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PII: DOI: Reference:	S0277-5387(17)30031-1 http://dx.doi.org/10.1016/j.poly.2017.01.018 POLY 12422			
To appear in:	Polyhedron			
Received Date:	12 October 2016			
Revised Date:	11 January 2017			
Accepted Date:	11 January 2017			



Please cite this article as: Z. Hao, A. Ma, B. Xu, W. Gao, Y. Mu, Cu(II) Complexes with Anilido-Imine ligands: Synthesis, Characterization and Catalysis on Reverse Atom Transfer Radical Polymerization of Styrene, *Polyhedron* (2017), doi: http://dx.doi.org/10.1016/j.poly.2017.01.018

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Cu(II) Complexes with Anilido-Imine ligands: Synthesis, Characterization and Catalysis on Reverse Atom Transfer Radical Polymerization of Styrene

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Abstract

Several bearing bidentate anilido-imine copper(II) complexes ligands $[(Ar'N=CHC_6H_4-NAr)Cu]_2(\mu-Cl)_2$ (Ar = Ar' = 2,6-Me_2C_6H_3 (1a); Ar = Ar' = 2,6-Et₂C₆H₃ (**1b**); Ar = 3,5-(CF₃)₂C₆H₃, Ar' = 2,6-ⁱPr₂C₆H₃ (**1d**); Ar = p-OMeC₆H₄, Ar' $= 2,6^{-i}Pr_2C_6H_3$ (1e)), (Ar'N=CHC_6H_4-NAr)CuCl (Ar = Ar' = 2,6^{-i}Pr_2C_6H_3 (1c)), and that bearing tridentate quinolinyl anilido-imine ligand $(2,6-^{i}Pr_{2}C_{6}H_{3}N=CHC_{6}H_{4}-NAr)CuCl$ (Ar = 8-quinolinyl (1f)) were synthesized via reactions of the corresponding ligands with ⁿBuLi and subsequent in-situ addition of CuCl₂. The X-ray diffraction analysis revealed that **1a** and **1d** are dinuclear, while **1f** with N, N, N-tridentate ligand is in monomeric form. In the presence of 2,2'-azobisisobutyronitrile (AIBN), these well-defined complexes showed moderate to high activities in reverse ATRP of styrene. High conversions up to 86.5% were obtained and polymers with controllable molecular weight and relatively narrow polydispersity were produced.

Keywords: Copper complexes; Reverse-ATRP; Anilido-imine ligands

1. Introduction

Atom transfer radical polymerization (ATRP), discovered independently by Sawamoto and Matyjaszewski in 1995, have received considerable attention in the controllable polymerization area due to its broad range of applicable monomers, high initiation efficiency, precise control of molecular weights, and mild reaction conditions.[1] In ATRP, some transition metal complexes were used to control the radical concentration at very low levels, thereby reduce the impact of irreversible bimolecular terminations through the establishment of a shuttle between the active radical chain and a dormant chain that is capped by a halogen atom.[1, 2] In this process, a lot of alkyl halide were used as the resource of radical. In order to minimize the amount of alkyl halide in the polymerization, the reverse ATRP using the conventional radical generator and metal complexes were developed.[3] Various complexes based on Cu,[4] Fe,[5] Ni,[6] and Ru[7] were widely investigated and used as catalyst in ATRP and reverse ATRP, in which the copper complexes have received special attention due to their high activities. On the other hand, it is well accepted that the ligands in the catalysis systems can not only solubilize the transition-metal complexes in the organic media but also adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer.[5a] In literatures, various ligands are used to support the metal complexes, in which the nitrogen ligands were mainly used for copper- and iron-mediate ATRP, while the phosphorus-based ligands are mostly used for other transition metals such as rhenium, ruthenium,

rhodium, nickel, and palladium. The nitrogen-based ligands work particularly well for copper-mediated ATRP, and it is well established that the coordination chemistry shows great influence on the catalysis behavior of the complexes. For example, the activity of copper complexes based on N-based ligands in ATRP decreases with the number of coordinating sites as well as the number of linking carbon- atoms.[1e]

Recently we focused on the anilido-imine ligands, which features easy preparation and fine-tuning of the steric and electronic properties at the metal centers. The rare-earth-metal,[13] aluminum and zinc,[14] nickle,[15] and chromium[16] complexes based on the anilido-imine ligands were proved to show moderate to high activities in ε -caprolactone (lactide) ring-opening polymerization, norbornene polymerization, and ethylene polymerization respectively. More recently, the iron(II) complexes supported by these ligands have been demonstrated to be active for the atom transfer radical polymerization (ATRP) of MMA. [17] Although, some copper complexes bearing anilido-imine ligands have been reported,[18] their structure features and catalysis performance were less focused. In extending this research, the current study reports on the synthesis and full characterization of Cu(II) complexes bearing anilido-imine ligands. The catalytic behaviors of these Cu(II) complexes toward reverse ATRP polymerization of styrene are also presented.

2. Experimental

2.1. General procedures and methods

All manipulations involving air and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk or dry box techniques. Toluene and hexane were dried over sodium/benzophenone and

distilled under nitrogen prior to use. Elemental analyses were performed on a Varian 12EL microanalyzer. NMR spectra were recorded on a Bruker-400 NMR spectrometer at room temperature in CDCl₃. The molecular weight and molecular weight distribution of the polymers were measured on a TOSOH HLC 8220 GPC at 40 °C using THF as eluent at a flow rate of 1.0 mL/min. Polystyrene standards were used for calibrations. The ligands L_aH , L_bH , L_cH , and L_fH were synthesized according to the literature.[17]

2.2 ligands preparation and characterization

2.2.1. Preparation of L_dH

An ⁿBuLi solution of hexane (8.3 mL, 16.5 mmol) was added to a THF (30 mL) solution of 3,5-bis(trifluoromethyl)aniline (3.44 g, 15 mmol) at -40 °C, and the mixture was allowed to warm to room temperature overnight and then transferred into a THF (20 mL) solution of *ortho*-C₆H₄F(CH=NC₆H₃ⁱPr₂-2,6) (2.83 g, 10 mmol) at room temperature. After stirring for 24 h at 50 °C, the reaction mixture was quenched with 20 mL of H₂O, The organic solution was dried with anhydrous MgSO₄ and the solvent was removed in vacuum to give a residue. Treatment of the residue with column chromatography on silica gel eluting with petroleum ether affords the L₄H as yellow powder. Yield 2.07 g (42%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 1.18 (d, 12H, CH(CH₃)₂), 2.97–3.03 (m, 2H, CH(CH₃)₂), 7.01 (t, 1H, Ar-*H*), 7.16–7.23 (m, 3H, Ar-*H*), 7.41–7.50 (m, 4H, Ar-*H*), 7.66 (s, 2H, Ar-*H*), 8.33 (s, 1H, Ar-C*H*=N), 11.56 (s, 1H, Ar-N*H*). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 23.56 (s, 4C, ArC(CH₃)₂), 28.20 (s, 2C, ArC(CH₃)₂), 113.66, 115.32, 119.60, 121.93, 123.35, 124.64, 125.05, 132.30,

132.61, 132.94, 133.27, 135.13, 138.18, 143.07, 144.05, 147.82, 165.68 (s, 1C, *C*H=N) ppm.

2.2.2. Preparation of LeH

An ⁿBuLi solution of hexane (8.3 mL, 16.5 mmol) was added to a THF (30 mL) solution of 4-methoxyaniline (1.85 g, 15.0 mmol) at -30 °C, and the mixture was allowed to warm to room temperature overnight. The resulted lithium-salt solution was slowly transferred into a solution of *ortho*-C₆H₄F(CH=NC₆H₄¹Pr₂-2,6) (2.83 g, 10.0 mmol) in 20 mL of THF at room temperature. After stirring for 12 h at 50 °C, the reaction was quenched with 15 mL of water, extracted with ethyl acetate, and evaporated to dryness in vacuum affording a yellow solid. The solid was crystallized from methanol to give L_eH as yellow crystals. Yield 2.75 g (71.2%). NMR (400 MHz, CDCl₃, 25 °C): δ 1.19 (d, 12H, CH(CH₃)₂), 3.02–3.09 (m, 2H, CH(CH₃)₂), 3.81 (s, 3H, Ar-OMe), 6.76 (t, 1H, Ar-H), 6.92 (d, 2H, Ar-H), 7.10–7.27 (m, 7H, Ar-H), 7.34 (d, 1H, Ar-H), 8.30 (s, 1H, Ar-CH=N), 10.92 (s, 1H, Ar-NH). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 23.57 (s, 4C, ArC(CH₃)₂), 28.11 (s, 2C, ArC(CH₃)₂), 55.54 (s, 1C, Ar-OCH₃), 112.15, 114.64, 116.16, 117.28, 123.11, 124.45, 125.29, 132.07, 133.69, 134.89, 138.19, 147.92, 148.61, 156.41, 165.49 (s, 1C, CH=N) ppm.

2.3. Preparation and characterization of copper complexes

2.3.1 Preparation of complex 1a

A hexane solution of ⁿBuLi (2.00 M in hexane, 0.50 mL, 1.0 mmol) was added dropwise to a solution of the free ligand L_aH (0.33 g, 1.0 mmol) in 20 mL of THF at -78 °C. After stirred for 1 h, the reaction mixture was gradually warmed to -40 °C

and then CuCl₂ (0.14 g, 1.0 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature and stirred overnight. Evaporation of the solvent and crystallization of the residues with toluene/hexane mixed solvent afford the copper complex **1a** as brown powder (0.63 g, 73.7%). Single crystals for X-ray analysis were grown from dichloromethane/hexane at -30 °C within several days as brown blocks. Anal. Calcd for C₄₆H₄₆Cl₂N₄Cu₂ (%): C, 64.78; H, 5.44; N, 6.57 Found: C, 64.65; H, 5.58; N, 6.62. IR(KBr): v (cm⁻¹) 3123s, 3009m, 1609m, 1578m, 1460m, 1399vs, 1227w, 1163s, 1087w, 1037w, 772m, 743m, 670w.

2.3.2 Preparation of complex 1b

Complex **1b** was prepared in a similar procedure to that for preparation of **1a**. Treatment of L_bH (0.39 g, 1.0 mmol) in 25 mL THF with ⁿBuLi (2.0 M in hexane, 0.50 mL, 1.0 mmol) and then in situ addition of CuCl₂ (0.14 g, 1.0 mmol) yield **1b** in a 74.6% yield (0.72 g). Anal. Calcd for C₅₄H₆₂Cl₂N₄Cu₂: C, 67.20; H, 6.48; N, 5.81. Found: C, 67.33; H, 6.58; N, 5.69. IR(KBr): v (cm⁻¹) 3130m, 2959s, 2834m, 1733s, 1460s, 1378s, 1243w, 1173m, 1071w, 837m, 814m, 744w, 619w.

2.3.3 Preparation of complex 1c

Following the same procedure described for **1a**, treatment of L_cH (0.44 g, 1.0 mmol) with ⁿBuLi (2.0 M in hexane, 0.50 mL, 1.0 mmol) and then in situ addition of CuCl₂ (0.14 g, 1.0 mmol) afford complex **1c** in a 76.7% yield (0.83 g). Anal. Calcd for $C_{31}H_{39}ClN_2Cu:C$, 69.12; H, 7.30; N, 5.20. Found: C, 68.94; H, 7.42; N, 5.03. IR(KBr): v (cm⁻¹) 3158m, 2979s, 2827s, 2737w, 1734s, 1462m, 1416vs, 1249w, 1174m, 992m, 832m, 734w, 612w.

2.3.3 Preparation of complex 1d

Following the same procedure described for **1a**, treatment of L_dH (0.49 g, 1.0 mmol) with ⁿBuLi (2.0 M in hexane, 0.50 mL, 1.0 mmol) and then in situ addition of CuCl₂ (0.14 g, 1.0 mmol) afford **1d** as brown powder (0.86 g, 72.8%). Single crystals for X-ray analysis were grown from hexane at -30 °C within several days as brown blocks. Anal. Calcd for C₅₄H₅₀Cl₂F₁₂N₄Cu₂: C, 54.92; H, 4.27; N, 4.74. Found: C, 54.80; H, 4.37; N, 4.59. IR(KBr): v (cm⁻¹) 3145m, 2971s, 2819m, 1728s, 1454m, 1401vs, 1264m, 1166m, 1006w, 969m, 809m, 748w.

2.3.3 Preparation of complex 1e

Following the same procedure described for **1a**, treatment of L_eH (0.39 g, 1.0 mmol) with ⁿBuLi (2.0 M in hexane, 0.50 mL, 1.0 mmol) and then in situ addition of CuCl₂ (0.14 g, 1.0 mmol) afford **1e** as brown powder (0.71 g, 73.4%). Anal. Calcd for $C_{52}H_{58}Cl_2Cu_2N_4O_2$: C, 64.45; H, 6.03; N, 5.78 Found: C, 64.60; H, 5.87; N, 5.92. IR(KBr): v (cm⁻¹) 3138m, 2953s, 2815m, 1739s, 1462m, 1399s, 1260m, 1143m, 1059w, 962m, 837m, 664w.

2.3.3 Preparation of complex 1f

Following the same procedure described for **1a**, treatment of L_fH (0.41 g, 1.0 mmol) with ⁿBuLi (2.0 M in hexane, 0.50 mL, 1.0 mmol) and then in situ addition of CuCl₂ (0.14 g, 1.0 mmol) afford **1f** as purple powder (0.40 g, 78.9%). Red crystals for X-ray analysis were grew from the mixture of toluene and dichloromethane/hexane at -30 °C within several days. Anal. Calcd for C₂₈H₂₈ClN₃Cu: C, 66.52; H, 5.58; N, 8.31. Found: C, 66.68; H, 5.44; N, 8.42. IR(KBr): v (cm⁻¹) 3131m, 2940w, 1590m, 1468s,

1395vs, 1340m, 1160s, 1089w, 832w, 740m, 657w.

2.4. Polymerizations

In the glovebox, a Schlenk tube was loaded with the catalyst and then corresponding equivalent of styrene, AIBN and toluene were added in sequence. The tube was then immersed in an oil at the desired temperature to polymerize under stirring. After the desired time, the reaction was poured into 30 mL of cold ethanol, filtered, washed with plenty of ethanol, and dried under vacuum.

2.5. Crystal structure determination

The crystals were mounted on a glass fiber using the oil drop. Data obtained with the ω -2 θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods, and refined with full-matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. All calculations were performed using the SHELXTL crystallographic software packages. [19]

3. Results and discussion

3.1. Synthesis and characterization of the Cu(II) complexes

The ligands L_aH , L_bH , L_cH , and L_fH were synthesized according to the literature and identified with NMR spectroscopy and elemental analyses. L_dH and L_eH were synthesized in a similar procedure *via* nucleophilic substitution of *ortho*-C₆H₄F(CH=NAr) with the corresponding aniline lithium salt. The NMR spectra

 L_dH and L_eH showed the characteristic resonance at 11.56 ppm and 10.92 ppm respectively assignable to the amine hydrogen atoms which attached to the imino nitrogen atom by a hydrogen bond. The diagnostic resonances around 165.6 ppm assignable to the carbon atoms in imino fragments are also comparable to the corresponding ones in other anilido-imine ligands.[14]



1c, Ar = Ar' = $2,6^{-i}$ Pr₂C₆H₃

Scheme 1. Synthesis of anilido-imino Cu(II) complexes

The lithium salt of anilido-imine ligands L_aLi~L_eLi were prepared in situ by treating the corresponding ligands with ⁿBuLi in THF at low temperature. Reactions of these lithium salts of anilindo-imine ligands with CuCl₂ afford the brown solution. Evaporating the solution to dryness and extracting the residue with toluene afford the anilido-imino copper complexes **1a~1e** in moderate to high yields as brown powder. These complexes were well identified by elemental analyses and IR spectroscopy. The molecular structure of **1c** was previously reported to be a monomer and the copper atom was in a trigonal-planar geometry.[18] The formation of the 15e tri-coordinated Cu(II) chloride may be ascribed to the stronger steric repulsion between the bulky substitutes on the two ligands. The crystals of **1a** and **1d** suitable for X-ray diffraction

analysis were grown from THF/hexane mixed solution. The molecular structures of **1a** and **1d** were established by X-ray diffraction analyses and their molecular structures are shown in Figure 1 and Figure 2 respectively with the selected bond lengths and angles in the captions. The crystallographic data in CIF format is shown in the supporting information. There are two metrically identical molecules in the unsymetric unit of 1d and only one molecule was dipicted in Figure 2. In contrast to 1c, both of 1a and 1d are dimmer consisted of two LCu ($L = L_a$ or L_d) units linked with each other by two chlorine bridges. In each molecular, the two copper atoms and two chloride atoms are coplanar forming a perfect square Cu₂Cl₂ core and the dihedral angles between the Cu₂Cl₂ square and the two coordinated ligand-planes are 50.68(21)° and 53.16(20)° for 1a, and 55.676(87)° and 57.741(76)° for 1d respectively $(63.676(73)^\circ)$ and $54.735(84)^\circ$ in the other molecule in **1d**). In each LCu unit the copper center is basically coplanar with its parental ligand and the geometry at each copper center could be described as a warped square-planar i.e., intermediate between tetrahedral and square planar. The geometry parameter τ_4 for the Cu center is 0.29(av) for **1a** and 0.31(av) for **1d**. Considering that the τ_4 value 1 for the tetrahedron and 0 for square-planar geometry, the copper centers in **1a** and **1d** are more closer to square-planar.[20] The two parent coordination planes in same molecular are oriented orthogonally to each other to minimize the compulsion between the ortho substitutes on the aryl ring. The Cu-Cl bond lengths (2.305(3)-2.320(2) Å in 1a and 2.2854(12)-2.3522(12) Å in **1d**) are slightly longer than those of Cu-Cl (2.1997(13)–2.2001(13) Å) in CuCl₂(Dipp-BIAN) [10a] as well as that of 2.1290(8) Å

in **1c**. In both complexes, the bond lengths of $Cu-N_{amino}$ are shorter than the corresponding value for $Cu-N_{imino}$ and their metric parameters are slightly longer than the corresponding one in **1c** respectively.



Figure 1. Perspective view of complex **1a** with thermal ellipsoids drawn at 30% probability level. Uncoordinated solvents and hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (deg.): Cu(1)–N(1) 1.913(9), Cu(1)–N(2) 1.931(7), Cu(2)–N(3) 1.904(8), Cu(2)–N(4) 1.946(8), Cu(1)–Cl(1) 2.305(3), Cu(1)–Cl(2) 2.320(2), Cu(2)–Cl(1) 2.315(2), Cu(2)–Cl(2) 2.313(3), N(1)–Cu(1)–Cl(1) 174.96(5), N(3)–Cu(1)–N(2) 175.49(7), N(1)–Cu(1)–N(3) 92.36(7).

C



Figure 2. Perspective view of complex 1d with thermal ellipsoids drawn at 30% probability level. Uncoordinated solvents and hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (deg.): Cu(1)–N(1) 1.902(3), Cu(1)–N(2) 1.942(3), Cu(2)–N(3) 1.914(3), Cu(2)–N(4) 1.943(3), Cu(1)–Cl(1) 2.3522(12), Cu(1)–Cl(2) 2.2885(12), Cu(2)–Cl(1) 2.2854(12), Cu(2)–Cl(2) 2.3418(12), N(1)–Cu(1)–N(2) 95.24(14), N(3)–Cu(2)–N(4) 94.45(15), Cl(1)–Cu(1)–Cl(2) 87.65(4), Cl(1)–Cu(2)–Cl(2) 87.98(4).

Similarly, reaction of the tridentate ligand L_fH with BuLi and subsequent addition of CuCl₂, after appropriate work up, gave the complex **1f** in moderate yield. Complex **1f** was also characterized with IR and elemental analysis. The crystals of **1f** that are suitable for X-ray diffraction were grown from hexane solution. The molecular structure of **1f** is shown in Figure 3 with the selected bond lengths and angles in the caption. Complex **1f** is monomer with copper atom coordinated by the N,N,N

tridentate ligands and one chlorine atom, and the geometry around Cu center could be described as distorted square plane (the two large angles in the N₃CuCl are 157.85 and 154.88° which are greatly larger than 109°.28' for an ideal tetrahedron, $\tau_4 = 0.19$). The Cu atoms is essentially coplanar with the quinolinyl plane but stay out of the anilido-imino coordination plane with the deviation of 0.6830(38) Å. The whole ligand is greatly twisted with the dihedral angle between the quinolinyl ring and anilido-imino parent plane of 32.14(9)°. The Cu–Cl bond lengths of 2.2326(10) Å is slightly shorter than those in **1a** and **1d**. The N_{quino}–Cu bond lengths (1.997(3) Å) is longer than the N_{quino}–Cu (1.967(3) Å) and the N_{amino}–Cu (1.939(3) Å), but these value are all comparable with those of 1.9873(3)–2.158(3) Å in the 2-imino-1,10-phenanthroline copper complexes.[18]



Figure 3. Perspective view of complex **1f** with thermal ellipsoids drawn at 30% probability level. Uncoordinated solvents and hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (deg.): Cu(1)-N(1) 1.939(3), Cu(1)-N(2) 1.967(3), Cu(1)-N(3) 1.997(3), Cu(1)-Cl(1) 2.2326(10), C(1)-N(1) 1.369(4);

N(1)-Cu(1)-N(3) 83.00(12), N(3)-Cu(1)-N(2) 154.88(12), N(1)-Cu(1)-N(3)

91.86(12), N(1)-Cu(1)-Cl(1) 157.84(10), N(2)-Cu(1)-Cl(1) 96.52(9).

	1a	1d	1f	
Formula	$C_{46}H_{46}Cl_2Cu_2N_4$	$C_{57}H_{57}Cl_2Cu_2F_{12}N_4$	C ₂₈ H ₂₈ ClCuN ₃	
Fw	852.85	1224.09	505.52	
cryst syst	Monoclinic	Triclinic	Monoclinic	
space group	P32	P-1	P2(1)/n	
<i>a</i> (Å)	11.3648(10)	12.7809(10)	8.4380(14)	
b (Å)	11.3678(10)	21.0161(17)	21.048(4)	
<i>c</i> (Å)	27.666(5)	23.0108(19)	14.177(2)	
a (deg)	90	107.848(1)	90	
β (deg)	90	97.755(1)	106.726(3)	
γ (deg)	120	96.852(1)	90	
<i>v</i> (Å ³)	3094.6(7)	5744.3(8)	2411.4(7)	
Ζ	3	4	4	
D _{calcd} (gcm⁻³)	1.373	1.4153	1.392	
µ (mm⁻¹)	1.197	0.912	1.038	
<i>F</i> (000)	1326	2513	1052	
$\theta_{\max}(\deg)$	26.02	26.02	28.30	
collected refins	16392	21949	14234	
Uniq reflns	7928	14056	5695	
R _{int}	0.0648	0.0327	0.0529	
GOF	0.974	1.0223	1.005	
<i>R</i> 1	0.0527	0.0620	0.0579	
w <i>R</i> 2	0.1048	0.1034	0.1370	
Largest diff peak, hole (e A^-3)	0.517, -0.295	0.9831, -0.7667	1.068, -0.323	

Table 1. Summary of crystallographic data for complexes 1a, 1d, and 1f.

3.2. ATRP polymerization of styrene with copper complexes

All the copper complexes were tested as catalysts for ATRP of styrene. The polymerizations were performed in toluene at 60–100°C with **1a–1f** as catalysts and AIBN as initiator. The polymerization results are summarized in Table 1. Initially, with 0.5 equivalent AIBN (1 equivalent initiator, Cu:[I] = 1 : 1), these complexes exhibit moderate activities and the conversions of 52.5%–59.3% are obtained (entry 1–6). The molecular weight of the resulted polymer are slightly larger than the calculated values with narrow PDI (from 1.47–1.58). However, with the increase of the ratio of Cu:[I] from 1:1 to 1:10, the conversions are gradually increased and up to

85.2% conversion is obtained (entry 6-9). Meanwhile the molecular weight distributions maintained almost intact. The control experiment shows that without the catalyst only 49.1% of monomer is consumed in 20 hours affording the polymer with broadened PDI (entry 10). At 80 °C and with 10 equivalent of initiator, complexes 1a, **1b** also show high activities giving the conversion of 82.5–85.2% in 20 hours with the molecular weight ranging from 12500–13300. Complex 1c with bulky ligands show relatively higher activity than that of **1b** and **1c** under the same conditions. Moreover, 1d, 1e without *ortho* substitutes on imino group show lower activities affording the conversion from 77.3 to 78.2%. This phenomenon presumably due to that the bulky groups around the metal center may make the complexes more stable and less decomposition. Notably, complex 1f with tridentate ligand shows 76.2% conversion in 20 h at 80 °C, which is lower than the corresponding bidentated analogous with ortho substitutes (1a, 1b, and 1c). The molecular structures suggests that the "blade" coordination of quinolinyl group does not give a full protection to the metal center. The polymerization temperature shows significant influence on the activity (entry 9, 16, 17). The conversion increased from 58.2% to 85.2% when the temperature goes from 60 °C to 80 °C, and then dropped to 71.2% when the temperature reached to 100 °C. The lower activity at 60 °C might due to the lower radical generating rate, while at 100 °C the lower activity probably due to the fast decomposition rate of the AIBN at high temperature. We suspect that the increasing viscosity of the reaction mixture causes a heterogeneity in the overall styrene concentration in solution which broad the distribution. To further investigate the living character of this catalytic

system, the dynamic of the polymerization was carried out. As shown in Figure 4, the M_n ; GPC values of the polymers increased linearly with the increase of monomer conversion. However the molecular weight distribution (M_w/M_n) was kept in narrow range suggesting the controllable nature of the polymerization.

Entry	Cat	[Cu]:[I]:[Sty]	Convertion (%) ^b	Mn(expt.) ^c × 10 ⁴	$M_{\rm n}({\rm calc.})$ × 10 ⁴	PDI
1	1a	1:1:200	56.8	1.45	1.18	1.54
2	1b	1:1:200	59.3	1.41	1.23	1.55
3	1d	1:1:200	54.7	1.39	1.14	1.47
4	1e	1:1:200	54.1	1.32	1.13	1.50
5	1f	1:1:200	52.5	1.30	1.09	1.48
6	1c	1:1:200	61.4	1.53	1.28	1.58
7	1c	1:2:1000	63.4	2.97	3.30	1.47
8	1c	1:5:1000	64.9	1.47	1.35	1.58
9	1c	1:10:1000	85.2	1.33	0.88	1.57
10	1c	0:10:1000	49.1	1.34	0.51	2.50
11	1a	1:10:1000	82.5	1.25	0.86	1.55
12	1b	1:10:1000	84.1	1.32	0.87	1.59
13	1d	1:10:1000	77.5	1.34	0.81	1.44
14	1e	1:10:1000	77.3	1.25	0.80	1.42
15	1f	1:10:1000	76.2	1.30	0.79	1.45
16 ^d	1c	1:10:1000	58.2	0.82	0.61	1.54
17 <i>°</i>	1c	1:10:1000	71.2	0.97	0.74	1.67
18	1c	1:10:500	83.8	0.72	0.44	1.48
19	1c	1:10:1500	86.5	2.10	1.35	1.60
20	1c	1:10:2000	85.7	2.16	1.78	1.63

Table 1. Polymerization of styrene with copper(II) complexes.

^{*a*}Polymerization conditions: Cat. = 10 μ mol based on Cu(II), toluene (5 mL), T = 80 °C, 20 h; ^{*b*}Isolated yield. ^{*c*}Determined by GPC relative to polystyrene standards. ^{*d*}T = 60 °C. ^{*e*}T = 100 °C



Figure 4. Plot of average-number molecular weight (M_{n, GPC}) and molecular weight

distribution (Mw/Mn) versus the conversion. Polymerization condition: [Cu]:[I]:[Sty] = 1:10:1000 at 80 °C.

4. Conclusions

Several copper complexes based on bidentate anilido-aldimino ligands and N,N,N,-tridentate quinolinyl anilido-aldimino ligand have been synthesized and used in reverse ATRP of styrene. These complexes show moderate to high activities and controllable characters. The *ortho* groups on imino moieties show great influence on the activities.

Acknowledgements

The authors would like to thank the National Natural Science Foundation of China (21574052, U1462111, and 51673078) and Jilin University (J1103302).

References

(a) J. S. Wang, K. Matyjasewski, J. Am. Chem. Soc. 117 (1995) 5614; (b) M. Kato,
M. Kamigaito, M. Sawamoto, T. Higashimura, Macromolecules 28 (1995) 1721; (c)
T.E. Patten, K. Matyjaszewski, Acc. Chem. Res. 32 (1999) 895; (d) M. Kamigaito, T.
Ando, M. Sawamoto, Chem. Rev. 101 (2001) 3689; (e) K. Matyjaszewski, J. Xia,
Chem. Rev. 101 (2001) 2921.

2. R. Poli, Angew. Chem. Int. Ed. 45 (2006) 5058.

(a) S. Zhu, W. Wang, W. Tu, D. Yan, Acta Polym., 50 (1999) 267; (b) J. Xia, K. Matyjaszewski, Macromolecules, 30 (1997) 7692; (c) J. S. Wang, K. Matyjaszewski, Macromolecules, 28 (1995) 7572.

4. (a) P. Li, K. Y. Qiu, Macromolecules, 35 (2002) 8906; (b) W. Zhang, X. Zhu, J.

Zhu, Z. Cheng, Macromol. Chem. Phys., 205 (2004) 806.

5. (a) L. Zhang, Z. Cheng, S. Shi, Q. Li, X. Zhu, Polymer, 49 (2008) 3054; (b) R.

Ferro, S. Milione, T. Caruso, A. Grassi, J. Mol. Catal. A: Chem., 307 (2009) 128; (c)

C. Hou, C. Ji, R. Qu, C. Wang, C. Sun, W. Zhou, M. Yu, J. App. Poly. Sci. 105 (2007)

1575.

6. (a) C. Granel, P. Dubois, R. Jérôme, P. Teyssié, Macromolecules, 29 (1996) 8576;

(b) H. Uegaki, Y. Kotani, M. Kamigaito, M. Sawamoto, Macromolecules, 30 (1997)

2249;(c) H. Uegaki, Y. Kotani, M. Kamigaito, M. Sawamoto, Macromolecules,

31 (1998) 6756; (d) G. Moineau, M. Minet, P. Dubois, P. Teyssié, T. Senninger, R. Jérôme, Macromolecules, 32 (1999) 27; (e) H. Uegaki, M. Kamigaito, M. Sawamoto, J. Polym. Sci. Part A: Polym. Chem. 37 (1999) 3003; (f) P. Li, K. Y. Qiu, Polymer, 43 (2002) 5873.

7. H. Takahashi, T. Ando, M. Kamigatio, M. Sawamoto, Macromolecules, 32 (1999)6461.

8. (a) G. Moineau, C. Granel, P. Dubois, Macromolecules, 31 (1998) 542; (b) P.
Lecomte, I. Drapier, P. Dubois, P. Teyssié, R. Jérôme, Macromolecules, 30 (1997)
7631.

9. (a) J. L. Wang, T. Grimaud, K. Matyjasewski, Macromolecules, 30 (1997) 6507; (b)A. K. Nanda, K. Matyjasewski, Macromolecules, 36 (2003) 1487.

(a) C. Fliedel, V. Rosa, C.I.M. Santos, P.J. Gonzalez, R.M. Almeida, C.S.B.
Gomes, P. T. Gomes, M.A.N.D.A. Lemos, G. Aullón, R. welter, T. Avilés, Dalton
Trans., 43(2014) 13041; (b) R. K. O'Reilly, V. C. Gibson, A. J. P. White, D. J.

Williams, J. Am. Chem. Soc., 125 (2003) 8450.

 S. A. Turner, Z. D. Remillard, D. T. Gijima, E. Gao, R. D. Pike, C. Goh, Inorg. Chem. 51 (2012)10762.

12. (a) A. Plichta, W. Li, K. Matyjaszewski, Macromolecules, 42 (2009) 2330; (b) O.

Bienemann, A. K. Froin, I. D. S. Vieira, R. Wortmann, A. Hoffmann, S.

Herres-Pawlis, Z. Anorg. Allg. Chem. 638(2012), 1683.

13.W. Gao, D. Cui, X. Liu, Y. Zhang, Y. Mu, Organometallics 27 (2008) 5889.

14. N. Yang, L. Xin, W. Gao, J. Zhang, X. Luo, X. Liu, Y. Mu, Dalton Trans., 41

(2012) 11454.

15. Z. Hao, N. Yang, W. Gao, L. Xin, X. Luo, Y. Mu, J. Organomet. Chem., 749 (2014) 350.

Z. Hao, B. Xu, W. Gao, Y. Han, G. Zeng, J. Zhang, G. Li and Y. Mu,Organometallics, 34 (2015) 2783.

17. Z. Hao, Y. Han, W. Gao, L. Xin, Y. Mu, Polyhedron, 83 (2014) 236.

 E. C. Brown, N. W. Aboelella, A. M. Reynolds, G. Aullón, S. Alvarez, W. B. Tolman, Inorg. Chem., 43 (2004) 3335.

19. G. M. Sheldrick, SHELXTL, Version 5.1, Siemens Industrial Automation, Inc., 1997.

20. L. Yang, D. R. Powell, R. P. Houser, Dalton Trans. (2007), 955.

Graphical abstract

Several copper complexes supported by bidentated and tridentated anilido-imine ligands were synthesized and used as catalysts for reverse ATRP of styrene.

