Metal-organic frameworks containing N-heterocyclic carbenes and their precursors
Chizoba I. Ezugwu^{a,b}, Nawsad Alam Kabir^{a,b}, Mehman Yusubov^c, Francis Verpoort^{a,b,c,d,*}

^a: *Laboratory of Organometallics, Catalysis and Ordered Materials, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing; Center for Chemical and Material Engineering, Wuhan University of Technology, Wuhan, People's Republic of China.*

^b: *Department of Applied Chemistry, Faculty of Sciences, Wuhan University of Technology, Wuhan 430070, People's Republic of China.*

^c: *National Research Tomsk Polytechnic University, Lenin Avenue 30, 634050 Tomsk, Russian Federation.*

^d: *Ghent University, Global Campus Songdo, 119 Songdomunhwa-Ro, Yeonsu-Gu, Incheon, Korea.*

Email: francis.verpoort@ghent.ac.kr

Abstract

Metal-organic frameworks (MOFs) are coordination networks formed by self-assembly of metal ions or clusters and organic linkers. The functionalities and versatilities of MOF materials are enhanced by designing the frameworks with linkers, which have extra active functional groups that can be modified presynthetically, in situ, or postsynthetically. The carbenic carbon in N-heterocyclic carbenes enhances the potential of MOFs synthesized from azolium-containing linkers. In this review, we provide a survey and discussion of N-heterocyclic carbene precursor-containing MOFs and their various applications. This review will guide researchers and synthetic chemists attempting to design MOFs from N-heterocyclic carbene precursors.

Keywords: MOFs, NHC precursors, Azolium-containing ligands, Postsynthetic modification.

Contents

1. Introduction
2. Metal-organic frameworks
3. Carbenes and NHCs

- 3.1 Stability and reactivity
- 4. NHC-metal bonds
 - 4.1. NHCs as σ - and π -donors and as π -acceptors
 - 4.2. Steric effect
- 5. Azolium-containing MOFs
 - 5.1 Why azolium-containing MOFs?
 - 5.2 Past work on azolium-containing MOFs
 - 5.3 Synthetic methods of incorporating azolium or NHC entities into MOFs
 - 5.4 Different azolium-containing ligands used for MOFs
- 6. PSM of azolium-containing MOFs
- 7. Applications
 - 7.1. Catalysis
 - 7.2. Adsorption of organic molecules
 - 7.3. Fuel cells
 - 7.4. Gas separation
- 8. Conclusions and outlook

1. Introduction

For a long time, traditional microporous inorganic and organic materials such as zeolites and activated carbons, respectively, have been useful in many industrial applications [1]. Some limitations of these traditional materials inspired synthetic chemists to use the molecular building block approach to generate analogous three-dimensional hybrid microporous materials with improved chemical, physical, and structural properties.

The emergence of metal-organic frameworks (MOFs) revolutionized the nanosciences with respect to the unlimited possibilities of combining the metal nodes and organic linkers to obtain the desired frameworks. The size of the resulting voids is determined by the length and functionality of the ligand. The exceptionally high surface area, large pore size, and chemical tunability of MOFs have resulted in their emergence in the forefront among microporous

materials. Owing to the rigid tetrahedral oxide skeletons of zeolites, the tunability of their pores is restricted, unlike that of MOFs, which can be easily tuned after synthesis. Consequently, the skyrocketing number of publications that report each year on MOFs is quite astounding [2]. MOFs are very interesting because of their versatile applications [3, 4]. Moreover, the functionalities and applicability of MOFs are enhanced by their being designed with a linker with an extra active site that can be modified presynthetically or postsynthetically. Azolium-containing ligands, which are precursors of N-heterocyclic carbenes (NHCs), are good examples of such linkers. Not only do NHCs immobilized in MOFs have the ability to increase the functionality of the frameworks and heterogenize the NHC complexes, but they also synergize the catalytic potentials of MOFs and NHC complexes.

The high σ -donor and low π -acceptor ability of NHCs augment their potential to tether to many metal ions. Although NHCs were thought to be pure NHC-to-metal $\sigma \rightarrow d$ donors, it has been realized that they are also involved in metal-to-NHC $d \rightarrow \pi^*$ and NHC-to-metal $\pi \rightarrow d$ donations when bonded to a metal [5]. NHC complexes have a wide range of applications, mainly in catalysis. Notwithstanding the fact that NHC complexes have efficient and wide catalytic applications, these catalysts are mainly homogeneous in nature. One of the ways of heterogenizing these catalysts is by the use of azolium-based linkers for the synthesis of the frameworks, followed by postsynthetic modification (PSM) by tethering a metal to the carbene carbons [6]. Alternatively, NHC complexes can be used as linkers for the synthesis of MOFs.

In this review, the literature on azolium-containing MOFs is summarized. The need for the use of azolium linkers for MOFs, PSM, and applications of these frameworks are discussed. This review will guide present and future researchers working on MOFs synthesized from NHC precursors.

2. Metal-organic frameworks

Improvements in a new class of porous coordination polymers, which is denoted as MOFs, have been witnessed recently [1]. An MOF is a coordination network with organic ligands containing potential voids [7]. Generally, these frameworks are known for their well-defined crystallographic and geometric structures [8]. MOFs have gained the attention of scholars because they do not collapse on removal of the guest molecules from the pores. This is an essential property, which allows such compounds to be used in different applications, such as gas

storage [3, 9], gas separations [8, 10], heterogeneous catalysis [11-13], and drug delivery [14, 15]. These structures consist of metal-based nodes [16] (single ions or clusters) bridged by organic linking groups to form one-, two-, or three-dimensional coordination networks [17, 18] (Fig. 1).

Most of the porous MOFs are built on metal clusters, usually referred to as “secondary building units” (SBUs) [20]. An SBU is a unit of “polynuclear clusters” constructed from two or more metal ions and multidentate carboxylate (or other coordination moiety) linkers [17]. The SBU is unique because it is usually not a reagent in the synthetic scheme, but is generated in situ under particular synthetic conditions [18]. The conceptual theory of the SBU has been introduced to help define the geometry adopted around the metal entities of MOFs. It is from the SBU that the ligands extend out in the ordered geometric array that forms the framework [17]. Usually transition metal ions are used as the metal centers of the SBU owing to the ability of transition metal ions to adopt a large variety of coordination numbers, resulting in a variety of geometries, ranging from linear to pentagonal-bipyramidal, as well as the distorted forms of each or them [17, 21-23]. First-row transition metals are most commonly used as the metal ions of MOFs because they have the following characteristics: fixed coordination geometry, high availability, low expense, and well-understood chemical bonding [22]. Besides these characteristics, the nature of the metal has an effect on both the catalytic and the adsorption properties of MOFs. A metal with known catalytic function should be incorporated if the constructed MOF is to have the desired catalytic property. On the other hand, for the construction of MOFs, the choice of the ligand in terms of functionality, shape, and size is considered. For example, ditopic ligands with a bend angle of 180° will have a propensity to form various molecular dimensional frameworks [24, 25].

Among the versatile applications of MOFs [26], gas storage is one of the most promising applications. The measurement of a gas isotherm is very important in order to determine the permanent porosity of the framework in which the pores are fully evacuated [23, 27-29]. Many MOFs are especially air sensitive and moisture sensitive following the evacuation of the pores, leading to the need for careful handling under an inert atmosphere if the best performance characteristics are to be obtained.

Type I isotherm shapes with little or no hysteresis are expected for frameworks with uniform micropores (Fig. 2) [18, 30, 31]. Figure 2 shows the considerable increase in the nitrogen isotherm among MOF-2, MOF-5, and MOF-177, and indicates that MOF-177 has a higher surface area than MOF-2 and MOF-5. These rigid structures can be used for molecular sieving by size exclusion of gas molecules [32].

Catalytic behavior has also been reported for MOFs [33, 34]. MOFs combine the benefits of both heterogeneous and homogeneous catalysis [35]. It is possible to prepare MOFs in which the catalytic functions are efficient at their three major components: the metal nodes, the organic linker, and the porous system. Catalysis at the void may occur by encapsulation of catalytically active noble metal nanoparticles inside the pores of the MOFs [36]. Unsaturated metal nodes in MOFs initiate catalysis at the nodes [37], and the use of linkers with an extra functional group that was not involved in framework synthesis results in catalysis at the organic linker [38].

3. Carbenes and NHCs

The carbenic carbon can be electrophilic or nucleophilic, and thus metal-carbene species have greatly impacted synthetic chemistry [39]. In 1964, Fischer and his students introduced carbenes into inorganic and organometallic chemistry [40]. The carbene complexes they discovered were characterized as having an electrophilic carbenic carbon, but later carbenic complexes with a nucleophilic carbenic carbon were isolated by Schrock [41]. Subsequently, Öfele [42] and Wanzlick and Schönherr [43] independently reported the first NHC-transition metal complexes [44, 45]. They independently produced these by use of a basic metal precursor to deprotonate an imidazolium salt to form imidazolin-2-ylidene complexes.

For a long time, carbenes were considered overreactive and short-lived molecules that could not be isolated without dimerization [46, 47]. However, interest in the use of these systems as ligands was limited until the isolation of a stable, crystalline NHC by Arduengo et al. [46] in 1991. NHC is a singlet carbene, with the carbene being incorporated in a nitrogen-containing heterocycle [45]. This first stable NHC was based on the imidazol-2-ylidene ring, having adamantyl groups as substituents on the nitrogen atoms (see Fig. 3). It has thermodynamic as well as kinetic stability in the absence of oxygen and moisture. This structure was thought to be

protected from dimerization by the steric hindrance of the adamantyl groups, but later the isolation of NHCs with N-substituents, far less bulky than adamantyl, clearly indicated that steric hindrance is not the only factor explaining the stability. Indeed, adequate electronic stabilization of the carbene center in imidazol-2-ylidenes is enough to isolate free NHCs even in the absence of steric protection [48].

Since this isolation, remarkable research efforts on the synthesis of NHCs, preparation of the corresponding metal complexes, and their applications in metal-based catalysts have been made in this field [49-56]. In addition, the organocatalytic applications of NHCs were reviewed by Enders et al. [57]. The most commonly encountered N-heterocycles are those that have imidazole rings. Their electron-rich heterocycle provides a suitable structure that stabilizes the carbene center [58, 59]. Generally, NHC ligands are formed by the deprotonation of an N,N'-disubstituted imidazolium (or other azolium) salt with a strong base, such as potassium *tert*-butoxide [60, 61]. Therefore, azolium-containing ligands, which comprise, for example, imidazolium, triazolium, and benzimidazolium, are precursors for the generation of NHC ligands. Besides the deprotonation of azolium salts, there are some other less commonly applied methods for the generation of free carbene [62].

Intrinsically, NHCs are characterized by strong σ -donor but poor π -acceptor abilities, which results in chemical stability and coordination versatility, hence allowing them to coordinate with many metals, ranging from alkaline-earth metals and transition metals to rare-earth metals. Furthermore, the easy introduction of chiral elements into NHCs and the facile preparation of their precursors have made chiral NHCs promising chiral ligands in metal-based asymmetric catalysis [49]. Notably, not only is the catalytic activity of NHC-derived second-generation catalysts better than that of first-generation catalysts in olefin metathesis, their catalytic activity can also be fine-tuned by varying the substituents [61]. This can be observed in the Grubbs second-generation catalysts shown in Fig. 4: **2** [63] and **4** [64].

3.1. Stability and reactivity

Owing to the σ -type lone pair and the vacant p-orbital in the singlet carbenes, they show nucleophilic and electrophilic reactivity, respectively, [65] unlike their triplet counterparts, which exhibit radical-like reactivity. Singlet carbenes fall into five categories: +M/+M, -M/-M,

$-M/+M$, $+M/-$ [59, 66], and the recently isolated aromatic *cyclo*-propylidenes [67]. This categorization is based on the mesomeric effects ($\pm M$) and the stabilization brought by each α -group. NHCs belong to the $+M/-$ group, which is stabilized simultaneously by a strong donation from a p-orbital substituent to the methylene empty p-orbital and by a weaker donation from the carbene's filled p-orbital to the substituent's empty p-orbital, thus constituting a push-pull effect [39]. The π -donation contributes less to the stability of a free NHC as the substantial σ charge transfer from the carbenic carbon to the more electronegative neighboring nitrogen atoms constitutes the major contributor to the stability [68]. Mesomerically, NHCs as singlet carbenes prefer a bent geometry [69].

Sterically stabilized imidazolidenes and imidazolylidenes are thermodynamically stable to the extent that they do not react with triplet dioxygen, even when the formation of the ketone appears to be very exothermic. Although Arduengo's group later obtained a stable imidazol-2-ylidene with little steric hindrance by replacing the bulky *N*-adamantyl with smaller methyl groups, the steric factor nevertheless contributes to the stability and reactivity of NHCs. Denk et al. [70] investigated the reactivity of 1,3-di-*tert*-butylimidazol-2-ylidene and 1,3-di-*tert*-butylimidazolin-2-ylidene toward H_2 , O_2 , H_2O , and CO . They reported that NHCs do not react with O_2 or CO , but are sensitive to air because they are attacked by H_2O , which leads to ring opening to give the formamides. NHCs with unsaturated backbones on C4 and C5 are stabler in water than their saturated counterparts. These carbenes hydrolyze either by nucleophilic attack of OH^- or through the insertion of carbene into H_2O , which leads to formamide by ring opening of a cyclic α -diamino methanol intermediate. Furthermore, they are unreactive toward oxidizing agents, such as CuO and HgO , even after prolonged heating. In the presence of platinum as a catalyst, NHCs react with hydrogen to form aminals, which are 1,1-hydrogenation products [39, 70].

NHCs display an ambivalent p-bonding character, thus functioning as a π -acid as well as a π -base [71]. This dual behavior is evident in dimerization, which is considered the simplest carbene reaction. For a system with low d-electron count such as a d^0 system, both π -donation and π -backdonation are important. But backdonation constitutes the major contribution to the p-interaction for systems with a high d electron count. Therefore, the NHC ligands in systems with a high d-electron count are best described as π -acids [71].

Notably, the substitutions on C4 and C5 together with the N–C–N bond are the main influential factors that determine the basicity of NHCs. Their basicity is not very dependent on electron delocalization. Hence, the acyclic bis(diisopropylamino) carbene ligand and the C–C saturated dimesitylimidazolidin-2-ylidene induce higher electron density at the metal atom than the C–C unsaturated *N,N*-di-(*R*)-imidazolin-2-ylidenes [72]. NHCs react with acids to form iminium salts, and they are among the most powerful neutral organic bases [73].

Dimerization in NHCs involves the attack of the occupied σ lone pair of one carbene center on the vacant p orbital of the second carbene center. Basically, the thermodynamic tendency to dimerize can be linked to the steric and electronic properties. Formation of monomeric NHC is favored by the appropriate increase of the steric bulk of the R substituent on the nitrogen atoms, but sterically too demanding NHC ligands often have a detrimental effect in catalysis. To establish a balance between the electronic effect and the steric effect on dimerization of NHCs, Poater et al. [74] came up with an equation that will assist in the calibration of these two effects. The π -delocalization is a necessary prerequisite for the aromaticity of NHCs with unsaturated backbones [75] and for the stability of NHCs in general. Surprisingly, two oxygen atoms, with electronegativity higher than nitrogen and sulfur, afford the lowest stabilization. This indicates that although the double bond in the backbone of the unsaturated NHCs contributes to their stability, the major contribution to carbene stabilization is due to $p\pi$ - $p\pi$ electron donation from the two nitrogen atoms to the carbene carbon atom [75].

The C4 and C5 CH groups of imidazole-2-ylidene are acidic, as exemplified by the replacement of their hydrogen atoms by halogens or deuterium [76]. An extraordinarily air stable NHC, 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene, is produced from the substitution of hydrogens at C4 and C5 of 1,3-dimesitylimidazol-2-ylidene by chlorides. The high stability of the chlorinated NHC was attributed to a π -electron donating effect of the chlorine lone pairs and to a σ -electron withdrawing effect due to the high electronegativity of the chlorine atoms. Consequently, this reduces and stabilizes the basicity of the σ lone pair at the carbene center [48]. Moreover, because of the acidity of the backbone, C4 and C5 of NHC have been osmylated [77].

4. NHC-metal bonds

Understanding the bonding of NHC to metal was a revealing experience for researchers. NHC-based catalysts were very stable under many catalytic conditions (e.g., temperature, pressure) although they presented carbene functionality. This ability initiated impressive academic and industrial efforts, and as a result, a great number of effective NHC-bearing catalysts with very different structures have been synthesized, some of which are better than their phosphine counterparts. Generally, NHC-metal complexes are synthesized by direct metalation or transmetalation. The latter usually involves the treatment of the imidazolium salt with Ag_2O to form the Ag-NHC complex, followed by transmetalation with the required metal salt, such as transmetalation of Ag-NHC complexes to bis(NHC)-Pd complexes [78]. The general structure of NHCs and some examples of their complexes are shown in Fig. 5. The flat heterocycle structure of NHCs is fan-shaped with substituents, R^1 and R^2 , and a metal atom, M, that may be freely rotated along the $\text{R}^1\text{-N}$, $\text{R}^2\text{-N}$, and C-M bonds, respectively (Fig. 9, 5) [49]. The strong σ -donating but weak π -accepting abilities of NHCs make their metal complexes fascinating catalysts in a plethora of reactions, including hydroacylation [79-82], the Suzuki-Miyaura reaction [83-88], hydrogenation [89, 90], and ruthenium-based olefin metathesis [91-96]. Herrmann et al. [97] reported the first application of NHCs as ligands in transition-metal catalysis, and Díez-González et al. [98] critically reviewed and categorized their catalytic applications in late-transition-metal complexes. Beyond catalysis, Mercks and Albrecht [99] reviewed other applications of NHC complexes.

4.1 NHCs as σ - and π -donors and as π -acceptors

The electronic effects on NHC-metal bonding are as important as steric effects. The importance that NHC precursor-containing ligands have acquired in practical applications spurred a remarkable amount of work focused on the understanding of the NHC-metal bond from an experimental to a theoretical point of view. The three orbital contributions to the NHC-metal bond are shown in Fig. 6.

NHC ligands are considered as simple pure σ -donors when coordinated to metal ions [100], through $\sigma \rightarrow d$ donation as shown in Fig. 6a. NHCs form stable adducts with main-group elements and rare-earth metals, such as aluminum, magnesium, and thallium [101-103], because these metal centers are incapable of π -backdonations and because NHCs have a pure σ -donor

character [44]. The beryllium ion, a Lewis-acidic metal ion, forms stable adducts with the carbene, 1,3-dimethylimidazolin-2-ylidene, further supporting the idea of pure $\sigma \rightarrow d$ donation by NHC, since no backdonation is possible in the case of beryllium [104]. The stability of this complex is enhanced by donation from the substituents of the carbene carbon atom (the nitrogen atoms in NHCs) to the pure acceptor beryllium metal. However, when the M–C(NHC) distances in the Mg–C(NHC), Ca–C(NHC), and Ba–C(NHC) complexes were studied, stronger σ -interactions were observed with the lighter alkaline-earth metals [48]. Additionally, Mungur et al. [105] indicated that the strength of the metal-carbene bond is predominantly electrostatic in nature. They discovered this by showing that the synthesized first s-block metal (lithium and magnesium) and uranium amido NHC complexes show significant distortion of the metal-carbene bond from the anticipated trigonal planar hybridization without any significant reduction in the strength of the bond. Pd–NHC complexes were synthesized from their respective imidazolium halide salts by the reaction of PdCl₂ with pyridine in the presence of K₂CO₃ as a base. By use of charge decomposition analysis to examine the nature of the NHC-metal bond in the complexes, it was revealed that the NHC ligands were effective σ -donors.

On the other hand, this idea of NHCs being only a pure σ -donor has changed since these ligands are electrically much more flexible than expected. Both the filled and the empty π -orbitals on the carbene as well as the NHC ring are involved in the bonding with metals.

Owing to the flexibility of NHC ligands, they can stabilize electron-deficient metals through a $\pi \rightarrow d$ donation as well as stabilize electron-rich metals by $d \rightarrow \pi^*$ backdonation [106].

In 1998, Boehme and Frenking [107] reported the first negligible metal-to-ligand π -backbonding interactions, $d \rightarrow \pi^*$ donation (Fig. 6b). By using theoretical density functional theory (DFT) approaches, Lee and Hu [108] studied Cr(CO)₅L complexes, with L being NHCs, phosphines, diaminocarbenes, and Fischer and Schrock type carbenes. They observed that the ligand-metal bonds of NHCs are much stronger than those of phosphines, and concluded that π -backdonation is negligible in NHC-metal bonding compared with the σ -donation.

On the basis of structural information, high π -metal interaction between metals and carbene ligands has been reported [109, 110]. Hu et al. [111, 112] used the recent development of modern DFTs and corresponding computer programs to compute the electronic structure of the synthesized NHC-metal complexes, and they evidenced that NHCs can accept electron density from electron-rich group 11 metal atoms, through a $d \rightarrow \pi^*$ backdonation scheme. Similar

conclusions were drawn from energy decomposition analysis calculations on group 11 complexes with NHC ligands [113]. The experimental as well as computational results show that the NHC is capable of acting as a π -accepting ligand when coordinated to the electron-rich U(III) ion [114]. Jacobsen et al. [115] compared the σ - and π -contributions in a series of NHC complexes in which the formal d-electron count ranges from d^0 to d^{10} . They reported that even for d^0 complexes there exists a considerable amount of metal-to-ligand π -backdonation. Also, they showed that backdonation constitutes the major contribution to the π -interaction for systems with a high d-electron count. Two techniques, Fourier transform IR spectroscopy and cyclic voltammetry, were used to observe structural and electronic changes, including deconvoluting σ - versus π -effects, on the NHC complex with a *p*-quinone moiety attached at the C4 and C5 positions (see Fig. 7) [116].

The *p*-quinone moiety fused to the imidazolyliene is sensitive to π -effects and is ideal for identifying π -backbonding of the metal complexes, while the *cis,cis*-1,5-cyclooctadiene ligand rapidly exchanges with two units of CO. After the analysis, a substantial π -backdonation was observed.

After the σ -donation and π^* -backdonation in the NHC-metal bond had been studied, it was found that the σ -donation is remarkably larger than the π^* -backdonation, and the σ/π^* ratios were calculated to be significantly larger than those calculated for classic Fischer carbene compounds. Although the influence of the π^* -backdonation is a bit stronger in silylene and germylene than in other carbene compounds, this donation is substantially negligible. Notably, the NHC-metal bond is mainly due to coulombic attraction between the lone-pair electrons at the carbene atoms and the positively charged metal atoms, but there are also significant covalent interactions from the donor lone-pair electrons. The charge decomposition analysis mainly confirmed the almost pure σ -donor character of the carbene ligands [48]. The nature of the NHC-metal bonding of a series of structurally diverse silver and gold amido-functionalized NHC complexes was examined by means of DFT studies, which revealed that the NHCs are good σ -donating ligands with relatively weaker π -accepting properties [117]. Electron donation from the carbene lone pair of the NHCs occurred at an unfilled p or s orbital of the metal (5p or 5s for Ag and 6p or 6s for Au).

Electron density analysis on the synthesized NHC complexes of Pt(II) indicates that more electron density is backdonated from the metal center to the saturated NHCs (1,3-bis(2,6-

diisopropyl)phenyl-4,5-dihydroimidazol-2-ylidene and 1,3-bis(2,4,6-trimethyl)phenyl-4,5-dihydroimidazol-2-ylidene) than to unsaturated NHC congeners (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) [118]. In addition, saturated NHCs are more σ -donating with respect to Pt(II) than their unsaturated counterparts. Therefore, the synergistic effect between π -backdonation and σ -donation present in the saturated NHC systems results in increased electron density at the Pt(II) center compared with the bonding situation in the unsaturated NHC systems. Consequently, saturated NHC binds more strongly to the metal than the corresponding unsaturated NHC. These observations go a long way to explaining the reason why the coordination of the unsaturated NHC catalysts to the substrate is usually more facile, although their stability is affected by the weaker bond they form with the metal. In contrast, saturated NHCs, with more strongly bound ligands, stabilize the catalyst but may also lower its reactivity, probably because they make the metal center a worse σ -acceptor and π -donor, which results in weaker interaction with many substrates [118].

NHCs do not only accept π -electrons from the metal during NHC-metal bonding, they also donate their π -electrons to the metal (see Fig. 6c). Jacobsen et al. [115] used DFT together with suitable bond analysis to indicate that for systems with a low d-electron count, both π -donation and π -backdonation are important in NHC-metal bonding. Explaining the absence of agnostic interactions in $\text{IrCl}(\text{ItBu})_2$ (where *ItBu* is 1,3-bis(*tert*-butyl)imidazol-2-ylidene), Cavallo et al. [106] reported that electron deficiency on the metal complex is better compensated by donation from the π -orbital of the NHC ligand than by donation from the σ -orbital of the C–H bond of the *tert*-butyl groups. In addition, Scott et al. [119] reported from molecular orbital analysis that the unusual stability of the 14-electron complex $[\text{Ir}(\text{ItBu})_2]\text{PF}_6$ is due to a remarkable donation of electron density from the filled π molecular orbital of the NHC ligands to the empty d orbitals of the iridium atom through $\pi \rightarrow d$ donation, hence explaining the strange stability of the 14-electron complex $[\text{Ir}(\text{ItBu})_2]\text{PF}_6$.

4.2 Steric effect

Basically, the combination of steric and electronic properties of an NHC ligand in a given coordination environment influences the stability of the carbene lone pair. From a structural point of view, one can conclude that the bulkiness of the groups bonded to the nitrogen atoms of

the NHC ligands and the short metal-carbon distances in these complexes enhance the steric congestion around the metal center when compared with tertiary phosphines.

The bond dissociation energy (BDE) of CO in the $\text{Ni}(\text{CO})_3(\text{NHC})$ systems was calculated to rationalize the different behaviors shown by the two groups of NHC-based complexes, the unsaturated and saturated NHC-based complexes. The difference between the two groups of NHC ligands was exclusively attributed to steric factors [120]. 1,3-Bis(adamantyl)imidazol-2-ylidene and *ItBu* are substantially bulkier than very bulky phosphine ligands and other NHC ligands.

Steric effects do not only play a fundamental role in determining the BDE of the NHC-metal bond, but can also alter the stability of the complexes completely. Cavallo et al. [106] reported that in the $\text{Cp}^*\text{Ru}(\text{NHC})\text{Cl}$ class (where Cp^* is $\eta^5\text{-C}_5\text{Me}_5$), the BDE of the NHC ligands is remarkably dependent on the bulkiness of the substituents in the *ortho* position of the aromatic rings of the ligands. However, in this class of $\text{Ni}(\text{CO})_3(\text{NHC})$ complexes studied, the stability depends on the bulkiness of the groups bound to the nitrogen atoms of the NHC ligands. With the less bulky 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene-based and 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene-based ligands, the saturated $\text{Ni}(\text{CO})_3(\text{NHC})$ complexes are stable, whereas with the bulky 1,3-bis(adamantyl)imidazol-2-ylidene-based and *ItBu*-based ligands, the 18-electron $\text{Ni}(\text{CO})_3(\text{NHC})$ complexes are destabilized so much that 16-electron $\text{Ni}(\text{CO})_2(\text{NHC})$ complexes are formed.

The concept of percent buried volume (the percentage of the volume occupied by ligand atoms in a sphere centered on the metal) was used to quantify the steric bulkiness of NHC and phosphine ligands (Fig. 8). This molecular descriptor can be considered as an analogue of Tolman's cone angle for tertiary phosphines [121]. The volume of this sphere represents the space around the metal atom that must be shared by the different ligands on coordination [122].

Basically, the bulkier a ligand is, the larger is the amount of the sphere the ligand will occupy: that is, the greater the buried volume. The putative metal atoms ruthenium and nickel were placed at a distance of 2.00 Å and 2.28 Å, respectively, from the coordinating carbon, and the bulkiness of the different ligands was determined with use of the sphere in Fig. 8 [106]. Although BDE is essentially controlled by the steric requirements of the ligands, the buried

volume showcases the different steric requirements of the different ligands. Structural and catalytic studies on (NHC)Pd(R-allyl)Cl complexes involving substitution of the allyl moiety show that the saturated 2,6-diisopropylphenyl (SIiPr)-containing complex undergoes far faster aryl amination reactions than its unsaturated IiPr analogue, which is attributed to the higher steric hindrance of the saturated SIiPr ligand [123, 124]. Nevertheless, an excessive steric pressure around the metal center can render the NHC-metal bond labile.

5. Azolium-containing MOFs

5.1. Why azolium-containing MOFs?

Designing MOFs with azolium-containing ligands not only increases the functionality of the frameworks but also generates electrostatic environments within the materials [125]. The positively charged azolium moieties tend to introduce this unusual ionic environment within the pores of the MOFs. Although the charged moieties induce a strong electronic interaction with ionic guest molecules in the pores of the MOFs, making the evacuation of the guest molecules difficult, these positively charged azolium components also generate proton conductivity in the materials [126].

Furthermore, the selectivity of gaseous molecules with different quadrupole moments and polarizabilities is enhanced by designing the MOFs with a charged azolium-containing ligand [127]. Gas molecules with a greater quadrupole moment and polarizability will be absorbed more owing to their significant favorable interaction with the framework. Also, the open metal sites and counterions augment this selectivity in the pore cavities [125]. The charged azolium moieties interact more with polar organic molecules (such as polar dyes), which can be useful for their separation [128].

The catalytic activity of MOFs can be derived by use of unsaturated metal nodes for the synthesis of the MOFs, by encapsulation of an active catalyst inside the pores of the MOFs, or by generation of MOFs that contain ligands which can tether catalytically active metal complexes [129, 130]. Use of an azolium-containing ligand will introduce a more functional part into the open framework structures, which may open a new chapter in the design of new MOFs. These MOFs can be modified presynthetically, in situ, or postsynthetically by metalation of their carbene to generate NHC complexes. Alternatively, deprotonation of the acidic methylene hydrogen of the azolium moieties inside the frameworks will afford neutral carbenes or NHCs

that can be stabilized by the two heteroatoms near the carbene center [126] (Fig. 9). The NHCs generated can be used as useful Lewis base catalysts in their own right or can be further metalated for other catalytic applications [125]. Unfortunately, generation of these NHCs in MOFs is still difficult owing to degradation of the framework following addition of the base used for deprotonation, inaccessibility of the carbene-precursor sites, and unwanted in situ metalation of the carbene during the synthesis of the MOFs [131].

NHCs have very high potential for using their carbenic carbons to coordinate with a lot of metals owing to their excellent σ -donor and weak π -acceptor ability. Thus, such ligands are applied in organometallic chemistry for the synthesis of highly active and very stable catalysts [132, 133], which are much superior to phosphine-based catalysts. These NHC catalysts have shown good control over carbon-carbon, carbon-oxygen, and carbon-nitrogen bond formation or deletion, by their effectiveness for an array of rearrangement, addition, and group-transfer reactions [57, 131, 134]. Nevertheless, most of these catalysts are homogenous in nature. The need to heterogenize these NHC-based catalysts for optimum and versatile application arises. Many efforts have been made to achieve this goal through immobilization, polymerization of the side chain, the design of azolium-containing MOFs, and other methods [135-138]. In MOFs, heterogeneous counterparts of some homogeneous catalysts are obtained by careful selection of the organic linker and metal ion or clusters. Like homogeneous Cu^{2+} coordination, complexes containing NHC are converted to their heterogeneous MOF counterparts [139]. Depending on the application, heterogeneous catalysts have the edge over their homogenous counterparts because heterogeneous catalysts are easily recyclable molecular catalysts with well-defined and predesigned active centers. Incorporation of NHC complexes into MOFs would yield reusable heterogeneous transition metal catalysts with permanent microporosity [140]. Another means of heterogenizing and enhancing the efficiency of these catalysts is by their incorporation into MOFs by use of the already synthesized catalyst as an organic spacer or by PSM of the MOFs. Of optimum importance is developing a heterogenization procedure that not only preserves the catalytic activities of the starting homogeneous catalyst but also improves its efficiency [131].

Incorporating NHC complexes into MOFs allows multiple catalytic sites to be created in close proximity that generally cannot be used simultaneously in solution (such as NHC and Lewis-acidic metal catalysts), thereby facilitating new patterns of catalytic reactivity. On the other hand, other intrinsic characteristics of NHC complexes are incorporated into the frameworks

synthesized from them, thus enhancing their applications. Importantly, dimerization, which limits the activity of homogeneous NHC catalysts, is sometimes circumvented by immobilization of the NHC in an MOF [141, 142].

5.2. Past work on azolium-containing MOFs

Some research work on MOFs synthesized with azolium-containing ligands and metal nodes has been reported. Azolium-containing ligands, which comprise imidazolium-, triazolium-, tetrazolium-, pyrazolium-, benzimidazolium-, oxazolium-, and thiazolium-containing ligands, are deprotonated to prepare the corresponding NHCs [143] as shown in Fig. 10. Imidazolium salts, such as imidazolium bromide, are obtained by the protonation or substitution at the nitrogen of the imidazole, thereby rendering the ring cationic.

The most commonly used azolium-containing MOF linkers are imidazolium ligands, although triazolium [144] and benzimidazolium [145] ligands have also been used. These frameworks have diversified structures, functionalities, and applications. The structural and functionality differences are influenced by some factors. Notably, the charge on the azolium-containing ligand can influence the structures of the MOFs owing to the requirement of charge balance. Burgun et al. [144] demonstrated this by comparing the coordination chemistry of a triazolium-containing ligand, 1,4-bis(4-benzoic acid)-1-methyl-1*H*-1,2,3-triazolium chloride, and that of an equivalent neutral triazole ligand, 1,4-bis(4-benzoic acid)-1*H*-1,2,3-triazole hydrochloride, with two metal salts, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. Furthermore, notwithstanding that the coordination number of the metal ion and the length of the ligand influence the morphology of the framework, the position of the azolium moiety in the ligand also immensely influences the structure of the frameworks for azolium-containing MOFs. As outlined in Scheme 1(a) and discussed below, the imidazolium-containing ligands for MOF synthesis can be categorized as having two design features [144]: (1) where the azolium or NHC entities form the core of the ligand [126, 128, 144] and (2) where the azolium or NHC entities are appended to existing linkers [141].

Generally, in the first category (Scheme 1(a)), the azolium or NHC entities are integrated in the core and bend the ligand (see Fig. 11), thus inducing unusual linker topologies in the MOFs.

The bent nature of the ligand results in unusual high interpenetrated structures, which sometimes makes it difficult to predict the final atomistic connectivity in the framework [145]. Subsequent

to this, the porosity of the resulting MOF is reduced. To this end, Sen et al. [127] envisioned using the strategy of mixed ligands to control interpenetration. They constructed a series of noninterpenetrated cationic MOFs by means of a rigid and angular tetracarboxylic acid ligand, 1,3-bis(3,5-dicarboxyphenyl)imidazolium, with different pyridine-based linkers.

By solvothermal reaction, they designed a framework that consists of two-dimensional layers that are further pillared by the linker to form three-dimensional bipillared-layer porous structures. They further used different lengths of the pillar linkers (pyridine based) to direct the pore modulation [127]. Furthermore, the charge of the azolium linker influences the porosity of the framework. For charge compensation, the resulting charged frameworks contain counterions in their pores, and thus guest-molecule inclusion may be blocked. Generally, the porosity of the resulting MOFs from these linkers is low.

The rigidity of the ligand influences the topology of the frameworks (Fig. 12). Rigid azolium-containing linkers with the azolium entities integrated in the core of the ligands have been reported for synthesis of MOFs (see Fig. 12b).

Sn et al. [146] formed a three-dimensional entangled MOF that consists of a threefold interpenetrated network by solvothermal reaction of 1,3-bis(4-carboxyphenyl)imidazolium with $\text{Cd}(\text{NO}_3)_2$. The parallel polycatenation of three such threefold interpenetrated networks formed the entangled three-dimensional structure as shown in Fig. 13. This structure is attributed to the bent nature of the ligand and the coordination mode of the metal ion.

On the other hand, Burgun et al. [147] constructed a three-dimensional MOF from Zn_4O SBUs that adopt an uncommon coordination environment surrounded by four pairs of azolium-containing linkers. This framework adopted a fourfold interpenetrated flexible three-dimensional diamondoid structure (see Fig 14).

Under solvothermal conditions, the reaction of the linker 1,3-bis(4-carboxyphenyl)imidazolium with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ afforded a three-dimensional framework with also an unusual SBU, Zn_8O [126]. This SBU coordinates to the six azolium ligands (Fig. 15) to generate a three-dimensional structure.

Isostructural one-dimensional MOFs, [silver ((4-picolyl)₂imidazolium)₂] hexafluorophosphate and [copper ((4-picolyl)₂imidazolium)₂] hexafluorophosphate, crystallize in a monoclinic system

[148]. The self-assembly of the bis(4-picolyl)imidazolium linker with the two single oxidation state metal ions, Cu(I) and Ag(I), resulted in the frameworks. The parallel stacking of the Ag(I) network is shown in Fig. 16.

A U-shaped imidazolium-containing ligand, 1,3-bis(3-carboxyphenyl)imidazolium chloride, was solvothermally reacted with zinc nitrate to construct an unusual undulating structure of a one-dimensional necklace-type framework (see Fig. 17) [129]. In addition, some other unusual zeolite-like geometries on the link component of the MOFs based on rigid linkers that have imidazolium integrated in the core of the ligand have been reported by Chun et al. [149, 150].

For azolium-containing MOFs with the azolium entities forming the core of a flexible ligand, the flexibility of the spacers allows the linkers to bend and rotate when they coordinate to metal centers, and this often causes structural diversity (Fig. 12a). On careful inspection of the reported cases, it was found that most of them were focused on imidazolium-based ligands. Wang et al. [151] used a symmetric flexible ligand, *N,N'*-diacetic acid imidazolium chloride, with $\text{Pb}(\text{NO}_3)_2$ in an aqueous solution at ambient temperature to build a twofold interpenetrating three-dimensional homochiral MOF (see Fig. 18a). Kong and Wu [152] used two flexible ligands containing an azolium moiety integrated in their core to construct MOFs. The distinct lamellar coordination networks of the ligands and metal cations afforded chiral frameworks (Fig. 18 b).

Owing to the degree of flexibility and conformational freedom, the ligand *N,N'*-diacetic acid imidazolium was used by Chai et al. [153] with lanthanide ions to synthesize a series of MOFs with different topological structures, as shown in Fig. 19.

Recently, Suresh et al. [154] tried to create a balance between rigidity and flexibility of the azolium ligand. They used rigid and flexible biscarboxylate-linked monoimidazolium salts, shown in Fig. 12c, to control the structural topologies in MOFs. Among the six frameworks they synthesized, three were isostructural one-dimensional structures, and the remaining three had different structures.

The second category when the azolium entities are appended to existing linkers induces access to “conventional MOF topologies” (Scheme 1(a)). Roberts et al. [141] prepared two biphenyl dicarboxylate-based linkers with one or two azolium groups (methyl imidazolium salts) appended at the 2 and 2' positions of the biphenyl. Solvothermal synthetic reaction of the ligand containing one azolium moiety with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ afforded a cubic network with Zn_4O nodes,

which is analogous to isorecticular MOF-9 (IRMOF-9). On the other hand, application of the linker with two azolium moieties under the same reaction conditions yielded a framework that is analogous to IRMOF-10. This difference in the number of azolium cores, one versus two, impacts the level of catenation of the MOFs, as can be observed in Fig. 20.

To obtain a linear azolium-containing ligand with the azolium moiety integrated into the linker backbone, Oisaki et al.[145] used a benzimidazolium core to generate a linear dicarboxylate by using cross-coupling reactions as a key step for the synthesis. Solvothermally, the synthesized ligand, 4,7-bis(4-carboxylphenyl)-1,3-dimethylbenzimidazolium tetrafluoroborate, was reacted with a zinc salt to construct an MOF-5-type structure (IRMOF-76) which is a noninterpenetrated cationic framework possessing imidazolium moieties on each linker. Not only do these design features induce the conventional topology of MOFs, they also circumvent the limitation of low porosity encountered for the bent ligand as shown in Fig. 21.

5.3. Synthetic methods of incorporating azolium or NHC entities into MOFs

Basically, there are three synthetic methods by which azolium or NHC entities are incorporated into MOFs (see Scheme 1(b)): (1) azolium salts (without metalation) [125, 126, 129, 144], (2) NHCs (metalation during the reaction) [147, 149, 150], or (3) premetalated NHCs [145]. Azolium salts without metalation have been incorporated into MOFs as monoimidazolium, bisimidazolium, or triazolium per ligand.

Generally, ionic MOFs are constructed when there is imbalance of charge between the positive charge of the metal and the negative charge of the organic linkers. Nevertheless, achieving targeted cationic MOFs is difficult because the excess cations are normally compensated by guest anions, usually the anions from the metal salt used during the synthesis [128]. The use of linker-containing salt opens up the possibility of such controlled design of cationic frameworks. Nickerl et al. [128] proposed an approach for the controlled synthesis of cationic MOFs by the use of an imidazolium salt linker. By solvothermal synthesis, they reacted the linker, 1,3-bis(4-carboxy-2,6-dimethylphenyl)-1*H*-imidazolium chloride, with zinc nitrate and copper nitrate to give two topologically different cationic frameworks, $[\text{Cu}(\text{Imid})(\text{H}_2\text{O})]^+$ and $[\text{Zn}_4(\text{Imid})_5]^{3+}$, respectively (where Imid is 1,3-bis(4-carboxy-2,6-dimethylphenyl)-1*H*-imidazolium). Sen et al.

[126, 146] used an imidazolium salt-containing ligand, 1,3-bis(4-carboxyphenyl)imidazolium chloride, to design two proton-conducting frameworks. Wang et al. [155] designed a charge-separated two-dimensional MOF from an imidazolium tricarboxylate ligand, *N*-(3,5-dicarboxyphenyl)-*N'*-(4-carboxylbenzyl)imidazolium chloride and a zinc(II) dimeric SBU.

An azolium salt-containing ligand, *N,N'*-bis(2,6-dimethyl-3,5-carboxylphenyl)imidazolium chloride, was used to synthesize a microporous framework material by solvothermal reaction with $\text{Cu}(\text{NO}_3)_3 \cdot 2.5\text{H}_2\text{O}$ [125]. Chun et al. [150] used cadmium nitrate as a metal salt and an azolium salt-containing ligand, 1,3-bis(4-carboxy-2,6-diisopropylphenyl)imidazolium chloride, to design a one-dimensional MOF with two carboxylates coordinated to a single cadmium ion and two chlorides functioning as bridging ligands between the cadmium units, as can be observed in Fig. 22. They reported that the central imidazolium salts were intact for PSM.

Chun et al. [149] worked in the same research direction by using cerium(III) nitrate with the same ligand as mentioned above [150] to construct three-dimensional supramolecular networks. Also, the imidazolium salts in the building blocks were intact during the self-assembly process and could be modified postsynthetically as shown in Fig. 23. As already mentioned, rigid and flexible biscalboxylate-linked monoimidazolium salts have been used for the synthesis of MOFs [154].

Work has been reported on the use of bisazolium salt-based linkers for synthesis MOFs. A flexible bisazolium anthracene spacer together with copper and zinc ions was used to construct three-dimensional MOFs [156]. Moreover, these MOFs have considerable luminescence properties owing to the azolium spacers, as shown in Fig. 24.

In 2011, Kong et al. [157] constructed two frameworks containing bisazolium linkers by reacting a mixture of the ligand 1,1'-methylenebis(3-(4-carboxyphenyl)-1*H*-imidazol-3-ium) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Later, the same research group [158] used another bisazolium salt linker, 1,1'-methylenebis(3-(4-carboxy-2-methylphenyl)-1*H*-imidazol-3-ium), to design a framework by the reaction of the ligand with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at room temperature. Also, semirigid bisazolium spacers were used by Roberts et al. [141] to synthesize MOFs.

Triazolium salt-containing linkers with carboxylate donors, 1,4-bis(4-benzoic acid)-1-methyl-1*H*-1,2,3-triazolium chloride, have been used by Burgun et al. [144] to design MOFs. They

incorporated the linker into the framework instead of the usual imidazolium linker to offer an opportunity to tune the electronic and catalytic properties of the resulting NHC.

In the synthetic method discussed above (incorporation of azolium salts without metalation), the MOFs synthesized contain azolium entities, which can undergo dative PSM with the desired metal to afford the corresponding NHC complexes in the framework. In an attempt to modify the MOFs, unidentified metal solids can be deposited either on the surface or inside the framework. Consequently, homogeneous distribution of the active metal sites requires clarification [149]. Also, the MOFs should be stable enough during the PSM process to avoid the collapse of the structure. PSM of such frameworks will be discussed in Section 6.

Secondly, azolium entities are incorporated into the MOFs as NHC complexes by in situ metalation during the synthesis, as can be observed in Scheme 1(b). As far as the authors are aware, the first in situ generation of an NHC-metal complex within a supramolecular network was reported by Chun et al. [150] in 2009. The two-dimensional MOF they assembled with copper(II) nitrate and 1,3-bis(4-carboxy-2,6-diisopropylphenyl)imidazolium chloride in dimethylformamide (DMF) under heating at a temperature of 110 °C contained two kinds of copper species, Cu(I) and Cu(II), within the structure. The Cu(II) formed the metal node, while the imidazolium proton was concomitantly abstracted during the self-assembly process, leading to the formation of NHC-Cu(I) complexes within the MOF. That is to say that there was reduction of Cu(II) to Cu(I) during the synthesis (Fig. 25) [150].

Sometimes, mixed metal salt synthesis is used in this method. Chun et al. [149] used 1,3-bis(4-carboxy-2,6-diisopropylphenyl)imidazolium chloride with mixed metal salts, cerium(III) nitrate and copper(I) oxide, to construct three-dimensional MOFs. Because Cu₂O shows chemical properties very similar to those of Ag₂O toward imidazolium salts, reaction of Cu₂O with imidazolium halides in the absence of a base to form NHC-copper halide complexes [150, 159] resulted in the three-dimensional MOFs being in situ decorated with NHC-copper species during the construction of the network. The NHC-copper species were formed within the MOFs as in their previous work [150] (Fig. 26).

In 2014, Burgun et al. [147], in situ generated the first bis(N-heterocyclic) complex linker during the synthesis of an MOF. The solvothermal reaction of 1,3-bis(4-carboxyphenyl)imidazolium

chloride with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ in DMF in situ generated the bis(NHC) complex linker and afforded a three-dimensional framework. Figure 27 depicts the bis(NHC) complex linker.

As illustrated in Scheme 1(b), premetalated NHC complexes are used to construct MOFs. Oisaka et al. [145] used the first premetalated NHC entities or metalloligand for the synthesis of MOFs. Before then, they had tried to use dative PSM to metalate the constructed MOF-5-type structure (IRMOF-76) discussed earlier, but did not succeed. Consequently, they metalated the ligand 4,7-bis(4-(*tert*-butoxycarbonyl)phenyl)-1,3-dimethylbenzimidazolium iodide by using pyridine with a Pd(II) source, a base, and an iodide source followed by the deprotection of the *tert*-butyl esters to afford the metal-NHC complex, [4,7-bis(4-carboxylphenyl)-1,3-dimethylbenzimidazol-2-ylidene](pyridyl)palladium(II) iodide. Then the metalloligand was solvothermally reacted with zinc salt to construct the desired metalated MOF, IRMOF-77 [145]. The permanent porosity of the framework was demonstrated via N_2 adsorption. The Langmuir and Brunauer-Emmett-Teller surface areas of the activated framework were 1610 and 1590 m^2g^{-1} , respectively. Hence, they used this strategy to immobilize Pd(II)-NHC organometallic complexes into MOFs without losing the porosity and structural order of the MOFs, as illustrated in Scheme 2.

5.4. Different azolium-containing ligands used for MOFs

Generally, transition metal ions and monovalent, divalent, trivalent, or tetravalent azolium-containing ligands are used for the synthesis of frameworks [160]. Multidentate carboxylic acids are excellent ligands for the synthesis, affording structures with a diverse range of topologies and conformations [161]. Notwithstanding this, nitrogen-coordination ligands are sometimes used [148, 162]. Occasionally, the coordination chemistry of imidazolium-based carboxylic acids differs significantly from that of conventional neutral carboxylic acids, by involving not only the coordination of the carboxylate groups but also, in many instances, coordination of the counteranion to the transition metal center or inclusion of the counteranion as a guest [163, 164]. Hitherto, most of the structures of monoazolium-containing ligands that have been reported for the synthesis of MOFs together with their metal ions are presented in Table 1. In these structures, the azolium entities form the core of the ligand, which contains two, three, and four carboxylic

functionalities (except entry 8) for coordination with the metal nodes, affording MOFs with different unusual morphologies.

Dicarboxylic acid ligands with bisazolium moieties integrated in the core are represented in Table 2. Also, these ligands induce unusual linker topologies as those represented in Table 2. The linkers represented in Tables 2 and 3 can undergo dative PSM. These linkers with bisazolium moieties contain more carbene functionalities available for dative PSM of the MOFs synthesized from them than those in Table 1. These linkers were applied as a single ligand during the synthesis of the MOFs, and the metal nodes used so far are Cu(II) and Zn(II).

The linkers represented in Table 3 allow access to conventional MOF topologies because the azolium entities are appended to existing linear linkers (Scheme 1(a)). Dative PSM has not been successful for the frameworks synthesized from these linkers.

6. PSM of azolium-containing MOFs

Some approaches have been reported to incorporate active unsaturated metal sites into MOFs. These approaches include the following: use of an organic linker that already contains the active metal site or metalloligand for the self-assembly process, with the active metal site not being affected by the synthetic process [165-167]; simultaneous generation of active unsaturated metal sites in the metal node during the self-assembly [168]; PSM of the linker by incorporation of active metal sites when the frameworks have already been designed [169]; and concomitant modification of the linker during the self-assembly process [149, 150, 170]. Postsynthetic methods, which are chemical modifications on the fabricated MOFs, are very useful because the solvothermal synthetic methods that are used to prepare most MOFs greatly limit the type of functional groups that can be introduced as part of the ligand monomer. This is because of the reactivity of such groups with metal ions. Furthermore, unlike other crystalline inorganic solids, MOFs contain organic ligands, which opens up the possibility of the use of the vast range of organic transformations developed by synthetic organic chemists. Functionalization can be achieved both in the interior and on exterior of the MOFs owing to their very high porosity [171].

Our sole interest is to discuss PSM of azolium-containing MOFs that is achieved by deprotonation and tethering the azolium group to the desired active metal in order to generate an NHC complex in an already synthesized framework. Many attempts to generate an NHC complex in an already constructed MOFs via PSM proved abortive. For example, Oisaki et al. [145] tried to use dative PSM to bind an organometallic complex to azolium-containing MOFs. The conditions they examined for PSM included treatment with a Brönsted base/ $\text{Ag}_2\text{O}/\text{Ag}_2\text{CO}_3$, or formation of $\text{CN}/\text{CCl}_3/\text{alkoxide}$ adducts followed by thermal re-elimination, but these were unsuccessful.

Although very little literature has reported successful results on the PSM of MOFs designed from azolium-containing ligands, we have attempted to review the reported work here. Kong et al. [157] used an azolium ligand containing two imidazolium moieties to synthesize two MOFs, $[\text{Cu}_2\text{L}_2(\text{MeOH})_2] \cdot 4\text{NO}_3 \cdot \text{H}_2\text{O}$, and $[\text{CuLCl}_2] \cdot \text{H}_2\text{O}$, where L is 1,1'-methylenebis(3-(4-carboxyphenyl)-1*H*-imidazol-3-ium). They reported that after the synthesis of the first MOFs, the imidazolium moieties were readily available to be deprotonated by PSM (Fig. 28), which was achieved by treating the framework with lead(II) acetate in tetrahydrofuran. By using inductively coupled plasma mass spectrometry, they indicated that about 76% of the azolium species in the MOFs were deprotonated, and thus about 11.0% of palladium was immobilized. The second synthesized framework was also postsynthetically modified with lead(II) acetate under the same reaction conditions. They showed that only 4.4% of palladium was immobilized on the framework, corresponding to about 24% of azolium in the MOF being deprotonated to anchor Pd(II) atoms.

In the subsequent year, Kong et al. [158] used the ligand 1,1'-methylenebis(3-(4-carboxy-2-methylphenyl)-1*H*-imidazol-3-ium) chloride with Zn(II) ion as the metal node to design a framework that was modified by partial deprotonation of the free imidazolium moieties with palladium(II) acetate to form Pd(II)-NHCs inside the framework. Also, they used both inductively coupled plasma mass spectrometry and ^1H -NMR spectroscopy to ascertain that 7.8% of palladium was immobilized in the framework. These postsynthetically modified MOFs by produced by Kong et al. [157, 158] were applied for catalysis, as will be discussed in the next section.

7. Applications

7.1. Catalysis

As already mentioned, incorporation of NHCs into a framework for catalytic applications does not only transform a homogeneous catalyst into its heterogeneous counterpart, it also allows multiple catalytic sites to be created in close proximity that generally cannot be used simultaneously in solution. Table 4 illustrates clear structure-property relations of azolium-containing MOFs in catalysis. This table will make the sections on catalytic applications of NHC precursor-containing MOFs clearer.

The modified MOF $[\text{Cu}_2\text{L}_2(\text{MeOH})_2] \cdot 4\text{NO}_3 \cdot \text{H}_2\text{O}$ discussed in Section 6 [157] can quantitatively catalyze the Suzuki-Miyaura cross-coupling reaction of bromobenzene and phenylboronic acids in toluene (Table 5, entry 1).

Also, as shown in Table 5, the framework can catalyze the coupling reactions of many phenylbromides or phenyliodides with phenylboronic acids. Electron-donating or electron-withdrawing groups attached to phenylboronic acids or phenylbromides affected the yield of the product. While the electron-donating groups on phenylboronic acids and phenylbromides generated products in good yield (Table 5, entries 2 and 3, and entries 5 and 6, respectively), the yield obtained with use of the electron-withdrawing group on phenylboronic acid was very low (Table 5, entry 4). Nonetheless, quantitative yield of the product was obtained with electron-withdrawing groups on phenylbromides (Table 5, entries 7 and 8). Furthermore, from Table 5, entries 9-12, the framework can quantitatively catalyze the coupling reaction of various phenyliodides and phenylboronic acids. By use of $\text{Pd}(\text{OAc})_2$ and Pd/C in place of the framework as a catalyst, the corresponding product yields were very low for entries 15 and 16, respectively. Thus, the NHC-anchored $\text{Pd}(\text{II})$ sites performed the catalytic activities of the framework (Table 4, entry 1).

The postsynthetically modified azolium-containing framework was also applied in the Suzuki-Miyaura cross-coupling reaction of phenylhalides with phenylboronic acids (see Table 4, entry 2) [158]. As shown in Table 4, entry 3, Table 6, and Scheme 3, the modified frameworks were very active for the Heck coupling reaction of various phenylhalides and olefins in dimethylacetamide in the presence of K_2CO_3 at 100 °C for 1 h. A schematic representation of various catalytic reactions of the postsynthetically modified framework is shown in Scheme 3.

Additionally, they quantitatively catalyzed both the hydrogenation of various olefins (Table 4, entry 4) and the reduction of nitrobenzene (Table 4, entry 5). Also, NHC-tethered Pd(II) sites perform the catalysis as shown in Table 4. Notably, their catalytic performance in the cross-coupling reaction was similar to that of the previous modified framework.

Lalonde et al. [131] reported a metal imidazole which is an important construct for MOFs, as a precursor to an NHC-like catalyst. They used *n*-butyl lithium to deprotonate tripodal $\text{Co}_3\text{Cl}_6(\text{L})_2$ (where L is 1,3,5-trimethylimidazole-2,4,6-triethylbenzene), thus exposing the NHC sites, which are competent as Brønsted base-type NHC catalysts (Table 4, entry 6). This MOF-based NHC-like catalysis performed faster and in higher yield the conversion of α,β -unsaturated ketone to the corresponding methyl ether than with a traditional homogeneous NHC catalyst. The catalysis occurs on the surface of the MOFs, and Scheme 4 illustrates the reaction.

In addition, catalytic hydroboration of CO_2 has been achieved by Burgun et al. [147] with use of NHC-containing MOFs. They reported that during the synthesis of the MOFs, the in situ generated Cu(I) bis(NHC) complex was an active catalyst for this reaction (Table 4, entry 7). Scheme 5 shows how the catalytic reaction occurs at the in situ generated Cu(I) bis(NHC) site. In the presence of pinacolborane (pin) and different amounts of the MOF, they conducted the catalytic reactions in tetrahydrofuran at 35 °C under a CO_2 atmosphere (1 atm). Afterward, the MOF catalyst was separated by filtration, and the product ($\text{HCO}_2\text{B}(\text{pin})$) formed was used as a formylating reagent for benzylamine, as can be observed in Table 7.

When 10 or 5 mol% (Table 7, entries 2 and 3, respectively) of the framework was used, 92% conversion was obtained. The catalyst has an advantage over the homogenous Cu(I)-NHC species because the framework-based catalyst can be easily recovered by filtration.

7.2. Adsorption of organic molecules

A cationic copper framework was applied in selective adsorption of organic molecules either bearing a carboxylic group or having an ionic nature [128]. The framework was used to selectively adsorb Nile blue from an ethanolic solution containing equimolar amounts of Nile blue and Nile red. Of importance in the adsorption is the ionic nature of the dye, and the main difference between Nile blue and Nile red is the ionic nature. The cationic nature of the linker

causes the formation of positively charged networks that activate the selective adsorption of ionic species (Table 8, entry 1).

Thereafter, by use of UV/vis spectroscopy, the amount of Nile blue desorbed by the framework at different times was monitored (Fig. 29).

Table 8 illustrates clear concise structure-property relations of azolium-containing MOFs in other applications beyond catalysis. This section and subsequent sections on applications are based on this table.

7.3. Fuel cells

Sen et al. [126] used AC impedance spectroscopy to measure the proton conductivity of an azolium-containing MOF. As can be observed in Fig. 30, the framework showed low conductivity up to the tetrahydrate stage, but addition of the fifth water molecule enhanced its conductivity significantly, with low activation energy, implying that water molecules in the channels played a vital role in the proton conduction. The conducting protons originate from the methylene protons of the imidazolium groups (Table 8, entry 2). Consequently, this MOF had high proton conductivity with a low activation energy that is comparable with that of Nafion presently used in fuel cells. It exhibited high thermal stability (~ 400 °C), while Nafion was stable below 80 °C. Therefore, the MOF has features that make it better than Nafion in fuel cell research. This MOF is relevant for clean energy applications because it exhibits significant proton conductivity at temperatures above 100 °C, which is desirable for fuel cell research. Sen et al. [146] used a different metal ion, Cd(II), to design a framework that did not give as high proton conductivity as compared with their previous framework with tZn(II) ion [126], a result which was attributed to low packing of the imidazolium moieties.

7.4. Gas separation

Notwithstanding the catalytic performance of azolium-containing MOFs, these frameworks have been applied in gas separation. The sorption studies conducted by Lee et al. [125] on a three-dimensional framework showed that it could separate CO₂ from CH₄ with high selectivity. Under optimal activation conditions of the MOF, 4 hours at 200 °C, the CO₂/CH₄ selectivity of the framework was extremely high (38) at low pressure (Fig. 31). The high selectivity was attributed to the interaction of CO₂ with open metal sites and the unusual ionic environment within the

MOF generated from the positively charged aromatic azolium components (Table 8, entry 3). Similarly, the selective adsorption of CO₂ over H₂ and CH₄ by an azolium-containing framework has been reported by Wang et al. [155], as presented in Table 8, entry 4.

Recently, a significant CO₂ adsorption capacity and selectivity over N₂ and CH₄ has been reported [127] with azolium-containing MOFs. An imidazolium-containing ligand was used with different lengths of pyridine-based linkers (pillar) to construct a series of MOFs as mentioned in Section 5.2. Notably, the N₂ adsorption capacity increases with increasing length of the pillar linkers. The highest selectivity was observed with the framework having the longest pillar linker (the excellent CO₂ adsorption selectivity suggests that these MOFs may have potential for the separation of CO₂ from industrial flue gas); see Fig. 32. Furthermore, variation in the electronic environment created by the imidazolium moieties, counterions and the accessibility to electron-rich double-pillar linkers of the MOFs permit selective CO₂ adsorption over N₂.

Importantly, N₂ molecules do not diffuse into the channels of the MOFs owing to their low polarizability and high thermal energy (Fig. 32). Preferential adsorption of CO₂ is due to its high quadrupole moment and polarizability (13.4×10^{-40} C m² and 26.3×10^{-25} cm³, respectively), which initiate strong electrostatic interactions with the charged MOFs [127]. In contrast, the selectivity of CO₂ over CH₄ is reversed. From the aforementioned results, it can be deduced that the electronic environment (Table 8, entry 5) plays a pivotal role in the selective sorption of CO₂ over N₂ and CH₄, notwithstanding that the pore sizes of the MOFs are large enough compared with the kinetic diameters of the other gas molecules (N₂ and CH₄).

8. Conclusions and outlook

The skyrocketing number of publications evolving in the field of MOFs each year result from their numerous applications. Although NHC complexes have a fascinating catalytic importance, most of the reported catalysts are homogeneous in nature. In this review, a critical examination of the essence of incorporating azolium-containing ligands in the synthesis of MOFs was done, and it has been established that these frameworks have interesting unique features. Although little research work has been accomplished on PSM of NHC precursor-containing MOFs, all the literature on the subject matter was examined.

Herein, the combined importance of NHCs and MOFs was used to propose some potential applications of NHC precursor-containing MOFs. Owing to the great possibilities of transmetalation from silver-NHC complexes to other metal-NHC systems, [159] PSM of azolium-containing MOFs by tethering the carbenes to silver ions would create a good route for the development of many other metal-tethered NHC-containing MOFs. This would open up more opportunities for the applications of postsynthetically modified frameworks. It is also worth noting that incorporation of a silver complex for transmetalation is always limited by the silver halide by-product generated, which is difficult to be removed, and thus contaminates the system. Furthermore, silver-NHC complexes have been applied as antimicrobial agents for wound healing, [159], and thus when incorporated into MOFs, the silver complexes would heterogenize and enhance their performance.

Louie and Grubbs [172] reported the use of iron-NHC complexes in atom transfer radical polymerization of styrene and methyl methacrylate. Incorporation of these complexes in MOFs may improve the polymerization process. On the other hand, NHC-rhodium catalysts have been applied in hydrosilylation [173] of acetophenone to produce the corresponding enantio-enriched silyl ether [98].

Notwithstanding that NHC precursor-based MOFs which have been postsynthetically modified with palladium were reported for excellent cross-coupling reactions [157, 158], modification of the framework with Ni(II) ions may also catalyze such reactions. [(NHC)Ni]-based complexes have been reported for C–C bond forming cross-coupling reactions that include Suzuki-Miyaura, Heck, and Kumada-Corriu reactions [98, 174]. Lozano-Vila et al. [96] critically reviewed ruthenium-based olefin metathesis catalysts that were derived from alkynes, and indicated the numerous catalysts that have been applied for this reaction. Consequently, PSM of azolium-containing frameworks with ruthenium ions may not only improve their catalytic performance but may also heterogenize them.

Use of a rigid unbent azolium-containing ligand or mixed ligand to construct a very high surface area and pore volume framework that can be modified presynthetically, in situ or postsynthetically by tethering the azolium moieties to the desired metal ions would be a valuable contribution to this field. Such a framework would have a synergistic effect in its application as an efficient catalyst and gas separator. Design of a reliable synthetic method for PSM of NHC precursor-containing MOFs would greatly assist in the development of this research area.

To this end, therefore, the future should see a strong surge in the synthesis and modification of NHC precursor-containing MOFs for numerous applications.

Acknowledgements

The authors to express their deep thanks to the “State Key Lab of Advanced Technology for Materials Synthesis and Processing” for financial support. F.V. acknowledges the Chinese Central Government for an “Expert of the State” position in the “Thousand Talents” program as well as the support of the National Science Foundation of China (no. 21172027). C.I.E. and N.A.K. express their deep appreciation to the Chinese Scholarship Council (CSC) for the financial support for their PhD study (grants 2013GXZ987 and 2012GXZ640, respectively).

Abbreviations

BDE: bond dissociation energy

Cp*: η^5 -C₅Me₅

DFT: density functional theory

DMF: dimethylformamide

Imid: 1,3-bis(4-carboxy-2,6-dimethylphenyl)-1*H*-imidazolium

IRMOF: isorecticular metal-organic framework

*Ir*Bu: 1,3-bis(*tert*-butyl)imidazol-2-ylidene

MOF: metal-organic framework

NHC: N-heterocyclic carbene

pin: pinacolborane

PSM: postsynthetic modification

SBU: secondary building unit

SIIPr: saturated 2,6-diisopropylphenyl

References

- [1] J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* 112 (2011) 869-932.
- [2] S. Keskin, S. Kızılel, *Ind. Eng. Chem. Res.* 50 (2011) 1799-1812.
- [3] L.J. Murray, M. Dincă, J.R. Long, *Chem. Soc. Rev.* 38 (2009) 1294-1314.
- [4] N.A. Khan, Z. Hasan, S.H. Jhung, *J. Hazard. Mater.* 244 (2013) 444-456.
- [5] L. Oehninger, R. Rubbiani, I. Ott, *Dalton Trans.* 42 (2013) 3269-3284.
- [6] D.T. Genna, A.G. Wong-Foy, A.J. Matzger, M.S. Sanford, *J. Am. Chem. Soc.* 135 (2013) 10586-10589.
- [7] S.R. Batten, N.R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M.P. Suh, J. Reedijk, *Pure Appl. Chem.* 85 (2013) 1715-1724.
- [8] S. Chaemchuen, N.A. Kabir, K. Zhou, F. Verpoort, *Chem. Soc. Rev.* 42 (2013) 9304-9332.
- [9] R.E. Morris, P.S. Wheatley, *Angew. Chem. Int. Ed.* 47 (2008) 4966-4981.
- [10] S. Chaemchuen, K. Zhou, N.A. Kabir, Y. Chen, X. Ke, G. Van Tendeloo, F. Verpoort, *Microporous Mesoporous Mater.* 201 (2015) 277-285.
- [11] J. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, *Chem. Soc. Rev.* 38 (2009) 1450-1459.
- [12] J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, *Chem. Soc. Rev.* 43 (2014) 6011-6061.
- [13] M. Opanasenko, *Catal. Today.* 243 (2015) 2-9.
- [14] M. Vallet-Regí, F. Balas, D. Arcos, *Angew. Chem. Int. Ed.* 46 (2007) 7548-7558.
- [15] J. Gordon, H. Kazemian, S. Rohani, *Mater. Sci. Eng., C* 47 (2015) 172-179.
- [16] N. Ahmad, A.H. Chughtai, H.A. Younus, F. Verpoort, *Coord. Chem. Rev.* 280 (2014) 1-27.
- [17] S. Kitagawa, R. Kitaura, S.i. Noro, *Angew. Chem. Int. Ed.* 43 (2004) 2334-2375.
- [18] J.L. Rowsell, O.M. Yaghi, *Microporous Mesoporous Mater.* 73 (2004) 3-14.
- [19] N. Ahmad, H.A. Younus, A.H. Chughtai, F. Verpoort, *Chem. Soc. Rev.* 44 (2015) 9-25.

- [20] J. Lee, Synthesis and Gas Sorption Study of Microporous Metal Organic Frameworks for Hydrogen and Methane Storage, ProQuest LLC, Michigan, 2007, pp. 1-31.
- [21] G. Férey, Chem. Soc. Rev. 37 (2008) 191-214.
- [22] S.R. Batten, S.M. Neville, D.R. Turner, Coordination polymers: design, analysis and application, Royal Society of Chemistry, Cambridge, 2009, pp. 144-183.
- [23] M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke, O.M. Yaghi, J. Solid State Chem. 152 (2000) 3-20.
- [24] D.J. Tranchemontagne, Z. Ni, M. O'Keeffe, O.M. Yaghi, Angew. Chem. Int. Ed. 47 (2008) 5136-5147.
- [25] J.-R. Li, D.J. Timmons, H.-C. Zhou, J. Am. Chem. Soc. 131 (2009) 6368-6369.
- [26] Y.-G. Sun, X.-M. Yan, F. Ding, E.-J. Gao, W.-Z. Zhang, F. Verpoort, Inorg. Chem. Commun. 11 (2008) 1117-1120.
- [27] H.K. Chae, D.Y. Siberio-Pérez, J. Kim, Y. Go, M. Eddaoudi, A.J. Matzger, M. O'Keeffe, O.M. Yaghi, Nature 427 (2004) 523-527.
- [28] H. Li, M. Eddaoudi, T.L. Groy, O. Yaghi, J. Am. Chem. Soc. 120 (1998) 8571-8572.
- [29] A.J. Fletcher, E.J. Cussen, T.J. Prior, M.J. Rosseinsky, C.J. Kepert, K.M. Thomas, J. Am. Chem. Soc. 123 (2001) 10001-10011.
- [30] C.X. Bezuidenhout, V.J. Smith, P.M. Bhatt, C. Esterhuysen, L.J. Barbour, Angew. Chem. 127 (2015) 1-6.
- [31] S. Takamizawa, W. Mori, M. Furihata, S. Takeda, K. Yamaguchi, Inorg. Chim. Acta. 283 (1998) 268-274.
- [32] L. Pan, K.M. Adams, H.E. Hernandez, X. Wang, C. Zheng, Y. Hattori, K. Kaneko, J. Am. Chem. Soc. 125 (2003) 3062-3067.
- [33] A.H. Chughtai, N. Ahmad, H.A. Younus, A. Laypkov, F. Verpoort, Chem. Soc. Rev. (2015) DOI:10.1039/c4cs00395k.
- [34] Y. Jiang, J. Huang, M. Hunger, M. Maciejewski, A. Baiker, Catal. Sci. Technol. 5 (2015) 897-902.
- [35] M.H. Beyzavi, C.J. Stephenson, Y. Liu, O. Karagiari, J.T. Hupp, O.K. Farha, Front. Energy Res. 2 (2015) 63.
- [36] L. Ma, W. Lin, in: M. Schröder (Ed.), Functional Metal-Organic Frameworks: Gas Storage, Separation and Catalysis, Springer Science+Business Media, New York, 2010, pp. 175-205.

- [37] S. Horike, M. Dinca, K. Tamaki, J.R. Long, *J. Am. Chem. Soc.* 130 (2008) 5854-5855.
- [38] J.E. Halls, A. Hernán-Gómez, A.D. Burrows, F. Marken, *Dalton Trans.* 41 (2012) 1475-1480.
- [39] P. de Frémont, N. Marion, S.P. Nolan, *Coord. Chem. Rev.* 253 (2009) 862-892.
- [40] E. Fischer, A. Maasböl, *Angew. Chem. Int. Ed. Engl.* 3 (1964) 580-581.
- [41] R.R. Schrock, *J. Am. Chem. Soc.* 97 (1975) 6577-6578.
- [42] K. Öfele, *J. Organomet. Chem.* 12 (1968) P42-P43.
- [43] H.W. Wanzlick, H.J. Schönherr, *Angew. Chem. Int. Ed. Engl.* 7 (1968) 141-142.
- [44] S. Díez-González, S.P. Nolan, *Coord. Chem. Rev.* 251 (2007) 874-883.
- [45] T. Weskamp, V.P. Böhm, W.A. Herrmann, *J. Organomet. Chem.* 600 (2000) 12-22.
- [46] A.J. Arduengo III, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.* 113 (1991) 361-363.
- [47] A.J. Arduengo III, M. Kline, J.C. Calabrese, F. Davidson, *J. Am. Chem. Soc.* 113 (1991) 9704-9705.
- [48] H. Jacobsen, A. Correa, A. Poater, C. Costabile, L. Cavallo, *Coord. Chem. Rev.* 253 (2009) 687-703.
- [49] F. Wang, L.-j. Liu, W. Wang, S. Li, M. Shi, *Coord. Chem. Rev.* 256 (2012) 804-853.
- [50] D. Enders, K. Breuer, G. Raabe, J. Runsink, J.H. Teles, J.P. Melder, K. Ebel, S. Brode, *Angew. Chem.* 107 (1995) 1119-1122.
- [51] D. Enders, H. Gielen, G. Raabe, J. Runsink, J.H. Teles, *Chem. Ber.* 129 (1996) 1483-1488.
- [52] D.M. Khramov, A.J. Boydston, C.W. Bielawski, *Angew. Chem.* 118 (2006) 6332-6335.
- [53] S. Kim, S.Y. Choi, Y.T. Lee, K.H. Park, H. Sitzmann, Y.K. Chung, *J. Organomet. Chem.* 692 (2007) 5390-5394.
- [54] A.M. Maj, L. Delaude, A. Demonceau, A.F. Noels, *J. Organomet. Chem.* 692 (2007) 3048-3056.
- [55] F. Glorius, G. Altenhoff, R. Goddard, C. Lehmann, *Chem. Commun.* (2002) 2704-2705.
- [56] F.E. Hahn, M.C. Jahnke, *Angew. Chem. Int. Ed.* 47 (2008) 3122-3172.
- [57] D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* 107 (2007) 5606-5655.
- [58] A. Tudose, A. Demonceau, L. Delaude, *J. Organomet. Chem.* 691 (2006) 5356-5365.
- [59] D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, *Chem. Rev.* 100 (2000) 39-92.
- [60] H. Catalysis, *Platin. Met. Rev.* 51 (2007) 212-214.
- [61] V.P. Reddy, A. Vadapalli, E. Sinn, N. Hosmane, *J. Organomet. Chem.* 747 (2013) 43-50.

- [62] T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.* 49 (2010) 6940-6952.
- [63] T. Ritter, M.W. Day, R.H. Grubbs, *J. Am. Chem. Soc.* 128 (2006) 11768-11769.
- [64] F.B. Hamad, T. Sun, S. Xiao, F. Verpoort, *Coord. Chem. Rev.* 257 (2013) 2274-2292.
- [65] J.-L. Mieusset, U.H. Brinker, *J. Org. Chem.* 73 (2008) 1553-1558.
- [66] A. Schmidt, T. Habeck, *Lett. Org. Chem.* 2 (2005) 37-39.
- [67] V. Lavallo, Y. Canac, B. Donnadieu, W.W. Schoeller, G. Bertrand, *Science* 312 (2006) 722-724.
- [68] A.J. Arduengo III, H.R. Dias, D.A. Dixon, R.L. Harlow, W. Klooster, T. Koetzle, *J. Am. Chem. Soc.* 116 (1994) 6812-6822.
- [69] D.J. Nelson, S.P. Nolan, *Chem. Soc. Rev.* 42 (2013) 6723-6753.
- [70] M.K. Denk, J.M. Rodezno, S. Gupta, A.J. Lough, *J. Organomet. Chem.* 617 (2001) 242-253.
- [71] J.F. Lehmann, S.G. Urquhart, L.E. Ennis, A.P. Hitchcock, K. Hatano, S. Gupta, M.K. Denk, *Organometallics* 18 (1999) 1862-1872.
- [72] K. Denk, P. Sirsch, W.A. Herrmann, *J. Organomet. Chem.* 649 (2002) 219-224.
- [73] I. Kaljurand, T. Rodima, I. Leito, I.A. Koppel, R. Schwesinger, *J. Org. Chem.* 65 (2000) 6202-6208.
- [74] A. Poater, F. Ragone, S. Giudice, C. Costabile, R. Dorta, S.P. Nolan, L. Cavallo, *Organometallics* 27 (2008) 2679-2681.
- [75] W.A. Herrmann, C. Koecher, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2162-2187.
- [76] P.L. Arnold, S. Pearson, *Coord. Chem. Rev.* 251 (2007) 596-609.
- [77] W.A. Herrmann, P.W. Roesky, M. Elison, G. Artus, K. Oefele, *Organometallics* 14 (1995) 1085-1086.
- [78] I. Özdemir, S. Demir, O. Şahin, O. Büyükgüngör, B. Çetinkaya, *J. Organomet. Chem.* 695 (2010) 1555-1560.
- [79] I.E. Markó, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant, J.-P. Declercq, *Science* 298 (2002) 204-206.
- [80] K. Hirano, A.T. Biju, I. Piel, F. Glorius, *J. Am. Chem. Soc.* 131 (2009) 14190-14191.
- [81] A.T. Biju, N.E. Wurz, F. Glorius, *J. Am. Chem. Soc.* 132 (2010) 5970-5971.
- [82] A.T. Biju, F. Glorius, *Angew. Chem. Int. Ed.* 49 (2010) 9761-9764.

- [83] N. Marion, E.C. Ecarnot, O. Navarro, D. Amoroso, A. Bell, S.P. Nolan, *J. Org. Chem.* 71 (2006) 3816-3821.
- [84] O. Navarro, R.A. Kelly, S.P. Nolan, *J. Am. Chem. Soc.* 125 (2003) 16194-16195.
- [85] O. Navarro, N. Marion, J. Mei, S.P. Nolan, *Chem. Eur. J.* 12 (2006) 5142-5148.
- [86] G. Altenhoff, R. Goddard, C.W. Lehmann, F. Glorius, *Angew. Chem.* 115 (2003) 3818-3821.
- [87] G. Altenhoff, R. Goddard, C.W. Lehmann, F. Glorius, *J. Am. Chem. Soc.* 126 (2004) 15195-15201.
- [88] S. Wuertz, F. Glorius, *Acc. Chem. Res.* 41 (2008) 1523-1533.
- [89] L.D. Vázquez-Serrano, B.T. Owens, J.M. Buriak, *Chem. Commun.* (2002) 2518-2519.
- [90] A.C. Hillier, H.M. Lee, E.D. Stevens, S.P. Nolan, *Organometallics* 20 (2001) 4246-4252.
- [91] T.M. Trnka, R.H. Grubbs, *Acc. Chem. Res.* 34 (2001) 18-29.
- [92] A. Fürstner, *Angew. Chem. Int. Ed.* 39 (2000) 3012-3043.
- [93] S.J. Connon, S. Blechert, *Angew. Chem. Int. Ed.* 42 (2003) 1900-1923.
- [94] C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* 109 (2009) 3708-3742.
- [95] N. Ledoux, B. Allaert, F. Verpoort, *Eur. J. Inorg. Chem.* 2007 (2007) 5578-5583.
- [96] A.M. Lozano-Vila, S. Monsaert, A. Bajek, F. Verpoort, *Chem. Rev.* 110 (2010) 4865-4909.
- [97] W.A. Herrmann, M. Elison, J. Fischer, C. Koecher, G.R. Artus, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2371-2374.
- [98] S. Díez-González, N. Marion, S.P. Nolan, *Chem. Rev.* 109 (2009) 3612-3676.
- [99] L. Mercks, M. Albrecht, *Chem. Soc. Rev.* 39 (2010) 1903-1912.
- [100] M. Niehues, G. Erker, G. Kehr, P. Schwab, R. Fröhlich, O. Blacque, H. Berke, *Organometallics* 21 (2002) 2905-2911.
- [101] A.J. Arduengo III, H.R. Dias, J.C. Calabrese, F. Davidson, *J. Am. Chem. Soc.* 114 (1992) 9724-9725.
- [102] H. Schumann, J. Gottfriedsen, M. Glanz, S. Dechert, J. Demtschuk, *J. Organomet. Chem.* 617 (2001) 588-600.
- [103] H. Nakai, Y. Tang, P. Gantzel, K. Meyer, *Chem. Commun.* (2003) 24-25.
- [104] W.A. Herrmann, O. Runte, G. Artus, *J. Organomet. Chem.* 501 (1995) C1-C4.
- [105] S.A. Mungur, S.T. Liddle, C. Wilson, M.J. Sarsfield, P.L. Arnold, *Chem. Commun.* (2004) 2738-2739.

- [106] L. Cavallo, A. Correa, C. Costabile, H. Jacobsen, *J. Organomet. Chem.* 690 (2005) 5407-5413.
- [107] C. Boehme, G. Frenking, *Organometallics* 17 (1998) 5801-5809.
- [108] M.-T. Lee, C.-H. Hu, *Organometallics* 23 (2004) 976-983.
- [109] J.C. Garrison, R.S. Simons, W.G. Kofron, C.A. Tessier, W.J. Youngs, *Chem. Commun.* (2001) 1780-1781.
- [110] A.A. Tulloch, A.A. Danopoulos, S. Kleinhenz, M.E. Light, M.B. Hursthouse, G. Eastham, *Organometallics* 20 (2001) 2027-2031.
- [111] X. Hu, Y. Tang, P. Gantzel, K. Meyer, *Organometallics* 22 (2003) 612-614.
- [112] X. Hu, I. Castro-Rodriguez, K. Olsen, K. Meyer, *Organometallics* 23 (2004) 755-764.
- [113] D. Nemcsok, K. Wichmann, G. Frenking, *Organometallics* 23 (2004) 3640-3646.
- [114] H. Nakai, X. Hu, L.N. Zakharov, A.L. Rheingold, K. Meyer, *Inorg. Chem.* 43 (2004) 855-857.
- [115] H. Jacobsen, A. Correa, C. Costabile, L. Cavallo, *J. Organomet. Chem.* 691 (2006) 4350-4358.
- [116] M.D. Sanderson, J.W. Kamplain, C.W. Bielawski, *J. Am. Chem. Soc.* 128 (2006) 16514-16515.
- [117] M.K. Samantaray, K. Pang, M.M. Shaikh, P. Ghosh, *Inorg. Chem.* 47 (2008) 4153-4165.
- [118] S. Fantasia, J.L. Petersen, H. Jacobsen, L. Cavallo, S.P. Nolan, *Organometallics* 26 (2007) 5880-5889.
- [119] N.M. Scott, R. Dorta, E.D. Stevens, A. Correa, L. Cavallo, S.P. Nolan, *J. Am. Chem. Soc.* 127 (2005) 3516-3526.
- [120] R. Dorta, E.D. Stevens, N.M. Scott, C. Costabile, L. Cavallo, C.D. Hoff, S.P. Nolan, *J. Am. Chem. Soc.* 127 (2005) 2485-2495.
- [121] C.A. Tolman, *Chem. Rev.* 77 (1977) 313-348.
- [122] A.C. Hillier, W.J. Sommer, B.S. Yong, J.L. Petersen, L. Cavallo, S.P. Nolan, *Organometallics* 22 (2003) 4322-4326.
- [123] M.S. Viciu, O. Navarro, R.F. Germaneau, R.A. Kelly, W. Sommer, N. Marion, E.D. Stevens, L. Cavallo, S.P. Nolan, *Organometallics* 23 (2004) 1629-1635.
- [124] N. Marion, O. Navarro, J. Mei, E.D. Stevens, N.M. Scott, S.P. Nolan, *J. Am. Chem. Soc.* 128 (2006) 4101-4111.

- [125] J.Y. Lee, J.M. Roberts, O.K. Farha, A.A. Sarjeant, K.A. Scheidt, J.T. Hupp, *Inorg. Chem.* 48 (2009) 9971-9973.
- [126] S. Sen, N.N. Nair, T. Yamada, H. Kitagawa, P.K. Bharadwaj, *J. Am. Chem. Soc.* 134 (2012) 19432-19437.
- [127] S. Sen, S. Neogi, A. Aijaz, Q. Xu, P.K. Bharadwaj, *Inorg. Chem.* 53 (2014) 7591-7598.
- [128] G. Nickerl, A. Notzon, M. Heitbaum, I. Senkovska, F. Glorius, S. Kaskel, *Cryst. Growth Des.* 13 (2012) 198-203.
- [129] R.S. Crees, M.L. Cole, L.R. Hanton, C.J. Sumby, *Inorg. Chem.* 49 (2010) 1712-1719.
- [130] P. Valvekens, F. Vermoortele, D. De Vos, *Catal. Sci. Technol.* 3 (2013) 1435-1445.
- [131] M.B. Lalonde, O.K. Farha, K.A. Scheidt, J.T. Hupp, *ACS Catal.* 2 (2012) 1550-1554.
- [132] H.A. Younus, W. Su, N. Ahmad, S. Chen, F. Verpoort, *Adv. Synth. Catal.* 357 (2015) 283-330.
- [133] H.A. Younus, N. Ahmad, W. Su, F. Verpoort, *Coord. Chem. Rev.* 276 (2014) 112-152.
- [134] D. Enders, T. Balensiefer, *Acc. Chem. Res.* 37 (2004) 534-541.
- [135] M. Mayr, B. Mayr, M.R. Buchmeiser, *Angew. Chem. Int. Ed.* 40 (2001) 3839-3842.
- [136] Y. Zhang, L. Zhao, P.K. Patra, J.Y. Ying, *Adv. Synth. Catal.* 350 (2008) 662-666.
- [137] Y. Zhang, L. Zhao, P.K. Patra, D. Hu, J.Y. Ying, *Nano Today*, 4 (2009) 13-20.
- [138] U. Díaz, M. Boronat, A. Corma, *Proc. R. Soc. A*, 468 (2012) 1927-1954.
- [139] I. Luz, F. Llabrés i Xamena, A. Corma, *J. Catal.* 285 (2012) 285-291.
- [140] I. Luz, F. Llabrés i Xamena, A. Corma, *J. Catal.* 276 (2010) 134-140.
- [141] J.M. Roberts, O.K. Farha, A.A. Sarjeant, J.T. Hupp, K.A. Scheidt, *Cryst. Growth Des.* 11 (2011) 4747-4750.
- [142] R.H. Crabtree, *Chem. Rev.* 115 (2015) 127-150.
- [143] W.A. Herrmann, T. Weskamp, V.P. Boehm, *Adv. Organomet. Chem.* 48 (2001) 1-69.
- [144] A. Burgun, C.J. Doonan, C.J. Sumby, *Aust. J. Chem.* 66 (2013) 409-418.
- [145] K. Oisaki, Q. Li, H. Furukawa, A.U. Czaja, O.M. Yaghi, *J. Am. Chem. Soc.* 132 (2010) 9262-9264.
- [146] S. Sen, T. Yamada, H. Kitagawa, P.K. Bharadwaj, *Cryst. Growth Des.* 14 (2014) 1240-1244.
- [147] A. Burgun, R.S. Crees, M.L. Cole, C.J. Doonan, C.J. Sumby, *Chem. Commun.* 50 (2014) 11760-11763.

- [148] I. T. Siraj, M.D. Spicer, *Int. J. Chem. Eng. Appl.* 4 (2013) 199-203.
- [149] J. Chun, H.S. Lee, I.G. Jung, S.W. Lee, H.J. Kim, S.U. Son, *Organometallics* 29 (2010) 1518-1521.
- [150] J. Chun, I.G. Jung, H.J. Kim, M. Park, M.S. Lah, S.U. Son, *Inorg. Chem.* 48 (2009) 6353-6355.
- [151] X.-W. Wang, L. Han, T.-J. Cai, Y.-Q. Zheng, J.-Z. Chen, Q. Deng, *Cryst. Growth Des.* 7 (2007) 1027-1030.
- [152] G.-Q. Kong, C.-D. Wu, *CrystEngComm* 14 (2012) 847-852.
- [153] X.-C. Chai, Y.-Q. Sun, R. Lei, Y.-P. Chen, S. Zhang, Y.-N. Cao, H.-H. Zhang, *Cryst. Growth Des.* 10 (2009) 658-668.
- [154] P. Suresh, C.N. Babu, G. Prabusankar, *Polyhedron* 89 (2015) 322-329.
- [155] S. Wang, Q. Yang, J. Zhang, X. Zhang, C. Zhao, L. Jiang, C.-Y. Su, *Inorg. Chem.* 52 (2013) 4198-4204.
- [156] P. Suresh, S. Radhakrishnan, C.N. Babu, A. Sathyanarayana, N. Sampath, G. Prabusankar, *Dalton Trans.* 42 (2013) 10838-10846.
- [157] G.-Q. Kong, X. Xu, C. Zou, C.-D. Wu, *Chem. Commun.* 47 (2011) 11005-11007.
- [158] G.-Q. Kong, S. Ou, C. Zou, C.-D. Wu, *J. Am. Chem. Soc.* 134 (2012) 19851-19857.
- [159] J.C. Garrison, W.J. Youngs, *Chem. Rev.* 105 (2005) 3978-4008.
- [160] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, *Nature* 423 (2003) 705-714.
- [161] Z.-J. Lin, J. Lü, M. Hong, R. Cao, *Chem. Soc. Rev.* 43 (2014) 5867-5895.
- [162] H. Guo, X. Guo, H. Zou, Y. Qi, R. Chen, L. Zhao, C. Liu, *CrystEngComm* 16 (2014) 7459-7468.
- [163] Z. Fei, T.J. Geldbach, D. Zhao, R. Scopelliti, P.J. Dyson, *Inorg. Chem.* 44 (2005) 5200-5202.
- [164] Z. Fei, T.J. Geldbach, R. Scopelliti, P.J. Dyson, *Inorg. Chem.* 45 (2006) 6331-6337.
- [165] S. Zhang, L. Han, L. Li, J. Cheng, D. Yuan, J. Luo, *Cryst. Growth Des.* 13 (2013) 5466-5472.
- [166] M.C. Das, S. Xiang, Z. Zhang, B. Chen, *Angew. Chem. Int. Ed.* 50 (2011) 10510-10520.
- [167] B.J. Burnett, P.M. Barron, W. Choe, *CrystEngComm* 14 (2012) 3839-3846.

- [168] A.O.z.r. Yazaydin, A.I. Benin, S.A. Faheem, P. Jakubczak, J.J. Low, R.R. Willis, R.Q. Snurr, Chem. Mater. 21 (2009) 1425-1430.
- [169] Z. Wang, S.M. Cohen, Chem. Soc. Rev. 38 (2009) 1315-1329.
- [170] S.-H. Cho, B. Ma, S.T. Nguyen, J.T. Hupp, T.E. Albrecht-Schmitt, Chem. Commun. (2006) 2563-2565.
- [171] S.M. Cohen, Chem. Rev. 112 (2011) 970-1000.
- [172] J. Louie, R.H. Grubbs, Chem. Commun. (2000) 1479-1480.
- [173] B.J. Truscott, A.M.Z. Slawin, S.P. Nolan, Dalton Trans. 42 (2013) 270-276.
- [174] J.C. Bernhammer, H.V. Huynh, Organometallics 33 (2014) 5845-5851.

Fig. 1. Combination of ligands and metal ions to synthesize MOF materials. Reprinted with permission from [19]. Copyright 2015 Royal Society of Chemistry.

Fig. 2. The nitrogen sorption isotherms were measured at 77 K and display type I behavior, as expected for compounds with uniform micropores. Reproduced with permission from [18].

Fig. 3. The first stable NHC ligand. Reprinted with permission from [46]. Copyright 1991 American Chemical Society.

Fig. 4. NHC-derived second-generation catalysts in olefin metathesis. Mes, mesityl; PCy₃, tricyclohexylphosphine. **1** and **2**, reprinted with permission from [63]. Copyright 2006 American Chemical Society. **3** and **4** reproduced with permission from [64]. Copyright 2013 Elsevier.

Fig. 5. Structure of a generic NHC-metal complex **5** and some examples of NHC-metal complexes **6** and **7**. **5** and **7** reproduced with permission from [49]. Copyright 2012 Elsevier. **6** reproduced with permission from [95]. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.

Fig. 6. The most important NHC molecular orbitals involved in the NHC-metal bonding. Reproduced with permission from [106].

Fig. 7. NHC complex with a *p*-quinone moiety attached at the C4 and C5 positions. Mes, mesityl. Reprinted with permission from [116]. Copyright 2006 American Chemical Society.

Fig. 8. The sphere dimensions used for determination of the buried volume. Reproduced with permission from [106].

Fig. 9. The carbene stabilization in MOFs by the two nitrogen atoms. Reprinted with permission from [126]. Copyright 2012 American Chemical Society.

Fig. 10. General example of conversion of azolium to NHC

Fig. 11. An example of a bent ligand when azolium forms the core.

Scheme 1. The strategies to prepare azolium-containing MOFs. (a) Two design features of azolium-containing ligands. (b) Synthetic methods of incorporating azolium or NHC entities into MOFs. The green ring symbolizes the azolium ring, the purple sphere symbolizes the postsynthetically added metal, and the yellow cube represents the metal node for the synthesis of the MOF.

Fig. 12. Rigidity and flexibility of azolium-containing ligands, where (a) contains two flexible carboxylate wings, (b) contains two rigid carboxylate wings, and (c) contains one rigid carboxylate wing and one flexible carboxylate wing. A blue sphere represents an imidazolium ring, a red sphere represents a carboxylate group, a green ring represents a flexible site, and a purple ring represents a rigid site. Reproduced with permission from [154].

Fig. 13. The polycatenated azolium-containing framework. Reproduced with permission from [146]. Copyright 2014 American Chemical Society.

Fig. 14. Perspective view of the diamond-like MOFs with the unusual coordination of the SBU, Zn_4O . Adapted with permission from [147]. Copyright 2014 Royal Society of Chemistry.

Fig. 15. Six metallomacrocycles connected to the core Zn_8O cluster. Reprinted with permission from [126]. Copyright 2012 American Chemical Society.

Fig. 16. Parallel stacking of the $\text{Ag}(\text{I})$ network. Hydrogen atoms, PF_6^- anion outside the ring structure, and hydrogen bonding omitted for clarity. Reproduced with permission from [148].

Fig. 17. Perspective view of the undulating structure of the one-dimensional necklace-type MOFs. Reprinted with permission from [129]. Copyright 2010 American Chemical Society.

Fig. 18. (a) A space-filling model showing the doubly interpenetrating three-dimensional chiral MOF. Reprinted with permission from [151]. Copyright 2010 American Chemical Society. (b) A space-filling representation of the three-dimensional supramolecular network. Adapted with permission from [152]. Copyright 2012 Royal Society of Chemistry.

Fig. 19. Different structures of the flexible azolium-containing MOFs. Reprinted with permission from [153]. Copyright 2009 American Chemical Society.

Fig. 20. Level of catenation dependent on the number of azolium cores. Reprinted with permission from [141]. Copyright 2011 American Chemical Society.

Fig. 21. Single-crystal structure of IRMOF-76 showing the linker. Reprinted with permission from [145]. Copyright 2010 American Chemical Society.

Fig. 22. Self-assembled supramolecular structure between the building block L and cadmium(II) nitrate in the DMF node. Reprinted with permission from [150]. Copyright 2009 American Chemical Society.

Fig. 23. Three-dimensional network structure formed by assembly of the azolium-containing ligand and Ce(III) (the bridging and nonbridging carboxylates are differentiated by red and green, respectively). Reprinted with permission from [149]. Copyright 2010 American Chemical Society.

Fig. 24. Flexible bis(carboxyimidazolium)anthracene spacer.

Fig. 25. Self-assembled supramolecular structure between NHC ligand and copper(II) nitrate. Reprinted with permission from [150]. Copyright 2009 American Chemical Society.

Fig. 26. X-ray structures of the NHC-copper-decorated three-dimensional network. Blue and violet balls indicate incorporated copper in building blocks and cerium connectors, respectively. Reprinted with permission from [149]. Copyright 2010 American Chemical Society.

Fig. 27. $[\text{CuL}_2]$ bis(NHC) linker. Adapted with permission from [147]. Copyright 2014 Royal Society of Chemistry.

Scheme 2. Premetalated NHC complexes for the synthesis of MOFs. Reprinted with permission from [140]. Copyright 2010 American Chemical Society.

Fig. 28. A view of the lamellar network of $[\text{Cu}_2\text{L}_2(\text{MeOH})_2]\cdot 4\text{NO}_3\cdot \text{H}_2\text{O}$ consisting of 80-membered macrocycle rings of the ligand bridging copper paddle-wheel subunits down the *c*-axis, showing the available imidazolium moieties (color code: cyan, Cu; red, O; blue, N; gray, C). Adapted with permission from [157]. Copyright 2011 Royal Society of Chemistry.

Scheme 3. The catalytic reactions of the modified frameworks. (a) Suzuki-Miyaura cross-coupling reaction, (b) Heck coupling reaction, and (c) hydrogenation of olefins. Adapted with permission from [158]. Copyright 2012 American Chemical Society.

Scheme 4. MOF-based NHC-like catalysis of α,β -unsaturated ketone to the corresponding methyl ether. Adapted with permission from [131]. Copyright 2012 American Chemical Society.

Scheme 5. Catalytic reaction at the Cu(I) bis(NHC) site. Reprinted with permission from [147]. Copyright 2014 Royal Society of Chemistry.

Fig. 29. Concentration of Nile blue in the supernatant solution after the copper framework had been put into excess of fresh ethanol. Reprinted with permission from [128]. Copyright 2012 American Chemical Society.

Fig. 30. Proton conductivity (σ) dependence on water uptake. Conductivity was measured with an increase (filled circles) and a decrease (open circles) of the water content. Reprinted with permission from [126]. Copyright 2012 American Chemical Society.

Fig. 31. The ideal adsorbed solution theory selectivity of CO₂ over CH₄ of the optimal activated framework at 298 K. Reprinted with permission from [125]. Copyright 2012 American Chemical Society.

Fig.32. CO₂, N₂, and CH₄ physisorption isotherms of activated MOFs at 273 K. Reprinted with permission from [127]. Copyright 2014 American Chemical Society.

Table 1

Monoazolium-containing linker with azolium forming the core

Entry	Name of linker	Structure of linker	Metal nodes	References
1	1,3-Bis(4-carboxyphenyl)imidazolium chloride		Zn(II), Cd(II)	[126, 129]
2	1,3-Bis(3-carboxyphenyl)imidazolium		Zn(II)	[129]

	chloride		
3	1,3-Bis(4-carboxy-2,6-dimethylphenyl)-1 <i>H</i> imidazolium chloride	Cu(II), Zn(II)	[128]
4	1,3-Bis(4-carboxy-2,6-diisopropylphenyl)imidazolium chloride	Cd(II), Cu(I), Ce(III)	[150]
5	<i>N,N'</i> -Bis(2,6-dimethyl-3,5-carboxylphenyl)imidazolium chloride	Cu(II)	[125]
6	<i>N</i> -(3,5-Dicarboxylphenyl)- <i>N'</i> -(4-carboxylbenzyl)imidazolium chloride	Zn(II)	[155]
7	1,3-Bis(3,5-dicarboxyphenyl)imidazolium chloride	Zn(II)	[127]
8	1,3-Bis(4-picolyl)imidazolium chloride	Ag(I), Cu(I)	[148]
9	1-(Carboxymethyl)-3-(4-carboxyphenyl)-1 <i>H</i> -imidazol-3-ium bromide	Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)	[154]

Table 2

Bisazolium-containing linker with azoliums forming the core

Entry	Name of linker	Structure of linker	Metal	Reference
-------	----------------	---------------------	-------	-----------

		nodes
1	1,1'-Methylenebis(3-(4-carboxyphenyl)-1 <i>H</i> -imidazol-3-ium)	Cu(II) [157]
2	1,1'-Methylenebis(3-(4-carboxy-2-methylphenyl)-1 <i>H</i> -imidazol-3-ium)	Zn(II) [158]
3	1,1'-(Anthracene-9,10-diylbis(methylene))bis(3-(carboxymethyl)-1 <i>H</i> -imidazol-3-ium) bromide	Cu(II), [156] Zn(II)

Table 3

Azolium-containing linker with azolium entities appended to existing linkers.

Entry	Name of linker	Structure of linker	Metal nodes	Reference
1	3-((4,4'-Dicarboxybiphenyl-2-yl)methyl)-1-methyl-1 <i>H</i> -imidazol-3-ium bromide		Cu(II), [141] Zn(II)	
2	3,3'-(4,4'-Dicarboxybiphenyl-2,2'-diyl)bis(methylene)bis(1-methyl-1 <i>H</i> -imidazol-3-ium) bromide		Cu(II)	[141]
3	4,7-Bis(4-carboxylphenyl)-1,3-dimethylbenzimidazium tetrafluoroborate		Zn(II)	[145]

Table 4

Structure-property relations of azolium-containing MOFs in catalysis.

Entry	Linker, L	MOF (formula)	Active site(s)	Reaction(s)	Reference
1	1,1'-Methylenebis(3-(4-carboxyphenyl)-1 <i>H</i> -imidazol-3-ium)	$\text{CuL}_{0.24}\text{L}_{0.76}\text{Pd}_{0.76}(\text{H}_2\text{O})_4(\text{NO}_3)_2$	NHC-anchored Pd(II)	Suzuki-Miyaura cross-coupling reaction of phenylhalides and phenylboronic acids	[157]
2	1,1'-Methylenebis(3-(4-carboxy-2-methylphenyl)-1 <i>H</i> -imidazol-3-ium)	$[\text{ZnL}_{0.42}\text{L}_{0.58}\text{Cl}_2\text{Pd}_{0.58}(\text{H}_2\text{O})_{1.16}] \cdot 9\text{H}_2\text{O}$	NHC-anchored Pd(II)	Suzuki-Miyaura coupling reaction of phenylhalides and phenylboronic acids	[158]
3	1,1'-Methylenebis(3-(4-carboxy-2-methylphenyl)-1 <i>H</i> -imidazol-3-ium)	$[\text{ZnL}_{0.42}\text{L}_{0.58}\text{Cl}_2\text{Pd}_{0.58}(\text{H}_2\text{O})_{1.16}] \cdot 9\text{H}_2\text{O}$	NHC-anchored Pd(II)	Heck coupling of aryl halides with olefins	[158]
4	1,1'-Methylenebis(3-(4-carboxy-2-methylphenyl)-1 <i>H</i> -imidazol-3-ium)	$[\text{ZnL}_{0.42}\text{L}_{0.58}\text{Cl}_2\text{Pd}_{0.58}(\text{H}_2\text{O})_{1.16}] \cdot 9\text{H}_2\text{O}$	NHC-anchored	Hydrogenation of olefins	[158]

	imidazol-3-ium)		Pd(II)		
5	1,1'-Methylenebis(3-(4-carboxy-2-methylphenyl)-1 <i>H</i> -imidazol-3-ium)	[ZnL _{0.42} L _{0.58} Cl ₂ Pd _{0.58} (H ₂ O) _{1.16}]·9H ₂ O	NHC- anchor ed Pd(II)	Reduction of nitrobenzene for the formation of aniline	[158]
6	1,3,5-Trimethylimidazole-2,4,6-triethylbenzene	[Co ₃ Cl ₆ (L) ₂]	NHC	Conjugative addition of alcohols to α,β - unsaturated ketones	[131]
7	1,3-Bis(4-carboxyphenyl)imidazolium	[Zn ₄ O{Cu(L) ₂ } ₂]	Cu(I) bis(NH C)	Hydroborati on of CO ₂	[147]

Table 5

The Suzuki-Miyaura cross-coupling reaction of phenylhalides and phenylboronic acids. Reproduced with permission from [157]. Copyright 2011 Royal Society of Chemistry.

Entry	R	X	R'	Yield (%)
1	H	Br	H	98
2	H	Br	3-CH ₃	93
3	H	Br	4-CH ₃ O	91
4	H	Br	4-CN	3.4
5	4-CH ₃	Br	H	84
6	4-CH ₃ O	Br	H	81
7	4-CHO	Br	H	>99
8	2-NO ₂	Br	H	99

9	H	I	H	99
10	H	I	3-CH ₃	97
11	H	I	4-CH ₃ O	95
12	4-CH ₃ O	I	H	91
13	4-CH ₃ O	Br	H	31
14	4-CH ₃ O	Br	H	24
15	4-CH ₃ O	Br	H	37
16	4-CH ₃ O	Br	H	8
17	H	Br	H	97
18	4-CH ₃ O	Br	H	43

Reaction conditions; MOF catalyzt., K₂CO₃, toluene, 70 °C, 12 h.

Table 6

Heck coupling of aryl halides with olefins. Adapted with permission from [158]. Copyright 2012 American Chemical Society.

Entry	X	R	R'	Yield (%)
1	Br	CHO	COO(CH ₂) ₃ CH ₃	>99
2	Br	CHO	Ph	>99
3	Br	NO ₂	COO(CH ₂) ₃ CH ₃	>99
4	Br	NO ₂	Ph	>99
5	I	H	COO(CH ₂) ₃ CH ₃	>99
6	I	H	Ph	>99
7	I	CH ₃ O	COO(CH ₂) ₃ CH ₃	>99
8	I	CH ₃ O	Ph	93(0.7)
9	I	NO ₂	COO(CH ₂) ₃ CH ₃	>99
10	I	NO ₂	Ph	>99
11	I	CH ₃ CO	COO(CH ₂) ₃ CH ₃	>99
12	I	CH ₃ CO	Ph	>99
13	I	H	COO(CH ₂) ₃ CH ₃	99(0.3)

Reaction conditions: MOF catalyst., K₂CO₃, dimethylacetamide, 100 °C, 1 h.

Table 7

N-Formylation of benzylamine using HCO₂B(pin) prepared by a [Zn₄O{Cu(L)₂}₂]-catalyzed hydroboration of CO₂. Reprinted with permission from [147]. Copyright 2014 Royal Society of Chemistry.

Entry	Cu catalyst	Cu (mol%)	Conversion (%)
1	None	0	6
2	[Zn ₄ O{Cu(L) ₂ } ₂]	10	92
3	[Zn ₄ O{Cu(L) ₂ } ₂]	5	92
4	[Zn ₄ O{Cu(L) ₂ } ₂]	1	66

Determined by ¹H NMR spectroscopy. 1 mol% Cu = 0.5 mol% MOF

Table 8

Structure-property relations of azolium-containing MOFs in other applications

Entry	Linker	MOF(Formula)	Active site(s)	Application(s)	Reference
1	Imid = 1,3-bis(4-carboxy-2,6-dimethylphenyl)-1 <i>H</i> -imidazolium	[Cu(Imid)(H ₂ O)] ⁺	Cationic imidazolium moiety	Selective adsorption of organic molecules bearing a carboxylic group or having an ionic nature	[128]

2	L = 1,3-bis(4-carboxyphenyl)imidazolium	$\{[(Zn_{0.25})_8(O)]Zn_6(L)_{12}(H_2O)_{29}(DMF)_{69}(NO_3)_2\}_n$	Methylene proton of the imidazolium moieties	proton conductivity	[126]
3	L = 1,3-bis(4-carboxyphenyl)imidazolium	$\{[Cd_2(L)_3(DMF)(NO_3)] \cdot (DMF)_3 \cdot (H_2O)_8\}_n$	Methylene proton of the imidazolium moieties	Proton conductivity	[146]
4	IMTA = imidazolium tetraacid = <i>N,N'</i> -bis(2,6-dimethyl-3,5-carboxylphenyl)imidazolium chloride	$[Cu_2(IMTA)(DMSO)_2] \cdot 2H_2O$	Ionic environment from the positively charged imidazolium moieties	To separate CO ₂ from CH ₄	[125]
5	DCPCBIm = <i>N</i> -(3,5-dicarboxylphenyl)- <i>N'</i> -(4-carboxylbenzyl)imidazolium	$\{Zn_2(DCPCBIm)_2 \cdot DMF\}_n$	Ionic environment from the positively charged imidazolium moieties	To separate CO ₂ from H ₂ and CH ₄	[155]
5	L = 1,3-bis(3,5-dicarboxyphenyl)imidazolium, bpy = 4,4'-bipyridine, dpe = 1,2-di(4-pyridyl)ethylene, bpb = 1,4-bis(4-pyridyl)benzene	$\{[Zn_2(L)(bpy)_2] \cdot (NO_3) \cdot (DMF)_6 \cdot (H_2O)_9\}_n$ $\{[Zn_2(L)(dpe)_2] \cdot (NO_3) \cdot (DMF)_3 \cdot (H_2O)_2\}_n$ $\{[Zn_2(L)(bpb)_2] \cdot (NO_3) \cdot (DMF)_3 \cdot (H_2O)_4\}_n$	Ionic environment from the positively charged imidazolium components and difference in pore sizes Ionic environment from the positively charged imidazolium components and difference in pore sizes Ionic environment from the positively charged imidazolium components and difference in pore sizes	Selective CO ₂ adsorption over N ₂ and CH ₄ Selective CO ₂ adsorption over N ₂ and CH ₄ Selective CO ₂ adsorption over N ₂ and CH ₄	[127] [127] [127]

Figures

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

a) $\text{NHC} \rightarrow \text{M} \quad \sigma\text{-donation}$

b) $\text{M} \rightarrow \text{NHC} \quad \pi^*\text{-back donation}$

c) $\text{NHC} \rightarrow \text{M} \quad \pi\text{-donation}$

Fig. 6

Fig. 7

Fig. 8

Fig. 9.

Fig. 10.

Fig. 11.

Fig. 12

Fig. 13 (1)

Fig. 13 (2)

Fig. 14

Fig. 15

Fig. 16

Fig. 17

Fig. 18. (1)

Fig. 18 (2)

Fig. 21

Fig. 22

Fig. 23

Fig. 24.

Fig. 25

Fig. 26

Fig. 27

Fig. 28

Fig. 29

Fig. 30

Fig. 31

Fig. 32

Scheme 1

Scheme 2

Scheme 3

Scheme 4

Scheme 5