



Research Article

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Bis-carbene metallic compounds: synthesis of imidazoline derivatives via cycloaddition reaction of isocyanides based on amidines

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Abstract

In an effort to develop new classes of NHC (N-heterocyclic carbenes) complexes, two imidazoline-anchored ligand systems have been synthesized. The process is superior owing to two approaches: (i) a new synthesized phase transfer catalyst, namely, 1,1'-benzene-1,4-diylidipyridinium dibromide (BDPDB) used to catalyze the phase-transfer Hoffmann reaction of two structurally varied amines, dodecylamine and 1-amino-9,10-anthraquinone. The reaction successfully gave the corresponding isocyanides that display the highest reactivity in reasonable to good yields. (ii) A cycloaddition-rearrangement reaction between amidines and isocyanides gives easy access to a diverse range of highly substituted 5- and 2-imidazolines. Furthermore, imidazoline based bis-NHC (N-heterocyclic carbenes) precursors were prepared and complexed to copper cation (5-Z and 2-Z, Chart 1).

Keywords: PTC; Isocyanides; MCRs {reductive elimination; oxidative addition}.

INTRODUCTION

Multicomponent reactions (MCRs) provide a powerful tool toward the one-pot synthesis in diverse environments and complex compounds on the one hand and small and 'drug-like' heterocycles on the other hand. No other single synthesis technology enables chemists to search such large chemical spaces as provided by MCRs. MCRs that involve isocyanides are by far the most versatile reactions in terms of scaffold's and number of accessible compounds ^[1].

Zhu *et al.* introduced a novel MCR for α -substituted isocyno acetic acid amides, primary amines and aldehydes or ketones to yield persubstituted oxazoles ^[2]. Nair and co-workers ^[3] have exploited the reaction between isocyanide, rarely used *N*-isocyanides, acetylenedicarboxylic acid diesters and aldehydes. They have observed a smooth formation of 2, 4-disubstituted 2-aminofuranes 4 and 3(5*H*)-pyrrolin-2-ones.

Huttner and co-workers — highly dedicated to MCRs — have used the abbreviation UDC for a combination of Ugi reaction, deboc (deprotection of an amine from the *tert*-butoxycarbonyl group) and cyclisation for a general sequence of reactions with regards to the variety of different scaffold's, such as diketo-piperazines, diketo-morpholines and *N*-substituted α -amino acids. Recently, they have described a novel scaffold's accessible by UDC: *N*-substituted benzimidazoles ^[4]. The U-4CR of mono-*tert*-butoxycarbonyl protected *o*-phenyldiamine, aldehydes or ketones, isocyanides, and carboxylic acids cyclize under acidic conditions to the corresponding benzimidazoles ^[5].

Three synthetic MCRs methodologies are most commonly applied for the preparation of NHC metal complexes: i) *in situ* deprotonation of the imidazolium by basic metalates or basic counter-ions, ii) high dissociation energies of an external base in a one pot reaction with the metal. Furthermore it is noteworthy, that there are also so-called 'ligand-free' versions, and iii) transmetallation of NHCs via silver complexes still show a large scale than phosphines for metals ^[6].

Therefore, when their free form could be isolated, their complexation was achieved in high yields. It has been shown that free NHCs are able to cleave dimeric metallic species and exchange phosphine or pyridine ligands such as $[(\eta^4\text{-cod})\text{RhCl}]_2$ ^[7].

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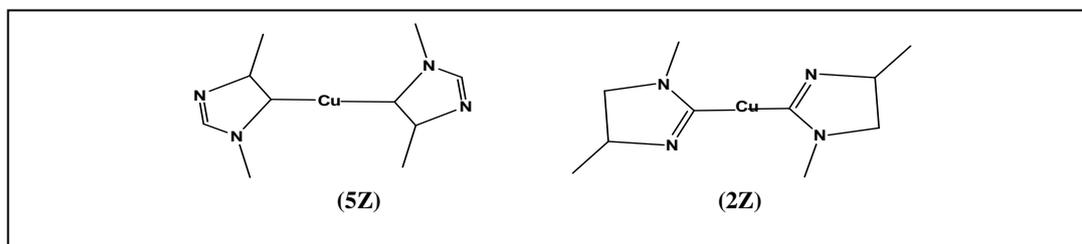


Chart 1: Copper-carbene-complexes of two novel amidines

The use of an external base to generate NHCs could be an efficient method in the presence of a metal precursor. Potassium *tert*-butoxylate and sodium hydride in THF at room temperature could be used to coordinate NHCs to $\text{Cr}(\text{CO})_6$ and to $\text{W}(\text{CO})_6$ *in situ* [8]. A large variety of bases ranging from triethylamine [9], lithium diisopropylamide [10] to phosphazene bases have been successfully used over the past years.

Recently, a method for preparing NHC metal complex via silver complex has been developed upon mixing the imidazolium salt with Ag_2O in CH_2Cl_2 at room temperature by Gopinath [11]. Subsequent reaction with a chloro-metal precursor has given the desired NHC metal complex that could be easily separated from AgCl , the latter being insoluble in THF [12-15].

Abnormal binding modes for NHC ligands: In 2001, Crabtree discovered an unexpected binding mode of NHCs. Instead of having coordination at the C(2) position of the NHC, the metal has been linked at C(4) or C(5). Since this publication, there have been an increasing number of reports of NHC with abnormal binding mode [16].

EXPERIMENTAL SECTION

MATERIALS

CuCl_2 was used as received from SISCO Research Laboratories Pvt. Ltd. India. England. Cyanothioacetamide obtained from El-Nasr Chemicals. 1, 4-Dibromobenzene, dodecyl amine ($\text{C}_{12}\text{H}_{25}\text{NH}_2$) and 1-amino-9, 10-anthraquinone supplied by Sigma Co. All other reagents were of high purity and used as purchased without any further purification. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Varian Gemini 200 MHz for $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ in CDCl_3 solution. Proton chemical shifts are reported in ppm downfield and carbon chemical shifts in ppm downfield using the resonance of the deuterated solvent as internal standard. Elemental analyses were carried out using a Perkin Elmer 2400. IR spectra were measured on a Perkin Elmer 1600 FT-IR 4000-400 cm^{-1} .

EXPERIMENTAL PROCEDURES

Phase transfer catalyst residue [1, 1'-Benzene-1, 4-diylidipyridinium dibromide (BDPDB)]

A flat-bottomed flask equipped with a magnetic stirrer, a dropping funnel, a thermometer, and an efficient reflux condenser was charged with 50 ml of 25% aqueous sodium hydroxide, 0.02 M (1.58 gm) of pyridine and 0.2 mM of prepared PTC [17-18], 0.01 M (2.36 gm) (excess) of dibromobenzene was added drop wise over a period of approximately 70 minutes at 50°C with stirring. After the addition of dibromobenzene was completed, stirring was continued for 70 minutes, and then the temperature was increased to 60°C for an additional 30 minutes. The layers were separated, and the organic layers were extracted with 50 ml of methanol. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed by distillation under reduced pressure.

$\text{C}_{16}\text{H}_{14}\text{N}_2\text{Br}_2$: IR ($\gamma\text{ cm}^{-1}$): 3397 (s), 3050 (s), 1657 (s), 1257 (s), 1214 (s); $^1\text{H NMR}$ (200 MHz, CDCl_3) δ (ppm) 9.2-8.5 (m, 5H, pyridinium), 7.38 (m, 4H aryl-H); (Found) Calc. %: C, (48.75) 48.76; H, (3.54) 3.55; Br, (40.58) 40.6; N, (7.10) 7.11.

Phase-transfer hoffmann reaction adducts [Aliph- and Ar-Isocyanides]

A round-bottomed flask equipped with a magnetic stirring bar, and a reflux condenser, was charged with a mixture of (2 M) 3.71 and 4.47 gm of aliphatic and aromatic amines respectively, (1 M) 1.19 gm of chloroform, and (0.005 M) of BDPDB in 150 ml of dichloromethane was added. 25% of Sodium hydroxide was added in portions in order to maintain efficient stirring. The reaction mixture was refluxed immediately and subsided within 70 minutes at 45°C . After the reaction flask was immersed in with 100 ml cold water, the organic layer was separated and retained, and the aqueous layer was extracted with dichloromethane. The dichloromethane solutions were combined and washed successively with 100 ml of aqueous 5% sodium chloride, and dried over anhydrous magnesium sulfate. The drying agent was collected, yielding of isocyanides was 93%, (based on chloroform) [19].

Ar-Isocyanide ($\text{C}_{15}\text{H}_8\text{NO}_2$): IR ($\gamma\text{ cm}^{-1}$): 3409 (s), 3227 (s), 2936, 2849, 1603, 1508, 1456, 1249 (s), 1163 (s), 829 (s, C-Cl); $^1\text{H NMR}$ (200 MHz, CDCl_3) δ (ppm) 7.6 (m, 2H, aryl- $\text{H}_{\text{isocyanide}}$). (Found) Calc. %: C, (76.8) 76.9; H, (3.2) 3.4; N, (5.98) 6.0; O, (13.68) 13.7.

Aliph-Isocyanide ($\text{C}_{13}\text{H}_{25}\text{N}$): IR ($\gamma\text{ cm}^{-1}$): 3337 (s), 2922, 2845, 1647, 1566, 1488, 1318 (s), 1151 (s), 725 (s, C-Cl); $^1\text{H NMR}$ (200 MHz, CDCl_3) δ (ppm) 3.3 (t, 2H, aliph- $\text{H}_{\text{isocyanide}}$). (Found) Calc. %: C, (79.9) 80; H, (12.7) 12.8; N, (7.1) 7.2.

5- and 2-Imidazolines

Solid-liquid PTC (without solvent) nucleophilic substitution condition was carried out at a concentration of 1 M of dichotomize or bisect from 5-, 2-imidazolines, via i] the treatment of (2 M) 3.91 and 4.66 gm of aliphatic and aromatic isocyanides respectively, in dry CH_2Cl_2 with cyanothioacetamide in the presence of sodium ethoxide. And ii] unless note otherwise, the imidoester residue has been formed in the intermediate step, at room temperature, to a stirred solution of the produced amidines. After the reaction mixture stirred at room temperature for an additional 3 h, the reaction mixture was then filtered and concentrated *in vacuo* [14].

5-Imidazoline ($\text{C}_{29}\text{H}_{35}\text{N}_2\text{O}_2$): IR ($\gamma\text{ cm}^{-1}$): 3329 (s), 3206 (s), 3075 (s), 2977, 2838, 2554, 1601 (s), 1502 (s), 1467 (s), 1247 (s); $^1\text{H NMR}$ (200 MHz, CDCl_3) δ (ppm) 3.5 (C_4 -imid.), 3.36 (C_5 -imid.); (Found) Calc. %: C, (78.7) 79; H, (7.9) 8; N, (6.2) 6.3; O, (7.1) 7.2.

2-Imidazoline ($\text{C}_{27}\text{H}_{32}\text{N}_2$): IR ($\gamma\text{ cm}^{-1}$): 3329 (s), 3075 (s), 2919, 2848, 2554, 1601 (s), 1502 (s), 1247 (s); $^1\text{H NMR}$ (200 MHz, CDCl_3) δ (ppm)

3.9 (C₄-imid.), 2.1 (C₅-imid.); (Found) Calc. %: C, (79.98) 80; H, (12.7) 13; N, (6.99) 7.

Imidazoline-complexes [5-Z & 2-Z]

Each of 0.01 mole of prepared ligands was separately dissolved in 50 ml of hot methanol after adding a solution of metal salt (Cu(II)) in hot methanol and then refluxed for 4 h. The complexes were precipitated and then filtered and air dried. Yields were in the range of 95% [13].

Copper complex of imidazolin-5-ylidene [5-Z] C₅₈H₇₂CuN₄O₄

IR (γ cm⁻¹): 3459 (iminium), 3394 (NR₃), 3265 (arom_{stretch}), 2920 (C-H, sp²), 2849 (C-H, sp³), 1644 (C=O_{quinone}), 1603 (C=C / C=N), 1509, 1461 (ring struct.), 1165-1031 (C-O-Ar_{asy, sy}), 1250 (Cu-C); ¹H NMR (200 MHz, CDCl₃) δ (ppm): 7.2-6.8 (m, 4H, aryl-H), 7.33-6.72 (m, quin.-H), 7.8-7.55 (m, quin.-H), 3.73 (s, 3H, CH₃), 2.6 (d, 1H, C₄-imid.), 1.7 (m, 1H, C₅-imid.), 1.8 (m, 1H, t-CH), 1.33 (m, 2H, CH₂), 1.3 (d, 2H, ⁺N-CH₂), 1.29 (m, 2H, CH₂), 1.1 (t, 3H, t-CH₃), 0.96 (t, 3H, CH₃). ¹³C NMR (200 MHz, CDCl₃) δ (ppm): 14.1 (2 CH₃), 21.4 (4 t-CH₃), 22.8 (2 CH₂-1), 25.4 (2 CH₂-2), 29.7 (10 CH₂), 31.9 (2 CH₂-2), 49 (2 C₅-imid.), 55.8 (2 ⁺N-CH₂), 72 (2 C₄-imid.), 160.7-114.3 (benz. ring), 182.2-109.9 (2 quin. ring). (Found) Calc. %: C, (18.99) 19; H, (22.9) 23; N, (17.9) 18; O, (19.9) 20; Cu, (19.9) 20.

Copper complex of imidazolin-2-ylidene [2-Z] C₅₄H₁₀₆CuN₄

IR (γ cm⁻¹): 3412 (iminium), 3373 & 1301 (NR₃), 3240 (arom_{stretch}), 2920 (C-H, sp²), 2848 (C-H, sp³), 1602 (C=C / C=N), 1507, 1457 (ring struct.), 1247 (Cu-C), 827 (p-disubs. benzene); ¹H NMR (200 MHz, CDCl₃) δ (ppm): 7-6.7 (m, 4H, aryl-H), 7.3 (s, 4H, aryl-H), 3.9 (d, 1H, C₄-imid.), 2.55 (t, 2H, C₅-imid.) 2.1 (m, 1H, CH), 1.33 (m, 2H, CH₂), 1.29 (m, 2H, CH₂), 0.96 (t, 3H, CH₃). ¹³C NMR (200 MHz, CDCl₃) δ (ppm): 14.1 (4 CH₃), 21.4 (4 t-CH₃), 22.8 (4 CH₂-1), 25 (2 CH₂), 25.7 (2 CH₂), 27.4 (2 CH₂-N-3), 28.4 (2 CH₂-N-2), 29.4 (6 CH₂), 29.7 (16 CH₂), 31.9 (4 CH₂-2), 48.2 (2 N-CH₂), 55.9 (2 CH₃), 66 (2 C₄-imid.), 75 (2 C₅-imid.), 157.9-114 (benz. ring), 137.8-126 (benz. ring). (Found) Calc. %: C, (18.8) 19; H, (37.9) 38; N, (19.9) 20; Cu, (22.9) 23.

RESULTS AND DISCUSSION

Properties of carbene ligands

N-heterocyclic carbenes can be obtained from the corresponding azolium salts, imidazolium, imidazolinium, triazolium, pyrazolium, benzimidazolium, thiazolium, and oxazolium salts by deprotonation. The functional groups can be introduced in the imidazole side chain by conventional synthetic methods. The ability of these carbenes to replace labile ligands is a big advantage in coordination chemistry. In situ, the deprotonation of C2 and C5, the main reasons for the success of N-heterocyclic carbenes in catalysis are their properties such as the strong σ -donating ability, a strong metal-carbon bond and poor π -accepting ability leading to the formation of many stable metal complexes used in organometallic chemistry and catalysis. The strong σ -donating and little or no π -backbonding ability of the carbene ligands leads to increased electron density at the metal centers for which NHC can generally be seen as alternatives to the widely used copper ligands. These heterocyclic carbene compounds have nucleophilic properties and possess a significant degree of electronic stability which may be derived from a combination of steric and electronic factors. The electronic factors operate via both π and σ modes. In the π mode, electron donation into the carbene out-of-plane p-orbital by the electron rich system (N=C=N) leads to a moderation of the electrophilic reactivity of carbenes. In the σ mode, additional stability for the carbene electron

pair may be gained from the σ electron-withdrawal effects on the carbene center by the more electronegative nitrogens.

The advantages associated with N-heterocyclic carbene complexes are: (i) cheap, (ii) easy to prepare, (iii) non-toxic, (iv) thermally stable and (v) exceptionally stable M-C bonds towards hydrolysis under high temperatures. The discovery and established of a novel class of carbenes have one or two π -donor substituents such as N or O, directly attached to the carbene carbon, and shows a typical behavior of stabilized metals in high formal oxidation states with additional donor ligands N-heterocyclic carbene complexes. The metals are differing by the polarity of the electron density with the $p\pi$ orbital of the carbene.

Studies have shown that carbenes are neutral species, with six electrons, with two non-bonding electrons in their valence shell, and are exist in two different geometries: either linear or bent, depending on the sp or sp² hybridization. The linear sp-hybridized carbene possess two non-bonding degenerate 2p orbitals at the carbon atom p_x, p_y orbitals. Most carbenes are bent and their frontier orbitals will be systematically called σ and $p\pi$. The non-bonding electrons can either be spin paired (singlet state) or have parallel spins in different orbitals (triplet state), however, only the states with one electron in both σ and $p\pi$ orbital assigning the carbene a triplet state or with the pair located in either the σ or the $p\pi$ orbital, resulting in a singlet state. The energy state has one electron in the σ and one in the $p\pi$, as for state, but with antiparallel spins [19]. The reactivity of carbenes depends on their ground state spin multiplicity, a singlet carbene with a free orbital and one filled with a pair of electrons can be seen as amphiphilic, potentially able to be attacked by either a nucleophile or an electrophile. The triplet carbenes with a single electron in each orbital are diradicals. Calculations by Hoffmann predicted that the bigger the gap between the σ and $p\pi$ orbital is, more likely the carbene will be in singlet state configuration, while a low energy gap will induce a triplet state carbene. Steric and electronic effects play an important role in the understanding of the reactivity of carbenes [20].

In **Schemes 1-3**, the syntheses of two different imidazolines are illustrated. As a first result, only amidine and isocyanide could be isolated. Also, performing the reaction at a high temperature was being unsuccessful. Second, the cycloaddition to amidines seems to be critically dependent on the acidity of the isocyanide proton. Finally, the resulted 5- and 2-imidazolines were used as precursors for N-heterocyclic carbenes containing two different C-back-bone substituents [17]. Indeed, one-pot reaction of them in the presence of only 0.2 mM of PTC has provided two structurally varied imidazolines in reasonable to good yields. In recent years, NHCs are almost exclusively referred to as donors. This is merely based on the fact that in most NHC complexes, the metal-carbene bond distances are close to that of a "normal" single bond. The metal-ligand interactions of 5-L and 2-L were analyzed using elemental analyses, FT-IR, ¹H & ¹³CNMR spectroscopy.

Abnormal binding modes for 5-Z & 2-Z

It is interesting to note that the size of the 1-anthraquinyl substituent is observed in **Schemes 1-3**. Possibly, deprotonation at C1 was hampered by insufficient resonance stabilization of the corresponding anion. To maximize the overlap between the lone pair at C1 and the aromatic substituent, a planar carbanion conformation must be realized in which that the anthraquinyl moiety and the imidazoliny ring are in the same plane. This seems next to impossible.

According to **Schemes 1-3**, 1-isocyanoanthraquinone might react intramolecularly with amidine to afford 5-Z. Alternatively, 2-Z could form intermolecularly with amidine in case of the intermediates.

Carbene complexes are thermodynamically stable and generally have diagnostic ^{13}C NMR chemical shift values between 210–230 ppm for the carbenic carbon. Typically, X-ray illustrated the structures of these molecules showing N-C-N bond angles of 101–102° [21].

All SaMBVCA calculations take Cartesian coordinates for ligand atoms only. Clavier and Nolan set all bond distances at 2.00 and 2.28 Angstroms for geometrically flexible NHCs.

Scheme 1: (intramolecular reaction of amidine)

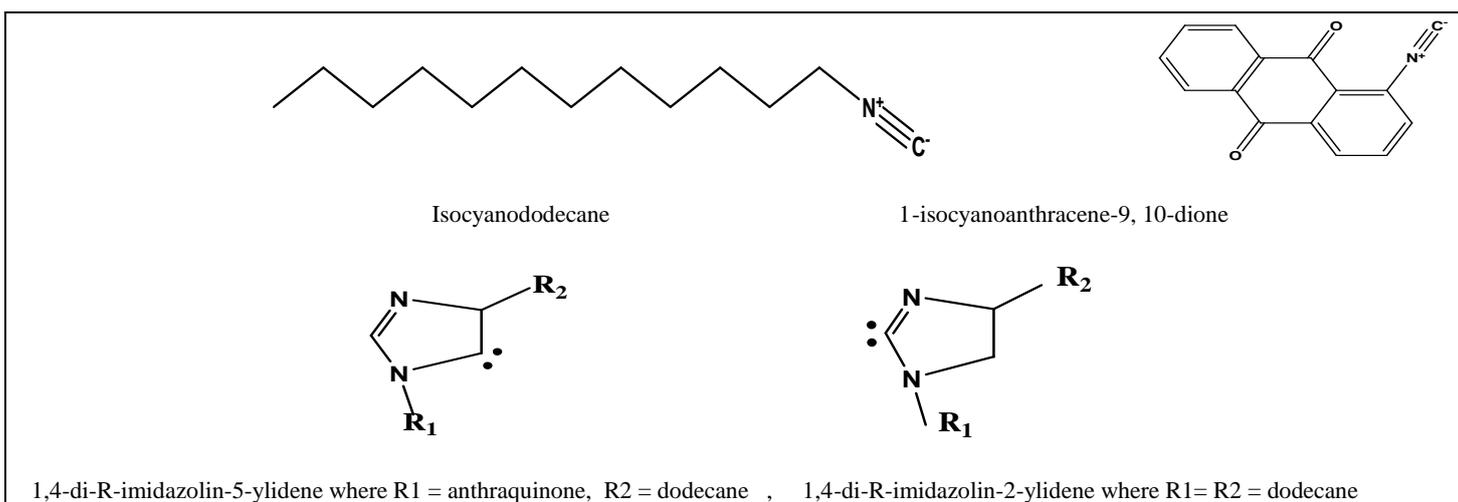
Absent of solvent and under phase-transfer reflux, 25% aqueous sodium hydroxide and 0.2 mM of prepared PTC are being used.



Scheme 2: (intramolecular reaction of amidine, cont.)

Dodecyl amine and 1-amino-9,10-anthraquinone maintains phase-transfer hoffmann reaction to give isocyanides: i] ptc , ii] NaOH as base, iii] $\text{CHCl}_3/\text{CH}_2\text{Cl}_2$ as solvent

Scheme 3: (intramolecular reaction of amidine, cont.)



CONCLUSION

It would not be an exaggeration to say that when designing a new process or a method of synthesis, which include reactions involving anions, one should consider PTC as the first choice. Compared to the conventional methods, this method is simple, gives high yield, has shorter reaction time, and is environmental friendly. Additionally, BDPDB was found to be an optimum catalyst for carbene insertion reaction. The utility of nucleophilic substitution conditions permits to form biscarbenes; meanwhile the catalysed-Hoffman reaction and multicomponent reaction (MCR) were used to prepare this type of copper complexes. The molecular structures of the representative metal-NHC and metal-carbene bonds of the desired complexes have elucidated and proved by elemental analyses, FT-IR, ^1H & ^{13}C NMR spectroscopy. In contrast to the common assumption that NHCs are pure σ -donors, the prepared complexes revealed a significant π -back-bonding in electron-rich metal NHC complexes and sterically stabilized.

The promising feature of that methodology is forming the isocyanides via dehydrogenation reaction and generating dichlorocarbene by the phase-transfer method. With less sterically hindered primary amines, a 1:1 ratio of amine to chloroform gives satisfactory results.

No conflict of interest: Nil

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