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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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ABSTRACT

Keywords: 1,4-Diazabutadiene ligands Dicopper(I) and dicopper(II) complexes Tunability of copper oxidation state Catalytic C-N and C-C coupling reactions Reaction of 1,4-diazabutadiene (p-RC₆H₄N = C(H)(H)C = NC₆H₄R-p; 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^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}], 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 1,4diazabutadiene 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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was to synthesize a group of mixed-ligand copper complexes containing 1,4-diazabutadiene as neutral ligand and chloride ion as anionic ligand. In order to achieve this target we selected cupric chloride as the source of copper, as it is capable of providing the CuCl fragment. In this paper we describe our observation on the interaction of the 1,4-diazabutadiene ligands with cupric chloride towards affording the mixed-ligand complexes, their characterization, and exploration of their catalytic efficiency for C-C and C-N bond formation.

2. Experimental

2.1. Materials

Copper(II) chloride dihydrate (CuCl₂·2H₂O) was procured from Merck, Mumbai, India. Glyoxal was obtained from SD Fine Chem, Mumbai, India, and the 4-R-anilines ($R = OCH_3$, CH_3 , H and Cl) were procured from Merck, Mumbai, India. The 1,4-diazabutadiene ligands (**L-R**) were prepared by condensation of glyoxal with the 4-R-anilines in hot methanol. Tetrabutylammonium hexafluorophosphate (TBHP) procured from Aldrich and AR-grade acetonitrile procured from Merck (India) were used in electrochemical work. All other chemicals and solvents were reagent grade commercial materials and were used as received.

2.2. Synthesis of complexes

2.2.1. $[{Cu^I(L-R)Cl}_2]$ complexes

The $[{Cu^I(L-R)Cl}_2]$ (**1-R**; R = OCH₃, CH₃, H and Cl) complexes were prepared by following a general procedure. Specific details are given below for a particular complex.

1-OCH₃: CuCl₂:2H₂O (200 mg, 1.17 mmol) was dissolved in methanol (25 ml), and a solution of **L-OCH₃** (318 mg, 1.18 mmol) in methanol (25 ml) was added to it. The solution was stirred at ambient temperature for 1 h, whereby a brown solution was obtained. The solution volume was reduced to half via evaporation under reduced pressure, and the concentrated solution was kept in a refrigerator for 12 h. The **1-OCH₃** complex separated as a greenish-brown crystalline solid, which was collected by filtration, washed with ether, and dried in air. Yield: 380 mg, 88%. *Anal.* Calc. for $C_{32}H_{32}N_4O_4Cl_2Cu_2$: C, 52.32; H, 4.36; N, 7.63. Found: C, 52.64; H, 4.34; N, 7.66%. ¹H NMR (500 MHz, CDCl₃) [36]: 3.74 (OCH₃); 6.87 (d, 2H, J = 8.5); 7.47 (d, 2H, J = 9.0); 8.27 (s, 1H). IR (cm⁻¹): 497, 528, 634, 719, 797, 825, 1024, 1110, 1166, 1252, 1296, 1360, 1458, 1503, 1585 and 1611.

1-CH₃: Yield: 335 mg, 85%. *Anal.* Calc. for *Anal.* Calcd. for $C_{32}H_{32}N_4Cl_2Cu_2$: C, 57.31; H, 4.78; N, 8.36. Found: C, 57.44; H, 4.53; N, 8.61%. ¹H NMR (500 MHz, CDCl₃): 2.21 (CH₃); 7.04 (d, 2H, *J* = 8.0); 7.32 (d, 2H, *J* = 8.5); 8.22 (s, 1H). IR (cm⁻¹): 499, 530, 670, 759, 797, 844, 988, 1110, 1176, 1252, 1300, 1362, 1458, 1503 and 1611.

1-H: Yield: 278 mg, 77%. *Anal.* Calc. for $C_{28}H_{24}N_4Cl_2Cu_2$: C, 54.72; H, 3.91; N, 9.12. Found: C, 54.50; H, 4.01; N, 9.11%. ¹H NMR (500 MHz, CDCl₃): 7.10 (t, 2H, J = 7.5); 7.28 (t, 1H, J = 7.0); 7.34 (d, 2H, J = 8.0); 8.26 (s, 1H). IR (cm⁻¹): 524, 613, 694, 759, 846, 954, 1024, 1075, 1208, 1275, 1345, 1447, 1485, 1536, 1591 and 1625.

1-Cl: Yield: 362 mg, 82%. *Anal.* Calc. for $C_{28}H_{20}N_4Cl_6Cu_2$: C, 44.68; H, 2.66; N, 7.45. Found: C, 44.64; H, 2.66; N, 7.48%. ¹H NMR (500 MHz, CDCl₃): 7.19 (d, 2H, J = 8.5); 7.40 (d, 2H, J = 8.5); 8.29 (s, 1H). IR (cm⁻¹): 540, 597, 683, 715, 750, 823, 1013, 1091, 1170, 1211, 1285, 1345, 1405, 1450, 1480, 1539, 1588 and 1635.

2.2.2. $[{Cu^{II}(L-R)Cl_2}_2]$ complexes

The $[{Cu^{II}(L-R)Cl_2}_2]$ (**2-R**; R = OCH₃, CH₃, H and Cl) complexes were prepared by following a general procedure. Specific details are given below for a particular complex.

2-OCH₃: CuCl₂:2H₂O (200 mg, 1.17 mmol) was dissolved in acetonitrile (25 ml), and a solution of L-OCH₃ (318 mg, 1.18 mmol) in acetonitrile (25 ml) was added to it. The solution was stirred at ambient temperature for 1 h, whereby a yellowish-brown solution was obtained. The solution volume was reduced to half via evaporation under reduced pressure, and the concentrated solution was kept in a refrigerator for 12 h. The **2-OCH₃** complex separated as a yellowish-brown crystalline solid, which was collected by filtration, washed with ether, and dried in air. Yield: 427 mg, 90%. *Anal.* Calcd. for $C_{32}H_{32}N_4O_4Cl_4Cu_2$: C, 47.70; H, 3.98; N, 6.96. Found: C, 47.45; H, 3.95; N, 6.99%. Magnetic moment, $\mu_{eff} = 2.43 \ \mu_B$. IR (cm⁻¹): 494, 550, 797, 839, 851, 902, 1022, 1172, 1259, 1299, 1371, 1459, 1503, 1519, 1591 and 1627.

2-CH₃: Yield: 375 mg, 86%. Anal. Calcd. for $C_{32}H_{32}N_4Cl_4Cu_2$: C, 51.82; H, 4.32; N, 7.56. Found: C, 52.05; H, 4.21; N, 7.43%. Magnetic moment, $\mu_{eff} = 2.49 \ \mu_B$. IR (cm⁻¹): 502, 559, 645, 763, 807, 847, 867, 1020, 1039, 1062, 1103, 1170, 1210, 1278, 1347, 1380, 1466, 1499 and 1634.

2-H: Yield: 322 mg, 80%. *Anal.* Calcd. for $C_{28}H_{24}N_4Cl_4Cu_2$: C, 49.05; H, 3.50; N, 8.18. Found: C, 49.45; H, 3.55; N, 8.17%. Magnetic moment, $\mu_{eff} = 2.41 \ \mu_B$. IR (cm⁻¹): 521, 585, 604, 623, 696, 759, 836, 852, 881, 916, 1002, 1028, 1071, 1175, 1208, 1300, 1312, 1342, 1447, 1483, 1584 and 1628.

2-Cl: Yield: 426 mg, 88%. *Anal.* Calcd. for $C_{28}H_{20}N_4Cl_8Cu_2$: C, 40.83; H, 2.43; N, 6.80. Found: C, 40.64; H, 2.40; N, 6.85%. Magnetic moment, $\mu_{eff} = 2.47 \ \mu_B$. IR (cm⁻¹): 535, 677, 715, 752, 819, 833, 874, 1014, 1091, 1167, 1208, 1345, 1412, 1456, 1482, 1590 and 1635.

2.3. Physical measurements

Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. IR spectra were obtained on a Perkin Elmer Spectrum Two IR spectrometer with samples prepared as KBr pellets. Magnetic susceptibilities were measured using a Sherwood MK-1 balance. ¹H NMR spectra were recorded in CDCl₃ solutions on a Bruker Avance DPX 500 NMR spectrometer using TMS as the internal standard. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical measurements were made using a CH Instrument model 600A electrochemical analyzer. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three electrode configuration. Electrochemical measurements were made under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. GC-MS analyses were performed using a Perkin Elmer CLARUS 680 instrument.

2.4. X-Ray crystallography

Single crystals of $[{Cu^{I}(L-OCH_{3})Cl}_{2}]$, $(1-OCH_{3})$ and $[{Cu^{II}(L-OCH_{3})Cl}_{2}]$, $(2-OCH_{3})$ were obtained by slow evaporation of solvent from solutions of the complexes in methanol and acetonitrile respectively. Selected crystal data and data collection parameters are given in Table 1. Data on both the crystals were collected on a Bruker SMART CCD diffractometer. X-ray data reduction and, structure solution and refinement were done using the SHELXS-97 and SHELXL-97 packages [37]. The structures were solved by the direct methods.

2.5. Application as catalysts

2.5.1. General procedure for C-N coupling reactions

In a typical run, an oven-dried 10 ml round bottom flask was charged with a known mole percent of catalyst and base, phenylboronic acid (1.2 mmol) and aniline (1.0 mmol) with ethanol (5 ml). The mixture was stirred at ambient temp (25 °C). After the specified time (5 h) stirring was stopped, water (20 ml) was added, and extraction with ether (2 × 10 ml) was done. The combined ether extract was washed with water (3 × 10 ml), dried over anhydrous Na₂SO₄, and filtered. Solvent was removed under vacuum. The residue was dissolved in hexane and analyzed by GC-MS.

Table 1

Crystallographic data for 1-OCH3 and 2-OCH3.

Complex	1-OCH ₃	2-OCH ₃	
Empirical formula	$C_{32}H_{32}N_4O_4Cl_2Cu_2$	C32H32N4O4Cl4Cu2	
Formula weight	734.62	805.52	
Crystal system	Monoclinic	Triclinic	
Space group	P21/c	Pī	
a (Å)	8.0130(14)	8.1280(8)	
b (Å)	11.717(2)	10.0921(10)	
c (Å)	34.489(7)	11.5611(11)	
α(°)	90	81.617(3)	
β(°)	95.018(11)	71.377(3)	
γC	90	69.912(3)	
V (Å ³)	3225.7(10)	843.32(14)	
Ζ	4	1	
$D_{\text{calcd.}}(\text{mg m}^{-3})$	1.513	1.586	
F(0 0 0)	1504	410	
λ (Å)	0.71073	0.71073	
Crystal size (mm ³)	0.16 imes 0.18 imes 0.25	$0.07\times0.08\times0.10$	
T (K)	296	296	
$\mu ({\rm mm}^{-1})$	1.527	1.621	
Collected reflections	38,422	27,872	
R _{int}	0.101	0.102	
Independent reflections	7781	3746	
R_1^{a}	0.0633	0.0479	
wR_2^{b}	0.1833	0.1507	
GOF ^c	0.92	0.90	

 $\label{eq:relation} \begin{array}{l} ^{a} \ R_{1} = \Sigma \ ||F_{o}| \cdot \ |F_{c} \ ||/\Sigma|F_{o}| \\ \\ ^{b} \ wR_{2} = \ [\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma \ [w(F_{o}^{2})^{2}]]^{1/2} \\ \\ ^{c} \ GOF = \ [\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}]/(M-N)]^{1/2}, \ \text{where } M \ \text{is the number of reflections} \end{array}$ and N is the number of parameters refined.

2.5.2. General procedure for nitroaldol reactions

In a typical run, an oven-dried 10 ml round bottom flask was charged with a known mole percent of catalyst, arylaldehyde (1.0 mmol) and nitroalkane (5.0 mmol) with acetonitrile (5 ml). The flask was placed in a preheated oil bath at required temp. After the specified time the flask was removed from the oil bath, water (20 ml) was added, and extraction with ether $(4 \times 10 \text{ ml})$ was done. The combined organic layers were washed with water (3 \times 10 ml), dried over anhydrous Na₂SO₄, and filtered. Solvent was removed under vacuum. The residue was dissolved in toluene and analyzed by GC-MS.

3. Results and discussion

3.1. Synthesis and characterization

As delineated in the introduction, the initial goal of the present study was to synthesize a group of mixed-ligand complexes of copper having both 1,4-diazabutadiene (L-R) and chloride ion in the coordination sphere. Accordingly reactions of the 1,4-diazabutadiene ligands were carried out with CuCl₂·2H₂O in methanol under stirring condition at ambient temperature (25 °C), and from each of these reactions a greenish-brown complex, depicted in general as 1-R, was obtained in good yield. Preliminary characterization of these complexes showed that they are diamagnetic, and their composition agrees well with the general formula Cu(L-R)Cl. In order to ascertain the composition of these complexes, as well as coordination mode of the 1,4diazabutadiene ligand in them, structure of a selected member of this family, viz. 1-OCH₃, was determined by X-ray crystallography. The structure is shown in Fig. 1 and some selected bond parameters are presented in Table 2. The structure reveals that 1-OCH₃ is actually a doubly chloro-bridged dicopper complex, in which copper is in +1oxidation state. Each copper is surrounded by a 1,4-diazabutadiene ligand coordinated in the usual mode (I, M = Cu), and two chloride ions. Disposition of the N,N-donor ligand and the two chlorides around each copper center is grossly tetrahedral in nature, as expected in four-coordinated copper(I) complexes, with a dihedral angle between the Cu



Fig. 1. Crystal structure of the [{Cu^I(L-OCH₃)Cl}₂] complex. Hydrogen atoms are omitted for clarity.

Table 2

Selected bond lengths (Å) and bond angles (°) for [{Cu^I(L-OCH₃)Cl}₂] and $[{Cu^{II}(L-OCH₃)Cl₂}_2].$

[{Cu ^I (L-OCH ₃)Cl} ₂] Bond distance (Å)			
Cu1-Cl1	2 3421(18)	Cu2-Cl1	2 2775(18)
Cu1-Cl2	2 2909(18)	Cu2-Cl2	2,3423(16)
Cu1-N1	2.072(5)	Cu2-N3	2,086(5)
Cu1-N2	2.094(4)	Cu2-N4	2.063(4)
C1-N1	1.281(7)	C17-N3	1.280(7)
C1-C2	1.436(8)	C17-C18	1.449(9)
C2-N2	1.291(7)	C18-N4	1.290(7)
C3-N1	1.426(7)	C19-N3	1.418(8)
C10-N2	1.415(8)	C26-N4	1.424(8)
D 1 1 (2)			
Bond angle (°)	00 55(10)	NO 0 0 N/4	00 50(10)
N1-Cu1-N2	80.55(18)	N3-Cu2-N4	80.50(18)
CII-CuI-CI2	104.07(6)	CII-Cu2-Cl2	104.49(6)
Cl1-Cu1-N1	115.79(14)	Cl1-Cu2-N3	121.07(14)
Cl1-Cu1-N2	112.01(13)	Cl1-Cu2-N4	117.49(14)
Cl2-Cu1-N1	121.23(14)	Cl2-Cu2-N3	111.61(13)
Cl2-Cu1-N2	122.60(14)	Cl2-Cu2-N4	121.27(13)
[{Cu ^{II} (L-OCH ₂)Cl ₂ } ₂]			
Bond distance (Å)			
Cu1-Cl1	2.2479(14)	C1-N1	1.282(5)
Cu1-Cl2	2.2929(11)	C1-C2	1.459(6)
Cu1-Cl2a	2.3465(13)	C2-N2	1.276(5)
Cu1-N1	2.004(3)	C3-N1	1.433(5)
Cu1-N2	2.276(3)	C10-N2	1.431(5)
D 1 1 (2)			
Bond angle (*)		ate a e ata	
N1-Cu1-N2	77.75(12)	CII-CuI-Cl2a	166.28(5)
CII-Cu1-Cl2	93.49(4)	CI2-Cu1-Cl2a	85.21(4)
CI1-Cu1-N1	89.15(10)	Cl2-Cu1-N1	169.17(11)
CII-Cu1-N2	100.01(9)	CI2-Cu1-N2	112.04(8)

(N-N) plane and the CuCl₂ plane close to 87.5°. The bond distances within the five membered Cu(N-N) chelate are normal, and are indicative of usual delocalization of the *n*-cloud over the N-C-C-N fragment. One Cu-Cl distance is found to be about 0.5 Å longer than the other, a feature quite common in doubly chloro-bridged dicopper complexes [38-42]. As all the four 1-R complexes were synthesized similarly and they show similar properties (vide infra), the remaining three 1-R ($R = CH_3$, H and Cl) complexes are assumed to have similar structures as 1-OCH₃. Molecular formula of the 1-R complexes is henceforth represented in general as [{Cu^I(L-R)Cl}₂]. Out of these four 1-R complexes, synthesis and crystal structure of 1-OCH₃ was reported

earlier by Diez-Gonzalez and co-workers [30]. They used cuprous chloride as the source of copper(I) and carried out the synthesis in dichloromethane under stirring condition at room temperature for overnight. While we started the synthesis taking L-OCH₃, cupric chloride as the copper source and methanol as the solvent, which provided the copper(I) complex **1-OCH₃** after 1 h of stirring at ambient temperature via *in situ* reduction of the metal center (*vide infra*).

It is interesting to note here that though a copper(II) source, viz. CuCl₂·2H₂O, was used in the synthesis, copper(I) complexes of type [{Cu^I(L-R)Cl}₂] were obtained as the end product, which indicates that the metal center has undergone one-electron reduction during the course of the synthetic reaction. In the absence of any recognized reducing agent during the synthesis, methanol appears to have served as the reductant. In order to verify it further, similar reactions between the same two reagents, viz. CuCl₂·2H₂O and the 1,4-diazabutadiene ligands, were carried out in acetonitrile under stirring condition at ambient temperature (25 °C), which afforded a group of reddish-brown complexes, represented as 2-R, in decent yields. The 2-R complexes are paramagnetic, and their microanalytical data found to be consistent with Cu(L-R)Cl₂ formulation. For an unambiguous characterization of these complexes, the crystal structure of 2-OCH₃ was determined, and the structure (Fig. 2) shows that 2-OCH₃ is also a doubly chloro-bridged dicopper complex. However, unlike in 1-OCH₃, here each copper is linked to three chloride ions, two of which are bridging and one is terminal. A 1,4-diazabutadiene ligand is coordinated in chelating mode to both the metal centers. Thus each copper is existing in +2 oxidation state in this complex. The N2Cl3 coordination sphere around each copper is distorted square pyramidal in nature. Besides the axial Cu-Cl length being slightly shorter, the observed bond parameters (Table 2) are found to compare well with those in 1-OCH₃. In view of the similarity in synthetic procedure and properties (vide infra), the other three 2-R ($R = CH_3$, H and Cl) complexes are believed to have similar structures as 2-OCH₃. Molecular formula of these 2-R complexes is represented in general as [{Cu^{II}(L-R)Cl₂}₂]. It is interesting to note that by simple variation of the solvent in synthesis, copper(I) or copper(II) complexes can be prepared predictably. It is also worth mentioning here that the isolated $[{Cu^{II}(L-R)Cl_2}_2]$ (2-R) complexes, on dissolution in methanol, are readily and quantitatively converted to the corresponding [{Cu^I(L-R)Cl}₂] (1-R) complexes [43]. As methanol is unable to reduce copper(II) directly in common



Fig. 2. Crystal structure of the $[{Cu^{II}(L-OCH_3)Cl_2}_2]$ complex. Hydrogen atoms are omitted for clarity.

paramagnetic, and the observed magnetic moment ($\mu_{eff} = 2.41 - 2.49 \mu_B$) is slightly lower than expected the spin-only value for two isolated copper(II) centers. This lowering of magnetic moment is attributable to antiferromagnetic interaction between the two copper(II) centers, which is well known in similar doubly chloro-bridged dicopper(II) systems [44].

Infrared spectra of the **1-R** and **2-R** complexes show many bands of varying intensities within 4000–450 cm⁻¹. Spectral data are presented in the experimental section. Besides small shifts in band positions, spectrum of each **1-R** complex is similar to that of the uncoordinated L-R ligand. Infrared spectra of the **2-R** complexes are also found to be grossly similar to those of the corresponding **1-R** analogue.

The **1-R** complexes are soluble in common organic solvents like methanol, ethanol, acetonitrile and dichloromethane, producing intense greenish-brown solutions. Electronic spectra of the **1-R** complexes were recorded in dichloromethane solutions. Spectral data are presented in Table 3. Each complex shows several intense absorptions spanning the visible and ultraviolet regions. The absorptions in the

$$L-R \xrightarrow{CuCl_2} [\{Cu^{II}(L-R)Cl_2\}_2] \xrightarrow{CH_3OH} [\{Cu^{II}(L-R)Cl_2\}_2] \xrightarrow{(L-R)Cl_2} + HCHO + 2HCI$$
(1)

cupric salts [44], we believe that $[{Cu}^{II}(L-R)Cl_2}_2]$ is generated first, even when methanol is used as the solvent for synthesis, which then undergoes one-electron reduction at each copper(II) center to afford the corresponding $[{Cu}^{I}(L-R)Cl_2]$ complexes (eq. 1). This hypothesis has been testified by identification of formaldehyde in the solution obtained from the interaction of $[{Cu}^{II}(L-R)Cl_2}_2]$ with methanol [45]. Similar reduction of copper(II) species to corresponding copper(I) complex is known in the literature [32].

3.2. Spectral properties

Magnetic susceptibility measurements show that the [{Cu^I(L-R)Cl}₂] (**1-R**) complexes are diamagnetic, as expected. ¹H NMR spectra of the **1-R** complexes, recorded in CDCl₃ solutions, show all the expected signals arising from the coordinated L-R ligands. ¹H NMR data are given in the experimental section. For **1-OCH**₃, **1-CH**₃ and **1-H** four signals are observed while for **1-Cl** three signals are found, which is consistent with the composition and stereochemistry of these complexes. The [{Cu^{II}(L-R)Cl}₂] (**2-R**) complexes are found to be

visible region are believed to be due to metal-to-ligand charge-transfer transitions, while those in the ultraviolet region are attributable to transitions within the diimine-ligand orbitals. The **2-R** complexes are found to be insoluble in dichloromethane, but soluble in methanol, ethanol and acetonitrile, producing yellowish-brown solutions. In methanol or ethanol solution, reduction of copper(II) to copper(I) was observed, associated with rapid change in solution color. Hence electronic spectra of the **2-R** complexes were recorded in acetonitrile solution. Each complex shows three intense absorptions (Table 3); one near 460 nm assignable to ligand-to-metal charge-transfer transition, and two in the ultraviolet region within 260 – 340 nm due to transitions within the diimine-ligand orbitals.

3.3. Electrochemical properties

Electrochemical properties of the dicopper(I) complexes (**1**-**R**) were studied by cyclic voltammetry in dichloromethane solution (0.1 M TBHP). Each complex showed three oxidative responses on the positive side of SCE, and two reductive responses on the negative side. The

Table 3

Electronic spectral and cyclic voltammetric data of the complexes.

Complex	Solvent	Electronic spectral data λ_{max} (nm) (ϵ (M ⁻¹ cm ⁻¹))	Cyclic voltammetric data ^a E, V vs SCE
1-OCH ₃ 1-CH ₃ 1-H 1-Cl 2-OCH ₃	dichloromethane dichloromethane dichloromethane dichloromethane acetonitrile	700 ^b (1400), 595 (4400), 559 ^b (3600), 506 (6100), 440 ^b (40900), 419 (42700), 248 (66700) 699 ^b (1200), 552 (3100), 525 (2600), 471 (4700), 410 ^b (40300), 400 (42000), 284 (54300) 698 ^b (1300), 530 (2200), 507 (1900), 462 (4100), 401 ^b (40900), 395 (42500), 288 (52800) 709 ^b (1100), 570 (1900), 545 ^b (1500) 486 (3600), 412 ^b (38800), 400 (40700), 301 (50400) 468 (3900), 317 ^b (16200), 272 (25000)	$\begin{array}{l} 1.87^{\rm c}, 0.90(266), 0.69(281), -0.86^{\rm d}, -1.36^{\rm d}\\ 1.90^{\rm c}, 0.89(261), 0.72(274), -0.97^{\rm d}, -1.45^{\rm d}\\ 1.88^{\rm c}, 0.92(268), 0.70(284), -0.84^{\rm d}, -1.40^{\rm d}\\ 1.91^{\rm c}, 0.98(266), 0.76(281), -0.86^{\rm d}, -1.37^{\rm d}\\ 1.50^{\rm c}, 0.55(112), -0.98^{\rm d}. \end{array}$
2-CH ₃	acetonitrile	458 (4200), 339 ^b (15700), 261 (22000)	-1.57^{a} 1.54^{c} , 0.61 (1 1 4), -0.94^{d} , -1.46^{d}
2-H	acetonitrile	452 (4000), 321 ^b (15100), 260 (19300)	$1.49^{\circ}, 0.70 (116), -0.80^{d},$
2-Cl	acetonitrile	473 (4500), 340 ^b (16900), 281 (23100)	-0.97, $-1.401.55^{\circ}, 0.79 (117), -0.71^{d},-0.96^{d}, -1.40^{d}$

^a Supporting electrolyte, TBHP; scan rate 50 mV s^{-1} .

^b Shoulder.

 $^{\rm c}~{\rm E}_{\rm pa}$ (anodic peak potential) value.

 d E_{pc} (cathodic peak potential) value.

Table 4

C-N cross-coupling reaction of arylboronic acids with aryl amines.^a



 $^{\rm a}$ Reaction conditions: catalyst (1.0 mol%), arylamine (1.0 mmol), arylboronic acid (1.2 mmol), solvent (5 ml).

^b Determined by GCMS.

^c The O-C coupled product was obtained in 73% yield.



cyclic voltammetric data are presented in Table 3, and representative voltammograms are shown in Fig. S1 (Supplementary material). The two successive oxidations observed near 0.70 V and 0.90 V are assignable respectively to Cu(I)-Cu(II) and Cu(II)-Cu(III) oxidations. The third irreversible oxidation near 1.90 V may be attributed to oxidation of the coordinated diimine ligand. The two reductions are assignable to successive one-electron reductions of the diimine fragment of the N,N-donor ligand. The diimine moiety is capable of undergoing two one-electron reductions producing a radical anion and a dianion respectively (eq. 2). These two reductions are observed in each complex as

irreversible responses near -0.90 V and -1.40 V.



Cyclic voltammetry on the dicopper(II) complexes (2-R) were carried out in acetonitrile solution (0.1 M TBHP), which showed two oxidative responses on the positive side of SCE, and two-to-three reductive

(2)



Scheme 1. Probable mechanism for the observed C-N cross-coupling reactions. N-N represents the coordinated 1,4-diazabutadiene ligand.

responses on the negative side (Table 3, Fig. S2 (Supplementary material)). The first oxidative response, observed within 0.55 - 0.79 V, is assigned to Cu(II)-Cu(III) oxidation. The second irreversible oxidation near 1.50 V is tentatively assigned to oxidation of the diimine ligand. The first reduction in the **2-OCH**₃ and **2-CH**₃ complexes, observed as an irreversible response near -0.96 V, has the profile indicating two overlapping reductions. This has become very apparent in the **2-H** and **2-Cl** complexes, where these two reductions are observed as two close but separate reductive responses within -0.71 to -0.97 V. These two reductions are attributed to Cu(II)-Cu(I) reduction and first reduction of the diimine ligand respectively. The second reduction of the diimine ligand is observed as an irreversible response within -1.40 to -1.57 V.

3.4. Catalytic activity

Copper complexes are well known to catalyze a wide variety of reactions [46–53]. Herein we have a family of dicopper(I) and a similar family of dicopper(II) complexes, and we have explored catalytic potential of these two group of complexes towards two different reactions. Catalytic activity of the dicopper(I) complexes (1-R) was examined towards Chan-Lam type C-N cross-coupling reactions between arylboronic acids and arylamines. We first examined C-N coupling between phenylboronic acid and *p*-toluidine using 1-OCH₃ as the catalyst. Table S1 (Supplementary material) provides information on the impact of various reaction parameters on the efficiency of this process. After several trials for optimization, it was observed that the best result is obtained with 1.0 mol% of catalyst, NEt₃ as base, ethanol as solvent, and stirring at 25 °C temperature for 5 h (entry 11, Table S1). Under the optimized condition the other three dicopper(I) complexes, *viz.* **1-CH**₃, **1-H** and **1-Cl**, were found to exhibit similar catalytic efficiency (entries 14–16, Table S1).

The scope of the reaction is shown in Table 4. As all the 1-R complexes have shown comparable catalytic efficiency, the results obtained with 1-OCH₃ are only highlighted here. Using the optimized reaction conditions, C-N coupling between three different arylboronic acids (p-X-C₆H₄-B(OH)₂; X = H, CH₃ and Cl) and five *para*-substituted anilines $(p-Y-C_6H_4-NH_2; Y = OCH_3, CH_3, H, Cl and NO_2)$ were attempted, and the corresponding C-N coupled products (*p*-X-C₆H₄-N(H)-C6H4-Y-*p*) were obtained in excellent (\geq 90%) yield (entries 1–15). When a bulkier arylamine, viz. 1-naphthylamine, was used, the yield remained comparable (entry 16). When 2-aminopyridine, having recognized pyridine-nitrogen donor site was used as substrate, the C-N coupled product was obtained in 92% yield (entry 17), indicating no visible influence of presence of donor site in the substrate. When 2-aminophenol was used, the expected C-N coupled product was obtained in poor (12%) yield, however a C-O coupled product was obtained in good (73%) yield (entry 18). In view of the relatively milder reaction conditions and lower catalyst loading, the observed catalytic efficiency of the dicopper(I) complexes is superior to majority of the copper catalysts [54-64]. For example, similar coupling using molecular copper(II) complexes are known to require higher catalyst loading and longer reaction time [55,60–63], and in few cases higher temperature [62,63], to afford the C-N coupled products in comparable yields.

In copper-catalyzed Chan-Lam type C-N cross-coupling reaction, the catalytic cycle is known to involve three different oxidation states of copper, viz. +1, +2 and +3. However, in majority of the reported

Table 5

Nitroaldol reaction between arylaldehydes and nitroalkanes.^a



Entry	Х	Y	R	R'	Yeild ^b , %
1	Н	Н	н	н	79
2	Н	CH_3	н	н	85
3	Н	Cl	н	н	81
4	Н	Н	CH_3	н	74
5	Н	CH_3	CH_3	н	79
6	Н	Cl	CH ₃	н	76
7	Н	Н	CH_3	CH_3	88
8	Н	CH_3	CH_3	CH_3	93
9	Н	Cl	CH_3	CH_3	87
10	OCH ₃	Н	н	н	61
11	OCH ₃	Н	CH_3	н	56
12	OCH ₃	Н	CH_3	CH_3	67
13	1-naphthaldehyd	1-naphthaldehyde		н	83
14	1-naphthaldehyd	1-naphthaldehyde		н	76
15	1-naphthaldehyd	1-naphthaldehyde		CH_3	87
16	pyridine-2-aldeh	pyridine-2-aldehyde		н	50
17	pyridine-2-aldehyde		CH_3	н	54
18	pyridine-2-aldeh	pyridine-2-aldehyde		CH_3	55
19	salicylaldehyde		н	н	68
20	salicylaldehyde		CH_3	Н	59
21	salicylaldehyde		CH_3	CH_3	63

 $^{\rm a}$ Reaction conditions: catalyst (4.0 mol%), arylaldehyde (1.0 mmol), nitroalkane (5.0 mmol), solvent (5 ml).

^b Determined by GCMS.

studies, copper(II) species were taken as the catalyst-precursor [54–64]. Our present work is, to our knowledge, the first instance where a molecular complex of copper(I) has been utilized as the pre-catalyst. Moreover, our dicopper(I) complexes are readily converted to the corresponding dicopper(I) complexes in ethanol solution, as in methanol [43], which vitiates their use as catalyst in the present reaction. A plausible mechanism for the observed C-N coupling reaction, that is essentially drawn from the one reported by Rao and Wu [54], is illustrated in Scheme 1. The dimeric copper(I) complex (1-R) is believed to provide the tri-coordinated

copper(I) species (A) [65], which marks the entry into the catalytic cycle. A undergoes aerial oxidation in moist solvent to generate the four-coordinated copper(II) species **B**. Transmetallation takes place upon interaction with arylboronic acis in the next step producing species **C**. Coordination of aniline generates five-coordinated copper(II) species **D**, which undergoes aerial oxidation to generate the copper(III) species **E**. Reductive elimination of the C-N coupled product from **E** regenerates the initial copper(I) species **A**, and thus the catalytic cycle continues. It may be noted here that in strictly unaerobic condition the coupling does not happen, and in the absence of base (NEt₃) the C-N coupling occurs but yield of the product decreases significantly, presumably due to consumption of aniline as base by boric acid generated along with conversion of **B** to **C**.

Catalytic activity of the dicopper(II) complexes (2-R) was examined towards nitroaldol reaction, which is a C-C bond formation reaction between arylaldehydes and nitroalkanes, and is also known as Henry reaction [66]. The nitroaldol reaction is a well respected C-C bond formation reaction that is usually base-catalyzed, but copper-catalyzed nitroaldol reactions are also gaining importance [67–76]. We began this type of C-C coupling reaction with benzaldehyde and nitromethane as substrates, and 2-OCH₃ as the catalyst. The experimental method was optimized (Table S2; Supplementary material), and the best result was obtained with 4.0 mol% of catalyst, acetonitrile as solvent, and heating at 50 °C for 1 h (entry 5, Table S2) [77]. Catalytic efficiency of the other three dicopper(II) complexes, *viz*. **2-CH**₃, **2-H** and **2-Cl**, was found to be comparable with that of **2-OCH**₃ (entries 10–12, Table S2).

The scope of the nitroaldol reaction, with 2-OCH₃ as the catalyst, is presented in Table 5. Using the optimized reaction conditions, C-C coupling between seven different arylaldehydes and three nitroalkanes were attempted, and in each case the corresponding C-C coupled product was obtained in good yield (entries 1-21). When para-substituted benzaldehydes or 1-naphthaldehyde were used as substrate, the expected nitroaldols were obtained in very good (74-93%) yield (entries 1-9 and 13-15). However, when arylaldehydes with recognized donor sites were chosen as substrate, the corresponding nitroaldols were obtained in relatively lower (50-68%) vield (entries 10-12 and 16-21). probably due to catalyst inhibition through coordination. The observed copper(II) catalyzed nitroaldol reactions are believed to proceed through sequences that are reported in the literature [67-75]. The catalytic activity of the dicopper(II) complexes is found to be comparable to that of the many other copper(II) species utilized for similar nitroaldol reactions [67,68,70-74]. For example, catalyst loading for nitroaldol reactions using molecular copper(II) complexes is found to be either similar to [70,74], or slightly higher [71-73] than, that of our dicopper(II) complexes for furnishing the coupled products in comparable yields. Significantly higher catalyst loading is also required in case of few other molecular copper(II) complexes [69,75]. However, in view of reaction time, our dicopper(II) complexes appear to be more efficient than others. As nitroaldol reaction is also known to be catalyzed by copper(I) species [78-81], we tried our dicopper(I) complex 1-OCH₃ as catalyst which afforded the expected product, but in very poor yield (entry 13, Table S2).

4. Conclusions

The present study shows that the 1,4-diazabutadiene ligands (L-R) undergo facile reaction with CuCl₂·2H₂O, and afford a group of doubly chloro-bridged dicopper complexes where oxidation state of copper is found to depend on the nature of solvent chosen for the synthesis. When methanol is used as solvent copper(I) complexes of type [{Cu^I(L-R)Cl}₂] (1-R) complexes are obtained; and methanol is found to serve as reducing agent for the metal center. When a solvent like acetonitrile is used that does not have reducing capacity like methanol, the +2 oxidation state of copper is retained in the resulting [$\{Cu^{II}(L-R)Cl_2\}_2$] (2-**R**) complexes. Quantitative conversion of any $[{Cu^{II}(L-R)Cl_2}_2]$ to the corresponding [{Cu¹(L-R)Cl}₂] can be achieved by simple dissolution of the former in methanol. This study also demonstrates that the dicopper (I) complexes (1-R) can efficiently catalyze Chan-Lam type C-N crosscoupling reactions between arylboronic acids and arylamines. The dicopper(II) complexes (2-R) display notable catalytic efficiency for nitroaldol type C-C bond formation reaction between arylaldehydes and nitroalkanes.

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Appendix A. Supplementary material

CCDC 1941330 (for $1-OCH_3$) and 1941331 (for $2-OCH_3$) contain the supplementary crystallographic data for this paper. Screening of experimental conditions for C-N coupling reactions (Table S1), screening of experimental conditions for nitroaldol reactions (Table S2), and cyclic voltammograms of 1-OCH3 and 2-OCH3 (Figs. S1 and S2).

Appendix B. Supplementary data

Supplementary data to this article can be found online at https:// doi.org/10.1016/j.ica.2019.119228.

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