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New Copper(II) Complexes as Efficient Catalysts for Olefin Aziridination: The Effect of Ligand Steric Hindrance on Reactivity

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Three new copper(II) complexes derived from the tridentate N_3 ligands 4-methyl-1-(pyrid-2-ylmethyl)-1,4-diazacycloheptane (L1), 1-(quinol-2-ylmethyl)-1,4-diazacycloheptane (L2), and 4-methyl-1-(quinol-2-ylmethyl)-1,4-diazacycloheptane (L3) have been prepared and examined as copper catalysts for olefin aziridination. In the X-ray crystal structures of the complexes $[Cu(L2)Cl_2]$ (**2**) and $[Cu(L3)Cl_2]$ (**3**) copper(II) adopts a trigonal-bipyramidal distorted square-based pyramidal geometry (TBDSBP) as seen from the values of the trigonality index τ (0.08 for **2** and 0.48 for **3**). The enhanced trigonal distortion in **3** is due to the presence of an N-Me group, the lone pair orbital of which is not oriented exactly along the $d_{x^2-y^2}$ orbital of copper(II). While $[Cu(L1)(H_2O)](ClO_4)_2$ (**1**) assumes a tetragonal geometry in solution, complexes **2** and **3** adopt a distorted tetragonal geometry, as revealed by UV/Vis and EPR spectral studies. The complexes undergo quasi-reversible Cu^{II}/Cu^{I} redox behavior in methanol solution. The ability of the complexes to mediate nitrene transfer from PhINTs to olefins to form *N*-tosylaziridines has been studied. The complexes are found to be efficient catalysts (in 5 mol-% amounts) for the aziridination of the reactive olefin styrene, with yields varying from 80 to 90% (with respect to PhINTs). They exhibit significant catalytic nitrene transfer reactivity (yields of 30 to 60%) also towards the less reactive olefins cyclohexene and cyclooctene. A remarkable observation is the significantly accelerated rate of aziridination by **3**, which is ascribed to the steric crowding around copper(II) imposed by the bulky quinolyl and N-Me groups of the tridentate ligand L3.

Introduction

Similar to epoxides, aziridine rings enjoy special attention in organic synthesis, particularly as intermediates[1,2] in the synthesis of amines and amino alcohols. Furthermore, naturally occurring azinomycin and mitomycin, which contain aziridines in their core, exhibit cytotoxic properties.[3] The development of new catalysts for the preparation of aziridines has therefore been an active area of investigation. Of the two different catalytic processes that lead to the formation of aziridines,[4–6] that involving addition of an "NR" nitrene unit to a C=C double bond (alkene; Scheme 1) has been more extensively studied than the other, which involves the addition of a "CR" carbene unit to a C=N (imine) bond. This reaction is often catalyzed by transition metals through coordination of the nitrene[4] or by Lewis acids through substrate activation.[5] In transition-metal-catalyzed olefin aziridination reactions, the most widely employed reaction (Scheme 1) has been nitrene transfer from (tosylimino)phenyliodinane (PhINTs).[7–9]

Scheme 1.

Many copper-based catalysts have been reported for nitrene-transfer reactions from PhINTs to alkenes, although they have rarely been structurally characterized.[4,10–14] Halfen et al. have systematically investigated[10] the structural and electronic factors that regulate the catalytic activity of copper complexes in such nitrene-transfer reactions. They used the complex $[Cu(i\text{Pr}_3\text{TACN})(O_2CCF_3)_2]$ to effect the near-quantitative aziridination of styrene derivatives. They also reported aziridination of olefins catalyzed by a series of square-based copper(II) complexes in which tetradentate pyridyl-appended diazacycloalkane ligands are meridionally coordinated.[13] In these complexes the axial coordination site(s) are either vacant or occupied by a readily displaced solvent or counterion, which facilitates the aziridination with the nitrene source PhINTs. The reactivity of the copper(II) complexes is significantly enhanced for aziridination of styrene when the ligand denticity is lowered from tetradentate to tridentate.[15] Very recently Vadernikov

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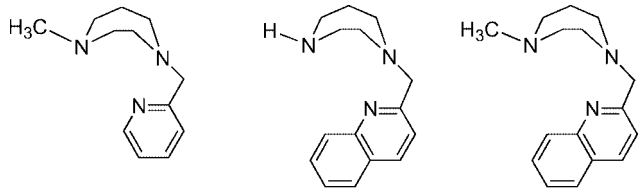
et al. have reported that coordinative unsaturation at copper is responsible for the very high catalytic activity of certain four-coordinate copper(II) chloride complexes of pyridine-based ligands.[16]

We decided to prepare copper(II) complexes of tridentate N_3 ligands and study them systematically to identify the key ligand structural and electronic properties for optimum copper catalyst performance. As the highly oxidized copper-nitrene species are suggested[10] to be stabilized by electron-rich and sterically hindered ligands, sterically hindering N–Me and quinolyl moieties were incorporated into the tridentate N_3 ligands (Scheme 2) chosen for the present study. The ring system of the ligand would provide resistance[13] towards oxidative degradation of the catalyst by the strongly oxidizing nitrene transfer agent PhINTs. The coordinative unsaturation as well as steric crowding around copper(II) in the present complexes is expected to lead to improved selectivity, reaction rates, and broad substrate tolerance. The X-ray crystal structures of two of the complexes were determined to establish the degree of coordinative unsaturation and distortion in the complexes. The solution structures of the complexes have been probed by employing spectroscopic and electrochemical methods to understand the effect of the ligand architecture on the copper(II) coordination geometry. All the complexes examined were found to be fast and efficient catalysts for the aziridination of styrene, cyclohexene, and cyclooctene when a high amount (5–10 equiv.) of olefin was treated with PhINTs (1 equiv.).



Scheme 2. Ligands employed for the present study.

Results and Discussion

Synthesis of Ligands and Complexes

The tridentate ligands L1–L3 were prepared as oils in good yields (50–70%) by stirring the appropriate diazacycloheptane (homopiperazine or *N*-methylhomopiperazine) with one equivalent of 2-picolyl chloride or 2-quinolyl chloride and two equivalents of triethylamine in ethanol at room temperature for three days. The copper(II) complexes of the ligands were prepared by the addition of either $CuCl_2{\cdot}H_2O$ or $Cu(ClO_4)_2{\cdot}6H_2O$ in methanol to a methanolic solution of the ligands; they were characterized by analytical and spectroscopic methods and studied as catalysts for aziridination reactions. The ligands occupy three coordination positions in the X-ray crystal structures of both **2** and **3**, with a chloride ion in the equatorial position. Conductivity studies revealed that complex **1** behaves as a 2:1 electrolyte (190 $\Omega^{-1}cm^2M^{-1}$) while **2** and **3** behave as 1:1 electrolytes (**2**, 98 and **3**, 86 $\Omega^{-1}cm^2M^{-1}$) in methanol solution, corresponding to dissociation 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.

Description of the Crystal Structures

An ORTEP view of the structures of complexes **2**·CH_3CN and **3**, along with the atom numbering schemes, are shown in Figures 1 and 2 respectively. Selected bond lengths and bond angles relevant to the copper coordination spheres are given in Table 1. In the complex **2**·CH_3CN copper(II) is bound to two chloride ions and two nitrogen atoms (N2 and N3) of the homopiperazine moiety and the nitrogen atom (N1) of the quinoline moiety of the tridentate ligand L2. The value of the structural index[17] τ (0.08) suggests that the pentacoordinate complex is very slightly distorted square pyramidal and the coordination geometry around copper(II) may be best described as trigonal-bipyramidal distorted square-based pyramidal (TBDSBP)[18] in which the square plane is constituted by the three nitrogen atoms (N1, N2, N3) of L2 and one chloride ion (Cl1) and the apical position occupied by the other chloride ion (Cl2). Two crystallographically independent complex molecules with the same chemical formula are present in the asymmetric unit cell of complex **3**. In both these molecules copper(II) is coordinated by three nitrogen atoms, two (N2 and N3) from the homopiperazine moiety and one (N1) from the quinoline moiety of ligand L3, and two chloride ions (Cl1 and Cl2), as in **2**·CH_3CN. The value of the structural index[17] τ (0.48) reveals that the coordination geometry around copper(II) in **3** is best described as TBDSBP in which the corners of the square plane are occupied by the three nitrogen atoms of L3 and one chloride ion (Cl1), and the apical position by the other chloride ion (Cl2). In fact, the coordination geometry lies exactly midway between trigonal-bipyramidal and square-pyramidal geometries. The value of the trigonality index τ for **3** is much higher than

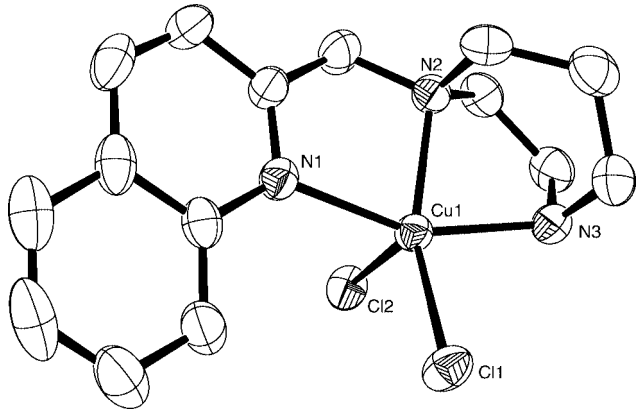


Figure 1. ORTEP drawing of $[Cu(L2)Cl_2]$ (**2**) showing the atom numbering scheme and the thermal motion ellipsoids (50% probability level).

that for **2**·CH_3CN, thus revealing that incorporation of the sterically hindering N–Me group in **3** leads to a greater geometrical constraint at copper(II). The Cu–N_{amine} distances in both **2**·CH_3CN and **3** are in the range expected[15] and, interestingly, they are longer in **3** (2.052, 2.068 Å) than those (2.036, 2.0392 Å) in **2**·CH_3CN, thus revealing that the lone pair orbitals of the N-Me group in **3** are not oriented exactly along the $d_{x^2-y^2}$ orbital of copper(II).[19] Further, the axial chloride ions in both **2**·CH_3CN and **3** are located further away from the metal (2.456 Å in **2** and 2.462 Å in **3**) than the equatorial chloride ions (2.272 Å in **2** and 2.304 Å in **3**). This is obviously because of the presence of two electrons in the d_{z^2} orbital of copper(II) in the square-based environments of both complexes. It is interesting to note that both **2**·CH_3CN and **3** are monomeric, which is in contrast to the dimeric structure of the complex [(L4)Cu(μ-Cl)$_2$-Cu(L4)], where L4 is 5-methyl-1-(2-pyridylmethyl)-1,5-diazacyclooctane, the pyridine analogue of ligands L2 and L3. The incorporation of the sterically hindering quinolyl moiety in place of the pyridyl moiety in L4 and that of the ethylene linker instead of propylene one in the homopiperazine backbone of L4 prevent the dimerization of both **2** and **3**. We have previously shown[20] that incorporation of a sterically hindering NMe_2 group in the place of a pyridine donor enhances the Fe–O–C bond angle in iron(III) complexes of certain tetradentate monophenolate ligands from 128.5° to 136.1°. The equatorial chloride ion in **2**·CH_3CN and **3** can be replaced by PhINTs, which leads to catalysis of aziridination reactions, as observed for copper(II) complexes of didentate ligands.[16]

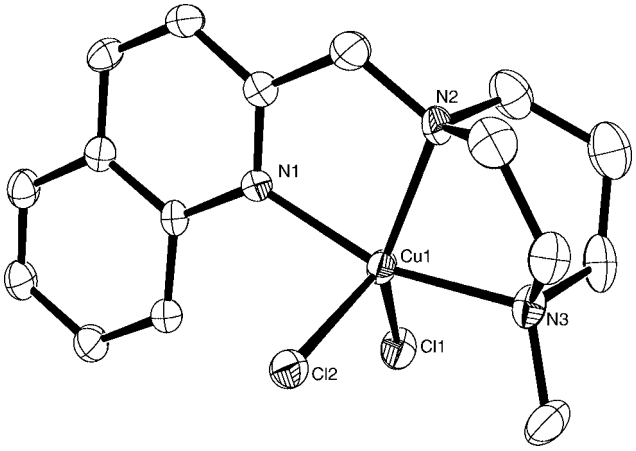


Figure 2. ORTEP drawing of [Cu(L3)Cl_2] (**3**) showing the atom numbering scheme and the thermal motion ellipsoids (50% probability level).

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

2		**3**	
Cu(1)–N(1)	2.135(2)	Cu(1)–N(1)	2.039(2)
Cu(1)–N(2)	2.0392(17)	Cu(1)–N(3)	2.052(2)
Cu(1)–N(3)	2.036(2)	Cu(1)–N(2)	2.068(2)
Cu(1)–Cl(1)	2.2722(9)	Cu(1)–Cl(1)	2.3043(8)
Cu(1)–Cl(2)	2.4556(9)	Cu(1)–Cl(2)	2.4620(8)
		Cu(2)–N(21)	2.045(2)
		Cu(2)–N(22)	2.056(2)
		Cu(2)–N(23)	2.068(2)
		Cu(2)–Cl(21)	2.3183(8)
		Cu(2)–Cl(22)	2.4299(8)
N(1)–Cu(1)–N(2)	81.19(6)	N(1)–Cu(1)–N(3)	161.28(10)
N(1)–Cu(1)–N(3)	154.90(7)	N(1)–Cu(1)–N(2)	83.05(9)
N(2)–Cu(1)–N(3)	76.59(7)	N(3)–Cu(1)–N(2)	78.23(10)
Cl(1)–Cu(1)–N(1)	103.67(5)	N(1)–Cu(1)–Cl(1)	100.72(7)
Cl(1)–Cu(1)–N(2)	149.96(5)	N(3)–Cu(1)–Cl(1)	92.69(7)
Cl(1)–Cu(1)–N(3)	90.23(5)	N(2)–Cu(1)–Cl(1)	133.78(8)
Cl(2)–Cu(1)–N(1)	93.78(4)	N(1)–Cu(1)–Cl(2)	91.92(7)
Cl(2)–Cu(1)–N(2)	101.96(5)	N(3)–Cu(1)–Cl(2)	94.24(7)
Cl(2)–Cu(1)–N(3)	102.04(5)	N(2)–Cu(1)–Cl(2)	111.03(8)
Cl(1)–Cu(1)–Cl(2)	107.19(2)	Cl(1)–Cu(1)–Cl(2)	114.82(3)
		N(21)–Cu(2)–N(22)	83.36(9)
		N(21)–Cu(2)–N(23)	161.08(10)
		N(22)–Cu(2)–N(23)	78.23(10)
		N(21)–Cu(2)–Cl(21)	102.24(7)
		N(22)–Cu(2)–Cl(21)	131.95(8)
		N(23)–Cu(2)–Cl(21)	93.37(7)
		N(21)–Cu(2)–Cl(22)	92.38(7)
		N(22)–Cu(2)–Cl(22)	117.75(7)
		N(23)–Cu(2)–Cl(22)	92.33(8)
		Cl(21)–Cu(2)–Cl(22)	109.72(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 appears to contain more than one band; this is typical of Cu^{II} located in a square-based environment, as evidenced from the X-ray crystal structures of complexes **2** and **3** (Table 2). On dissolution in methanol, only one ligand-field feature is observed (640–760 nm, Figure 3) for all the complexes, which suggests changes in their coordination geometries such as dissociation of the axial chloride ion in solution. The ligand-field energies of complexes **2** and **3** are much lower, with higher molar absorptivities, than those of **1**, thereby indicating that the replacement of the pyridyl moiety in **1** by the bulky quinolyl moiety in **2** and **3** leads to an enhancement of the distortion in the square-pyramidal geometry towards trigonal bipyramidal. Further, the ligand-field energy of **3** is lower, and the molar absorptivity higher, than those of **2**, as expected from the weaker σ-coordination of N(3), as explained above, and due to the steric hindrance imposed by the N-Me group leading to a more distorted coordination geometry, as evident from the X-ray structures of the complexes. A similar decrease in ligand-field energy has been observed upon replacing an NHMe group by an NMe_2 group in the coordination sphere of copper(II) complexes of tridentate pyridine-based ligands.[19]

The polycrystalline EPR spectra of complexes **1** and **2** are axial while that of **3** is rhombic, which is consistent with the distorted square-based geometry found in the X-ray crystal structure of **3**. The frozen solution spectra (Figure 4) of all the complexes are axial [$g_{\|} > g_{\perp} > 2.0$, $G = (g_{\|} - 2)/(g_{\perp} - 2) = 3.0–4.3$],[21] which is usual for mononuclear tetragonal copper(II) complexes with a $d_{x^2-y^2}$ ground state.[22] Copper(II) complexes with a square-based CuN_4 coordination sphere exhibit $g_{\|}$ and $A_{\|}$ values of around

Table 2. Electronic and EPR spectroscopic 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 methanol)	Solid	Frozen[c] solution
$[Cu(L1)(H_2O)](ClO_4)_2$ (**1**)	545–645	642 (150) 268 (34310)[d]	$g_\parallel$ 2.223 $g_\perp$ 2.109	$g_\parallel$ 2.227 $A_\parallel$ 186 $g_\perp$ 2.066 $g_\parallel/A_\parallel$ 119 G 3.43
$[Cu(L2)Cl_2]$ (**2**)	650–750	730 (195) 270 (33280)[d] 235 (35845)[d] 203 (34710)[d]	$g_\parallel$ 2.198 $g_\perp$ 2.147	$g_\parallel$ 2.225 $A_\parallel$ 146 $g_\perp$ 2.052 $g_\parallel/A_\parallel$ 152 G 4.32
$[Cu(L3)Cl_2]$ (**3**)	700–850	758 (270) 275 (27430)[d] 238 (36005)[d]	g_3 2.162 g_2 2.136 g_1 2.078	$g_\parallel$ 2.231 $A_\parallel$ 130 $g_\perp$ 2.077 $g_\parallel/A_\parallel$ 171 G 3.00

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

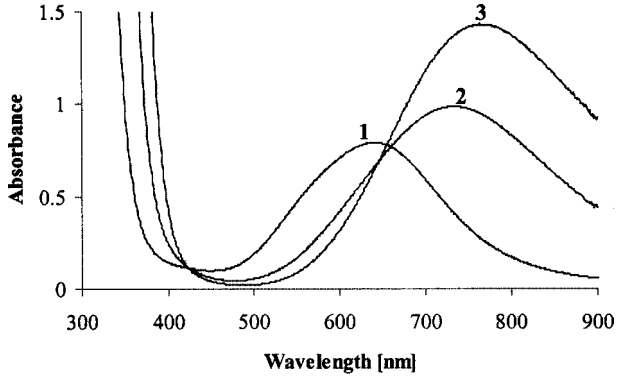


Figure 3. Electronic absorption spectra of complexes **1**–**3** in methanol solution. Concentration of the complexes: 5×10^{-3} M.

2.200 and 200×10^{-4} cm^{-1}, respectively. Replacement of a coordinated nitrogen in this chromophore by oxygen (solvent methanol) is expected to enhance the $g_\parallel$ value and decrease the $A_\parallel$ value. Thus, the $g_\parallel$ (2.225–2.231) and $A_\parallel$ (180–130×10^{-4} cm^{-1}) values of **1**–**3** are suggestive of the presence of a square-based $[Cu(N_3)Cl]^+$ chromophore.[19] Interestingly, the $A_\parallel$ values of **2** and **3** are much lower than that of **1**, which suggests that the coordination geometries in them are strongly distorted from planarity. In fact, the values of their $g_\parallel/A_\parallel$ quotient (152 cm for **2** and 171 cm for **3**) is higher than that for **1** (117 cm). This suggests a large deviation from a perfectly square-planar geometry ($g_\parallel/A_\parallel$ = 105–135 cm)[23] because of the incorporation of sterically demanding quinolyl moiety in **2** and **3** in place of the pyridyl moiety in **1**. Further, the $g_\parallel$ and $A_\parallel$ values of **2** are lower and higher, respectively, than those for **3**, and the $g_\parallel/A_\parallel$ value for **2** is lower than that for **3**. This reveals that the distortion from a square-based geometry in **3** is higher than that in **2** because of the sterically hindering N-Me substitution, which is consistent with the above X-ray structures and electronic spectral results.

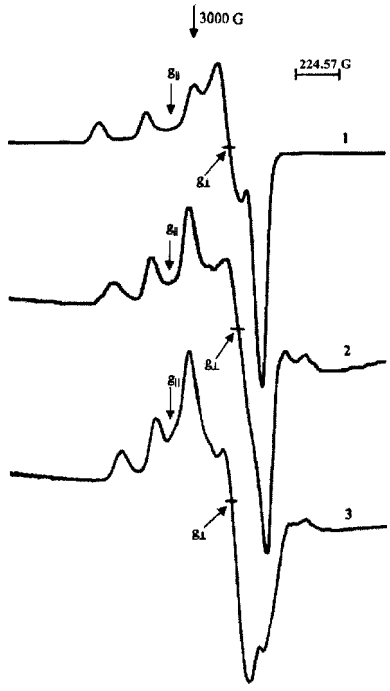


Figure 4. X-band EPR spectra of complexes **1**–**3** at 77 K in methanol/acetone (4:1 v/v) glass.

Electrochemical Properties

The electrochemical data obtained for the present complexes in methanol solution using TBAP as supporting electrolyte are collected in Table 3. The cyclic (CV) and differential pulse voltammograms (DPV) were recorded using Pt as working electrode and Ag/AgCl as reference electrode. For all the complexes the Cu^{II} to Cu^{I} reduction (E_{pc}, –0.325 to –0.475 V) is associated with a reoxidation peak (E_{pa}, –0.244 to –0.318 V) in the reverse scan. The value of the limiting peak-to-peak separation (ΔE_p = 158–

Table 3. Electrochemical data[a] for copper(II) complexes at 25 ± 0.2 °C in methanol solution.

Complexes	E_{pc} [V]	E_{pa} [V]	$E_{1/2}$ [V] CV	DPV[b]	ΔE_p [mV]	i_{pa}/i_{pc}	D [10^{-6} cm^2 s^{-1}]
$[Cu(L1)(H_2O)](ClO_4)_2$ (**1**)	–0.476	–0.318	–0.397	–0.378	158	0.6	3.4
$[Cu(L2)Cl_2]$ (**2**)	–0.454	–0.244	–0.349	–0.336	210	0.9	4.2
$[Cu(L3)Cl_2]$ (**3**)	–0.326	–	–0.164[c]	–0.252	–	–	5.8

[a] Potential measured vs. non-aqueous $Ag/AgNO_3$ reference electrode; add 0.544 V to convert to standard hydrogen electrode (SHE); Fc/Fc^+ couple: $E_{1/2}$ = 0.038 V (CV), ΔE_p = 88 mV; scan rate: 50 mV s^{-1}; supporting electrolyte: tetrabutylammonium perchlorate (0.1 M); complex concentration: 1×10^{-3} M. [b] Differential pulse voltammetry (DPV); scan rate: 1 mV s^{-1}; pulse height: 50 mV. [c] Potential at half-height $E_{p1/2}$.

210 mV) is higher than that for the Fc/Fc^+ 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 considerable stereochemical reorganization of the coordination sphere occurs on electron transfer. The Cu^{II}/Cu^{I} redox potentials follow the trend **3** > **2** > **1** (Figure 5). This reveals the importance of the sterically hindering quinolyl moiety in destabilizing the Cu^{II} form of **2**, thereby facilitating the electron transfer. Similarly, the incorporation of the sterically hindering and weakly σ-bonding N-Me group in **2** to obtain **3** further destabilizes the Cu^{II} oxidation state, which is consistent with the X-ray structures of the complexes. Similar results have been observed by incorporating an NMe_2 group in the copper(II) complexes of certain pyridine-based linear N_3 ligands.[19]

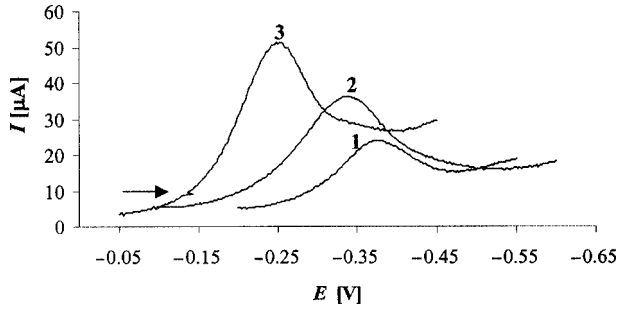


Figure 5. Differential pulse voltammograms of complexes **1**–**3** in methanol solution at 25 °C at a scan rate of 0.05 V s^{-1}. Complex concentration: 0.001 M.

Application to Catalytic Olefin Aziridination Reactions

The newly synthesized copper(II) complexes **1**–**3** were examined for their ability to catalyze the aziridination of olefins, especially styrene, cyclohexene, and cyclooctene, using PhINTs as the nitrene source; the results are collected in Table 4. When a 10:1 olefin:PhINTs ratio was employed with a catalyst loading of 5 mol-%, all the complexes gave high yields (85–90%) for the aziridination of the most reactive olefin styrene. However, when the olefin:PhINTs ratio was decreased to 5:1, slightly lower yields (75–80%) were obtained. When this ratio was decreased from 5:1 to 1:1 as for **3**, the yield decreased further. A remarkable observation is the significantly accelerated rate of aziridination of styrene (within an hour) for complex **3**. The presence of labile ligands and the coordinative unsaturation around copper(II) promotes faster coordination of PhINTs to copper(II) (otherwise slow) and is responsible for the high yield and reduced reaction times. In fact, on treatment of **3** with excess PhINTs in acetonitrile solution, the ligand-field band is shifted from 799 to 794 nm with enhanced absorptivity, thus suggesting the coordination of PhINTs to copper(II). Further, the persistence of the blue or green color of the reaction mixtures after dissolution of PhINTs reveals that the resting state of the catalyst is always Cu^{II}. According to the very recently proposed mechanism for copper-catalyzed aziridination,[16] the coordination of =NTs to copper(II) is required for intramolecular electron transfer. This leads to the formation of PhI and a highly reactive copper-nitrene radical-like intermediate [$(L3)Cu^{II}$=NTs], which is then involved in consecutive nitrene transfer to olefin. Obviously, the steric crowding around copper(II) imposed by the bulky quinolyl moiety and the N-Me group (see above) of the tridentate ligand would stabilize this intermediate and facilitate the aziridination. Also, it would prevent any side reactions like recoordination of chloride. In fact, when aziridination was performed for complex **3** after the removal of two chloride ions by treatment with $AgNO_3$, the reaction time decreased further, as expected, but with no change in yield. It is interesting to note that the incorporation of a sterically hindering NMe_2 group in the place of a pyridine donor enhances the dioxygenase activity of iron(III) complexes of certain tetradentate monophenolate ligands.[20] No change in yield was observed with a decrease in the olefin:PhINTs ratio; however, the reaction becomes faster (completed within 30 min).

Aziridination of the less reactive cyclohexene was performed with 5 mol-% catalyst loading. When the olefin:PhINTs ratio was 5:1, all the complexes showed a good yield of more than 60%. It is remarkable that the yield of aziridine observed for cyclohexene is higher than those for other complexes available in the literature (except $[Cu(MeCN)_4]ClO_4$, 77%).[4] Also, and interestingly, no allylic sulfonamide insertion product was obtained. The complexes also catalyze the aziridination of the other less reactive olefin *cis*-cyclooctene, although the yield is very low (30–45%). When the olefin:PhINTs ratio was decreased from 10:1 to 5:1, the yield was also reduced. Again, complex **3** catalyzes the aziridination (within an hour) faster than the other two complexes.

Table 4. Results of catalytic aziridination studies using copper(II) complexes **1**–**3**.

Olefin	Catalyst[a]	Equiv. of olefin	Yield [%][b]	Time [h]
	**1**	10	90	3
		5	80	2
	2	10	85	3
		5	80	3
	3	10	85	1
		5	75	1
		4	84	1
		2.5	53	0.5
		1	18	0.5
	3 + 2 equiv.	4	80	0.5
	of $AgNO_3$	2.5	53	0.5
		1	25	0.5
	**1**	5	64	3
	2	5	68	3
	3	5	60	3
	**1**	10	42	10
		5	35	24
	2	10	38	6
		5	35	6
	3	10	38	1
		5	30	1

[a] 5 mol-% vs. PhINTs. [b] Isolated yields of *N*-tosylaziridine after purification with respect to 0.3 mM of PhI=NTs used.

Conclusions

Copper(II) complexes of three new tridentate N_3 ligands have been isolated. Two of them have been structurally characterized to contain the meridionally coordinated ligand, and the incorporation of a sterically hindering quinolyl moiety and N-Me donor group in the ligand leads to a strong trigonal distortion of the copper(II) coordination geometries. All the complexes exhibit significant catalytic nitrene transfer reactivity with PhINTs towards three olefins. While good yields (above 80%) were obtained for the reactive olefin styrene, yields exceeding 60% were obtained for less reactive cyclohexene; however, lower yields (30–45%) were obtained for cyclooctene. The present findings confirm that both the degree of coordinative unsaturation and the steric congestion in copper-based systems are important factors that determine their catalytic activity. It is fascinating to note that the use of low-coordinate copper(II) species with distorted geometries as catalysts dramatically accelerates the aziridination (reaction times 0.5–1 h) for reactive as well as less reactive olefinic substrates. This finding could be expected to pave the way for the rational design of new and more active catalysts for aziridination and related group-transfer reactions.

Experimental Section

Materials and Methods: $CuCl_2·2H_2O$, cyclohexene, triethylamine, (Merck, India), *p*-toluenesulfonamide, iodosobenzene diacetate (Merck, Germany), *tetra*-butylammonium bromide (G. F. Smith), *N*-methylhomopiperazine, homopiperazine, 2-picolylchloride hydrochloride, 2-quinolylchloride hydrochloride, $Cu(ClO_4)_2·6H_2O$, and *cis*-cyclooctene (Aldrich) 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.[7] *tetra*-Butylammonium perchlorate (TBAP) was prepared by the addition of sodium perchlorate to a hot ethanol solution of *tetra*-butylammonium bromide. The product was recrystallized from aqueous ethanol and was tested for the absence of bromide. ^{1}H NMR spectra were obtained using a Bruker 200 MHz spectrometer at room temperature. ^{1}H NMR chemical shifts are reported relative to TMS and are referenced to residual solvent peaks. Electronic absorption spectra were acquired using a Varian 300 spectrophotometer (200–900 nm). FTIR spectra (4000–400 cm^{-1} range, KBr pellets) were recorded with a Jasco FT-IR spectrometer. EPR spectra were recorded with a JEOL JES-TE 100 X-band spectrometer, the field being calibrated with diphenylpicrylhydrazyl (dpph). The g_0 and A_0 values were estimated at ambient temperature and $g_\parallel$ and $A_\parallel$ at 77 K. The values of $g_\perp$ and $A_\perp$ were computed as $1/2(3g_0 - g_\parallel)$ and $1/2(3A_0 - A_\parallel)$ 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 methanol using 0.1 M TBAP as supporting electrolyte. Elemental analyses were performed at Bharathiar University, Coimbatore. Conductivity measurements on methanolic solution of the complexes were made using an Elico conductivity bridge.

Caution! Perchlorate salts of transition metal complexes containing organic ligands are potentially explosive and should be prepared in small quantities and handled with appropriate precautions. While no difficulties were encountered with the complexes reported herein, due caution should be exercised.

4-Methyl-1-(pyrid-2-ylmethyl)-1,4-diazacycloheptane (L1): An aqueous solution (5 mL) of NaOH (0.40 g, 10 mmol) was added dropwise to an aqueous solution (10 mL) of 2-picolyl chloride hydrochloride (0.82 g, 5 mmol) at 0 °C. An aqueous solution (10 mL) of *N*-methylhomopiperazine (0.57 g, 5 mmol) was then added to this mixture over 15 min. The mixture was stirred in a loosely sealed flask at room temperature for three days. The reaction mixture was then extracted with $CHCl_3$ (3 × 50 mL). The organic layer was washed with saturated sodium hydrogen carbonate solution, evaporated, and then dried (Na_2SO_4). The organic solvent was removed on a rotary evaporator to yield the crude product as a pale-yellow oil. The pure product was obtained by extracting the oil once again with ethyl acetate. The product obtained was used as such for the complex preparation. Yield: 0.58 g (56%). $C_{12}H_{19}N_3$ (205.16): calcd. C 70.20, H 9.33, N 20.47; found C 70.15, H 9.48, N 20.37. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.64–7.29 (m, 4 H), 3.95 (s, 2 H), 2.48 (m, 4 H), 2.36 (m, 4 H), 1.49 (quint, 2 H), 2.27 (br. s, 3 H) ppm. IR: $\tilde{\nu}$ = 3023 (m), 2983 (s), 2888 (w), 1467 (m), 1407 (s), 1240 (m), 941 (s), 779 (s) cm^{-1}.

1-(Quinol-2-ylmethyl)-1,4-diazacycloheptane (L2): The ligand L2 was synthesized by a slightly modified procedure that was reported for the preparation of the monosubstituted diazocyclooctane li-

gands.[24] Triethylamine (1.01 g, 10 mmol) was added to 2-quinolyl chloride hydrochloride (1.07 g, 5 mmol) in ethanol (25 mL) at 0 °C, and a solution of homopiperazine (2.00 g, 20 mmol) in ethanol (10 mL) was added slowly to this mixture with stirring. The whole mixture was refluxed for 2 h. The solution was stirred for 2 d at room temperature and the ethanolic solution was removed on a rotary evaporator to dryness. Water was added to the residue and the pH of the solution was adjusted to 10 with sodium carbonate. The solution was extracted with chloroform and the extracts were dried with sodium sulfate. The ligand was isolated as a yellow oil after rotary evaporation of the chloroform extracts. Yield: 0.75 g (61%). $C_{15}H_{19}N_3$ (241.16): calcd. C 74.65, H 7.94, N 17.41; found C 74.55, H 8.13, N, 17.32. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.02–7.36 (br. m, 6 H), 3.93 (s, 2 H), 2.65 (m, 2 H), 2.55 (m, 2 H), 2.45 (m, 2 H), 2.33 (m, 2 H), 1.51 (quint, 2 H), 2.91 (br. s, NH) ppm. IR: $\tilde{\nu}$ = 3432 (br), 3010 (s), 2884 (s), 1432 (s), 1230 (w), 760 (s), 629 (s) cm^{-1}.

4-Methyl-1-(quinol-2-ylmethyl)-1,4-diazacycloheptane (L3): A slightly different procedure was followed for the synthesis of L3. Triethylamine (1.01 g, 10 mmol) was added to 2-quinolyl chloride hydrochloride (1.07 g, 5 mmol) in ethanol (25 mL) at 0 °C. A solution of *N*-methylhomopiperazine (0.57 g, 5 mmol) in ethanol (10 mL) was added to this mixture slowly with stirring. The whole mixture was refluxed for 2 h and then stirred for 2 d at room temperature. The ethanolic solution was removed on a rotary evaporator to dryness, water was added to the residue, and the pH of the solution was adjusted to 10 with sodium carbonate. The solution was extracted with chloroform and the extracts were dried with sodium sulfate. The ligand was isolated as dark yellow oil after rotary evaporation of the chloroform extracts. Yield: 0.98 g (77%). $C_{16}H_{21}N_3$ (255.17): calcd. C 75.26, H 8.29, N 16.46; found C 75.33, H 8.15, N 16. 52. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.27–7.32 (br. m, 6 H), 3.98 (s, 2 H), 2.46 (m, 4 H), 2.36 (m, 4 H), 1.49 (quint, 2 H), 2.27 (br. s, 3 H) ppm. IR: $\tilde{\nu}$ = 3054 (s), 2981 (s), 2865 (s), 1459 (s), 1215 (w), 766 (s), 628 (s) cm^{-1}.

[Cu(L1)(H$_2$O)](ClO$_4$)$_2$ (1): A solution of L1 (0.21 g, 1 mmol) in methanol (15 mL) was treated with $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1 mmol) to obtain a deep-blue color. After 15 min of stirring, diethyl ether was allowed to diffuse into the solution. After a period of several days blue crystals of the product were deposited. Yield: 0.32 g (56%). $C_{12}H_{21}Cl_2CuN_3O_9$ (484.01): calcd. C 28.07, H 3.85, N 8.93; found C 28.11, H 3.78, N 8.98. IR: $\tilde{\nu}$ = 3451 (br), 2923 (w), 2869 (w), 1610 (s), 1089 (br, ClO_4^-), 890 (s), 626 (s, ClO_4^-) cm^{-1}.

[Cu(L2)Cl$_2$] (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 (0.24 g, 1 mmol) instead of L1. The pure product was isolated as blue crystals. Yield: 0.19 g (47%). $C_{15}H_{19}Cl_2CuN_3$ (374.04): calcd. C 47.94, H 5.10, N 11.18; found C 47.78, H 5.23, N 11.21. IR: $\tilde{\nu}$ = 3442 (br), 3235 (s), 2927 (s), 2884 (s), 1481 (w), 786 (s), 634 (s) cm^{-1}. X-ray diffraction quality crystals of **2**·CH_3CN were obtained by the vapor diffusion of diethyl ether into a solution of the complex in acetonitrile.

[Cu(L3)Cl$_2$] (3): This complex was prepared by the addition of L3 (0.26 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, the solution was layered with diethyl ether. Green crystals were deposited after two days. Yield: 0.26 g (65%). $C_{16}H_{21}Cl_2CuN_3$ (388.05): calcd. C 49.30, H 5.43, N 10.78; found C 49.42, H 5.38, N 10.71. IR: $\tilde{\nu}$ = 3442 (br), 3079 (w), 2981 (m), 2869 (m), 1610 (s), 782 (s), 634 (s) cm^{-1}. Suitable single crystals of **3** for X-ray diffraction were obtained by slow evaporation of the methanolic solution of the complex.

Catalytic Aziridinations. Styrene: Aziridinations were performed by stirring mixtures of PhINTs (0.3–0.4 mmol), styrene (10 to 1 equiv. vs. PhINTs), and the copper catalyst (5 mol% vs. PhINTs) in 2 mL of anhydrous CH_3CN under a dry N_2 atmosphere as reported previously.[10] At the completion of the reactions, the clear, pale-green solutions were passed through a short column of neutral alumina to remove copper species, eluted with ethyl acetate, and the eluates were evaporated to yield oily residues. These crude product mixtures (of iodobenzene, 2-phenyl-1-tosylaziridine, and *p*-toluenesulfonamide) were treated with hexane to produce the crude aziridine products, which were recrystallized from hexane/diethyl ether mixtures at –20 °C. The 2-phenyl-1-tosylaziridine obtained was characterized by ^{1}H NMR spectroscopy and the data were identical with those reported in the literature.[13]

Cyclooctene: Aziridinations were performed as described above by stirring mixtures of PhINTs (0.3–0.4 mmol), the olefin (10 to 5 equiv. vs. PhINTs), and the copper catalyst (5 mol-% vs. PhINTs) in 2 mL of anhydrous CH_3CN. At the completion of the reactions, the clear, pale-green solutions were passed through a short column of neutral alumina to remove copper species, eluted with ethyl acetate, and the eluates were evaporated to yield semi-solid residues. These crude product mixtures were treated with hexane, and the resultant mixtures were filtered to remove *p*-toluenesulfonamide. The filtrates were evaporated and dried overnight under vacuum to yield the pure aziridine products. ^{1}H NMR spectroscopic data confirmed the formation of the aziridine.

Cyclohexene: Aziridinations were performed as described above by stirring mixtures of PhINTs (0.3–0.4 mmol), the olefin (5 equiv. vs. PhINTs), and the copper catalyst (5 mol-% vs. PhINTs) in 2 mL of anhydrous CH_3CN. At the end of the reaction, flash column chromatography (3 × 18 cm silica, 4:1 hexane/ethyl acetate) yielded the aziridine as a white crystalline solid. The *N*-(*p*-tolylsulfonyl)-7-azabicyclo-[4.1.0]heptane obtained was characterized by ^{1}H NMR spectroscopy and the data were identical with those reported in the literature.[4e]

X-ray Crystallography: The single-crystal diffraction experiments for **2**·CH_3CN were carried out on a Bruker SMART APEX CCD diffractometer at room temperature. The SMART[25] program was used for collecting frames of data, indexing reflections, and determining the lattice parameters; SAINT[25] was used for integration of the intensity of reflections and scaling; SADABS[25] was used for absorption correction, and the SHELXTL[25] program for space group and structure determination and least-squares refinements on F^2. The structure was solved by the heavy-atom method. Other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares. Most of the hydrogen atoms were located from the difference Fourier map and refined isotropically, except for the hydrogen atoms of the lattice acetonitrile molecule, which was placed at a geometrical position. For **3**, the intensity data were collected at 173 K on a Stoe Image Plate Diffraction System.[26] Image plate distance: 70 mm; φ oscillation scans: 0–200°; step: Δφ = 1.0°; exposure time: 3 min; 2θ range: 3.27–52.1°; $d_{min.}$–$d_{max.}$ = 12.45–0.81 Å. The structure was solved by direct methods using the programme SHELXS-97.[27] The refinement and all further calculations were carried out using SHELXL-97.[28] The H atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. There are two independent molecules per asymmetric unit (Z = 8, Z' = 2). A multi-scan absorption correction was applied using the MULscanABS routine in PLATON;[29] transmission factors:

Table 5. Crystal data and structure refinement details for $[Cu(L2)Cl_2]$ (**2**) and $[Cu(L3)Cl_2]$ (**3**).

	2·CH_3CN	**3**
Empirical formula	$C_{15}H_{19}Cl_2CuN_3 \cdot C_2H_3N$	$C_{16}H_{21}Cl_2CuN_3$
Formula weight	416.84	389.80
Crystal system	monoclinic	monoclinic
Crystal size [mm]	$0.10 \times 0.16 \times 0.24$	$0.27 \times 0.23 \times 0.23$
Space group	$P2_1/C$ (no. 14)	$P2_1/n$
a [Å]	13.641(4)	16.6495(11)
b [Å]	11.138(3)	10.7723(6)
c [Å]	12.613(3)	18.9392(14)
α [°]	90.000	90.000
β [°]	107.966(4)	105.767(8)
γ [°]	90	90
V [Å]^3	1822.9(8)	3269.0(4)
Z	4	8
λ [Å] (Mo-K_α)	0.71073	0.71073
D_{calc} [g cm^{-3}]	1.519	1.584
Goodness-of-fit on F^2	1.032	1.040
Number of reflections measured	10552	25289
Number of reflections used	4231	6382
Number of L.S. restraints	0	0
Number of refined parameters	294	399
Final R indices [$I > 2\sigma(I)$]		
R_1[a]	0.0334	0.0332
wR_2[b]	0.0931	0.0837

[a] $R_1 = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$. [b] $wR_2 = \{[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^4)]^{1/2}\}$.

$T_{min.}/T_{max.}$ = 0.6675/0.7138. Relevant crystallographic information for **2** and **3** are summarized in Table 5.

CCDC-609006 (for **2**) and -609007 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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