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Recent Development of Carbenes: Synthesis, Structure, Photophysical Properties and Applications

Arunava Manna, Abhineet Verma, Sumit K. Panja and Satyen Saha

Abstract

Carbenes are highly reactive intermediates in organic synthesis. These divalent carbon species are generally transient in nature and cannot be isolated. However, they can form stable metal complexes. Later on, the development of N-heterocyclic carbene (NHC) and other stable carbene led to the application of these carbon (II) donor ligands in the synthesis of complex natural products, transition metal catalysis, organo-catalysis and several other synthetic methodologies. Here in this short review, we will discuss the brief history of the development of carbenes, synthesis of stable carbenes (NHC in particular), and their applications in natural products synthesis transition metal chemistry/organometallics. In addition to synthesis and application, the chapter will consist of a detailed structural analysis of carbenes and exciting photophysics of this class of compounds. Special emphasis will be given to electronic structure. The role of carbene in the development of luminescent NHC transition metal complexes, the tuning of emission properties as well as their active role as photocatalysts in the reduction of CO₂ will also be discussed.

Keywords: carbene, N-heterocyclic carbene, electronic structure, photophysics, applications

1. Introduction

Carbenes are divalent carbon compounds which are generally highly reactive organic intermediates with six valence electrons having the general formula R²C or R¹R²C [1, 2]. Carbenes are classified as either singlets or triplets, depending upon their electronic structure. Most carbenes are very short lived, although persistent carbene are also known.

Carbene generally have either linear (as an extreme case) or bent geometry with sp² hybridized central carbon atom. These structures are related to electronically different orbital coupled states of central carbon atom in carbene. The orbital coupling between sp-hybrid orbitals and other two energetically degenerated p-orbitals results linear geometry of carbene (**Figure 1**). In other case, the hybrid sp²

Figure 1. Geometry (linear and bent) and hybridization of carbene; Single head arrow indicates electron.

orbitals (δ orbitals) coupled with a p orbital ($p\pi$ orbital) promotes bent geometry of carbene (**Figure 1**).

The arrangement of two nonbonding electrons in carbene is extremely important to reactivity of carbene. The two different electronic states are obtained from different arrangement of two nonbonding electrons in carbene. These electronic states are related to triplet and singlet state of carbene.

1.1 Triplet state of carbene

From two nonbonding electrons, one electron occupies in empty δ orbitals and another electron resides in empty $p\pi$ with parallel spin orientation ($\delta^1 p\pi^1$: $3B_1$). If electronic spin orientation is antiparallel, then the carbene is no longer triplet carbene ($\delta^1 p\pi^1$: $1B_1$) (**Figure 2**).

1.2 Singlet state of carbene

When the two nonbonding electrons occupy as a lone-pair in the empty δ orbital, then the $p\pi$ orbital is being vacant ($\delta^2 p\pi^0$: $1A_1$ state). If these two nonbonding electrons are present in $p\pi$ orbital as a lone pair with empty δ -orbital, then $1A_1$ state is also created with $\delta^0 p\pi^2$ electronic configuration. Interestingly, the $\delta^2 p\pi^0$ ($1A_1$ state) is considered as a more stable state than the $\delta^0 p\pi^2$ (another $1A_1$ state) where the lone-pair occupies the $p\pi$ orbital (**Figure 2**).

The stability of singlet state ($\delta^2 p\pi^0$ ($1A_1$ state))) is explained on the basis of significant energy difference between δ and $p\pi$ orbital (>2.0 eV).¹ Singlet carbenes show the amphiphilic behavior (nucleophilic and electrophilic character) due to the presence of a sp^2 hybridized lone-pair and of a vacant p-orbital.

Initially, carbene were so reactive that they were only considered as reaction intermediates or transition states. They could not be isolated and were only indirectly studied, often by trapping them in the presence of suitable reagents. However, now carbene can be stabilized and isolated by forming complexes with transition metals. They act as ligands for organometallic complexes. Two types of carbene-metal complex are known and they are Fischer and Schrock-type complexes (**Figure 3**).

Figure 2. Triplet and singlet carbenes: electronic configurations. Arrows: electrons.

Figure 3.
 General structure of Fischer and Schrock Carbene with examples.

Figure 4.
 Synthesis of Fischer carbene and their application in organic synthesis.

The Fischer carbene, which were first described in 1960s, form complexes with low valent or lower oxidation state of metal and are versatile reagents for organic synthesis due to presence of electrophilic carbon center (Figure 4). The Schrock-type compounds (first reported in the early 1970s) play an important role in olefin metathesis due to present of nucleophilic carbon center (Figure 5).

2. Types of N-heterocyclic carbene (NHC) ligands

The structure of carbene depends upon the nature of ligands.

Schrock Carbene Complexes

- Unlike the Fischer complexes, Schrock complexes do not have a heteroatom to stabilise "carbocationic" character and are *nucleophilic* at carbon

- The most common examples are:

Figure 5.
Synthesis of Schrock's carbene and their application as catalyst.

Figure 6.
A 4-membered N-heterocyclic carbene ligand 2,6-diisopropyl-substituted substituents.

2.1 4-Membered NHC

Grubbs et al. was the first group to develop the 4-membered NHC [3] (**Figure 6**). It was found that for the isolation of carbene carbon steric shielding was very much important. The 2, 6-diisopropyl-substituted constituents led to the successful isolation of the free NHC [3, 4]. The vibrational, $\nu(\text{CO})$ values of the corresponding Rhodium dicarbonyl complex ($\nu(\text{CO})$ in toluene: 2080 and 1988 cm^{-1}) show that its σ -electron donating properties is slightly less than the dihydroimidazol-2-ylidene analogue [5].

2.2 5-Membered NHC

5-membered ring systems were most and widely reported NHC carbene so far [6–11]. This is due to the fact that 5-membered ring system is sterically more stable and hence provide the extra stability to the NHC as well as improving its catalytic

Figure 7.
Imidazol-2-ylidenes and imidazolidin-2-ylidenes.

properties [8, 9]. Some of the scaffolds used for the preparation of 5-membered NHC were imidazole-2-ylidenes Imes (L2), IPr (L3), Icy (L4), ItBu (L5), and IAd (L6) and the imidazolidin-2-ylidenes SIMes (L7) and SiPr (L8) presented in **Figure 7**.

IBiox system of NHC ligands have been well explored and readily derived from bioxazolines (**Figure 8**) (L9–L13) [5, 6] probably due to the two reasons. (1) The 4,5-dioxygen substitution affects the ligand's electronic properties. The electron donating capability is similar to electron-rich phosphines like PtBu_3 , but slightly less electron-rich than other imidazolium-based N-heterocyclic carbene. It is fascinating that all IBiox ligands have the similar or same electronic properties. There are several salient features among the ligands (L10–L13):

- all of them have a rigid tricyclic backbone
- the presence of the substituents R1 and R2 on the peripheral rings. These groups shield the carbene carbon, and can cause the metal's coordination sphere either to expand or to contract.
- the cycloalkyl substitution on the rigid tricyclic backbone enable the IBiox ligands to become sterically demanding, while being flexible at the same time (flexible steric bulk) [5–7].

Figure 8.
Some of the most widely applicable 5-membered NHC.

Figure 9.
Important feature for the IBiox NHC ligands.

A salient feature of these carbenes (NHC ligands) is that steric bulkiness of the ligands can be modified according to the uses without affecting the electronic character of carbene which is an ideal criterion for selection of ligands (**Figure 9**). It is an important and a unique property for such monodentate ligands as compared to monodentate phosphines where increasing the size of the phosphine ligands can affect both their steric and electronic properties.

N-heterocyclic carbene based on Benzimidazolium (**Figure 8**) **L14–L16** [12–16] and **L17** [17] are an important as well as interesting classes of carbenes, though less commonly explored classes of NHC. The synthetic challenges limited the scope to only three electronically different ligands (**L14–L16**) and no sterically tunable benzimidazolium-derived N-heterocyclic carbene [18, 19].

Weiss et al. was the first person to develop and introduce the Bipyridocarbene (**L18** and **L19**) which is a highly electron-rich NHC (**Figure 8**) [20, 21]. This is evident from the strong high-field shift of its carbene signal (196 ppm) in the ^{13}C NMR spectrum [22]. But the instability of this compound limited its application in catalysis. On the other hand, Kunz et al. showed that tert-butyl substitution can lead to the formation of more stable NHC (**L19**) and also reported for the first time, the X-ray structural analysis of these types of carbene [23]. Later on, Lassaletta et al. [8] and Glorius et al. [7] independently developed imidazo [1,5-a] pyridine-3-ylidenes. These can be viewed as benzannulated imidazolin-2-ylidenes **L2–L6**. These ligands form electron-rich carbene as seen in IR spectra. The $\nu(\text{CO})$ for cis-(CO) $_2$ RhCl with R $_1$, R $_2$ = Me was found to be 2079 and 2000 cm^{-1} .

The structures of some other interesting carbene ligands (**L20**) and (**L21**) based on imidazolium backbone are also shown. These ligands showed different reactivity in the palladium-catalysed α -arylation of propiophenone because of their structural features.

2.3 6- and 7-Membered NHC

6 or 7 membered ring carbenes of N-heterocyclic such as 1,3-disubstituted pyrimidin- 2-ylidenes **L23** [24–27], perimidine-based carbene **L24** [28], **L25–L27** [29] or chiral 7-membered NHC **L28** [30] have only rarely been reported (**Figure 10**). The different electronic properties of NHCs are due to the different backbone structures and in the topology of the substituents on the NHC. Richeson et al. validated this by incorporating a naphthyl ring system in ligand **L25**. This modification changed the shape of the NHC [28]. The value of the N-C carbene–N

Figure 10.
 Some most and widely applicable six and seven-membered NHC.

bond angle increased from 100 to 110° in 5 membered to 115.3° in 6 membered ring. The carbene N–R angle α is also reduced from 122 to 123° in (L2–L6) and (L7 & L8) to 115.5° in L24, which had a steric influence of the N-substituents on the carbene carbon. Based on the $\nu(CO)$ values of the corresponding cis-(CO)₂RhCl complex, ligand L24 is an even stronger electron donor than the dihydroimidazol-2-ylidenes L7 & L8, but weaker than the acyclic carbene C(NiPr₂)₂.

Borazines, also known as “inorganic benzene” and isoelectronic with benzene are excellent scaffolds for highly stable heterocycles. When the borane moiety is “exchanged” with an iso-electronic carbene moiety one can obtain NHC L25–L27. There have been reports on the synthesis of such stable complexes of these ligands but their catalytic properties have been not explored yet.

The first synthesis of a 7-membered NHC ligand was reported by Stahl et al. very recently [29, 30]. Even though NHC L28 could not be isolated as a free carbene, palladium complexes of L28 were isolated and their structures fully characterized. Ligand L28 is C₂ symmetric and because of a torsional twist it shows the Möbius-aromatic character of the 8 π -electron carbene heterocycles [31].

2.4 Bi- and multi-dentate NHC

In addition to these monodentate ligands, several multi-dentate ligands have been synthesized and used for various applications. The rigid bidentate benzimidazole-based N-heterocyclic carbene was used in the synthesis of conjugated organometallic polymers which show interesting electronic and mechanical properties [32]. Another application of such bidentate NHC was the formation of stable chelate complexes. One such palladium-NHC complex was used in the catalytic conversion of methane to methanol [33]. The stability of the complexes is a pre-requirement for such applications as the reaction takes place in an acidic medium (trifluoroacetic acid) at high temperatures (80°C) in the presence of strong oxidizing agents like potassium peroxodisulfate.

Similar stable metal-chelate complexes were reported using tri- and tetra-dentate ligands. Iron (III) and chromium (III) form complexes of the structure [M(L29)₂]⁺ with the tripodal tricarbene ligand L29 (Figure 11) [34].

On the other hand, the development of macrocyclic ligands was found to be challenging. Hahn et al. successfully synthesized tetracarbene ligands having crown

Figure 11.
A tridentate ligand (L29).

ether topology in a template-controlled synthetic approach. Initially, a transition metal complex with four unsubstituted benzimidazol-derived NHC **L14** to **L16** (R, X = H) was formed. The carbene ligands are not stable when separated from the transition metal. Then, the carbene ligands were linked by a template-controlled cyclization of alkyl or aryl isocyanides and finally, the desired product was synthesized.

3. Synthesis

While the first report on the synthesis of carbene dates back to the 1920s, N-Hetero carbene (NHC) was discovered, from independent research works by Ofele [35], Wanzlick [36], and Lappert [37] in 1960s. A (phosphino)-(silyl) carbene was the first stable carbene to be synthesized which led to the tremendous flourishment in carbene chemistry (**Figure 12**: left) [36, 38, 39]. After long time from discovery of carbene, Arduengo et al. reported for the first time the isolation of metal-free N-heterocyclic carbene in 1991 (**Figure 12**: right) [40–44].

After the synthesis and isolation of stable free NHC, carbene chemistry has attracted much more attention in recent times and scientists began to look for new NHC ligands and the synthesis of stable NHC. Prior to this carbene were thought to be highly reactive to be isolated and thus it limited the studies on carbene. But the stability, isolation of NHC and the ease of synthesis from cheap and easily available precursors such as imidazolium salts, made the field advance rapidly in the last three decades. The stability of Arduengo-type free carbene owes to the presence of two heteroatoms in the molecule. The inductive effect of these heteroatoms stabilize the carbene [45]. The chemistry, structure, and properties of these “classical” heterocyclic carbene have been reviewed elaborately [46, 47]. The diverse applications of NHC have prompted the design and development of novel NHC structures. However, NHC are obtained generally from their suitable precursors. Thus, the facile, diverse synthesis of the NHC precursors is of great importance in order to get

Bertrand's carbene

Arduengo's N-heterocyclic carbene

Figure 12.
First isolated stable carbene compound.

Figure 13.
 Different strategies of carbene synthesis.

NHCs of various designs. Depending on NHC precursors their synthesis can be divided into the following major categories (**Figure 13**):

- a. Deprotonation of azolium salts
- b. Elimination reactions from imidazolines
- c. Desulfurization of imidazol- and benzamidazol-2-thiones

Two of the most commonly used NHC scaffolds are imidazolin-2-ylidene and its saturated version, imidazolidin-2-ylidene. In both the cases, the two nitrogen atoms are substituted with alkyl and aryl groups either in a symmetrical or in an asymmetrical way [37]. One of the easiest and widely used methods for the preparation of NHCs is the deprotonation of imidazolium or imidazolinium salts with strong bases such as sodium hydride [38], potassium tert-butoxide [39], or potassium bis(trimethylsilyl)amide [40].

The azolium salts can be also be prepared by the following routes namely,

3.1 N-alkylation of heterocycles

The first approach is simple and straightforward; the successive alkylation of the nitrogen atom in these heterocycles generates the quaternary N atoms which are excellent NHC precursors. The various methodologies for synthesis of imidazole, oxazole, thiazole, and other five membered heterocyclic rings have been reviewed extensively [48–53].

3.2 Symmetrical synthesis of imidazolinium salts as NHC precursors

Symmetrical synthesis of imidazolinium salts as NHC precursors can be achieved by various methods. One such example is shown in **Figure 14** [54] following condensation reduction route. This is widely applicable for a variety of primary amines [55–64].

3.3 Unsymmetrical synthesis of imidazolinium salts as NHC precursors

Unsymmetrical synthesis of imidazolinium salts as NHC precursors similarly have been prepared following different methods. The uses of oxalyl chloride or

Figure 14.
Synthesis of symmetrical NHC precursor.

derivatives give more flexibility leading to the synthesis of unsymmetrical imidazoliums. Mol and co-workers synthesized the mixed adamantyl/mesityl N-heterocyclic precursor 1-(1-adamantyl)-3-mesityl-imidazolium chloride. At first, oxalyl chloride was reacted with mesityl amine to afford the intermediate acyl chloride which on successive reaction with another amine afforded the desired compound (**Figure 15**) [65, 66]. A small library of imidazolium derivatives were prepared having groups with various steric or electronic properties using this method [67–72].

Similarly, the unsaturated azolinium salts have been prepared by (a) alkylation of the nitrogen atom of imidazolium, (b) symmetric and (c) unsymmetrical synthesis of such salts.

Paraformaldehyde has been extensively used for the synthesis of both unsaturated and saturated NHC precursors as shown in **Figure 16** [73]. There are several other strategies for the preparation of such azolium salts as NHC precursors which have been nicely reviewed [54]. The deprotonation method of generating carbene

Figure 15.
Synthesis of unsymmetrical NHC precursor.

Figure 16.
Synthesis of unsaturated azolinium based NHC precursors.

from imidazolium salts using a strong base is generally performed in-situ so that the air sensitive free or ligated carbene is not isolated. But sometimes, the use of such a strong base and harsh reaction conditions leads to unwanted side-reactions. Thus to avoid those unnecessary complications, elimination of hydrogen atoms from imidazolinium salts are undertaken to provide NHC carbene.

Alternatively, less common routes involve reduction of thiourea derivatives, pyrolysis of an NHC – volatile compound adduct or release of NHC.

3.3.1 NHC·CO₂ zwitterions

The carbon dioxide adducts of NHCs can be prepared easily by passing carbon dioxide gas into a free carbene solution, and then evaporating the solvent. They are comparatively air stable and can be stored for a long time. Imidazol(in)ium-2-carboxylate derivatives act as an excellent NHC precursor for the synthesis of NHC-transition metal complexes by releasing carbon dioxide during thermolysis. The steric effect on N substituent and other electronic, steric factors affecting the stability of such precursors has been also studied [74]. Later on, imidazol(in)ium hydrogen carbonates have been shown as another excellent source of NHCs when they lose H₂CO₃ upon heating [75–79].

3.3.2 NHC – metal adducts

Another important NHC precursor is silver (I) complexes of NHC. There have been several types of such complexes like: Imidazolin-2-ylidene involving imidazole ring with substituents at the nitrogen atoms, Benzimidazol-2-ylidenes having a benzene ring fused with the imidazole moiety, imidazolidin-2-ylidenes- and related heterocycles. The first Ag (I)–NHC adduct was reported by Arduengo in the early 90s by the reaction of Ag(I) salt with a free NHC [80]. Later, the uses of Ag(OAc) and Ag₂O as silver base were reported to synthesize various Ag(I)–NHCs. These silver bases are used for the deprotonation of azolium salts, and generation of Ag(I)–NHCs in situ. These Ag(I)–NHC complexes easily decompose under thermolysis to provide the free carbenes for various applications. One limitation to this approach is the use of silver metal in stoichiometric amounts. The different synthetic routes as well the structural diversity and the applications of such precursors have been well established in the carbene literature [81].

3.3.3 Other NHC precursors

In addition to the above mentioned adducts there are reports of similar complexes of NHC namely the chloroform and pentafluorobenzene adducts of 1,3-dimesitylimidazolidin-2-ylidene (SIMes). They are stable at room temperature and afford the corresponding NHC on thermolysis [82, 83]. One such example is SIMes (H)(O-t-Bu) which can produce the corresponding NHC at room temperature. The alcohol adducts of triazolin-5-ylidene and imidazolidin-2-ylidene also proved to be excellent NHC precursors [84, 85] (**Figure 17**).

4. Photophysical studies of N-heterocyclic carbene

New efficient light-emitting materials related to iridium(III) and platinum(II) complexes have attracted research area and wide range of applications in OLED and WOLED technologies. The suitable ligand based iridium(III) and platinum(II)

Figure 17.
Various strategies for generation of carbene.

complexes allow tailoring the emission properties for specific application in organic light emitting devices (OLEDs) and white organic light emitting devices (WOLEDs).

In particular, extensive investigations have been carried out on iridium(III) and platinum(II) complexes as triplet emitters in OLEDs. In OLEDs, significant progress has been achieved for making highly efficient and stable green and red emitters. But further advancement in recent progress of solid state full-colored OLED displays and WOLEDs appliances is also required in the research area of blue and white light emitting iridium(III) and platinum(II) complexes.

4.1 Photophysical studies of N-heterocyclic carbene platinum(II) complexes

Here N-heterocyclic carbene platinum(II) complexes are selected to investigate their photophysical properties (**Figure 18**). Selected N-heterocyclic carbene platinum(II) complexes have shown distinct absorption bands in 325–405 nm region with higher extinction coefficients (order of 10^3 or 10^4). These complexes are known as either blue, bluish green, or green emitters depending on emission bands within the 430–530 nm region with large Stokes shifts.

The [Pt^{II}(C[^]N[^]C)Cl][PF₆] complex shows strong absorption bands at 272 nm and moderately intense bands at 364 nm with higher extinction coefficients ($\epsilon \sim 10^3$ – 10^4) in acetonitrile (**Figure 19**). The high-energy intense absorption band (277–291 nm) is assigned as $\pi \rightarrow \pi^*$ transitions (IL: Intra ligand) of the C $\equiv$ CR and C[^]N[^]C pincer ligands, whereas the low-energy absorption band (band (383–471 nm)) is observed due to presence of the $d\pi(\text{Pt}) \rightarrow \pi^*$ (C[^]N[^]C)] transitions, and $[\pi(\text{C} \equiv \text{CR}) \rightarrow \pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})]$ transition, considered as metal-to-ligand charge-transfer (MLCT), ligand-to-ligand charge-transfer (LLCT), mixed with the $\pi \rightarrow \pi^*$ transitions (IL) of the C[^]N[^]C pincer ligands [75–79].

A blue-shifted absorption band (383 nm) of Complex 1 with the alkylalkynyl ligand is observed compared to Complex 3 (appeared at 405 nm) with the phenylalkynyl because of weak π -donating ability of alkylalkynyl ligand. The

Figure 18.
Structures of pyridine-based N-Heterocyclic Carbene Platinum(II) Complexes (1–6).

Figure 19.
UV-Vis spectra of pyridine-based N-Heterocyclic Carbene Platinum(II) Complexes 1–6 in ACN at 298 K
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absorption band is redshifted due to increasing the π -electron-donating property of arylalkynyl ligand is assigned as MLCT/ LLCT transition.

The MLCT/LLCT absorption band is sensitive towards polarity of the solvents and shows a blue shifted absorption band from DCM (382 nm) to ACN (376 nm). A negative solvatochromism is observed in Pt (II)–polypyridine [82, 83], and Pt (II)–bzimpy complexes [76, 79] because of decreasing dipole moment during electronic transition.

Non-emissive nature of $[\text{Pt}^{\text{II}}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{Cl}][\text{PF}_6]$ complex in ACN is can be explained on the basis of low-energy d-d ligand field (LF) states, and effective quenched $^3\text{MLCT}/^3\text{IL}$ state [86]. In contrast to the $[\text{Pt}^{\text{II}}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{Cl}][\text{PF}_6]$ complex, the tridentate pyridine-based N-heterocyclic carbene ligand based alkynylplatinum(II) complexes 1–5 (**Figure 18**) exhibit strong luminescence in solution with gaussian shaped emission bands (range: 497–631 nm) (**Figure 20**). Only alkynylplatinum(II) complex 6 (**Figure 18**) shows non-emissive character in solution. Interestingly, all alkynylplatinum(II) complexes 1–6 (**Figure 18**) have shown emissive character at low temperature in solid state and glass matrices at 77 K.

The large Stokes shifts and lifetimes in the microsecond are originated from triplet energy state. The emission bands are appeared from an predominantly $^3\text{MLCT}$ excited state of $[\text{d}\pi(\text{Pt}) \rightarrow \pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})]$ transition, along with $^3\text{LLCT}$ $[\pi(\text{C} \equiv \text{CR}) \rightarrow \pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})]$ transition (**Figure 20**). Moreover, CT band and emission band of these metal complexes is altered depending on the nature of the substituted phenyl ring of alkynyl ligands in solution.

The intense luminescence from green to yellow and high PL quantum yield of alkynylplatinum(II) complexes 1–5 can be readily achieved by alternation of alkynyl ligands. The electron-rich moiety quenches the luminescence from $^3\text{MLCT}$ excited state via photoinduced electron transfer (PET) process is responsible for non-emissive property of complex 6 in solution [82, 83]. Depending upon increasing the polarity of the solvents, excited state ($^3\text{MLCT}/^3\text{LLCT}$) is lesser stabilized compared to its ground state, leading to a blue shift of absorption spectra in solution, shows negative solvatochromism for alkynylplatinum(II) complex 2. A red shift of the emission band state (559–640 nm) has also been observed for complexes 2–4 in solid at room temperature. The low-energy emission band (559–640 nm) is originated from triplet states (due to presence of metal to-ligand charge transfer (MMLCT) character) of alkynylplatinum(II) complexes 2–4 due to presence of significant contribution from $\text{Pt} \cdots \text{Pt}$ interaction in solid state [86].

Figure 20. Normalized emission spectra of pyridine-based N-Heterocyclic Carbene Platinum(II) Complexes 1–5 in ACN at 298 K (Reprinted with permission from *Chem. Eur. J.* 2013, 19, 10,360–10,369. Copyright@ 2013 Wiley-VCH).

4.2 N-heterocyclic carbene Ir (III) complexes and their applications to deep-blue phosphorescent organic light-emitting diodes

Absorption and emission spectra of N-heterocyclic carbene Ir (III) complexes 1–3 (**Figure 21**) are measured in DCM (**Figure 22**). The absorption band at around 320 nm is due to overlap of the $\pi \rightarrow \pi^*$ transition of triazolate chelate, the benzyl (carbene) and pyridyl (triazolate fragment) and considered as LLCT transition. Furthermore, spin-orbit coupling is enhanced by iridium and plays significant role on triplet absorption cross section.

N-heterocyclic carbene Ir (III) complexes 1–3 (**Figure 21**) show emission band at 461, 460, and 458 nm, respectively in DCM. The weak phosphorescence intensity of complex 1 is observed at 392 nm and also indicated by its low quantum efficiency (QE) (only 5.0×10^{-4}). It is observed that the fluorescence quantum yield of complex 2 and 3, is much higher than that of complex 1. The radiative lifetimes of N-heterocyclic carbene Ir (III) complexes 1–3 confirm their phosphorescent nature. The nonradiative decay rate constants (k_{nr}) are found to be 1.2×10^9 , 3.5×10^6 and $7.0 \times 10^5 \text{ s}^{-1}$ with large differences in quantum efficiency for complex 1–3 respectively.

5. Applications

The carbene chemistry became more popular for their applications as organocatalysts [87, 88] and transition metal catalysts in the synthesis of complex

Figure 21.
 Structures of N-heterocyclic carbene iridium (III) complexes (1–3).

Figure 22.

Absorption and fluorescence spectra of 1 (—), 2 (....) and 3 (—) in CH_2Cl_2 at 298 K (Reprinted with permission from *Angew. Chem. Int. Ed.* 2008, 47, 4542. Copyright© 2008 Wiley-VCH).

Figure 23.

Types of oxidation reactions catalyzed by NHC-metal complexes.

molecules [89, 90]. The N-heterocyclic carbene (NHCs) is widely used in organometallic chemistry during the last few years [47]. A brief summary of the applications include:

5.1 Oxidation reactions catalyzed by NHC-metal complexes

They can be employed for various types of oxidation reactions like (a) Oppenauer-Type Alcohol Oxidation [91] where smaller R groups show catalytic activity, (b) Palladium-Catalyzed Aerobic Alcohol Oxidation [92] or (c) Wacker-Type Oxidation [93] as shown in **Figure 23**.

In addition, NHC metal complexes have been extensively used for **oxidative cleavage of alkenes** [94] as well as **oxidation of methane** [33]. In this regard, it has been observed that electron deficient alkenes react slower than electron rich alkenes. The NHC-Ru complex remains stable throughout the course of oxidation reaction (**Figure 24**).

Figure 24.
 NHC-Ru complex catalyzed oxidation of alkene.

5.2 Palladium catalyzed reactions

NHCs are also frequently used in **Palladium catalyzed reactions** forming C-C bonds. Mori et al. reported the use of NHC ligand in allylic alkylation with excellent yield [95] (**Figure 25**).

Another important application has been the α -arylation of carbonyl compounds at moderate temperature and short reaction time [96]. The same strategy has been applied for esters and amides [60, 97] (**Figure 26**).

Besides these, NHC act as great ligands for Pd catalyzed various coupling reactions like Heck reaction [98], Negishi reaction [99], Sonagashira reaction [100], Suzuki-Miyaura reaction [101], Stille coupling [102], and Buchwald-Hartwig reaction [103].

The NHC ligands act as good catalysts for tandem coupling reactions as well [104]. The reaction proceeds via amination route (**Figure 27**).

5.3 NHC Complexes in Olefin Metathesis

After the development of Grubbs I catalyst several modifications were carried out to develop more efficient catalysts. In this regard, NHC-Ruthenium complex

Figure 25.
 Use of NHC ligands in allylic alkylation.

Figure 26.
 NHC mediated coupling reaction.

Figure 27.
 NHC-metal complex for tandem coupling reactions.

was synthesized for RCM [105]. But the initial design did not show marked difference in activity compared to Grubbs I catalyst, Later on, some combination catalysts were developed which showed greater activity and selectivity [106–109]. Nowadays, these second-generation Grubbs' olefin metathesis catalysts are widely used for metathesis reactions (**Figure 28**).

5.4 NHC as ligands in asymmetric synthesis

There are different approaches for inducing chirality by NHC ligands. One of the ways is N-substituents containing centers of chirality. But initially this method did not show great stereoselectivity [110] but later on the development of bidentate ligands enhanced the enantioselectivity. Grubbs et al. developed another method wherein, NHC ligands had the chiral elements within the N-heterocycles [111]. These ligands showed great selectivity. Another interesting method involves an element of chirality like axial chirality or planer chirality to make the NHC ligands as stereo directing ligands for asymmetric synthesis [112, 113] (**Figure 29**).

5.5 NHC as organocatalysts

Carbene can act as an organocatalyst was demonstrated long back in 1940s [114]. Since then, several attempts have been undertaken to develop NHC mediated Benzoin, Acyloin condensation reactions [115–119] (**Figure 30**).

Figure 28.
NHC ligands in metathesis reactions (a) first complex (b) combination catalysts.

Figure 29.
(a) Chiral NHC ligand structure, (b) synthesis of chiral ligand.

Figure 30.
NHC ligands used as organocatalysts.

6. Conclusion

Carbene has been all along an important reactive intermediate in organic chemistry but the development of N-Heterocyclic carbene has revolutionized the field of organic synthesis. NHC owing to their ease and flexibility of synthesis, their interesting structural properties and in particular their stability have received a great deal of attention within the last few years. There are several strategies for the development of stable and versatile NHC ligands. We have highlighted in this book chapter some general synthetic strategies for the synthesis of some interesting NHC. Along with the discussion on the different strategies adopted in the synthesis of NHC, we focused primarily on some of the salient features of their structures and photophysical properties. Finally, we focus briefly on the various uses of NHC in organic synthesis. Over the years, NHCs have been extensively studied for several applications in organic transformations. Herein, we have very briefly touched upon some of those reactions.

The recent advances in the design of novel ligands, development of interesting structures of NHC enable their exciting potential applications in organic synthesis in the future.

Author details

Arunava Manna^{1*}, Abhineet Verma¹, Sumit K. Panja^{1,2} and Satyen Saha^{1*}

¹ Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi, UP, India

² Tarsadia Institute of Chemical Science, Uka Tarsadia University, Bardoli, Gujarat, India

*Address all correspondence to: arunavam@bhu.ac.in
and satyen.saha@gmail.com

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