Synthesis and Structural Characterization of Trifluoromethyl-Substituted β-Ketoimino Copper(II) Complex and Its Catalytic Behavior for Methyl Acrylate Polymerization¹

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Abstract—A new trifluoromethyl-substituted bis(β -ketoimino)copper complex (II) was synthesized and characterized by FTIR, elemental analysis, and X-ray diffraction (CIF file CCDC no. 1023178). XRD refinement revealed that the copper complex adopted a perfect central symmetric square planar structure with the copper center coordinated by two *trans* β -ketoimine ligands with delocalized double bonds. On activation with modified methylaluminoxane (MMAO), the bis(β -ketoimino)copper complex can polymerize methyl acrylate effectively. Introduction of trifluoromethyl group into the N-aryl ring of the ligands, which leads to strong electron-withdrawing effect, can improve significantly the catalytic activities. The activity of II/MMAO can reach 89.4 kg/mol Cu h, which is among the highest values reported for copper complexes in acrylic monomer polymerization.

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INTRODUCTION

Copper complexes have been widely used in many fields [1–7]. For example, in life science, some copper complexes have shown biological activities of anticancer, antibacterial, antiviral, antitumor or carrying oxygen. In the field of catalysis, copper complexes can catalyze many organic reactions, such as the selective oxidation of hydrocarbons, alcohols and phenols, the cyclopropanation of olefins, mimic enzyme catalysis and so on.

Copper complexes can also be used for the polymerization or copolymerization of polar monomers, which has been an interesting and challenging field [8, 9]. In the past decade, much attention has been focused on the performance of late-transition-metal complexes due to their weaker oxophilicity, greater tolerance to functional group and thus generally less sensitive to deactivation by polar species than early-transitionmetal complexes [10-16]. Among the late-transitionmetal complexes, copper complexes are attractive candidates since they are cheaper, air-stable, and easy to prepare. However, compared with the nickel and palladium complexes, much less attention has been paid to copper complexes for catalyzing the polymerization of polar monomers. R.T. Stibrany et al. reported good activity of bis(benzimidazole) copper(II)/MAO (MAO = methylaluminoxane) system for the homo- and copolymerizations of ethylene and methyl acrylate [17-19]. The activity of MAO-activated [1,2-bis(4,4-dimethyl-2oxazolin-2-yl)ethane]copper(II) dichloride for the polymerization of acrylates and their copolymerization with ethylene was reported in [20]. Bis(salicylaldiminate)copper(II) complexes can also be used to catalyze the homo and copolymerizations of ethylene and methyl methacrylate [21]. Wu's group found that bis(β-ketoamino)copper/MAO could catalyze the homo- and copolymerization of methyl acrylate and 1-hexene [22]. The copper complexes ligated by N-tripodal [23], salicylaldiminate [24] or 2-(pyrazol-3-yl)-6-(pyrazolate)pyridine [25] ligands were also efficient catalyst precursors for methacrylate polymerization. During the last few years, β -ketoimine ligands have

During the last few years, β -ketoimine ligands have received some attention and been applied in organometallic complexes due to their ease of preparation and modification of both the steric and electronic effects [26–28]. However, copper complexes with β -ketoimine ligand are rarely reported. Recently we have been committed to finding some novel early and late transition non-metallocene catalysts with excellent catalytic performances by regulating the coordination environments of the central metal with electronic effects or synergistic steric and electronic effect of substituents on ligands [29–33]. The substituents in ligands have great influence on the structure and catalytic activity of the complexes, which include the steric

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effects of alkyl substituents and electronic effects of halogen substituents. However, relative to the steric effects of alkyl-substituents, the electronic effects of halogen substituents received much less attention in complexes design and catalytic behavior research [34–39]. Here we studied the electronic effects to the copper complexes with β-ketoimine ligands and reported the synthesis methyl- (I) and trifluoromethyl-substituents (II) bis(β-ketoimino)copper complexes, structure, and methyl acrylate (MA) polymerization activity of a new complex II. We found that the trifluoromethyl-substitution exerted significant influences on the structure and MA polymerization activity of the copper complexes.

EXPERIMENTAL

General procedures. All work involving air- and/or moisture-sensitive compounds was carried out with standard Schlenk techniques. Modified methylaluminoxane (MMAO), 7% aluminum in a heptane solution, was purchased from Akzo Nobel Chemical, Inc. All other commercial chemicals are used as received. The ¹H NMR spectra of ligands were recorded on a Bruker Avance III 400 MHz spectrometer with tetramethylsilane as an internal standard. IR spectra of the ligands and copper complexes were collected on a Nicolet Nexus 470 FT–IR spectrometer. Elemental analyses were carried out using Vario EL 111.

Synthesis of 4-(o-tolylamino)pent-3-en-2-one (HL¹). A mixture of 2-methylaniline (2.14 g, 0.02 mol), acetyl acetone (2.10 g, 0.021 mol) and p-toluenesulfonic acid (0.02 g) in toluene (100 mL) was refluxed for 12 h, with azeotropic removal of water using a Dean-stark trap. After removing the solvent, the crude product was washed by 30 mL water and extracted three times each by 40 mL diethyl ether. The ether solution was washed one or two times by a little dilute hydrochloric acid to eliminate raw materials and the byproduct diketiminate. The organic solution was then washed by water, dried by Na₂SO₄ and removed of Et₂O. 2.90 g product was obtained with 76.7% yield. ¹H NMR (400 MHz; CDCl₃; δ ppm): 12.35 (s., 1H, NH), 7.19 (m., 4H, Ph), 5.21 (s., 1H, CH), 2.29 (s., 3H, PhCH₃), 2.12 (s., 3H, CHCOCH₃), 1.88 (s., 3H, $CHCNCH_3$).

IR (KBr; v, cm⁻¹): 3432 (N–H), 1597 (C=O), 1560 (C=C).

For C₁₂H₁₅NO

anal. calcd., %:	C, 76.16;	Н, 7.99;	N, 7.40.
Found, %:	C, 76.07;	H, 7.78;	N, 7.44.

Synthesis of 4-((2-(trifluoromethyl)phenyl)amino)pent-3-en-2-one (HL²). Following a similar procedure, HL² was obtained in 76.5% yield. ¹H NMR (400 MHz; CDCl₃; δ , ppm): 12.66 (s., 1H, N*H*), 7.41 (m., 4H, Ph), 5.47 (s., 1H, C*H*), 2.30 (s., 3H, CHCOC*H*₃), 2.21 (s., 3H, CHCNC*H*₃).

IR (KBr; v, cm⁻¹): 3432 (N–H), 1597 (C=O), 1560 (C=C).

For C ₁₂ H ₁₂ NOF ₃			
anal. calcd., %:	C, 59.26;	Н, 4.97;	N, 5.76.
Found, %:	C, 59.37;	H, 5.02;	N, 5.83.

Synthesis of complex I. A mixture of ligand HL^1 (0.76 g, 4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.38 g, 2 mmol) in methanol (50 mL) was refluxed for 5 h. After removal of methanol solvent, the crude product was recrystallized in toluene to obtain 0.67 g black solid with 76% yield.

IR (KBr; v, cm⁻¹): 3422 w, 2921 w, 1577 s, 1530 s, 1414 s, 1274 w, 1187 w, 1019 w, 936 w, 781 m.

For C24H28N2O2Cu

anal. calcd., %:	C, 65.51;	H, 6.41;	N, 6.37.
Found, %:	C, 65.47;	H, 6.92;	N, 6.49.

Synthesis of complex II. Complex was prepared via a procedure similar to that for complex I in 70% yield.

IR (KBr; v, cm⁻¹): 3416 w, 2965 w, 1573 s, 1522 s, 1453 s, 1411 s, 1316 s, 1264 w, 1196 w, 1158 s, 1113 s, 1056 w, 946 w, 760 m.

For	\mathbf{C}	ц	NL	\cap	C_{11}	
гoг	C_{24}	П 22	112	\mathbf{U}_{2}	Cu.	г6

anal. calcd., %:	C, 52.60;	Н, 4.05;	N, 5.11.
Found, %:	C, 52.50;	Н, 4.16;	N, 5.02.

Polymerization of MA. A flame-dried Schlenk flask was thrice purged with N_2 and a desired amount of freshly distilled toluene was transferred into the flask (placed in an oil bath at a designated temperature). MA monomer and MMAO were injected into the flask using a syringe and the mixture was stirred for 5 min. The polymerization was started by adding the copper complex solution in toluene with a syringe. After a desired time, the polymerization was quenched with acidified ethanol (100 mL, 10 vol % HCl in ethanol). The precipitated polymer was filtered off, washed with ethanol, and then dried under vacuum overnight at 50°C to constant weight.

X-ray structure determinations. Crystal data obtained with the ω -2 θ scan mode were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å). Structure II was solved using direct methods, whereas further refinements with full-matrix least squares on F^2 were obtained with the SHELXL-97 program package. All nonhydrogen atoms were refined aniso-



Molecular structure of complex II.

tropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Crystallographic data (excluding structure factors) for structure II have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1023178; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

By referring previous works [30], we synthesized the β -ketoimino ligands bearing methyl- and trifluoromethyl-substituents by reacting acetylacetone with substituted aniline in toluene. The corresponding copper complexes were obtained in good yields by reacting the ligands with cupric acetate in methanol according to the following Scheme:



Scheme.

These black copper complexes are stable in air and soluble in toluene, CH_2Cl_2 and THF. The ligands were characterized by ¹H NMR, FTIR and elemental analysis, and the copper complexes were measured by FTIR and elemental analysis. The crystal of **II** suitable for X-ray crystallography were obtained by slow evaporation from toluene solution. The molecular struc-

ture was shown in figure. The crystallographic data together with the collection and refinement parameters are summarized in Table 1.

The crystal structure of complex II showed that the complex had a 2:1 ligand to metal ratio. Furthermore, the two β -ketoimino ligands acted as bidentate N,O-chelators and lie in the *trans* conformation to

Parameter	Value
Formula weight	547.98
Temperature	296(2)
Crystal system	Orthorhombic
Space group	Pbca
<i>a</i> , Å	7.902(2)
b, Å	14.504(3)
Volume, Å ³	2432.6(10)
Ζ	4
ρ , mg/m ³	1.496
μ , mm ⁻¹	0.967
<i>F</i> (000)	1116
Crystal size	$0.45 \times 0.40 \times 0.40$
θ Range, deg	1.92-25.02
Index ranges	$-9 \le h \le 8,$
	$-17 \le k \le 12,$
	$-24 \le l \le 25$
Reflections collected	12570
Independent reflections (R_{int})	2151 (0.0343)
Reflections with $I > 2\sigma(I)$	1476
Completeness to θ , %	99.9
Goodness-of-fit on F^2	1.016
Number of refinement parameters	162
Final <i>R</i> indices $(I > 2\sigma(I))$	0.0358, 0.0878
<i>R</i> indices (all data)	0.0593, 0.1017
Largest diff. peak and hole, $e \text{ Å}^{-3}$	0.341, -0.292

 Table 1. The crystal data and structure refinement parameters for complexes II

create two six-membered chelate rings (Cu–O–C– C–C–N). The bond distances of C(8)–C(9) and C(9)–C(10) are 1.406(4) and 1.361(4) Å, respectively, which are between that of single and double bonds, suggesting that the double bond of C=C is delocalized. The bond length of C(10)–O(1) is 1.276(4) Å, which is longer than ordinary C=O bond (1.23 Å), showed that the C=O double bond was also delocalized. Thus an N–C–C–C–O conjugated big π -bond has been formed.

Four-coordinated Cu(II) complexes are usually characterized by a square planar coordination that may distort to a pseudo-tetrahedral geometry [40]. Furthermore, the steric hindrance and the electronic characteristics of the substituents on the imine moieties also influence the planarity. For example, 2,6-diisopropyl-substituted β -ketoimino copper complex reported by Wu's group adopted a distorted square planar coordination geometry. However, unlike the most [N,O] chelated copper complexes with distorted square planar structures, the *o*-CF₃ derivative **II** exhibited perfect square planar geometry and central symmetric structure. The dihedral angle between Cu(1)O(1)N(1) and C(1)C(2)C(3)C(4)C(5)C(6) planes is 86.79°, indicating that the two imine-aryl rings are almost perpendicular to the N–Cu–O plane. The Cu–O and Cu–N bond lengths are 1.893(2) and 1.986(2) Å, respectively, and the angle of NCuO is 91.36(9)°, siminar to that of analogous [N,O] copper(II) complexes.

Copper complexes can be used as catalyst precursors for polar monomer polymerization. Recently Wu et al. reported that bis(ketoamino)copper complexes with alkyl substituents could catalyze the polymerization of MA with moderate activity when activated with MAO [22]. We found that the introduction of electron-drawing trifluoromethyl group into N-aryl rings of ligand can improve greatly the catalytic activities, and the results are summarized in Table 2.

The Al/Cu molar ratio and reaction temperature apparently influence the catalytic activity of **II**. It cannot catalyze the polymerization of MA without MMAO, showing that the cocatalyst MMAO has a pivotal role. With the usage of MMAO increased, the activities of complex **II** increased to a maximum (52.6 kg/mol Cu h) at an Al/Cu molar ratio of 100 and then decreased (entry 2–5 of Table 2). The molecular weights of obtained PMA have similar change trends with the increase of Al/Cu molar ratio, but the molecular weight distributions decreased gradually.

A clear change in activity of **II**/MMAO at different temperatures was also observed, as shown in entry 4 and 6–8 of Table 2. When the reaction temperatures increased from 25 to 75°C, the polymerization activities increased gradually to a maximum at 65°C and then decreased, while the polymers have the highest molecular weight of 119 kg/mol at 45°C, and higher and lower temperatures would lower the molecular weight. The catalyst need to be activated at a certain temperature, so increase of temperatures can increase the activity. But too high a temperature may destroy the structure of copper complex, resulting in the reduction of catalytic activity. Similar phenomenon had been found in alkyl-substituted bis(β -ketoamino)copper complex by Wu et al. [22].

We have previously introduced fluorine atoms into the *N*-aryl moiety of some early transition metal complexes (mono β -diiminato titanium complexes [29] and bis(β -ketoimino) titanium complexes [30]) and observed significant electronic effect of the fluorosubstituents upon the structure and catalytic activity of the titanium complexes as well as the property of the obtained polymer. The trifluoromethyl substitution of the *N*-aryl moiety also exerted great influence to bis(β -ketoimino)copper complexes for MA polymerization. Complex I with the methyl substitution showed an activity of 20.7 kg/mol Cu h, which was similar to the results reported by Wu et al. [22]. Introduction of trifluoromethyl group into the *N*-aryl ring of ligand, however, appreciably improved the activi-

Entry	Catalyst	Temperature, °C	Al/Cu	Time, h	Product, g	Activity, kg/mol Cu h	$M_w \times 10^4$	M_w/M_n
1	Ι	65	100	3	1.2454	20.7	8.2	2.27
2	II	65	0	3	0	0		
3	II	65	50	3	0.2676	4.5	3.4	2.26
4	II	65	100	3	3.1574	52.6	6.0	1.83
5	II	65	200	3	2.1985	36.6	4.1	1.46
6	II	25	100	3	2.4811	41.4	5.9	2.39
7	II	45	100	3	2.9728	49.6	11.9	2.20
8	II	75	100	3	2.9081	48.5	4.9	2.02
9	II	65	100	1	1.7886	89.4	6.1	1.77
10	II	65	100	2	2.5664	64.2	6.9	2.22
11	II	65	100	4	3.3207	41.5	6.8	1.48

 Table 2. The results of MA polymerization at different polymerization conditions*

* Reaction conditions: toluene solvent, catalyst 20 µmol, MA 5 mL, solution total volume 25 mL.

ties. Under the same reaction conditions, the catalytic activity of **II** can reach 52.6 kg/mol Cu h, more than twice that of **I**. The calculated activity can even reach 89.4 kg/mol Cu h at one hour reaction time. To the best of our knowledge, this is the highest value reported so far for copper complexes in acrylic monomer polymerization.

In summary, a new β -ketoimine ligand with trifluoromethyl-substitution on the *N*-aryl moiety and its corresponding copper complex were synthesized in good yields and characterized. XRD characterization revealed that the copper(II) were coordinated by two *trans* β -ketoimino ligands with delocalized double bonds and the copper complex II adopted a perfect central symmetric square planar structure with copper as the center. The MMAO-activated copper complexes can polymerize MA effectively. The electron-withdrawing effect of trifluoromethyl group improved significantly the catalytic activities. The activity of II/MMAO can reach 89.4 kg/mol Cu h, which is the highest value reported so far for copper complexes in acrylic monomer polymerization.

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