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Stefano Gulli, Jean-Claude Daran, Rinaldo Poli. Synthesis and Structure of Four-Coordinate Copper(II) Complexes Stabilized by β -Ketiminato Ligands and Application in the Reverse Atom-Transfer Radical Polymerization of Styrene. European Journal of Inorganic Chemistry, 2011, 2011 (10), pp.1666-1672. 10.1002/ejic.201001203 . hal-03158346

HAL Id: hal-03158346

<https://hal.science/hal-03158346>

Submitted on 3 Mar 2021

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Synthesis and structure of Four-coordinate copper(II) complexes stabilized by β -ketiminato ligands and application in the reverse Atom-Transfer Radical Polymerization of styrene


Stefano Gulli,^[a] Jean-Claude Daran,^[a] and Rinaldo Poli^{*[a,b]}

Keywords: Copper(II) / Functionalized β -ketiminato ligands / Controlled Radical Polymerization / ATRP / Polystyrene

The reaction of CuCl_2 with $\text{R}_2\text{NCH}_2\text{CH}_2\text{NHC}(\text{Me})=\text{CHCO}(\text{Me})$ ($\text{R} = \text{Me}$, HL^1 ; or Et , HL^2) in the presence of Et_3N leads to the formation of complexes $\text{CuCl}(\text{L}^n)$ ($n = 1, 2$). While the solid state structure of compound **2** is mononuclear with a close to square planar arrangement of the ClON_2 donor set, compound **1** adopts a dinuclear di- μ -chlorido arrangement where two mononuclear units having essentially the same arrangement as in **2** establish loose axial $\text{Cu}\cdots\text{Cl}$ interactions, each one of them with the Cl atom of the other one. Compounds **1** and **2** have been tested as reversible

trapping agents for the controlled radical polymerization of styrene under a reverse ATRP approach. Reversible Cl atom transfer leading to a controlled polymerization process is observed, although the controllability is negatively affected by slow radical trapping. A moderate effect on the polymerization rate, once all the radical initiator is consumed, was observed in the presence of excess pyridine (10 equiv per Cu) and interpreted on the basis of the stabilization of the Cu^{I} system.

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Introduction

Copper coordination chemistry with multidentate ligands has recently experienced a revival after the discovery^[1] and intensive development^[2–5] of Cu-mediated controlled radical polymerization. This polymerization strategy rests on the reversible trapping of the growing radical chain, which is accomplished by transfer of a halogen atom from a $\text{Cu}^{\text{II}}\text{-X}$ compound, yielding the corresponding Cu^{I} complex and the halogen-terminated radical chain. The technique is therefore named “atom transfer radical polymerization” (ATRP). The process can be started from stable Cu^{I} complexes, usually made in situ from CuX ($\text{X} = \text{Cl}$ or Br) and a suitable multidentate ligand, plus a halogenated compound $\text{R}_0\text{-X}$ as initiator, in the presence of the polymerizable monomer (so-called ATRP conditions). Alternatively, it can be started from a stable Cu^{II} complex (also usually made in situ from CuX_2 and the appropriate ligand) and a standard radical source, in the presence of the monomer (so-called reverse ATRP conditions).

A recent review, focused on the structural aspects of copper-catalyzed ATRP, shows that the complexes used for this purpose are inevitably made by mixing CuX and CuX_2 with neutral supporting ligands, therefore always containing a halogen atom in the coordination sphere.^[6] Occasionally, the halide is displaced to yield cationic complexes, such as for instance $[\text{Cu}(\text{bipy})_2]^+[\text{OTf}]^-$ or $[\text{Cu}(\text{Me}_6\text{TREN})]^+[\text{OTf}]^-$,^[8] but the introduction of the anionic

functionality into the multidentate ligand itself does not seem to have so far attracted much attention. We wish to explore here the use of anionic multidentate ligands for copper coordination chemistry, starting with the tridentate “ XL_2 ” type. This is the minimum denticity likely to provide stable complexes in both oxidation states, since the $\text{Cu}^{\text{II}}\text{Cl}(\text{XL}_2)$ coordination environment is well established, for instance in Tp^*CuCl ($\text{Tp}^* = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{borate}$),^[9] and the putative 3-coordinate $\text{Cu}^{\text{I}}\text{XL}_2$ system resulting from the halogen atom transfer may be stabilized by dimerization or by monomer coordination, as for instance in $[\text{Tp}^*\text{Cu}]_2$ or $\text{Tp}^*\text{Cu}(\text{olefin})$ complexes.^[10, 11]

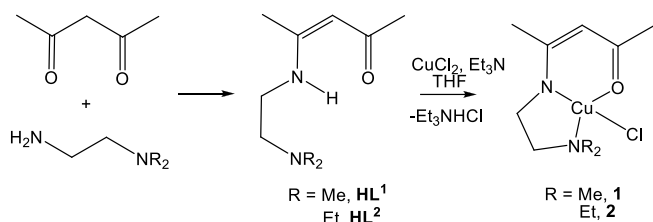
One of the simplest ways to introduce an anionic functionality in a chelating ligand is through deprotonation of a β -diketone such as acetylacetone. Since Cu has greater affinity to N ligands, modification of acetylacetone by introduction of a diamine was envisaged, to yield amine-functionalized β -ketimines, a well known class of ligands that has already been used to generate Cu^{I} derivatives.^[12–15] We report here the synthesis and structural characterization of new copper(II) complexes incorporating these ligands, as well as a preliminary exploration of their ability to control the radical polymerization of styrene under reverse ATRP conditions.

Results and Discussion

Condensation of acetylacetone with one equivalent of $\text{R}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ($\text{R} = \text{Me}$, Et) yielded ligands HL^1 and HL^2 as shown in Scheme 1.^[16–19] Both ligands have recently been used in coordination chemistry with both main group^[17, 19] and transition metals.^[12, 15, 20] The reaction of these ligands with anhydrous CuCl_2 in THF, in the presence of one equivalent of triethylamine, provides a high-yield entry into complexes $\text{CuCl}(\text{L}^1)$, **1**, and $\text{CuCl}(\text{L}^2)$, **2**.

Complex **2** has already been recently described.^[12] It was synthesized in unreported yields by direct interaction of CuCl_2 and HL^2 in acetone at 60–65°C without use of a base and it was only

characterized by IR spectroscopy. Our method uses NEt_3 , allowing the elimination of the generated HCl as Et_3NHCl , which precipitates in THF and can be easily removed by filtration, while the reaction is complete in less than 2 h at room temperature. The two compounds show a sharp EPR spectrum in dichloromethane solution at room temperature (Figure 1a), with the expected 1:1:1:1 hyperfine splitting caused by the $I = 3/2$ Cu nucleus. The dimethylamino derivative **1** reveals also an additional and barely discernible superhyperfine splitting, which may be caused by coupling to one of the N atoms (^{14}N : $I = 1$). The g tensor is tetragonal, as revealed by the spectrum taken at 120 K (Figure 1b), with a large a_{\parallel} and a non discernible a_{\perp} .



Scheme 1.

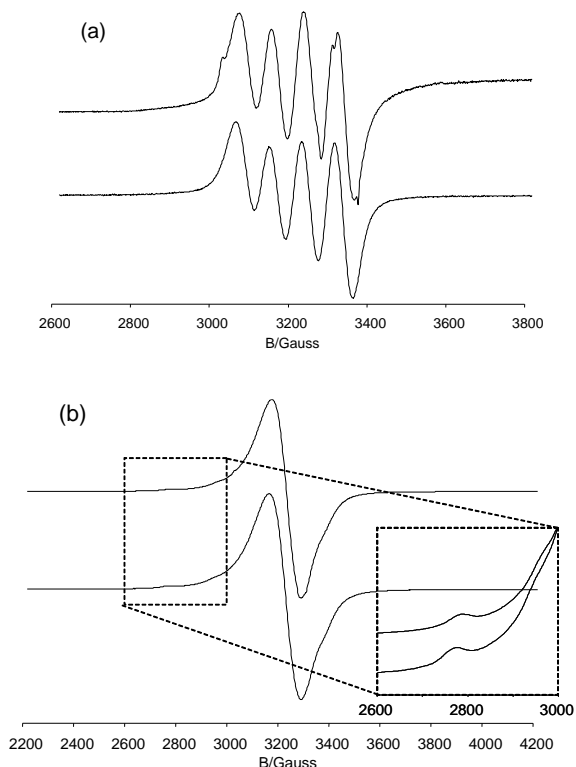


Figure 1. EPR spectra of compounds **1** (below) and **2** (above) in CH_2Cl_2 solution: (a) at room temperature; (b) at 120K.

Both complexes have been structurally characterized by X-ray diffraction. The structural chemistry of these molecules presents an interesting feature related to the nuclearity. Compound **2** is mononuclear and four-coordinate, with a close to square planar coordination geometry. When considering the plane of the electronically delocalized $\text{Cu}(\beta\text{-ketiminato})$ moiety, the donor N atom of the Et_2N moiety deviates only slightly ($0.203(2)$ Å) on one side of the plane, whereas the Cl atom deviates to a greater extent ($0.933(1)$ Å) in the other direction. The *trans* N1-Cu-Cl angle is significantly smaller than 180° [$163.62(4)^\circ$], but the O-Cu-N2

angle is also rather small. The Cl-Cu-O plane makes a dihedral angle of $21.47(7)^\circ$ with the N1-Cu-N2 plane. This distortion appears quite natural for this specific coordination environment. A search on the Cambridge Data Base for other 4-coordinate Cu complexes with a ClON_2 donor set has revealed 42 mononuclear geometries, for which the average value of this specific dihedral angle is $11 \pm 7^\circ$.

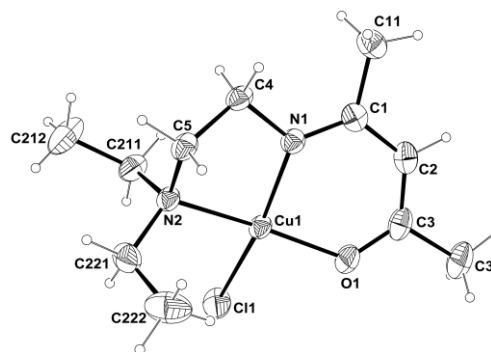


Figure 2. An ORTEP view of the molecule of compound **2**, also showing the numbering scheme used. Thermal ellipsoids are drawn at the 50 % probability level. Main geometrical parameters: Cu-Cl, $2.2458(4)$; Cu-O, $1.9126(10)$; Cu-N1, $1.9404(12)$; Cu-N2, $2.0563(12)$ Å; Cl-Cu-O, $91.92(4)$; Cl-Cu-N1, $163.62(4)$; Cl-Cu-N2, $93.46(4)$; O-Cu-N1, $92.92(5)$; O-Cu-N2, $166.32(5)$; N1-Cu-N2, $85.38(5)^\circ$.

Compound **1**, on the other hand, is dinuclear, with bridging Cl atoms and 5-coordinate Cu centers. The bridging Cu_2Cl_2 moiety is in fact quite asymmetric, with very different Cu-Cl distances. The shorter Cu-Cl distance is only slightly lengthened relative to the Cu-Cl distance in compound **2**. Upon closer look, it is clear that the compound can be described as the dimerization of $\text{CuCl}(\text{L}^1)$ moieties that have a geometry very closely related to that of the mononuclear compound **2**, through loose Cu-Cl^i and $\text{Cu}^i\text{-Cl}$ interactions. Indeed, the coordination geometries around the Cu center in **1** and **2** are strikingly similar, including the deviation of the Cl-Cu-N1 angle from linearity and the dihedral angle between the N1-Cu-N2 and Cl-Cu-O planes from coplanarity ($15.19(6)^\circ$).

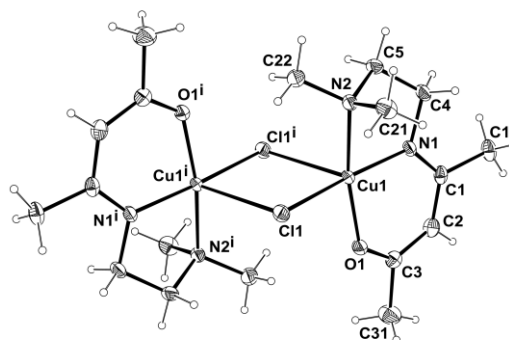


Figure 3. An ORTEP view of the molecule of compound **1**, also showing the numbering scheme used. Thermal ellipsoids are drawn at the 50 % probability level. Main geometrical parameters: Cu-Cl, $2.3202(4)$; Cu-Clⁱ, $2.8442(4)$; Cu-O, $1.917(1)$; Cu-N1, $1.9642(13)$; Cu-N2, $2.0610(13)$ Å; Cl-Cu-Clⁱ, $85.77(1)$; Cl-Cu-O, $88.97(3)$; Cl-Cu-N1, $170.47(4)$; Cl-Cu-N2, $92.65(4)$; Clⁱ-Cu-O, $97.56(4)$; Clⁱ-Cu-N1, $103.40(4)$; Clⁱ-Cu-N2, $95.25(4)$; O-Cu-N1, $92.34(5)$; O-Cu-N2, $167.17(5)$; N1-Cu-N2, $84.02(5)^\circ$.

An interesting question therefore arises: why this nuclearity difference? The existence of the Cu-Clⁱ interactions demonstrates the preference of a dinuclear structure, but their weakness suggests that their establishment may be discouraged by small perturbations. For compound **2**, for which the shortest intermolecular contacts of the Cl atom are established with C-H bonds of neighboring diethylaminoethyl moieties, the small perturbation is undoubtedly caused by the steric repulsion that the ethyl substituents would experience in a dinuclear structure. Indeed, the space filling model of compound **1**, shown in Figure 4, indicates how one of the NMe₂ methyl groups in one half of the molecule (right arrow) finds itself in close proximity with the methyl group of the keto group in the other half of the molecule (left arrow), suggesting that a similar structure may not be sufficiently favoured with the bulkier NEt₂-substituted ligand. It is then also interesting to re-examine the related mononuclear Cu structures containing a ClON₂ ligand set already described in the literature, to identify the perturbation impeding dimerization in those cases.

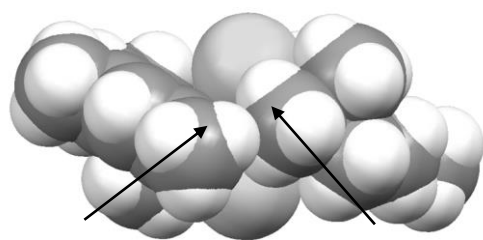


Figure 4. A space-filling view of the structure of compound **1**.

For a few compounds, the authors reported a 4-coordinate structure without realizing the presence of a loose axial interaction with an interstitial solvent molecule. This is the case for a few “methanol solvates”, with Cu-O distances to the axially bonded MeOH ligand as little as 2.27 Å.^[21-23] For another three compounds, the structure was described as mononuclear but it is in fact halide-bridged dinuclear, just like **1**, with “loose” Cu-X distances of 2.61^[24] and 2.84^[25] Å (X = Cl), or 3.09^[26] Å (X = Br). In other cases, although axial donor atoms are far away for detection as bonding interactions (distance greater than the sum of van der Waals radii), the donor atom (Cl but sometimes also O) is correctly positioned to provide some axial electron density to the Cu center in 2D or 3D packing arrangements.^[27-32] Interesting situations are presented by other structures that, like that of compound **2**, are genuinely mononuclear, without significant additional contacts to the 4-coordinate Cu^{II} center. A few of these are polyaromatic compounds with delocalized planar ligands, which always display a π -stacking arrangement.^[33-40] This indicates that intermolecular π -stacking interactions provide better stabilization to the crystal structure than the halide-bridge formation. In other cases, the dinuclear structure simply does not form because of the presence of a bulky group near the Cu center, either an NEt₂ group like in compound **2**,^[41, 42] or another bulky group.^[31, 43, 44]

The structure of compound **1** is identical to that of compound [Cu(L¹)(O₂CPh)]₂,^[15] where the benzoate ligand occupies the same position as the Cl ligand in **1** by adopting a bridging monodentate ($\kappa^1:\mu$) coordination mode, also with very different distances to the two Cu atoms (1.984(2) Å for the strong equatorial bond, 2.788 Å for the loose axial bond). The Cu-N2 bond (2.064(3) Å) is essentially identical to that in **1**, whereas the Cu-N1 bond (1.914(3) Å) is significantly shorter and the Cu-O1 (1.944(3) Å) is

significantly longer. The structure of **2**, on the other hand, may be directly compared with that of compound CuCl[Et₂NCH₂CH₂N-C(Me)CHC(Ph)O], the two compounds differing only by the nature of the substituent at the keto position (Ph vs. Me).^[31] In the Ph substituted compound, the Cu-Cl distance is significantly longer (2.300 Å), while the Cu-N1 distance (1.956 Å) is marginally longer and the Cu-O (2.107 Å) and Cu-N2 (1.992 Å) distances are marginally shorter. The *trans* Cl-Cu-N1 angle (164.8°) is quite similar to that in **1**.

Compounds **1** and **2** have been tested as controlling agents for the radical polymerization of styrene under reverse ATRP conditions. The first experiments carried out at 80°C, with primary radicals generated from 2,2'-azobisisobutyronitrile (AIBN, $t_{1/2}$ = ca. 70 min), are shown in Figure 5a.

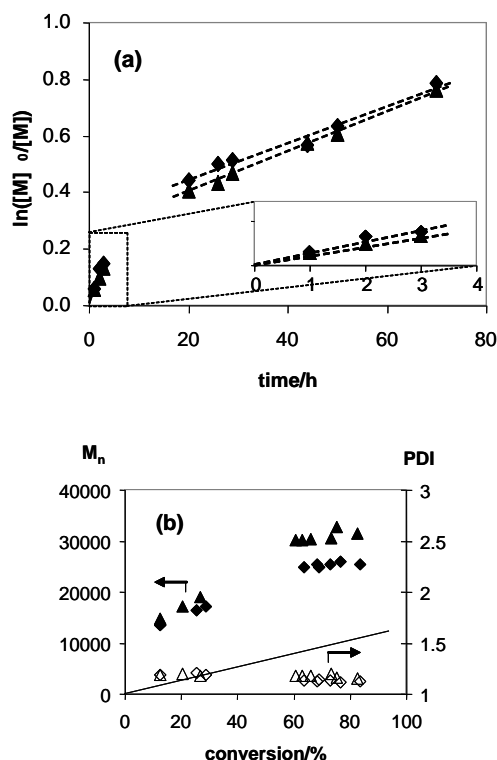


Figure 5. (a) First-order kinetic plot and (b) M_n (filled symbols) and PDI (hollow symbols) vs. conversion for the radical polymerization of styrene in the presence of compounds **1** (triangles) or **2** (diamonds). The straight line in plot (b) indicates the theoretical molecular weight ($M_{R^+} + M_M \cdot (n_M/n_{Cu}) \cdot p + M_{Cl}$; where M_{R^+} , M_M and M_{Cl} are the molar masses of primary radical, monomer and Cl atom, respectively, p is the degree of conversion, and (n_M/n_{Cu}) is the molar ratio of monomer and Cu). Conditions: 50% (v/v) in toluene, 80°C, [styrene]:[AIBN]:[Cu] = 200:0.8:1.

Several features of the two plots shown in Figure 5 deserve discussion. The first and most important one is that polymerization occurs and is sustained well beyond the time required to completely consume the radical initiator (6-7 h) in the presence of both compounds. Together with the continued increase of the number-average molecular weight and the low polydispersities of the resulting polymers at high conversion, this represents evidence that the radical chains are continuously generated from a dormant species and that the polymerization is controlled. Note that the first order kinetics plot indicates linearity in the high conversion region (after completely consuming the initiator), in agreement with a constant radical concentration in solution and with the occurrence of the ATRP mechanism. At low conversions (short times), on the other hand, the polymerization is faster. In addition, the molecular

weights at low conversions are much greater than the expected values, but subsequently continue to grow at approximately the expected growth rate, while the polydispersity remains narrow throughout the polymerization process (< 1.2), see Figure 5b. This phenomenon can be ascribed to a slow trapping rate, generating chains of much higher molecular weight than expected during the initial phase of initiator decomposition. The relatively long initial phase of initiator decomposition (6-7 half-lives, namely 6-7 hours) entails the continuous generation of new radical chains throughout this period, but the molecular weight distribution does not appear to be too negatively affected by this initial phase or poor control.

The polymerization proceeds at approximately the same rate in the presence of compounds **1** and **2**, both before and after depletion of the radical initiator (see Figure 5a), indicating that the activation/deactivation equilibrium is very similar for both copper compounds. In relation to the above described structural study of the two Cu^{II} complexes, it is clear that the weak dichlorido-bridged interaction revealed for compound **1** does not play a major role in this process, as also indicated by the identical EPR spectroscopic properties of the two compounds in solution.

The putative Cu^{I} catalyst generated by Cl atom transfer to the radical chain is a three-coordinated complex where the constraints of the ligand bite do not allow the metal center to adopt a preferred trigonal planar configuration. Although, as mentioned in the introduction, the complex may be stabilized by dimerization or by coordination of a monomer molecule, we wondered whether the addition of Lewis bases such as pyridine (py) or bipyridine (bipy) could affect the polymerization rate and controllability.

Because of the identical solution properties and polymerization results of compounds **1** and **2**, additional experiments in the presence of py or bipy were only carried out with the ethyl-substituted complex **2**. The results (Figure 6) indicate a negligible effect on the reaction rate when using only 1 equiv of either additive. The difference between the three experiments may be considered to fall within the margins of the experimental error. The trends of M_n and PDI as a function of conversion were also sensibly identical for the three experiments. When the py/Cu ratio was increased to 10, however, the polymerization was significantly retarded in the second period, after full consumption of the initiator, whereas the behaviour was once again identical before full consumption of the radical initiator. Therefore, it appears that the three-coordinate Cu^{I} complex generated by Cl atom transfer, $\text{Cu}(\text{L})_2$, can be stabilized by the Lewis base additive as shown in Scheme 2, the overall effect being a shift of the deactivation equilibrium toward the Cu^{I} form. The absence of a notable effect on the rate during the first polymerization period is in agreement with the prediction that the Lewis additive action is restricted to the Cu^{I} stabilization and does not affect the rate of Cl atom transfer from compound **2** to the growing radical chain (deactivation, k_d).

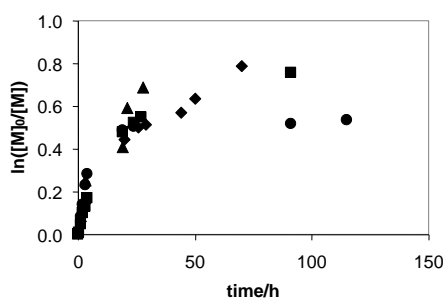
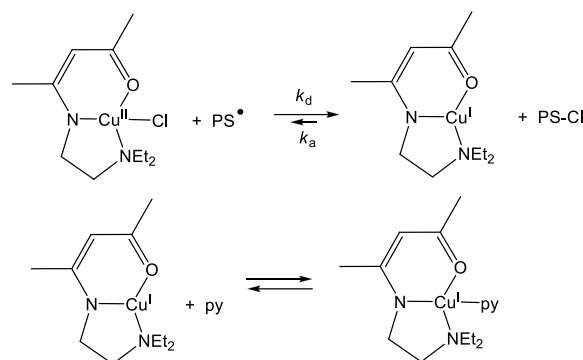


Figure 6. First-order kinetic plot for the radical polymerization of styrene in the presence of compound **2** alone (diamonds) or together with py (1 equiv, triangles; 10 equiv, spheres) or bipy (1 equiv, squares). Conditions are the same as in Figure 5.

An additional experiment was carried out in the presence of compound **2** and py (1 equiv) at lower temperature (30°C). In this case, 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), V-70, was used as radical initiator ($t_{1/2} = 10$ h). The results are compared with those obtained at 80°C in Figure 7. The polymerization rate is slower as expected. Once again, the process is sustained beyond the time needed to fully deplete the radical initiator (ca. 70 h for V-70 at 30°C), with a visible breakpoint in the reaction rate, indicating reversible reactivation of the dormant chains by atom transfer to Cu^{I} . However, the controllability is not improved, as shown by the fact that the polymer M_n is still large relative to the theory while the PDI is greater relative to the experiment at 80°C . The reason for this result is that, while controllability in the second polymerization period is expected to increase, the lower temperature also causes a slower deactivation rate, negatively affecting the molecular weight distribution in the first polymerization period.



Scheme 2.

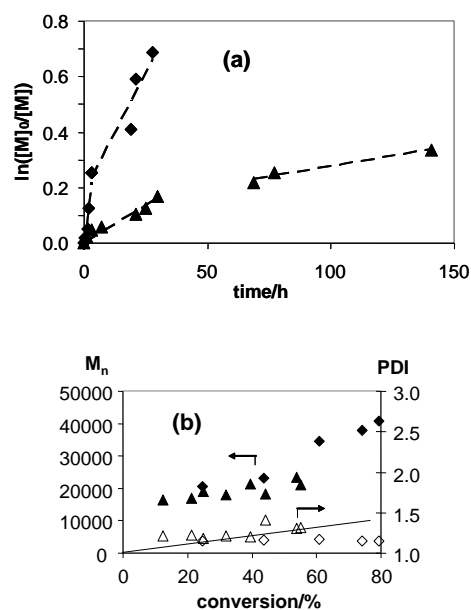


Figure 7. (a) First-order kinetic plot and (b) M_n (filled symbols) and PDI (hollow symbols) vs. conversion for the radical polymerization of styrene in the presence of compound **2** and py (py/Cu = 1) at 80°C (diamonds) and 30°C (triangles). The straight line in plot (b) indicates the theoretical molecular weight ($M_{R^*} + M_{M^*}(n_M/n_{Cu}) \cdot p + M_{Cl}$; where M_{R^*} , M_{M^*} and M_{Cl} are

the molar masses of primary radical, monomer and Cl atom, respectively, p is the degree of conversion, and (n_M/n_{Cu}) is the molar ratio of monomer and Cu. Conditions for the experiment at 30°C: 50% (v/v) in toluene, [styrene]:[V-70]:[Cu] = 200:0.8:1.

The slow radical trapping by complexes **1** and **2** may be directly related to the unsuitable geometry of the three-coordinate Cu^I species that is formed by Cl atom transfer. As it has been previously pointed out, the best systems for rapid radical deactivation, which is crucial for good controllability, are those where the coordination geometry changes in a minimal way on going from $L_n/Cu^{II}-Cl$ to L_n/Cu^I , while the electronic properties and the coordination geometry of the L_n coordination sphere are most suitable to the Cu^I species. In our case, the situation is quite the opposite, since the L^1 and L^2 ligands yield a suitable coordination environment for the Cu^{II} system in combination with the Cl atom but are not at all adapted to the Cu^I system.

Conclusions

We have prepared and characterized two neutral 4-coordinated Cu^{II} monochloride complexes, disclosing new structural features related to weak intermolecular $Cu\cdots Cl$ bonding and discussing the criteria allowing this interaction to occur in these and other related complexes previously described in the literature. These complexes have been tested as reversible trapping agents for growing polystyrene radical chains under reverse ATRP conditions. While the systems are negatively affected by a slow trapping rate, the principle of reversible atom transfer leading to a controlled radical polymerization has been demonstrated. The trapping rate is expected to be accelerated by using other tridentate “ XL_2 ” ligands with greater bites, thus adapting to a trigonal planar coordination for Cu^I , or perhaps even better by moving to tetradentate “ XL_3 ” ligand that would stabilize Cu^I in a tetrahedral environment. Research in our laboratory is now oriented along these directions.

Experimental Section

General: All solvents used in the reactions were distilled under argon. The NMR spectra were recorded on Bruker ARX 250 and AV300 instruments. Chemical shifts are expressed in ppm downfield from Me_4Si . Coupling constants are given in Hertz. The EPR spectra were measured on a Elexsys E500 BRUKER spectrometer (X-band) equipped with both a frequency-meter and gauss-meter. Acetylacetone, *N,N*-dimethylethylenediamine, *N,N*-diethylethylenediamine and $CuCl_2$ were purchased from Sigma-Aldrich and used as received. Styrene (Sigma-Aldrich) was dehydrated by passing through a neutral alumina column and then stirred on CaH_2 for 1 day, followed by distillation under argon.

Synthesis of $Me_2NCH_2CH_2NHC(Me)=CHC(Me)=O$, HL^1

In a 500 ml round-bottomed flask equipped with a condenser, 29.3 g (0.29 mol) of acetyl acetone and 26 g (0.29 mol) of *N,N*-dimethylethylenediamine in 250 ml of benzene were refluxed for 48 h to yield an intense yellow solution. The conversion was monitored through measurement of the water removed from the reaction through a Dear-Stark apparatus. The reaction starts immediately, as suggested by the color change but two days of reflux were necessary to complete it. The solvent was then removed to yield an intense yellow-colored liquid. Distillation at 115 °C yielded the product as a yellow oil. Yield: 47.1 g (95.5%). 1H -NMR (C_6D_6 , 250 MHz): δ 11.1 (s(br), 1H, NH), 4.98 (s, 1H, $CH_3CCHCCH_3$), 2.93 (q, 2H, $J = 6.2$ Hz, $NHCH_2CH_2$), 2.15 (t, 2H, $J = 6.5$ Hz, $NHCH_2CH_2$), 2.08 (s, 3H, CH_3CO), 2.06 (s, 6H, $N(CH_3)_2$), 1.63 (s, 3H, CH_3CN). ^{13}C -NMR (C_6D_6 , 62.90 MHz): δ 193.6, 161.5, 95.0, 58.9, 45.2, 40.9, 28.7, 18.4.

Synthesis of $Et_2NCH_2CH_2NHC(Me)=CHC(Me)=O$, HL^2

In a 500 ml round-bottomed flask equipped with a condenser, 29.3 g (0.29 mol) of acetylacetone and 34 g (0.29 mol) of *N,N*-diethylethylenediamine in 250 ml of benzene were refluxed for 48 h to yield an intense yellow solution. The conversion was monitored through measurement of the water removed from the reaction through a Dear-Stark apparatus. The reaction starts immediately, as suggested by the color change but two days of reflux were necessary to complete it. The solvent was then removed to yield an intense yellow-colored liquid. Distillation at 145°C yielded the product as a yellow oil. Yield: 49.7 g (87.6%). 1H -NMR (C_6D_6 , 300 MHz): δ 11.1 (s, 6H), 4.98 (s, 1H, $CH_3CCHCCH_3$), 2.93 (q, 2H, $J = 6.2$ Hz, $NHCH_2CH_2$), 2.37 (q, 4H, $J = 7.2$ Hz, $N(CH_2CH_3)_2$), 2.34 (t, 2H, $J = 6.6$ Hz, $NHCH_2CH_2$), 2.08 (s, 3H, CH_3CO), 1.64 (s, 3H, CH_3CN), 0.98 (t, 6H, $J = 7$ Hz, $N(CH_2CH_3)_2$). $^{13}C\{^1H\}$ -NMR (C_6D_6 , 75.47 MHz): δ 193.5, 161.4, 95.0, 52.9, 47.3, 41.5, 28.7, 18.5, 12.1.

Synthesis of compound $CuCl(L^1)_2$, **1**

To a solution of $CuCl_2$ (5 g, 0.038 mol) in 10 ml of THF, a solution of HL^1 (7.5 g, 0.038 mol in 10 ml of THF) was added, followed by stirring for 1 h at room temperature. The solution became dark green. Then, 5.5 ml (0.04 mol) of Et_3N was added, followed by stirring for another 1 h, resulting in the formation of a white precipitate ($Et_3NH^+Cl^-$), which was then removed by filtration. The solvent was partially removed under reduced pressure to about 5 ml and slow diffusion of hexane gave black crystals suitable for analysis and for the X-ray diffraction analysis. Yield: 9.1 g (98.1%). Anal. Calcd. for $C_9H_{17}ClCuN_2O$: C, 40.30; H, 6.39; N, 10.44 %. Found: C, 39.6; H, 6.8; N, 10.3 %. EPR (CH_2CH_2 , rt): $g = 2.097$; $a_{Cu} = 83.4$ G. EPR (CH_2CH_2 , 120 K): $g_{\parallel} = 2.20$ ($a_{\parallel} = ca. 190$ G), $g_{\perp} = 2.08$.

Synthesis of compound $CuCl(L^2)_2$, **2**

To a solution of $CuCl_2$ (5 g, 0.038 mol) in 10 ml of THF, a solution of HL^2 (6.5 g, 0.038 mol in 10 ml of THF) was added, followed by stirring for 1 h at room temperature. The solution became dark green. Then, 5.5 ml (0.04 mol) of Et_3N was added, followed by stirring for another 1 h, resulting in the formation of a white precipitate ($Et_3NH^+Cl^-$), which was removed by filtration. The solvent was partially removed under reduced pressure to about 5 ml and slow diffusion of hexane gave black crystals suitable for analysis. Yield: 4.8 g (57.9%). Anal. Calcd. for $C_{11}H_{21}ClCuN_2O$: C, 44.59; H, 7.14; N, 9.45 %. Found: C, 44.0; H, 7.7; N, 9.4 %. EPR (CH_2CH_2 , rt): $g = 2.098$; $a_{Cu} = 81.4$ G. EPR (CH_2CH_2 , 120 K): $g_{\parallel} = 2.20$ ($a_{\parallel} = ca. 180$ G), $g_{\perp} = 2.09$.

Standard procedure for the polymerization experiments

The polymerizations were conducted in pre-dried Schlenk flasks. The solids (complexes, initiators and bipyridine) and a stirring bar were added, and then the flask was sealed with a glass septum. Oxygen was removed from the flask by applying vacuum and backfilling with argon (three cycles). The monomer and the solvents (pyridine, toluene and dodecane) were added via syringe. The solution was degassed by three freeze-pump-thaw cycles. A first sample was removed as reference and the flask immersed in an oil bath held by thermostat at the desired temperature. At timed intervals, samples were removed from the flask by syringe and diluted into THF. Every sample was filtered through neutral alumina to remove the catalyst. A small amount of this THF solution was used to determine the monomer conversion by gas chromatography (GS) with dodecane as an internal standard. From the remaining sample, the polymer product was precipitated by adding into excess MeOH. The precipitate was collected and analyzed by GPC-SEC.

X-ray crystallography

A single crystal of each compound was mounted under inert perfluoropolyether on the tip of a glass fibre and cooled in the cryostream of either an Oxford-Diffraction XCALIBUR CCD diffractometer for **1** or an Oxford-Diffraction GEMINI CCD diffractometer for **2**. Data were collected using the monochromatic $MoK\alpha$ radiation ($\lambda = 0.71073$). The structures were solved by direct methods (SIR97)^[45] and refined by least-squares procedures on F^2 using SHELXL-97.^[46] All H atoms attached to carbon

were introduced in calculation in idealised positions and treated as riding models. The drawing of the molecules was realised with the help of ORTEP32.^[47] The crystal data and structure refinement parameters for both compounds are listed in Table 1.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 800731 & 800732. 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).

Table 1. Crystal data for compounds **1** and **2**.

Compound	1	2
Empirical formula	C ₉ H ₁₇ ClCuN ₂ O	C ₁₁ H ₂₁ ClCuN ₂ O
Formula weight	268.24	296.30
Temperature, K	180(2)	180(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P 2 ₁ /n	P 2 ₁ /n
a, Å	10.2397(4)	10.2616(3)
b, Å	9.6133(4)	9.7014(3)
c, Å	12.3296(5)	14.1431(4)
α, °	110.201(4)	103.053(3)
Volume, Å ³	1139.03(8)	1371.59(7)
Z	4	4
D (calcd), Mg/m ³	1.564	1.435
Abs. coeff., mm ⁻¹	2.122	1.770
F(000)	556	620
Crystal size, mm ³	0.12x0.11x0.07	0.44x0.34x0.31
Theta range, °	2.75 to 28.32°	3.48 to 29.12°
Reflts collected	12338	15349
Unique reflts [R(int)]	2646 (0.0266)	3263 (0.0228)
Completeness, %	93.3	94.2
Abs. correction	Multi-scan	Multi-scan
Max. / min. transm.	1.00000, 0.74280	1.00000, 0.86185
Refinement method	F ²	F ²
Data / restr. / param.	2416 / 0 / 131	3204 / 0 / 149
Goodness-of-fit on F ²	1.101	1.103
R, wR2 [I>2σ(I)]	0.0224, 0.0601	0.0217, 0.0607
R, wR2 (all data)	0.0264, 0.0616	0.0289, 0.0619
Resid. density, e.Å ⁻³	0.287 and -0.611	0.415 and -0.269

Supporting Information: Tables of conversions, molecular weights and polydispersity index for the all polymerization experiments (2 pages).

Acknowledgments

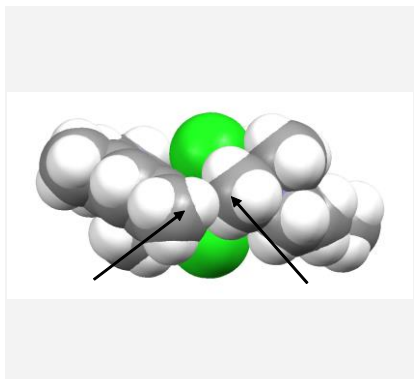
We are grateful to the Agence National de la Recherche (Programme ANR Blanc "OMRP", 2010-13), the Centre National de la Recherche Scientifique (CNRS) and the Institut Universitaire de France (IUF) for support of this work and to the Politecnico, Milan, Italy for an Erasmus exchange fellowship to SG. We also thank Dr. Zhigang Xue and Mr Andrés F. Cardozo for technical assistance.

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Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Neutral monochloride Cu^{II} complexes with dialkylaminoethyl-functionalized β -ketiminato ligands have been synthesized and shown to control the radical polymerization of styrene under reverse ATRP conditions. A structural comparison between the dimethyl and diethylamino compounds reveals a delicate balance between mononuclear and dinuclear arrangements in the solid state.



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Synthesis and structure of 4-coordinate copper(II) complexes stabilized by β -ketiminato ligands and application in the reverse ATRP of styrene

Keywords: Copper / Functionalized β -ketimidato ligands / Controlled Radical Polymerization / ATRP / Polystyrene

