



Research paper

Copper complexes of 1,4-diazabutadiene ligands: Tuning of metal oxidation state and, application in catalytic C-C and C-N bond formation

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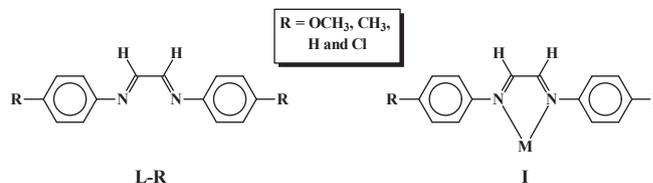
1,4-Diazabutadiene ligands
Dicopper(I) and dicopper(II) complexes
Tunability of copper oxidation state
Catalytic C-N and C-C coupling reactions

ABSTRACT

Reaction of 1,4-diazabutadiene ($p\text{-RC}_6\text{H}_4\text{N}=\text{C}(\text{H})(\text{H})\text{C}=\text{NC}_6\text{H}_4\text{R}$; R = OCH₃, CH₃, H and Cl; abbreviated as L-R) with CuCl₂·2H₂O in methanol at ambient temperature (25 °C) affords a group of doubly chloro-bridged dicopper complexes of type [Cu^I(L-R)Cl]₂, designated as 1-R. Similar reaction carried out in acetonitrile furnishes a family of doubly chloro-bridged dicopper complexes of type [Cu^{II}(L-R)Cl₂]₂, designated as 2-R. Molecular structures of 1-OCH₃ and 2-OCH₃ have been determined by X-ray crystallography. While copper(I) is having a nearly tetrahedral N₂Cl₂ coordination sphere in 1-OCH₃, the N₂Cl₃ coordination sphere around copper (II) is distorted square pyramidal in nature in 2-OCH₃. Isolated 2-R complexes, on dissolution in methanol, are found to undergo facile reduction of the metal center to generate the corresponding 1-R complexes. The 1-R and 2-R complexes show intense absorptions in the visible and ultraviolet regions. Cyclic voltammetry on the 1-R and 2-R complexes shows both metal-centered and ligand centered redox responses. The 1-R complexes are found to efficiently catalyze C-N cross-coupling reactions between arylboronic acids and aryl amines; while the 2-R complexes display notable catalytic efficiency for nitroaldol reactions.

1. Introduction

The present work has originated from our continued interest in the synthesis of designed transition metal complexes, and their utilization in catalysis [1–8]. Though complexes of the platinum group of metals are undoubtedly most favorite catalysts for majority of the reactions, complexes of the first row transition metals are gradually finding importance in this field of catalysis, primarily owing to their ease of formation and inexpensive metal sources [9–13]. We have also been active along this direction, and prepared few copper and nickel based systems that showed notable catalytic properties towards C-C and C-N bond formation reactions [14–16]. Accessibility of different oxidation states of copper (*viz.* +1 to +3), associated with possible variation of coordination number around the metal center, has endowed copper based systems as favorite candidates for exploring their catalytic potential. Encouraged by our own observations, as well as by the works of others, on the development of copper based molecular systems and their utilization as catalyst in useful reactions [16,17–20], we planned to synthesize copper complexes of a group of 1,4-diazabutadiene ligands, which



are abbreviated in general as L-R, where R depicts the *para*-substituent in the aryl ring. Four different substituents (R = OCH₃, CH₃, H and Cl), with different electron withdrawing properties, were chosen to study their influence, if any, on the redox properties of the complexes. The selected ligands are known to bind to metal centers as bidentate N,N-donors forming five-membered chelate ring (I) [21–25]. The α -diimine fragment in these ligands has considerable π -acidity, and hence they are capable of stabilizing metals in relatively low oxidation states [26,27]. Though copper complexes with some diimine ligands are reported [28–35], and catalytic application of some of them is known [29,31–34], a comprehensive study on copper complexes of the 1,4-diazabutadiene ligands, with particular reference to their catalytic application in C-N and C-C bond formation reactions which is our final goal, seems to have remained unexplored. The initial target of this work

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