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The key role of R–NHC coupling (R = C, H, heteroatom) and M–NHC bond cleavage in the evolution of M/NHC complexes and formation of catalytically active species

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Complexes of metals with N-heterocyclic carbene ligands (M/NHC) are typically considered the systems of choice in homogeneous catalysis due to their stable metal–ligand framework. However, it becomes obvious that even metal species with a strong M–NHC bond can undergo evolution in catalytic systems, and processes of M–NHC bond cleavage are common for different metals and NHC ligands. This review is focused on the main types of the M–NHC bond cleavage reactions and their impact on activity and stability of M/NHC catalytic systems. For the first time, we consider these processes in terms of NHC-connected and NHC-disconnected active species derived from M/NHC precatalysts and classify them as fundamentally different types of catalysts. Problems of rational catalyst design and sustainability issues are discussed in the context of the two different types of M/NHC catalysis mechanisms.

1. Introduction

Homogeneous metal catalysis is a highly valuable tool of modern organic synthesis. It is used for preparation of fine chemicals, pharmaceuticals and agrochemicals, transformations of natural compounds, syntheses of monomers, polymers and advanced materials.[1] Metal catalysts facilitate hundreds of unique C–C and C-heteroatom bond-forming reactions under mild conditions and with high selectivities.[2]

Tremendous progress in fine organic synthesis has been achieved owing to the development of well-defined, stable and easy to use precatalysts based on the complexes of transition metals with organic ligands.[3] Important roles of these ligands are numerous: they stabilize active metal species, ensure their solubility, secure favorable electronic states of the metal center, provide sterically defined binding pockets for reagents and substrates, and control chemo-, regio-, stereo- and enantioselectivity during the reaction.[4,5] In addition, multifunctional ligands can participate in metal–ligand cooperative catalysis,[6] or purposefully change properties of a catalyst under the action of an external stimulus (pH, light, oxidation-reduction, *etc.*).[4,5]

Over the last three decades, N-heterocyclic carbenes (NHCs) have been increasingly appreciated as excellent ligands for metal catalysis.[5,7–18] Global impact of N-heterocyclic carbene (NHC) ligands is comparable with the impact of phosphines in the 1970s through the 1990s.[5] The main benefits of NHCs over phosphines and some other ligands are their relatively easy preparation, lower toxicity, high tunability of electronic and steric parameters, ability to incorporate many additional functions, and, undoubtedly, the enhanced stability of M/NHC complexes arising from strong metal–NHC bonding with a variety of transition metals.[11,12,19] In addition, M/NHC complexes are typically less prone to reversible dissociation than complexes with phosphine ligands and are less sensitive to oxidation in solution.[11,12]

Nevertheless, M/NHC complexes may undergo decomposition during catalysis, with the cleavage of the metal–NHC bond despite its high strength.[20–25] Reductive elimination of NHC ligands was described by Cavell and co-workers.[26] It was noted that the processes of M–NHC bond cleavage may cause deactivation of M/NHC catalytic systems.[20–23,25]

However, it has been recently demonstrated that M–NHC bond cleavage may also produce "ligandless" active metal species and thus can be considered as M/NHC precatalyst activation.[27] Further studies revealed a diverse range of metal species without NHC ligands in a variety of M/NHC-catalyzed reactions and these literature will be considered in the present review.

Indeed, as one may expect, the reactions of metal–NHC bond cleavage have a great impact on the activity and stability of

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M/NHC catalytic systems. The processes of catalyst evolution *via* reductive elimination of NHC ligands (known as R–NHC couplings) drastically change the nature of catalytically active species. Other types of M–NHC bond cleavage were also described and may affect ligand environment of metal centers. In-depth analysis of literature including recent publications shows a number of R–NHC bond formations and several types of M–NHC bond cleavage reactions, which can have remarkable importance for catalysis. We believe the time is ripe now to analyze the impact of these processes on catalytic reactions. In this review we provide systematization of representative M–NHC bond cleavage reactions as well as discuss their potential influence on catalysis. Distinction between the NHC-connected and NHC-disconnected active species is of great importance to design highly efficient M/NHC catalytic systems.

2. State-of-the-art catalysis by metal complexes with NHC ligands

The general concept of M/NHC catalysis has long been based on the assumption of high stability of the M–C_{NHC} framework during catalysis. NHCs were considered as supporting ligands that stabilize and at the same time activate the metal centers. The active centers were commonly imagined as activated molecular $(NHC)_nM(L)_x$ complexes (Fig. 1) by analogy with phosphine complexes.

Here we discuss that M/NHC complexes show variable behavior, and the paths of their activation are diverse. The mechanisms of M/NHC catalysis can be divided into two main types depending on the structure of the active centers (Fig. 1):

(i) The NHC-connected mechanisms with active centers containing a typical metal–C_{NHC} sigma bond;

(ii) The NHC-disconnected mechanisms with active centers containing no metal–C_{NHC} sigma bonds.

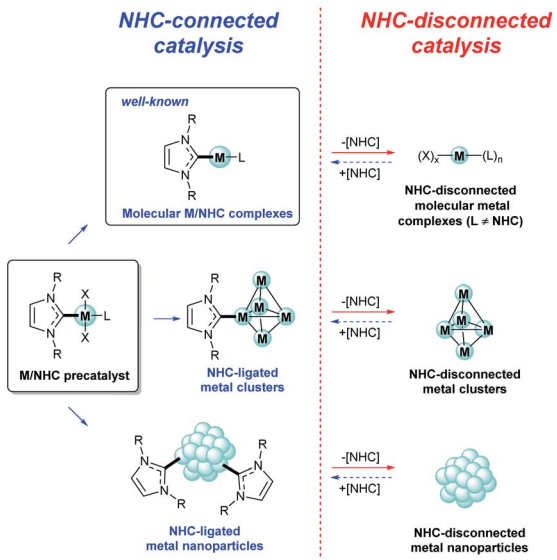


Fig. 1 Two types of active species in NHC-connected and NHC-disconnected modes of M/NHC catalysis.

It should be noted, that similar discussions related to well-defined homogeneous catalysts *vs.* cocktail-type behavior are ongoing in recent years for other types of catalysts.[24,28–44] However, M/NHC catalysis is a least studied topic in the area of dynamic catalysis, since until recently only molecular mode was predominantly considered.

First, let us briefly consider the main features of the above mentioned two types of M/NHC catalysis.

2.1. NHC-connected mechanisms

Undoubtedly, NHC-connected mechanisms, in which active metal species contain NHC ligands connected with metal atoms *via* the M–C_{NHC} bond, play an important role in M/NHC catalysis. In these mechanisms, active centers are usually represented by molecular M/NHC complexes (molecular M/NHC catalysis, Fig. 1). NHC–ligated metal clusters and nanoparticles may form in the course of catalytic process as a result of partial M/NHC complexes decomposition.[45] The NHC–ligated metal clusters and nanoparticles can also act as NHC-connected active centers (Fig. 1).[46–48] For example, recent study demonstrated significant impact of the NHC ligand structure on the catalytic activity of Pd/Al_2O_3 heterogeneous catalysts composed of NHC–ligated Pd nanoparticles in bromobenzene hydrogenolysis and Buchwald–Hartwig amination of aryl halides.[46] Comparative DFT calculations for neat and NHC–ligated Pd_{13} clusters revealed that coordinated NHCs convey electron density to nanoclusters thus lowering the energy barriers of aryl halide oxidative addition.[46] Similar effects were observed in electrochemical reduction of CO_2 on NHC–ligated Pd electrodes; the role of coordinated NHCs was supported by DFT calculations of the reaction pathways on surface models of Pd(111) and Pd(111)–NHC.[47]

The main feature of the NHC-connected mechanisms is that, after pre-catalyst activation (Fig. 2A), the M–C_{NHC} framework directly participates in the catalytic cycle, or, more specifically, in transition states of the catalyzed reaction (Fig. 2B). Under this condition, electronic and steric parameters of the NHC ligand directly influence the metal center and significantly affect the activation energy.

Typical examples of catalytic systems operating by the NHC-connected mechanisms are Pd/NHC- and Ni/NHC-catalyzed cross-coupling and CH-functionalization reactions of non-activated aryl chlorides *e.g.* the Buchwald–Hartwig amination,[10,18,49–52] C–S cross-coupling of thiols,[53–55] CH–arylation of ketones,[56,57] among several other examples.

Catalytic efficacy of M/NHC complexes in the reactions operating by the NHC-connected mechanisms is highly dependent on the electronic effect and steric bulkiness of the NHC ligands.

2.2. NHC-disconnected mechanisms

The alternative, NHC-disconnected mode, is often mentioned as "NHC-free" catalysis or "ligandless" M/NHC catalysis.[24] The name indicates that the active metal species (molecular metal complexes, metal clusters, or metal nanoparticles) are formed by decomposition of M/NHC precatalysts and contain no metal–

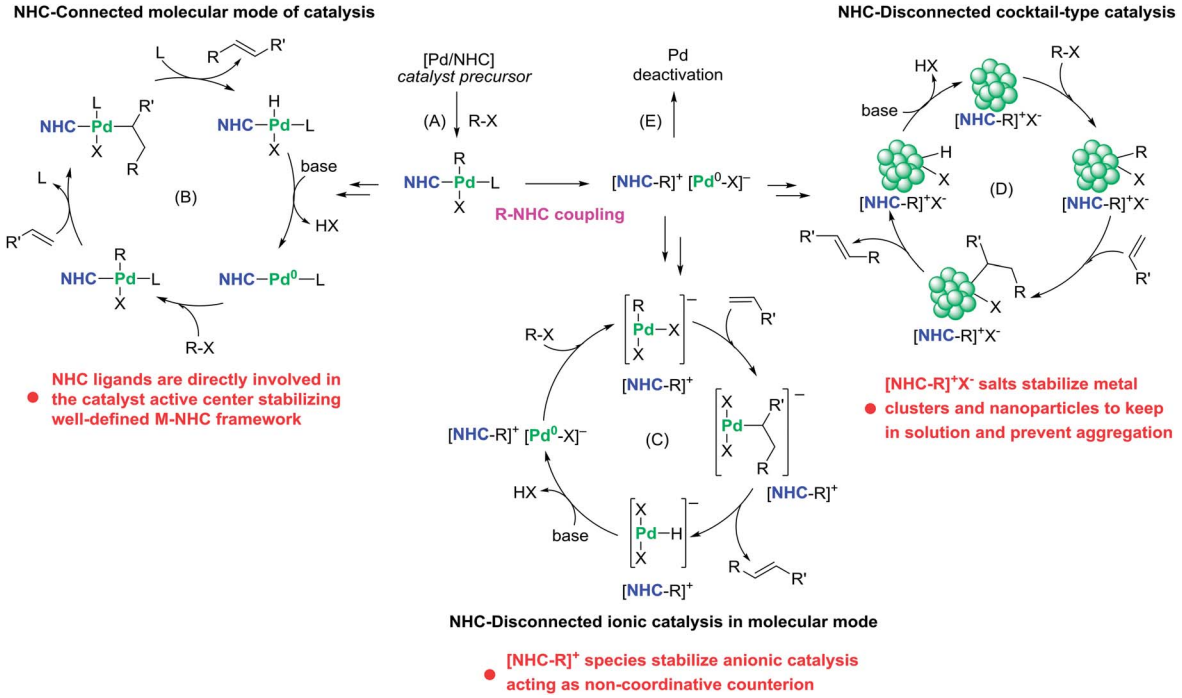


Fig. 2 Different modes of operation of Pd/NHC complexes are shown using the Mizoroki–Heck reaction as an example: (A) – initial stage of precatalyst activation; (B) – NHC-connected molecular catalysis; (C) – NHC-disconnected molecular catalysis; (D) – NHC-disconnected cocktail-type catalysis involving nanoparticles; (E) – catalyst degradation after R–NHC coupling (other pathways of catalyst degradation also exist in each of the catalytic cycles; not shown here to avoid picture overload).

C_{NHC} sigma bonds (Fig. 1).[27,54,58–64] In this type of mechanisms, M/NHC complexes serve as precursors or reservoirs of the active metal species. The metal–C_{NHC} framework breaks at the activation stage and it does not participate in the catalytic cycle. A typical example of NHC-disconnected metal catalysis is Pd/NHC catalyzed Mizoroki–Heck reaction (Fig. 2).[27,58,59,62]

At the activation stage, Pd/NHC complexes suffer reductive elimination of NHC ligands *via* C–NHC coupling or H–NHC coupling to give azolium salts $[NHC\text{–}R]^+X^-$ (R = H, aryl, *etc.*),[27,59,62] or *via* O–NHC coupling under the action of strong oxygen bases to give azolones.[58] The NHC-disconnected Pd(0) active species, that form after the Pd–C_{NHC} bond cleavage, effectively catalyze the Mizoroki–Heck reaction. Under certain reaction conditions and Pd/NHC loadings, molecular M/NHC catalysis cannot be neglected (Fig. 2B);[62] however, in such cases, the homogeneous NHC-disconnected catalysis by ionic Pd complexes (Fig. 2C)[62] or the cocktail-type NHC-disconnected catalysis by nanoparticles (Fig. 2D) come into effect and make the main contribution to the product formation.[27,59]

The efficacy of M/NHC complexes in the catalytic systems operating by NHC-disconnected mechanisms depend on the rate of the metal–C_{NHC} bond cleavage and the stability of the forming NHC-disconnected active metal species (considered further in Section 4).[27,59,62]

Overall, it is evident that the metal–C_{NHC} bond cleavage reactions may have paramount impact on the catalytic systems operating by NHC-connected and NHC-disconnected catalytic mechanisms. Understanding the M–NHC bond cleavage reactions is pivotal for the efficient tuning of activity and stability of the M/NHC catalytic systems.

3. Organometallic chemistry behind the H–NHC, C–NHC and X–NHC couplings

M/NHC complexes can undergo metal–C_{NHC} bond cleavage to give different products depending on the structure of the complex and reaction conditions (Table 1). Here we attempt to classify these reactions considering the type of forming R–NHC bond (C–NHC, H–NHC, and X–NHC), the changes in oxidation state of the metal at the stage of M–C_{NHC} bond cleavage, and some other features of the plausible reaction mechanism. It should be emphasized that the number of detailed studies of the M–NHC bond cleavage reactions is still limited (either by R–NHC coupling or direct M–NHC bond dissociation). Some of the reports elucidate the major NHC conversion products without accounting for the metal-containing products, which complicates conclusions on the stoichiometry and mechanism of reaction.

3.1. Metal–NHC bond cleavage reactions with the metal reduction

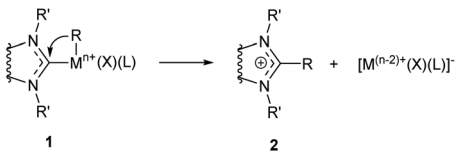
Reductive M–NHC bond cleavage reactions are typical for complexes of metals in higher oxidation states with a higher redox potential. Such reactions are very important for M/NHC catalysis as they lead to formation of ligandless M^0 species which can serve as alternative active centers.[24] On the other

Table 1 A summary of representative studies on M–NHC bond cleavage reactions leading to the formation of R–NHC species (R = C, H, X; respectively in the table columns)

Metal	M–NHC → C–NHC	M–NHC → H–NHC	M–NHC → X–NHC
Li	C_{sp^2}–NHC[104] C_{sp^3}–NHC[105,108]	Ref. 105–109	P–NHC[110] As–NHC[110]
Na	C_{sp^3}–NHC[111]	—	—
Mg	—	Ref. 112	—
Al	C_{sp^2}–NHC[113,114] C_{sp^3}–NHC[120]	Ref. 115–119	—
Ga	—	Ref. 105 and 116	—
Ge	—	Ref. 121 and 122	B–NHC[122]
In	—	Ref. 116 and 119	—
Tl	—	—	Cl–NHC[123] Br–NHC[123]
Sc	C_{sp^2}–NHC[124]	—	—
Y	—	Ref. 125	—
Ce	—	Ref. 125	—
Eu	C_{sp^2}–NHC[126]	—	—
Cr	—	Ref. 127	I–NHC[127]
Mo	—	Ref. 127–130	I–NHC[127]
W	—	Ref. 127	—
Mn	—	Ref. 131	—
Fe	C_{sp}–NHC[132] C_{sp^2}–NHC[80,135,138]	Ref. 133–136	B–NHC[137]
Ru	C_{sp^2}–NHC[73,74,139]	Ref. 140–143	—
Co	—	Ref. 144	O–NHC[145]
Rh	C_{sp^2}–NHC[75–79,146] C_{sp^3}–NHC[147]	Ref. 147–149	—
Ir	—	—	B–NHC[150]
Ni	C_{sp^2}–NHC[72,151] C_{sp^3}–NHC[67,82,155,156]	Ref. 152 and 153	B–NHC[154] P–NHC[157] S–NHC[99,100]
Pd	C_{sp^2}–NHC[27,58,61,62,82,155,156,158–165] C_{sp^3}–NHC[26,82,155,156,160,166,173–175]	Ref. 59,165–171	O–NHC[97,172] Cl–NHC[83] Si–NHC[175]
Pt	—	Ref. 59 and 176	—
Cu	C_{sp^2}–NHC[71,81,177]	Ref. 71,178–182	O–NHC[71,181–183] Br–NHC[81,101,184] Cl–NHC[101,184] I–NHC[101] N–NHC[103] P–NHC[185] S–NHC[186–188]
Ag	—	Ref. 189–205	B–NHC[205] N–NHC[206] S–NHC[207,208]
Au	—	Ref. 209	—
Zn	C_{sp^2}–NHC[210–212]	Ref. 212 and 213	—

hand, these reactions often lead to formation of metal precipitates and cause deactivation of M/NHC catalytic systems.[22,23,25]

3.1.1. Reductive elimination of NHC ligand(s) *via* C–NHC coupling. Reductive elimination of NHC and R ligands from complexes **1** (R = alkyl, aryl, alkenyl, alkynyl, acyl, *etc.*) is a highly important and the most studied type of M–NHC bond cleavage reactions (Table 1). The process results in formation of new C–C bond between NHC and R (Scheme 1).[22,23,25,58,60] Complexes **1** are typical catalytic intermediates found in the vast majority of M/NHC catalysed reactions. Decomposition of M/NHC catalysts *via* C–NHC coupling was detected in Mizoroki–Heck[27,62,65] and Suzuki–Miyaura[66] couplings, in the oligomerizations of alkenes and alkynes,[67–70] in CH-functionalizations of heterocycles,[71] and in many other reactions.[23,25] The C–NHC coupling reactions accompanied by two-electron reduction of the metal center were observed experimentally for Pd^{II},[22,23,25]



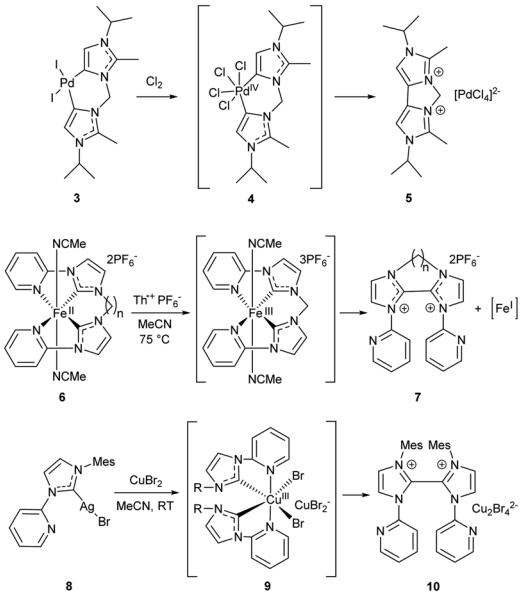
Scheme 1 General scheme of the NHC reductive elimination reactions.

Ni^{II},[22,23,25,72] Ru^{II},[73,74] Rh^{III},[75–79] Fe^{III} (ref. 80) and Cu^{III} (ref. 71 and 81) complexes. In the case of M^{II}/NHC complexes **1**, the NHC-disconnected M^0-containing products are often unstable and prone to formation of metal nanoparticles in the absence of external oxidizers ($n = 2$, Scheme 1).

The C–NHC coupling reactions were most extensively studied for Pd^{II}/NHC complexes (Table 1 column 2). These reactions proceed *via cis* arrangement of NHC and R groups; kinetic studies and DFT calculations are consistent with the concerted reductive elimination mechanism.[82] Susceptibility of (NHC)Pd(R)(Br)Py complexes to R–NHC coupling decreases as R = vinyl > ethynyl > Me ~ Ph.[58] The calculated energy barriers of Ph–NHC coupling is in the range of 17.9–25.1 kcal mol^{-1} for different NHCs.[64] In many catalytic reactions conducted at 50–100 °C such barriers are readily overpassed and the stability of complexes is determined by thermodynamic factors. Reversibility of the C–NHC coupling was confirmed experimentally on an example of the CH_3–NHC bond activation catalyzed by palladium nanoparticles.[61] Bulky N-substituents in NHC ligands usually increase the activation barriers;[58] however, the effects of bulkiness can be more complex, as a significant increase in steric bulkiness can induce dissociation of the stabilizing co-ligands. For example, DFT calculations of Ph–NHC coupling in (NHC)Pd(Ph)(I)DMF complexes predicted lower $\Delta E^{\neq}$ for the bulky IPr ligand (19.2 kcal mol^{-1}) than for the non-bulky IMe ligand (20.9 kcal mol^{-1}) owing to the splitting of DMF molecule from the complex with IPr ligand.[64]

The effect of metal and its oxidation state on the C–NHC coupling efficiency has been evaluated by DFT calculations for M^{II}/NHC and M^{IV}/NHC complexes of Ni, Pd and Pt.[60] The results indicate that thermodynamic and kinetic stabilities of both M^{II} and M^{IV} complexes **1** against C–NHC coupling decrease as Pt > Pd > Ni. Besides, complexes **1** with a higher oxidation state of the metal are thermodynamically and kinetically less stable than corresponding complexes with metals in lower oxidation states. Thus, in $(NHC)_2M^{IV}(Ph)(Br)_3$ complexes (NHC = 1,3-dimethylimidazol-2-ylidene), Ph–NHC coupling is facilitated dramatically from Pt ($\Delta G^{\neq}$ = 37.5 kcal mol^{-1}, ΔG = −36.9 kcal mol^{-1}) to Pd ($\Delta G^{\neq}$ = 18.3 kcal mol^{-1}, ΔG = −61.5 kcal mol^{-1}) and Ni ($\Delta G^{\neq}$ = 4.7 kcal mol^{-1}, ΔG = −80.2 kcal mol^{-1}). In similar complexes $(NHC)_2M^{II}(Ph)(Br)$, corresponding values change in a smaller extent from Pt ($\Delta G^{\neq}$ = 50.1 kcal mol^{-1}, ΔG = 34.0 kcal mol^{-1}) to Pd ($\Delta G^{\neq}$ = 30.8 kcal mol^{-1}, ΔG = 15.8 kcal mol^{-1}) and Ni ($\Delta G^{\neq}$ = 30.1 kcal mol^{-1}, ΔG = 16.6 kcal mol^{-1}). The poor thermodynamic and kinetic stabilities of the regular Pd^{IV} and Ni^{IV} complexes **1** against R–NHC coupling indicate high probability of the M^{IV}–NHC bond cleavage and implementation of the NHC-disconnected catalytic scenario in the reactions comprising M^{IV} intermediates.[60]

A similar decrease in the stability against R–NHC coupling was observed for the bis-C–NHC couplings in Pd, Fe and Cu complexes (Scheme 2). Treatment of Pd^{II}/NHC complex **3** with chlorine results in formation of cyclic 4,4-biimidazolium salt **5** and release of Pd^{II} species; the reaction apparently proceeds *via* reductive elimination of both NHC ligands from the Pd^{IV}/NHC intermediate **4**.[83] Reductive elimination of both NHC ligands in

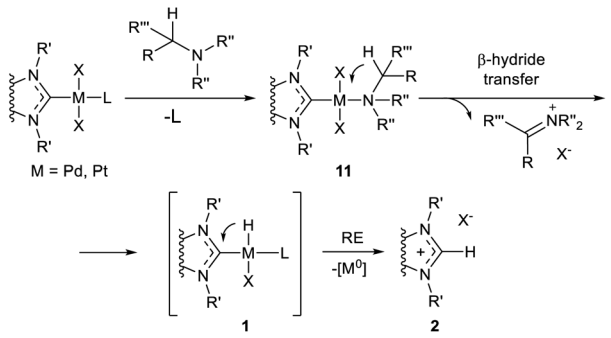


Scheme 2 The C_{NHC}–C_{NHC} coupling reactions in bis-NHC complexes of metals in higher oxidation states.[80,81,83]

the stable bis-NHC Fe^{II} complexes **6** upon one-electron oxidation with Th^+ gives dicationic 2,2′-biimidazolium salts **7**, presumably along with unstable Fe^{I} species that has not been isolated.[80] A similar C–C coupling leading to compound **10** occurs between two NHC ligands in the bis-NHC Cu^{III} complex **9** that forms *in situ* from the silver complex **8**.[81]

It should be noted that C–NHC coupling reactions have great importance for accessing various functionalized heterocycles.[84–89] Numerous metal-catalyzed CH-functionalizations of nitrogen heterocycles like alkylation, arylation and *etc.* in fact proceed *via* R–NHC coupling of *in situ* formed M–NHC complexes in which heterocyclic substrate acts as a protic NHC–ligand.[86–89]

3.1.2. Reductive elimination of NHC ligand(s) *via* H–NHC coupling. The H–NHC coupling reactions proceed by reductive elimination of H and NHC ligands from the hydride M/NHC complexes type **1** (R = H) to give azolium cations $[NHC–H]^+$ which represent protonated NHCs (Scheme 1, Table 1 column 3).[27,59,62] Hydride complexes **1** (R = H) are typical catalytic intermediates in various hydrogenation/dehydrogenation reactions, Mizoroki–Heck reactions, C–H bond functionalizations, *etc.* The hydride complexes can also be derived from M/NHC precatalysts under the action of aliphatic amines (used as mild bases in many catalytic systems), alcohols, DMF and other solvents that can donate hydride ions.[27,54,59,62] For example, aliphatic amines, especially tertiary amines, induce facile decomposition of M^{II}/NHC complexes (M = Pd, Pt) to give metal nanoparticles and azolium salts **2** (Scheme 3).[54,59] Formation of the hydride complexes **1** *via* β-hydride transfer from aliphatic group of coordinated amine in an intermediate complex **11** was proposed as the key stage and was supported by observation of $[(NHC)PdH]^+$ ions in ESI-MS during online MS monitoring of the reaction progress.[59] Formation of the hydride complexes **1**



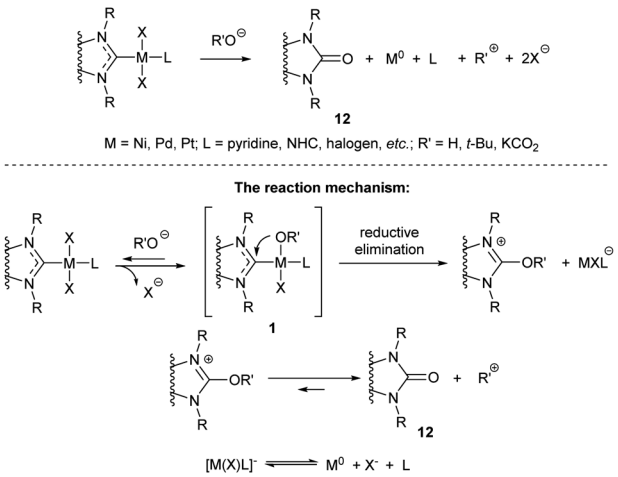
Scheme 3 The aliphatic amine-induced H–NHC coupling of M^{II}/NHC complexes.[54,59]

in methanol solutions of Pd/NHC precatalysts was demonstrated by online ESI-MS experiments, with strong signals corresponding to the $[(NHC)PdX_2H]^-$ ion and azolium cations $[NHC–H]^+$ observed in negative and positive ion modes, respectively.[62] The mechanism involving β-hydride transfer from the methyl group of methanol was confirmed by experiments with CH_3OH-d_n ($n = 1, 3, 4$).[62]

Theoretical modeling of the H–NHC coupling and reverse reaction for Ni, Pd and Pt complexes by DFT methods have been reported.[62,90,91] Predicted activation and reaction energies vary depending on the structure of complexes **1** (R = H); however, all of the studies emphasize the endergonic character of the H–NHC coupling reactions. For example, a low activation barrier of H–NHC coupling ($\Delta G^{\neq} = 6.3$ kcal mol^{-1}), with corresponding reaction energy of $\Delta G = 4.4$ kcal mol^{-1}, were calculated for (NHC)Pd(H)I (NHC = 1,3-dimethylbenzimidazol-2-ylidene); the reaction leads to ionic aggregate $[NHC–H]^+[PdI]^-$. The reversibility of the H–NHC coupling has been confirmed experimentally.[21,92,93] Bulky N-substituents in the NHC ligands usually stabilize the Pd/NHC hydride complexes **1**.[92,94–96] This finding indirectly supports the reductive elimination mechanism (H–NHC coupling) as the predominant pathway of the observed decomposition of hydride complexes **1** into $[NHC–H]^+$ cations and Pd^0 species in solutions at moderate temperatures. The alternative mechanism (dissociation of Pd^{II}/NHC or Pd^0/NHC complexes) would mean a positive correlation between decomposition and steric bulkiness, which contradicts the experimental findings. It should be noted, however, that the alternative pathway to azolium salts **2** *via* the M–NHC bond dissociation and NHC ligand protonation must not be excluded in many cases.

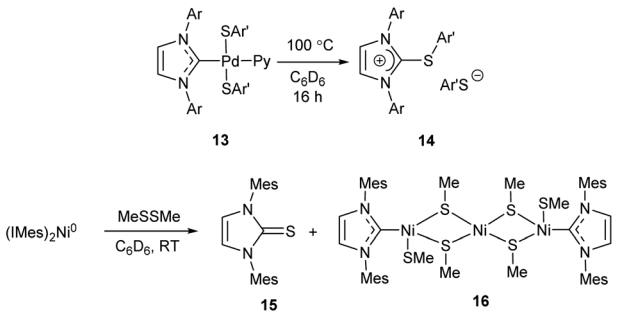
3.1.3. Reductive elimination of NHC ligand(s) *via* X–NHC coupling. Reductive eliminations of NHC ligands with the formation of heteroatom–C_{NHC} bonds are relatively understudied (Table 1 column 4). One important type of such reactions is O–NHC coupling (Scheme 4).[58] It is promoted by strong oxygen-containing bases (alkali metal hydroxides, alkoxides, carbonates, *etc.*) used in many catalytic systems.

The M^{II}/NHC complexes (M = Ni, Pd, Pt) react by reductive elimination of RO and NHC ligands to give M^0 species that are typically transformed into metal precipitates and $[NHC–OR]^+$ cations; the latter afford azolones (the oxo-substituted azoles)



Scheme 4 The oxygen-base-mediated O–NHC coupling reactions of M/NHC complexes.[97]

via dissociation or solvolysis of the R–O bond (Scheme 4).[58] In this reaction, NHC ligands play a role of two-electron intramolecular reductants of the coordinated metal dications. The reaction mechanism was confirmed by experiments with ^{18}O labelled potassium hydroxide and observation of key intermediates **1** (R = OH, M = Pd) by ESI-MS with their direct transformations into azolones **12** in MS/MS experiments (Scheme 4).[58] Among the studied metal complexes, Pd complexes were found to be the most reactive, and thus more prone to the base-induced O–NHC coupling. Mono-NHC complexes and the halogen-bridged Pd complexes containing non-bulky N-substituents were decomposed by KOH or ^{t}BuOK within 10–20 min at 40–100 °C, while bis-NHC complexes (L = NHC) and the complexes with bulky substituents in NHC ligands suffered appreciable conversions only within several hours. S–NHC coupling was observed in the reactions of arylthiols with Pd^{II}/NHC and Ni^{II}/NHC, as well as in the reactions of *S*,*S*′-dimethyl disulfide with $(IMes)_2Ni^0$ complex (Scheme 5).[55,98,99] For example, *S*-aryl-imidazolium salt **14** was afforded by heating dithiolate complex **13** in C_6D_6 (Scheme 5).[98] Compound **14** very likely forms *via* reductive elimination of NHC and thiolate ligands.[98] The reaction of $Ni^0(Mes)_2$ complex with MeSSMe affords imidazoline-2-thione **15** along with the trinuclear S-bridged complex **16**.[99] Imidazoline-2-thione **15** is reportedly

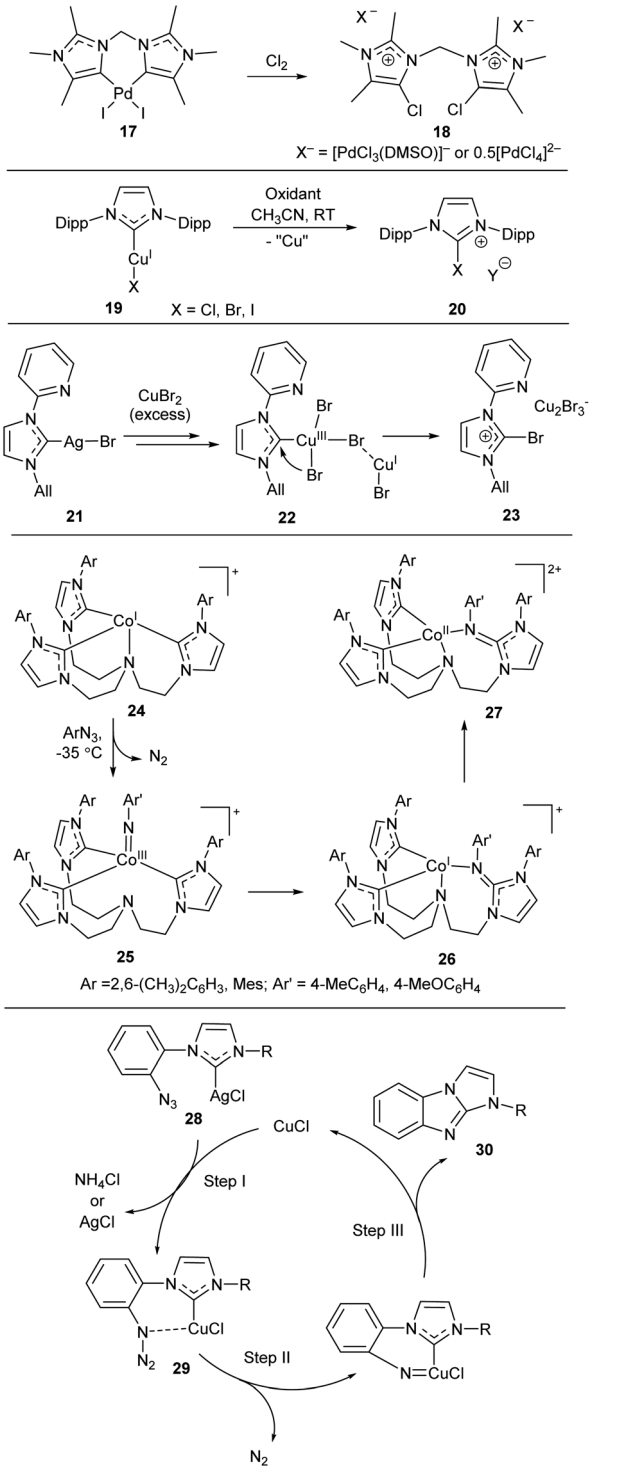


Scheme 5 Major products of S–NHC coupling reactions.[98,99]

formed by Ni/NHC-catalyzed hydrothiolation of alkynes.[100] Remarkably, trinuclear Pd complexes similar to **16** were observed in the reactions of Pd–PEPPSI complexes with arylthiols, along with 2-arylthioimidazolium salts analogous to **14**.[55,98] The undesired S–NHC coupling can significantly affect the stability of M/NHC complexes during catalysis of C–S bond formation and activation reactions. However, the detailed evaluation is difficult, as the mechanisms of these reactions are still poorly studied. In the first instance, formation of azoline-2-thiones implies the cleavage of *S*-aryl and *S*-alkyl bonds in the starting thiols or disulfides;[99,100] the mechanism of this cleavage is unclear. Secondly, reductive elimination of SR and NHC ligands from M^{II}/NHC complexes should produce NHC-disconnected M^0 species, no isolation or detection of which have ever been reported. Complexes **16**, the only metal-containing products of determined structure reported for this process (Scheme 5),[55,98,99] apparently are not the final products of S–NHC coupling. It is quite probable, that the forming NHC-disconnected M^0 species are unstable under the reaction conditions and further react with sulfur compounds to give metal polysulfides.[100] Overall, the S–NHC coupling reactions require detailed mechanistic investigation.

Halogen–NHC coupling is also of great interest (Scheme 6).[23,25,81,83] For example, treatment of Pd/NHC complex **17** with chlorine affords salt **18**, very likely by reductive elimination of Cl and NHC from the Pd^{IV} intermediate similar to **4**.[83] The authors emphasize the critical influence of a slight change in the NHC bulkiness on the pathway of Pd^{IV}/NHC intermediates decomposition (Schemes 2 and 6). Oxidation of (NHC)Cu^{I}X complexes **19** with various oxidizers afforded $[NHC–X]^{+}Y^{-}$ salts **20**.[101] DFT calculations supported the high probability of the reductive elimination mechanism.[101] Br–NHC coupling was also observed in reaction of Ag/NHC complex **21** with excess of $CuBr_2$ (Scheme 6).[81] The proposed mechanism of this reaction includes formation of Cu^{III}/NHC complex **22** which suffers reductive elimination of Br and NHC ligands to give imidazolium salt **23**. This mechanism was supported by DFT calculations.[81]

N–NHC bond-forming reactions may proceed by nitrene insertion into M–NHC bond.[102,103] For example, interaction of arylazides with Co^{I}/NHC complexes **24** results in formation of corresponding Co^{III}/NHC intermediates **25** successfully isolated and characterized at low temperatures (Scheme 6).[102] Intermediates **25** undergo nitrene insertion into the Co–NHC bond (considered formally as reductive elimination of nitrene and NHC ligands) to give Co^{I}/NHC complexes **26** (detected and characterized *in situ*). Complexes **26** are unstable and undergo disproportionation to give Co^{II} complexes **27** and other products.[102] A similar intramolecular reaction yields Cu^{I}/NHC complexes **29** from Ag/NHC complexes **28** *in situ* (Scheme 6).[103] Subsequent transformations lead to compound **30**; a plausible mechanism for this sequence was supported by DFT calculations.[103]

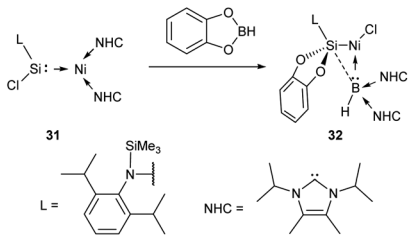


Scheme 6 Representative examples of X–NHC coupling reactions.[81,83,101–103]

3.2. Cleavage of the metal–NHC bond with oxidation of the metal

Reports on metal oxidation at the M–NHC bond cleavage stage are rare. Certain oxidizer-induced reactions may very well proceed with metal oxidation at the M–NHC bond cleavage stage; however, no substantial mechanistic evidence on this point is available.

The interaction of [bis(NHC)](silylene)Ni^{0} complex **31** with catechol borane producing Ni^{II} complex **32** is an intriguing example of oxidative cleavage reaction (Scheme 7).[154] DFT



Scheme 7 The oxidative Ni–NHC bond cleavage reaction.[154]

calculations show that the concerted transfer of Cl from Si to Ni and NHC from Ni to B is a key event in this multistep reaction.[154]

3.3. Cleavage of the metal–NHC bond without alteration in the oxidation state of the metal

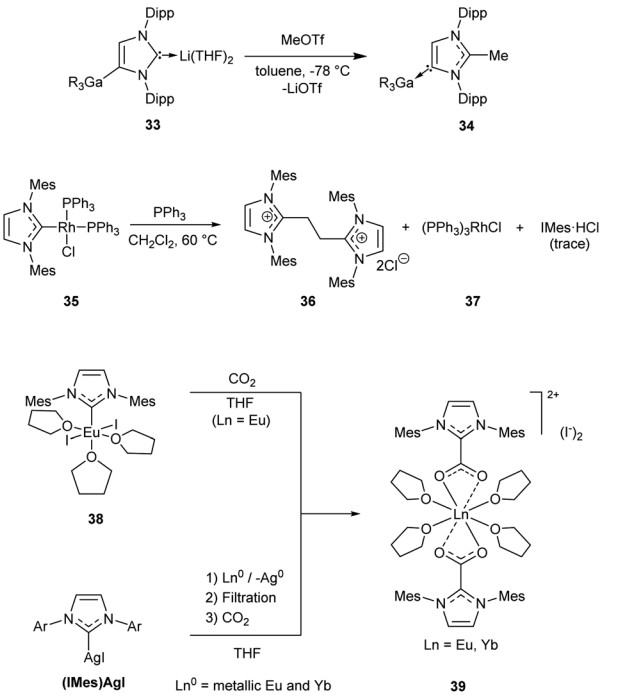
The majority of such reactions can be conventionally classified as (i) M–NHC bond dissociation or (ii) insertion into M–NHC bond. Alternative mechanisms (notably substitution of the metal species through an attack at the carbene carbon) can also be encountered in the literature;[23,25,183] it should be noted that mechanistic details are frequently missing.

3.3.1. C–NHC bond forming reactions. These reactions typically proceed under the action of C-electrophiles, similarly for the complexes of metal cations with NHC ligands and free NHCs. For example, treatment of Li/NHC[105,108] or Na/NHC[111] with MeOTf leads to formation of Me–NHC compounds, for instance product **34** from Li/NHC complex **33** (Scheme 8, Table 1 column 2). The M–NHC bond dissociation preceding the reaction with electrophile can be promoted by the NHC ligand displacement in the presence of alternative ligands capable of coordination with the metal. For example, Rh^{I}/NHC complex **35** reacts with 1,2-dichloroethane (DCE) in the presence of triphenylphosphine to give compound **36** and complex **37**, and no reaction is observed in the absence of phosphine (Scheme 8).[147] The authors assume that phosphine promotes a reversible substitution of NHC ligand which subsequently reacts with DCE. Free NHCs react to afford **36** in high yields under the same conditions.[147]

Treatment of a Eu^{II}/NHC complex **38**, or Yb^{II}/NHC complex prepared *in situ* from (IMes)AgI, with CO_2 affords insertion products **39** (Scheme 8).[126] Similar reactions were described for Sc^{III}/NHC complexes.[124] Reductions of CO_2 with hydride Zn^{II}/NHC complexes are accompanied by formation of zwitterionic NHC–COO adducts.[210,211]

Facile insertions of aldehydes, isocyanates, and carbodiimides into Al^{III}–NHC bond can also be found in the literature.[113,114,120]

3.3.2. The H–NHC bond-forming reactions. Protonolysis is a common M–NHC bond cleavage reaction that leads to formation of azolium salts $[NHC–H]^{+}X^{-}$ and NHC-disconnected metal species. It can be considered as reverse reaction to the formation of M/NHC complexes from azolium salts $[NHC–H]^{+}X^{-}$ (NHC proligands) and metal precursors. Protonolysis can be induced by protic acids, protic solvents or acidic products of the catalyzed reaction. It should be emphasized that for the M/NHC complexes prone to oxidative addition, the alternative pathway of $[NHC–H]^{+}X^{-}$ salt formation may combine the oxidative addition of protic compound with subsequent H–NHC coupling (Section 3.1).

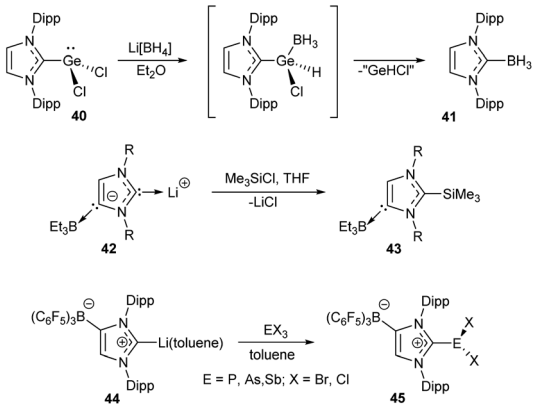


Scheme 8 Representative examples of C–NHC bond forming reactions without alteration of the metal oxidation state.[105,126,147]

Protonolysis reactions proceed very easily for Li/NHC[105,108] and Mg/NHC[112] complexes. Other complexes, including Ag^{I}/NHC,[191,193,197–199,201] Al^{III}/NHC,[119] In^{III}/NHC,[119] Y^{III}/NHC[125] and Ce^{III}/NHC,[125] Mn^{I}/NHC, Zn^{II}/NHC,[213] Mo^{VI}/NHC[130] and Ni^{II}/NHC,[214] are also susceptible to protonolysis; the efficiency depends on the structure of NHC ligands, co-ligands and reaction conditions (Table 1 column 3). For example, $(NHC)_2NiX_2$ complexes (X = Cl, Br, I) suffer facile hydrolysis in aqueous MeCN or THF at 70 °C to give azolium salts and $Ni(OH)_2$.[214] Half-life of the complex decomposition reactions varies from several minutes for the complexes with non-bulky NHCs to about 2 days for $(IMes)_2NiCl_2$.[214]

Even quite stable Pd^{II}/NHC[168,170] and Ru^{II}/NHC[141,215] complexes suffer protonolysis under highly acidic conditions to give azolium salts and the corresponding NHC-disconnected M^{II} species. Remarkably, protolytic cleavage of the Pd^{II}–C_{NHC} bond induced by traces of DCl can be occasionally observed in $CDCl_3$ solution at 40 °C.[215]

3.3.3. The X–NHC bond-forming reactions. In these reactions, heteroatom reagents are thought to act as Lewis acids. Transformations of M–NHC to B–NHC bonds have been reported for Li/NHC,[108] Fe^{II}/NHC[137] and Ge^{II}/NHC[122] complexes (Table 1 column 4). For example, reaction between Ge^{II}/NHC complex **40** and $LiBH_4$ in Et_2O affords NHC–BH_3 adduct **41** (Scheme 9).[122] Reaction of complex **42** with Me_3SiCl affords compound **43** (Scheme 9).[108] A similar adduct was detected by



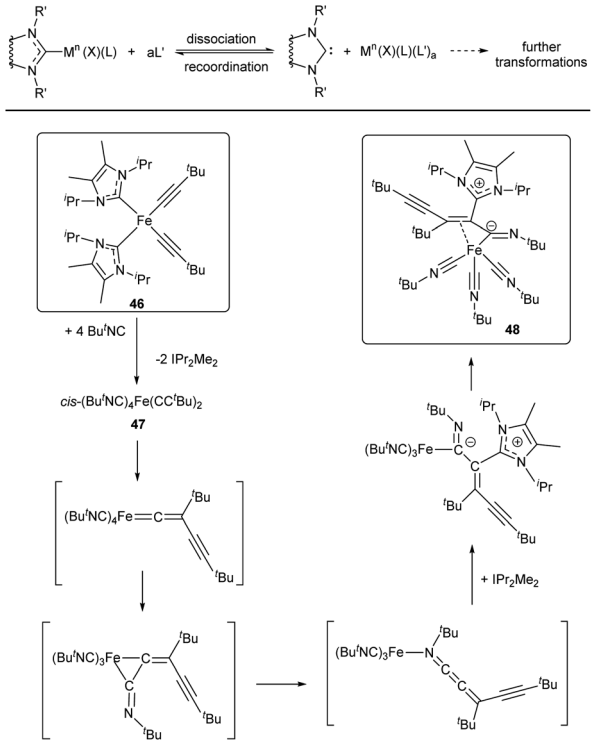
Scheme 9 Representative examples of the X–NHC bond forming reactions preserving oxidation state of the metal.[108,110,122]

NMR in a C_6D_6 solution of $[Pd(I^tBu)_2]$ complex and Me_3SiI after 40 day storage at room temperature;[175] the authors suggested that the NHC–$SiMe_3$ adduct was formed *via* Pd–NHC dissociation and subsequent reaction of the free NHC with Me_3SiI. Facile reactions of PCl_3, PBr_3, $SbCl_3$ and $AsCl_3$ with Li/NHC adducts **44** afford the corresponding P–NHC, Sb–NHC and As–NHC products **45** (Scheme 9).[110]

Pd–NHC bond cleavage in Pd^{II}/NHC complexes under the action of molecular iodine can be also mentioned in this context.[216] In this reaction, NHC is oxidized with iodine to give the NHC·I_2 adduct, while Pd atom retains the 2+ oxidation state. Two feasible mechanisms for this reaction were proposed on the basis of DFT calculations.[216] One of them involves direct electrophilic attack of I_2 at the Pd–NHC bond followed by formation of the NHC·I_2 adduct. The second mechanism involves dissociation of the Pd–NHC bond and subsequent electrophilic attack of I_2 at the free NHC.

3.3.4. The M–NHC bond dissociation and ligand displacement. The M–NHC bond dissociation energies are usually high.[11,12,14,19] They typically fall within the range of 20–47 kcal mol^{-1}, depending on the metal M and NHC bulkiness.[217] Nevertheless, NHCs are capable of facile dissociation from the metal complexes.[25] The M–NHC bond dissociation can be facilitated by the presence of other molecules capable of binding with the releasing NHCs and metal species. Notably, certain ligands (phosphines, CO, isonitriles, *etc.*) promote M–NHC dissociation *via* ligand displacement.[25,138,218–220] Catalytic poisons that capture metals can shift the equilibrium and thus facilitate the M/NHC complexes decomposition.[221] Parameters of the equilibrium and the rates of ligand exchange obviously depend on the relative energies of dissociation of M–NHC and M–L′ bonds (Scheme 10), concentrations, solvent, temperature and the presence of ancillary species.

It should be noted that, although M–NHC bond dissociation does not affect the metal oxidation state, the formed NHC-disconnected metal species may undergo subsequent redox transformations (Scheme 10). To illustrate this point, an interesting case of Fe^{II}/NHC complex **46** reacting with Bu^{t}NC to give compound **48** can be mentioned.[138] This reaction may be



Scheme 10 General scheme of the M–NHC bond cleavage reactions induced by dissociation of NHC ligands and reaction of complex **46** with ^{t}BuNC.[138]

considered as a simple ligand displacement with subsequent transformations of the released species. At the first stage of the reaction, NHC is displaced by Bu^{t}NC ligand. Dissociation of the Fe^{II}–NHC bond thus results in formation of free NHCs and complex **47**, which undergoes a cascade of migratory insertion and migration reactions accompanied by reduction of Fe^{II} and nucleophilic addition of NHC at the final step (Scheme 10).

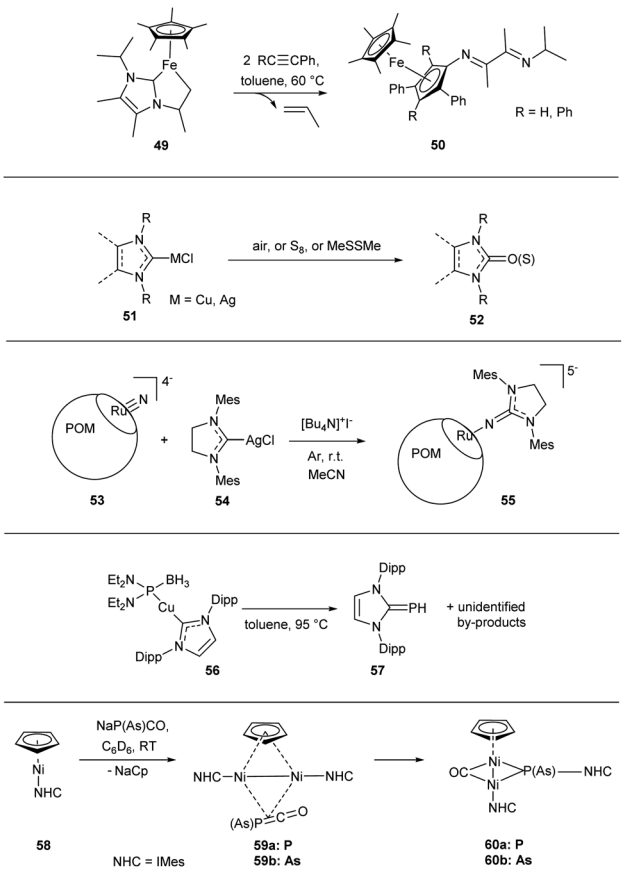
3.4. Other cases of the metal–NHC bond cleavage

Some M–NHC bond cleavage reactions are not attributable to any of the considered types but nevertheless highly relevant.

These include various transformations leading to the NHC ring opening products;[23,25] the mechanisms are multistep and often puzzling. For example, transformation of complex **49** under the action of alkynes leads to compound **50** and is accompanied by release of propylene (Scheme 11).[132]

Oxidation of M/NHC complexes **51**, leading to formation of O–NHC bond and affording imidazoline-2-ones **52** or related substances, certainly deserves attention.[172,181,182,222] For example, homogeneous aerobic oxidation of Cu^I/NHC complexes can be used for preparative synthesis of cyclic ureas (Scheme 11).[181] The reaction is highly sensitive to the NHC steric bulkiness and possibly includes a reductive elimination step. Similar reactions of Cu^I/NHC and Ag^I/NHC complexes with sulfur afford azoline-2-thions.[186–188,207] The mechanisms of these reactions remain unexplored.

Formation of N–NHC bond between ruthenium(VI) nitride-containing polyoxometalate $[PW_{11}O_{39}Ru^{VI}N]^{4-}$ **53**



Scheme 11 Representative examples of the C–NHC and X–NHC bond forming reactions with unclear mechanisms.

and (NHC)AgCl complex **54** in the presence of iodide leads to compound **55** (Scheme 11).[206] The presence of iodide is prerequisite; the authors suggest that iodide ensures reduction of Ru^{IV} to Ru^{III} in the presence of Ag/NHC complex.

Formation of P–NHC and As–NHC bonds is an option as well (Scheme 11). For example, Cu^{I}/NHC complex **56** transforms into phosphaalkene **57** in good yields under heating in toluene at 95 °C.[185] Interaction of Ni^{I}/NHC complex **58** with NaPCO or NaAsCO affords binuclear Ni^{I} complexes **60** *via* intermediates **59**.[157] The mechanisms of these reactions remain unexplored.

4. Rational catalyst design for the tuning of M/NHC catalytic systems

As it follows on from the above discussion, M/NHC complexes can decompose *via* diverse range of M–NHC bond cleavage reactions, and this phenomenon is common for most of the metals and NHC ligands. To a greater or a lesser extent, R–NHC coupling inevitably takes place in catalytic systems and can be quite influential to take it into account.

Given the possibility of M–NHC bond cleavage, what criteria should be used when selecting an M/NHC catalyst to ensure effective catalysis of a particular reaction? What changes in the structure of M/NHC complexes and catalytic conditions would enhance the efficacy of a catalytic system?

We believe that the type of catalytic mechanism is the primary thing to be taken into account. In particular, the NHC-connected and NHC-disconnected modes of catalysis may require quite different optimization approaches.

4.1. The NHC-connected catalysis

M–NHC bond cleavage may represent a serious obstacle for the classical, NHC-connected metal catalysis. This mode of catalysis is dependent on the M–NHC bond stability, as the M–NHC framework participates in catalytic cycle and notably in transition states of the catalyzed reaction. As some excellent reviews on the molecular M/NHC catalysis are available,[7–12,18] we will only briefly consider the properties of catalytic systems that are relevant to the problem of M–NHC bond cleavage.

Catalytic efficacy of M/NHC complexes is highly dependent on:

(i) Electronic and steric parameters of M/NHC complexes, especially the NHC ligands; (ii) the ease of M/NHC complexes activation; (iii) the M–NHC bond stability, both at the activation stage and during the catalytic cycle.

The great success of M/NHC complexes as catalysts is primarily due to the strong sigma electron-donating ability of NHC ligands, which ensures the strong metal–NHC bonding[8,9] and usually accelerates the oxidative addition step. The electron-donating properties of NHCs are chiefly determined by heterocyclic moiety and to a smaller extent by substituents.[8,19,217] The ligands with non-aromatic NHC core (especially the expanded ring NHCs, "abnormal" NHCs, or NHCs with electron-donating groups conjugated with the aromatic N-heterocycle) typically reveal higher sigma electron-donating ability.[11,12,223] Nevertheless, even NHCs with electron-withdrawing groups are sufficiently rich in electron density, *e.g.* to ensure the activation of chloroarenes.[8]

Steric properties of NHCs are evidently more significant for the tuning of M/NHC catalysts in a variety of cross-coupling, addition and CH-activation reactions.[8,9,224] High catalytic activity has been observed for mono-NHC complexes comprising NHC ligands with the bulky and flexible *N*-aryl or *N*-alkyl substituents like, for example, 2,6-diisopropylphenyl.[8,9,18,50,225,226] Such "bulky-yet-flexible"[49,226] NHC ligands typically provide a sufficiently high buried volume (V_{bur}),[11,19,224] and their performance is commonly interpreted in terms of the "flexible steric bulk" concept.[49,227] According to this concept, effective ligands should be electron-rich and "small enough to accept sterically hindered substrates yet sufficiently bulky to support mono-ligation and promote reductive elimination",[228] and the "flexible steric bulk" should allow "the ligands to adapt to the changing needs of the catalytic cycle".[229] In this line, bisoxazoline-derived N-heterocyclic carbene ligands were introduced (IBiox, Fig. 3).[226,229] The IBiox ligands revealed excellent performance in Pd-catalyzed Suzuki–Miyaura coupling between sterically hindered aryl chlorides and boronic acids; the reaction provides access to tetra-*ortho*-substituted biaryls.[229] Cyclic (alkyl)(amino)carbenes (CAACs) demonstrated good

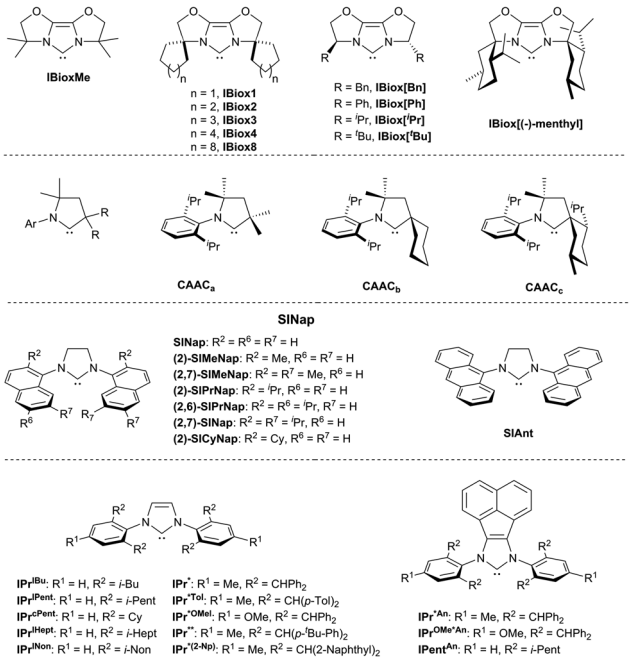


Fig. 3 Major types of bulky-yet-flexible NHC ligands used in M/NHC catalysis.

activity in Pd-catalyzed α-arylation of ketones with non-hindered arylchlorides.[230] However, the most common recognition have been received by families of *N*,*N*′-bis-[2,6-(di-isopropyl)phenyl]imidazol-2-ylidene (IPr) and its saturated analog 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene (SIPr) (Fig. 3).[12,18,49,50,226] The examples include SINap,[231,232] ITent (Tent seems to reflect tentacular structure),[18,49,233] IPr*,[50,234] IPent^{An},[235] IPr*^{An}[236] and other bulky-yet-flexible NHC ligands. Metal complexes with these ligands show superior catalytic activity in various cross-coupling reactions. Besides the N-substituents, heterocyclic core of NHCs also contributes to V_{bur}.[224] For instance, the expanded ring NHCs[237] usually have slightly higher V_{bur} compared to the corresponding imidazol-2-ylidene NHCs with the same N-substituents.[224] Imidazol-2-ylidene ligands with Cl[238] and N(Alk)$_2$[239–242] substituents at C4 and C5 of imidazole ring show enhanced activity in many cross-coupling reactions, apparently due to a buttressing effect of these groups on the N-substituents.[238,242]

It has been commonly believed that steric bulkiness facilitates reductive elimination. However, DFT calculations show that IPr ligands can also facilitate oxidative addition of aryl halides, owing to favorable intramolecular π–π and C–H/π interactions between ArCl and bulky N-substituents (steric attraction) that decrease the activation barriers.[243] Thus, bulky groups can accelerate not only the reductive elimination, but also the oxidative addition step.[243] Moreover, it was revealed experimentally that bulky NHCs with aromatic N-substituents like IPr and IMes provide better activation of Pd nanoparticles in the Pd catalyzed hydrogenolysis of bromobenzene than NHCs with alkyl N-substituents (ICy, IMe).[46] X-ray photoelectron spectra revealed that NHCs with aromatic N-substituents provide higher donation of electron density to Pd nanoparticles than NHCs with aliphatic N-substituents. The effect was explained by DFT calculations, which showed that NHCs like IPr and IMes bind to Pd nanoclusters not just by the carbene carbon but also by aromatic N-substituents *via* their delocalized π-orbitals.[46] Such coordination facilitates the transfer of electron density from NHCs to Pd nanoclusters and lowers the activation barriers of aryl halide oxidative addition.[46] Thus, NHC ligands with bulky aromatic N-substituents can also promote oxidative addition to the NHC-connected metal clusters and nanoparticles.

However, correlation between steric bulkiness and catalytic activity is not straightforward and optimum dependence is observed oftentimes.[49,226] For example, in the Suzuki–Miyaura coupling of 2-chloromesitylene with 2,6-dimethylbenzene boronic acid activity of Pd complexes with ITent ligands increased significantly from IPr to IPent, then it decreased from IPent to IHept and INon. A similar effect, with the highest activity for IHept, was observed in Buchwald–Hartwig amination.[49] In C–S cross-couplings between aryl halides and thiols, the excessively bulky IPr* and IPr*OMe ligands provide lower reaction rates but higher selectivity than IPr.[54] In reactions of alkyne hydrothiolation, Pd and Ni complexes with IMes ligand show better catalytic performance than corresponding complexes with the bulkier IPr and SIPr ligands.[100,244]

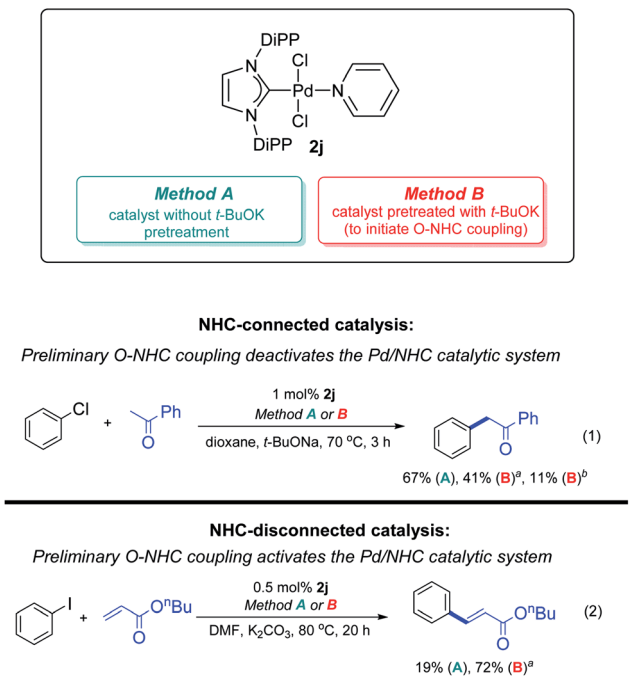
The next important factor in the catalytic performance of M/NHC complexes is the ease of their activation under catalytic conditions.[25] Well-defined and stable M/NHC precatalysts often require transformation into active form capable of catalysis. Activation can include only removing of throw-away ligand, for example chloride in (NHC)AuCl complexes, and may be facilitated by more bulky NHC and external activators like silver salts used for capture halide ions.[25] In many cases the activation requires reduction of a stable M^{n+2}/NHC precatalyst to active M^n/NHC species that enter the oxidative addition step. For example, Pd^{II}/NHC complexes must be reduced to Pd^0/NHC complexes which activate aryl halide and thus initiate C–S cross-coupling with thiols.[98] Reduction of the metal is usually accomplished by using external reducing agents or sacrificial ligands. The ease of activation is essential for the catalytic output.[55,98,245] Hardly activated Pd^{II}/NHC precatalysts are highly prone to formation of the catalytically inactive thiolate complexes and Pd–NHC bond breaking products associated with deactivation of the catalytic system.[55,98]

Stability of M–NHC bond is a very important point, both at the activation stage and during catalysis. Foremost, if metal can change its oxidation degree by 2 in catalytic conditions, activators and typical reagents can induce reductive elimination of NHC ligands from the M/NHC catalyst. C–NHC, H–NHC and X–NHC couplings are highly probable in such systems. For example, ESI-MS monitoring of various Pd/NHC complexes with IMes, IPr, SIpr and other typical ligands in DMF solution of iodobenzene at 100 °C revealed decomposition of the complexes and facile formation of the Ph–NHC coupling products.[64] H–NHC coupling represents a problem during the activation of M/NHC complexes with hydride donors, *e.g.* alcohols or aliphatic amines.[54,59,62] Strong bases, *e.g.* alkali metal

alkoxides and hydroxides used in many catalytic systems, may trigger O–NHC coupling.[97] The effect of O–NHC coupling on the catalytic performance of PEPPSI–IPr precatalyst was assessed in the reaction of acetophenone CH-arylation with chlorobenzene. Simple preheating of PEPPSI–IPr **2j** with *t*-BuOK for 10 min and 3 h at 100 °C led to, respectively, 26% and 56% decrease in the yields of CH–arylation product (Scheme 12).[97] It should be remembered that M/NHC complexes with metals in the highest oxidation states, *e.g.* Ni^{IV} and Pd^{IV}, are susceptible to the reductive elimination of NHC, and the use of such complexes in catalytic systems with assumed participation of M^{IV} species may be inefficient due to their low stability.[60] It should also be noted that activated M^0/NHC complexes are usually susceptible to M–NHC bond dissociation and prone to ligand displacement and elimination, which may trigger formation of metal clusters and nanoparticles.[25]

Thus, suppression of the undesirable M–NHC bond cleavage is generally beneficial for the NHC-connected metal catalysis, and to protect this bond by rational catalyst design is challenging.

Reductive elimination of NHC ligands can be suppressed by building them up with bulky-yet-flexible moieties; this approach also helps to minimize formation of dimeric M–M species.[25] However, bulky NHC ligands and strongly binding co-ligands can hinder reductive activation.[25] In such cases, the use of ancillary sacrificial ligands as internal reductants for pre-catalyst activation is feasible. For example, allyl, cinnamyl and related anions are used as convenient sacrificial ligands which



Scheme 12 Possible impacts of O–NHC coupling on the Pd-catalyzed C–C coupling reactions. Method A: pretreatment of the catalyst with *t*-BuOK for 10 min at 100 °C. Method B: pretreatment of the catalyst with *t*-BuOK for 3 h at 100 °C. Adapted with permission.[97] Copyright © 2018 Royal Society of Chemistry.

can activate Pd^{II}/NHC and Ni^{II}/NHC complexes under the action of alkoxide anions.[57,246,247] The use of cinnamyl or η^3-indenyl sacrificial ligands in combination with a bulky NHC ligand ensures facile precatalyst activation while suppressing the formation of Pd^{I}–Pd^{I} dimeric species.[248,249]

Morpholine as a sacrificial co-ligand for the base-induced activation of Pd^{II}/NHC complexes in C–S cross-coupling reactions was successfully used.[55] Preparation of the aliphatic amine complexes in advance turned out to be redundant, as a variety of primary and secondary amines in combination with strong bases can be used directly for the activation of Pd–PEPPSI complexes in C–S cross-coupling reactions.[54] Strong bases (*e.g.* potassium *tert*-butoxide) deprotonate the NH group of Pd-coordinated amine in the *in situ* formed amino complexes and facilitate β-hydride transfer from amine to Pd. Besides, the base accelerates reductive elimination of HX from the forming hydride intermediates (NHC)PdHXL thus decreasing their concentration and suppressing the undesirable H–NHC coupling.[54]

Undesirable formation of (NHC)PdHXL intermediates can be suppressed, in some reactions, by using special additives serving as reversibly coordinating ligands. For example, it was disclosed recently that deactivation of Pd/NHC catalysts in Negishi reaction of alkylzinc reagents can be effectively diminished by the addition of LiBr.[165] Excess of bromide ions help to keep Pd atom coordinately saturated in (NHC)Pd(Alkyl)(Aryl)Br catalytic intermediates thus preventing β-hydride transfer from alkyl group to Pd leading to hydride complexes responsible for catalyst deactivation *via* H–NHC coupling.[165]

Stability of M/NHC complexes against reductive elimination of NHC ligands can be enhanced by the use of chelated NHC–ligands.[250–252] For example, certain complexes with the tridentate pyridine-bridged bis-NHC ligands resist Me–NHC coupling even at 150 °C.[250] However, stability of chelated NHC complexes significantly depends on steric factors and can be affected by bulky N-substituents (*e.g.* ^{t}Bu).[250] Moreover, stable tridentate ligands can hinder coordination of reagents to the metal by reducing the availability of vacant coordination sites.[25] For this reason, bidentate chelated NHC ligands that contain a second donor functionality less strongly binding with the metal center and capable of reversible dissociation (oxygen, nitrogen, sulfur, phosphine, or other hemilabile group) may be a better option for certain catalytic systems.[5,25,253–255]

Overall, rational balance between steric bulkiness and flexibility of NHC ligand, combined with the ease of the throw-away ligands elimination and the use of effective activators, is a prerequisite for high efficacy of the NHC-connected metal catalysis.

4.2. The NHC-disconnected catalysis

One may doubt concerning the benefits of the use of M/NHC complexes in reactions catalyzed by NHC-disconnected metal species. Indeed, the NHC-disconnected mode implies the breakage of the M/NHC complex. Isn't it better to use some cheaper metal salts or complexes?

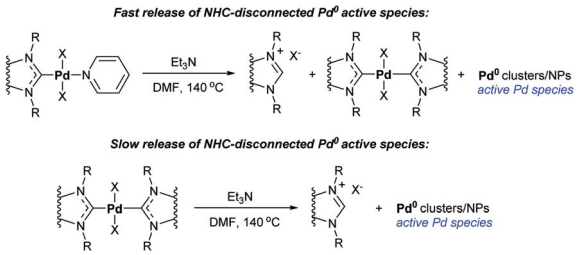
Apparently, there are quite a few reactions proceeding in the mode of NHC-disconnected metal catalysis, in which the M/NHC complexes can be successfully replaced with cheaper metal compounds. For example, in the Pd catalyzed Mizoroki–Heck reaction of butyl acrylate with iodobenzene relatively cheap $Pd(OAc)_2$ combined with a tetraalkylammonium salt $[Bu_4N]^+Br^-$ (Pd nanoparticle stabilizer) demonstrated efficacy no worse than Pd/NHC complexes in the same conditions.[27] However, in certain catalytic systems operating by NHC-disconnected metal catalysis, the use of M/NHC precatalysts is reasonable, because of unique features provided by $[NHC–R]^+$ counterions and $[NHC–R]^+X^-$ salts stabilization mechanisms (Fig. 2C and D).

The NHC-disconnected metal catalysis can be conventionally described as ligandless.[38–40,43,256] In this mode, performance of a catalytic system depends significantly on the rate of active metal species formation and their working concentration in solution.[38,40,43,256] In the reactions driven by M^0 active species, agglomeration of M^0 nanoparticles into inactive metal precipitates poses a serious problem.[39] A well-known example of this effect is formation of palladium black in Pd-catalyzed reactions. Actual concentrations of active M^0 species in such systems depend on the rates of their formation from a precatalyst as related to their stability.[38,40,43,256] In many cases, concentration of M^0 active species significantly affects their stability, with higher concentrations enhancing the rates of agglomeration thus destabilizing the catalytic system.[38,256]

The use of M/NHC complexes allows fine tuning of the rates of M^0 active species formation; at the same time, organic products of M/NHC decomposition may act as stabilizers for the active metal species despite the M–NHC bond absence (see Fig. 2 as an example).

The main impact of M/NHC precatalyst structure concerns the rate of formation of NHC-disconnected active metal species. This rate strongly depends on the rate of the M–NHC bond cleavage which, in turn, depends on the structure of the NHC ligand and co-ligands.[27,54,58–60,62,63,97] M/NHC complexes with bulky NHC ligands (or bis-NHC complexes,[59] especially chelated[250]) are usually more resistant to R–NHC coupling and therefore decompose slower than NHC complexes with non-bulky NHC ligands. For example, the rate of Mizoroki–Heck reactions shows inverse relationship with the stability of Pd/NHC precatalyst.[27,250]

Decomposition of Pd–PEPPSI–IPr precatalyst *via* O–NHC coupling by preheating with *t*-BuOK enhances its catalytic performance significantly (Scheme 12).[97] Moreover, catalysis of Mizoroki–Heck reactions by Pd–PEPPSI complexes in the presence of aliphatic amine bases has been shown to proceed by a previously unknown mechanism of the active species generation that provides enhanced robustness of the formed catalytic systems (Scheme 13).[59] Heated with tertiary aliphatic amines (*e.g.* triethylamine) under typical conditions of the Mizoroki–Heck reaction, Pd–PEPPSI complexes undergo the amine-induced H–NHC coupling. The reaction is channeled as follows: at first, Pd–PEPPSI precatalyst reacts with amine to give a primary pool of active metal clusters or nanoparticles while releasing a primary portion of NHC ligand in the form of



Scheme 13 Reactions of fast and slow release of the NHC-disconnected Pd^0 active species in the catalytic systems with Pd–PEPPSI precatalyst and triethylamine.[59]

azolium salt $[NHC–H]^+X^-$ (Scheme 13). The released NHC reacts promptly with the Pd/NHC species in solution to produce a relatively stable bis-NHC complex $Pd(NHC)_2X_2$, this process can also occur due to Pd–NHC bond dissociation. The second channel involves sluggish decomposition of the formed bis-NHC complex for continuous production of the azolium salt and active Pd clusters or nanoparticles (Scheme 13). Thus, the bis-NHC complex acts as a molecular reservoir of active metal species. The observed combination of fast- and slow-release channels ensures prolonged performance of the catalytic system. The efficiency of this approach and the correctness of its mechanistic interpretation were confirmed experimentally; the setting included repeated cycles of filtration of the reaction mixture and reloading with fresh substrates.[59]

As mentioned above, another benefit of using M/NHC precatalysts for the NHC-disconnected catalysis concerns stabilization of active metal species with azolium salts derived from NHC-ligands. The M–NHC bond cleavage *via* H–NHC coupling, protonolysis or C–NHC coupling produces azolium salts $[NHC–R]^+X^-$. Azolium salts are well-known stabilizers of metal nanoparticles.[257,258] Imidazolium cations formed *via* C–NHC coupling provide enhanced stability against strong bases and are known as highly promising subclass of ionic liquids.[72]

Thus, active metal clusters and nanoparticles formed from M/NHC precatalysts can be effectively stabilized *in situ* by azolium salts. This mechanism was proposed for Pd/NHC catalysis in Mizoroki–Heck reaction[27] and confirmed experimentally for Rh/NHC catalyzed hydrogenation of arenes. Under conditions of arene hydrogenation, by means of *ex situ* and *operando* XAFS studies, scanning transmission electron microscopy and IR spectroscopy, it was revealed that [(CAAC)Rh(COD)Cl] complexes form Rh nanoparticles stabilized with the cations of protonated CAAC (Fig. 4), which function as active centers for the arene hydrogenation.[148,149] Moreover, CAAC-derived products adsorbed on Rh nanoparticles were shown to play a key role in providing high chemoselectivity of fluorinated arenes hydrogenation.[259] Remarkably, azolium cations can effectively stabilize anionic $[PdX_3]^-$ complexes released from Pd/NHC precatalysts in Mizoroki–Heck reactions at low Pd loadings (0.1 mM concentrations and below).[62] Ionic complex $([NHC–Ph]^+)_2[Pd_2X_6]^{2-}$, formed by fast Ph–NHC coupling and isolated from the reaction mixture, was recognized as a new type of ionic palladium precatalysts for

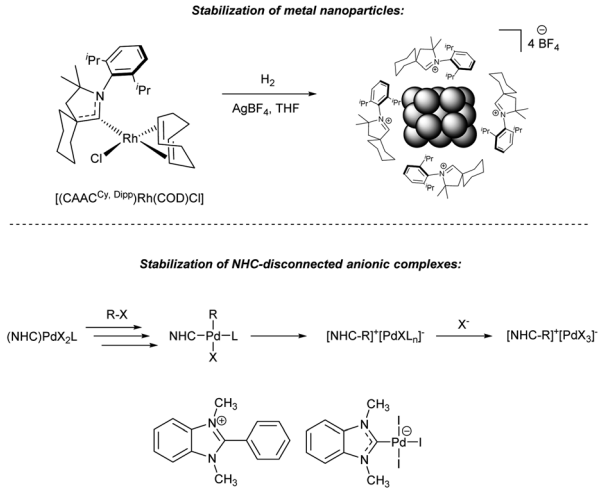


Fig. 4 Stabilization of the NHC-disconnected active metal species with azolium salts formed from M/NHC precatalysts. (a) Rh nanoparticles in the [(CAAC)Rh(COD)Cl]-catalyzed arene hydrogenation;[148,149] (b) anionic Pd complexes in Mizoroki–Heck reaction.[62]

Mizoroki–Heck reaction. In this case, the $[NHC–Ph]^+$ cation acts as ionic stabilizer for NHC-disconnected active species; the ionic state prevents aggregation and progressive deactivation of the catalyst in diluted solutions.[62]

Overall, in certain catalytic systems M/NHC precatalysts can provide high catalytic performance owing to the regulated release of NHC-disconnected M^0 active species and their *in situ* stabilization by azolium salts and non-coordinative cations derived from the NHC ligands.

5. Recycling and sustainability aspects of M/NHC systems

Consideration of catalyst recycling highlights a long-standing contradiction in the area of M/NHC catalysis. On one hand M/NHC complexes were believed to be highly stable, while on the other hand the number of successful recycling experiments is drastically limited. In fact, molecular M/NHC complexes are not considered as easily recyclable catalysts.[260–265] The topic disclosed in the present review sheds some light on this problem. Indeed, catalyst evolution readily takes place during M/NHC-catalyzed reactions and in many cases the complexes can not be recycled in initial state. It should be mentioned that supported heterogenized M/NHC catalysts were studied for several reactions to perform recycling,[266–270] however it is a different approach which is not considered in details here.

Among the three possible pathways for M/NHC catalysis, catalyst recycling in the NHC-connected molecular mode (Fig. 2B) is less studied. Many M/NHC complexes are stable under catalytic conditions and retain their activity due to the strong M–NHC bond. However, a few only can be recovered in their initial form after the reaction. (NHC)NiCl(Cp) complexes were used in a regioselective Markovnikov-type thiol-yne click reaction.[100] (IMes)NiCl(Cp) complex was found to be the most active catalyst. However, its recovery, although technically possible, was profoundly inefficient. The losses were due to IMes-S coupling that acted as the major catalyst decomposition pathway during the reaction.

Of note, there is another possible option, which includes a different type of supported heterogenized NHC systems. Heterogenized systems have been reviewed previously and are not considered here (corresponding reviews can be found elsewhere[269,270]).

Recycling with NHC-disconnected molecular catalysis involving ionic species (Fig. 2C) is more feasible, although yet not explicitly explored. One of the major pathways to irreversibly eliminate NHC from the coordination sphere of palladium is Ar–NHC coupling. This process leads to ionic pair that can be stabilized in solution by either decreasing the concentration or increasing the ionic strength. Adjustment of these parameters allowed efficient isolation of the $[NHC–Ph]^+[NHC–PdI_3]^-$ (NHC = 1,3-dimethylbenzimidazol-2-ylidene) ionic complex from the reaction mixture; it was successfully reused for five consecutive cycles without loss of catalytic activity (Fig. 5).[62]

With increasing cycle number, the $[NHC–Pd(I)_3]^-$ was progressively transformed into ligandless $[PdI_3]^-$, although the $[NHC–Ph]^+[PdI_3]^-$ became detectable by TLC, NMR and ESI-MS after the fifth cycle only. A solid dimer of this complex with $[Pd_2I_6]^{2-}$ anion readily dissociates in solution. In the studied Mizoroki–Heck reaction, H–NHC coupling acts as a reversible pathway to the molecular NHC–Pd bonded mode of catalysis, whereas Ph–NHC coupling promotes formation of a stabilizing non-coordinating cation to keep the metal in its active form.

Noteworthy, leaching driven formation of NHC-disconnected ionic systems might be a promising method to achieve catalyst recycling. C–C and C–H oxidative additions to

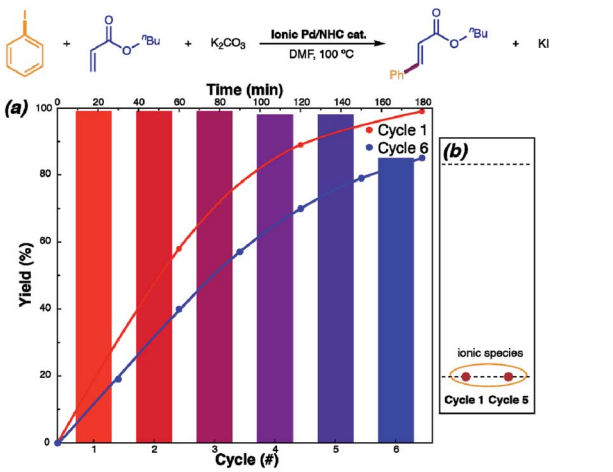
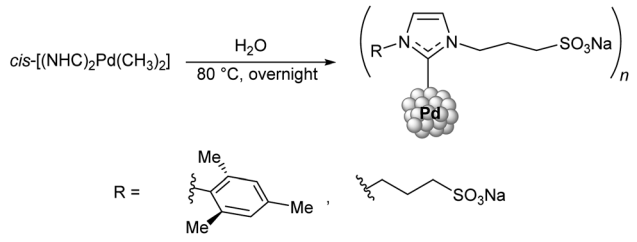


Fig. 5 Ionic Pd/NHC-catalyzed Mizoroki–Heck reaction with counterion stabilization: mechanism, recycling, and scope. The reaction was examined for recovery of the ionic Pd/NHC complex. (a) Reaction profiles for a sequence of cycles, with cycle 6 performed after 3 week storage of the isolated catalyst. (b) Model TLC analysis of the ionic Pd/NHC complex catalyst recovered after cycles 1 and 5. Adapted with permission.[62] Copyright ©2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.



Scheme 14 Synthesis of water-soluble Pd NPs by thermal decomposition of the dimethyl bis-NHC complexes.[166]

palladium nanoparticles promote separation of individual metal complexes and their leaching into liquid phase. The heating of $[NHC–Me]^+$ salt with aryl halides in the presence of palladium nanoparticles, copper or nickel salts leads to formation of $[NHC–Ar]^+X^-$ salts, that is a vivid example of the C–C bond oxidative addition-driven leaching.[61]

In the meantime, high concentrations of precatalyst promote sintering of the NHC-disconnected palladium, and catalyst recycling in the metal cluster pathway (Fig. 2D) can be achieved. In general, it follows the more developed approach, available for cocktail-type systems.

Some NHC–Pd–R complexes are thermally labile but capable of forming water-resistant nanoparticles stabilized by NHC ligands. A protocol for obtaining Pd nanoparticles (NPs) from $(NHC)_2PdMe_2$ (NHC = 3-sodium sulfonatopropyl substituted imidazolylidene) was developed by water-mediated thermal decomposition of the complex at 80 °C (Scheme 14).[166] This reaction yields both NHC–Me and NHC–H products (corresponding to about 60% and 40% of the conversion, respectively). The metal-free NHC species eventually bind to the forming Pd NPs, which makes them water-soluble. The resulting Pd NPs successfully catalyzed 10 consecutive cycles of styrene hydrogenation in water, and no degradation of the catalyst by precipitation of bulk palladium was observed during the reaction.

Although it is usually not accentuated, leaching that affects nanoparticle catalysts in the systems with NHC–H precursors might be classified as NHC ligand-assisted leaching due to activation of the C–H bond by either a base or direct M^0 oxidative addition.

To summarize this section, recycling of M/NHC complexes for re-use in the further reaction is on the early stages of development. More in depth studies are required to develop efficient recycling protocols and solve sustainability problem. Revealing the nature of active species is the key-requirement for successful recycling.

6. Conclusions

M/NHC complexes have been long considered as robust homogeneous catalysts with catalytic performance substantially dependent on the enhanced strength of the $M–C_{NHC}$ bond. It is currently becoming clear that the M–NHC bonds are susceptible to facile cleavage even under mild conditions. The integrity of the M–NHC framework can be violated by reactions of reductive elimination, protonolysis and ligand displacement. The analysis carried out in this article shows that M–NHC bond cleavage phenomenon is typical for most of the metals and NHC ligands and may significantly affect the catalysis. Among the considered reactions (Table 1), the H–NHC bond formation may be a reversible step, while many cleavage reactions with the formation of C–NHC and X–NHC bonds may not be reversible under catalytic conditions.

The impact of the M–NHC bond breakage on a catalytic system largely depends on the mode of its functioning (Fig. 2). Many M/NHC-catalyzed reactions proceed by NHC-connected mechanisms where the M–NHC framework directly participates in catalytic cycle, notably affecting transition states of the transformation. In such cases, the M–NHC bond cleavage is highly undesirable as it ultimately leads to deactivation of the catalytic system.

However, a number of reaction systems operate in the NHC-disconnected catalysis mode, with M/NHC complexes acting as precursors of active species. In such systems, M–NHC bond cleavage leads to the generation of active centers and, thus, represents a process of catalyst activation. Rational M/NHC catalyst design should therefore account for the type of catalytic mechanism.

In the systems that operate in the mode of NHC-connected metal catalysis, the structure of the M/NHC catalyst has to ensure a combination of high catalytic activity with sufficient stability of the M–NHC framework. At present, the most reliable approaches are based on the rational balance between the steric bulkiness and flexibility of NHC ligands combined with the use of easily eliminated throw-away co-ligands and effective activators. A new promising approach is to use chelating NHC ligands that, in addition to the strongly binding NHC carbon, contain a mild donor site capable of switchable coordination/decoordination with the metal.

In the systems that operate in the mode of NHC-disconnected metal catalysis, the M/NHC precatalyst should provide the optimal rate of M–NHC bond breaking to release the active metal species. At the same time, the products of M/NHC decomposition have to ensure effective stabilization of the active species (unless it is ensured by the use of ancillary stabilizers).

Processes of M–NHC bond cleavage can change molecular M/NHC catalytic system to nano-sized dimension. Nanoparticles bearing NHC frameworks are actively studied and found their applications in many fields, including materials science, which is not a subject of this review. Alongside, clusters being a transition between nanoparticles and molecular systems are of high importance. Many clusters were proposed to possess high catalytic properties, however studies of well-defined metal clusters with NHC ligands are yet very limited. Thus, pronounced developments in this area are anticipated in the near future.

We hope that this review will draw attention of researchers to the problem of M–NHC framework lability and promote the development of new effective approaches for the rational design of M/NHC catalytic systems.

Conflicts of interest

There are no conflicts to declare.

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