



Cu(I)-N heterocyclic carbene complexes: Synthesis, catalysis and DFT studies



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ABSTRACT

The structural, spectroscopic and catalytic properties of the two Cu(I) complexes $[\text{Cu}_2(\text{L1})_2](\text{PF}_6)_2$ (**1**) and $[\text{Cu}_2(\text{L2})_2](\text{PF}_6)_2$ (**2**), bearing proligands 2,6-bis-(N-methylimidazolium)pyrazine hexafluorophosphate (**L1**) and 2,6-bis-(N-methylbenzimidazolium)pyrazine hexafluorophosphate (**L2**), have been investigated. The solid state structure of **1** has been determined by X-ray diffraction studies, while DFT computation technique has been used to optimize structure **2**. From molecular orbital calculations using TD-DFT, the absorption bands are assigned to metal to ligand charge transfer (MLCT) along with some inter ligand charge transfer (ILCT) transitions. Complexes **1** and **2** possess very weak Cu(I)–Cu(I) interactions within the reported distance 2.947–3.020 Å. They are expected to have luminescent properties due to Cu(I)–Cu(I) interactions. Preliminary studies revealed both complexes to possess catalytic efficiency in general hydrosilylation reactions.

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1. Introduction

N-heterocyclic carbenes (NHCs) have established as a leading class of ligands with outstanding performance in metal-catalyzed reactions [1]. They are strong σ -donors and are known to be better alternative of phosphine compounds due to air and moisture stability. In most of the cases, NHC compounds are very inexpensive to prepare and formless undesired products during catalysis and thus become predominantly useful during catalysis [2]. NHCs are more powerful σ -donors than the closely related phosphine ligands, forming stronger bonds to transition metals and thereby also leading to electron-rich metal centres [3]. The metals which mostly participate in catalysis get stabilized by the ancillary ligand NHC through ‘push–pull’ mechanism (strong σ -donor by carbene carbon but π -accepting by N of imidazole ring) and remain as centres of ‘curiosity’ [4] during molecular designing. Interestingly, most studies focusing on catalysts incorporating NHC ligands have

revolved around the platinum metal groups [5], though other groups of metals also offer ample of scopes. Copper is relatively less expensive than platinum group metals and has a long history in catalysis [6] which motivated us for the current studies.

Beyond catalysis, many researchers in NHC field are focusing on (i) the development of novel NHC ligands [7], (ii) applications of NHCs as fluorescent materials [8], and (iii) metal-NHC complexes in biomedical applications [9]. The fluorescent materials have ample of scope of use as photosensitizers in dye-sensitized solar cells and have thus played a pivotal role in developing light-to-energy conversion technology [10]. In materials science, phosphorescent metal complexes of Ir(III), Ru(II), Os(II), Au(I), Au(III), Ag(I) etc. supported by 2-phenylpyridine [11] have received a lot of attention as these are emerging luminescent materials for new light emitting devices used in mobile phones, PCs, and TVs [10]. Over the past decade, a broad range of silver(I) complexes supported by NHCs have been synthesized and explored for their potentially useful photo-physical properties [12], though comparatively fewer Cu(I)-NHC complexes have been studied [13]. Indeed, stability of Cu(I) remains a challenge, because of the strong σ -donor nature of NHC where Cu(I) is weak electron acceptor than Cu(II). But proper

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designed NHC can stabilize Cu(I).

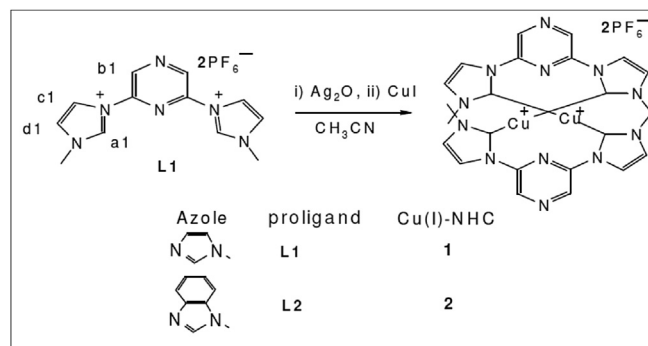
We have focused on pyrazine functionalized pincer-carbenes [9a,14] because of their excellent chelating effect and reactivities. Catalytic hydrosilylation of carbonyl compounds, which leads to alcohols, is a useful synthetic method for the reduction of carbonyl groups by main-group hydrides. We have studied the efficacy of our Cu(I)-NHCs as catalyst for this transformation. Additionally, luminescent properties of the complexes (which is arises because of Cu—Cu interaction as shown in Chart 1) have been investigated and DFT studies have been performed to understand orbital participation and to explain the electronic properties.

2. Results and discussion

2.1. Synthetic strategy and spectral characterization

The precursors 2, 6-bis(N-methylimidazol-2-yl)pyrazine dichloride and 2, 6-bis(N-methylbenzimidazol-2-yl)pyrazine dichloride were obtained by the reported procedure [9a]. The formation of imidazolium salts was confirmed from the presence of imidazolium carbene singlet signal at 9.44 and 9.73 ppm for proligands **1** and **2** respectively. The designing of imidazolium/benzimidazolium salts of pyrazine was taken up because of the fact that the electron withdrawing (π -acidic) character of pyrazine facilitates the formation of carbene and allows the comparison of the iso-electronic character with other pincer carbenes like 2,6-bis(N-methylimidazolium)pyridine dichloride. In addition to the base added externally, the extra N present in pyrazine increases the basicity of the reaction medium during catalysis [14].

The Cu(I) complex **1** has been synthesized by silver-carbene transfer method [15] as described in Scheme 1 without isolating the Ag-carbene from the solvent. The formation of Cu(I)-NHCs was confirmed by the disappearance of imidazolium C₂-H signal at 9.44 and 9.73 ppm (for **1** and **2**) and downfield shift of other aromatic protons; more downfield shift was observed in case of **2**. ¹³CNMR spectra of the complexes showed downfield shift of carbon signals (ca. 1.5–12 ppm) from those of the free ligands. The absorption spectrum of **1** in acetonitrile showed a strong absorption band ($\epsilon = 22\,000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) and weaker shoulders ($\epsilon = 6200\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) at 305 nm and 425 nm. The deep orange complexes **1/2** are air and moisture sensitive, but stable in nitrogen atmosphere in dry condition. The orange colour turned to deep green in air after 10–12 h; after ¹HNMR analysis it was observed that the mixture contained the free proligand and an unidentified Cu salt.



Scheme 1. Synthesis of complexes **1** and **2**.

2.2. Structural description of the complexes

The molecular view of **1** is shown in Fig. 1. Crystallographic parameters are listed in Table 1 and selected bond parameters are listed in Tables 2 and 3. The molecule crystallized with triclinic symmetry and *P*-1 space group. There are three crystallographically independent dinuclear complex cations in the asymmetric unit of

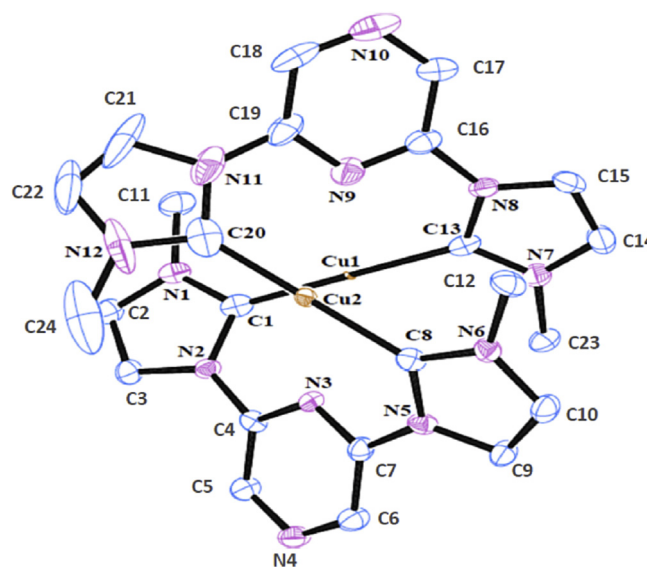


Fig. 1. ORTEP view of single crystal X-ray structure of complex **1** [H atoms and PF₆⁻ have been removed for clarity].

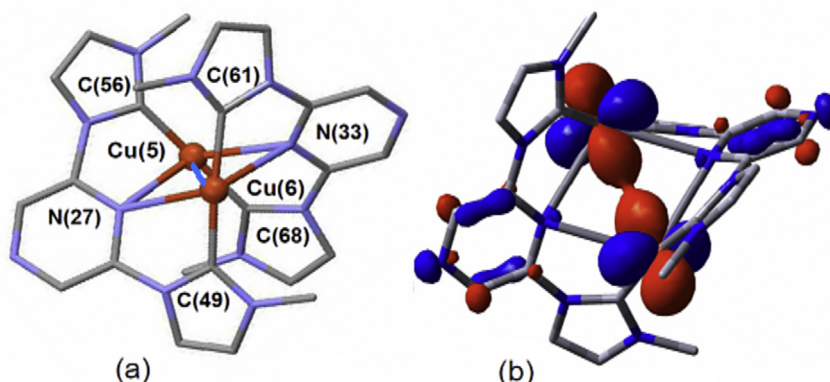


Chart 1. Key structural feature Cu—Cu interaction shown by (a) solid state structure and (b) DFT studies.

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