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# Preparation of Diamine- $\beta$ -diketiminato Copper(II) Complexes and their Application in Reverse Atom-Transfer Radical Polymerization of Styrene

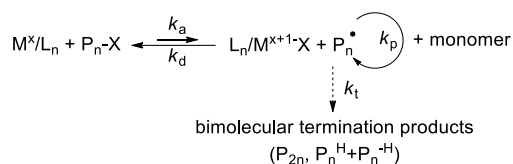
Yohan Champouret,<sup>[a]</sup> Stefano Gulli,<sup>[a]</sup> Jean-Claude Daran<sup>[a]</sup> and Rinaldo Poli\*<sup>[a,b]</sup>

**Keywords:** Copper /  $\beta$ -diketiminato ligands / controlled radical polymerization / polystyrene / ARGET ATRP

Compound **1** ( $\text{Et}_2\text{NCH}_2\text{CH}_2\text{N}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{NHCH}_2\text{CH}_2\text{NEt}_2$  (HL), after conversion to the  $\text{Li}^+$  salt by MeLi, reacts with  $\text{CuCl}_2$  in toluene to yield  $\text{CuCIL}$  (**1**). The compound adopts a 4-coordinate  $\text{CuClN}_3$  environment with a pendant amino arm. The same reaction with  $\text{CuCl}$ , as well as reactions of  $\text{CuCl}$  or  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$  with LiL, leads to disproportionation with deposition of metallic copper. Crystals of compounds  $[\text{CuL}][\text{CuCl}_2]$  (**2**) and  $[\text{CuL}]\text{BF}_4$  (**3**) were isolated in minor amounts from these reactions. The  $[\text{CuL}]^+$  ion in these compounds has a 4-coordinate  $\text{CuN}_4$  environment.

Compound **2** was also obtained in good yields from the reaction between equivalent amounts of **1** and  $\text{CuCl}$ . Compound **1** was used to control the radical polymerization of styrene under ARGET ATRP conditions in the presence of glucose as reducing agent and bromoethylbenzene as initiator. The polymerization behavior indicates that the controlling ability of this system is negatively affected by its slow trapping rate and by the disproportionation of the  $\text{CuL}$  catalyst.

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Supporting information for this article is available on the WWW under <http://www.eurjic.org/> or from the author.



Scheme 1. Equilibrium controlling the radical polymerization by the atom transfer mechanism.

## Introduction

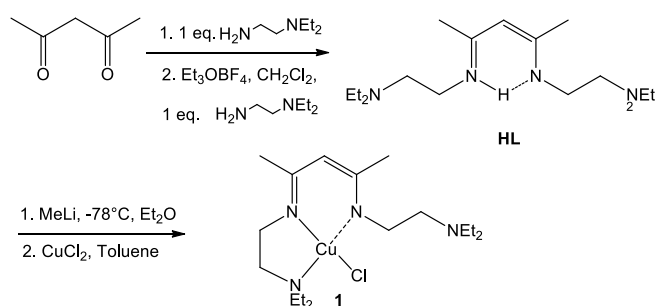
Since its discovery in 1995,<sup>[1-2]</sup> metal-catalyzed radical polymerization has grown to become a powerful method to access high added-value functionalized polymers for a multitude of specialty applications.<sup>[3-8]</sup> The technique, also named Atom Transfer Radical Polymerization (ATRP) rests on controlling the radical concentration at very low levels, thereby reducing the impact of irreversible bimolecular terminations, through the establishment of a shuttle between the active radical chain and a dormant chain which is capped by a halogen atom. The equilibrium between these two species is insured by a metal complex that can reversibly abstract the halogen atom from the dormant chain and therefore generate a new metal complex with one additional ligand (the halide) with an increase of the formal oxidation state by one unit. This mechanism is illustrated in Scheme 1. Two common approaches to start the polymerization are from either the left hand side of the equilibrium (the  $\text{M}^x/\text{L}_n$  complex plus a suitable alkyl halide initiator, so called “ATRP conditions”) or from the right hand side (the oxidized  $\text{L}_n/\text{M}^{x+1}-\text{X}$  complex plus a suitable radical generating initiator, so-called “reverse ATRP conditions”). The most versatile and convenient metal system for this process has proven to be  $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$  because of low cost, efficiency, facility of catalyst assembly *in situ* from simple copper halide salts and suitable ligands, and availability of a large variety of neutral multidentate ligands that allow the system to be tuned for application to a variety of different monomers and operating conditions, even though limitations exist.

The combination of  $\text{CuX}$  ( $\text{X}$  = halide; mostly Cl and Br have been used) with neutral supporting ligands is the simplest method to afford a wide variety of catalysts but can only lead to systems that contain a halogen atom in the coordination sphere or to cationic complexes when the halide ion dissociates.<sup>[9]</sup> Little attention has so far devoted to the development of ATRP  $\text{Cu}^{\text{I}}$  catalysts containing the anionic functionality embedded in the multidentate ligand itself, mostly limited to tris(pyrazolyl)borate derivatives.<sup>[10-12]</sup> This leads to halide-free neutral catalysts that are of interest because they may avoid ligand redistribution processes that are observed for the  $\text{CuX}/\text{L}_n$  systems under certain conditions.<sup>[13]</sup> We have recently explored the use of a tridentate “ $\text{XL}_2$ ” type ligand, the amino- $\beta$ -ketiminato ligand obtained by deprotonation of  $\text{R}_2\text{NCH}_2\text{CH}_2\text{NHC}(\text{Me})\text{CHC}(\text{Me})\text{O}$  ( $\text{R} = \text{Me}, \text{Et}$ ) and have reported the synthesis of corresponding  $\text{CuCl}(\text{XL}_2)$  complexes and their preliminary application to the reverse ATRP of styrene.<sup>[14]</sup> In this contribution, we wish to extend the study to a tetradentate diamino- $\beta$ -diketiminato ligand. We report the synthesis of unprecedented  $\text{Cu}^{\text{II}}$  complexes containing the ligand  $[\text{Et}_2\text{NCH}_2\text{CH}_2\text{N}(\text{Me})\text{CHC}(\text{Me})\text{NCH}_2\text{CH}_2\text{NEt}_2]^-$  ( $\text{L}^-$ ), our attempts to generate a corresponding  $\text{Cu}^{\text{I}}$  complex, and the performance of the  $\text{Cu}^{\text{II}}$  complex  $\text{CuCIL}$ , **1**, as a controlling agent for the polymerization of styrene.

## Results and Discussion

### (a) Synthesis and characterization

The pro-ligand HL was prepared by a previously reported two-step procedure as shown in Scheme 2.<sup>[15]</sup> The reaction of HL with MeLi in ether affords the lithium salt LiL that can react *in situ* with anhydrous CuCl<sub>2</sub> to give purple LCuCl (**1**) in moderate yields (Scheme 2), isolated as a hygroscopic microcrystalline purple powder, which changes color to brown upon absorption of water. However, well formed crystals of **1** are stable in air without any color change even after a few months.



Scheme 2. Procedure for the synthesis of HL and LCuCl (**1**).

Complex **1** is soluble in most organic solvents yielding deep purple solutions. It has been characterized by mass spectrometry, by IR and EPR spectroscopies, by elemental analysis and by single crystal X-ray diffraction. The molecular ion is not revealed by the mass spectrometric study, the highest peak corresponding to the loss of one chloride ligand, [M - Cl]<sup>+</sup> at *m/z* = 358. The IR spectrum (see figure 1S in the SI) does not change upon exposure to moist air, except for the appearance of bands corresponding to coordinated water. Hence, the color change can be attributed to a change of the coordination environment of the Cu<sup>II</sup> ion but the chemical nature of the CuLCl moiety remains intact. The C=N stretching vibrations, which are observed as the most intense bands at 1619 and 1561 cm<sup>-1</sup> for the free ligand, become less intense and are red-shifted to 1557 and 1523 cm<sup>-1</sup> in the Cu<sup>II</sup> complex.

Single crystals of **1** suitable for the X-ray analysis could be grown from pentane solutions by slow evaporation or by hot filtration followed by cooling to -20°C. The molecular structure of **1** is depicted in Figure 1. The complex is mononuclear with a four coordinated copper(II) centre bound by one chlorine atom and three N atoms of L (two N atoms of the β-diketiminato moiety and one of the two amino N atoms) while one amine arm remains pendant. The geometry around the copper centre can best be described as a distorted square plane with trans N1-Cu-Cl1 and N2-Cu-N3 angles significantly smaller than 180° [161.87(13)° and 154.94(10)°, respectively]. The Cl1-Cu-N3 plane makes a dihedral angle of 25.48° with the N1-Cu-N2 plane. This structural type is quite typical for a 4-coordinated Cu<sup>II</sup> complex,<sup>[16-23]</sup> fully analogous to that of the complex with a tridentate amine-β-ketiminato ligand, [Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NC(Me)CHC(Me)O]CuCl, which also displays similar Cu-Cl (2.2458(4) Å) and Cu-N distances (1.9404(12) Å to the ketiminato N atom, 2.0563(12) Å to the amino N atom).<sup>[14]</sup> In the latter contribution, it was specifically shown that this 4-coordinate geometry is stabilized by bulky groups against the possible dimerization with formation of loose Cu...Cl axial interactions, which were on the other hand seen for the related [Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NC(Me)CHC(Me)O]CuX complexes (X = Cl,<sup>[14]</sup> O<sub>2</sub>CPh<sup>[24]</sup>) as well as for other related complexes.<sup>[25-27]</sup> For the present structure, the bulky ethyl groups and the pendant diethylaminoethyl arm are presumably preventing the formation of such loose Cl-bridged dimer.

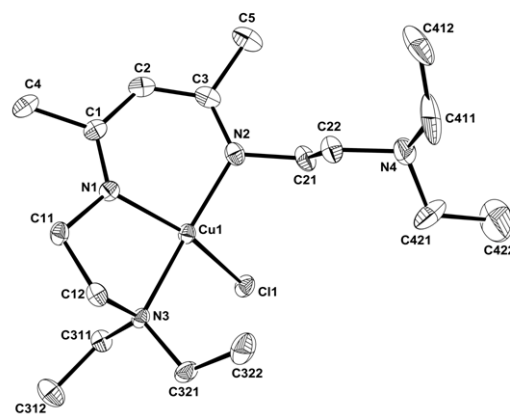


Figure 1. ORTEP view of compound **1**. Thermal ellipsoids are drawn at the 50% probability level. Main geometrical parameters: Cu1-Cl1 2.2641(10), Cu1-N3 2.067(3), Cu1-N1 1.914(3), Cu1-N2 1.938 (3); Cl1-Cu1-N1 154.94(10) Å; Cl1-Cu1-N3 93.20(9), Cl1-Cu1-N2 97.46(10), N3-Cu1-N2 161.87(13), N3-Cu1-N1 83.88(12), N1-Cu1-N2 92.40(14)°.

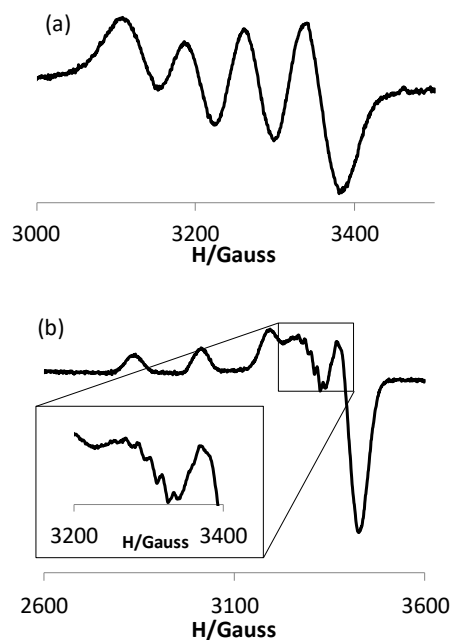


Figure 2. X-band EPR spectra of compound **1** in toluene. (a) Room temperature. (b) Frozen solution at 115K.

The EPR spectra of **1** in toluene solution at room temperature and frozen at 115K are shown in Figure 2. In the isotropic room temperature spectrum, only the coupling to the <sup>63</sup>Cu and <sup>65</sup>Cu nuclei (*I* = 3/2) is observed. The frozen spectrum shows an essentially tetragonal tensor (with a slight orthorhombic distortion) with *g<sub>x,y</sub>* >> *g<sub>z</sub>* > 2.0 and *A<sub>||</sub><sup>Cu</sup>* > *A<sub>⊥</sub><sup>Cu</sup>* (the latter is not discernible), which is characteristic of a ground state with the unpaired electron in the *d<sub>x2-y2</sub>* orbital. This is common to other Cu complexes with similar coordination geometry, notably Cu<sup>II</sup> complexes with isoindoline based ligands that also display a 4-coordinate CuClN<sub>3</sub> environment.<sup>[28]</sup> The fine structure that can be discerned on the perpendicular component (see inset of Figure 2b) is due to superhyperfine coupling to the <sup>14</sup>N nuclei. The spectrum has been simulated to a reasonable level (see SI). However, the presence of three chemically distinct N atoms is not unambiguously

demonstrated by the simulation. The best fitting is obtained when using three g values, two A values for Cu (x, z) and only one A value for two undistinguishable N atoms (details in the Experimental section). Coupling to the third N atom (probably the less strongly coordinated amino atom) was not visible.

The synthesis of the copper(I) complex CuL was attempted by a strategy completely analogous to that described in Scheme 2, using CuCl instead of CuCl<sub>2</sub>. The reaction, however, resulted in the formation of a copious amount of Cu<sup>0</sup>. The same result was obtained upon using [Cu(CH<sub>3</sub>CN)<sub>4</sub>]BF<sub>4</sub> as substrate in toluene. This result could be caused by disproportionation of the initially formed Cu<sup>I</sup> product, or by overreduction because of the interaction of the formed CuL with the Li<sup>+</sup> salt that is still present in solution. An alternative strategy consisted of reacting HL with CuCl in the presence of NEt<sub>3</sub> to trap the HCl by-product. Indeed, when using THF as solvent, the precipitation of white Et<sub>3</sub>NH<sup>+</sup>Cl<sup>-</sup> occurred as expected, but a disproportionation reaction was still observed, although more slowly (over several hours) under these conditions. This indicates that overreduction accelerates the formation of Cu<sup>0</sup>, but the CuL product is also prone to slow disproportionation. Upon rapid work-up of the solution after filtration of Et<sub>3</sub>NH<sup>+</sup>Cl<sup>-</sup>, we were not able to isolate the putative CuL compound. Only a few crystals of the mixed-valence Cu<sup>I</sup>/Cu<sup>II</sup> compound **2** (from the CuCl/HL/NEt<sub>3</sub> reaction) or the Cu<sup>II</sup> complex **3** (from the LiL/[Cu(CH<sub>3</sub>CN)<sub>4</sub>]BF<sub>4</sub> reaction) were obtained from the various crystallization attempts. Disproportionation of β-diketiminato Cu<sup>I</sup> complexes has also been previously observed by other authors and attributed to an insufficient steric bulk of the substituent on the ligand N donor atoms.<sup>[29]</sup> In the present case, it is likely that the coordination of the two NH<sub>2</sub>NH<sub>2</sub>NEt<sub>2</sub> arms is not sufficiently strong to stabilize the Cu<sup>I</sup> center in a 4-coordinate environment, particularly in view of the fact that the planarity of the β-diketiminato ligand, which extends to the first C atom on each aminoethyl arm, does not allow the CuL structure to adopt the preferred tetrahedral coordination geometry.

The nature of compounds **2** and **3** was revealed by single crystal X-ray diffraction analyses. The two structures contain the same cation and will be therefore discussed together. Both complexes contain two independent cations and two independent anions in the asymmetric unit, each pair of like ions having essentially the same geometrical parameters. For the structure of **2** both cation-anion pairs are located in a general position whereas one pair is in a general position and the second one sits on a crystallographic twofold axis for the structure of **3**. A view of one of these independent pairs is provided in Figure 3 for compound **2** and in Figure 4 for compound **3**. In the case of complex **2**, the typical coordination geometry observed for each fragment unambiguously identifies the CuCl<sub>2</sub> fragment as an anion of Cu<sup>I</sup> because of the linear geometry [Cl-Cu-Cl angles of 179.08(8)° around Cu(3) and 179.49(8)° around Cu(4)]. Consequently, the CuL fragment must consist of a cation of Cu<sup>II</sup>, which is identical to the [CuL]<sup>+</sup> fragment in complex **3**. The [CuCl<sub>2</sub>]<sup>-</sup> anion is preceded in over 100 other salts, of which we found fourteen containing a Cu<sup>II</sup> cation in the Cambridge Structural Database. These cations are mostly 5-coordinate complexes,<sup>[30-41]</sup> but there are also two examples of 4-coordinate complexes like the cation of compound **2** in the structures of the chloro-(2,6-bis((1,3-di-*tert*-butylimidazolin-2-imino)methyl)pyridine)copper(II) and [Cu(Ph<sub>3</sub>AsO)<sub>4</sub>]<sup>2+</sup> salts.<sup>[42-43]</sup>

The relevant geometric parameters of the cations in the two structures are reported and compared in Table 1. For both complexes, L acts as a tetradentate ligand through the four nitrogen atoms to yield a slightly distorted (towards a butterfly) square

coordination geometry, very close to that adopted by **1** (Figure 1) and by many other 4-coordinate Cu<sup>II</sup> complexes as already cited above. The range of the *trans* N-Cu-N angles is between 161 and 163° for compound **2** and between 156 and 165° for compound **3**. The (β-diketiminato)Cu plane (e.g. N11-Cu1-N14 in Figure 3) and the other CuN<sub>2</sub> plane involving the two amino groups (e.g. N12-Cu-N13 in Figure 3) form dihedral angles of 22.7° and 19.5° in complex **2** and 20.5° and 29.7° in complex **3**.

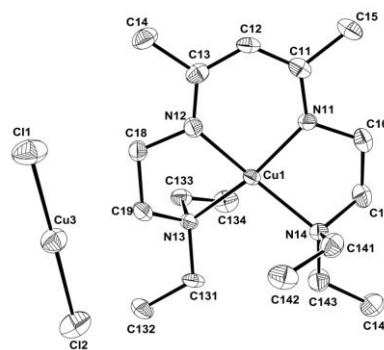


Figure 3. ORTEP view of one of the two independent cation-anion pairs in the structure of complex **2**. Thermal ellipsoids are drawn at 50% probability level.

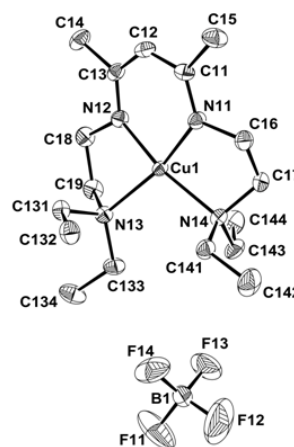
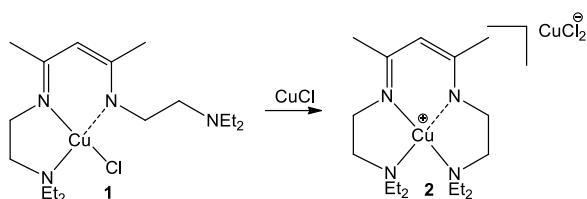


Figure 4. ORTEP view of one of the two independent cation-anion pairs in the structure of complex **3**. Only one orientation of the disordered BF<sub>4</sub><sup>-</sup> ion is shown. Thermal ellipsoids are drawn at 50% probability level.

Table 1. Selected metric parameters (distances in Å, angles in °) for the [CuL]<sup>+</sup> cations in the structures of compounds **2** and **3**.

	Complex <b>2</b>		Complex <b>3</b>	
	n = 1	n = 2	n = 1	n = 2
Cu(n)-N(n1)	1.927(4)	1.930(4)	1.9252(15)	1.9053(14)
Cu(n)-N(n2)	1.934(5)	1.923(4)	1.9260(14)	
Cu(n)-N(n3)	2.104(4)	2.109(4)	2.1140(15)	
Cu(n)-N(n4)	2.124(4)	2.130(4)	2.0936(14)	2.1040(14)
N(n1)-Cu(n)-N(n2)	92.85(18)	92.58(18)	93.04(6)	93.80(8)
N(n1)-Cu(n)-N(n3)	161.28(17)	162.88(17)	161.37(6)	156.11(6)
N(n1)-Cu(n)-N(n4)	83.89(17)	83.92(17)	84.57(6)	85.89(6)
N(n2)-Cu(n)-N(n3)	83.60(18)	84.25(18)	82.49(6)	
N(n2)-Cu(n)-N(n4)	161.65(18)	162.14(18)	164.99(6)	
N(n3)-Cu(n)-N(n4)	105.01(16)	104.00(16)	104.24(6)	103.85(8)

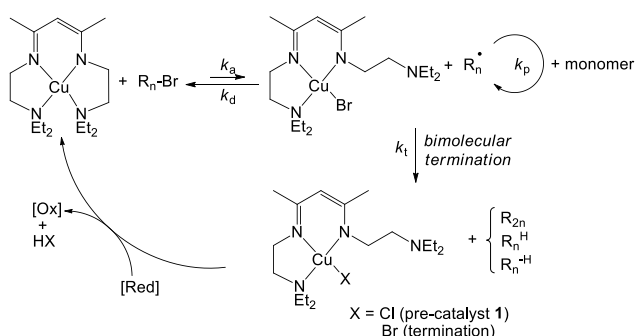
Once the formulation of **2** as a mixed-valence Cu<sup>I</sup>-Cu<sup>II</sup> salt became evident from the X-ray structural analysis, the compound was prepared in bulk quantities by a logical approach, which consists of the reaction of equivalent amounts of complex **1** and CuCl in THF at room temperature (Scheme 3). In this reaction, CuCl acts as a Lewis acid by extracting the chlorido ligand from compound **1**, which allows the pendant NEt<sub>2</sub> group to coordinate and yield the 4-coordinate [CuL]<sup>+</sup> cation. The success of this synthetic strategy might also hint to the possible mechanism of its formation in the initial attempt aimed at synthesizing CuL. The mass spectrum of compound **2** in the positive mode reveals the *m/z* peak of the CuL<sup>+</sup> ion, identical to the spectrum of compound **1**, while the spectrum in negative mode shows the *m/z* peak of the CuCl<sub>2</sub><sup>-</sup> ion.



Scheme 3. Synthesis of [CuL][CuCl<sub>2</sub>] (**2**).

### (b) Controlled radical polymerization

The new copper complex **1** was tested in the controlled radical polymerization of styrene by the atom transfer strategy. Since the target copper(I) complex could not be isolated and the synthetic studies revealed its high propensity to disproportionation, the polymerization was carried out using **1** under ARGET (Activators ReGenerated by Electron Transfer) ATRP conditions.<sup>[44-46]</sup> The reducing agent chosen to generate the copper(I) *in situ* as well as to regenerate it during the polymerization process was glucose, while (1-bromoethyl)benzene (BEB) was selected as the initiator. The principle of the ARGET ATRP involves the *in situ* generation of the Cu<sup>I</sup> catalyst from the corresponding oxidatively stable Cu<sup>II</sup> halide by the action of a reducing agent. Subsequently, the Cu<sup>I</sup> complex activates the initiator by the normal ATRP equilibrium.<sup>[8]</sup> The use of an excess of reducing agent serves to insure that the Cu<sup>II</sup> species accumulating when the radicals irreversibly terminate is continuously reduced to regenerate the Cu<sup>I</sup> activator species. The process is summarized in Scheme 4 for the action of the 1/BEB combination. A well controlled polymerization should reveal a first order consumption of monomer (constant radical concentration insured by the persistent radical effect),<sup>[47]</sup> a linear growth of the molecular weight with the conversion in close agreement with the value calculated from the molar monomer/initiator ratio, and a narrow dispersity ( $\bar{D} = M_w/M_n$ ).



Scheme 4. Mechanism of action of compound **1** in ARGET ATRP.

The results of ARGET ATRP of styrene using **1** are presented in Figure 5. The first-order kinetics plot (Figure 5, top) shows better linearity when the polymerization is carried out at 80°C. As expected, the polymerization is faster at 110°C initially, but subsequently slows down at higher conversions, eventually becoming even slower than the polymerization conducted at 80°C. The polymer number average molecular weight increases linearly with conversion at both temperatures, as noticeable in Figure 5 (bottom) and the polymer dispersities are reasonably low (smaller than 1.40 at > 60% conversion). However, the observed *M<sub>n</sub>* are greater than the theoretical values (for instance, at 80°C and 63% conversion *M<sub>n,exp</sub>* = 96640 g/mol vs. *M<sub>n,theo</sub>* = 32740 g/mol, *f* = 0.34; at 110°C and 67% conversion *M<sub>n,exp</sub>* = 80960 g/mol vs. *M<sub>n,theo</sub>* = 35085 g/mol, *f* = 0.43). This observation shows that the polymerization is negatively affected by a high tendency to bimolecular terminations, reducing the number of active chains to a greater extent as the polymerization progresses. This must result from an insufficient rate of radical trapping (*k<sub>d</sub>* in Scheme 4). Note that the catalyst disproportionation process would only lead to a decrease of the catalyst concentration and this may potentially affect the polymerization rate but not the initiator efficiency factor (*f*). The greater *M<sub>n</sub>* (low initiator efficiency) must necessarily be related to a decrease of active chains through bimolecular terminations. It seems that this phenomenon is more or less equally important at the two temperatures. In fact, *f* is greater at the higher temperature, suggesting that trapping becomes more efficient (greater *k<sub>d</sub>*) as the temperature increases. The trend observed for the polymerization rate, on the other hand, can be rationalized by a faster catalyst loss through the disproportionation process at the higher temperature. The amount of catalyst and the degree of disproportionation were apparently too small to visually confirm the formation of metallic copper.

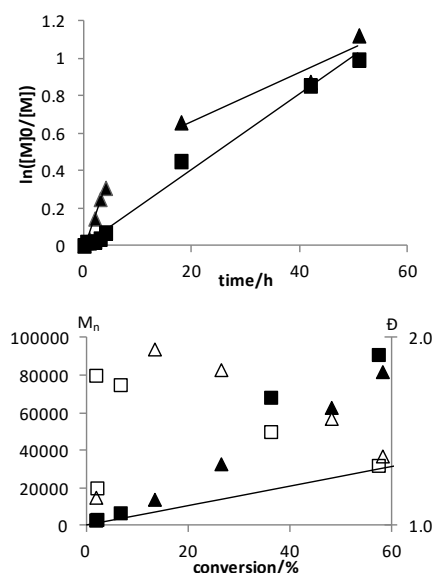


Figure 5. First-order kinetic plot (top) and *M<sub>n</sub>* (filled symbols) and dispersity index ( $\bar{D}$ ; empty symbols) versus conversion (bottom) for the radical polymerization of styrene in the presence of CuClL. *T* = 110°C (triangles) or 80°C (squares). [Styrene]:[BEB]:[Glucose]:[Cu] = 500:1:2:1. The straight line in the second plot indicates the theoretical molecular weight with *M<sub>n,theo</sub>* = ([M]<sub>0</sub>/[BEB]<sub>0</sub>)\*conversion.

We have recently reported a slow trapping rate also for the reverse ATRP of styrene with related Cu<sup>II</sup> complexes containing the tridentate β-ketoiminato ligands R<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NC(Me)-CHC(Me)O (R = Me, Et), which adopt a distorted square planar

geometry similar to that of compound **1**, even when run in the presence of additional ligands such as pyridine or bipy.<sup>[14]</sup> In that case, we argued that the addition of a second amino arm could improve the catalyst performance by providing a smaller reorganizational energy upon halogen atom transfer from CuXL to CuL. However, as shown by the structural analysis of compound **1** in this contribution, this compound is not able to accept the coordination of the additional amino arm and therefore still requires a significant reorganization during the atom transfer process, thereby maintaining a high activation energy. Furthermore, the geometry of the tetracoordinated L ligand on the Cu<sup>I</sup> complex does not appear suitable for the stabilization of the preferred tetrahedral geometry of Cu<sup>I</sup>, whereas it fits quite well with the distorted square planar geometry preferred by [Cu<sup>II</sup>L]<sup>+</sup>. This factor is presumably responsible for the insufficient stabilization of the CuL complex, leading to disproportionation.

## Conclusions

Cu<sup>II</sup> complexes containing the tetradentate mononegative diamino- $\beta$ -diketiminato ligand Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NC(Me)CHC(Me)-NCH<sub>2</sub>CH<sub>2</sub>NEt<sub>2</sub> (L<sup>-</sup>), namely CuCIL and [CuL]<sup>+</sup>, have been synthesized and fully characterized. An analogous Cu<sup>I</sup> complex CuL could be generated in solution but could not be isolated because of its susceptibility to disproportionation. Contrary to our hope, this CuL/CuCIL system is not suitable for an efficient control of atom transfer radical polymerization and we have identified two reasons for this shortcoming. The first one is the tendency of the Cu<sup>I</sup> species to disproportionate. The second one is a slow trapping rate for the CuXL (X = Cl, Br) species as shown by the results of the styrene polymerization run under ARGET ATRP conditions. Both these reasons are probably related to the unsuitable coordination geometry of the L ligand. Improvement of this "halogen-free" CuN<sub>4</sub> coordination environment for application to ATRP requires further ligand design, in order to create a coordination environment better suited to Cu<sup>I</sup> and work in this directly is currently underway.

## Experimental Section

**General.** All solvents were freshly distilled under argon prior to use. NMR spectra were recorded with Bruker DPX 300 and AV 300 instruments. Chemical shifts are expressed in ppm downfield from Me<sub>4</sub>Si. EPR spectra were measured with a Bruker Elexsys E 500 spectrometer (X-band) equipped with both a frequency meter and a gauss meter. The elemental analyses were performed on a Perkin Elmer 2400 instrument by the analytical services of the LCC Toulouse. Size exclusion chromatography (SEC) of polystyrene was carried out in filtered THF (flow rate: 1 ml/min) at 35°C on a 300x7.5 mm PL gel 5micrometer mixed-D column (polymer laboratories), equipped with multiangle light scattering (minidawn Tristar, Wyatt Technology Corporation) and refractive index (RI2000, Sopares) detectors. The isolated polymer samples were dissolved in THF and the polymer solutions were filtered (pore size = 0.45  $\mu$ m) before chromatographic analysis. The columns were calibrated against linear polystyrene standards (Polymer Laboratories). Acetylacetone, N,N-diethylethylenediamine, 1-bromoethyl(benzene), glucose, MeLi (1.6 M solution in Et<sub>2</sub>O), CuCl and CuCl<sub>2</sub> were purchased from Sigma–Aldrich and used as received. [Et<sub>3</sub>O][BF<sub>4</sub>] was prepared as previously described.<sup>[48]</sup> Styrene (Sigma–Aldrich) was dehydrated by passing through a neutral alumina column and then stirred in the presence of CaH<sub>2</sub> for 1 day, followed by distillation under argon.

**Synthesis of CuLCl, 1.** To a cooled solution (-78°C) of HL (697 mg, 2.35 mmol) in dried Et<sub>2</sub>O (15 ml), MeLi (1.46 mL, 1 equiv) was added dropwise.

Stirring at -78°C for 2 h and then at r.t. overnight afforded a yellow solution of the lithium salt LiL. The solution was evaporated to dryness under vacuum and the residue was dissolved in toluene (15 mL). In a separated Schlenk flask, CuCl<sub>2</sub> (316 mg, 1 equiv) was suspended in toluene (2 ml) and the lithium salt solution was added dropwise through a cannula to afford a purple solution. After 2 h stirring at room temperature, the solvent was removed under vacuum. The residual solid was recrystallized by dissolution in hot pentane, filtration through Celite and standing overnight at -80 °C to afford **1** as purple crystals. Yield: 370 mg (40%). Anal. % Calcd for C<sub>17</sub>H<sub>35</sub>CuClN<sub>4</sub>: C, 51.76; H, 8.94; N, 14.20. Found: C, 51.7; H, 8.9; N, 14.0. MS (FAB, MNBA): m/z 358 [M-Cl]<sup>+</sup>. EPR (CH<sub>2</sub>Cl<sub>2</sub>, X band): room temperature: g = 2.100 (a<sub>Cu</sub> = 75 G); 115K: g<sub>x</sub> = 2.07 (A<sub>x</sub><sup>Cu</sup> = 10 G), g<sub>y</sub> = 2.04 (A<sub>y</sub><sup>2N</sup> = 18 G), g<sub>z</sub> = 2.006 (A<sub>z</sub><sup>Cu</sup> = 179 G) (the reported g and A values for the 115K spectrum derive from the simulation, see SI).

### Attempted syntheses of complex CuCl.

**(a) From CuCl, HL and NEt<sub>3</sub>.** To a stirred solution of CuCl (0.5 g, 5.05 mmol) in 5 mL of dry THF, a solution of HL (1.5 g, 5.05 mmol in 5 mL of dry THF) was added and the resulting solution was stirred for 30 minutes. The solution became dark yellow. Then, 0.7 mL (5.05 mmol) of dry Et<sub>3</sub>N was added to the solution and stirring was continued for another hour, during which time the color turned to red. The white Et<sub>3</sub>NH<sup>+</sup>Cl<sup>-</sup> precipitate that had formed was removed by filtration. The solvent was then partially removed under reduced pressure to about 5 mL and slow diffusion of dry ether at -20°C afforded a few brownish crystals of [CuL][CuCl<sub>2</sub>], **2**.

**(b) From [Cu(CH<sub>3</sub>CN)<sub>4</sub>]BF<sub>4</sub> and LiL.** To a cooled solution (-78°C) of HL (410 mg, 1.38 mmol) in dried Et<sub>2</sub>O (6 mL), MeLi (0.86 mL, 1 equiv) was added dropwise. Stirring at -78°C for 2 h and then at r.t. overnight afforded a yellow solution of the lithium salt LiL. The solution was evaporated to dryness under vacuum and the residue was dissolved in toluene (6 mL). In a separated Schlenk flask, [Cu(CH<sub>3</sub>CN)<sub>4</sub>]BF<sub>4</sub> (434 mg, 1 equiv) was suspended in toluene (2 mL) and the lithium salt solution was added dropwise through a cannula to afford a dark-green solution that turned night blue after 15 min stirring. After 3 h stirring at room temperature, the solution was filtered and placed overnight at -20°C to afford a few red crystals of [CuL][BF<sub>4</sub>], **3**.

**Synthesis of [CuL][CuCl<sub>2</sub>], 2.** A purple solution of **1** (91 mg, 0.23 mmol) in dried THF (8 mL) was added dropwise to CuCl (23 mg, 1 equiv) at room temperature. Stirring at r.t. for 8 h afforded a red precipitate. The supernatant was removed by filtration and the red precipitate was dried under vacuum. The residual red solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and slow diffusion of ether gave **2** as red crystals. Yield: 68 mg (60%). Anal. % Calcd for C<sub>17</sub>H<sub>35</sub>Cu<sub>2</sub>Cl<sub>2</sub>N<sub>4</sub>: C, 41.38; H, 7.15; N, 11.35. Found: C, 41.2; H, 7.3; N, 10.9. MS (ESI positive): m/z 358 [CuL]<sup>+</sup>. MS (ESI negative): m/z 135 [CuCl<sub>2</sub>]<sup>-</sup>.

**Procedure for ARGET-ATRP.** Complex **1** (17.3 mg, 0.044 mmol), glucose (15.9 mg, 2 equiv), BEB (6  $\mu$ L, 1 equiv), styrene (2.5 mL, 500 equiv) and anisole (2.5 mL) were introduced in a Schlenk flask under a protective argon atmosphere. The flask was degassed by three freeze-pump-thaw cycles and then immersed in an oil bath preheated at the desired temperature. At the desired time, the Schlenk flask was rapidly immersed in an ice bath before sample withdrawal. The monomer conversion was determined gravimetrically after removal of the solvent and unconverted monomer under vacuum.

**X-ray Crystallography.** A single crystal of each compound was mounted under inert perfluoropolyether on the tip of a glass fiber and cooled in the cryostream of either an Oxford-Diffraction XCALIBUR CCD diffractometer (for **1** and **3**) or an Oxford-Diffraction GEMINI CCD diffractometer (for **2**). The data were collected by using monochromatic Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 180(2) K. The structures were solved by direct methods (SIR97)<sup>[49]</sup> and refined by least-squares procedures on F<sup>2</sup> using SHELXL-97.<sup>[50]</sup> All H atoms attached to carbon atoms were introduced in calculated idealized positions and treated as riding models. The drawing of the molecules was realized with the help of ORTEP32.<sup>[51-52]</sup>

The crystal data and structure refinement parameters for the three compounds are listed in Table 2. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 852833 - 852835. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

Table 2. Crystal data and refinement parameters for all compounds.

Compound	CuCIL (1)	[CuL][ClCl <sub>2</sub> ] (2)	[CuL][BF <sub>4</sub> ] (3)
Empirical formula	C <sub>17</sub> H <sub>35</sub> ClCuN <sub>4</sub>	C <sub>34</sub> H <sub>70</sub> Cl <sub>4</sub> Cu <sub>4</sub> N <sub>8</sub>	C <sub>17</sub> H <sub>35</sub> CuN <sub>4</sub>
M <sub>r</sub>	394.48	986.94	445.84
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbca	P2 <sub>1</sub> /c	C 2/c
a [Å]	17.1959(13)	18.7208(5)	29.3723(15)
b [Å]	8.0359(6)	17.3653(4)	13.6327(4)
c [Å]	29.479(2)	13.0819(3)	16.8855(7)
β [°]	90	90.978(2)	111.723(5)
V [Å <sup>3</sup> ]	4073.5(5)	4252.21(18)	6281.2(5)
Z	8	4	12
D <sub>calcd.</sub> [Mgm <sup>-3</sup> ]	1.286	1.542	1.414
Abs. coeff. [mm <sup>-1</sup> ]	1.209	2.260	1.087
F(000)	1688	2056	2820
Crystal size [mm]	0.50x0.21x0.02	0.62x0.50x0.40	0.58x0.41x0.24
θ range [°]	3.01 to 26.37	2.94 to 26.37	2.88 to 28.41
Refl. collectd	22479	53358	23865
Unique refl. [R(int)]	4152 (0.0876)	8685 (0.0479)	6416 (0.0262)
Completeness [%]	99.8	99.9	99.9
Abs. corr.	Semi-empirical	Semi-empirical	Semi-empirical
Max./min. transm.	1.0000/0.7144	1.0000/0.5296	1.0000/0.6865
Refinement method	F <sup>2</sup>	F <sup>2</sup>	F <sup>2</sup>
Data/restr./param.	4152/10/252	8685/0/463	6416/76/412
Goodness-of-fit (F <sup>2</sup> )	1.107	1.349	1.055
R, wR2 [I > 2σ(I)]	0.0593, 0.1037	0.0562, 0.1402	0.0276/0.0734
R, wR2 (all data)	0.0888, 0.1115	0.0685, 0.1451	0.0337/0.0734
Resid. dens. [eÅ <sup>-3</sup> ]	0.455, -0.437	1.041, -1.094	0.582, -0.422

**Supporting Information** (see footnote on the first page of this article): IR spectrum of compound 1 before and after exposure to moist air.

## Acknowledgments

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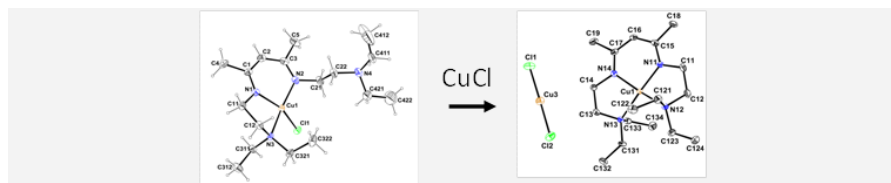
### Diamine- $\beta$ -diketiminato Copper(II)

**Yohan Champouret, Stefano Gulli,  
Jean-Claude Daran and Rinaldo Poli\***

..... Page No. – Page No.

Preparation of Diamine- $\beta$ -diketiminato  
Copper(II) Complexes and their  
Application in Reverse Atom-Transfer  
Radical Polymerization of Styrene

**Keywords:** Copper /  $\beta$ -diketiminato  
ligands / controlled radical polymerization  
/ polystyrene / ARGET ATRP



The coordination chemistry of copper  
with a diamine- $\beta$ -diketiminato ligand (a  
monoanionic N<sub>4</sub> donor), is explored in

view of developing atom transfer radical  
polymerization with halogen-free Cu<sup>I</sup>  
catalysts.