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Olefin aziridination by copper(II) complexes: Effect of redox potential on catalytic activity

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ABSTRACT

A series of new copper(II) complexes of four sterically hindering linear tridentate 3N ligands *N′*-ethyl-*N′*-(pyrid-2-ylmethyl)-*N,N*-dimethylethylenediamine (L1), *N′*-benzyl-*N′*-(pyrid-2-ylmethyl)-*N,N*-dimethylethylenediamine (L2), *N′*-benzyl-*N′*-(6-methylpyrid-2-yl-methyl)-*N,N*-dimethylethylenediamine (L3) and *N′*-benzyl-*N′*-(quinol-2-ylmethyl)-*N,N*-dimethylethylenediamine (L4) have been isolated and examined as catalysts for olefin aziridination. The complexes $[Cu(L1)Cl_2]\cdot CH_3OH$ **1**, $[Cu(L2)Cl_2]\cdot CH_3OH$ **2**, $[Cu(L3)Cl_2]\cdot 0.5\ H_2O$ **3** and $[Cu(L4)Cl_2]$ **4** have been structurally characterized by X-ray crystallography. In all of them copper(II) adopts a slightly distorted square pyramidal geometry as inferred from the values of trigonality index (τ) for them (τ: **1**, 0.02; **2**, 0.01; **3**, 0.07; **4**, 0.01). Electronic and EPR spectral studies reveal that the complexes retain square-based geometry in solution also. The complexes undergo quasireversible Cu(II)/Cu(I) redox behavior ($E_{1/2}$, −0.272 − −0.454 V) in acetonitrile solution. The ability of the complexes to mediate nitrene transfer from PhINTs and chloramine-T trihydrate to olefins to form *N*-tosylaziridines has been studied. The complexes **3** and **4** catalyze the aziridination of styrene very slowly yielding above 80% of the desired product. They also catalyze the aziridination of the less reactive olefins like cyclooctene and *n*-hexene but with lower yields (30–50%). In contrast to these two complexes, **1** and **2** fail to catalyze the aziridination of olefins in the presence of both the nitrene sources. All these observations have been rationalized based on the Cu(II)/Cu(I) redox potentials of the catalysts.

1. Introduction

The chemistry of aziridines, the smallest heterocycles similar to epoxides, has been attracting the interest of synthetic organic chemists due to their greater potential as the building blocks of biologically significant nitrogen containing compounds that exist in numerous natural products [1]. Some natural products that contain aziridine rings are shown to exhibit anti-cancer and anti-tumor activities also [2–8]. Aziridines can be obtained by reacting olefins with suitable nitrene sources like (tosylimino)phenyliodinane (PhINTs) [9–21], iodobenzene diacetate ($PhI(OAc)_2$) [22] tosyl azide (TsN_3) [23], chloramine-T (TsNClNa) [24,25] etc. in the presence of catalysts (Scheme 1). A number of catalysts mostly based on copper [26] have been reported; however, structurally characterized copper catalysts are rare. The complex $[Cu(i\text{-}Pr_3TACN)(O_2CCF_3)_2]$ with the tridentate 3N ligand was found to effect the quantitative aziridination of styrene derivatives [27]. Halfen et al. utilized the copper(II) complexes of both tetradentate and tridentate nitrogen containing ligands and showed that the reactivity of the copper(II) complexes is significantly enhanced for aziridination of styrene when the ligand denticity is lowered from tetradentate to tridentate [28,29]. They also suggested that the axial coordination site(s) either vacant or occupied by a readily displaced solvent or counterion facilitates the aziridination with the nitrene source PhINTs. Vadernikov et al. also reported maximum yield of aziridines with copper(II) complexes of bidentate ligands and suggested that coordinative unsaturation at copper is responsible for the very high catalytic activity [30].

The most employed and the best reagent till date for the olefin aziridination reaction by copper catalysts is PhINTs. However, it suffers from certain drawbacks. The synthesis of PhINTs involves two steps [31] and iodobenzene is obtained as the byproduct during aziridination and so a search for better reagents other than PhINTs has resulted. An obvious alternative is chloramine-T trihydrate ($TsNClNa\cdot(H_2O)_3$), which gives NaCl as the byproduct, and it is cheaper and readily available [27]. Taylor et al. reported [31] a yield of about 76% for the aziridination of olefins using a Cu(I) catalyst of the ligand *N*-(2-pyridinylmethylene)-1-pentanamine. In this procedure, chloramine-T trihydrate is used as such without dehydrating it as reported by Komatsu [33]. Bromamine-T has been also used as a nitrene precursor [34,35]. Hutchings et al.

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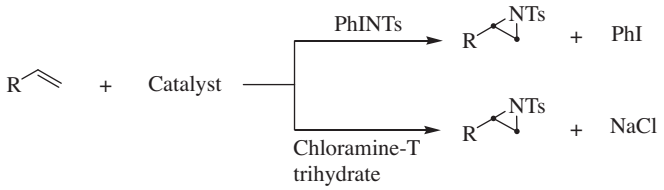


Scheme 1. Olefin aziridination using Cu(II) complexes.

examined the potential of both chloramine-T and bromamine-T as a nitrene source in the asymmetric aziridination with copper-exchanged zeolite and found that PhINTs is far superior [36].

In our laboratory we have already investigated [37] the aziridination of olefins using Cu(II) complexes of cyclic tridentate 3N ligands as catalysts and the strongly oxidizing PhINTs as nitrene source. All the complexes were found to be fast and efficient catalysts when a high (10–5) olefin:PhINTs ratio was used. Also we have shown that ligand steric hindrance plays a vital part in accelerating the reaction rate and providing higher yields of aziridines. In continuation of the above study to determine whether electronic effects or steric factors are responsible for the increased product yield and minimum reaction time, the electron rich and sterically hindering $-NMe_2$, 6-methylpyridyl and quinolyl moieties have been incorporated in the open chain tridentate 3N ligands (Scheme 2) chosen for the present study. The coordinative unsaturation as well as steric crowding around copper(II) in the present complexes is expected to lead to improved selectivity, reaction rate and broad substrate tolerance. Since copper halides are till now the best catalysts reported, we have examined and compared the nitrene sources PhINTs and chloramine-T trihydrate in the presence of Cu(II) chloride complexes of the 3N ligands. The X-ray crystal structures of the complexes have been determined to establish the degree of coordinative unsaturation and distortion in the complexes. The solution structures of the complexes have been asserted by employing spectroscopic and electrochemical methods to understand the effect of ligand architecture on copper(II) coordination geometry. The more sterically hindered complexes **3** and **4** are found to catalyze the aziridination of olefins more efficiently than **1** and **2** and this observation correlates with the higher ability of the former complexes to stabilize Cu(I) or destabilize the Cu(II) oxidation state in solution.

2. Experimental section

2.1. Materials and methods

$CuCl_2{\cdot}2H_2O$ (Merck, India), pyridine-2-carboxaldehyde, quinoline-2-carboxaldehyde, 6-methyl-pyridine-2-carboxaldehyde, *N′*-ethyl-*N,N*-dimethylethylenediamine, *N′*-benzyl-*N,N*-dimethylethylenediamine, chloramine-T trihydrate, sodium triacetoxyborohydride, styrene, *cis*-cyclooctene, *n*-hexene, *tetra-n*-butylammonium bromide (Aldrich), *p*-toluene sulfonamide and iodosobenzenediacetate (Merck, Germany), were used as received. Styrene was distilled from KOH pellets at 25 °C under vacuum (0.3 Torr) and was stored at −20 °C. Anhydrous acetonitrile was used in catalytic aziridinations and was handled and stored under N_2. The iodinane PhINTs was prepared by a modified literature procedure and was stored in the dark [31]. *tetra-n*-Butylammonium perchlorate (TBAP) was prepared by the addition of perchloric acid to a aqueous solution of *tetra-n*-butylammonium bromide. The product was recrystallised from aqueous ethanol and was tested for the absence of bromide. Elemental analyses were performed on a Perkin–Elmer Series II CHNS/O analyzer 2400. ^{1}H NMR spectra were obtained using a Bruker 200 MHz spectrometer at room temperature. ^{1}H NMR chemical shifts are reported versus TMS and are referenced to residual solvent peaks. Electronic absorption spectra were acquired using a Agilent Diode Array Spectrophotometer (200–1100 nm). FTIR spectra (4000–400 cm^{-1} range, KBr pellets) were recorded on a Jasco FT-IR spectrometer. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMX 6/1 spectrometer, the field being calibrated with diphenylpicrylhydrazyl (dpph). The g_0 and A_0 values were estimated at ambient temperature and $g_{||}$ and $A_{||}$ at 77 K. The values of $g_\perp$ and $A_\perp$ were computed as $\frac{1}{2}(3g_0 - g_{||})$ and $\frac{1}{2}(3A_0 - A_{||})$, respectively. Electrochemical experiments were conducted using a EG & G PAR 273 Potentiostat/Galvanostat with EG & G M270 software, using a platinum sphere working electrode, an $Ag/AgNO_3$ reference electrode, and a platinum plate auxiliary electrode. Cyclic voltammograms were obtained in acetonitrile using 0.1 M TBAP as supporting electrolyte. Conductivity measurements on acetonitrile solution of the complexes were made using Elico conductivity bridge.

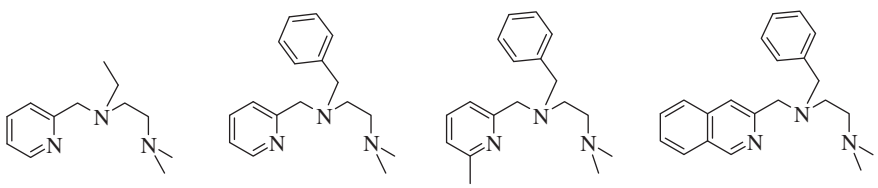
2.2. Synthesis of ligands

2.2.1. *N′*-ethyl-*N′*-pyrid-2-ylmethyl-*N,N*-dimethylethylenediamine (L1)

Pyridine-2-carboxaldehyde (0.535 g, 5 mmol) and *N′*-ethyl-*N,N*-dimethylethylenediamine (0.580 g, 5 mmol) were mixed in 1,2-dichloroethane (20 mL). Sodium triacetoxy borohydride (1.49 g) was added to the above solution and the reaction mixture was stirred at room temperature for 42 h. The reaction was quenched with saturated aqueous sodium bicarbonate and the product was extracted with ethyl acetate. The ethyl acetate extract was dried and the solvent was evaporated to give yellow oil. The product obtained was used as such for the complex preparation. Yield, 0.67 g, 65%. *Anal.* Calc. for $C_{12}H_{21}N_3$ (207.17). δ_H (200 MHz; $CDCl_3$) 8.53–7.18 (m, 4H), 3.76 (s, 2H), 2.63 (q, 4H), 2.43 (m, 4H), 2.21 (s, 6H), 1.06 (t, 3H) ppm.

2.2.2. *N′*-benzyl-*N′*-pyrid-2-ylmethyl-*N,N*-dimethylethylenediamine (L2)

The ligand L2 was prepared using the same procedure employed for L1, except that the amine used here was *N′*-benzyl-*N,N*-dimethylethylenediamine (0.89 g, 5 mmol). Yield, 1.08 g, 80%. *Anal.* Calc. for $C_{17}H_{23}N_3$ (269.19). δ_H (200 MHz; $CDCl_3$) 8.64–7.29



Scheme 2. Ligands employed for the present study.

(m, 4H), 7.06–7.14 (m, 6H), 3.95 (s, 2H), 2.46 (m, 4H), 3.62 (s, 3H), 2.27 (br s, 6H) ppm.

2.2.3. N′-benzyl-N′-(6-methylpyrid-2-ylmethyl)-N,N-dimethylethylenediamine (L3)

The ligand L3 was prepared by the same procedure used for L1, except that the aldehyde used here was 6-methyl-pyridine-2-carboxaldehyde (0.63 g, 5 mmol). Yield, 0.84 g, 60%. *Anal.* Calc. for $C_{18}H_{25}N_3$ (285.41). δ_H (200 MHz; $CDCl_3$) 7.81–7.18 (m, 3H), 7.07–7.14 (m, 6H), 3.95 (s, 2H), 2.46 (m, 4H), 3.62 (s, 2H), 2.55 (s, 3H), 2.27 (br s, 6H) ppm.

2.2.4. N′-benzyl-N′-quinol-2-ylmethyl-N,N-dimethylethylenediamine (L4)

The ligand L4 was prepared using the same procedure employed for L1, except that the aldehyde used here was 2-quinoline carboxaldehyde (0.79 g, 5 mmol). Yield, 0.64 g, 40%. *Anal.* Calc. for $C_{21}H_{25}N_3$ (319.44). δ_H (200 MHz; $CDCl_3$) 9.09–7.29 (m, 6H), 7.07–7.14 (m, 6H), 3.95 (s, 2H), 2.46 (m, 4H), 3.62 (s, 2H), 2.27 (br s, 6H) ppm.

2.3. Preparation of copper(II) complexes

2.3.1. $[Cu(L1)Cl_2]\cdot CH_3OH$ (**1**)

A solution of L1 (0.21 g, 1 mmol) in methanol (15 mL) was treated with $CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol) to obtain a deep blue color solution. After 15 min of stirring, diethyl ether was allowed to diffuse into the solution. Blue crystals of the product were deposited after standing for a period of several days. Yield, 0.32 g, 56%. *Anal.* Calc. for $C_{13}H_{25}N_3Cl_2CuO$ (373.81): C 41.77; H 6.74; N 11.24. Found: C 41.70; H 6.77; N 11.28%. IR: $\bar{\nu}$ = 3525(b), 2925(s), 2360(w), 1590(s), 908(s) cm^{-1}.

2.3.2. $[Cu(L2)Cl_2]\cdot CH_3OH$ (**2**)

A procedure analogous to that used to prepare **1** was followed, using $CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol) and L2 (0.27 g, 1 mmol) instead of L1. The pure product was isolated as pale green precipitate. Yield, 0.19 g, 47%. *Anal.* Calc. for $C_{18}H_{27}N_3Cl_2CuO$ (435.88): C 49.60; H 6.24; N 9.64. Found C 49.62; H 6.28; N 9.58%. IR: $\bar{\nu}$ = 3502(b), 2925(s), 2362(w), 1515(s), 1344(w), 904(s) cm^{-1}. X-ray diffraction quality crystals of **2** were obtained by the vapor diffusion of diethylether into the complex dissolved in methanol.

2.3.3. $[Cu(L3)Cl_2]\cdot 0.5\cdot H_2O$ (**3**)

A procedure analogous to that used to prepare **1** was followed, using $CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol) and L3 (0.28 g, 1 mmol) instead of L1. The solution was stirred which results in the formation of green colored precipitate after one hour and it was filtered. Yield, 0.21 g, 50%. *Anal.* Calc. for $C_{18}H_{26}N_3Cl_2CuO_{0.5}$ (426.87): C 50.65; H 6.14; N 9.84. Found: C 50.60; H 6.13; N 9.90%. IR: $\bar{\nu}$ = 3315(b), 2925(s), 1735(s), 1446(s), 939(s), 634 (s) cm^{-1}. X-ray diffraction quality crystals of **3** were obtained by the vapor diffusion of diethylether into the complex dissolved in acetonitrile.

2.3.4. $[Cu(L4)Cl_2]$ (**4**)

This was prepared by the addition of L4 (0.32 g, 1 mmol) in methanol (15 mL) to a methanolic solution of $CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol) with stirring. After 15 min of stirring, green colored precipitate was obtained. It was filtered and washed with diethyl ether. Yield, 0.26 g, 65%. *Anal.* Calc. for $C_{21}H_{25}N_3Cl_2Cu$ (453.9): C 55.57; H 5.55; N 9.26. Found: C 55.62; H 5.38; N 9.38%. IR: $\bar{\nu}$ = 3546(b), 2925(w), 1467(s), 1031(s), 773(s) cm^{-1}. Suitable single crystals of **4** for X-ray diffraction were obtained by diffusion of diethyl ether into the methanolic solution of the complex.

2.4. Catalytic aziridination

Aziridination of the reactive as well as the non-reactive olefins like styrene, cyclooctene, 1-hexene were performed using the nitrene sources, PhINTs and chloramine-T trihydrate by the procedures reported previously [28,32]. Aziridinations were performed by stirring mixtures of PhINTs or chloramine-T trihydrate (0.3–0.4 mmol), olefins (5 equiv versus nitrene source), and the copper catalyst (5 mol% versus nitrene source) in 2 mL of anhydrous CH_3CN under a dry N_2 atmosphere. All the products obtained were characterized by ^1H NMR spectroscopy.

Table 1
Crystal data and structure refinement details for the complexes **1–4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{13}H_{25}Cl_2CuN_3O$	$C_{18}H_{27}Cl_2CuN_3O$	$C_{36}H_{52}Cl_4Cu_2N_6O$	$C_{21}H_{25}Cl_2CuN_3$
Formula weight	373.81	435.87	853.72	453.90
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Crystal size (mm)	0.07 × 0.09 × 0.17	0.28 × 0.14 × 0.08	0.41 × 0.26 × 0.21 mm	0.09 × 0.12 × 0.32
Space group	*P*21/*c*	*P*21/*c*	*P*$\bar{1}$	*C*2/*c*
a (Å)	7.3916(8))	9.035(5)	10.8374(11)	32.363(3)
b (Å)	12.5856(15)	24.322(13)	12.3977(13)	11.4343(12)
c (Å)	17.679(2	9.561(5)	16.0820(16)	13.0705(14)
α (°)	90	90.000	107.351(2)	90
β (°)	91.575(2)	99.093(10)	101.618(2)	112.928(2)
γ (°)	90	90	102.710(2)	90
V (Å^3)	1644.0(3)	2074.6(19)	1927.4(3)	4454.6(8)
Z	4	4	2	8
λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
D_{calc} g cm^{-3}	1.510	1.395	1.471	1.354
Goodness-of-fit on F^2	1.18	1.063	1.074	0.96
Number of reflections measured	8124	7688	16709	13044
Number of reflections used	2893	2695	8745	5162
Number of L.S. restraints	0	0	0	0
Number of refined parameters	186	230	448	243
Final *R* indices [$I > 2\sigma(I)$]				
*R*1[a]	0.0595	0.1061	0.0398	0.0739
*wR*2[b]	0.1451	0.2272	0.0914	0.1698

[a] $R_1 = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$.
[b] $wR2 = \{[\Sigma(w(F_o^2 - F_c^2)\}\text{^}\{2\})/\Sigma(wF_o\text{^}\{4\})]^{1/2}\}$.

2.5. X-ray crystallography

X-ray single-crystal diffraction data for all the copper(II) complexes were collected on a Bruker SMART Apex diffractometer equipped with CCD area detector at 273 K for **1**, **2** and **3** and at LN temperature (100 K) for **4** with Mo Kα radiation (λ, 0.71073 Å). A crystal of suitable size was immersed in paraffin oil and then mounted on the tip of a glass fiber and cemented using epoxy resin. The crystallographic data were collected in Table 1. For all the complexes, the SMART [50–52] program was used for collecting frames of data, indexing the reflections, and determination of lattice parameters; SAINT [50–52] program for integration of the intensity of reflections and scaling; SADABS [50–52] program for absorption correction, and the SHELXTL [53] program for space group and structure determination, and least-squares refinements on F^2. The structure was solved by heavy atom method. Other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares analysis. Hydrogen atoms attached to the ligand moiety were located from the difference Fourier map and refined isotropically.

In the case of **4**, there was no evidence of crystal decay during data collection, even though the crystal was very unstable on exposure to atmosphere. After locating the complex moiety, a large number of diffused scattered peaks with residual electron density ranging from 4.0 $Å^{-3}$ to 2.0 $Å^{-3}$ was observed in the difference Fourier map, which can be attributed to disordered solvent molecule (diethylether/methanol) used for crystallization, present in the crystal lattice. Attempts were made to model this, but were unsuccessful since the residual electron density peaks obtained was diffused and there were no obvious major site occupations for the solvent molecules. PLATON/SQUEEZE [54,55] was used to correct the data for the presence of the disordered solvent. A potential solvent accessible volume of 629.8 Å [9–13] was found. A total of 141 electrons per unit cell worth of scattering were located in the void. This electron counts correspond to approximately three molecules of diethylether and one molecule of methanol present in the unit cell. Thus, the structure of the compound revealed that in addition to the refined copper complex, tentatively three disordered diethylether and one methanol molecules as solvent of crystallization may be present in the unit cell corresponding to 144 electrons/per unit cell, whose contribution was removed from the modified reflection data by SQUEEZ program. For this compound, full-matrix least-squares refinement of all non-hydrogen atoms with anisotropic temperature factors were carried out till the convergence reached. All the H atoms were positioned geometrically and treated as riding atoms. With the modified data set final cycles of least-squares refinements improved both the *R*-values and Goodness of Fit significantly.

3. Results and discussion

3.1. Synthesis of ligands and complexes

The tridentate ligands L1–L4 were prepared as oils in good yields by the reductive amination of the corresponding aldehydes like pyridine-2-carboxaldehyde, 6-methyl-pyridine-2-carboxaldehyde and quinoline-2-carboxaldehyde with the trisubstituted ethylenediamines in the presence of sodium triacetoxyborohydride. The copper(II) complexes of the ligands were readily prepared in good yields by the addition of $CuCl_2·H_2O$ in methanol to methanolic solutions of the ligands. All of them are soluble in common organic solvents like methanol and acetonitrile. They were characterized by analytical and spectroscopic methods and studied as catalysts for olefin aziridination. In the X-ray crystal structures the ligands occupy three meridional coordination positions and the two chloride ions in the remaining positions. Also, conductivity studies reveal that the complexes behave as 1:1 electrolytes ($130\ \Omega^{-1}\ cm^2\ M^{-1}$) in acetonitrile solution corresponding to the displacement of the axial chloride to give $[Cu(L)Cl]^+$ ions. The longer equatorial chloride can dissociate in solution in the presence of the substrates and facilitate aziridination reaction.

3.2. Structures of the copper(II) complexes

The ORTEP representation of the structures of $[Cu(L1)Cl_2]·CH_3OH$ **1**, $[Cu(L2)Cl_2]·CH_3OH$ **2**, $[Cu(L3)Cl_2]·0.5\ H_2O$ **3** and $[Cu(L4)Cl_2]$ **4** are shown in Figs. 1–4, respectively along with atom numbering scheme. The crystallographic data were collected in Table 1 and the relevant bond lengths and bond angles for the complexes are

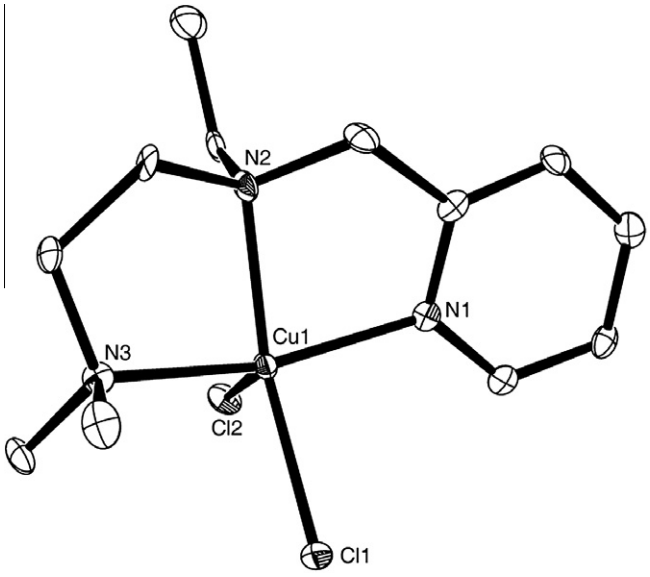


Fig. 1. ORTEP drawing of $[Cu(L1)Cl_2]$ **1** showing the atom numbering scheme and the thermal motion ellipsoids (50% probability level).

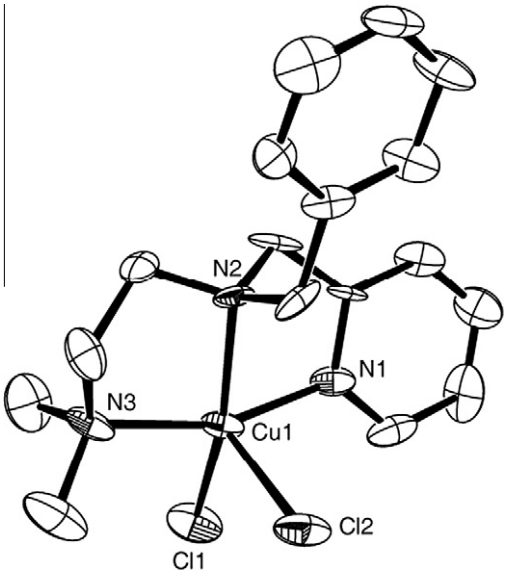


Fig. 2. ORTEP drawing of $[Cu(L2)Cl_2]$ **2** showing the atom numbering scheme and the thermal motion ellipsoids (50% probability level).

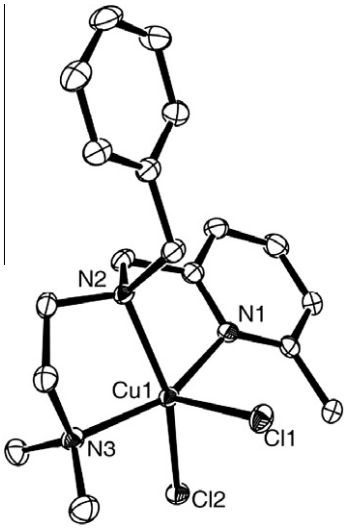


Fig. 3. ORTEP drawing of $[Cu(L3)Cl_2]$ **3** showing the atom numbering scheme and the thermal motion ellipsoids (50% probability level).

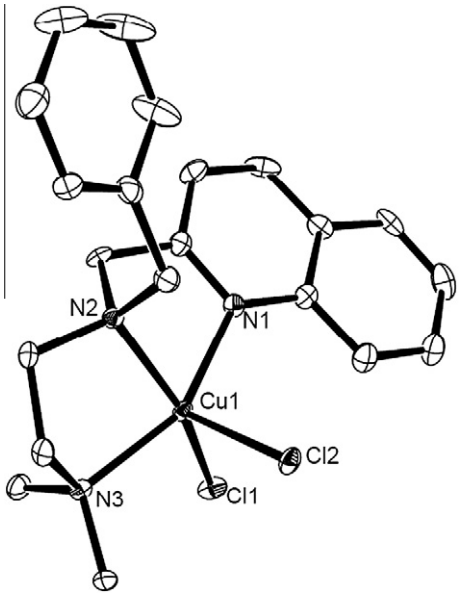


Fig. 4. ORTEP drawing of $[Cu(L4)Cl_2]$ **4** showing the atom numbering scheme and the thermal motion ellipsoids (50% probability level).

given in Table 2. The complex $[Cu(L1)Cl_2]\cdot CH_3OH$ **1** crystallises in the space group of $P21/c$ with one methanol molecule of crystallization. In **1** copper(II) is coordinated by two nitrogen atoms (N2, N3) of the ethylenediamine moiety and the pyridyl nitrogen (N1) of ligand L1, and two chloride ions (Cl1, Cl2). The value of the structural index [38] (τ, 0.02) reveals that the coordination geometry around copper(II) is best described as trigonal bipyramidal distorted square-based pyramidal (TBDSBP) [39–41] with the corners of the square plane being occupied by the three nitrogen atoms and a chloride ion (Cl1), and the apical position by the other chloride ion (Cl2). The coordination of N2 and N3 nitrogens of the ethylenediamine moiety is sterically hindered by the presence of *N*-alkyl substituents. On incorporating an ethyl substituent on N2 in $[Cu(L5)Cl_2]$ **5**, where L5 is *N,N*-dimethyl-*N′*-(pyrid-2-ylmethyl)ethylenediamine [42], to give **1**, the lone pair orbital on it becomes improperly oriented towards Cu(II) and consequently the Cu–N2 bond (2.0319(14) Å) in **5** is elongated to 2.086(4) Å in **1**.

Table 2
Selected bond lengths [Å] and angles [°] for **1**, **2**, **3** and **4**.

	1	2	3	4
Bond lengths				
Cu(1)–N(1)	2.016(4)	2.028(11)	2.046(2)	2.069(4)
Cu(1)–N(2)	2.086(4)	2.113(9)	2.1004(19)	2.088(4)
Cu(1)–N(3)	2.064(4)	2.053(12)	2.067(2)	2.069(4)
Cu(1)–Cl(1)	2.2759(14)	2.297(4)	2.2793(6)	2.3073(15)
Cu(1)–Cl(2)	2.5377(14)	2.542(4)	2.4914(7)	2.4139(13)
Cu(2)–N(4)			2.048(2)	
Cu(2)–N(5)			2.102(2)	
Cu(2)–N(6)			2.058(2)	
Cu(2)–Cl(3)			2.2762(6)	
Cu(2)–Cl(4)			2.4643(7)	
Bond angles				
N(1)–Cu(1)–N(2)	80.52(16)	81.0(4)	79.92(8)	79.40(15)
N(1)–Cu(1)–N(3)	161.06(17)	158.7(4)	156.84(8)	153.58(14)
N(2)–Cu(1)–N(3)	85.67(16)	84.7(4)	84.43(8)	83.89(15)
Cl(1)–Cu(1)–N(1)	94.36(12)	96.9(3)	100.99(6)	94.22(12)
Cl(1)–Cu(1)–N(2)	159.67(11)	100.7(3)	101.39(6)	154.13(11)
Cl(1)–Cu(1)–N(3)	94.14(12)	101.2(3)	98.76(6)	91.96(11)
Cl(2)–Cu(1)–N(1)	93.06(12)	93.4(3)	95.04(6)	104.11(11)
Cl(2)–Cu(1)–N(2)	103.37(11)	159.5(3)	152.75(6)	102.92(11)
Cl(2)–Cu(1)–N(3)	102.74(11)	94.5(3)	91.08(6)	99.46(11)
Cl(1)–Cu(1)–Cl(2)	96.51(5)	99.57(14)	105.86(2)	102.94(5)
N(4)–Cu(2)–N(5)			79.13(8)	
N(4)–Cu(2)–N(6)			154.50(8)	
N(5)–Cu(2)–N(6)			83.67(8)	
Cl(3)–Cu(2)–N(4)			93.51(5)	
Cl(3)–Cu(2)–N(5)			151.37(6)	
Cl(3)–Cu(2)–N(6)			92.64(6)	
Cl(4)–Cu(2)–N(4)			105.99(6)	
Cl(4)–Cu(2)–N(5)			102.24(6)	
Cl(4)–Cu(2)–N(6)			95.92(6)	
Cl(3)–Cu(2)–Cl(4)			106.39(2)	

The complex $[Cu(L2)Cl_2]\cdot CH_3OH$ **2** crystallises with one methanol molecule of crystallization. In this complex, the coordination geometry around copper(II) is best described as trigonal bipyramidal distorted square-based pyramidal (TBDSBP) with the corners of the square plane being occupied by the three nitrogen atoms (N1, N2, N3) and one chloride ion (Cl2), and the apical position by the other chloride ion (Cl1). It is very much similar to that of complex **1**, but has a lower trigonal constraint at Cu(II) as evident from the lower value of the structural index τ (0.01) in **2**. When the *N*-ethyl substituent in $[Cu(L1)Cl_2]$ **1** is replaced by the bulkier *N*-benzyl substituent as in **2**, the Cu–N2 bond (2.113(9) Å) in **2** becomes longer than in **1**, as expected [43], and consequently the Cu–N3 bond (2.053(12) Å) in **2** becomes shorter than that in **1**. As observed in **1**, the Cu–N_{py} bond (2.028(11) Å) in **2** is shorter than that (2.0308(13) Å) in **5**. The weaker coordination of ethyl and benzyl substituted N2 in **1** and **2**, respectively results in the stronger coordination of pyridine nitrogen atom to copper.

The unit cell of the triclinic crystals of $[Cu(L3)Cl_2]\cdot 0.5\ H_2O$ **3** contains two crystallographically independent molecules along with one water molecule. In both the molecules copper(II) possesses a trigonal bipyramidal distorted square-based pyramidal (TBDSBP) coordination geometry, which is very similar to that of all the above complexes. The τ values for both the molecules (0.07 and 0.05) are slightly higher than those for **1** and **2** clearly indicating that the steric bulk of the 6-methyl group on the pyridyl moiety confers enhanced constraints on copper(II). The coordination of pyridine nitrogen to copper is hindered by 6-methyl group in **3** leading to a Cu–N_{py} bond distance (2.046(2), 2.048(2) Å) longer than that (**2**, 2.016 Å) in the analogous complex **2**. The incorporation of the benzyl substituent on N2 in $[Cu(L6)Cl_2]$ **6**, where L6 is *N,N*-dimethyl-*N′*((6-methyl)pyrid-2-ylmethyl)ethylenediamine [32], to give **3** leads to weakening of the Cu–N2 bond (**3**, 2.1004(19); **6**, 2.006(3) Å) obviously due to the improper orientation of the lone pair orbital on N2.

In **4** copper(II) is coordinated by three nitrogen atoms, two from the ethylenediamine moiety (N2, N3) and one (N1) from the quinolyl moiety of the ligand L4, and two chloride ions (Cl1, Cl2). The value of τ (0.01) reveals that the coordination geometry around copper(II) is almost square-based pyramidal with the corners of the square plane being occupied by the three nitrogen atoms and one chloride ion (Cl1), and the apical position by the other chloride ion (Cl2). The Cu–N_{qui} (Cu–N1; 2.069(4) Å) and the Cu–NMe_2 (Cu1–N3; 2.069(4) Å) bond distances are equal and are shorter than the Cu–N_{amine} distance (Cu–N2; 2.088(4) Å). On replacing the pyridyl moiety in **2** by the sterically hindering quinolyl moiety to obtain **4**, the Cu–N_{qui} bond becomes longer suggesting the effect of steric hindrance from the benzene ring fused with the pyridyl ring. It is interesting to note that the Cu(II) coordination geometry in [Cu(L7)Cl_2] **7**, where L7 is 4-methyl-1-(quinol-2-ylmethyl)-1,4-diazacycloheptane [37], is strongly distorted from square planar geometry towards trigonal bipyramidal geometry (τ, 0.48) obviously due to the presence of sterically constrained diazepane backbone connecting the N2 and N3 nitrogen donor atoms in L7.

The Cu–N_{py}/Cu–$N_{me\text{-}py}$ bond in the complexes **1**–**3** (**1**, 2.016(4); **2**, 2.028(11); **3**, 2.046(2) Å) is shorter than the Cu–N_{amine} bond distance (**1**, 2.086(4); **2**, 2.113(9); **3**, 2.1004(19) Å), which is expected of the sp^2 and sp^3 hybridisations respectively of the pyridine and amine nitrogen atoms. Also, in all the above square-based pyramidal complexes **1**–**4**, the apical Cu–Cl bond is longer than the equatorial Cu–Cl bond obviously due to the presence of two unpaired electrons in the d_z2 orbital of Cu(II).

3.3. Spectral properties

The solid state reflectance spectra of all the complexes show a broad ligand field feature (540–850 nm) in the visible region, which is typical of Cu(II) located in a square-based environment as evidenced from the X-ray crystal structures of the complexes (Table 3). On dissolution in acetonitrile, only one ligand field feature is observed (above 700 nm, Fig. 5) for all the complexes. This suggests a negligible change in coordination geometry on dissolu-

Table 3
Electronic and EPR spectral data for the copper(II) complexes.

Complexes	Electronic spectra[a] λ_{max}/nm (ε_{max}/M^{-1} cm^{-1})		EPR spectra[b]	
	Solid	Solution (in acetonitrile)	Solid	Frozen solution[c]
[Cu(L1)Cl_2] **1**	650–800	750 (215) 461 (192) 270 (32634)[d]	$g_{\|\|}$ 2.223 $g_{\perp}$ 2.13	$g_{\|\|}$ 2.37 $A_{\|\|}$ 177 $g_{\perp}$ 2.12 $g_{\|\|}/A_{\|\|}$ 133
[Cu(L2)Cl_2] **2**	650–800	765 (240) 270 (28483)[d]	$g_{\|\|}$ 2.23 $g_{\perp}$ 2.09	$g_{\|\|}$ 2.36 $A_{\|\|}$ 187 $g_{\perp}$ 2.07 $g_{\|\|}/A_{\|\|}$ 126
[Cu(L3)Cl_2] **3**	750–900	792 (274) 272 (27290)[d]	$g_{\|\|}$ 2.226 $g_{\perp}$ 2.056	$g_{\|\|}$ 2.29 $A_{\|\|}$ 172 $g_{\perp}$ 2.080 $g_{\|\|}/A_{\|\|}$ 133
[Cu(L4)Cl_2] **4**	750–900	780 (225) 276 (65254)[d] 238 (49779)[d]	$g_{\|\|}$ 2.25 $g_{\perp}$ 2.10	$g_{\|\|}$ 2.262 $A_{\|\|}$ 158 $g_{\perp}$ 2.103 $g_{\|\|}/A_{\|\|}$ 142

[a] Concentration, 4×10^{-3} M for ligand field and 2×10^{-5} M for ligand based transitions.
[b] $A_{\|}$ in 10^{-4} cm^{-1}.
[c] Acetonitrile: acetone (4:1 v/v) glass at 77 K.
[d] π–π^* Transitions within the ligand.

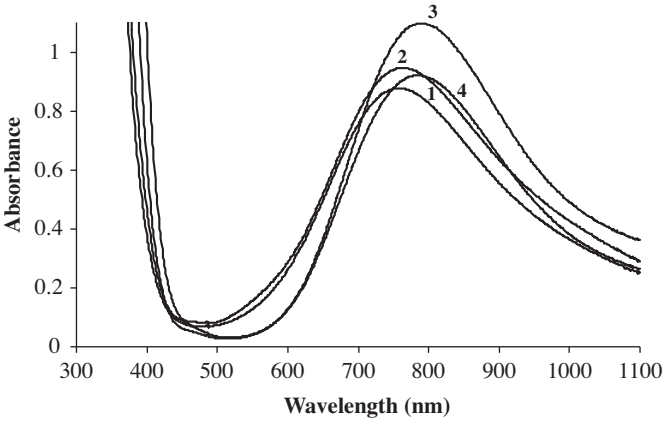


Fig. 5. Electronic absorption spectra of all the complexes in acetonitrile solution. Concentration of the complexes: 4×10^{-3} M.

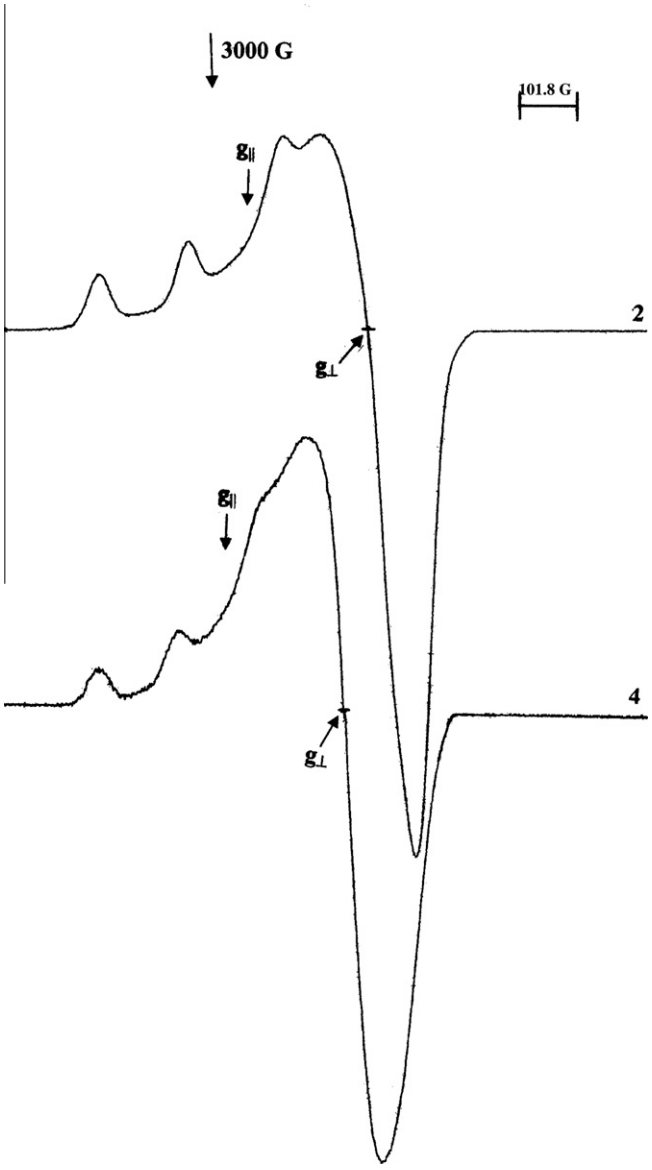


Fig. 6. X band EPR spectra of complexes **2** and **4** at 77 K in acetonitrile/acetone (4:1 v/v) glass.

Table 4
Electrochemical data[a] for copper(II) complexes at 25 ± 0.2 °C in acetonitrile solution.

Complexes	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)		ΔE_p (mV)	i_{pa}/i_{pc}	D (10^{-6} cm^2 s^{-1})
			CV	DPV[b]			
[Cu(L1)Cl$_2$] **1**	−0.542	−0.378	−0.460	−0.454	164	0.9	5.1
[Cu(L2)Cl$_2$] **2**	−0.472	−0.348	−0.410	−0.404	124	0.8	6.1
[Cu(L3)Cl$_2$] **3**	−0.432	−0.176	−0.304	−0.308	256	0.6	3.6
[Cu(L4)Cl$_2$] **4**	−0.378	−0.190	−0.284	−0.272	188	0.8	3.7

[a] Potential measured vs. non-aqueous Ag/AgNO$_3$ reference electrode; add 0.544 V to convert to standard hydrogen electrode (SHE); F_c/F_c^+ couple, $E_{1/2}$, 0.038 V (CV), ΔE_p, 88 mV; scan rate 0.05 V s^{-1}; supporting electrolyte, *tetra-N*-butylammonium perchlorate (0.1 M); complex concentration, 1×10^{-3} M.
[b] Differential pulse voltammetry (DPV), scan rate 0.005 V s^{-1}, pulse height 50 mV.

tion. Further, the ligand-field energy of the complexes **1**–**4** are lower, and the molar absorptivities are higher than those of **5** and **6** [32], which is expected of the weaker σ-coordination of N2 nitrogen atom on account of the steric hindrance imposed by the *N*-ethyl or *N*-benzyl substituents on it.

The polycrystalline EPR spectra of **1**–**4** are axial, which is consistent with the square-based geometry found in the X-ray crystal structures of the complexes. The frozen-solution spectra (Fig. 6) of all the complexes are axial [$g_{||} > g_\perp > 2.0$, $G = (g_{||} - 2)/(g_\perp - 2) = 2.5 - 4.0$] [44,45], which is usual for mononuclear tetragonal copper(II) complexes with $d_x2_{-y}2$ ground state [46]. Copper(II) complexes with square-based CuN_4 coordination sphere exhibit $g_{||}$ and $A_{||}$ values around 2.200 and 200×10^{-4} cm^{-1}, respectively and replacement of a coordinated nitrogen in this chromophore by oxygen (solvent methanol) is expected to enhance the $g_{||}$ value and decrease the $A_{||}$ value. Thus the $g_{||}$ (2.262–2.237) and $A_{||}$ (187–158 $\times 10^{-4}$ cm^{-1}) values of **1**–**4** are suggestive of the presence of a square based CuN_3Cl/CuN_3O chromophore [42]. The values of $g_{||}/A_{||}$ quotient for all the complexes (**1**; 133, **2**; 126, **3**; 133, **4**; 142 cm) are in the range for complexes with a perfect square planar coordination geometry ($g_{||}/A_{||}$, 105–135 cm) [47], which is consistent with the above X-ray crystal structures and electronic spectral results.

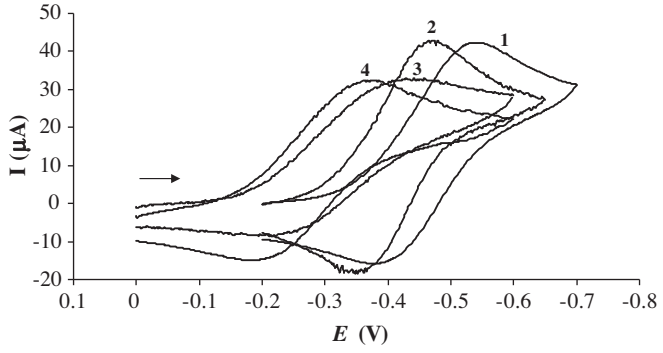


Fig. 7. Cyclic voltammograms of **1**, **2**, **3** and **4** in acetonitrile solution at 25 °C at 0.05 V s^{-1} scan rate. Complex concentration: 0.001 M.

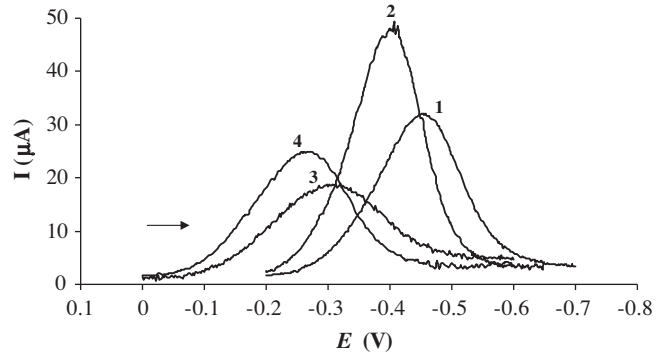


Fig. 8. Differential pulse voltammograms of **1**, **2**, **3** and **4** in acetonitrile solution at 25 °C at 0.005 V s^{-1} scan rate. Complex concentration: 0.001 M.

3.4. Electrochemical properties

The electrochemical data obtained for the present complexes in acetonitrile solution using TBAP as supporting electrolyte are collected in Table 4. The cyclic (CV) and differential pulse voltammograms (DPV) have been recorded using Pt as working electrode and Ag/AgNO$_3$ as reference electrode. For all the complexes the Cu(II) to Cu(I) reduction (E_{pc}, −0.378 − −0.542 V) is associated with a reoxidation peak (E_{pa}, −0.176 − −0.378 V) in the reverse scan (Fig. 7). The values of the limiting peak-to-peak separation (ΔE_p, 124–256 mV) are higher than that for F_c/F_c^+ couple (ΔE_p, 88 mV) under identical conditions. This suggests that the heterogeneous electron-transfer process in the present complexes is far from reversible and that on electron transfer considerable stereochemical reorganization of the coordination sphere occurs [37]. The observed Cu(II)/Cu(I) redox potentials follow the trend **4** > **3** > **2** > **1** (Fig. 8). Upon replacement of the *N*-ethyl group in **1** by the *N*-benzyl group in **2**, the redox potential becomes slightly more positive. With the replacement of the pyridyl group in **2** by 6-methylpyridyl group as in **3** and by quinolyl moiety as in **4**, there is an enormous positive shift in the $E_{1/2}$ value. This reveals the importance of sterically hindering quinolyl and 6-methylpyridyl moieties in destabilizing the Cu(II) forms of **3** and **4**, thereby rendering the $Cu^{II} \rightarrow Cu^{I}$ electron transfer more facile.

Table 5
Results of catalytic aziridination studies using copper(II) complexes **1**–**4**.

Olefin	Entry	Catalyst[a]	Olefin equiv	Yield (%)[b]	
				PhINTs	Chloramine-T trihydrate
Styrene	1	**1**	5	32	–
	2	**2**	5	24	–
	3	**3**	5	90	75
	4	**4**	5	85	63
cis-Cyclooctene	5	**1**	5	–	–
	6	**2**	5	–	–
	7	**3**	5	56	50
	8	**4**	5	48	45
n-Hexene	9	**1**	5	–	–
	10	**2**	5	–	–
	11	**3**	5	42	40
	12	**4**	5	30	30

[a] 5 mol% vs. PhINTs or chloramine-T trihydrate.
[b] Isolated yields of *N*-tosylaziridine after purification with respect to 0.3 mM of PhINTs or chloramine-T trihydrate used.

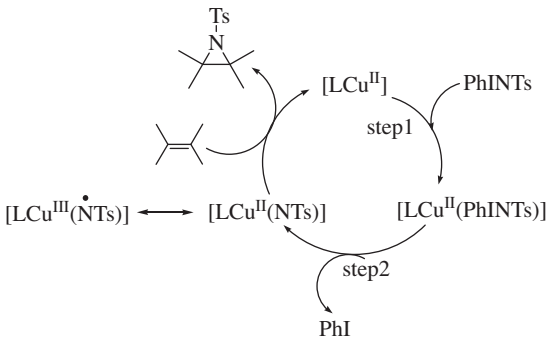
3.5. Olefin aziridination with PhINTs and chloramine-T trihydrate

The copper(II) complexes **1**–**4** were examined for their ability to catalyze the aziridination of olefins, especially styrene, *cis*-cyclooctene and *n*-hexene as model substrates using PhINTs and chloramine-T trihydrate as the nitrene sources and the results are collected in Table 5. When a 5:1 olefin:PhINTs ratio is employed with a catalyst loading of 5 mol%, **1** and **2** give only 24–32% yield while **3** and **4** give higher yields (85–90%) for the aziridination of styrene the most reactive olefin. However, the reaction is slow and is completed only after 12 h. When a 5:1 olefin:PhINTs ratio was employed with a catalyst loading of 5 mol% for the less reactive olefins like *cis*-cyclooctene and *n*-hexene, **1** and **2** fail to give the desired aziridine but yield *p*-toluenesulfonamide as the major product. On the other hand, **3** and **4** gave yield of about 30–56% of the desired aziridine. However, the reaction is slow and is completed after 24 h only. When the aziridination of olefins by the complexes is performed after the removal of both the coordinated chloride ions by using $AgNO_3$, the yield decreases further (results not reported here).

When a 5:1 olefin:chloramine-T trihydrate ratio is employed with a catalyst loading of 5 mol% for the reactive olefin styrene, the desired aziridine is not formed and mainly *p*-toluenesulfonamide is obtained for **1** and **2**. In fact, it has been reported already that some side products like styrene epoxides may be formed if chloramine-T trihydrate is used as the nitrene source. On the other hand, **3** and **4** gave about 63–75% yield of the desired aziridine. Also, the reaction required three days for completion. When a 5:1 olefin:chloramine-T trihydrate ratio is employed with a catalyst loading of 5 mol% with the less reactive olefins like *cis*-cyclooctene and *n*-hexene, **1** and **2** fail to give the desired aziridine while low yields of aziridine (30–50%) are observed for **3** and **4**. Thus, PhINTs is a nitrene transfer reagent much better than chloramine-T trihydrate for the present complexes to obtain the aziridines in good yield. Though chloramine-T trihydrate is harmless and easily available, the yields of the aziridines are less than the side products. Also, though PhINTs is a better source for the nitrene transfer catalysis by the present complexes, good yields are obtained only for styrene.

According to the recently proposed mechanism for copper-catalyzed aziridination [30], the coordination of PhINTs to copper(II) is required for intramolecular electron transfer leading to the formation of PhI and a highly reactive copper-nitrene radical-like intermediate [(L)Cu^{II}=NTs], which is then involved in consecutive nitrene transfer to olefin (Scheme 3). We have shown [37] that the steric crowding around copper(II) imposed by the bulky quinolyl moiety and the *N*-Me group of certain diazapane-derived tridentate 3N ligands would confer steric constraints on Cu(II) coordination geometry and hence facilitate the quick transfer of the =NTs from the metallo-nitrene intermediate to the olefins leading to the observed decrease in the reaction time with an increase in yield. Thus the complex **7** of the ligand containing the sterically congested diazepane backbone imposes greater steric constraints around copper(II) leading to the highest aziridination rate and yield among the complexes investigated. On the other hand, the incorporation of the bulky ligand moieties like quinolyl and 6-methyl-pyridyl in the less sterically congested ethylenediamine backbone fail to impose any significant steric constraints on the copper(II) coordination geometry in **1**–**4** (see above). So, all the present complexes would be expected to be less efficient catalysts for aziridination and thus **1** and **2** fail to effect aziridination. Interestingly, **3** and **4** catalyze the aziridination of olefins to give quantitative yields of aziridine, however, with decreased rates of reaction. The wide difference in reactivities can be illustrated based on the ability of the present ligands to destabilize Cu(II) oxidation state in solution. Thus the $E_{1/2}$ values of **3** and **4** (**3**, −0.308 V; **4**, −0.272 V) are more positive than those of **1** and **2** (**1**, −0.454 V; **2**, −0.404 V) suggesting that the ligands in the former complexes destabilize the Cu(II) oxidation state more than those in the latter. This leads to enhanced ability of the former complexes to facilitate the transfer of =NTs from the metallo-nitrene intermediate to olefins resulting in better yields of the aziridine. However, their efficiency is much lower than the diazapane-based ligand in **7** the Cu(II)/Cu(I) redox potential ($E_{1/2}$, −0.252 V) of which is more positive than that of the present complex. This suggests that the Cu(II)/Cu(I) redox potentials rather than the trigonal constraint on the copper(II) coordination geometry may be used to illustrate the ability of copper(II) complexes to catalyze the aziridination of olefins.

Also, the catalytic activity of the present complexes can be explained on the basis of the ability of the 3N ligands to stabilize the Cu(I) oxidation state in solution. Theoretical calculations [48] have suggested that Cu(I) rather than Cu(II) as the active oxidation state for aziridination. However, for the present complexes, the green color of the reaction mixture persists even after dissolution of the PhINTs indicating that the catalyst resting state is Cu(II) but evidences [48] show a favorable path for conversion of Cu(II) to Cu(I) when they interact with alkenes under the reaction conditions. It should be noted that a Cu(I)–alkene complex has been isolated and structurally characterized [49]. The Cu(I) species thus generated in situ would then react with PhINTs to form the reactive Cu(III)–nitrene intermediate [9–13] constituting a Cu(I)/Cu(III) reaction cycle and the reaction proceeds with the consecutive nitrene transfer from the radical-like intermediate to olefins. The sterically hindered ligands in **3** and **4** with higher Cu(II)/Cu(I) redox potentials would be expected to facilitate Cu(I)-alkene and hence the metallo-nitrene intermediate formation more than **1** and **2** do leading to their higher catalytic ability. Similarly, the diazapane-based complex **7** with a Cu(II)/Cu(I) redox potential higher than the present complexes functions as a more efficient catalyst. Also, the present complexes of sterically hindering ligands would form less stable adducts with the less reactive alkenes leading to lower reactivity.



Scheme 3. Proposed mechanism [30] of aziridination by Cu(II) complexes.

4. Conclusions

Copper(II) complexes of four new sterically hindering linear tridentate 3N ligands have been isolated. All of them have been structurally characterized to possess square pyramidal coordination geometry involving meridional coordination of the ligands. The incorporation of sterically hindering quinolyl or 6-methylpyridyl moieties or $-NMe_2$ donor group in the ligand fails to confer any significant distortion on the copper(II) coordination geometries but imposes varying tendencies on them to destabilize Cu(II) species. Also, the complexes exhibit varying catalytic nitrene transfer reactivity towards three olefins when PhINTs and chloramine-T

trihydrate are used as nitrene sources. It emerges from the present study that the catalytic activity – both the yield and rate of aziridination reaction – is largely determined by the ability of the ligands to destabilize Cu(II) oxidation state or stabilize Cu(I) oxidation state of the copper(II) complexes. This finding is expected to pave the way for a rational design of new and more active catalysts for aziridination and related group transfer reactions.

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Appendix A. Supplementary material

CCDC 680240, 680241, 680242 and 680243 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.08.051.

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