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Liberation of *N*-Heterocyclic Carbenes (NHCs) from Thermally Labile Progenitors: Protected NHCs as Versatile Tools in Organo- and Polymerization Catalysis

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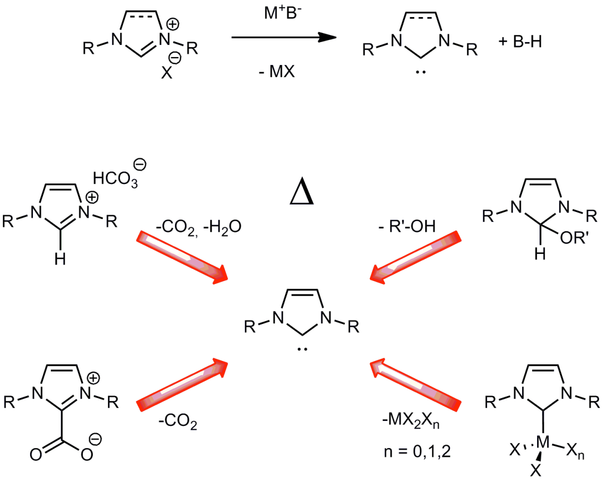
This mini-review describes the thermal in situ generation of *N*-heterocyclic carbenes (NHCs) from various heat sensitive precursors for use in organocatalysis and in polymer chemistry. Thermally labile progenitors such as azolium hydrogen carbonates, NHC-CO_2-adducts, alcohol-protected NHCs and NHC-metal complexes are discussed and compared in their scope and limitations. Advantageous aspects like enhanced stability, controlled release by external stimuli, latency and co-catalysis by the protecting groups are illuminated in numerous examples, stressing the versatility and adaptability that can be achieved by protected NHCs. Emerging strategies to harness the reactivity of NHCs are also briefly touched to provide an outlook where future developments are to be expected.

Introduction

The ascent of *N*-heterocyclic carbenes (NHCs) from mere lab curiosities to the important class of chemical compounds they represent today has been rapid and spectacular. After being first successfully isolated and characterized by Arduengo in 1991,[1] NHCs were soon implemented as powerful ligands in transition metal chemistry where they enhanced complex stability, expanded the scope of substrates and enabled a step change in catalyst design.[2,3] This was certainly helped along by the good accessibility of diverse NHC structures, which can be finely tuned with regard to steric demand and electronic properties and usually require only few synthetic steps to completion.[4,5] More recently, the ability of NHCs to stabilize unusual oxidation states and radicals has also found increasing interest.[6]

The second boost for the popularity of NHCs is linked to their inherent nucleophilic[7] and Brønstedt-basic properties,[8] which renders them powerful organocatalysts, both for organic synthesis and polymerizations.[9,10] The Breslow-type umpolung reactions as found in benzoin condensations or Stetter reactions[11] are most iconic for NHC organocatalysis, but the number of NHC-mediated processes has multiplied over the last years, encompassing now mechanisms as different as transesterifications,[12] activation of esters,[13] conjugate addition,[14] cyclopropenylation,[15] formation of carbonates,[16] group-transfer-polymerization of acrylates[17] or lactam polymerization,[18] among many others. Recently, intermediates of NHC-catalysed Breslow-type reactions have also been isolated.[19]



Scheme 1: Conventional generation of NHCs by the use of bases (top) and thermal liberation of NHCs as discussed in this review.

The breadth of catalytic transformations that can be brought about by NHCs coupled with their facile preparation renders them also promising candidates for large scale applications, where metal-free conditions are much desired, both from economical and environmental reasons. However, NHCs as highly reactive and sensitive compounds would require a careful handling that excludes protic contamination. Furthermore, the long-time stability of NHCs can be severely limited and would probably necessitate temperature-controlled storage. Isolated NHCs can also be viscous oils, which can be problematic for efficient handling.

In order to retain the favourable properties of NHCs but eliminate some of the challenges that arise from the use of free NHCs, it has become quite common to generate NHCs in situ by addition of base (alcoholates, amides, hydrides) to a protonated precursor compound (Scheme 1, top). This method is especially useful in organic chemistry, however, many substrates cannot tolerate the presence of a strong base. The

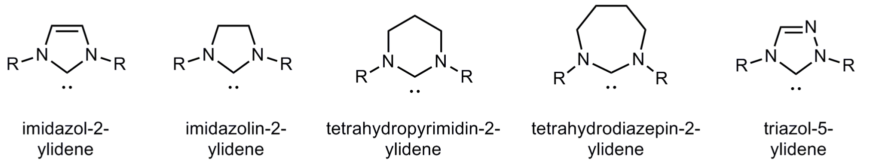
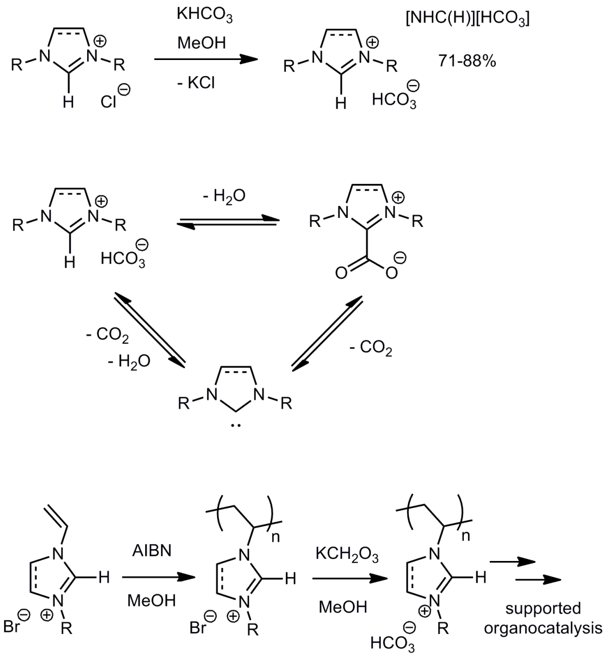


Figure 1: Some frequently encountered types of NHC.



Scheme 2: Preparation of [NHC(H)][HCO_3] (top), correlation of azolium hydrogen carbonates, NHC-CO_2-adducts and free NHCs (middle) and polymer supported NHC-precursor (bottom)[27,30].

same is true for most polymerizations, where the added base could compete with the generated NHC for initiation of reactions. Residues of base or the protonated base can act as undesired ligands when the NHC is intended to coordinate to a metal complex. Finally, on larger scale the addition of base would complicate the setup by demanding purification steps (removal of precipitates) and producing considerable amounts of waste, the more so since the base has to be present at least in stoichiometric amounts, but usually in excess to the NHC.

An elegant venue that can be taken to avoid these difficulties is the application of heat-sensitive NHC-progenitors (Scheme 1, bottom). In recent years, much effort has been put into the development of such compounds. The main advantages of thermal in situ liberation of NHCs can be summarized as follows: (i) the protected NHCs display a much higher stability and storability, where in some cases also ambient conditions are tolerated, (ii) the externally controlled release of NHCs by a heat stimulus enables latent, on-demand catalysing and polymerizing systems, (iii) the activation temperatures can be modulated and (iv) depending on the nature of the protecting group, it is possible that after cleavage from the NHC the protecting group actively participates in the catalysis. Overall, the use of thermally labile NHC-precursors is attractive because a heating step is easily incorporated in a reactor system and often necessary anyway.

According to the type of protection group (PG) that is applied, the subsequent discussion is subdivided into chapters dealing with heat-sensitive (1) protonated precursors, (2) NHCs protected by small molecules, (3) NHCs protected by organic compounds and (4) metal complexes bearing NHC ligands. Most of the following discussion will be based on the well investigated imidazole- and imidazolin-derivatives, but also the ring-expanded six- or seven-membered NHCs and triazolylidenes will be encountered (Figure 1). However, it should be underlined that NHC-, or more generally, carbene-chemistry is much more diverse than that.[20] Acyclic diaminocarbenes,[21] thiazol-2-ylidenes,[22] alkyl(amino)carbenes[23] or diamidocarbenes[24] are further enriching examples, not to speak of the remote, mesoionic or abnormal NHC motifs that receive continuously growing interest.[25] Obviously, in these emerging areas the knowledge about the catalytic properties of the carbenes is still in its infancy, and accordingly the protection chemistry is not developed yet. Still, the more classical NHCs show an intriguing width of protection strategies, which allows for adapting the thermolabile precatalysts to the challenge at hand, as will be discussed below. It should be noted that the thermal behaviour of masked NHCs may vary considerably with the system under observation; it is thus not possible to state one generally valid activation- or deprotection temperature for a certain compound. The physical state (solid or dissolved) and the chemical environment (polarity of the solvent and reactivity of the substrates) have both been repeatedly described to massively influence the conditions for thermal release of the NHCs.

1 Protonated NHC-precursors

C-2-Protonated NHC-precursors (*e.g.*, *N,N'*-dialkylated azolium salts) are typically not compounds that can be converted into free NHCs by heating; instead it is known that at elevated temperatures dealkylation occurs, which can be useful under certain circumstances.[26] However, Taton and co-workers have demonstrated that azolium salts with a suitable counter ion can indeed serve as a source for NHCs that does not require further addition of deprotonating agents.[27] By choice of the basic counter ion HCO_3^-, the NHC-precursor can eliminate H_2O and CO_2 ("H_2CO_3"), providing access to free NHCs. TGA measurements in the solid state showed these compounds ([NHC(H)][HCO_3], Scheme 2) to be stable up to at least 100°C. Onset of loss of water and carbon dioxide depended on the substituents R, and in one case direct proof for the liberation of a free carbene was found.[28] Azolium hydrogen carbonates can result from hydrolysed NHC-CO_2-adducts[29] (which will be discussed in the following chapter), but can be more readily accessed by facile anion metathesis of commercially available

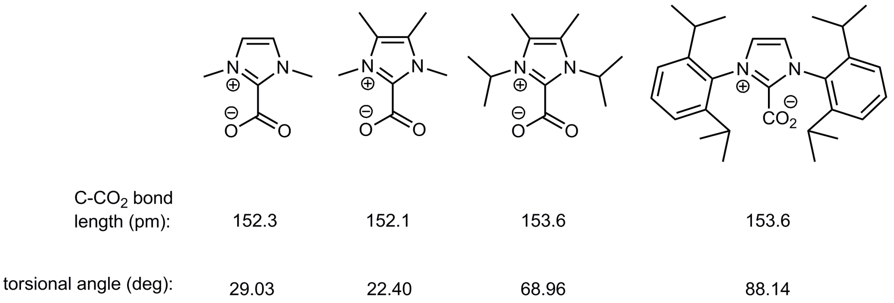
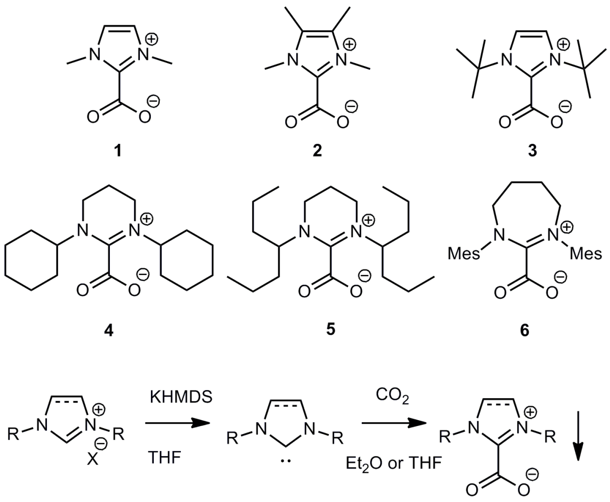


Figure 2: Torsional angles and C-CO_2 distance and their dependence on the steric demand of the *N*-substituent [35].



Scheme 3: Some examples for CO_2-protected NHCs and the commonly applied synthetic route (bottom).

azolium halides with potassium hydrogen carbonate (Scheme 2). It is thus not necessary to generate free NHCs prior to subsequent protection, which distinguishes this method from most other protection strategies. Potentially, this could be used to introduce functionalities in the precatalyst that cannot abide the presence of a free NHC.

Interestingly, NMR experiments revealed a solvent-dependent equilibrium of [(NHC(H)][HCO_3] and its corresponding NHC-CO_2-adduct.[27] Compounds of the type [(NHC(H)][HCO_3] can be stored without special precautions under ambient conditions, rendering this type of precursor very robust and interesting for application on supports, as was recently demonstrated by using recyclable polymers with pendant NHC-precursor functionalities (Scheme 2, bottom).[30] The downside, however, of these azolium hydrogen carbonates is that their inertness to humidity comes at the price of reduced activity. Indeed, several applications of typical NHC-mediated reactions (benzoin condensation, cyanosilylation, polymerization of lactones) showed a general order of catalysing ability of [(NHC(H)][HCO_3] < NHC-CO_2 < free NHC.[28,31] Furthermore, the loss of water during the liberation reaction renders the hydrogen carbonates not applicable in situations where the process is sensitive to protic impurities (like anionic polymerizations) and requires the addition of molecular sieves to protect the NHC from deactivation. The insufficient solubility of the salt can also hamper effective generation of the free NHCs.[31] It has also to be underlined that HCO_3^- is no innocent counter ion, and care has to be taken to differentiate between situations where the anion is the (catalysing) active part, in contrast to cases where a carbene is formed.[32]

Though usually at elevated temperature [(NHC(H)][HCO_3] shows increased activity, also at room temperature substrate or monomer conversion has been reported.[27,28,31] The latency of the precursor seems to be corrupted by the "self-deprotonating" property that is inherent to this system by the basic counter ion, which is not surprisingly more evident in solution than in the solid state. This could be very beneficial when low-temperature processes are necessary, for example to suppress side reactions that are favoured at higher temperature, yet truly thermally latent catalysis cannot be realized this way.

2 NHCs protected by small molecules

NHC-CO_2-adducts (NHC-carboxylates) have developed to be the most popular thermolabile NHC-precursors since their introduction in 2003/2004 (Scheme 3).[33] Nowadays, they certainly represent the best understood type of protected NHC.[34] One reason for that is the straightforward synthesis, which does involve free NHCs, but can be applied to almost any NHC-structures, provided they are not too sterically encumbered or too electron poor.[34,35] The compounds are usually received as colourless or yellowish amorphous powders or crystalline materials. Many carbon dioxide protected NHCs have been described to be inert towards limited exposure to air and humidity, but hydrolysis can occur (see previous chapter) and especially alkyl-substituted adducts seem sensitive towards deactivation with water.[35] The solubility of NHC-CO_2-adducts can be problematic in some cases, though this property is readily influenced by choice of more flexible *N*-substituents (see for example compound **5**, Scheme 3).[36] Louie and co-workers have investigated the behaviour of numerous imidazolium-carboxylates (bulk) when heated and correlated the TGA results with the crystal structures of the corresponding compounds.[35] It was found that the steric demand of the *N*-substituents is decisive for the ease of decarboxylation. This observation was attributed to the fact that larger substituents force the CO_2-moiety out of the plain of the imidazolium ring, which breaks conjugation and accordingly facilitates loss of carbon dioxide (see Figure 2 for examples of torsional angles). Consequently, in case of 1,3-di-*tert*-butylimidazolium-2-

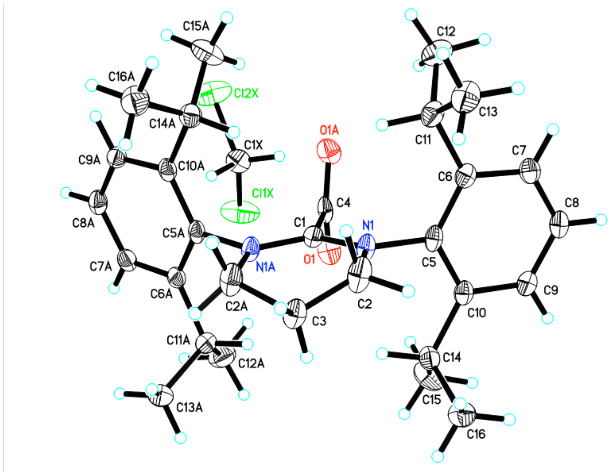


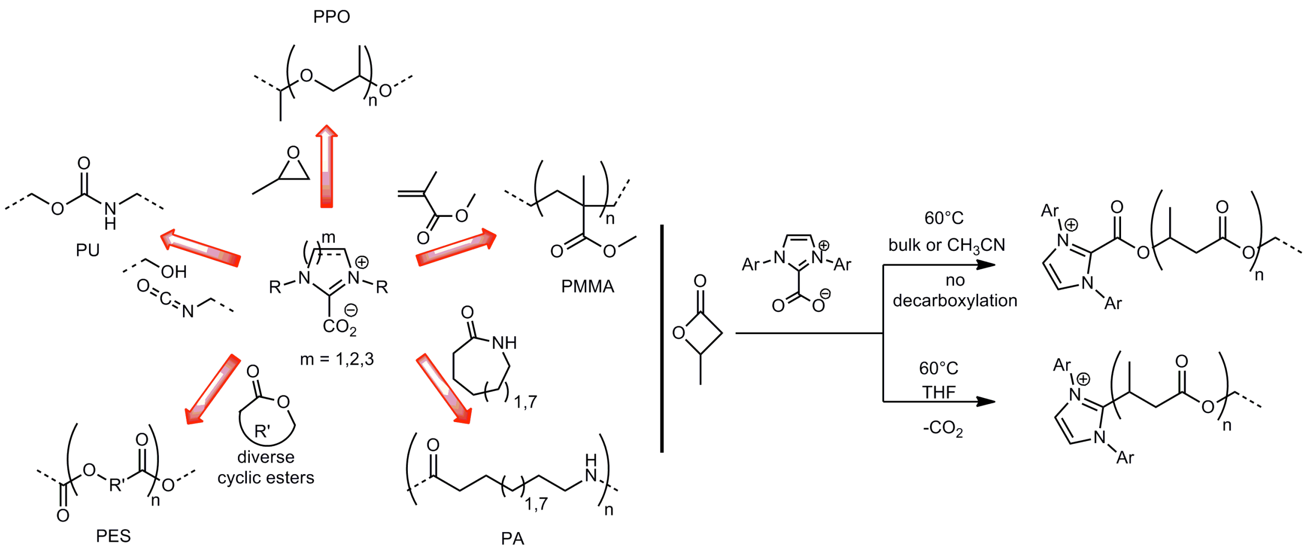
Figure 3: Crystal structure of tetrahydropyrimidin-2-ylidene derivative with bulky 2,6-di*iso*propylphenyl substituents. Torsional angle: 85.70°, C-CO_2 bond length = 154.9 pm [36].

carboxylate (**3**) the PG is lost beginning at around 70°C, while in contrast the methyl-bearing homologue (**1**) is stable up to 120°C with subsequent degradation, presumably without liberating the free NHC. In case of very bulky substituents, the CO_2-plane can be almost perpendicular to the ring system, which is also true for the related tetrahydropyrimidinium-2-carboxylates (Figure 3).[36] Increasing the electron density at the carbene carbon, for example by methylation of the imidazolium ring in C4 and C5 position (as in **2**), stabilizes the NHC-carboxylate and raises the deprotection temperature.[34,35] At room temperature, exclusion of water provided, NHC-CO_2-adducts remain stable for long periods of time, up to years without loss of PG or degradation occurring.[18] It should also be noted that NHC-carboxylates can coordinate to $MBPh_4$ (M = Li, Na), which *lowers* the decarboxylation temperature considerably.[37]

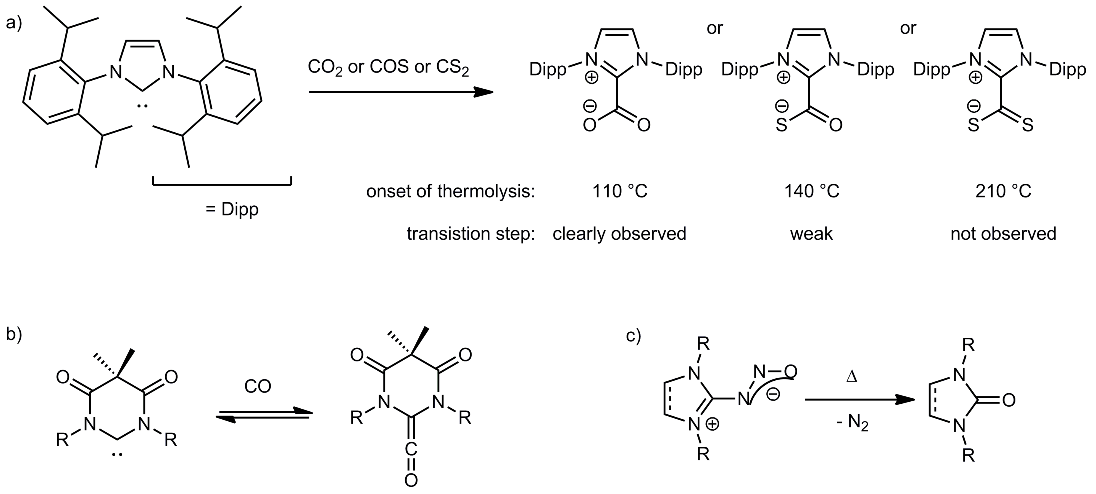
However, above discussion should not lead to the assumption that thermodynamically very stable NHC-CO_2-adducts with small *N*-substituents always degrade before releasing the free NHC. This is, if at all, only valid in solid state measurements in the absence of solvent or substrates. Indeed, as will be obvious in the following examples, the presence of suitable reaction partners can lower decarboxylation temperatures down to room temperature. Most probably this can be explained by at least three superimposed principles that govern the decarboxylation temperature. These are on the one hand the purely structural arguments as discussed above, which depend on the torsional angle of CO_2 relative to the heterocyclic ring (conjugation effect) and steric pressure on the PG in general, which destabilizes the CO_2-adduct. Combined with the electron-richness of the NHC this can lead to a reliable estimation of the bulk decarboxylation temperature. In solution, the situation complicates somewhat. The structural influences still apply, but depending on the solvents, decarboxylation is much facilitated. This is referred to by some authors as "solvation effect"[27] and may originate from a destabilization of the charge-separated state, which is found in the zwitterionic NHC-carboxylates. THF seems to be one solvent that promotes loss of carbon dioxide, while more polar solvents will retard the formation of non polar (CO_2) and weakly polar (NHC) dissociation products (see below). Thirdly, it has been recognized early on that in solution a very small concentration of free NHC can sometimes exist, as demonstrated by the cross-over experiments conducted by Louie.[33b] This means that the free NHC can be removed from the equilibrium, for example by formation of a very stable NHC-metal complex or by incorporation into a polymer chain. As a consequence, the activation temperatures may also depend on the *reactivity* of the parent NHCs. At present, all three effects together make it very difficult to gauge the decarboxylation temperatures for an individual system in advance, though it would be highly desirable to be able to calculate the deprotection process for a given application, especially in view of large scale use.

In polymer chemistry, where the advantages of latent and/or robust catalysts are especially pronounced,[38] NHC-carboxylates have recently enjoyed a massive increase of interest (Scheme 4). Taton,[31] Plasseraud,[39] Thomas[40] and Buchmeiser[41] reported in 2013 the polymerization of cyclic ester monomers, using CO_2-protected NHCs as precatalysts. While Taton and co-workers observed activity at room temperature in THF using ε-caprolactone (ε-CL) as monomer, Buchmeiser and co-workers investigated a large array of different NHC-carboxylates and found a pronounced latent behaviour for bulk polymerizations of ε-CL at lower temperature, while at 70°C the polyester was readily formed. As a consequence of the broad structural versatility of the accessible NHC-CO_2-adducts, it was furthermore possible to modulate the activity of the precatalysts by appropriate choice of the ring size and *N*-substituents of the NHC.[41] Interestingly, Plasseraud suggested a non-innocent role of the lost CO_2, which, when remaining in the reaction vessel, could regulate the concentration of free NHC or cause deactivating side reactions like the formation of carbonates from the reaction of an alcoholate and CO_2.[39] Thomas elegantly demonstrated via MALDI-ToF experiments that polymerization of the reactive β-butyrolactone (β-BL) at 60°C is initiated by the NHC-*carboxylate* when using bulk conditions or acetonitrile as solvent, while in THF the free NHC starts the polymerization (Scheme 4).[40] At higher temperatures (80°C), competing initiation by the free NHC is observed in cases where otherwise initiation by the carboxylate would be favoured. A bench-top reaction setup was used, enabled by the favourable inertness of the precatalyst (1,3-dimesitylimidazolium-2-carboxylate) towards air and humidity.

NHC-carboxylates have also been used as NHC-progenitors for the group transfer polymerization[31] (GTP) and the direct polymerization[36] of methyl methacrylate. While in the former case a controlled polymerization was possible at room temperature, the latter case allowed for a "switching on" from the latent state by heating (60-85°C). Note that both polymerizations are mechanistically completely different: while in GTP the liberated NHC interacts with a hypervalent Si-based transfer agent, the direct polymerization requires the NHC to achieve a conjugate addition on the monomer, thus initiating a zwitterionic polymerization. Still, in both cases NHC-carboxylates can be used as practically useful catalyst precursors.



Scheme 4: Recent examples for CO_2-protected NHCs in polymerization reactions (left) and Thomas' polymerization of β-BL with decarboxylation of the precatalyst controlled by the choice of solvent (right). PPO = polypropylene oxide; PMMA = polymethyl methacrylate; PA = polyamide; PES = polyester; PU = polyurethane [18,31,36,39-44].



Scheme 5: a) Comparison of the thermal stability of NHC-CO_2, -COS and –CS_2-adducts; b) reversible bonding of diamidocarbene to CO; c) NHC-N_2O-adduct and its thermal degradation to urea derivative [24,53-57].

Further examples include the application of CO_2-adducts in the synthesis of polyurethanes,[42] where full thermal latency was achieved, and, very recently published, the rather sluggish oligomerization of propylene oxide was likewise based on in situ generation of NHCs from their corresponding carboxylates.[43]

Finally, CO_2-protected NHCs have been applied for the synthesis of polyamides from lactams by anionic ring-opening polymerization, where the liberated NHC acts as a deprotonating agent.[18,44] As both monomer (ε-caprolactam or laurolactam) and the precatalyst are solids, a ready-to-polymerize composition can be effortlessly prepared. These mixtures were found to be storable over months without losing polymerization activity, which could be started by simple heating to 180-220°C. It is noteworthy that NHC catalysis is not limited to mild temperature regimes. The implementation of free, non-protected NHCs in such a single-component system would not have been feasible, underlining once again the practical advantages that can be gained from thermolabile NHC-precursors.

Apart from polymer chemistry, NHC-carboxylates have also been used as NHC-transfer agents for ruthenium complexes (transfer occurred at room temperature),[45] various other metal compounds,[46] carboxylative cyclization of propargylic alcohol[47] or coupling of epoxides with CO_2.[16] Of course, the interaction of NHCs and CO_2 can be seen under the perspective of CO_2-fixation and –activation. Numerous catalytic circles have been proposed to proceed via NHC-carboxylates, and capture or reversible storage of carbon dioxide by NHC-based systems has been a focus of attention for several years now.[48] NHC-carboxylates supported on a polymer backbone have been used for standard reactions like benzoin condensation and

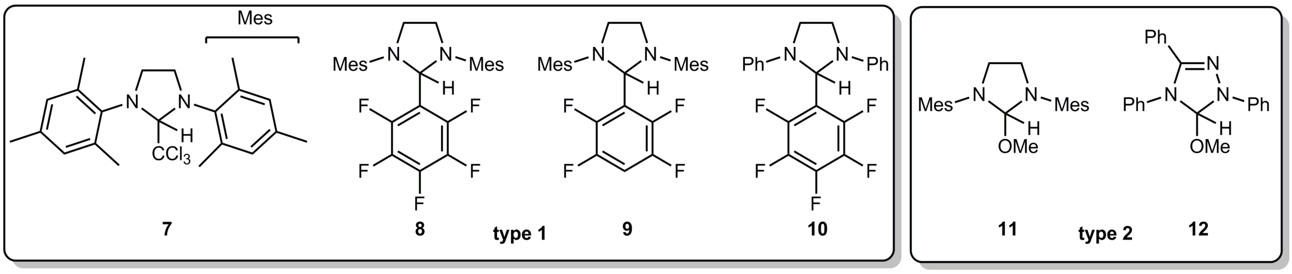
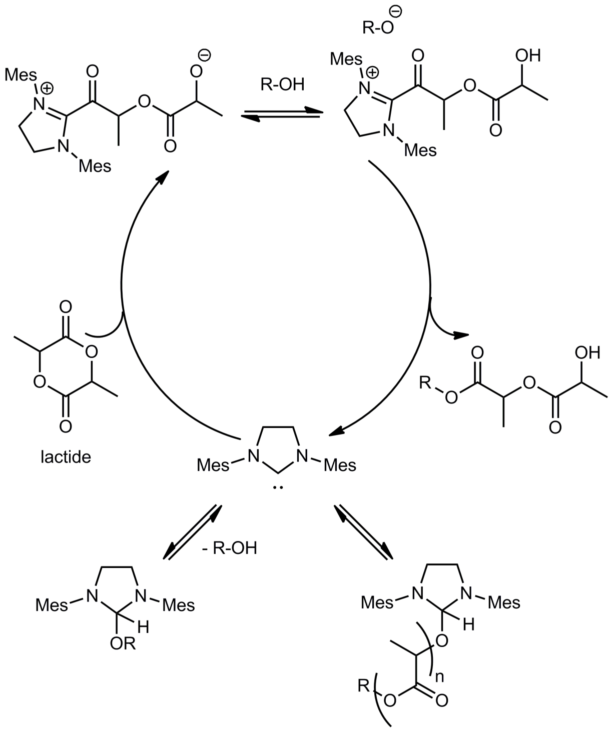


Figure 4: NHCs protected as adducts of halogenated organic compounds and alcohols [54,63-65].



Scheme 6: Polymerization of lactide by a single-component NHC-alcohol-system [63].

transesterifications,[49,50] the trimerisation of isoyanates[50] and were applied to prepare polymer-supported metal catalysts that proved useful in several catalytic transformations.[50] Very recently, Hans et al. have described a number of NHC-catalysed Michael additions using CO_2-protected pre-catalysts.[51]

Compared to CO_2, other small-molecule PGs have received much less attention.[52] The heavier homologue, CS_2, was found to form very stable adducts with NHCs, yielding impressively large and red crystals.[53] Therefore, this class of compounds is problematic for in situ liberation of NHCs, but addition of CS_2 has been advantageously used for efficient quenching of NHC-mediated reactions.[54] As can be expected, the properties of carbonylsulfide-protected (COS) NHCs are intermediate between NHC-CO_2 and NHC-CS_2 compounds.[55] A direct comparison between these different adducts is shown in Scheme 5. Upon heating, thermolysis starts much sooner for the carboxylate and a clear cut transition step can be observed by TGA, which is indicative of the formation of a free NHC. In contrast, the CS_2-adduct completely degrades after onset of thermolysis.

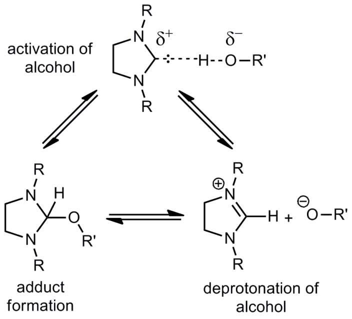
The unusual electronic situation that was observed in Bielawski's diamidocarbenes enabled the coordination of carbon monoxide to an NHC (Scheme 5).[24] The π-system, that is very electron poor in DACs compared to other NHCs, can act as a π-acid powerful enough to generate a backbonding-like situation. This is very different from the ability to bind CO_2, which is essentially a pure σ-donation. The interaction with CO, however, was relatively weak and the free NHC was reported to be in equilibrium with its "CO-protected" counterpart at room temperature (ratio 2:1). In this context it is very instructive to compare these findings with investigations by Bertrand and co-workers, who showed that CO-adducts of acyclic and cyclic alkyl amino carbenes can be stable in the solid state but also in solution.[56]

Finally, a rather interesting adduct can be formed by NHCs in combination with nitrous oxide (N_2O).[57] The compounds were found to include bent N_2O with a considerably weakened N-N bond and a coordinative flexibility (N-donor, O-donor and chelating N,O-donor). Though these adducts were mostly stable at room temperature, heating resulted in the formation of the corresponding ureas under loss of nitrogen (Scheme 5), so at present adducts of this kind cannot serve as sources for NHCs.

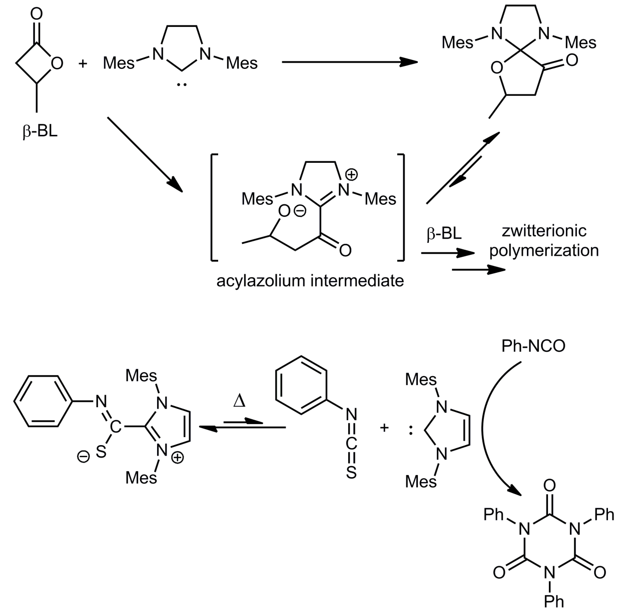
3 NHCs protected by organic compounds

Alcohols and chloroform have been the first PGs to be employed in NHC chemistry (Figure 4). Wanzlick himself has described several examples already in the 1960s, which he intended to use for isolation of the free carbenes.[58] Though this did not happen in the desired way due to the dimerising propensity of the NHCs he used, the interaction of NHCs with alcohol functionalities und acidic C-H-moieties has remained an intensively researched field, and the apparent ease of application has led to frequent use of NHCs protected formally by MeOH or $CHCl_3$ in organometallic synthesis and polymerization catalysis. The preparation of compounds as depicted in Figure 4 can in principle involve either direct addition to an NHC[59] or alternatively be achieved by cyclisation of diamines and suitably substituted aldehydes.[54] α-Elimination subsequently delivers the catalytically active NHC. It should be underlined that the PG will usually remain in the reaction setup, unlike the small molecules discussed above.

Nyce et al. have described the use of type 1 protected NHCs for the polymerization of lactide to yield the corresponding polyester at elevated temperatures.[54] A complex interplay between PG and NHC structure was found. While in some



Scheme 7: Extreme formulations of NHC-alcohol interaction.



Scheme 8: NHC-spirocycle as used for the polymerization of lactones (top) and isothiocyanate-adducts for high-temperature cyclotrimerisation of isocyanates [66,67].

cases no monomer conversion was observed, irrespective of the applied temperature (PG = benzene, trifluoromethane, *p*-nitrobenzene among others), compound **8** displayed acceptable activity at 65°C, while **9** required 110°C to reach 66% yield after 24 h. **10**, where the steric pressure on the PG is smaller than in **8**, was used at 144°C over 12 h to finally yield 68% of isolated polyester. As a general summary, the authors stated that pentafluorobenzene-adducts can achieve stability in solution at room temperature, while the $CHCl_3$-adducts (**7**) dissociate much more readily.[54] Overall, the activity of type 1 protected NHCs in the polymerization of lactides is inferior to that of free NHCs.[60]

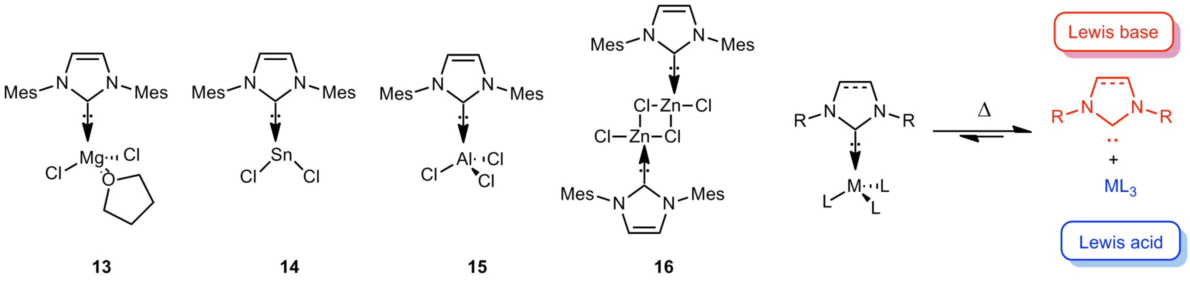
Alcohol adducts have been used frequently to transfer NHCs as ligands to metal complexes, for example in case of ruthenium alkylidenes[61] or rhodium and iridium compounds.[62] However, the contamination with alcohol limits the applicability of this method to metals with low oxophilicity, which is why alcohol-NHC-adducts are increasingly substituted by NHC-carboxylates.

Waymouth and Hedrick used adducts of 1,3-dimesitylimidazolin-2-ylidene and a range of different alcohols, again for the polymerization of lactide (Scheme 6).[63] The compounds are stable solids. In solution, however, they were found to quickly release the free NHC and the protecting alcohol even at 25°C. Accordingly, monomer conversion was swift, resulting in near-quantitative consumption within two hours. As alcohols are usually added in the ring-opening polymerization of cyclic esters as initiators, the NHC-adducts served in this case in a single-component setup, introducing both catalyst and initiator via the same compound. In consecutive studies it was demonstrated that the stability of type 2 adducts can be influenced by choice of the parent NHC.[64] Triazol-5-ylidene derivative **12** (Figure 4) was elegantly used for switching the polymerization on and off repeatedly, simply by varying the temperature between 25°C and 90°C. The polymerization rates were rather low in the latter case, which necessitated long reaction times, again highlighting the compromise that has to be negotiated between latency and activity.

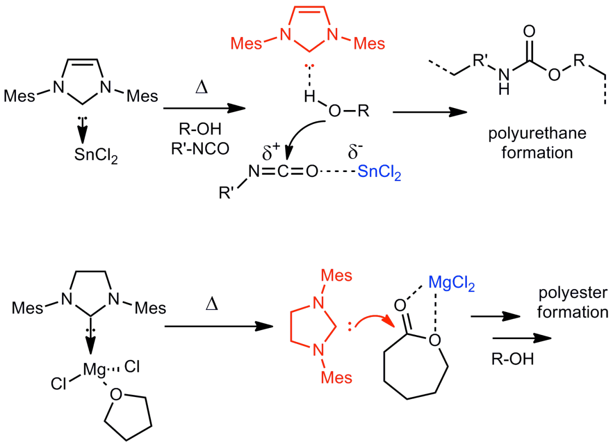
NHC-alcohol-adducts have been much exploited in the past, yet the parameters influencing their formation are not well understood (Scheme 7). Apart from adduct formation, literature descriptions range from "activation" of alcohols to their deprotonation by NHCs.[41] Depending on the partaking NHCs and alcohols, it seems reasonable to assume complex equilibria to exist between all three extreme formulations. It can be well conceived that sterically encumbered NHCs or alcohols will destabilize any adduct formation or lower the dissociation temperatures. Furthermore, the equilibrium should be well shifted in the direction of ion formation if strongly Brønstedt-basic NHCs or low-pK_a alcohols are used. In view of the many situations where NHCs and OH-functionalities interact, however, detailed investigations are needed to map out the interplay of carbene structure and alcohol moiety in a more systematic way. Generally speaking, the breadth of available alcohols is a favourable aspect in this type of chemistry, though their simultaneous release with the NHC cannot be tolerated by all systems (some anionic polymerizations, depending on the propagating species, oxophilic early transition metals, organometallics sensitive to protic compounds). Furthermore, solubility issues seem to be absent and the synthesis of NHC-alcohol-adducts is not complicated. Thermal stability, on the other hand, is usually rather low, so truly latent catalysis can be achieved only in special cases. Notably, investigations concerning polyurethane formation found type 1 and type 2 protected NHCs (Figure 4) to be not thermally latent.[42,65]

Moving away from alcohols, the addition of 1,3-dimesitylimidazolin-2-ylidene to β-BL has been reported to result in an NHC-spirocycle.[66] This compound efficiently initiated the polymerization of β-lactones, yet the reaction already occurred at room temperature, most likely because the spirocycle can ring-open to a zwitterionic species that is able to grow by monomer consumption (Scheme 8).

Interestingly, Bielawski and co-workers have found that adducts of NHCs and isothiocyanates can serve as thermally labile precursors for NHC-mediated polymerizations and the trimerization of isocyanates (Scheme 8).[67] Adduct formation was observed to be heavily favoured ($K_{eq} = 5.94 \times 10^{14}\ M^{-1}$ at 25°C) and working temperatures of at least 100°C were required to gain acceptable catalytic activity. Further it was



Scheme 9: Metal salt-protected NHCs for the thermally latent polyurethane synthesis (**13-16**) and general activation scheme for thermolabile NHC complexes (right) [42,65].



Scheme 10: Preparation of polyurethanes (top) and poly(ε-caprolactone) (bottom) by thermolabile precatalysts based on NHC-metal complexes. As the monomers are different, the best Lewis acid for activation also varies [41,42,65].

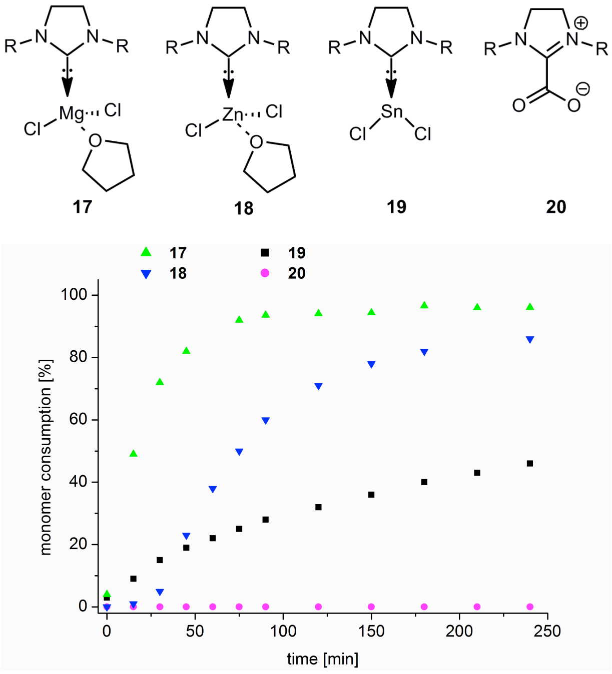


Figure 5: Monomer consumption during thermally induced polymerization of ε-CL (70°C) using homologous NHC-metal complexes as precatalysts. R = mesityl [41].

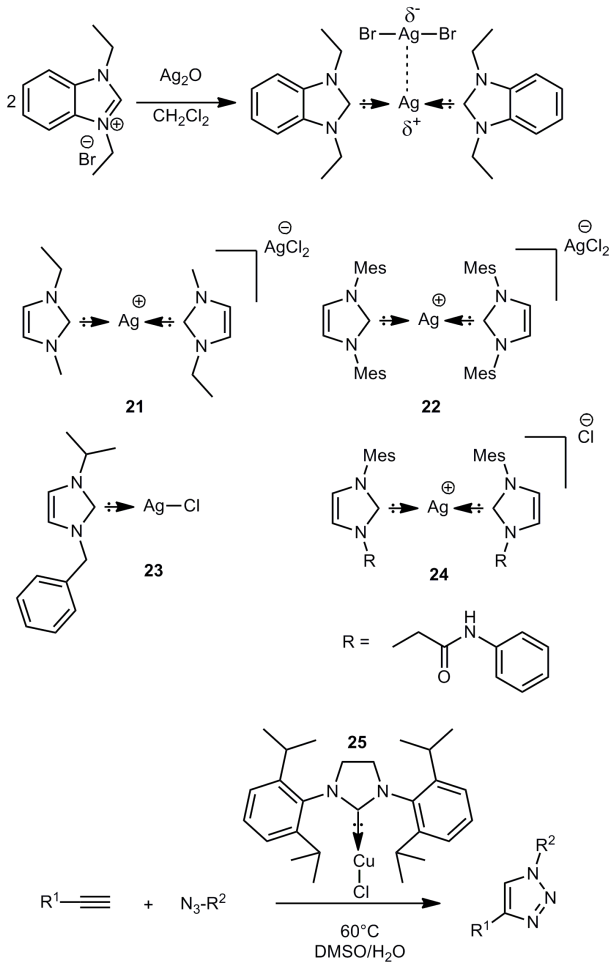
demonstrated that the electronic nature of the PG affected the adduct stability: more electron rich isothiocyanates, which are expectedly less prone to nucleophilic attack by the NHC, displayed a somewhat higher activity due to reduced stability of the adduct.

4 NHCs protected by metal compounds

In principle, every metal complexation of an NHC can be considered as protection as long as it can be reverted by reasonable measures, for example by way of heating. The somewhat unusual point of view taken on these complexes- understanding the NHC as main actor and designation of the metal as mere PG- favours the use of inexpensive, non-toxic and rather weakly coordinating metal ions.[68] Indeed, to gain truly latent behaviour a balance between proper association of the metal ion and the NHC at lower temperatures and a facile release at elevated temperatures has to be maintained. However, it should also be taken into account that the metal ions will stay in temperature dependant equilibrium with the NHC (Scheme 9). At the same time, the “free” metal ion can act as a Lewis acid and influence the reaction or polymerization, thereby changing its role from passive protecting group to active part of the chemical process. This can lead to a situation where Lewis base (NHC) and Lewis acid (metal ion) support each other in their catalytic activity with the result of enhanced activity. This principle has been described by Scheidt as cooperative Lewis acid/NHC catalysis in several complex organic reactions and has also found application in similar form in polymer chemistry.[69,70] Transferred to *latent* catalysis, this means that it is possible to circumvent a frequently encountered problem, which is the reduced activity that is usually the price for (thermo-)latent properties.[38] By suitable choice of PG, NHC and substrates it is possible to induce thermal stability to a metal-NHC complex, where after activation (dissociation) the catalytic activity of the NHC is not hampered by competing coordination to the metal but contrary it profits from Lewis acid activation of the substrate. Examples for this will be found below.

For the simplest possible metal-derived PGs, alkali metal ions, some descriptions exist.[71] Not surprisingly, the coordination seems too weak to serve as true protection of the carbene functionality in a latent fashion. However, more stable complexes can be synthesized if the NHC is chelating via a pendant alkoxide group.[72]

Other main group metals have received more attention and delivered truly thermolabile NHC complexes. Mg(II) served as



Scheme 11: Preparation of NHC-Ag(I) complexes using the facile “Ag$_2$O-route” (top), thermolabile silver(I)-NHC compounds for the polymerization of LA (**21**-**24**, middle) and a latent catalyst for copper-mediated “click-“reactions (bottom) [75,80-81,83].

a labile PG in the complex **13** (Scheme 9), which can in principle be synthesized in one step or by using NHC-carboxylates as transfer agents.[41,65] Interestingly, direct comparison of **13** with other Zn-, Sn-, and Al-protected NHCs (**14**-**16**) as precatalysts in the preparation of polyurethanes has underlined the influence of the PG on catalysis. Though generally pronounced latent behaviour was found with inactivity at room temperature and fast polymerization at 65°C, the polymerization rates were heavily controlled by the metal PG. The zinc and tin complexes were most active in polymer formation, while the magnesium-protected NHCs displayed only modest activity. The aluminium complexes proved to be instable in the presence of alcohols.[42,65] The difference in behaviour can probably be related to a better Lewis acid activation of the isocyanate moiety by Sn(II) and Zn (II) compared to Mg(II).

It is instructive to compare this case (see Scheme 10) with the polymerization of ε-caprolactone (ε-CL) by a homologous row of MgCl$_2$-, ZnCl$_2$-, SnCl$_2$- and CO$_2$-protected 1,3-dimesitylimidazolin-2-ylidene (Figure 5, **17**-**20**).[41] As can be seen, the activity of the metal-free precatalyst (**20**) is almost non-existent, while introduction of a metal-derived PG has a strong accelerating effect. Quite unexpectedly, Mg(II) is much superior to Zn(II) and Sn(II) in this particular polymerization process, thus showing an inverse order of activity compared to polyurethane formation. As both the reaction conditions and the parent NHC are the same in Figure 5, the difference in activity must solely depend on the joint action of metal salt and NHC. Obviously, according to the HSAB-principle,[73] the small and hard magnesium ion is more effective in coordination to the lactone, thereby removing electron density and rendering the monomer more prone to nucleophilic ring opening by the thermally liberated NHC. It should also be noted that **18** shows an induction time at 70°C (Figure 5), while the MgCl$_2$-bearing homologue does not, mirroring the stronger coordination of the NHC to Zn(II) compared to Mg(II). The same effect is also observed at room temperature; while **18** is perfectly latent over prolonged time, **17** entails slow monomer conversion. However, both precatalysts can be “switched on” by heating. At 130°C, controlled and rapid polymerization occurs, yielding quantitative amounts of polyester after only 5 minutes reaction time.[41]

In this context, a detailed investigation by Chen and co-workers also deserves attention.[74] A range of different Lewis bases, among them NHCs, have been used in combination with Lewis acids like AlCl$_3$, Al(C$_6$F$_5$)$_3$ or B(C$_6$F$_5$)$_3$ to polymerize diverse lactones and acrylates. Strongly enhanced polymerization rates were achieved by the cooperative influence of NHC and Lewis acid in some cases. The reagents, however, where not added as discrete complexes but separately (free NHC), so it remains unclear whether related protected NHCs would be active in a similar manner.

Silver complexes represent the most important class of labile NHC complexes.[75] The most popular route to Ag(I)-NHC compounds is the “Ag$_2$O” method (Scheme 11), which allows for directly converting precursor salts into the metal complex.[76] This synthetic strategy is very advantageous, because the intermediate generation of free NHCs is avoided. Silver(I)-protection can thus be used to transfer NHCs to metal compounds, even if the NHCs are not stable in their free form. A further positive aspect is that most reactions do not require special precautions with respect to protective gas atmosphere or solvent purification. NHC transfer and NHC characterization still remain the most frequent application for the readily available silver(I) complexes.[77] The rich structural diversity can also influence the transfer behaviour, which can be different for mono- and bis-NHC silver complexes.[78] A more recent development is the rapidly growing field of Ag(I)-NHC complexes as anti-infective agents; there, the (thermo-)labile character of these compounds is used for a slow release of antibacterial Ag$^+$ ions.[79]

The silver complexes have also been used directly for catalysis. In reports on lactide (LA) polymerization by Sentman et al., the liquid precursor **21** (Scheme 11) was found to catalyze the reaction between 40°C and 100°C with an optimum at 60°C (in toluene), where after 12 h 90% conversion was achieved (NHC:LA = 1:100).[80] The intermediacy of free NHCs was proven by capturing with CS$_2$. In accordance with the observations that were discussed in the chapters above concerning the difference of deprotection temperatures in

Table 1: Pointed summary of the properties of different protected NHCs.

NHC precursor	potential advantages	downsides
azolium hydrogen carbonates	very robust precatalyst, simple synthesis which does not include free NHC, metal-free	limited solubility, low reactivity, generation of protic byproduct (H_2O), reactive at RT in solution, non-innocent counter ion
NHC-carboxylates	robust, metal-free precursor, full thermal latency and controlled release possible, only CO_2 as byproduct	solubility can be problematic, decarboxylation depends on many factors and may require bulky NHC, synthesis goes via free NHC
NHC-alcohol-adducts	broad array of PG, facile preparation, single-component system in case alcohol acts as initiator, metal-free	protic byproduct (R-OH), limited (or no) thermal stability in solution, full latency only in some cases
NHC- metal complexes	near unlimited number of potential PGs, modulation of thermal stability/reactivity/pot times by choice of metal compound, Ag(I)-complexes very easy to prepare, enable cooperative/dual catalysis, usually good solubility	metal contamination, may hydrolyse, may entail “metal-based” catalysis

RT = room temperature

absence and presence of substrates, compound **22** did not show any weight loss in TGA (unlike **21**) below 250°C. And yet, **22** catalysed the polymerization of LA to near quantitative conversion, albeit slowly (72 hours, 100°C). Samantaray et al. investigated LA polymerization in the bulk, using compounds **23**-**24** (Scheme 11).[81] Both compounds were found to polymerize in a temperature range between 100-180°C, which enabled isolation of near-quantitative yields after 4 h of reaction. Again a discrepancy between TGA measurements and actual catalytical activity was observed, which prompted the authors to invoke a metal mediated mechanism.[81] No co-initiating alcohol was used, which makes it hard to compare these results with others.

As a concluding remark on the polymerization of cyclic esters it should be underlined that a low observed activity of a protected NHC-precatalyst cannot necessarily be attributed to difficult or incomplete deprotection. The activity is also strongly influenced by the NHC itself; indeed it is possible to render a free NHC completely inactive by choice of the “wrong” *N*-substituents.[82] Special care must therefore be taken when comparing two progenitors with differing parent NHCs, as the overall activity is a function of both deprotection and inherent catalytic power of the carbene. Of course, this generally applies to all processes mediated by in situ generated catalysts.

As a final example for a thermolabile coinage metal NHC complex, [NHC(CuCl)] (**25**) was found to be stable in DMSO for a week, while heating to 60°C led to a release of CuCl to catalyse a typical “click” reaction (Scheme 11).[83] Interestingly, in THF or isopropanol no latency was found, and high conversions were achieved at room temperature already.

Conclusions

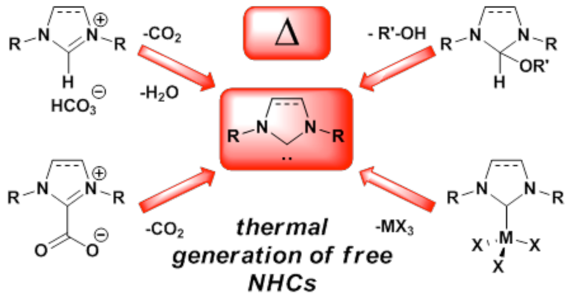
In Table 1, the advantages and disadvantages of several classes of protected NHCs are summed up in order to serve as a guideline for choosing the most suitable precatalyst for an intended application. One very fundamental difference is of course the division into metal-free and metal-containing protected NHCs. While the former can provide access to organocatalysis with all the connected benefits, the latter might also be found to be a very attractive alternative. Apart from being co-catalysing PGs, the implementation of non-toxic and readily available metal compounds might very well eliminate purification steps of the product and economic concerns regarding the costly consumption of metal resources. Control over the deprotection temperatures has been shown to be in need of more research efforts, yet it is clear that here again a major division can be made between protected NHCs were the *NHC* has to be manipulated in order to modulate the activation temperatures (azolium hydrogen carbonates, NHC-carboxylates) and strategies that allow for variation of the *PG* (NHC-alcohol-adducts, metal complexes). Though it is very convenient to apply the findings for CO_2-protected NHCs and increase the steric bulk for more facile loss of carbon dioxide, it might well be that this same manipulation renders the NHC not useful for the intended catalysis. Especially if the reaction is not flexible with regard to the applied temperature, the use of metal-protected NHCs can provide a more facile access to precatalysts with higher or lower propensity towards dissociation and liberation of the NHC.

It must furthermore be considered that azolium hydrogen carbonates and NHC-CO_2 adducts release byproducts that can be easily removed, while metal salts or alcohols will reside in the reaction system. When a robust process can tolerate protic impurities, NHC-aclohol-adducts or azolium hydrogen carbonates can be interesting choices. For more sensitive applications, NHC-carboxylates or NHC-metal complexes are recommended.

The important issue of solubility seems problematic for [NHC(H)][HCO_3] and in some cases for NHC-CO_2, while such difficulties are absent or easily circumvented in the case of alchohol-adducts and metal complexes. Interestingly, silver (I) complexes and azolium hydrogen carbonates give access to protected NHCs without prior generation of a free NHC, via the “Ag_2O-route” or anion metathesis, respectively. Truly thermally latent reactions, that can be “switched on” by heating are at the moment realized best by using NHC-carboxylates or suitable NHC-metal complexes.

In conclusion, the development of protected NHCs has already proven very fruitful for a number of applications. Increased stability, facile handling and externally controlled, heat-induced reactions pave the way for future large-scale NHC (organo-)catalysis. The research on thermolabile NHC-adducts is also interconnected to related fields, especially the activation of small molecules. The methods that exist at present to create labile NHC-progenitors complement each other and offer broad venues for intelligent precatalyst design. It must be expected that NHCs will rise in importance in the years to come, and so will strategies to control their reactivity and triggered release.

ToC Figure and Text



The thermally triggered release of catalytically active, free NHCs from various heat-sensitive progenitors is discussed.

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Notes and references

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1 A. J. Arduengo, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361-363.

2 W. A. Herrmann, M. Elison, J. Fischer, C. Köcher and Artus, G. R. J., *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 2371-2374.

3 a) F. Glorius, *N-Heterocyclic Carbenes in Transition Metal Catalysis*, Springer Berlin Heidelberg, 2007, vol. 21; b) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612-3676; c) C. S. J. Cazin, *N-Heterocyclic carbenes in transition metal catalysis and organocatalysis*, Springer, Dordrecht, London, op. 2011.

4 For reviews on NHCs, see: a) F. E. Hahn and M. C. Jahnke, *Angew. Chem. Int. Ed.*, 2008, **47**, 3122-3172; b) T. Dröge and F. Glorius, *Angew. Chem. Int. Ed.*, 2010, **49**, 6940-6952; c) D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723-6753; d) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39-92.

5 L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz and V. César, *Chem. Rev.*, 2011, **111**, 2705-2733.

6 See for example: C. D. Martin, M. Soleilhavoup and G. Bertrand, *Chem. Sci.*, 2013, **4**, 3020–3030.

7 a) B. Maji, M. Breugst and H. Mayr, *Angew. Chem.*, 2011, **123**, 7047-7052; b) H. Mayr, S. Lakhdar, B. Maji and A. R. Ofial, *Beilstein J. Org. Chem.*, 2012, **8**, 1458-1478.

8 E. M. Higgins, J. A. Sherwood, A. G. Lindsay, J. Armstrong, R. S. Massey, R. W. Alder and A. C. O'Donoghue, *Chem. Commun.*, 2011, **47**, 1559-1561.

9 For NHCs in organocatalysis, see: a) N. Marion, S. Díez-González and S. P. Nolan, *Angew. Chem. Int. Ed.*, 2007, **46**, 2988–3000; b) D. Enders, O. Niemeier and A. Henseler, *Chem. Rev.*, 2007, **107**, 5606–5655; c) S. J. Ryan, L. Candish and D. W. Lupton, *Chem. Soc. Rev.*, 2013, **42**, 4906–4917.

10 For NHCs in organopolymerization, see: M. Fèvre, J. Pinaud, Y. Gnanou, J. Vignolle and D. Taton, *Chem. Soc. Rev.*, 2013, **42**, 2142–2172.

11 R. Breslow, *J. Am. Chem. Soc.*, 1958, **80**, 3719–3726; b) H. Stetter, *Angew. Chem. Int. Ed. Engl.*, 1976, **15**, 639–647; c) X. Bugaut and F. Glorius, *Chem. Soc. Rev.*, 2012, **41**, 3511-3522.

12 a) G. A. Grasa, R. M. Kissling and S. P. Nolan, *Org. Lett.*, 2002, **4**, 3583–3586; b) G. W. Nyce, J. A. Lamboy, E. F. Connor, R. M. Waymouth and J. L. Hedrick, *Org. Lett.*, 2002, **4**, 3587–3590.

13 For a recent overview, see: P. Chauhan and D. Enders, *Angew. Chem. Int. Ed.*, 2014, **53**, 1485–1487.

14 C. Fischer, S. W. Smith, D. A. Powell and G. C. Fu, *J. Am. Chem. Soc.*, 2006, **128**, 1472–1473.

15 J. P. Moerdyk and C. W. Bielawski, *J. Am. Chem. Soc.*, 2012, **134**, 6116–6119.

16 H. Zhou, W.-Z. Zhang, C.-H. Liu, J.-P. Qu and X.-B. Lu, *J. Org. Chem.*, 2008, **73**, 8039–8044.

17 a) M. D. Scholten, J. L. Hedrick and R. M. Waymouth, *Macromolecules*, 2008, **41**, 7399–7404; b) J. Raynaud, A. Ciolino, A. Baceiredo, M. Destarac, F. Bonnette, T. Kato, Y. Gnanou and D. Taton, *Angew. Chem. Int. Ed.*, 2008, **47**, 5390–5393.

18 S. Naumann, F. G. Schmidt, M. Speiser, M. Böhl, S. Epple, C. Bonten and M. R. Buchmeiser, *Macromolecules*, 2013, **46**, 8426–8433.

19 a) A. Berkessel, S. Elfert, V. R. Yatham, J.-M. Neudörfl, N. E. Schlörer and J. H. Teles, *Angew. Chem. Int. Ed.*, 2012, **51**, 12370–12374; b) A. Berkessel, V. R. Yatham, S. Elfert and J.-M. Neudörfl, *Angew. Chem. Int. Ed.*, 2013, **52**, 11158–11162; c) B. Maji and H. Mayr, *Angew. Chem. Int. Ed.*, 2013, **52**, 11163–11167.

20 M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem. Int. Ed.*, 2010, **49**, 8810–8849.

21 V. P. Boyarskiy, K. V. Luzyanin and V. Y. Kukushkin, *Coord. Chem. Rev.*, 2012, **256**, 2029–2056.

22 A. J. Arduengo, J. R. Goerlich and W. J. Marshall, *Liebigs Ann./Recueil*, 1997, 365–374.

23 V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu and G. Bertrand, *Angew. Chem.*, 2005, **44**, 5705–5709.

24 T. W. Hudnall and C. W. Bielawski, *J. Am. Chem. Soc.*, 2009, **131**, 16039–16041.

25 R. H. Crabtree, *Coord. Chem. Rev.*, 2013, **257**, 755–766.

26 a) F. Ricciardi, W. A. Romanchick and M. M. Joullié, *J. Polym. Sci., Polym. Lett. Ed.*, 1983, **21**, 633–638; b) H. Maka, T. Spychaj and R. Pilawka, *Ind. Eng. Chem. Res.*, 2012, **51**, 5197–5206.

27 M. Fèvre, J. Pinaud, A. Leteneur, Y. Gnanou, J. Vignolle, D. Taton, K. Miqueu and J.-M. Sotiropoulos, *J. Am. Chem. Soc.*, 2012, **134**, 6776–6784.

28 M. Fèvre, P. Coupillaud, K. Miqueu, J.-M. Sotiropoulos, J. Vignolle and D. Taton, *J. Org. Chem.*, 2012, **77**, 10135–10144.

29 N. J. Bridges, C. C. Hines, M. Smiglak and R. D. Rogers, *Chem. Eur. J.*, 2007, **13**, 5207–5212.

30 P. Coupillaud, J. Pinaud, N. Guidolin, J. Vignolle, M. Fèvre, E. Veaudecrenne, D. Mecerreyes and D. Taton, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, **51**, 4530-4540.

31 M. Fèvre, J. Vignolle and D. Taton, *Polym. Chem.*, 2013, **4**, 1995–2003.

32 a) Y.-S. Choi, Y. N. Shim, J. Lee, J. H. Yoon, C. S. Hong, M. Cheong, H. S. Kim, H. G. Jang and J. S. Lee, *Appl. Catal. A*, 2011, **404**, 87–92; b) Q. F. Yue, C. X. Wang, L. N. Zhang, Y. Ni and Y. X. Jin, *Polym. Degrad. Stab.*, 2011, **96**, 399–403.

33 a) J. D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi and R. D. Rogers, *Chem. Commun.*, 2003, 28–29; b) H. A. Duong, T. N. Tekavec, A. M. Arif and J. Louie, *Chem. Commun.*, 2004, 112–113.

34 For extensive DFT calculations on NHC- and CO_2-bonding, see: M. J. Ajitha and C. H. Suresh, *J. Org. Chem.*, 2012, **77**, 1087–1094.

35 B. R. van Ausdall, J. L. Glass, K. M. Wiggins, A. M. Aarif and J. Louie, *J. Org. Chem.*, 2009, **74**, 7935–7942.

36 S. Naumann, F. G. Schmidt, R. Schowner, W. Frey and M. R. Buchmeiser, *Polym. Chem.*, 2013, **4**, 2731–2740.

37 B. R. van Ausdall, N. F. Poth, V. A. Kincaid, A. M. Arif and J. Louie, *J. Org. Chem.*, 2011, **76**, 8413–8420.

38 S. Naumann and M. R. Buchmeiser, *Macromol. Rapid Commun.*, 2014, **35**, 682–701.

39 A. Hoppe, F. Sadaka, C.-H. Brachais, G. Boni, J.-P. Couvercelle and L. Plasseraud, *Beilstein J. Org. Chem.*, 2013, **9**, 647–654.

40 E. Brulé, V. Guérineau, P. Vermaut, F. Prima, J. Balogh, L. Maron, A. M. Z. Slawin, S. P. Nolan and C. M. Thomas, *Polym. Chem.*, 2013, **4**, 2414–2423.

41 S. Naumann, F. G. Schmidt, W. Frey and M. R. Buchmeiser, *Polym. Chem.*, 2013, **4**, 4172–4181.

42 B. Bantu, G. M. Pawar, U. Decker, K. Wurst, A. M. Schmidt and M. R. Buchmeiser, *Chem. Eur. J.*, 2009, **15**, 3103–3109.

43 R. Lindner, M. L. Lejkowski, S. Lavy, P. Deglmann, K. T. Wiss, S. Zarbakhsh, L. Meyer and M. Limbach, *ChemCatChem*, 2014, **6**, 618–625.

44 S. Naumann, S. Epple, C. Bonten and M. R. Buchmeiser, *ACS Macro Lett.*, 2013, **2**, 609–612.

45 a) A. Tudose, A. Demonceau and L. Delaude, *J. Organomet. Chem.*, 2006, **691**, 5356–5365; b) X. Sauvage, A. Demonceau and L. Delaude, *Adv. Synth. Catal.*, 2009, **351**, 2031–2038.

46 a) A. M. Voutchkova, L. N. Appelhans, A. R. Chianese and R. H. Crabtree, *J. Am. Chem. Soc.*, 2005, **127**, 17624–17625; b) A. M. Voutchkova, M. Feliz, E. Clot, O. Eisenstein and R. H. Crabtree, *J. Am. Chem. Soc.*, 2007, **129**, 12834–12846.

47 Y. Kayaki, M. Yamamoto and T. Ikariya, *Angew. Chem. Int. Ed.*, 2009, **48**, 4194-4197.

48 Seee for example: a) H. Zhou, W.-Z. Zhang, Y.-M. Wang, J.-P. Qu and X.-B. Lu, *Macromolecules*, 2009, **42**, 5419–5421; b) M. Vogt, J. E. Bennett, Y. Huang, C. Wu, W. F. Schneider, J. F. Brennecke and B. L. Ashfeld, *Chem. Eur. J.*, 2013, **19**, 11134–11138; c) L. Gu and Y. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 914–915; d) Z. Guo, N. R. Song, J. H. Moon, M. Kim, E. J. Jun, J. Choi, J. Y. Lee, C. W. Bielawski, J. L. Sessler and J. Yoon, *J. Am. Chem. Soc.*, 2012, **134**, 17846–17849; e) H. Zhou, Y.-M. Wang, W.-Z. Zhang, J.-P. Qu and X.-B. Lu, *Green Chem.*, 2011, **13**, 644–650; f) A. B. Bocarsly, Q. D. Gibson, A. J. Morris, R. P. L'Esperance, Z. M. Detweiler, P. S. Lakkaraju, E. L. Zeitler and T. W. Shaw, *ACS Catal.*, 2012, **2**, 1684–1692; g) S. N. Riduan, Y. Zhang and J. Y. Ying, *Angew. Chem.*, 2009, **48**, 3322-3325.

49 J. Pinaud, J. Vignolle, Y. Gnanou and D. Taton, *Macromolecules*, 2011, **44**, 1900–1908.

50 G. M. Pawar and M. R. Buchmeiser, *Adv. Synth. Catal.*, 2010, **352**, 917–928.

51 M. Hans, L. Delaude, J. Rodriguez and Y. Coquerel, *J. Org. Chem.*, 2014, **79**, 2758–2764.

52 For NHC-small molecule interaction, see also: U. Siemeling, C. Färber, C. Bruhn, M. Leibold, D. Selent, W. Baumann, M. von Hopffgarten, C. Goedecke and G. Frenking, *Chem. Sci.*, 2010, **1**, 697–704.

53 L. Delaude, A. Demonceau and J. Wouters, *Eur. J. Inorg. Chem.*, 2009, 1882–1891.

54 G. W. Nyce, S. Csihony, R. M. Waymouth and J. L. Hedrick, *Chem. Eur. J.*, 2004, **10**, 4073–4079.

55 M. Hans, J. Wouters, A. Demonceau and L. Delaude, *Eur. J. Org. Chem.*, 2011, 7083–7091.

56 V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller and G. Bertrand, *Angew. Chem. Int. Ed.*, 2006, **45**, 3488–3491.

57 A. G. Tskhovrebov, B. Vuichoud, E. Solari, R. Scopelliti and K. Severin, *J. Am. Chem. Soc.*, 2013, **135**, 9486–9492.

58 H. W. Wanlick, *Angew. Chem*., 1962, **74**, 129-134.

59 A. J. Arduengo, J. C. Calabrese, F. Davidson, H. V. Rasika Dias, J. R. Goerlich, R. Krafczyk, W. J. Marshall, M. Tamm and R. Schmutzler, *Helv. Chim. Act.*, 1999, **82**, 2348–2364.

60 E. F. Connor, G. W. Nyce, M. Myers, A. Möck and J. L. Hedrick, *J. Am. Chem. Soc.*, 2002, **124**, 914–915.

61 a) S. Randl, S. Gessler, H. Wakamatsu and S. Blechert, *Synlett*, 2001, **3**, 430–432; b) T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Wilhelm, M. Scholl, T.-L. Choi, S. Ding, M. W. Day and R. H. Grubbs, *J. Am. Chem. Soc.*, 2003, **125**, 2546–2558.

62 K. Denk, P. Sirsch and W. A. Herrmann, *J. Organomet. Chem.*, 2002, **649**, 219–224.

63 S. Csihony, D. A. Culkin, A. C. Sentman, A. P. Dove, R. M. Waymouth and J. L. Hedrick, *J. Am. Chem. Soc.*, 2005, **127**, 9079–9084.

64 a) O. Coulembier, A. P. Dove, R. C. Pratt, A. C. Sentman, D. A. Culkin, L. Mespouille, P. Dubois, R. M. Waymouth and J. L. Hedrick, *Angew. Chem. Int. Ed.*, 2005, **44**, 4964–4968. b) O. Coulembier, B. G. G. Lohmeijer, A. P. Dove, R. C. Pratt, L. Mespouille, D. A. Culkin, S. J. Benight, P. Dubois, R. M. Waymouth and J. L. Hedrick, *Macromolecules*, 2006, **39**, 5617–5628.

65 B. Bantu, G. Manohar Pawar, K. Wurst, U. Decker, A. M. Schmidt and M. R. Buchmeiser, *Eur. J. Inorg. Chem.*, 2009, 1970–1976.

66 W. Jeong, J. L. Hedrick and R. M. Waymouth, *J. Am. Chem. Soc.*, 2007, **129**, 8414–8415.

67 B. C. Norris, D. G. Sheppard, G. Henkelman and C. W. Bielawski, *J. Org. Chem.*, 2011, **76**, 301–304.

68 On NHC-metal bonding, see: H. Jacobsen, A. Correa, A. Poater, C. Costabile and L. Cavallo, Coord. Chem. Rev., 2009, 253, 687–703.

69 D. T. Cohen and K. A. Scheidt, *Chem. Sci.*, 2011, **3**, 53-57.

70 E. Piedra-Arroni, A. Amgoune and D. Bourissou, *Dalton Trans.*, 2013, **42**, 9024-9029.

71 R. W. Alder, M. E. Blake, C. Bortolotti, S. Bufali, C. P. Butts, E. Linehan, J. M. Oliva, A. G. Orpen and M. J. Quale, *Chem. Commun.*, 1999, 241–242.

72 a) P. L. Arnold, M. Rodden, K. M. Davis, A. C. Scarisbrick, A. J. Blake and C. Wilson, *Chem. Commun.*, 2004, 1612–1613; P. L. Arnold, M. Rodden and C. Wilson, *Chem. Commun.*, 2005, 1743–1745.

73 a) S. Woodward, *Tetrahedron*, 2002, **58**, 1017–1050; b) T.-L. Ho, *Tetrahedron*, 1985, **41**, 3–86; c) T.-L. Ho, *Chem. Rev.*, 1975, **75**, 1–20.

74 Y. Zhang, G. M. Miyake, M. G. John, L. Falivene, L. Caporaso, L. Cavallo and E. Y.-X. Chen, *Dalton Trans.*, 2012, **41**, 9119–9134.

75 For reviews, see: a) J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978–4008; b) I. J. Lin and C. S. Vasam, *Coord. Chem. Rev.*, 2007, **251**, 642–670.

76 H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972–975.

77 For some typical examples, see: a) V. Sashuk, L. H. Peeck and H. Plenio, *Chem. Eur. J.*, 2010, **16**, 3983–3993; b) C. C. Scarborough, B. V. Popp, I. A. Guzei and S. S. Stahl, *J. Organomet. Chem.*, 2005, **690**, 6143–6155; c) M. Iglesias, D. J. Beetstra, J. C. Knight, L.-L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi and I. A. Fallis, *Organometallics*, 2008, **27**, 3279–3289.

78 U. Hintermair, U. Englert and W. Leitner, *Organometallics*, 2011, **30**, 3726–3731.

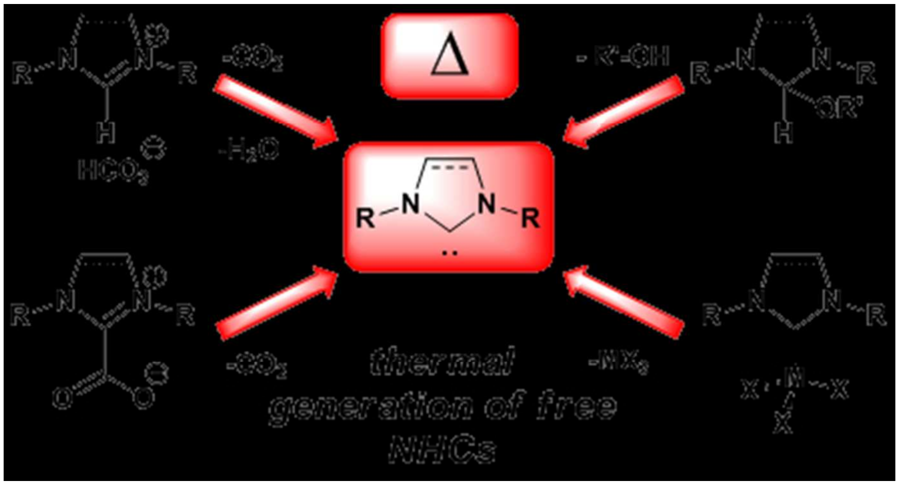
79 a) A. Kascatan-Nebioglu, M. J. Panzner, C. A. Tessier, C. L. Cannon and W. J. Youngs, *Coord. Chem. Rev.*, 2007, **251**, 884–895; b) L. Oehninger, R. Rubbiani and I. Ott, *Dalton Trans.*, 2013, **42**, 3269–3284.

80 A. C. Sentman, S. Csihony, R. M. Waymouth and J. L. Hedrick, *J. Org. Chem.*, 2005, **70**, 2391–2393.

81 M. K. Samantaray, V. Katiyar, K. Pang, H. Nanavati and P. Ghosh, *J. Organomet. Chem.*, 2007, **692**, 1672–1682.

82 N. E. Kamber, W. Jeong, S. Gonzalez, J. L. Hedrick and R. M. Waymouth, *Macromolecules*, 2009, **42**, 1634–1639.

83 S. Díez-González, E. D. Stevens and S. P. Nolan, *Chem. Commun.*, 2008, 4747–4749.



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