

Synthesis, Characterization, and Catalytic Behavior of Copper Complexes with Fluorosubstituted β -Ketoimine Ligands

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ABSTRACT: A series of β -ketoimine ligands with various fluorine substitutions on the *N*-aryl ring and the corresponding copper complexes were synthesized. The fluorosubstituents exerted significant effects on the structures and catalytic activities of the copper complexes. X-ray diffraction revealed that the copper(II) central ions were coordinated by two trans-oriented β -ketoimino ligands with delocalized double bonds. Complex **2b** (with mono-*o*-fluorosubstitution on the *N*-aryl moiety) adopted a central symmetric square planar structure, whereas complex **2f** (with bis-*o*-fluorosubstitution) had a distorted square planar structure with a dihedral angle of 28.2°. The Cu—N bond length in **2f** was appreciably shorter than that in **2b**. When activated by modified methylaluminoxane, the copper complexes effectively polymerized methyl acrylate. Furthermore, substitution with more fluorine atoms resulted in a higher activity. The catalytic activity of the pentafluorosubstituted complex **2h** reached 57.5 kg (mol of Cu)⁻¹·h⁻¹ under optimized conditions; this was the highest value reported up to this point for copper complexes in acrylic monomer polymerization. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41178.

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INTRODUCTION

The polymerization or copolymerization of polar monomers catalyzed by organometallic complexes has been an interesting and challenging field.^{1–9} In the past decade, much attention has been focused on the study of late-transition-metal complexes because of their weaker oxophilic properties, greater tolerance to functional groups, and thus lesser sensitivity to deactivation by polar species compared to early-transition-metal complexes. Group VIII catalysts, in particular, nickel- and palladium-based complexes,^{10–27} have been widely investigated; nevertheless, the majority of the catalytic systems usually produce polymers with low-polar monomer contents and often with low molecular weights and branched structures.

Among the late transition metals, copper presents an attractive candidate as a polymerization active center, especially for the polymerization or copolymerization of functional monomers. Furthermore, copper complexes are cheaper, more air stable, and easier to prepare. However, relatively less attention has been paid to copper complexes for catalyzing the polymerization of polar monomers. Stibrany and coworkers^{28–31} of Exxon–Mobil first found that copper complexes activated by methylaluminoxane

(MAO) could catalyze the copolymerization of olefin and polar monomers. Subsequently, they reported good activity of bis(benzimidazole)copper(II)/MAO systems for the homopolymerization and copolymerization of ethylene and methyl acrylate (MA).^{32–34} The activity of MAO-activated [1,2-bis(4,4-dimethyl-2-oxazolin-2-yl)ethane] copper(II) dichloride for the polymerization of acrylates and their copolymerization with ethylene was reported by Sen et al.³⁵ Bis(salicylaldimate)copper(II) complexes were found to catalyze the homopolymerization and copolymerization of ethylene and methyl methacrylate.³⁶ Wu et al.³⁷ found that bis(β -ketoamino)copper/MAO could catalyze the homopolymerization and copolymerization of MA and 1-hexene. The copper complexes ligated by *N*-tripodal,³⁸ salicylaldimate,³⁹ or 2-(pyrazol-3-yl)-6-(pyrazolate) pyridine⁴⁰ ligands were also efficient catalyst precursors for methacrylate polymerization.

During the last few years, β -ketoimine ligands have received some attention and have been applied in organometallic complexes because of their ease of preparation and modification of both the steric and electronic effects.^{41–43} However, copper complexes with β -ketoimine ligands have scarcely been reported. Recently, we synthesized some novel early- and late-transition-nonmetallocene catalysts with excellent catalytic performances

by regulating the coordination environments of the central metal with electronic or synergistic steric and electronic effects of the substituents on ligands.^{44–49} The substituents in ligands have great influence on the structure and catalytic activity of the complexes; this stems from the steric effect of alkyl substituents or the electronic effect of halogen substituents. However, relative to the steric effect of alkyl substituents, the electronic effect of halogen substituents has received less attention in complex design and catalytic behavior research.^{50–55} In this study, we examined the electronic effects of a novel class of bis(β -ketoimine)copper complexes containing fluorine substitution on the *N*-aryl ring, and we report their synthesis, structure, and MA polymerization activity. The fluorosubstitution pattern was found to significantly influence the structure of the complexes and the polymerization activity for MA.

EXPERIMENTAL

Materials

All work involving air- and/or moisture-sensitive compounds was carried out with standard Schlenk techniques. Methylaluminoxane (MMAO; 7% aluminum in a heptane solution) was purchased from Akzo Nobel Chemical, Inc. All other commercial chemicals were used as received.

Characterization

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 with a Nicolet Nexus 470 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were carried out with a Vario EL 111 instrument. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of poly(methyl acrylate) (PMA) were determined at 40°C with an Agilent GPC-50 chromatograph with standard polystyrene as a reference and tetrahydrofuran (THF) as a solvent at a flow rate of 1.0 mL/min.

Crystal Structure Determination

Crystal data were collected on a Bruker Smart Apex Charge-coupled Device diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The structure was solved with 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 anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Polymerization of MA

A flame-dried Schlenk flask was purged three times with N_2 , and a desired amount of freshly distilled toluene was transferred into the flask (which was placed in an oil bath at a desired temperature). The MA monomer and MMAO were injected into the flask with a syringe, and the mixture was stirred for 5 min. The polymerization was started by the addition of a 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 *in vacuo* overnight at 50°C to a constant weight.

Synthesis of the Ligands

4-(*o*-tolylamino)Pent-3-en-2-One (1a). A mixture of 2-methylaniline (2.14 g, 0.02 mol), acetyl acetone (2.10 g, 0.021 mol), and *p*-toluene sulfonic acid (0.02 g) in toluene (100 mL) was refluxed for 12 h with the azeotropic removal of water with a Dean–Stark trap. After the solvent was removed, the crude product was washed with 30 mL of water and extracted three times each with 40 mL of diethyl ether (Et₂O). The ether solution was washed one or two times by dilute hydrochloric acid to eliminate raw materials and the byproduct diketiminate. The organic solution was then washed with water, dried with anhydrous Na₂SO₄, and removed with Et₂O. An amount of 2.90 g of the product was obtained with a 76.7% yield.

¹H-NMR (400 MHz, CDCl₃, δ): 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, CHCNCH₃). IR (KBr, cm⁻¹): 3432 (N–H), 1597 (C=O), 1560 (C=C). ANAL. Calcd for C₁₂H₁₅NO: C, 76.16%; H, 7.99%; N, 7.40%. Found: C, 76.07%; H, 7.78%; N, 7.44%.

4-[(2-fluorophenyl)amino]Pent-3-en-2-One (1b). Following the previous procedure (for 1a), we obtained 1b in a 74.2% yield.

¹H-NMR (400 MHz, CDCl₃, δ): 12.25 (s, 1H, NH), 7.18 (m, 4H, Ph), 5.26 (s, 1H, CH), 2.11 (s, 3H, CHCOCH₃), 1.94 (s, 3H, CHCNCH₃). IR (KBr, cm⁻¹): 3439 (N–H), 1616 (C=O), 1569 (C=C). ANAL. Calcd for C₁₁H₁₂FNO: C, 68.12%; H, 6.28%; N, 7.34%. Found: C, 68.38%; H, 6.26%; N, 7.25%.

4-[(3-fluorophenyl)amino]Pent-3-en-2-One (1c). Following the previous procedure (for 1a), we obtained 1c in a 72.5% yield.

¹H-NMR (400 MHz, CDCl₃, δ): 12.51 (s, 1H, NH), 7.28 (m, 4H, Ph), 5.23 (s, 1H, CH), 2.19 (s, 3H, CHCOCH₃), 2.05 (s, 3H, CHCNCH₃). IR (KBr, cm⁻¹): 3439 (N–H), 1616 (C=O), 1569 (C=C). ANAL. Calcd for C₁₁H₁₂FNO: C, 68.12%; H, 6.28%; N, 7.34%. Found: C, 68.52%; H, 6.41%; N, 7.21%.

4-[(4-fluorophenyl)amino]Pent-3-en-2-One (1d). Following the previous procedure (for 1a), 1d was obtained in a 71.4% yield.

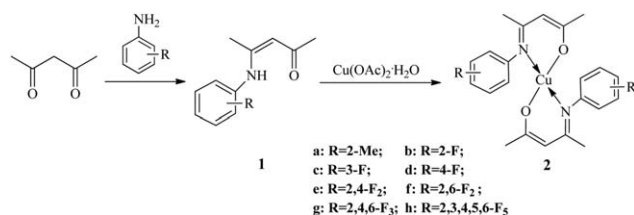
¹H-NMR (400 MHz, CDCl₃, δ): 12.35 (s, 1H, NH), 7.08 (m, 4H, Ph), 5.20 (s, 1H, CH), 2.11 (s, 3H, CHCOCH₃), 1.94 (s, 3H, CHCNCH₃). IR (KBr, cm⁻¹): 3439 (N–H), 1616 (C=O), 1569 (C=C). ANAL. Calcd for C₁₁H₁₂FNO: C, 68.12%; H, 6.28%; N, 7.34%. Found: C, 68.36%; H, 6.27%; N, 7.23%.

4-[(2,4-difluorophenyl)amino]Pent-3-en-2-One (1e). Following the previous procedure (for 1a), 1e was obtained in an 83.1% yield.

¹H-NMR (400 MHz, CDCl₃, δ): 12.08 (s, 1H, NH), 7.09–7.37 (m, 3H, Ph), 5.26 (s, 1H, CH), 2.12 (s, 3H, CHCOCH₃), 1.85 (s, 3H, CHCNCH₃). IR (KBr, cm⁻¹): 3439 (N–H), 1609 (C=O), 1568 (C=C). ANAL. Calcd for C₁₁H₁₁F₂NO: C, 62.66%; H, 5.37%; N, 6.45%. Found: C, 63.05%; H, 5.41%; N, 6.56%.

4-[(2,6-difluorophenyl)amino]Pent-3-en-2-One (1f). Following the previous procedure (for 1a), 1f was obtained in an 86.4% yield.

¹H-NMR (400 MHz, CDCl₃, δ): 12.45 (s, 1H, NH), 7.32–7.38 (m, 3H, Ph), 5.46 (s, 1H, CH), 2.26 (s, 3H, CHCOCH₃), 2.15



Scheme 1. Synthesis of the β -ketoimine ligands with fluorine substitution and the corresponding copper complexes.

(s, 3H, CHCNCH₃). IR (KBr, cm⁻¹): 3439 (N—H), 1609 (C=O), 1568 (C=C). ANAL. Calcd for C₁₁H₁₁F₂NO: C, 62.66%; H, 5.37%; N, 6.45%. Found: C, 62.55%; H, 5.25%; N, 6.63%.

4-[(2,4,6-trifluorophenyl)amino]Pent-3-en-2-One (1g). Following the previous procedure (for **1a**), **1g** was obtained in an 84.2% yield.

¹H-NMR (400 MHz, CDCl₃, δ): 11.73 (s, 1H, NH), 6.75 (m, 2H, Ph), 5.32 (s, 1H, CH), 2.12 (s, 3H, CHCOCH₃), 1.98 (s, 3H, CHCNCH₃). IR (KBr, cm⁻¹): 3439 (N—H), 1609 (C=O), 1568 (C=C). ANAL. Calcd for C₁₁H₁₀F₃NO: C, 57.55%; H, 4.47%; N, 6.05%. Found: C, 57.64%; H, 4.40%; N, 6.11%.

4-[(perfluorophenyl)amino]Pent-3-en-2-One (1h). Following the previous procedure (for **1a**), **1h** was obtained in a 64.5% yield.

¹H-NMR (400 MHz, CDCl₃, δ): 12.12 (s, 1H, NH), 5.67 (s, 1H, CH), 2.26 (s, 3H, CHCOCH₃), 2.16 (s, 3H, CHCNCH₃). IR (KBr, cm⁻¹): 3439 (N—H), 1609 (C=O), 1568 (C=C). ANAL. Calcd for C₁₁H₈F₅NO: C, 49.82%; H, 3.04%; N, 5.28%. Found: C, 49.76%; H, 3.00%; N, 5.19%.

Synthesis of Copper Complexes

Complex 2a. A mixture of ligand **1a** (0.76 g, 4 mmol) and Cu(OAc)₂·H₂O (0.38 g, 2 mmol) in methanol (50 mL) was refluxed for 5 h. After the removal of the methanol solvent, the crude product was recrystallized in toluene to obtain 0.67 g of a black solid with a 76% yield.

IR (KBr, cm⁻¹): 3422 (w), 2921 (w), 1577 (s), 1530 (s), 1414 (s), 1274 (w), 1187 (w), 1019 (w), 936 (w), 781 (m). ANAL. Calcd for C₂₄H₂₈CuN₂O₂: C, 65.51%; H, 6.41%; N, 6.37%. Found: C, 65.47%; H, 6.92%; N, 6.49%.

Complex 2b. Complex **2b** was prepared via a procedure similar to that used for complex **2a** in an 80% yield.

IR (KBr, cm⁻¹): 3448 (w), 2922 (w), 1577 (s), 1526 (s), 1408 (s), 1274 (w), 1187 (w), 1019 (w), 938 (w), 780 (m). ANAL. Calcd for C₂₂H₂₂CuF₂N₂O₂: C, 58.99%; H, 4.95%; N, 6.25%. Found: C, 58.70%; H, 5.29%; N, 6.20%.

Complex 2c. Complex **2c** was prepared via a procedure similar to that used for complex **2a** in a 76% yield.

IR (KBr, cm⁻¹): 3448 (w), 2922 (w), 1577 (s), 1526 (s), 1408 (s), 1274 (w), 1187 (w), 1019 (w), 938 (w), 780 (m). ANAL. Calcd for C₂₂H₂₂CuF₂N₂O₂: C, 58.99%; H, 4.95%; N, 6.25%. Found: C, 58.69%; H, 5.27%; N, 6.10%.

Complex 2d. Complex **2d** was prepared via a procedure similar to that used for complex **2a** in a 77% yield.

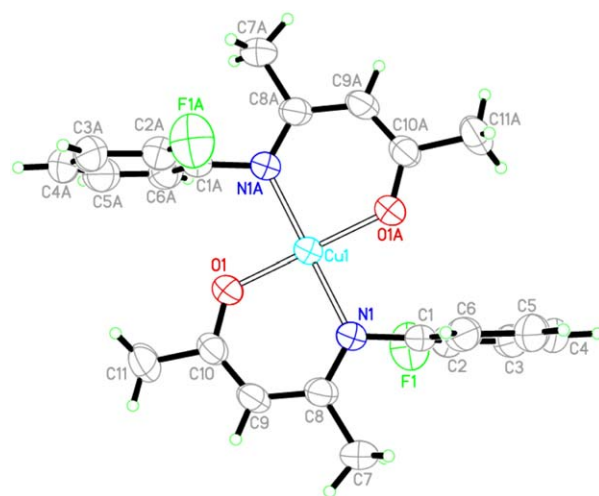


Figure 1. Molecular structure of complex **2b**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

IR (KBr, cm⁻¹): 3448 (w), 2922 (w), 1577 (s), 1526 (s), 1408 (s), 1274 (w), 1187 (w), 1019 (w), 938 (w), 780 (m). ANAL. Calcd for C₂₂H₂₂CuF₂N₂O₂: C, 58.99%; H, 4.95%; N, 6.25%. Found: C, 58.76%; H, 5.34%; N, 6.17%.

Complex 2e. Complex **2e** was prepared via a procedure similar to that used for complex **2a** in an 82% yield.

IR (KBr, cm⁻¹): 3441 (w), 2924 (w), 1576 (s), 1524 (s), 1404 (s), 1275 (w), 1195 (w), 1003 (w), 941 (w), 780 (m). ANAL. Calcd for C₂₂H₂₀CuF₄N₂O₂: C, 54.60%; H, 4.17%; N, 5.79%. Found: C, 54.58%; H, 4.30%; N, 5.67%.

Complex 2f. Complex **2f** was prepared via a procedure similar to that used for complex **2a** in an 86% yield.

IR (KBr, cm⁻¹): 3441 (w), 2924 (w), 1576 (s), 1524 (s), 1404 (s), 1275 (w), 1195 (w), 1003 (w), 941 (w), 780 (m). ANAL. Calcd for C₂₂H₂₀CuF₄N₂O₂: C, 54.60%; H, 4.17%; N, 5.79%. Found: C, 54.52%; H, 4.30%; N, 5.67%.

Complex 2g. Complex **2g** was prepared via a procedure similar to that used for complex **2a** in a 68% yield.

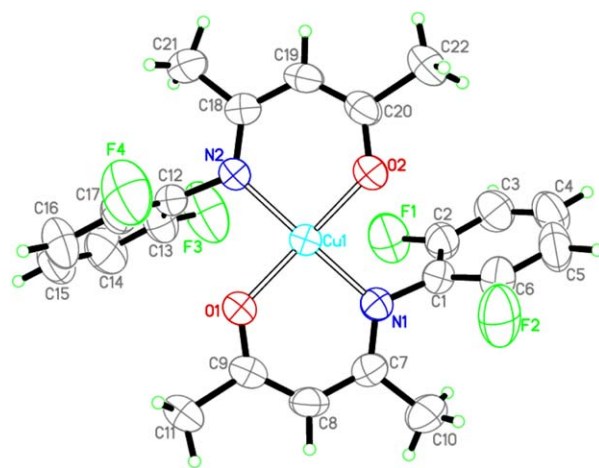


Figure 2. Molecular structure of complex **2f**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Crystal Data and Structural Refinement for Complexes **2b** and **2f**

	2b	2f
Empirical formula	C ₂₂ H ₂₂ F ₂ N ₂ O ₂ Cu	C ₂₂ H ₂₀ F ₄ N ₂ O ₂ Cu
Formula weight	447.96	483.94
Temperature	296 (2)	296 (2)
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n
<i>a</i> (Å)	10.165 (4)	10.9032 (16)
<i>b</i> (Å)	7.199 (3)	10.4206 (16)
<i>c</i> (Å)	14.111 (6)	19.347 (3)
α (°)	90	90
β (°)	94.701 (8)	97.804 (8)
γ (°)	90	90
Volume (Å ³)	1029.2	2182.1 (6)
<i>Z</i>	2	4
Density (Mg/m ³)	1.446	1.473
Absorption coefficient (mm ⁻¹)	1.099	1.055
<i>F</i> (000)	462	988
Crystal size	0.30 × 0.21 × 0.21	0.35 × 0.30 × 0.30
θ range (°)	2.38–25.04	2.03–25.05
Index range	-12 ≤ <i>h</i> ≤ 10, -8 ≤ <i>k</i> ≤ 8, -16 ≤ <i>l</i> ≤ 15	-12 ≤ <i>h</i> ≤ 12, -12 ≤ <i>k</i> ≤ 12, -14 ≤ <i>l</i> ≤ 23
Completeness to θ	99.9%	100%
Goodness of fit on <i>F</i> ²	1.029	1.012
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0286, 0.0898	0.0395, 0.0878
<i>R</i> indices (all data)	0.0332, 0.0942	0.0636, 0.0988
Largest difference between the peak and hole (e/Å ⁻³)	0.324, -0.277	0.297, -0.291

Z: number of formula units per unit cell; *F*(000): number of electrons per unit cell; θ : diffraction angle; *h*, *k*, *l*: reflection indices; *F*²: square of structure factors; *R*: residual factors; *I*: diffraction intensities; σ : standard deviations. The data in the parentheses represents the deviations of the last digit.

IR (KBr, cm⁻¹): 3450 (w), 2925 (w), 1569 (s), 1494 (s), 1404 (s), 1280 (w), 1172 (w), 1039 (w), 943 (w), 768 (m). ANAL. Calcd for C₂₂H₁₈CuF₆N₂O₂: C, 50.82%; H, 3.49%; N, 5.39%. Found: C, 50.61%; H, 3.56%; N, 5.22%.

Complex 2h. Complex **2h** was prepared via a procedure similar to that used for complex **2a** in 58% yield.

IR (KBr, cm⁻¹): 3445 (w), 2927 (w), 1576 (s), 1508 (s), 1400 (s), 1039 (w), 986 (w), 771 (m). ANAL. Calcd for C₂₂H₁₄CuF₁₀N₂O₂: C, 44.64%; H, 2.38%; N, 4.73%. Found: C, 44.50%; H, 2.63%; N, 4.72%.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Copper Complexes

The fluorosubstituted β -ketoimino ligands were synthesized by the condensation of acetyl acetone and fluorosubstituted aniline in toluene according to our previous works;⁴⁵ these could react

further with cupric acetate in methanol to obtain the corresponding copper complexes in good yields. These black copper complexes are stable in air and soluble in toluene, CH₂Cl₂, and THF. The synthetic route of the ligands and complexes is shown in Scheme 1.

The ligands were characterized by ¹H-NMR, FTIR spectroscopy, and elemental analysis, and the copper complexes were measured by FTIR spectroscopy and elemental analysis. These copper complexes could not be analyzed by ¹H-NMR because of the paramagnetic character of the Cu(II) complex. The crystals suitable for X-ray crystallography were obtained by slow evaporation from the toluene solution. The structures of complexes **2b** and **2f** are shown in Figures 1 and 2, respectively, which reveal the formation of Cu(II) complexes with a 2:1 ligand-to-metal stoichiometry. The crystal data and details of data collection and refinement are summarized in Table I, and the selected bond lengths and bond angles are listed in Table II.

It was found that both complexes **2b** and **2f** showed the same four-coordinate environment around the copper atom in which the two β -ketoimino ligands acted as bidentate N,O chelators and were in the trans conformation to create two six-membered chelate rings (Cu—O—C—C—N). In complex **2b**, the bond distances of C7—C8, C8—C9, and C9—C10 were 1.516, 1.410, and 1.370 Å, respectively. The C8—C9 and C9—C10 bond lengths were between single and double bonds; this meant that the double bond of C=C was delocalized. The bond length of C10—O1 was 1.281 Å, which was longer than the ordinary C=O bond (1.23 Å), so the C=O double bond was also delocalized, and an N—C—C—O conjugated big π bond was formed.

It is well known that four-coordinated Cu(II) complexes are usually characterized by a square planar coordination that may

Table II. Selected Bond Lengths (Å), Bond Angles (°), and Dihedral Angles at Cu (°) for Complexes **2b** and **2f**

2b		2f	
Cu(1)—O(1A)	1.9064	Cu(1)—O(2)	1.894
Cu(1)—O(1)	1.9064	Cu(1)—O(1)	1.904
Cu(1)—N(1)	2.0017	Cu(1)—N(1)	1.967
Cu(1)—N(1A)	2.0018	Cu(1)—N(2)	1.968
N(1)—C(8)	1.324		
O(1)—C(10)	1.281		
C(7)—C(8)	1.516		
C(8)—C(9)	1.410		
C(9)—C(10)	1.370		
C(10)—C(11)	1.515		
O(1A)—Cu(1)—O(1)	180.0	O(2)—Cu(1)—O(1)	158.55
O(1A)—Cu(1)—N(1)	88.62	O(2)—Cu(1)—N(1)	90.09
O(1)—Cu(1)—N(1)	91.39	O(1)—Cu(1)—N(1)	92.89
O(1A)—Cu(1)—N(1A)	91.38	O(2)—Cu(1)—N(2)	92.48
O(1)—Cu(1)—N(1A)	88.61	O(1)—Cu(1)—N(2)	91.61
N(1)—Cu(1)—N(1A)	180.0	N(1)—Cu(1)—N(2)	160.90
Dihedral angle at Cu (°)	0		28.20

Table III. Results of MA Polymerization with Different Copper Complexes and Different Polymerization Conditions^a

Entry	Complex	Temperature (°C)	Al/Cu	Time (h)	Product (g)	Act.[kg (mol of Cu) ⁻¹ h ⁻¹]	M _w /10 ⁴	M _w /M _n
1	2f	65	0	5	0	0		
2	2f	65	50	5	3.2302	32.3	6.1	1.46
3	2f	65	100	5	3.7990	38.0	11.2	1.61
4	2f	65	150	5	3.5861	35.8	7.4	1.58
5	2f	65	200	5	2.7564	27.6	6.1	1.79
6	2f	25	100	5	2.7258	27.3	6.1	1.90
7	2f	35	100	5	3.1180	31.2	7.3	1.70
8	2f	45	100	5	3.2871	32.9	10.2	1.77
9	2f	55	100	5	3.4662	34.7	10.9	1.65
10	2f	75	100	5	3.0491	30.5	5.1	1.74
11	2f	85	100	5	1.6767	16.8	4.9	1.59
12	2a	65	100	3	1.2454	20.7		
13	2b	65	100	3	1.6943	28.2	7.8	1.78
14	2c	65	100	3	1.8410	30.7	8.4	1.79
15	2d	65	100	3	2.0266	33.8	8.8	1.77
16	2e	65	100	3	2.6025	43.4	8.4	1.72
17	2f	65	100	3	2.7436	45.7	6.6	1.80
18	2g	65	100	3	3.1873	53.1	8.9	1.77
19	2h	65	100	3	3.4490	57.5	6.5	1.84

^aReaction conditions: toluene solvent, catalyst = 20 μmol, MA = 5 mL, solution total volume = 25 mL, Act. = Activity.

distort into a pseudo-tetrahedral geometry.⁵⁶ Furthermore, the steric hindrance and the electronic characteristics of the substituents on the imine moieties also influenced the planarity. The ortho-F derivative **2b** exhibited a perfect square planar geometry [O(1)—Cu(1)—O(1A) = 180°, N(1)—Cu(1)—N(1A) = 180°] and central symmetric structure, whereas a slightly distorted square planar geometry was observed in the case of the difluoro derivative **2f** with the diagonal angles deviated from the expected value of 180° (O1—Cu—O2 = 158.55°, N1—Cu—N2 = 160.90°). The dihedral angle between the Cu(1)O(1)N(1) and Cu(1)O(2)N(2) planes in complex **2f** was 28.2°; this was smaller than those of the other N,O-chelated copper(II) complexes, probably because of the smaller steric hindrance of fluoro atoms.

The Cu—O and Cu—N bond distances in **2b** and **2f** are in the ranges 1.89–1.90 and 1.96–2.00 Å, respectively, and the angles of N—Cu—O were in the range 91–93°; this was similar to the analogous [N,O]copper(II) complexes. It was noticeable that the Cu—N length in **2f** (1.967 Å) was obviously shorter than that in **2b** (2.0017 Å) with increasing fluorine atoms in the imine moiety; this may have been due to the stronger electron-withdrawing effect of more fluoro atoms. The reduction in the Cu—N bond distances suggested stronger coordination between the ligands and copper, which may have had significant effects on the catalytic performances.

MA Polymerization

Copper complexes can be used as catalyst precursors for the polymerization of polar monomers. Recently, Wu et al.³⁷ reported that bis(ketoamino)copper complexes with alkyl substituents could catalyze the polymerization of MA with moder-

ate activity when activated with MAO. We found that the introduction of fluorine atoms into the *N*-aryl ring of ligands greatly improved the catalytic activity, and the results are summarized in Table III.

Effect of the Polymerization Conditions. Copper complex **2f** was selected to catalyze MA polymerization under different conditions. The polymerization conditions, such as the Al/Cu molar ratio and the reaction temperature, had great effects on the catalytic activity and the properties of the produced PMA. The effects of the Al/Cu ratio are shown in Figure 3. The Al/Cu molar ratio influenced not only the catalytic activity but also the molecular weight of the polymer. The catalyst **2f**/MMAO demonstrated the highest catalytic activity [38.0 kg (mol of Cu)⁻¹ h⁻¹] and produced the PMA with the highest molecular weight of 11.2 × 10⁴ g/mol at an Al/Cu molar ratio of 100. A ratio of larger or smaller than 100 decreased the catalytic activity and lowered the molecular weight of the PMA. Moreover, complex **2f** had no catalytic activity for MA polymerization without MMAO; this showed that the cocatalyst MMAO played a crucial role in exerting the catalytic activity of the copper complexes.

Clear changes in the activity of **2f**/MMAO and the molecular weight of PMA at different temperatures were also observed, as shown in Figure 4. When the reaction temperature increased from 25 to 85°C, the polymerization activity increased gradually to a maximum at 65°C and then decreased rapidly. A similar trend was observed for the molecular weight of the produced polymer. However, the molecular weight distributions of PMA were almost constant (within 1.4–1.9 under different

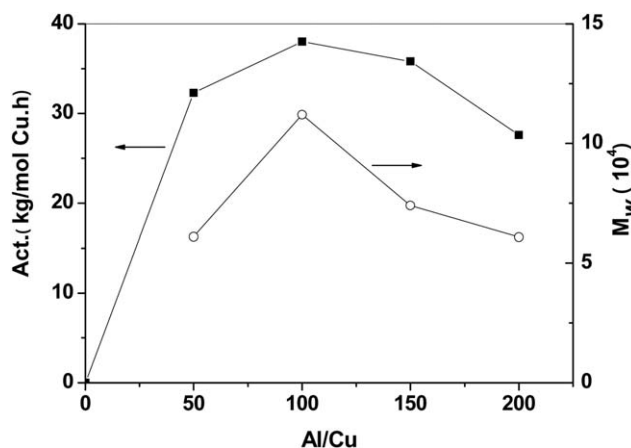


Figure 3. Effects of the Al/Cu molar ratio upon the catalytic activity of complex **2f** and the molecular weight of PMA.

conditions); this confirmed that the catalyst had a single active center. The catalyst need to be activated at a certain temperature, so the increase in the temperature increased the activity. However, too high a temperature reduced the catalytic activity, as was also found for alkyl-substituted bis(β -ketoamino)copper complex by Wu et al.³⁷

Effect of the Fluorosubstituents. We previously introduced fluorine atoms into the *N*-aryl moiety in early-transition-metal complexes [mono β -diiminato titanium complexes⁴⁴ and bis(β -ketoimino) titanium complexes⁴⁵] and observed significant electronic effects of fluorosubstituents on the structure and catalytic activity of the titanium complexes. The fluorine substitution pattern on the *N*-aryl moiety also exert a great influence on the bis(β -ketoimino)copper complexes for MA polymerization, and the results are shown in Figure 5.

All of the fluorosubstituted bis(β -ketoimino)copper complexes efficiently catalyzed the MA polymerization. Complex **2a** with a methyl group showed an activity of $20.7 \text{ kg (mol of Cu)}^{-1} \text{ h}^{-1}$, which was similar to results reported by Wu et al.³⁷ The introduction of fluoro atoms into the *N*-aryl rings of ligands, however,

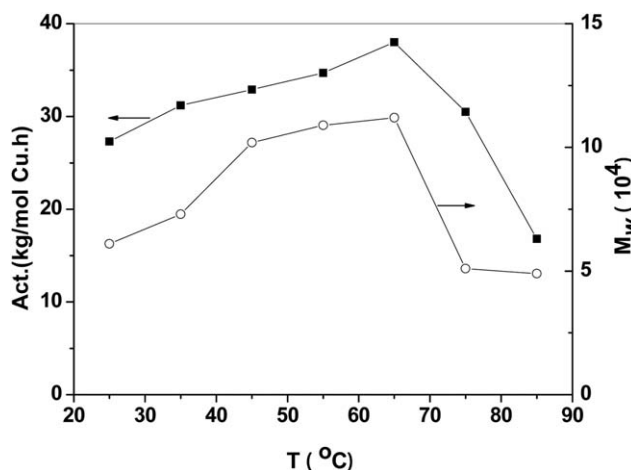


Figure 4. Effects of the temperature (T) on the catalytic activity of complex **2f** and molecular weight of PMA.

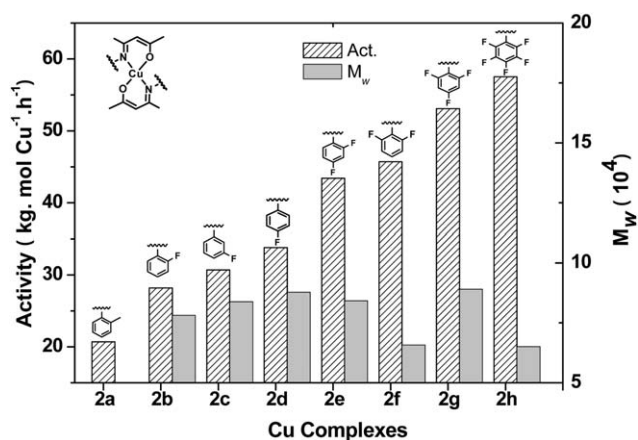


Figure 5. Effects of the fluorosubstituents on the catalytic activity of the Cu complexes and molecular weight of PMA.

appreciably improved the catalytic activities. The catalytic activity of complexes **2b–2d** with only one fluorine substitution of the *N*-aryl moiety were about $30 \text{ kg (mol of Cu)}^{-1} \text{ h}^{-1}$, and the activity of the difluoro derivatives **2e** and **2f** reached $43\text{--}45 \text{ kg (mol of Cu)}^{-1} \text{ h}^{-1}$. The trifluoro derivative **2g** exhibited a still higher activity of $53.1 \text{ kg (mol of Cu)}^{-1} \text{ h}^{-1}$, and the activity of the pentafluoro derivative **2h** increased further to $57.5 \text{ kg (mol of Cu)}^{-1} \text{ h}^{-1}$; this was almost three times that of **2a**. To the best of our knowledge, this was the highest value reported so far for copper complexes in acrylic monomer polymerization. It was obvious that the number of fluorosubstituents on the *N*-aryl moiety significantly affected the catalytic activities of the corresponding copper complexes; however, the position of the fluorosubstituents on the *N*-aryl rings had no obvious influence; that is, the copper complexes had the same amount of fluorosubstituents on the *N*-aryl ring but at different positions showed almost the same catalytic activities (e.g., **2b**, **2c**, and **2d**; **2e** and **2f**). The presence of the electron-withdrawing fluorosubstituents on the ligands increased the electrophilicity of the central Cu(II) and thus may have benefited the interaction of the metal and monomer. A similar effect was also found for nitro groups by Raspolli et al.³⁹ in bis(salicylaldimine)copper complexes for the catalysis

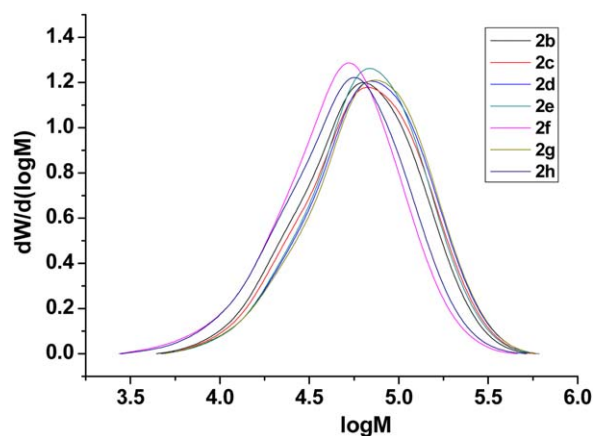


Figure 6. GPC curves of PMA catalyzed by different Cu complexes. W = weight percent; M = weight-average molecular weight. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of *n*-butyl methacrylate polymerization. Furthermore, M_w and the molecular weight distribution (M_w/M_n) were also not apparently influenced by the concentration of the fluorosubstituents, which were about $6.5\text{--}9 \times 10^4$ and $1.7\text{--}1.9$ g/mol, respectively (shown in Figure 6).

CONCLUSIONS

A series of β -ketoimine ligands with various fluorosubstitution patterns on the *N*-aryl moiety and their corresponding copper complexes were synthesized in good yield and characterized in detail. The structures and catalytic performances of the complexes were significantly affected by the fluorine substitution. X-ray diffraction characterization revealed that copper(II) was coordinated by two trans β -ketoimino ligands with delocalized double bonds. The copper complex **2b** with *o*-fluorosubstitution adopted a central symmetric square planar structure, whereas the difluoro derivative **2f** took a distorted square planar structure with a dihedral angle of 28.2° . The Cu—N length in **2f** was shorter than that in **2b** because of the strong electron-withdrawing effect of the increased fluorine substitution on the *N*-aryl moiety. The MMAO-activated copper complexes effectively polymerized MA. Fluorosubstituents on the ligands improved the catalytic activity, and when a greater number of fluorine atoms was introduced, the activities were higher. However, the position of the fluorosubstituents on the *N*-aryl rings had no obvious influence. The highest activity was obtained with the pentafluoro derivative **2h**; it reached 57.5 kg (mol of Cu) $^{-1}$ h $^{-1}$. This was the highest value reported so far for copper complexes in the acrylic monomer polymerization.

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