)(ICy)] and [Rh(COD)(ICy)$_2$]$^+$ in the hydrogenation of cyclohexene and 1-octene [92]. They found that the tested complexes are not useful for hydrogenation because they undergo decomposition during the reaction or present low activity. They also assumed that the combination of a strong σ-donor (carbene) and a strong π-acceptor (CO) ligand largely deactivates the metal center, and dihydrogen is not activated. When phosphines were used as additional ligands, a postulated three-coordinated active inter-



20

Fig. 20. Proposed structure of the [RhH(bmim-y)(CO)(P(OCH$_2$CF$_3$)$_3$)$_2$] complex.

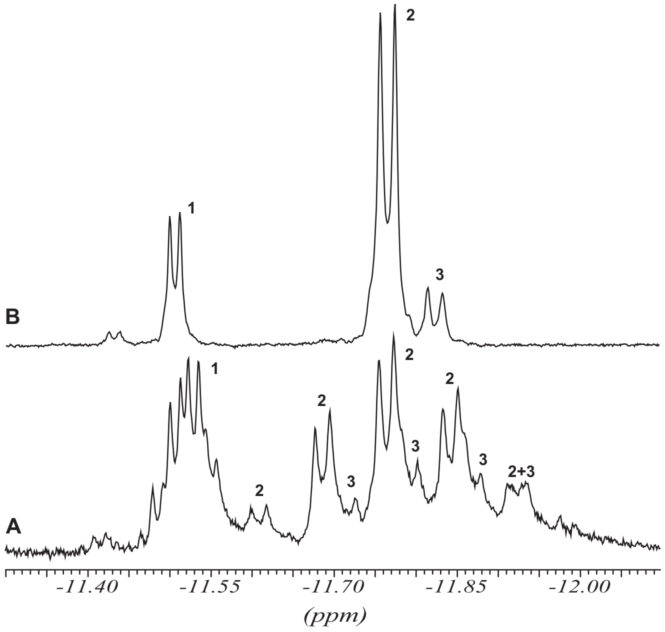


Fig. 21. ^{1}H NMR (A) and ^{1}H{^{31}P} (B) NMR spectra in the hydrido region. 1-[RhH(CO)(P(OCH$_2$CF$_3$)$_3$)$_3$], 2- [RhH(P(OCH$_2$CF$_3$)$_3$)$_4$], 3- [RhH(bmim-y)(CO)(P(OCH$_2$CF$_3$)$_3$)$_2$].

mediate could be more stable and, in fact, good results were obtained in cyclohexene hydrogenation performed in the presence of PPh_3. However, in this series of experiments, the best results were obtained for an *in situ* formed catalyst composed of [Rh(COD)Cl(NHC)] and dppe and $NaBPh_4$. No decomposition of the catalyst was observed, and its activity was close to the $[RhCl(PPh_3)_3]$ [92].

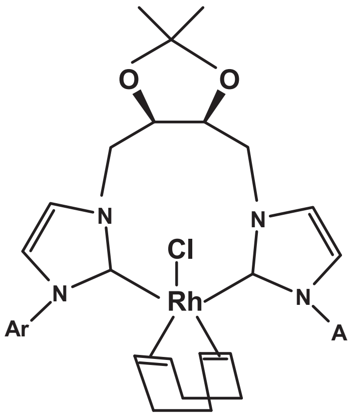
Complex **2b** was applied for hydrogenation of *trans*-methylstilbene and methyl-2-acetamidoacrylate at 50 bar of H_2, however the ee's were very low [70]. The Rh^0 species was evidenced as the active catalyst, formed after reductive elimination of corresponding imidazolium salt [70]. The very slow rates of transfer hydrogenation between acetophenone and 2-propanol were noted when Rh–NHC–imine complex was used as a catalyst. This finding is consistent with the formation of colloidal Rh^0 metal under reactions conditions [93,94].

A moderate activity of $[RhCl(IMes)(PPh_3)_2]$ in hydrogenation of cyclohexene was reported [95]. A way to improve its catalytic activity was to apply a CuCl co-catalyst acting as a phosphine scavenger [18,96]. In the hydrogenation of isosaffrole, such system was more active than Wilkinson's catalyst. An increase in TOF/h^{-1} from 36 to 430 caused by the addition of CuCl is very spectacular for $[RhCl(IMes)(PPh_3)_2]$, whereas CuCl has only very small influence on the catalytic activity of $[RhCl(PPh_3)_3]$ [18].

Rhodium complex bearing an NH, NR-stabilized N-heterocyclic carbene and PPh_3 ligands exhibited catalytic activity in hydrogenation of 1-octene [97]. In a competitive experiment with 1-dodecene and 3-butenoic acid ester, the clear preference of hydrogenation of oxygenated substrate was observed due to the presence of NH functionality in the NHC ligand [97].

The results obtained by the Messerle group show that NHC–pyrazolyl chelate ligands are suitable for the design of active rhodium catalysts of styrene hydrogenation [98]. Such complexes showed moderate activity with complete conversion of the substrate within 50 min in all cases. It should be mentioned that NHC–pyrazolyl ligands do not create big steric hindrance around the metal centre, which can be important for substrate coordination. Consequently, complexes containing the smallest ligands were the fastest catalysts, and complexes which contained a tert-butyl group on the NHC donor had much slower reaction rates. It was concluded that the steric bulk of the ligands had a significant effect on the hydrogenation activity of the complexes [98]. However, most probably not only steric hindrance but also electronic effects play an important role. This supposition is supported by the fact that a bis-NHC rhodium complex was totally inactive in hydrogenation under conditions applied for complexes with NHC–pyrazolyl chelating ligands [99]. On the other hand [Rh(NHC)(cod)Cl] complexes bearing functionalized carbene ligands based on 6- and 7-membered rings catalyze hydrogenation of 1-cyclooctadiene and 2-methyl styrene with molecular hydrogen under ambient temperature [100].

Rhodium complexes containing bis-NHC ligands of C_2 symmetry with two imidazolin-2-ylidene moieties at chiral dioxolane backbone have been successfully applied in hydrogenation of (E)-diethyl 2-R-succinates with ee's up to 99% [101] (Fig. 22). This is the first example of the use of rhodium complex with chiral biscarbene ligand in asymmetric hydrogenation with excellent enantioselectivity. High enantioselectivities have been obtained earlier for a range of functionalized olefins in hydrogenation catalyzed by rhodium complex containing NHC ligand with phosphane group bonded to N-atom [102]. In contrast, rhodium complexes with chiral 3,3′-substituted biisoquinoline-based NHC ligands did not show any optical induction in hydrogenation of methyl 2-acetamidoacrylate [103]. Similarly, rhodium complexes bearing monodentate NHC ligands derived from 2,2′-bipiperidine and partially reduced biisoquinoline showed significant activity in hydrogenation of methyl-2-acetamidoacrylate, however without any optical induction [104].



21

Fig. 22. Rhodium complex with bis-NHC ligand used in asymmetric hydrogenation [101].

9. Conclusions

From analysis of the published results, it can be concluded that Rh–NHC complexes catalyze hydroformylation of alkenes and vinyl-arenes under relatively harsh conditions, namely a pressure of over 50 atm and a temperature higher than 80 °C. This can be related to the fact that the strong electron-donor properties of NHC ligands facilitate the activation of dihydrogen and the formation of hydrido complexes, but they may also hinder the coordination/insertion of olefin, which is the rate-determining step for most rhodium-catalyzed hydroformylation systems. Moreover, the stability of Rh–NHC bonding is critical in the presence of H_2 as a result of possible protonation of C2 with formation of imidazolium cations. Chelating bis-NHC ligands are expected to be more stable in this respect.

Strong electron–donor properties of the NHC ligand can be reduced through modification of the NHC ring by means of insertion of another nitrogen atom into the N-heterocyclic ring or through the addition of electron-withdrawing substituents at the N atom. In both cases, during the hydroformylation reaction, alkene conversion increased compared with a non-modified NHC ligand, although the *l*/*b* ratio remained low and close to 1. In contrast, the application of an Rh–NHC complex together with a properly selected phosphorus ligand makes it possible to enhance the conversion of olefin and selectivity to normal aldehyde in the case of aliphatic olefin. However, such a positive effect was observed only for some combinations of a strongly electron–donor NHC and a more electron-withdrawing phosphine or phosphite. It is worth emphasizing that already in these cases even a small excess of the phosphorus ligand is sufficient to improve the results of hydroformylation, in contrast to classic rhodium systems which require much higher amounts of phosphane. One can propose that improvement in the selectivity of hydroformylation in Rh–NHC–phosphane systems is based on both electronic and steric effects as could be deduced from the unusual square pyramidal structure of the Rh–NHC hydrido complex.

Acknowledgement

This work has been performed in a frame of COST D40 programme and supported by the Polish Ministry of Science and Higher Education (N164/COST/2008).

References

[1] J.M. Praetorius, C.M. Crudden, Dalton Trans. (2008) 4079.
[2] S. Diez-Gonzalez, N. Marion, S.P. Nolan, Chem. Rev. 109 (2009) 3612.
[3] A.S. Veige, Polyhedron 27 (2008) 3177.
[4] C.D. Frohning, C.W. Kohlpaitner, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogenous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Two Volumes, vol. 1, VCH Weinheim, 1996, p. 27.
[5] B. Cornils, in: J. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer, Berlin, 1980.
[6] P.W.N.M. van Leeuven, C. Claver (Eds.), Rhodium Catalysed Hydroformylation, Kluwer Academic Publisher, Dordrecht, 2000.
[7] I. Thatchenko, in: G. Wilkinson, A.G.F. Stone, W.E. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon, Oxford, 1982, p. 101.
[8] W.G. Parshall, Homogenous Catalysis: The Application and Chemistry of Catalysis by soluble Transition Metal Complexes, Wiley, New York, 1980.
[9] M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, J. Mol. Catal. A: Chem. 104 (1995) 17.
[10] D. Evans, J.A. Osborn, G. Wilkinson, J. Chem. Soc. A (1968) 3133.
[11] D. Evans, G. Yagupsky, G. Wilkinson, J. Chem. Soc. A (1968) 2660.
[12] C.K. Brown, G. Wilkinson, J. Chem. Soc. A (1970) 2753.
[13] A.M. Trzeciak, J.J. Ziółkowski, Coord. Chem. Rev. 190–192 (1999) 883.
[14] L.A. van der Veen, P.C.J. Kamer, P.W.N.M. van Leeuven, Organometallics 18 (1999) 4765.
[15] R.P.J. Bronger, S.M. Silva, P.C.J. Kamer, P.W.N.M. van, Leeuven, Dalton Trans. (2004) 1390.
[16] C.P. Casey, E.L. Paulsen, E.W. Beuttenmueller, B.R. Proft, L.M. Petrovich, B.A. Matter, D.R. Powell, J. Am. Chem. Soc. 118 (1997) 11817.
[17] A.M. Trzeciak, T. Głowiak, R. Grzybek, J.J. Ziółkowski, J. Chem. Soc. Dalton Trans. (1997) 1831.
[18] C.M. Crudden, D.P. Allen, Coord. Chem. Rev. 248 (2004) 2247.
[19] W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290.
[20] S.P. Nolan (Ed.), N-heterocyclic Carbenes in Synthesis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006.
[21] N-Heterocyclic carbenes in transition metal catalysis, in: F. Glorius (Ed.), Topics in Organometallic Chemistry, Springer-Verlag, Berlin/Heidelberg, 2007.
[22] R. Corberan, E. Mas-Marza, E. Peris, Eur. J. Chem. (2009) 1700.
[23] C.A. Tolman, Chem. Rev. 77 (1977) 313.
[24] F.R. Heck, D.S. Breslow, J. Am. Chem. Soc. 83 (1961) 4023.
[25] C.P. Casey, L.M. Petrovich, J. Am. Chem. Soc. 117 (1995) 6007.
[26] R.P.J. Bronger, P.C.J. Kamer, P.W.N.M. van Leeuwen, Organometallics 22 (2003) 5358.
[27] M. Sparta, K.J. Borve, V.R. Jensen, J. Am. Chem. Soc. 129 (2007) 8487.
[28] G. Kiss, J.E. Mozeleski, C.K. Nadler, E. Van Driessche, C. De, Roover, J. Mol. Catal. A: Chem. 138 (1999) 135.
[29] S.C. van der Slot, P.C.J. Kamer, P.W.N.M. van Leeuwen, A.J. Iggo, B.T. Heaton, Organometallics 20 (2001) 430.
[30] K. Nozaki, T. Matsuo, F. Shibahara, T. Hiyama, Organometallics 22 (2003) 594.
[31] M. Kuil, T. Solmer, P.W.N.M. van Leeuwen, H.N.J. Reek, J. Am. Chem. Soc. 128 (2006) 11344.
[32] P.W.N.M. van Leeuwen, Homogeneous Catalysis, Understanding the Art, Kluwer, Dortrecht, 2004 (Chapter 8).
[33] A.M. Trzeciak, E. Mieczyńska, J.J. Ziółkowski, Top. Catal. 10/11 (2000) 461.
[34] A.M. Trzeciak, J.J. Ziółkowski, R. Choukroun, J. Organomet. Chem. 525 (1996) 145.
[35] R.L. Pruett, J.A. Smith, J. Org. Chem. 34 (1969) 327.
[36] R.L. Pruett, J.A. Smith, W.V. Charleston, US Patent 3527809, Union Carbide Corporation (1970).
[37] R.L. Pruett, Adv. Organomet. Chem. 17 (1979) 1.
[38] A.M. Trzeciak, J.J. Ziółkowski, J. Mol. Catal. 48 (1988) 319.
[39] A.M. Trzeciak, J.J. Ziółkowski, J. Organomet. Chem. 464 (1994) 107.
[40] A.M. Trzeciak, E. Wolszczak, J.J. Ziółkowski, New J. Chem. 20 (1996) 365.
[41] P.W.N.M. van Leeuwen, C.F. Roobeek, J. Organomet. Chem. 258 (1983) 343.
[42] S.N. Poelsma, P.M. Maitlis, J. Organomet. Chem. 451 (1993) C15.
[43] N. Yoshinura, Y. Tokito, European Patent 223103 (1987) (to Kuraray).
[44] C. Köcher, W.A. Herrmann, J. Organomet. Chem. 532 (1997) 261.
[45] A.A. Tukov, A.T. Normand, M.S. Nechaev, Dalton Trans. (2009) 7015.
[46] M. Srebro, A. Michalak, Inorg. Chem. 48 (2009) 5361.
[47] T. Jongsma, G. Challa, P.W.N.M. van Leeuwen, J. Organomet. Chem. 421 (1991) 121.
[48] E. Billig, A.G. Abatjoglou, R.D. Bryant, U.S. Patent 4 668 651; European Patent Appl. 213 639, 1987 (to Union Carbide) Chem. Abstr. 107 (1987) 7392.
[49] E. Billig, A.G. Abatjoglou, D.R. Bryant, R.E. Murray, J.M. Maher, U.S. Patent 4 599 206 (to Union Carbide) Chem. Abstr. 109 (1988) 233177.
[50] C.P. Casey, G.T. Whiteker, M.G. Malville, L.M. Petrovich, J.A. Garney Jr., D.R. Powell, J. Am. Chem. Soc. 114 (1992) 5535.
[51] M. Kranenburg, Y.E.M. van der Burgt, P.C.J. Kamer, P.W.N.M. van, Leeuwen, Organometallics 14 (1995) 3081.
[52] A.C. Hillier, W.J. Sommer, B.S. Yong, J.L. Petersen, L. Cavallo, S.P. Nolan, Organometallics 22 (2003) 4322.
[53] M. Poyatos, P. Uriz, J.A. Mata, C. Claver, E. Fernandez, E. Peris, Organometallics 22 (2003) 440.
[54] A.C. Chen, L. Ren, A. Decken, C.M. Crudden, Organometallics 19 (2000) 3459.
[55] M.T. Zarka, M. Bortenschlager, K. Wurst, O. Nuyken, R. Weberskirch, Organometallics 23 (2004) 4817.
[56] S. Dastgir, K.S. Coleman, A.R. Cowley, M.L.H. Green, Organometallics 25 (2006) 300.
[57] M. Bortenschlager, M. Mayr, O. Nuyken, M.R. Buchmeiser, J. Mol. Catal. A: Chem. 233 (2005) 67.
[58] S.A. Llewellyn, M.L.H. Green, A.R. Cowley, Dalton Trans. (2006) 4164.
[59] J.M. Praetorius, M.W. Kotyk, J.D. Webb, R.Y. Wang, C.M. Crudden, Organometallics 26 (2007) 1057.
[60] A. Gual, C. Godard, S. Castillon, C. Claver, Tetrahedron: Asymmetry 27 (2010) 1135.
[61] N. Sakai, S. Mano, K. Nozaki, H. Takaya, J. Am. Chem. Soc. 115 (1993) 7033.
[62] K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, H. Takaya, J. Am. Chem. Soc. 119 (1997) 4413.
[63] D. Gleich, W.A. Herrmann, Organometallics 18 (1999) 4354.
[64] R. Tanaka, K. Nakano, K. Nozaki, J. Org. Chem. 72 (2007) 8671.
[65] K. Nozaki, Y. Ito, F. Shibahara, E. Shirakawa, T. Otha, H. Takaya, T. Hiyama, J. Am. Chem. Soc. 120 (1998) 4051.
[66] H.J.G. Buisman, A.L. Van der Veen, J.G.W. de Lange, P.C.J. Kamer, P.W.N.M. van Leeuwen, D. Vogt, Organometallics 16 (1997) 2929.
[67] T.A. Axtell, J. Klosin, A.K. Abboud, Organometallics 25 (2006) 5003.
[68] T.A. Axtell, J.C. Colbey, J. Klosin, T.G. Whiteker, A. Zanotti-Gerosa, A.K. Abbout, Angew. Chem. Int. Ed. 44 (2005) 5834.
[69] R. Lai, J.-C. Daran, A. Heumann, A. Zaragori-Benedetti, E. Rafi, Inorg. Chem. Acta 362 (2009) 4849.
[70] M.S. Jeletic, M.T. Jan, I. Ghiviriga, K.A. Abboud, A.S. Veige, Dalton Trans. (2009) 2764.
[71] H. Song, L.-N. Lu, G. Zi, J. Organomet. Chem. 694 (2009) 1493.
[72] S.C. Zinner, W.A. Herrmann, F.E. Kuhn, J. Organomet. Chem. 693 (2008) 1543.
[73] W.A. Herrmann, J. Fischer, M. Elison, C. Kőcher, DE 4447068 (1994) (to Hoechst).
[74] M. Bortenschlager, J. Schutz, D. von Preysing, O. Nuyken, R. Weberskirch, J. Organomet. Chem. 690 (2005) 6233.
[75] S. Dastgir, K.S. Coleman, A.R. Cowley, M.L.H. Green, Dalton Trans. (2009) 7203.
[76] W. Gil, A.M. Trzeciak, J.J. Ziółkowski, Organometallics 27 (2008) 4131.
[77] A. Neveling, G.R. Julius, S. Cronje, C. Esterhuysen, H.G. Raubenheimer, Dalton Trans. (2005) 181.
[78] S.P. Downing, P.J. Pogorzelec, A.A. Donopoulos, D.J. Cole-Hamilton, Eur. J. Inorg. Chem. (2009) 1816.
[79] W. Gil, K. Boczoń, A.M. Trzeciak, J.J. Ziółkowski, E. Garcia-Verdugo, S.V. Luis, V. Sans, J. Mol. Catal. A: Chem. 309 (2009) 131.
[80] A.M. Trzeciak, J. Organomet. Chem. 390 (1990) 105.
[81] A.M. Trzeciak, T. Głowiak, J.J. Ziółkowski, J. Organomet. Chem. 552 (1998) 159.
[82] L.A. Van der Veen, P.C.J. Kamer, P.W.N.M. van, Leeuwen, Organometallics 18 (1999) 4765.
[83] A. Solsona, J. Suades, R. Mathieu, J. Organomet. Chem. 669 (2003) 172.
[84] S.C. van der Slot, J. Duran, J. Luten, P.C.J. Kamer, P.W.N.M. van, Leeuwen, Organometallics 21 (2002) 3873.
[85] S.C. van der Slot, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Fraanje, K. Goubitz, M. Lutz, A.L. Spek, Organometallics 19 (2000) 2504.
[86] S.C. van der Slot, P.C.J. Kamer, P.W.N.M. van Leeuwen, J.A. Iggo, B.T. Heaton, Organometallics 20 (2001) 430.
[87] J.D. Scholten, J. Dupont, Organometallics 27 (2008) 4439.
[88] S. Douglas, J.P. Lowe, M.F. Mahon, J.E. Warren, M.K. Whittlesey, J. Organomet. Chem. 690 (2005) 5027.
[89] X. Yu, H. Sun, B.O. Patrick, B.R. James, Eur. J. Inorg. Chem. (2009) 1752.
[90] J.M. Praetorius, R. Wang, C.M. Crudden, Eur. J. Inorg. Chem. (2009) 1746.
[91] J. Huang, E.D. Stevens, S.P. Nolan, Organometallics 19 (2000) 1194.
[92] W.A. Herrmann, G.D. Frey, E. Herdtweck, H. Steinbeck, Adv. Synth. Catal. 349 (2007) 1677.
[93] H. Jong, B.O. Patrick, M.D. Fryzuk, Can. J. Chem. Rev. Can. Chem. 86 (2008) 803.
[94] G. Dyson, J.-C. Frison, A.C. Whitwood, R.E. Douthwaite, Dalton Trans. (2009) 7141.
[95] G.A. Grasa, Z. Moore, K.L. Martin, E.D. Stevens, S.P. Nolan, V. Paquet, H. Lebel, J. Organomet. Chem. 658 (2002) 126.
[96] D.P. Allen, C.M. Crudden, L.A. Calhoun, R. Wang, A. Decken, J. Organomet. Chem. 69 (2005) 5736.
[97] N. Meier, F.E. Hahn, T. Pape, C. Siering, S.R. Waldvogel, Eur. J. Inorg. Chem. (2007) 1210.
[98] M.J. Page, J. Wagler, B.A. Messerle, Dalton Trans. (2009) 7029.
[99] B.A. Messerle, M.J. Page, P. Turner, Dalton Trans. (2006) 3927.
[100] A. Binobaid, M. Iglesias, D.J. Beetstra, B. Kariuki, A. Dervisi, I.A. Fallis, K.J. Cavell, Dalton Trans. (2009) 7099.
[101] A. Arnanz, C. Gonzalez-Arellano, A. Juan, G. Villaverde, A. Corma, M. Iglesias, F. Sanchez, Chem. Commun. 46 (2010) 3001.
[102] E. Bappert, G. Helmchen, Synth. Lett. (2004) 1789.
[103] D. Baskakov, W.A. Herrmann, E. Herdtweck, S.D. Hoffmann, Organometallics 26 (2007) 626.
[104] W.A. Herrmann, D. Baskakov, E. Herdtweck, S.D. Hoffmann, T. Bunlaksananusorn, F. Rampf, L. Rodefeld, Organometallics 25 (2006) 2449.