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Review

Supported *N*-heterocyclic carbene complexes in catalysis

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Contents

Abstract

N-Heterocyclic carbenes (NHCs) have been known to be outstanding ligands for a variety of organometallic complexes that are key components in catalysis. For the past 10 years, interest has grown towards tethered versions of this type of ligands onto a variety of supports including polymers and silica. In this report, we review current approaches to supported NHC-based complexes and catalysts. In particular, supported versions of olefin metathesis catalysts and palladium catalysts for coupling chemistries are described. While the first supported NHC catalysts have been reported less than 10 years ago, this blossoming area has increased exponentially since then and offers interesting perspectives for the future of supported catalysts.

Keywords: Catalysis; *N*-Heterocyclic carbene; Support; Ruthenium; Palladium

1. Introduction

1.1. N-Heterocyclic carbene in catalysis

The first report of an *N*-heterocyclic carbene was published in 1961 by Wanzlick, followed by several reports from Öfele and Lappert in the 1970s [1–8]. In these articles, the authors reported the synthesis of a five-membered ring *N*-heterocyclic carbene that is able to form complexes with a variety of metals. Early work on the metal complexes, conducted by Lappert et al. showed promising results, but the difficulty in generating and isolating the carbene complex as well as potential applications set back the development of this new ligand [1–4]. 20 years later, the first synthesis of a stable *N*-heterocyclic carbene was realized by Arduengo [9–12]. The breakthrough by Arduengo et al. in 1991 revived the interest for this new ligand species. Since then, an exponential number of publications have been reported using NHCs as key ligands for a wide variety of organometallic

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complexes that can be utilized as catalysts for a spectrum of reactions [13–16]. This particular class of ligands has several advantages over the closely related phosphine ligands [13,15–19]. Specifically, they have a greater thermal and air stability and lower toxicity, making them ideal candidates for catalysis.

The vast majority of reported NHC–metal complexes in catalysis have been utilized in olefin metathesis [20,21]. The second and third generation Grubbs catalysts that contain NHCs are the corner stones of today's extensive use of olefin metathesis in organic and polymer chemistry. The second area of interest of NHC-based complexes are in the palladium catalyzed coupling chemistry [22–28]. All these reports contributed to the wide use of NHCs for a diverse set of catalytic transformations [13,15,18–20,29,30]. Fig. 1 outlines some representative examples of the most common NHC that are used extensively as ligands in catalysis.

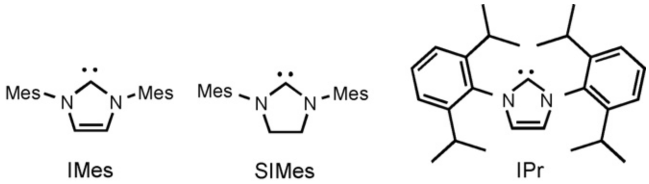

Fig. 1. Common NHC-ligands used in catalysis.

1.2. Supported catalysis

Recycling is becoming significantly more important nowadays as environmental harms increase and as resources are becoming scarcer. Chemists continue to develop new catalysts that are more efficient, robust and devise new methods to recover and reuse them. Towards this goal, the immobilization of well known catalysts onto supports often facilitates the recycling of

Table 1
Summary of supported NHC complexes that have been utilized as catalysts in the literature

Entry	Catalyst	Support	Solubility	Support site	Catalyst type	References
1	**1**	Poly(styrene) beads	Insoluble	Type A	Second generation Grubbs	[36]
2	**2**	Poly(divinyl benzene)	Insoluble	Type A	Second generation Grubbs	[48,49]
3	**3**	Merrifield resin	Insoluble	Type B	Second generation Grubbs	[32]
4	**4**	Poly(ethylene glycol) dimethylacryl amide copolymer resin	Insoluble	Type D	Second generation Grubbs–Hoveyda	[50]
5	**5**	Monolithic support	Insoluble	Type B	Second generation Grubbs	[38,39]
6	**6**	Monolithic support	Insoluble	Type E	Second generation Grubbs–Hoveyda	[45]
7	**7**	Poly(styrene)-divinyl benzene	Insoluble	Type C	Second generation Grubbs	[38]
8	**8**	Poly(styrene)-divinyl benzene	Insoluble	Type E	Second generation Grubbs–Hoveyda	[51]
9	**9**	Poly(styrene)-divinyl benzene/monolithic	Insoluble	Type E	Second generation Grubbs–Hoveyda	[52]
10	**10**	Butyl-diethyl silyl poly(styrene) resin	Insoluble	Type D	Second generation Grubbs–Hoveyda	[53]
11	**11**	Poly(vinyl pyridine)	Insoluble	Type C	Third generation Grubbs	[55]
12	**12**	Dendrimer with Si core	Soluble	Type D	Second generation Grubbs–Hoveyda	[56]
13	**13**	Poly(oxa-norbornene)	Soluble	Type D	Second generation Grubbs–Hoveyda	[57]
14	**14**	Poly(ethylene glycol)	Soluble	Type D	Second generation Grubbs–Hoveyda	[46]
15	**15**	Fluorous poly(acrylate)	Soluble	Type D	Second generation Grubbs–Hoveyda	[58]
16	**16**	Poly(ethylene glycol)	Soluble	Type D	Second generation Grubbs–Hoveyda	[47]
17	**17**	Poly(2-oxazoline)	Soluble	Type D	Second generation Grubbs–Hoveyda	[60]
18	**18**	Silica	Insoluble	Type D	Second generation Grubbs–Hoveyda	[61]
19	**19**	Silica	Insoluble	Type B	Ruthenium complex for the synthesis of furan	[35]
20	**20**	Silica	Insoluble	Type B	Second generation Grubbs	[62,63]
21	**21**	Silica	Insoluble	Type E	Second generation Grubbs	[64]
22	**22**	Silica	Insoluble	Type D	Second generation Grubbs–Hoveyda	[65]
23	**23**	Silica	Insoluble	Type B	Second generation Grubbs	[66]
24	**24**	Wang resin	Insoluble	Type G	Pd complex	[40]
25	**25**	Clay	Insoluble	Type F	Pd complex	[68,69]
26	**26**	Tenta Gel*	Insoluble	Type F	Pd complex	[70]
27	**27**	Poly(styrene) resin	Insoluble	Type I	Pd complex	[72,73]
28	**28**	Poly(styrene) resin	Insoluble	Type F	Pd complex	[74,75]
29	**29**	Poly(2-oxazoline)	Soluble	Type I	Pd complex	[76]
30	**30–32**	Poly(styrene)-divinyl benzene	Insoluble	Type F, H, I	Pd complex	[77]
31	**33**	Poly(styrene) resin	Insoluble	Type H	Pd Complex	[78]
32	**34–36**	Poly (norbornene)	Soluble	Type I	Pd complex	[79]
33	**37**	Silica	Insoluble	Other	Pd complex	[80]
34	**38**	Maghemite nanoparticle	Soluble	Type I	Pd complex	[81]
35	**39**	Silica	Insoluble	Type I	Pd complex	[33]
36	**40**	Poly(2-oxazoline)	Soluble	Type I	Rh complex for hydro-formylation	[43]
37	**41**	Silica	Insoluble	Type I	Rh complex for addition of phenyl boronic acid to benzaldehydes	[44]

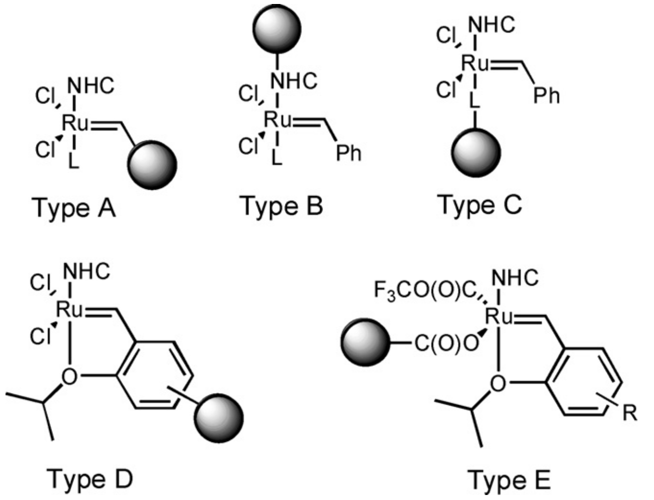

Fig. 2. Strategies to tether Ru–NHC complexes onto supports. The tethering 'type' classification corresponds to column 5 in Table 1.

these catalysts. As described above, organometallic NHC complexes have shown great performances in a wide variety of reactions, demonstrating their usefulness in the synthesis of complex molecules that have applications ranging from drug precursors to polymers. These vital applications make the NHC ligand a perfect candidate to be supported. However, it must be demonstrated that the catalytic activity of the supported NHC complexes does not change with the nature of the support. Several research groups have made significant contributions towards the synthesis of supported NHC complexes and shown that the catalytic activity is indeed maintained [31–34]. Over the past five years, NHCs have been grafted onto different supports ranging from monolithic supports to soluble poly(styrene)s [31,32,34–45]. Table 1 summarizes all supported NHC complexes that have been synthesized and utilized in catalysis. Table 1 also mentions the different attachment strategies for catalysts immobilization. These strategies are described in more details in Figs. 2 and 18. Most of these supported systems use ruthenium or palladium as the metal center. However, several examples were published that use rhodium for hydroformylations and the addition of phenyl boronic acid to an aldehyde. Herein, we present an extensive overview of the supported NHC system that have been published to date [45,46].

2. Supported Ru–NHC complexes

N-Heterocyclic carbenes have been supported on a variety of soluble and insoluble polymers ranging from poly(ethylene glycol) to poly(styrene) resin [38,47–49]. In this review, we categorized the supports by their solubility in the reaction media. We divided the support into two groups. First, we will discuss the synthesis and activity of polymeric supports that are insoluble under the reaction conditions, i.e., heterogeneous catalysts. Then, we will outline the different soluble polymeric supports under reaction conditions and their activity toward a variety of catalytic reactions. In the last part, we will discuss the use of silica as a support. In this chapter, we will examine the processes that research groups invented to support NHC–ruthenium based catalyst and the advantages and drawbacks of each supports. For all supports, a variety of tethering strategies have been used ranging from the attachment of the catalysts to the support through the NHC to supports through the alkylidine [32,38]. These strategies are outlined below in Fig. 2.

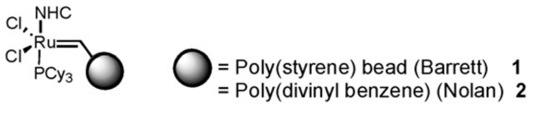

Fig. 3. Second generation Grubbs catalyst tethered through the alkylidine.

2.1. Polymeric supports

2.1.1. Insoluble polymers

In 2000, Barrett and coworkers reported the first immobilization of the second generation Grubbs catalyst for olefin metathesis on an insoluble polymeric support (**1**) (Fig. 3) [38]. Using vinyl modified poly(styrene) beads as the support, they immobilized the catalyst via the alkylidine. While the catalyst leaves the support during the catalysis, the system was designed to capture the ruthenium moiety after complete reaction. The authors called this proposed mechanism "boomerang mechanism". They used the supported catalyst in the ring-closing metathesis (RCM) of several common diene reagents. In all cases, they were able to get quantitative conversions for up to three catalytic cycles. This support strategy allowed for the minimization of the amount of ruthenium contamination in the final product.

Following this report, Nolan and coworkers published a similar system using poly(divinyl benzene) as the support (**2**) [50,51]. In this study, the authors supported the second generation Grubbs catalyst using a small library of NHCs. They were able to show that their supported catalysts were as active as their small molecules analogues in the ring-closing metathesis of a variety of activated and non-activated diallyl malonates. Furthermore, the authors demonstrated that they are able to recycle the supported NHC complex up to three times. However, a significant decrease in the yields was observed after the second cycle.

Also in 2000, Blechert and coworkers reported the synthesis and support of the second generation Grubbs catalyst through the *N*-heterocyclic carbene (**3**) [34]. Contrary to Barrett and Nolan's design, the catalyst is permanently immobilized on the support allowing potentially for a full recovery of the complex after catalysis. The support used in this system was a poly(styrene)-based Merrifield resin (Fig. 4). It allows for easy removal of the catalyst via simple filtration methods. The authors explored the activity of this supported catalyst in the olefin metathesis reactions of a wide variety of reagents. They reported near quantitative conversions for all reagents, from RCM of the simple diallyl malonate to the cross-metathesis of the cyclohexyl acetylene with allyl trimethyl silane demonstrating the utility of this supported catalyst.

Following this report, Blechert and coworkers published also a supported Grubbs–Hoveyda catalyst (Compound **4**, Fig. 5) [52]. To support the Grubbs–Hoveyda catalyst, they used the

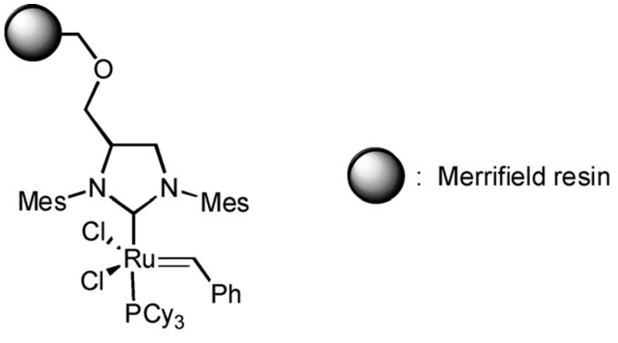

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Fig. 4. Second generation Grubbs catalyst tethered on insoluble Merrifield resin by Blechert et al.

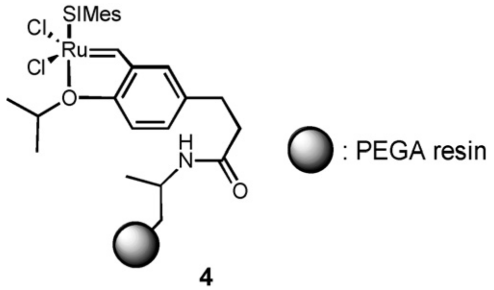

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Fig. 5. Second generation Grubbs–Hoveyda catalyst tethered on insoluble PEGA resin by Blechert et al.

phenyl carbene to anchor the catalyst onto a poly(ethylene glycol) dimethylacrylamide copolymer resin (PEGA) [52]. This specific support allows for the catalysis to be carried out in water or methanol. The authors demonstrated in their study the activity of their supported catalyst in the cross metathesis (CM) of a variety of allene and the RCM of a library of allyl malonates. However, the catalyst had some limitations depending on the solvent and the reagents used. For example, the CM of unprotected glycoside in methanol mostly yielded alkene isomerisation products.

The majority of contributions on supported olefin metathesis catalysts have been reported by Buchmeiser et al. [31,32,40,41,47,53,54]. In 2001, Buchmeiser's group reported for the first time the use of monolithic supports to immobilize the second generation Grubbs catalyst (Compound **5**, Fig. 6) [40,41]. By copolymerizing norbornene and 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*-*endo*-dimethanonaphtalene, the Buchmeiser group synthesized a solid matrix from which they anchored the catalyst. This design allowed them to easily remove

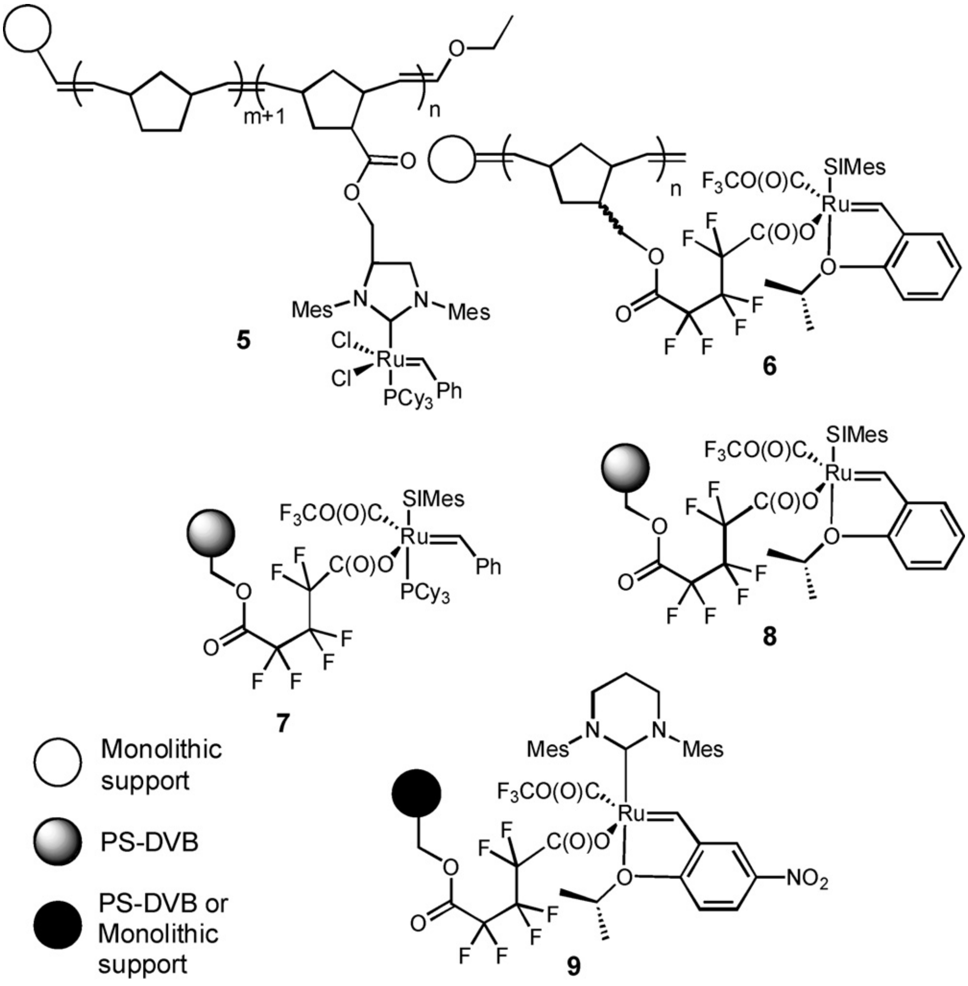

Fig. 6. Supported ruthenium carbene reported by Buchmeiser et al.

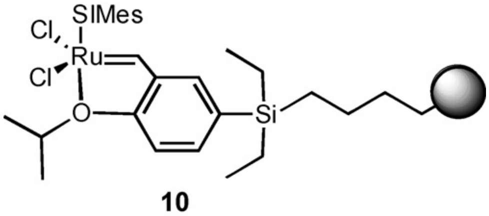

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Fig. 7. Butyldiethylsilyl poly(styrene) (PS-DES) resin supported second generation Grubbs–Hoveyda catalyst by Grela et al.

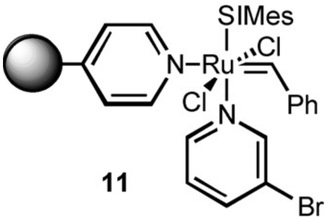

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Fig. 8. Poly(vinylpyridine) supported third generation Grubbs' catalyst by Kirschning et al.

the catalyst at the end of the reaction by filtration. They showed in their study the versatility of their supported catalyst by carrying out RCM of some common allyl malonates with reasonable yields but also the ring-opening metathesis polymerization (ROMP) of norbornene and cyclooctene obtaining polymers with molecular weights of up to 45,000 and 2,500 and PDIs as low as 1.2 and 1.7, respectively. This new supported system offers other useful applications including the use of immobilized catalysts in a continuous flow reactor or as an insoluble catalyst in combinatorial chemistry. Using the same support, Buchmeiser et al. synthesized different supported Grubbs–Hoveyda type catalysts (Compounds **6**–**9**, Fig. 6) [47,53,54]. Buchmeiser's group reported the first Hoveyda–Grubbs-type catalyst used heterogeneously in a continuous flow reactor (Compound **6**, Fig. 6). A new family of NHCs was also synthesized and supported onto poly(styrene)-divinyl benzene (PS-DVB) and monolithic supports (Compound **9**, Fig. 6) by the Buchmeiser group [54]. They investigated this supported catalyst in the ring-opening cross metathesis of numerous reactants and obtained promising results with high turn-over numbers.

A similar system was reported by Grela et al. who supported the Grubbs–Hoveyda catalyst on a PS-DES resin (Fig. 7) [55]. Promising results were reported in the RCM of allyl malonate as well as the formation of macrocycles. However, low levels of ruthenium were detected after the catalysis (<0.1 wt.%) suggesting at least partial decomposition of the supported complex.

In 2002, Gibson et al. used poly(styrene) to microencapsulate the second generation Grubbs catalyst [56]. The authors showed an easy method to immobilize any Grubbs catalyst while getting good overall yields for the RCM of a small library of diethyl diallyl malonates. Furthermore, they were able to recycle their catalyst up to four cycles for the RCM of tosyl diallylamine. However, a significant loss of activity (only 54% conversions) was observed after the third cycle.

Recently, Kirschning et al. reported the first supported third generation Grubbs catalyst using poly(vinylpyridine) as the support [57]. The catalyst was anchored to the support through one of the pyridines (Fig. 8). The authors obtained nearly quantitative conversions in the RCM of various substituted allyl malonates. Furthermore, they also reported the reusability of their catalyst. However, a sharp decline in conversions after the third run, (from 90% to 65% for diallyl malonate) was observed.

2.1.2. Soluble polymers

The study of soluble supports to anchor metathesis catalyst started to spur interest in early 2000 [58]. By having a supported catalyst that is soluble in the reaction media, it was hypothesized that the catalyst should behave more like its homogeneous small-molecule analogue. This property would allow for better selectivities and better yields while having the possibility of removing the supported catalyst and recycling it. In this section, we present the different soluble supports used to anchor olefin metathesis catalysts in particular the Grubbs–Hoveyda catalyst.

In early 2000, Hoveyda et al. reported the synthesis of a new supported Grubbs–Hoveyda catalyst [58]. They synthesized a dendritic-type support with four catalytic sites at the peripheral (Compound **12**, Fig. 9). The authors reported high activities for their systems towards metathesis reactions such as RCM, ROM and CM. Furthermore, they were able to recycle their catalyst by simple filtration methods. However, a decrease in the ruthenium content in the catalytic system was observed after each cycle. Nevertheless, they were still able to get excellent yields with 87% conversions for the RCM of tosyl diallylamine after six cycles.

Two years later, Blechert et al. reported a soluble polymer supported Grubbs–Hoveyda catalyst [59]. The polymer support was synthesized as a terpolymer using poly(oxanorbornene). By using ROMP, they were able to control the polymerization, and ultimately, the ratio of each co-monomer (Fig. 10). By using this terpolymer, Blechert and coworkers could control the metal loading and the solubility of the system. Another advantage of this system was the apparent ability of the polymer to scavenge residual decomposed ruthenium, allowing them to remove the metal from the product after the reaction. The authors tested their supported catalyst towards the RCM of a variety of diallyl malonates and seven membered ring precursors and were able to get quantitative conversions at room temperature within

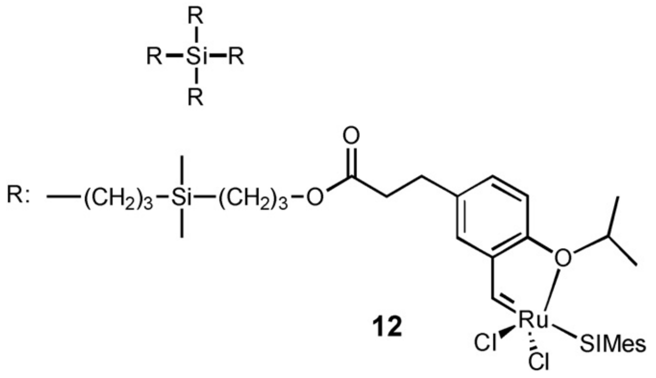

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Fig. 9. Dendrimer supported second generation Grubbs–Hoveyda catalyst reported by Hoveyda et al.

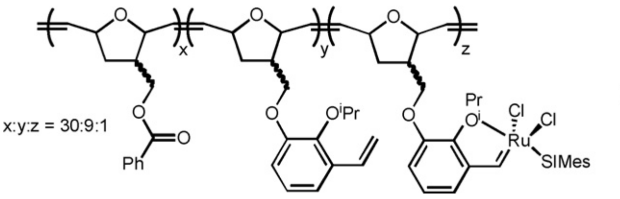

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Fig. 10. Poly(oxanorbornene) supported Grubbs–Hoveyda catalyst.

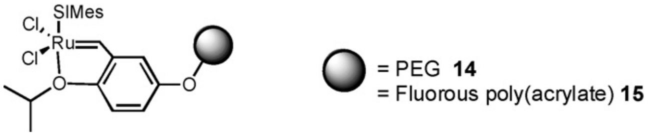

Fig. 11. PEG (**14**) and fluorous poly(acrylate) (**15**) supported second generation Grubbs–Hoveyda catalysts.

hours. Furthermore, the authors were able to recover and recycle their polymer supported catalyst by precipitation. They reported quantitative yields for the RCM of tosyl diallylamine up to seven cycles with a slight decrease of activity from the catalyst after the fifth cycle. Overall, this supported catalyst showed outstanding results for the RCM of several different reactants.

The first PEG supported second generation Grubbs–Hoveyda catalyst was reported by Lamaty et al. (Compound **14**, Fig. 11) [48]. This report follows earlier work by Yao et al. who supported the first generation of the Grubbs–Hoveyda catalyst via the alkylidene onto PEG [43]. By using the intrinsic solubility properties of the PEG support, Lamaty and coworkers were able to recover their polymer supported catalyst. Using a “boomerang” type system, they carried out the RCM of tosyl diallylamine and *N*-allyl allylglycine. Their system yielded above 80% conversions for up to five cycles in the RCM of tosyl diallylamine. Unfortunately, after each cycle, a loss of ruthenium was noticed, suggesting that not all of the catalyst was recovered on the support after completion of the reaction.

Following their earlier report of a supported Grubbs–Hoveyda catalyst with an imidazolium salt tag for use in ionic liquids, Yao et al. investigated a biphasic system that would allow them to remove their supported catalyst from the reaction solution by carrying out a simple extraction (Compound **15**, Fig. 11) [60]. The authors synthesized a poly(acrylate) using two different monomers, one with a perfluoroalkyl group and the second one with the Grubbs–Hoveyda type catalyst. The resulting polymer supported catalyst could be removed after complete reaction by a fluorous extraction. To study the activity of their catalyst, Yao et al. carried out RCM reactions with a wide variety of diallyl amylates and macrocyclic precursors and some CM reactions of common reactants. The catalyst showed high reactivity for these transformations with near quantitative conversions for most of the reactants. To test the activity of the extracted recycled polymer, Yao et al. investigated the RCM of two tosyl diallylamines, one giving a five membered ring and the other a seven membered ring. The catalyst showed outstanding activity with near quantitative conversion for up to twenty cycles for each substrate.

The Yao group also reported a dimer type supported second generation Grubbs–Hoveyda catalyst [49]. Improving on the “boomerang” work by Lamaty et al., which had considerable ruthenium loss after each cycle [48], Yao et al. synthesized a more robust system. They anchored the catalyst through the alkoxy phenyl carbene using ester linkages (Fig. 12). It has been shown previously that the electronic structure of the alkoxy group on this carbene determines the stability of the ruthenium complex [61–63]. To investigate the activity of their catalytic system, Yao et al. carried out the RCM on the same aforementioned reactants described above for their fluorous-based system. The supported catalyst yielded nearly quantitative conversions for all substrates studied and could be recycled up to thirteen times without noticeable loss of activity. The authors also investigated several CM reactions to demonstrate the versatility of their system. They obtained up to 88% conversions when a series of acrylates was used as reactants. Yao et al. have presented several reports that showed outstanding results towards RCM and CM, presenting the easy synthesis of different supported second generation Hoveyda–Grubbs catalysts on multiple supports [49,60].

More recently, Weberskirch and coworkers introduced an amphiphilic polymer, with hydrophilic and hydrophobic pendants forming micelles, to support the second generation Grubbs–Hoveyda catalyst (Fig. 13) [64]. The goal of their study was to present a highly active RCM catalyst that could be recycled and used in aqueous media. To test the catalytic activity of their catalyst, the authors used one of the common diethyl diallyl malonates as a benchmark substrate. Conversions of 90% were achieved within an hour. Unfortunately, recycling of the catalyst was not as successful, falling to 49% conversions for the second and even down to 9% conversions for the fifth cycle. However, their catalyst is one of the most active catalysts for the RCM in water, and allows for partial removal of the catalyst after the reaction.

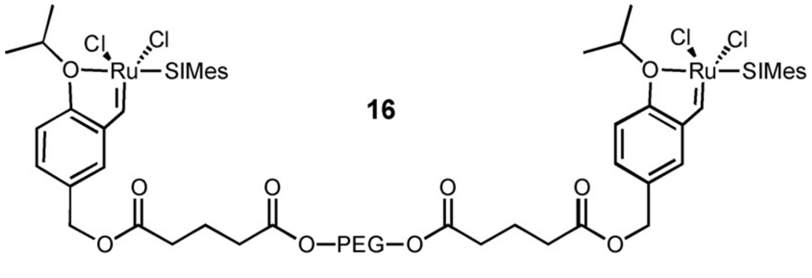

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Fig. 12. PEG supported second generation Grubbs–Hoveyda catalyst by Yao et al.

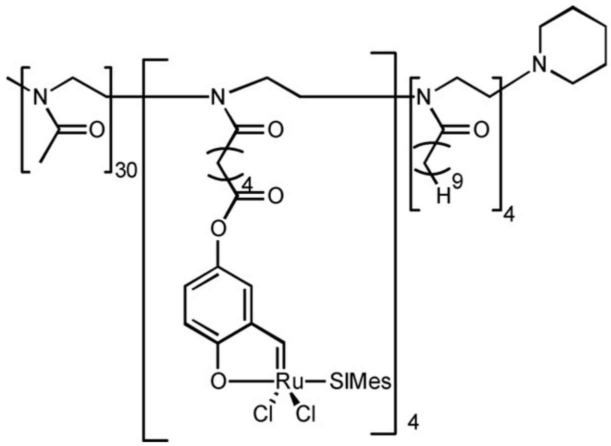

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Fig. 13. Amphiphilic polymer supported second generation Grubbs–Hoveyda catalyst by Weberskirch et al.

2.2. Silica supports

In 2001, Hoveyda et al. introduced the first silica supported NHC complex (Fig. 14) [65]. They used a monolith of porous sol–gel as a support that allowed them to remove their catalyst after the reaction giving the final products with high purity. This support allowed them to screen easily a wide variety of reagents for RCM and ROMP. They carried out RCM of a variety of functionalized cyclopentene and cyclohexene substrate precursors. Their catalytic system showed overall high activity towards the RCM of these reactants with quantitative conversions for the majority of them. Another reaction studied by Hoveyda et al. is the more demanding tandem ring-opening metathesis/cross metathesis (ROM–CM). The system had some erratic success getting yields from as low as 10% to full conversions with a wide array of reactants. Furthermore, the authors were able to show that their catalyst yielded quantitative conversions towards the RCM of *N*-allyl-*N*-tosylmethacrylamide for up to fifteen cycles. They showed that they could use the catalytic system for RCM and then use the same system for the tandem reaction ROM–CM with near quantitative conversions for both reactions. However, some loss of ruthenium was detected after each cycle. Overall, Hoveyda et al. presented a convenient system that allowed for an easy screening of different reactants for different transformations.

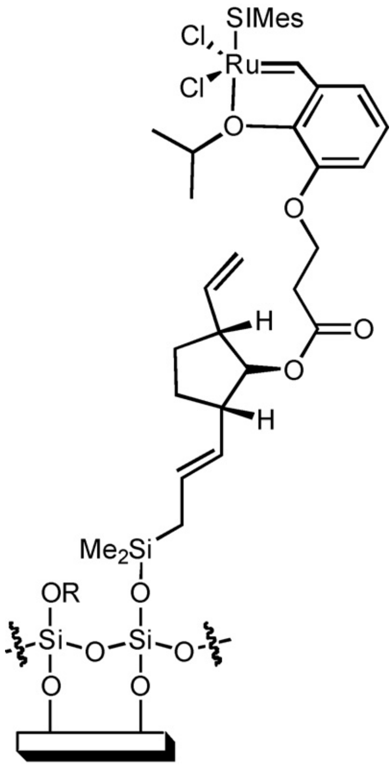

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Fig. 14. Silica supported second generation Grubbs–Hoveyda catalyst developed by Hoveyda et al.

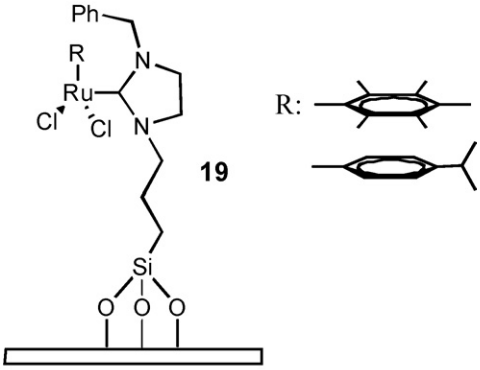

Fig. 15. Silica supported ruthenium complex by Cetinkaya et al.

In 2002, Cetinkaya et al. introduced a different silica supported NHC complex (Fig. 15). They synthesized three ruthenium NHC complexes for the synthesis of 2,3-dimethylfuran from 3-methylpent-2-en-4-yn-l-ol [37]. They were able to show that their catalysts were as active as the small molecule analogue. They demonstrated the possibility to recycle their catalysts in the formation of the furan for up to five cycles with yields around 90% for each cycle.

Buchmeiser and coworkers described in two reports a new strategy to support the second generation Grubbs catalyst, resulting in higher stabilities and good catalytic activities (Fig. 16) [66,67]. The first report established the synthesis and immobilization of Grubbs' second generation catalyst (Compound **20**, Fig. 16). The catalyst was anchored through the NHC carbene ligand, and preliminary results for the catalytic activity of the system towards RCM were reported. Using diethyl diallylmalonate, Buchmeiser et al. demonstrated that their silica immobilized system was as active as their monolithic system reported earlier. Following on this report, Buchmeiser et al. presented the immobilization of the second generation Grubbs catalyst through the exchange of one of the chlorines (Compound **21**, Fig. 16) [68]. They showed that this strategy increases the stability of their system resulting in very low ruthenium leaching. To test the catalytic activity of their system, the authors carried out the RCM with diethyl diallylmalonate resulting in low TON of up to 90. In contrast, the same reaction using a monolithic support yielded TON of up to 940.

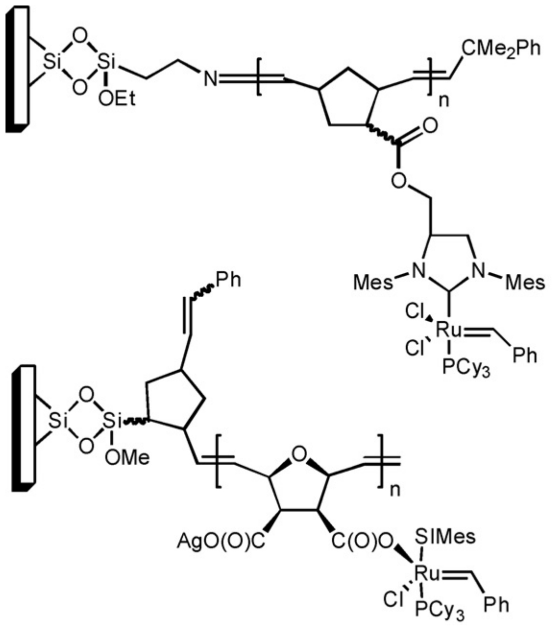

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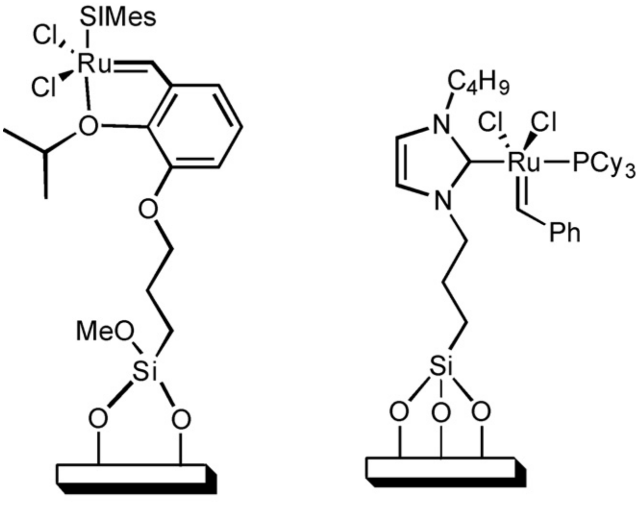
Fig. 16. Silica supported second generation Grubbs catalysts reported by Buchmeiser et al.

More recently, Blechert and coworkers reported the synthesis of the second generation Grubbs–Hoveyda catalyst supported on silica (Compound **22**, Fig. 17) [69]. They anchored the catalyst through a phenyl-ether *meta* to the Schrock carbene. The substitution pattern on the phenyl ring determines the stability of the complex as established by Blechert et al. and others previously [62,63]. Blechert and coworkers reported very high activities towards general metathesis of a variety of reactants. Although the recycling experiment for the RCM of tosyl diallylamine showed slow leaching of ruthenium into the reaction solution, they demonstrated the high activity of the catalyst by having 76% conversions for up to four cycles using a catalyst loading of only 0.15 mol%.



22 **23**

Fig. 17. Silica supported second generation Grubbs–Hoveyda and Grubbs catalysts.

The most recent report on silica supported Grubbs' second generation catalyst was published by Shi et al. (Compound **23**, Fig. 17) [70]. They reported the synthesis and anchoring of the catalyst through one of the arms of the NHC to SBA-15. The authors argued that their immobilization strategy prevented the catalyst from decomposing under reaction conditions. They tested the catalytic activity of their system towards the RCM of a variety of reagents from diethyl diallylmalonate to the precursors of several fifteen membered rings resulting in quantitative conversions for the majority of substrates. Shi et al. also showed the recyclibility of their system for the RCM of diethyl diallylmalonate, with 95% conversion for up to five cycles.

Over the past five years, various ruthenium-based olefin metathesis catalysts have been supported on a number of soluble and insoluble supports. It has been shown that the different supported Grubbs-based catalysts were as efficient as the small molecule analogues with the added advantage of recyclability. The soluble supported system offered the advantage of a homogeneous catalyst with the ability to remove the metal species at the end of the reaction. The insoluble supports demonstrated good overall activities for RCM and CM. The ease to remove these supported catalysts opens the door to industrial applications.

3. Supported Pd–NHC

The support of Pd–NHC complexes is of utmost importance because of the high activity of these complexes in coupling chemistry. Coupling chemistry is vital in the synthesis of complex molecules for the drug and fine chemical industries. Supporting these complexes allows for easy removal of the toxic metal and the possibility of recycling the metal catalysts. Several groups have investigated this topic by supporting palladium complexes on a variety of supports, from poly(styrene) to clay [71]. However, in contrast to supported Ru–NHC complexes, the literature in this area is limited. Hereafter, we describe the pioneering work of several groups using polymer and silica supports as well as the recent advances in this area. Below are the most common tethering strategies outlined for supported Pd–NHC complexes (Fig. 18).

3.1. Polymer supports

The first report of a polymer supported NHC–Pd complexes was provided by Herrmann and coworkers in 2000 [42]. They used a di-NHC chelate ligand coordinated to a palladium halide complex (Fig. 19). The authors anchored this complex through the NHC ligand onto an insoluble poly(styrene)-based Wang resin. They studied the catalytic activity of their system for the Heck reaction. By carrying out several coupling reactions with activated and non-activated arylbromides, they were able to get quantitative conversions for most of the substrates tested. Furthermore, the authors also conducted recycling experiments for the coupling reaction of 1-(4-bromo-phenyl)-ethanone with styrene yielding near quantitative conversions for up to fifteen cycles. However, Herrmann et al. noticed small amounts of

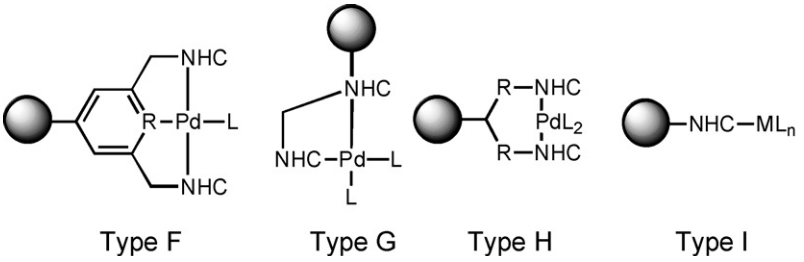
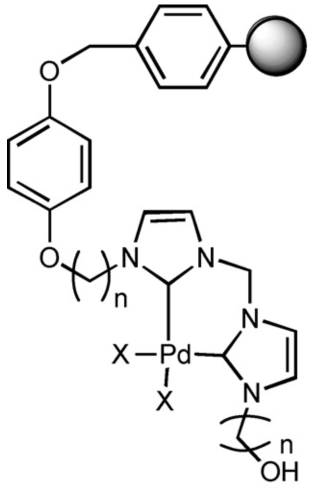


Fig. 18. Strategies to tether Pd–NHC complexes onto supports. The tethering ‘type’ classification corresponds to column 5 in Table 1.



n = 3, X = Br
n = 2, X = I

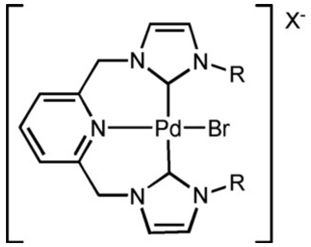
24

Fig. 19. Wang resin supported Pd–NHC complex developed by Herrmann et al.

palladium leaching after each cycle suggesting, at least, partial decomposition.

Three years later, Peris et al. and Fernandez et al. reported the first clay supported NHC–Pd complexes [72,73]. They synthesized a palladacycle CNC pincer with two NHC ligands for Heck and Sonogashira couplings (Fig. 20). An easy method to immobilize pincer NHC–Pd complexes onto clays was reported by using a solvent impregnation method. An immobilization of up to 1.7% of the complex was obtained. The catalytic Heck coupling of styrene with phenyl iodide resulted in 95% conversions within two hours. Recycling experiments were carried out resulting in up to 14% conversions after the third cycle. However, the study of the reaction showed an induction period of up to 2 min. This result coupled with the recycling results suggests that some palladium is leaching out after each cycle.

Finally, Sonogashira couplings using the same catalysts were investigated. The authors studied the coupling reactions of activated and non-activated benzyl halides with ethynyl-benzene with good overall yields. Furthermore, they also investigated the stability of their system by recycling it twice with similar yields for the coupling reaction of phenylacethylene with iodobenzene.



R = Bu, Me, Bn; X^- = Br^-, BF_4^-

25

Fig. 20. Clay supported Pd–NHC complexes reported by Peris et al. and Fernandez et al.

In 2004, Steel et al. introduced a CNC pincer like complex anchored to an insoluble Tenta Gel® (poly(ethylene glycol) resin) (Fig. 21) [74]. They tested the catalytic activity of their system towards the Suzuki coupling of bromo and iodobenzenes with phenylboronic acid and the Heck coupling of iodobenzene with *t*-butyl acrylate. In the case of iodobenzene, they were able to get near quantitative conversions. However, only up to 57% conversions were obtained when bromobenzene was used as reactant. Following this test, Steel et al. carried out recycling experiment for the same reactions. They were able to recycle their catalyst up to fourteen times without any apparent loss of activity. The authors also tested by ICP if palladium leaching was occurring during the reaction. They reported ’non meaningful’ amounts of leached palladium (0.05–3 ppb) during the catalysis. However, it has been demonstrated that less than 0.05 ppb in solution can catalyze quantitatively the Suzuki coupling of alkyl halides [75].

Two different systems were reported by Lee et al.. In the first report, the NHC was anchored through one of its arm (Compound **27**, Fig. 22). The goal of the authors was to synthesize a polymer supported catalyst for the Suzuki couplings in aqueous solutions [76]. They studied the activity of their system towards the Suzuki coupling of phenylboronic acid with aryl halides and compared the reactivity of the catalyst in water and in DMF/water mixtures. Up to 95% conversions for the coupling of aryl iodide with phenyl boronic acid in a mixture of water and DMF at 50 °C were observed. Following this report, Lee et al. reported a similar system using poly(styrene) resin as the support with similar catalytic activities [77].

Following these reports, in 2005, Lee et al. published a complete study of their supported NHC–Pd complex supported onto poly(styrene) (Fig. 22) [78]. After careful catalyst character-

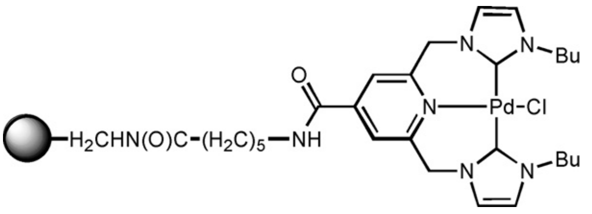


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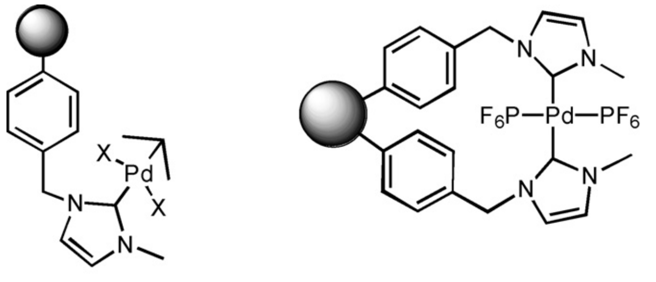
Fig. 21. Tenta Gel supported Pd–NHC complex reported by Steel et al.



27 **28**

Fig. 22. Poly(styrene) resin supported Pd–NHC complexes reported by Lee et al.

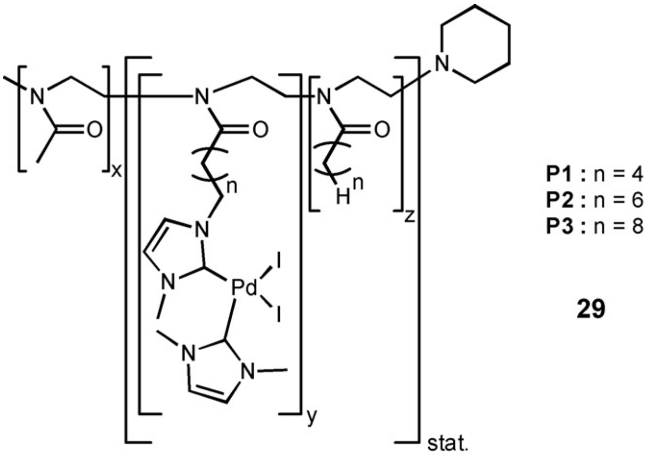


Fig. 23. Poly(2-oxazoline) supported Pd–NHC complex reported by Weberskirch et al.

ization through SEM, ICP and EDX, Lee et al. studied the catalytic activity of their catalysts towards the Suzuki couplings of phenyl boronic acid with iodobenzene. They showed that they could recycle the supported catalysts up to ten times with 92% yield. Furthermore, they also investigated the activity of their system for the Suzuki coupling of a variety of activated and non-activated aryl iodides and bromides with phenyl boronic acid and showed that their catalytic system could convert a variety of the reactants with very good yields (>90%). Finally, Lee et al. reported their novel catalysts in the Heck reaction using a variety of solvents and bases [79]. In general, DMA and TBA were the best solvent and base. The reactivity of this catalytic system towards the Heck coupling of a variety of aryliodides with *n*-butylacrylate was investigated. The catalyst was highly reactive with yields up to 95% for several of the coupling reactions and recycling of the system for up to six cycles with 94% conversions for the reaction of iodobenzene with *n*-butylacrylate were obtained.

In close analogy to their report of a supported olefin metathesis catalyst onto poly(2-oxazoline), Weberskirch and coworkers presented a supported Pd–NHC complex onto the same support (Fig. 23) [80]. Again, this water soluble amphiphilic polymer with hydrophobic pendant chains, containing the Pd–NHC complexes, forms micelles. Weberskirch et al. investigated the activity of their catalyst in the Suzuki and Heck coupling reactions in water. For the Heck transformation, they optimized their system for each polymer by screening different bases and different reaction temperatures for the coupling of styrene with iodobenzene. The authors reported the highest TOF ($2700\,h^{-1}$) with quantitative conversions for the Heck catalysis of iodobenzene with styrene using K_2CO_3 at 110 °C in water. A similar process has been implemented for the Suzuki transformation of activated and non-activated aryl halides (iodide and bromide) with phenyl boronic acid. TOF up to $5200\,h^{-1}$ were obtained with quantitative conversions for the Suzuki reaction in water at 110 °C. Following this report, Weberskirch et al. fully characterized the system using gel-permeation chromatography, TEM and dynamic light scattering [36]. They determined the size of the micelle aggregates to be 10–30 nm.

Finally, they conducted recycling experiments for the Heck catalysis of iodobenzene with styrene at 90 °C with K_2CO_3 as the base. Decreased conversions from 89% for the first cycle to 76% for the third one were obtained. The authors argued that the separation of the micelles from the product might play a role in the lower conversions for the later cycles.

More recently, Luis et al. reported the synthesis of two different Pd–pincer complexes precursors containing two imidazolium salts as well as a simple imidazolium supported on poly(styrene-divinyl benzene) resins (PS-DVB) that are precursors to NHC ligands (Fig. 24) [81]. After metallation with $Pd(OAc)_2$, Luis and coworkers studied the catalytic activity of their catalysts towards the Heck reaction of activated and non-activated aryl iodides and bromides with styrene and *para*-methyl ester styrene. They reported quantitative conversions for several of their reactions except for the coupling of bromobenzene with *para*-methylester styrene and of 1-bromo-4-methoxy-benzene with *para*-methylester styrene where no conversions were reported. Finally, they recycled their supported catalysts and reported quantitative conversions for the Heck catalysis of iodobenzene with styrene up to the fifth cycle. It is important to note that the authors noticed significant palladium leaching during the catalysis suggesting at least partial catalyst decomposition.

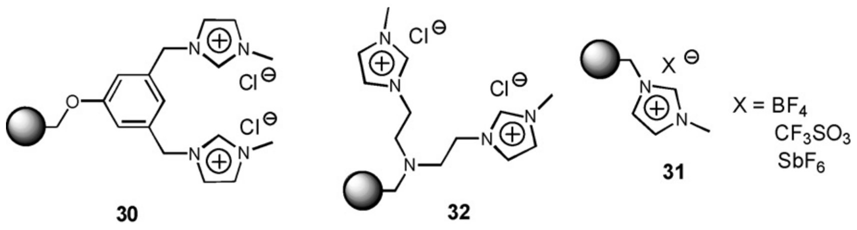


Fig. 24. PS-DVB supported imidazolium salts, Pd–NHC complex precursors, described by Luis et al.

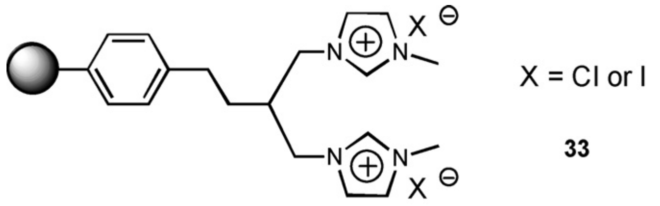


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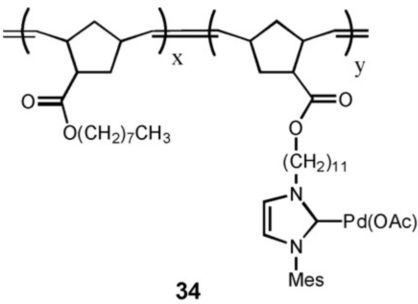
Fig. 25. Poly(styrene) resin supported Pd–NHC complex precursor reported by Luo et al.

A similar catalyst precursor was immobilized by Luo et al. onto poly(styrene) (Fig. 25) [82]. Luo and coworkers carried out several experiments to optimize their system by modifying the base and solvent for the Suzuki reaction of 4-bromoanisole with phenylboronic acid. Using the optimal conditions determined previously, 1:1 water:DMF and using Na_2CO_3 as a base, they investigated the activity of their catalyst for the Suzuki reaction of a variety activated and non-activated aryl bromides with different phenylboronic acids. They reported overall good conversions for all substrates with their catalyst. Finally, they recycled their catalytic system for the coupling of 4-bromoanisole with phenylboronic acid with 94% conversions up to five times.

Recently, Weck and Sommer reported the synthesis of supported Pd–NHC complexes on poly(norbornene) (Fig. 26) [83]. They used the highly controlled ring-opening metathesis polymerization (ROMP) of palladium functionalized norbornenes to tune the catalyst loading and solubility of their system. They synthesized three different Pd–NHC complexes and studied their activity in the Sonogashira, Suzuki and Heck catalyses. Good overall yields (>90%) were reported when using activated and non-activated aryl halides for the Sonogashira and Suzuki coupling reactions. However, leaching of Pd from the support was detected while carrying out the Heck coupling of iodobenzene with *n*-butyl acrylate. Weck and Sommer carried out several leaching test for each supported catalyst. For these leaching tests three different poisons were used, poly(vinylpyridine), mercury, and Quadra Pure®, a commercially available metal scavenger. Kinetic studies have been carried out using the different poisons to determine the active catalytic species. The overall result from these tests showed that supported NHC–Pd(dba) complex is less stable than its homologues NHC–Pd(OAc)$_2$ and NHC–Pd(allyl)Cl. Weck and Sommer studied three different Pd–NHC complexes and showed the overall stability of two of the complexes by carrying out a diverse set of leaching experiments.

3.2. Silica supports

In 2003, Zhang et al. reported the first supported Pd–NHC catalyst trapped in silica gel (Fig. 27) [84]. The goal of their study was to support a highly active catalyst for the Suzuki coupling onto a solid support to be used in aqueous media. In this study, they synthesized a double pincer-type complex with four NHCs. The support used was either silica gel or alumina. They studied the activity of their supported catalyst towards the Suzuki transformation with a variety of reagents. By using activated and non-activated aryl bromides and chlorides as well as aryl boronic acids, they demonstrated high activities of their catalyst. The conversions obtained with their system varied from quantitative conversions for the coupling of chloro-benzaldehyde with phenyl boronic acid to 55% conversions for the sterically



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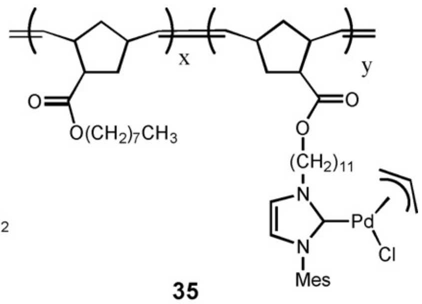

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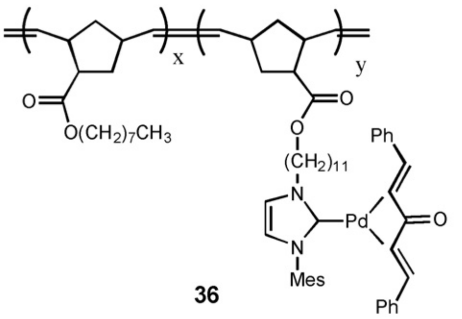

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Fig. 26. Poly(norbornene) supported Pd complexes reported by Weck and Sommer.

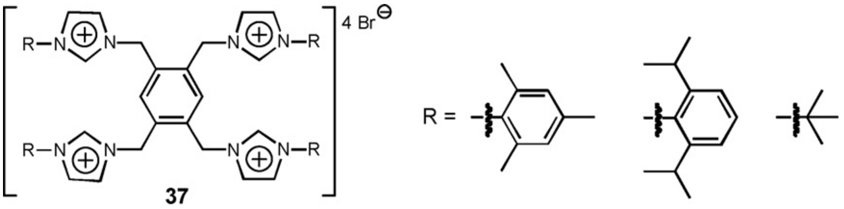

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Fig. 27. NHC precursors for Pd-complexes that have been physisorbed and trapped in silica gel as described by Zhang et al.

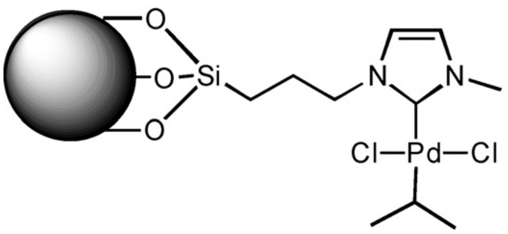

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Fig. 28. Silica coated maghemite supported Pd–NHC complexes reported by Gao et al.

demanding coupling of 1-bromo-2-methoxy-naphthalene with 2,5-methoxy phenylboronic acid.

Two years later, Gao et al. reported the first silica coated nanoparticle supported Pd–NHC [85]. In this study, Gao et al. synthesized superparamagnetic maghemite (γ-Fe_2CO_3) to support the palladium complex (Fig. 28). The small size of these nanoparticles (~11 nm) allowed them to be partially soluble in organic solvents, making them homogeneous under reaction conditions. The authors carried out Suzuki, Heck and Sonogashira reactions of common reagents. The different coupling reactions yielded close to quantitative conversions with iodo and bromo-aryls. Furthermore, the nanoparticles could be removed from the reaction vessel using a small permanent magnet. When performing recycling experiment, the conversions for each coupling reactions slightly declined after each cycle yielding 93%, 92% and 89% for the Suzuki, Heck and Sonogashira coupling respectively for the fifth cycle.

The most recent report on Pd–NHC complexes supported on insoluble supports comes from Karim and Enders who described the immobilization of an NHC–Pd complex/ionic liquid matrix onto silica (Fig. 29) [35]. They studied the activity of the catalytic system towards the Heck catalysis of aryl iodide with alkyl acrylates and showed that their catalytic system was highly active with nearly quantitative conversions for most of the Heck transformations studied. They finally recycled their catalyst three times yielding up to 89% conversions after 26 h for the third cycle.

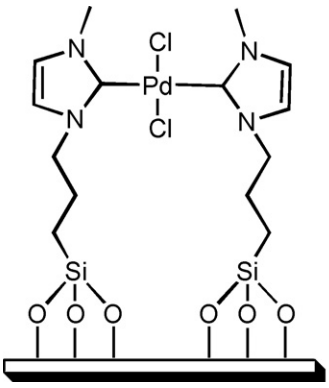

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Fig. 29. Silica supported Pd–NHC complexes reported by Karimi and Enders.

The study of supported NHC–Pd complexes predominantly focused on the investigations of catalysts for coupling reactions. In general, the different studies showed promising results. The use of insoluble supports allows for easy removal of the catalysts with the possibility to use the insoluble catalysts in continuous flow reactors. However, the activity for more challenging substrate was lower than their small molecule analogues. On the other hand, the use of soluble supports produced more active catalyst but lacked the easy removal that insoluble supports offer.

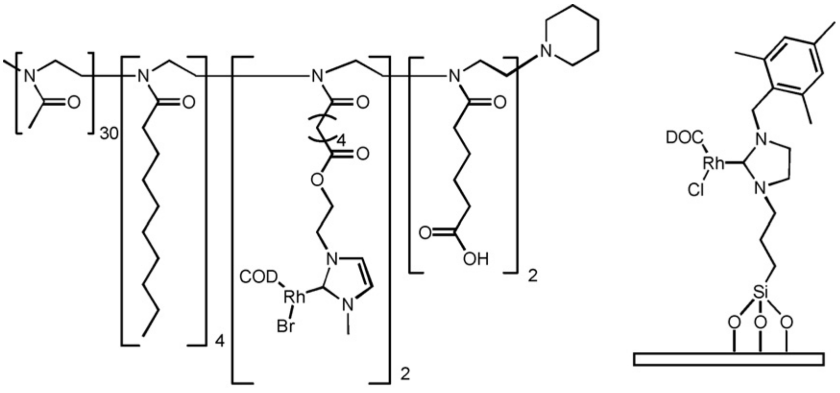
4. Miscellaneous NHC

As described above, over the past 6 years, supported palladium and ruthenium NHC complexes have been described as outstanding catalysts for olefin metathesis and coupling transformations. However, also other metal/NHC supported complexes have been described in the literature. Weberskirch et al. and Özdemir et al. demonstrated that supported Rh–NHC complexes are active catalysts for hydroformylations and the additions of phenyl boronic acids to benzaldehydes.

In 2004, Weberskirch and coworkers reported the first Rh–NHC immobilized catalyst [45]. Using their previously described amphiphilic block copolymer as support, Weberskirch et al. synthesized a supported Rh–NHC complex (Compound **40**, Fig. 30) for the hydroformylation of 1-octene under aqueous conditions. They investigated the recyclibility of their system for the hydroformylation reaction of 1-octene and obtained 22% yields for the first cycle. However, the yields increased up to 43% for the fourth cycle. They report the successful recycling of their polymer up to four times with TOF up to 2360 h^{-1} and the easy removal of the product by simple decantation.

Finally, in 2005, Özdemir et al. reported the synthesis and immobilization onto silica of a Rh–NHC complex (Compound **41**, Fig. 30) for the addition of phenyl-boronic acid to benzaldehydes [46]. Using activated and non-activated benzaldehyde, they investigated the activity of their catalytic system and found reasonable yields for the reaction with up to 89% conversion.

While the examples of other metals but Pd and Ru are very limited in the literature, the reported examples are highly encouraging. Since non-supported NHC ligands have been coordinated



40 41

Fig. 30. Supported Rh–NHC complex.

to a variety of metals, one would expect an increase in the research on supported NHC ligands with other metals.

5. Conclusions

The interest for NHC-based complexes has been increasing exponentially for the past 10 years. The versatility and stability of NHC ligands offers new possibilities in catalysis. Supported versions of these very potent catalysts may lead to important innovations in particular in light of their commercialization. Careful attention has been geared towards supporting the Grubbs catalyst for metathesis reactions. A large number of research groups have demonstrated outstanding results with tethered Ru–NHC catalysts using a variety of supports ranging from silica SBA-15 to diverse polymeric resins. The study of the supported catalyst systems gave great inside information on the ability to recycle the catalyst. Furthermore, recycling studies have been carried out with the majority of the described systems and very promising results were reported that could yield to potential industrial applications. Unfortunately, the loss of ruthenium during the catalysis seems inherent to the reaction and unavoidable, even though, several group showed that they could limit the leaching of ruthenium considerably.

The second area that drew a lot of attention is the support of Pd–NHC complexes for coupling reactions. Diverse types of supports have been used ranging from clay and silica to nanoparticles. Significant progress has been made towards the support of efficient coupling catalyst using NHC as a ligand. The literature concerning these systems is not as numbered as the one for the supported Ru–NHC systems. However, the studies published showed very promising results for the use of Pd–NHC supported catalyst and their recycling abilities. Unfortunately, the vast majority of these studies did not carry out significant catalyst stability and/or leaching studies. Over the past years a number of reports have been published that question the stability of homogeneous palladium catalysts for coupling reactions [75,86]. To make a real impact in the field, researchers have to carry out stabilities studies of their supported Pd–NHC catalysts to prove unambiguously that their catalysts are (a) stable and (b) the catalytic active species.

Clearly the future for supported NHC complexes in catalysis is bright. In less than 10 years, the field moved from its infancy to a highly mature area of supported catalysis. Based on the importance of NHC ligands in homogeneous and non-supported catalysis, one can expect a significant increase in literature reports on this topic.

Acknowledgements

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References

[1] D.J. Cardin, B. Çetinkaya, E. Çetinkaya, M.F. Lappert, J. Chem. Soc. Dalton Trans. (1973) 514.
[2] D.J. Cardin, B. Çetinkaya, E. Çetinkaya, M.F. Lappert, E.W. Randall, E. Rosenberg, J. Chem. Soc., Dalton Trans. (1973) 1982.
[3] B. Çetinkaya, E. Çetinkaya, M.F. Lappert, J. Chem. Soc. Dalton Trans. (1973) 906.
[4] B. Çetinkaya, P. Dixneuf, M.F. Lappert, J. Chem. Soc. Chem. Commun. (1973) 206.
[5] K. Öfele, J. Organomet. Chem. 72 (1968) P42.
[6] H.W. Wanzlick, Angew. Chem., Int. Ed. Engl. 7 (1962) 75.
[7] H.-W. Wanzlick, H.-J. Kleiner, Angew. Chem. 73 (1961) 493.
[8] H.-W. Wanzlick, H.-J. Schönherr, Angew. Chem. Int. Ed. Engl. 7 (1968) 141.
[9] A.J. Arduengo III, Ace Chem. Res. 32 (1999) 913.
[10] A.J. Arduengo III, F. Davidson, H.V.R. Dias, J.R. Goerlich, D. Khasnis, W.J. Marshall, T.K. Prakasha, J. Am. Chem. Soc. 119 (1997) 12742.
[11] A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.
[12] A.J. Arduengo III, R. Krafczyk, R. Schmutzler, Tetrahedron 55 (1999) 14523.
[13] D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39.

[14] A. Fürstner, Angew. Chem. Int. Ed. Engl. 39 (2000) 3012.
[15] W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290.
[16] W.A. Herrmann, C. Kocher, Angew. Chem. Int. Ed. Engl. 36 (1997) 2162.
[17] J. Huang, L. Jafarpour, A.C. Hillier, E.D. Stevens, S.P. Nolan, Organometallics 20 (2001) 2878.
[18] M. Regitz, Angew. Chem. Int. Ed. Engl. 35 (1996) 725.
[19] F.K. Zinn, M.S. Viciu, S.P. Nolan, Annu. Rep. Progr. Chem. Sect. B: Org. Chem. 100 (2004) 231.
[20] R.H. Grubbs, Tetrahedron 60 (2004) 7117.
[21] T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18.
[22] A.C. Frischa, A. Zapfa, O. Brielb, B. Kayserb, N. Shaikha, M. Beller, J. Mol. Catal. 214 (2004) 231.
[23] W.A. Herrmann, M. Elison, J. Fisher, C. Köcher, G.R.J. Artus, Angew. Chem. Int. Ed. Engl. 34 (1995) 2371.
[24] W.A. Herrmann, C.P. Reisinger, M. Spiegler, J. Organomet. Chem. 557 (1998) 93.
[25] H. Lebel, M.K. Janes, A.B. Charette, S.P. Nolan, J. Am. Chem. Soc. 126 (2004) 5046.
[26] O. Navarro, R.A.I. Kelly, S.P. Nolan, J. Am. Chem. Soc. 125 (2003) 16194.
[27] A.-E. Wang, J. Zhong, J.-H. Xie, K. Li, Q.-L. Zhou, Adv. Synth. Catal. 346 (2004) 595.
[28] R.H. Grubbs, Angew. Chem. Int. Ed. Engl. 45 (2006) 3760.
[29] A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C. Yang, S.P. Nolan, J. Organomet. Chem. 653 (2002) 69.
[30] F.E. Hahn, Angew. Chem., Int. Ed. 45 (2006) 1348.
[31] M.R. Buchmeiser, New J. Chem. 28 (2004) 549.
[32] M.R. Buchmeiser, Catal. Today 105 (2005) 612.
[33] A.H. Hoveyda, D.G. Gillingham, J.J.V. Veldhuizen, O. Kataoka, S.B. Garber, J.S. Kingsbury, J.P.A. Harrity, Org. Biomol. Chem. 2 (2004) 8.
[34] S.C. Schürer, S. Gessler, N. Buschmann, S. Blechert, Angew. Chem. Int. Ed. 39 (2000) 3898.
[35] B. Karimi, D. Enders, Org. Lett. 8 (2006) 1237.
[36] D. Schönfelder, K. Fischer, M. Schmidt, O. Nuyken, R. Weberskirch, Macromolecules 38 (2005) 254.
[37] B. Çetinkaya, N. Gürbüz, T. Seçkin, I. Özdemir, J. Mol. Catal. 184 (2002) 31.
[38] M. Ahmed, A.G.M. Barrett, D.C. Braddock, S.M. Cramp, P.A. Procopiou, Synlett 7 (2000) 1007.
[39] J.-W. Kim, J.-H. Kim, D.-H. Lee, Y.-S. Lee, Tetrahedron Lett. 47 (2006) 4745.
[40] M. Mayr, B. Mayr, M.R. Buchmeiser, Angew. Chem. Int. Ed. 40 (2001) 3839.
[41] M. Mayr, B. Mayr, M.R. Buchmeiser, Stud. Surf. Sci. Catal. 143 (2002) 305.
[42] J. Schwarz, V.P.W. Bohm, M.G. Gardiner, M. Grosche, W.A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, Chem. Eur. J. 6 (2000) 1773.
[43] Q. Yao, Angew. Chem. Int. Ed. 39 (2000) 3896.
[44] Q. Yao, M. Rodriguez, Tetrahedron Lett. 45 (2004) 2447.
[45] M.T. Zarka, M. Bortenschlager, K. Wurst, O. Nuyken, R. Weberskirch, Organometallics 23 (2004) 4817.
[46] I. Özdemir, N. Gürbüz, T. Seçkin, B. Çetinkaya, Appl. Organomet. Chem. 19 (2005) 633.
[47] T.S. Halbach, D.F. Stefan Mix, S. Maechling, J.O. Krause, C. Sievers, S. Blechert, O. Nuyken, M.R. Buchmeiser, J. Org. Chem. 70 (2005) 4687.
[48] S. Varray, R. Lazaro, J. Martinez, F. Lamaty, Organometallics 22 (2003) 2426.
[49] Q. Yao, M. Rodriguez, Tetrahedron Lett. 45 (2004) 2447.
[50] L. Jafarpour, M.-P. Heck, C. Baylon, H.M. Lee, C. Mioskowski, S.P. Nolan, Organometallics 21 (2002) 671.
[51] L. Jafarpour, S.P. Nolan, Org. Lett. 2 (2000) 4075.
[52] S.J. Connon, S. Blechert, Bioorg. Med. Chem. Lett. 12 (2002) 1873.
[53] J.O. Krause, S.H. Lubbad, O. Nuyken, M.R. Buchmeiser, Macromol. Rapid Commun. 24 (2003) 875.
[54] L. Yang, M. Mayr, K. Wurst, M.R. Buchmeiser, Chem. Eur. J. 10 (2004) 5761.
[55] K. Grela, M. Tryznowski, M. Bienek, Tetrahedron Lett. 43 (2002) 9055.
[56] S.E. Gibson, V.M. Swamy, Adv. Synth. Catal. 344 (2002) 619.
[57] K. Mennecke, K. Grela, U. Kunz, A. Kirschning, Synlett 19 (2005) 2948.
[58] S.B. Garber, J.S. Kingsbury, B.L. Gray, A.H. Hoveyda, J. Am. Chem. Soc. 122 (2000) 8168.
[59] S.J. Connon, A.M. Dunne, S. Blechert, Angew. Chem. Int. Ed. 41 (2002) 3835.
[60] Q. Yao, Y. Zhang, J. Am. Chem. Soc. 126 (2004) 74.
[61] J.S. Kingsbury, J.P.A. Harrity, P.J. Bonitatebus Jr., A.H. Hoveyda, J. Am. Chem. Soc. 727 (1999) 791.
[62] A. Michrowska, R. Bujok, S. Harutyunyan, V. Sashuk, G. Dolgonos, K. Grela, J. Am. Chem. Soc. 126 (2004) 9318.
[63] M. Zaja, S.J. Connon, A.M. Dunne, M. Rivard, N. Buschmann, J. Jiricek, S. Blechert, Tetrahedron 59 (2003) 6545.
[64] M.T. Zarka, O. Nuyken, R. Weberskirch, Macromol. Rapid Commun. 25 (2004) 858.
[65] J.S. Kingsbury, S.B. Garber, J.M. Giftos, B.L. Gray, M.M. Okamoto, R.A. Farrer, J.T. Fourkas, A.H. Hoveyda, Angew. Chem. Int. Ed. 40 (2001) 4251.
[66] M. Mayr, M.R. Buchmeiser, K. Wurst, Adv. Synth. Catal. 344 (2002) 712.
[67] M. Mayr, B. Mayr, M.R. Buchmeiser, Des. Monomers Polym. 5 (2002) 325.
[68] J.O. Krause, S. Lubbad, O. Nuyken, M.R. Buchmeiser, Adv. Synth. Catal. 345 (2003) 996.
[69] D. Fischer, S. Blechert, Adv. Synth. Catal. 347 (2005) 1329.
[70] L. Li, J.-L. Shi, Adv. Synth. Catal. 347 (2005) 1745.
[71] Y.R. de Miguel, J. Chem. Soc. Per kin Trans. 1 (2000) 4213.
[72] E. Mas-Marzá, A.M. Segarra, C. Claver, E. Peris, E. Fernandez, Tetrahedron Lett. 44 (2003) 6595.
[73] M. Poyatos, F. Márquez, E. Peris, C. Claver, E. Fernandez, New J. Chem. 27 (2003) 425.
[74] P.G. Steel, C.W.T. Teasdale, Tetrahedron Lett. 45 (2004) 8977.
[75] N.T.S. Phan, M.V.D. Sluys, C.W. Jones, Adv. Synth. Catal. 348 (2006) 609.
[76] J.-W. Byun, Y.-S. Lee, Tetrahedron Lett. 45 (2004) 1837.
[77] J.-H. Kim, B.-H. Jun, J.-W. Byun, Y.-S. Lee, Tetrahedron Lett. 45 (2004) 5827.
[78] J.-H. Kim, J.-W. Kim, M. Shokouhimehr, Y.-S. Lee, J. Org. Chem. 70 (2005) 6714.
[79] M. Shokouhimehr, J.-H. Kim, Y.-S. Lee, Synlett 4 (2006) 618.
[80] D. Schönfelder, O. Nuyken, R. Weberskirch, J. Organomet. Chem. 690 (2005) 21.
[81] B. Altava, M.I. Burguete, E. García-Verdugo, N. Karbass, S.V. Luis, A. Puzary, V. Sans, Tetrahedron Lett. 47 (2006) 2311.
[82] T. Kang, Q. Feng, M. Luo, Synlett 15 (2005) 2305.
[83] W.J. Sommer, M. Weck, Adv. Synth. Catal. 2006, in press.
[84] Y. Zhao, Y. Zhou, D. Ma, J. Liu, L. Li, Y. Zhang Tony, H. Zhang, Org. Biomol. Chem. 1 (2003) 1643.
[85] P.D. Stevens, G. Li, J. Fan, M. Yen, Y. Gao, J. Chem. Soc. Chem. Commun. (2005) 4435.
[86] J.G. de Vries, J. Chem. Soc. Dalton Trans. (2006) 421.