Bis(β-ketoamino) copper complexes for vinyl polymerization of norbornene: Correlation between precursor structure and catalytic activity

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ABSTRACT

A novel fluorinated bis(β-ketoamino) copper complex was synthesized and characterized. Norbornene polymerizations with bis(β-ketoamino) copper complexes activated with methylaluminoxane (MAO) were investigated. The highest catalytic activity up to now reported for copper based systems in norbornene polymerization was achieved using fluorinated bis(β-ketoamino) copper/MAO. The influence of precursor structure including steric and electronic effects on catalytic activity for norbornene polymerization was evaluated in detail. Bulky steric substituents and strong electron-withdrawing groups can enhance catalytic activity of precursor for norbornene polymerization through a dissociative mechanism. The influences of polymerization parameters such as polymerization temperature and Al/Cu ratio on norbornene polymerization with bis(β-ketoamino) copper catalysts were also examined. Norbornene polymerization catalyzed by bis(β-ketoamino) copper complexes/MAO proceeded on Cu(I) species through a coordination/insertion mechanism to produce vinyl-addition polynorbornene.

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1. Introduction

Interests in polymers of cyclic olefins such as norbornene (NBE) (bicyclo[2.2.1]hept-2-ene) have increased dramatically over the past decade. The attractive properties of this addition type of polymer such as high chemical resistance, good UV resistance, low dielectric constant, high glass transition temperature, excellent transparency, large refractive index, and low birefringence have been the reasons for the increased interest [1–7]. Driven by industrial application, vinyl-addition polymerization of norbornene has already been reported using many transition metal precursors including titanium [8,9], zirconium [10,11], iron [12], nickel [13–18], palladium [19–21], cobalt [22,23] and chromium [24,25]. Recently, Janiak and Bao have given a full literature and patent account on the work describing the addition polymerization of norbornene [26,27].

Compared with nickel and palladium based catalysts, copper based complexes have been scarcely reported as a kind of precursors for norbornene polymerization. To date, only several copper complexes bearing [N,O] donors such as salicylaldiminate [28], pyrazolone-amine [29,30], 2,5-diamino-1-4-benzoquinonediimine [31], phenoxy-imidazole [32], and hydroxyindanimine [33] ligands have been reported for norbornene polymerization. Moderate catalytic activities (10–100 kg PNBE/(mol Cu h)) were achieved, and a coordination/insertion mechanism for norbornene polymerization catalyzed by these copper catalysts was presented [28–33].

During the past few years, β-ketoamine ligand has been focused and widely applied in the organometallic field [34–36]. However, copper complex bearing β-ketoamine ligand is not prepared and characterized yet. Prior to this work, we have synthesized bulky bis(β-ketoamino) copper(II) complexes and investigated their homo- and copolymerizations of methyl acrylate and 1-hexene in the presence of MAO, and an insertion-triggered radical mechanism was also proposed [37]. We further report herein the preparation of a new copper(II) complex bearing fluorinated β-ketoamino ligand. To gain more insight into the correlation between precursor structure and catalytic activity for norbornene polymerization, the influence of steric and electronic effects on catalytic activity for norbornene polymerization was evaluated in detail.

2. Experimental

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with standard vacuum-line, Schlenk, or glovebox techniques.

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2.1. Materials

Toluene and hexane were dried over sodium metal and distilled under nitrogen. Dichloromethane and chlorobenzene was dried and distilled from calcium hydride. 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione was purchased from Aldrich. 2,6-Diisopropylaniline (Aldrich 90%) and 2,6-dimethylaniline (Aldrich 97%) were distilled prior to use. Norbornene (bicyclo-[2.2.1]hept-2-ene; Acros) was purified by distillation over potassium and used as a solution in chlorobenzene. MAO (methylaluminoxane solution, 10 wt.% in toluene) was purchased from Aldrich. Copper complexes **1** and **2** were prepared by our previous reported method [37]. Other commercially available reagents were purchased and used without purification.

2.2. Norbornene polymerization

In a typical procedure, the appropriate MAO solution was introduced into a chlorobenzene solution of norbornene in a 50 mL round-bottom glass flask. Chlorobenzene and copper complexes solution in dichloromethane were syringed into the well-stirred solution in order, and the total reaction volume kept 20 mL. The reaction was continuously stirred for an appropriate period at polymerization temperature. Polymerizations were terminated by addition of the acidic methanol (methanol–HCl, 95:5). The resulting precipitated polymers were collected and treated by filtering, washing with methanol several times, and drying in vacuum at 60 °C to a constant weight.

2.3. Characterization

Elemental analyses were performed on a Vario EL microanalyzer. ^{1}H NMR and ^{13}C NMR spectra of ligand were carried out on a Bruker 500 MHz instrument at room temperature in CDCl$_3$. ^{1}H NMR and ^{13}C NMR spectra of the polymers in o-dichlorobenzene-d_4 were recorded on a Bruker 500 MHz spectrometer. GPC analyses of the molecular weight and molecular weight distribution (MWD) of the polymers were performed on a PL-GPC 220 instrument with standard polystyrene as the reference and with 1,2,4-trichlorobenzene (TCB) as the eluent at 150 °C. FT-IR spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer. Differential scanning calorimetry (DSC) analysis was conducted with a Perkin-Elmer DCS-7 system. The DSC curve was recorded at a heating rate of 10 °C/min. The cooling rate was 10 °C/min. TGA data was measured with a TG-290C thermal analysis system instrument under a nitrogen atmosphere up to 600 °C at heating rate of 10 °C/min. Wide-angle X-ray diffraction (WAXD) curve of the polymer powder was obtained using a D/Max-IIIA powder X-ray diffractometer.

2.4. Crystal structure determination

Crystal data obtained with the ω–2θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The structure was solved using direct methods, while further refinements with full-matrix least squares on F^2 were obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

2.5. Synthesis of copper complex 3

Titanium tetrachloride (TiCl$_4$) diluted in dry hexane (8 mL, 27.8 mmol) was dropped into the stirring 100 mL of 2,6-diisopropylaniline (14.2 mL, 75 mmol) solution in dry hexane at 0 °C under nitrogen. A yellow-brown precipitate formed immediately, and the mixture was left to stir for overnight under nitrogen. 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (3.5 mL, 25 mmol) was then injected slowly to the mixture which turned orange-brown. After refluxing for another 8 h, the mixture became yellow-brown. The precipitate was removed by filtration and the filtrate was treated by a water/hexane extraction. The organic phase was evaporated to dryness, and the resulting solid was recrystallized in methanol to yield a bright yellow needle crystalline solid **L3**, which was filtered off and dried. Yield: 3.85 g, 42%. Anal. Calc. For C$_{17}$H$_{19}$F$_6$NO: C, 55.59; H, 5.21; N, 3.81. Found: C, 55.68; H, 5.32; N, 3.70. ^{1}H NMR (CDCl$_3$, 500 MHz), δ (ppm): 11.64 (b, 1H, –NH), 7.37 (t, 1H, p-C$_6H_3$), 7.20 (d, 1H, m-C$_6H_3$), 6.05(s, 1H, CH=), 2.94 (2H, –CH(CH$_3$)$_2$), 1.26 (d, 6H, –CH_3), 1.13 (d, 6H, –(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 125 MHz), δ (ppm): 180.6, 155.1, 136.5, 146.4, 1301.0, 129.8, 123.6, 120.0, 117.7, 115.4, 87.2, 28.9, 25.2, 21.6.

Ligand **L3** (3.67 g, 10 mmol) was allowed to react with Cu(OAc)$_2$·H$_2$O (1.00 g, 5 mmol) in 200 mL methanol at the refluxing temperature for 2 h. After cooling, the solid was collected by removing solvent in vacuum and recrystallized from the toluene/methanol solution to give copper complex **3** as brown crystals in 91% yield (3.62 g). Anal. Calc. For C$_{34}$H$_{36}$F$_{12}$N$_2$O$_2$Cu: C, 51.29; H, 4.56; N, 3.52. Found: C, 51.38; H, 4.27; N, 3.46. FT-IR (cm^{-1}): 2965(w), 2930(w), 2867(w), 1612(m), 1588(m), 1540(s), 1513(m), 1469(s), 1386(w), 1365(w), 1332(m), 1317(m), 1268(s), 1190(s), 1140(s), 1112(m), 1097(m), 1054(w), 956(m), 933(w), 853(m), 786(s), 759(m), 740(m), 701(m), 616(m).

3. Results and discussion

### 3.1. Synthesis of copper complexes and molecular structure

Copper complexes **1** and **2** were synthesized following our previously reported method [37]. New fluorinated β-ketoamine ligand **L3** was prepared by condensation of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione and 2,6-diisopropylaniline aniline in the presence of TiCl$_4$ due to strong electron-withdrawing CF$_3$ groups. The desired bulky copper complex **3** was obtained by the reaction of Cu(OAc)$_2$·H$_2$O with two equivalents of the fluorinated β-ketoamine ligand in methanol (see Scheme 1).

New copper complex **3** bearing two fluorinated β-ketoamino ligands was characterized by the elemental analysis and FT-IR. NMR analysis failed due to the paramagnetic character of the Cu(II) complex, which is similar to other copper(II) complexes bearing [N,O] ligands [37].

Crystal suitable for X-ray crystallography of **3** was obtained by slow evaporation from methanol/toluene solution. The data collection and refinement data are summarized in Table 1. ORTEP diagram is shown in Fig. 1 along with selected bond lengths and bond angles [38]. Complex **3** shows the four-coordinate environment around the copper atom where the two fluorinated ligands lie in the *trans* conformation to create two slightly distorted six-membered coordination planes. Like copper complex **2** with non-fluorinated ligands [37], copper complex **3** also adopts a distorted square planar coordination geometry. However, the presence of strong electron-withdrawing CF$_3$ groups causes a slight decrease in the bond lengths of Cu–O (1.88 Å *vs* 1.89 Å) and a slight increase in the bond lengths of Cu–N (1.99 Å *vs* 1.97 Å). Besides, the angle of N–Cu–O (∼93°) of copper complex **3** is smaller than that of **2** [37].

3.2. Norbornene polymerization

Bis(β-ketoamino) copper complexes **1**–**3** were investigated as precursors for norbornene polymerization. In the presence of
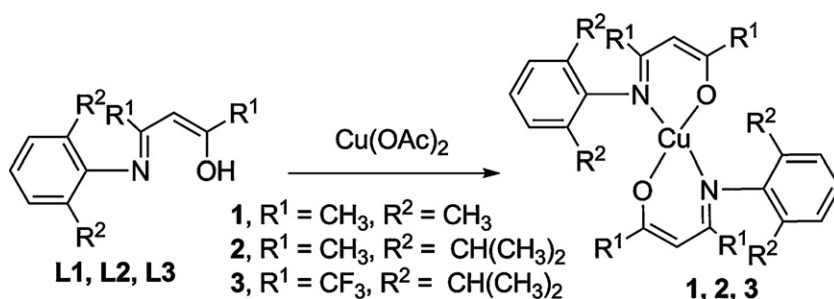
Scheme 1. Structure of bis(β-ketoamino) copper complexes.

Table 1
Crystallographic data for copper complex **3**.

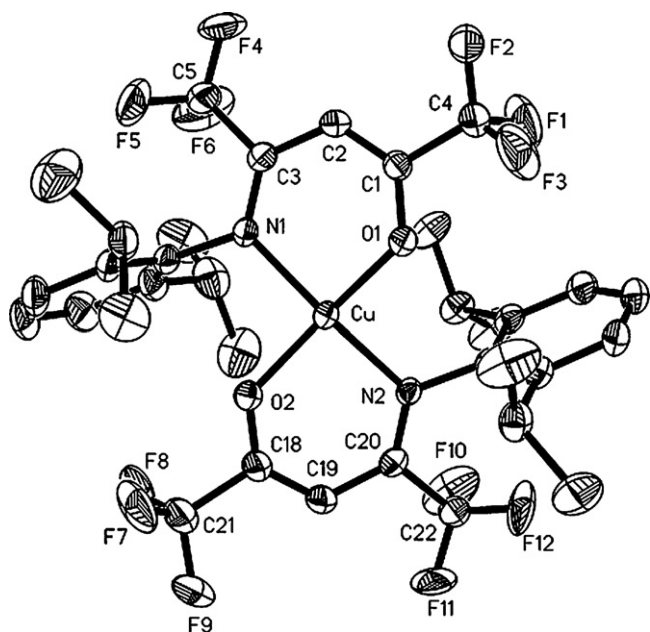|	
Empirical formula	$C_{34}H_{36}F_{12}N_2O_2Cu$
Formula weight	796.19
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	P-1
a (Å)	10.696(6)
b (Å)	11.719(6)
c (Å)	15.854(8)
α (°)	69.046(8)
β (°)	88.823(8)
γ (°)	76.279(8)
Volume (Å³)	1798.5(16)
Z	2
Density (mg/m³)	1.470
Absorption coefficient (mm⁻¹)	0.702
$F(000)$	814
Crystal size (mm)	$0.30 \times 0.25 \times 0.20$
θ range (°)	1.91–26.00
Index ranges	$-13 \le h \le 13, -13 \le k \le 14, -18 \le l \le 19$
Completeness to θ (26.00)	97.7%
Goodness-of-fit on F^2	0.943
Final R indices [$I>2\sigma(I)$]	0.0413, 0.0944
R indices (all data)	0.0614, 0.1015
Largest diff. peak and hole (e/Å⁻³)	0.375, −0.309

Fig. 1. ORTEP diagram of copper complex **3** with the thermal ellipsoids shown at 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu–N(1), 1.988(2); Cu–N(2), 1.993(2); Cu–O(1), 1.880(2); Cu–O(2), 1.881(2); O(1)–Cu–N(1), 92.99(9); O(2)–Cu–N(2), 92.80(9); O(1)–Cu–O(2), 154.64(10); N(1)–Cu–N(2), 156.24(9).
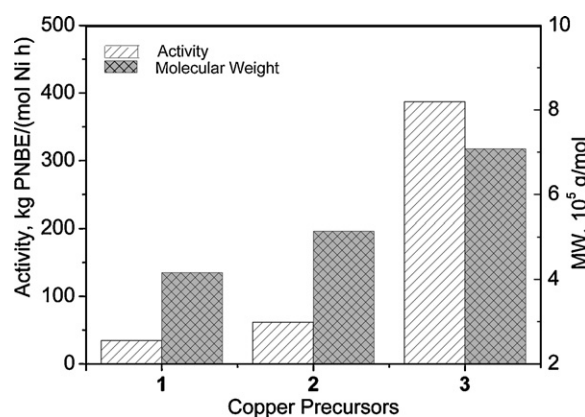
MAO, three copper complexes **1–3** exhibited appreciable activities for norbornene polymerization. The steric and electronic characteristics of the chelate ligands play an important role in the catalytic performances. Fig. 2 clearly shows that the order of the values of catalytic activities for norbornene polymerization catalyzed by **1–3**/MAO is **3 > 2 > 1** under the same conditions. **1** with N-2,6-dimethylphenyl group showed the lower activity for norbornene polymerization than **2** with N-2,6-diisopropylphenyl group, suggesting that bulky substituent on N-aryl moiety can enhance catalytic activity for norbornene polymerization. Compared with **2**, **3** with CF₃ groups exhibits obviously high catalytic activity for norbornene polymerization. The presence of electron-withdrawing CF₃ groups on the backbone of chelate ligands significantly increases the catalytic activity which reaches 387 kg PNBE/(mol Cu h), the highest value up to now reported for copper based catalytic systems in norbornene polymerization. Carlini also reported the presence of electron-withdrawing nitro groups on the ligand markedly increased the activity of the bis(salicylaldiminato) copper catalysts [28]. Generally, the fluorinated bis(β-ketoamino) copper catalyst **3** exhibit high catalytic activity which are comparable to those of bis(β-ketoamino) nickel catalysts [39]. Therefore, the introduction of bulky substituents and electron-withdrawing groups can enhance catalytic activity of bis(β-ketoamino) copper complex for norbornene polymerization.

Besides, the steric and electronic characteristics of the chelate ligands also affect the molecular weights of the produced polymers. The M_w value of the obtained polymer shows a similar tendency to catalytic activity under the same polymerization conditions (see Fig. 2). The highest molecular weight of the produced polymer (7.08×10^5 g/mol) was achieved using **3**/MAO catalytic system.

Fig. 2. Influence of precursor structure on norbornene polymerization with copper complexes **1–3**/MAO. Polymerization conditions: catalyst addition, 2 μmol; Al/Cu = 2000; polymerization temperature, 70 °C; reaction time, t = 1 h; norbornene addition, 4 g; solvent, 20 mL chlorobenzene.

Table 2
Norbornene polymerizations with copper complexes **1–3**/MAO at various conditions.[a]

Entry	Precursor	T_p (°C)	Al/Cu (mol/mol)	Activity[b]	M_w[c]	M_w/M_n
1	**1**	70	0	–	–	–
2	**1**	70	500	9.0	1.84	2.14
3	**1**	70	1000	24.5	3.59	2.70
4	**1**	70	2000	34.5	4.16	3.16
5	**1**	70	3000	28.0	3.81	2.82
6	**1**	30	2000	6.0	2.21	2.42
7	**1**	50	2000	20.0	3.06	2.53
8	**1**	90	2000	26.5	3.35	2.63
9	**2**	70	0	–	–	–
10	**2**	70	500	16.5	3.04	2.32
11	**2**	70	1000	39.0	3.75	2.59
12	**2**	70	2000	61.5	5.14	3.42
13	**2**	70	3000	53.0	4.90	2.97
14	**2**	30	2000	10.0	2.78	2.48
15	**2**	50	2000	30.5	3.89	2.61
16	**2**	90	2000	46.0	4.82	2.93
17	**3**	70	0	–	–	–
18	**3**	70	500	47.5	4.76	2.63
19	**3**	70	1000	206.5	5.81	2.93
20	**3**	70	2000	387.0	7.08	3.76
21	**3**	70	3000	213.0	6.02	3.05
22	**3**	30	2000	27.5	3.57	2.59
23	**3**	50	2000	104.5	5.34	2.82
24	**3**	90	2000	315.5	6.51	3.31

[a] Polymerization conditions: reaction time, $t = 1$ h; addition of copper complex, 2 μmol; norbornene addition, 4 g; NBE/Cu, 21276; solvent, 20 mL chlorobenzene.
[b] In units of kg PNBE/(mol Ni h).
[c] In units of 10^5 g/mol.

3.3. Influence of Al/Cu ratio

When copper complexes **1–3** were employed for norbornene polymerization in the absence of any activators (entries 1, 9, and 17, Table 2), no catalytic activity was observed. Also in this case, under the adopted conditions, no catalytic activity was observed when MAO was employed in the absence of copper precursors. When copper complexes were activated with MAO, appreciable catalytic activities were always observed to yield polynorbornene without formation of oligomeric products. Therefore, the activator MAO is essential to norbornene polymerization, and copper precursor and activator MAO cooperate in norbornene polymerization process.

Influence of Al/Cu mole ratio was further investigated at the fixed temperature (70 °C), and the results are listed in Table 2. Three catalytic systems **1–3**/MAO showed the same tendency. When Al/Cu ratio was 500, low activities for norbornene polymerization were observed. With an increase in Al/Cu ratio from 500 to 3000, the catalytic activities for norbornene polymerization increased, and then decreased. An optimum Al/Cu ratio was 2000 for bis(β-ketoamino) copper/MAO catalytic systems.

Besides, Al/Cu ratio also influenced the molecular weight of the obtained polynorbornene. All of the catalytic systems showed the same tendency. With an increase in Al/Cu ratio, the molecular weights of polynorbornenes increased, and then decreased. When Al/Cu ratio was 2000, the highest molecular weights were observed. This result suggests that excess MAO (Al/Cu > 2000) gives rise to easy chain transfer.

3.4. Influence of polymerization temperature

The reaction temperature also strongly affected the catalytic activities, and the results of norbornene polymerizations using **1–3**/MAO at various temperatures were summarized in Table 2. For **1–3**/MAO catalytic systems, small amount of polymer were produced and low catalytic activities were observed when reaction temperature was 30 °C. With an increase in the reaction temper-
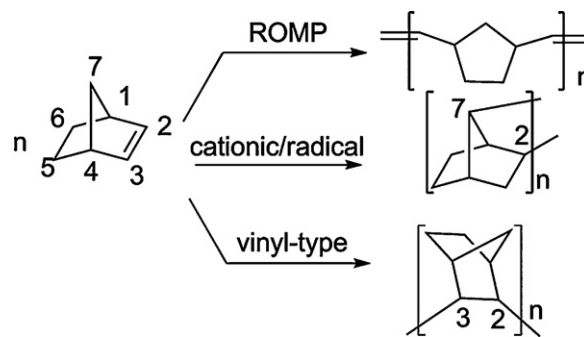
Scheme 2. Three mechanisms of norbornene polymerization.

ature, the catalytic activities obviously increased. Three copper complexes showed the highest activity for norbornene polymerization at 70 °C. The higher temperature (90 °C) caused a decrease in the catalytic activity for the norbornene polymerization because of the instability or decomposition of the active species, thus suggesting 70 °C is the optimum working temperature. The polymerization temperature also affected the molecular weights of the polymers. The M_w value of the obtained polymer increased, and then decreased with an increase in the reaction temperature. When polymerizations were carried out at 70 °C, the highest molecular weights of the obtained polymer were observed. This result suggests that chain transfer or termination begins to accelerate above 70 °C.

3.5. Polynorbornene characterizations

All of the obtained polymers catalyzed by bis(β-ketoamino) copper catalysts are soluble in organic solvents such as chlorobenzene, 1,2-dichlorobenzene. FT-IR spectrum revealed no traces of double bond, which often appear at 1680–1620, 966 and 735 cm^{-1}, while the existence of vibration bands of bicyclics of norbornene at 941 cm^{-1}. ^{1}H NMR spectrum (0.85–2.50 ppm) also proved no traces of any double bond (5.1, 5.3 ppm) [40], ensuring the occurrence of vinyl-type polymerization rather than ring-opening metathesis polymerization. ^{13}C NMR spectrum also further confirmed that the obtained polymers were vinyl-type polynorbornene. Several signals were observed from 28 to 55 ppm. The resonances of methenes and methines appear at 29.4–33.0 ppm for C_5 and C_6, 35.5–38.5 ppm for C_7, 38.8–42.8 ppm for C_1 and C_4, and 46.1–54.0 ppm for C_2 and C_3. The ^{13}C NMR spectrum is similar to that reported by another copper catalysts [32,33] and bis(β-ketoamino) nickel catalysts [39].

TGA curves of the obtained polynorbornenes showed that the polymer samples were stable up to 450 °C. Attempts to measure glass transition temperature (T_g) of polynorbornene from DSC curves were unsuccessful, DSC spectra not evidencing well-defined endothermic signals upon heating to the decomposition temperature. The wide-angle X-ray diffraction analysis of the obtained polynorbornene showed no indication of crystallinity.

3.6. Mechanistic consideration

Two possible mechanisms for the copper-mediated polymerization of olefins are radical and coordination/insertion [41–43]. Currently, all authors tended to think norbornene polymerization with copper based catalysts proceed through a coordination/insertion mechanism [28–32]. In fact, ring-opening metathesis polymerization (ROMP) can be safely ruled out according to NMR and FT-IR spectra of the obtained polynorbornene, but distinguishing between 2,3-addition and 2,7-addition fashion is difficult (see Scheme 2). Additionally, norbornene polymerization

through a radical mechanism typically forms low molecular weight or oligomeric products [16,26]. Our results show that no oligomeric products were obtained during norbornene polymerization, and the molecular weights of the obtained polynorbornenes are high up to 10^5 g/mol. Therefore, an insertion-triggered radical mechanism for norbornene polymerization using bis(β-ketoamino) copper/MAO can also be excluded [37].

Though a vinyl-addition coordination/insertion mechanism for norbornene polymerization catalyzed by bis(β-ketoamino) copper/MAO can be identified, distinguishing true active species between Cu(II) and Cu(I) is still worthwhile and interesting. The above control experiments showed that no reaction took place in the absence of MAO or bis(β-ketoamino) copper precursor, indicating both MAO and copper precursor were necessary for norbornene polymerization. EPR determination showed an silent Cu(I) was formed from an initial Cu(II) precursor with strong EPR signal by addition of MAO [37]. This result is well consistent with other Cu(II) precursor analogs by treatment of MAO [28,44]. Given the reduction behavior of MAO, the reduction of the late transition metal was analogous to what was recently observed in the case of Fe(III), Ni(II), and Pd(II) complexes upon activation of MAO [45–47]. It is accepted that TMA contained in MAO play a reducing role and oligomeric MAO has a stabilizing effect in the M(II) → M(I) (M = Ni, Pd, Cu) reduction process. Therefore, mixing bis(β-ketoamino) copper precursor and MAO will lead to form of Cu(I) species for norbornene polymerization. A Pd(I) species was recently reported as a highly active norbornene precursor [47].

The formation of Cu(I) species is strongly indicative of the abstraction of two β-ketoamino ligands by MAO. A ^{19}F NMR was carried out to test the formation of free ligand in copper precursor solution after addition of 200 equiv. MAO. Two signals at −65.2 ppm and −73.0 ppm clearly present, which are same to signals of ligand, proving occurrence of ligand abstraction. Increasing reaction temperature in the region from 0 to 70 °C leads to an increasing activity, also indicating ligand abstraction is favorable at high temperature. Additionally, a copper(II) complex chelating salen-type Schiff base ligand after activation with MAO was recently reported as a norbornene polymerization catalyst, indirectly suggesting the removal of ligand [48]. To further verify to Cu(I) species for norbornene polymerization, CuCl and CuCl$_2$ salts were used to polymerize norbornene in the combination of MAO (10 μmol CuCl, 4 g monomer, 1000 Al/Cu, 2 h, 20 mL chlorobenzene). No catalytic activities were observed in both systems, and metal depositions on the bottom of the reaction flask were ascertained. This is result from the over-reduction of copper salt to Cu(0) under the adopted conditions [28]. Hence, ligand plays an important role in stabilizing Cu(I) complex. Also note that metal depositions can take place in bis(β-ketoamino) copper(II)/MAO system without monomer, suggesting norbornene can also stabilize Cu(I) by coordination to metal center [49,50].

Combining the above experimental result, the activation process of the precursors may be formulated in the following pathway (Scheme 3). Addition of MAO to bis(β-ketoamino) copper(II) precursor results in the abstraction of one ligand and form of LCu(I)–NBE complex. Mixing MAO and CuCl or CuCl$_2$ causes an over-reduction of copper metal to give metal deposition due to the lack of stabilization of ligand. Another ligand of LCu(I)–NBE complex can be further removed, and a Cu(I) active species for norbornene can be formed, which is stabilized by the coordination of norbornene monomers. The polynorbornene is produced through the insertion polymerization in Cu(I) active species. Similar formation of highly active "nake" Pd^{2+} species for norbornene polymerization by chloride abstraction and ligand redistribution was also reported by Janiak [51,52].

According to the proposed activation pathway, the influence of ligand effect on activity can be obviously attributed to the kinetic activation effect [53]. Since bulky ligands are more labile than their
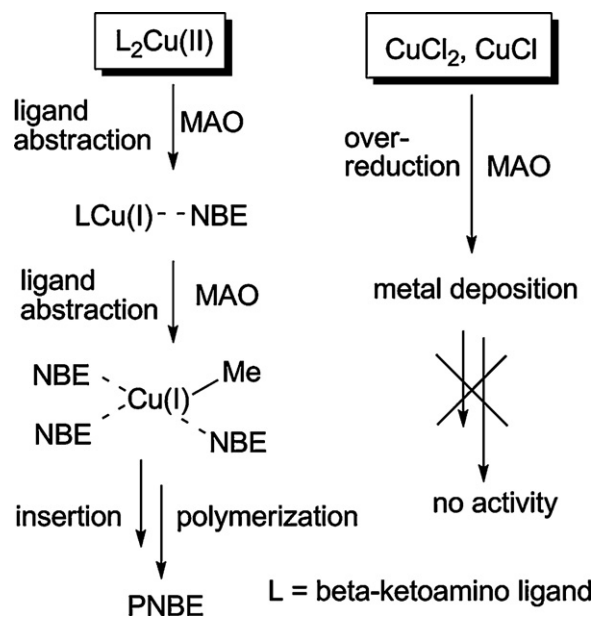
Scheme 3. Proposed activation pathway of bis(β-ketoamino) copper(II) activated by MAO.

less bulky analogs, bulky substituents on ligand can enhance catalytic activity of bis(β-ketoamino) copper complexes through a dissociative mechanism. Besides, electron-withdrawing CF$_3$ groups make ligands be more easily abstracted because of weak bound interaction to metal, thus significantly increasing the catalytic activity. This result is also supported by Cu–ligand bond strength (see crystal data).

In combination of our previous polymerization of methyl acrylate, bis(β-ketoamino) copper/MAO catalytic system exhibits a dual behavior toward the polymerization of polar methyl acrylate and nonpolar norbornene. Bis(β-ketoamino) copper/MAO is capable of polymerizing methyl acrylate by a radical mechanism and norbornene by a coordination/insertion mechanism, respectively. To the best of our knowledge, this is the first illumination that copper based catalytic system can operate different mechanisms for polar acrylate and nonpolar norbornene monomers. Similar behavior of palladium pentafluorophenyl complexes has also been observed [54].

4. Conclusion

We have developed bis(β-ketoamino) copper complexes as precursors for norbornene polymerizations. Under optimum reaction conditions (*T* = 70 °C, Al/Cu = 2000), the highest catalytic activity (387 kg PNBE/(mol Cu h)) up to now reported for copper based systems in norbornene polymerization is achieved using fluorinated bis(β-ketoamino) copper/MAO. The presence of bulky substituents on *N*-aryl moiety and the introduction of electron-withdrawing groups on the precursors can enhance their catalytic performances through a dissociative mechanism. Bis(β-ketoamino) copper/MAO catalytic systems are capable of polymerizing methyl acrylate by an insertion-triggered radical mechanism and norbornene on Cu(I) active species by a coordination/insertion mechanism, respectively. The obtained polynorbornenes are characterized by high molecular weight and vinyl-type structure.

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