

Syntheses, structures and catalytic activity of copper(II) complexes bearing *N,O*-chelate ligands

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Abstract

Copper complexes [Cu(Lⁿ)₂] **1–4** bearing *N,O*-chelating β-ketoamine ligands Lⁿ based on condensation products of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone with aniline (L¹), α-naphthylamine (L²), *o*-methylaniline (L³), and *p*-nitroaniline (L⁴), respectively, were synthesized and characterized by IR, ¹H NMR and X-ray crystallography (except **2**). They were shown to catalyze the vinyl polymerization of norbornene when activated by methylaluminumoxane (MAO). Both steric and electronic effects are important and influential factors contributing to the catalytic activity of the complexes with the order of **2** > **4** > **3** > **1**.

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Keywords: Copper complex; β-Ketoamine; Polymerization; Catalytic activity; Norbornene

1. Introduction

In recent years there has been an intense search for new-generation catalysts for the polymerization of olefins in both academic and industrial research laboratories [1], especially those containing late transition metals. Compared with the metallocenes based on early transition metals, the late transition metal catalysts are less oxophilic and thus less easily poisoned by polar monomeric contaminants [2]. Among these, copper(II) complexes present some interesting properties in both homo- and copolymerization of olefins with functional monomers [3]. Copper alkene chemistry is well explored in the literature [4], yet Cu-complexes used as catalysts in olefin polymerization are not well documented and the structure of the reactive center is still not yet disclosed. There were reports that Cu(II) complexes with benzamidinate [5] or benzimidazolyl [6] ligands have been used for ethylene polymerization but with low cata-

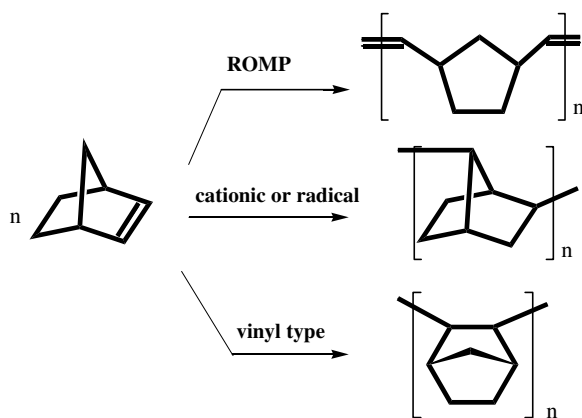
lytic activities. Copper(II) catalysts based on α-diimine [7] could produce very high-molecular-weight polyethylenes with moderate activity, which are probably the first such catalysts reported in the academic literature, although some have been described in patents [3b].

Complexes containing ligands of *N,O*-chelate are particularly interesting and challenging for catalysis by mixed-donor-ligand-complexes, such as the Ni-based systems were shown to be effective in ethylene polymerization [8]. β-Ketoamines are important members of the family of *N:O* bidentate ligands [9] because of their ease of preparation and simple modification of both steric and/or electronic effects. Presently, although the luminescent and magnetic properties and the biological activity [10] of β-ketoamino Cu-complexes have been reported, the catalytic activity toward olefin polymerizations, particularly of the bicyclic olefin bicyclo[2.2.1]het-2-ene, better known by its trivial name norbornene (NBE), to our knowledge, has not been observed before.

The catalytic polymerization of NBE has been reported to go through three pathways [1d,11] as shown in Scheme 1

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Scheme 1. Schematic representation of the three polymerization processes for norbornene (Ref. [1d]).

[1d]: the ring-opening metathesis polymerization (ROMP), the cationic or radical polymerization, and the vinylic polymerization. Catalysts containing Pd [12], Ni [13], or Co [14] and many others have been reported for vinyl-type polymerization of NBE, but none of copper complexes has been documented. The significance of this type of polymerization lies in the fact that the polymers formed will have good mechanical property, high heat resistivity and good solubility in organic solvents [1d]. Such systems may also find use in the copolymerization of NBE/olefins. In order to explore this void field of β -ketoamine-Cu(II) catalysts, herein a series of copper(II) complexes have been synthesized, characterized, and their catalytic activities reported for the first time.

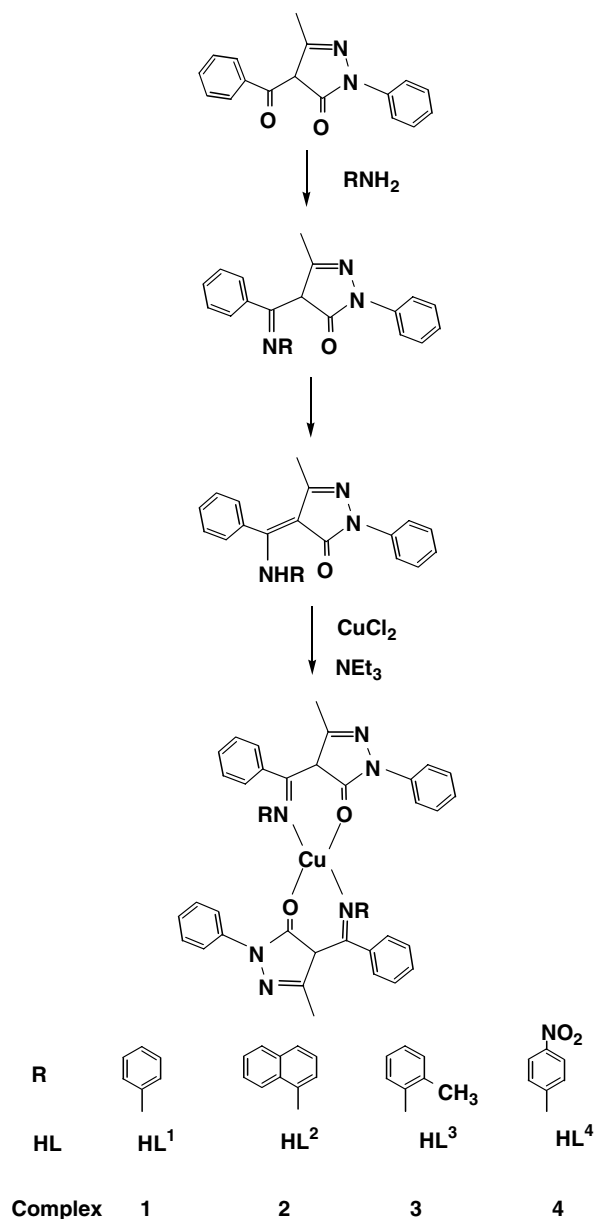
2. Results and discussion

2.1. Synthesis and characterization

The three new β -ketoamine ligands **HL**¹, **HL**³ and **HL**⁴ were synthesized by condensation of the corresponding amines (see Section 3) with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone in good yields. Their enamine conformation has been exemplified by the single crystal structural study of a member of **HL**ⁿ obtained with β -methylphenylamine [15]. **HL**¹–**HL**⁴ are very soluble in CH_2Cl_2 and CHCl_3 , but moderately soluble in hot EtOH and MeOH.

When the deprotonated (by triethylamine) ligands **L**ⁿ ($n = 1, 3, 4$) were allowed to react with CuCl_2 or $\text{Cu}(\text{NO}_3)_2$ in either 2:1 or 1:1 molar ratio, the respective bis(β -ketoamino)copper(II) complexes [CuL_2^n] **1**, **3** and **4** (Scheme 2) in 70–80% yields were obtained, respectively, suggesting that the composition of the products are sensitive neither to the type of anion nor to the ligand-to-metal ratio under these reaction conditions. Ligand **HL**² and complex **2** were also prepared for catalytic studies, which have been reported before [16].

Complexes **1**–**4** showed $\nu_{\text{C=O}}$ absorptions in range 1595–1597 cm^{-1} , while multiple strong absorptions in range 1560–1380 cm^{-1} could be caused by the C=N and C=C



Scheme 2. Reaction scheme for the syntheses of ligands **HL**ⁿ and the complexes **1**–**4**.

groups. The large red shift of the absorptions for the carbonyl bonds as compared to that for the ligands (1620–1644 cm^{-1}) may have been caused by coordination thus weakening of the bonds, and also by the delocalization of the conjugated six-membered chelate rings. Thermogravimetric analysis (TGA) in the range 25–600 °C showed that **1**–**4** have similar weight loss patterns. The framework decomposes at temperature over 320 °C where an abrupt weight loss was observed, followed by a final weight loss in the 390–600 °C range.

2.2. Crystal structures

The structure of **1** is shown in Fig. 1, while those of **3** and **4** are similar and were shown in Figs. 2 and 3, respectively. Selected atomic distances and bond angles are listed

in Table 1. The structure of **2** was not determined since the complex has been reported previously [16]. In the complexes, the four-coordinate copper atom is arranged in a distorted square-planar geometry where the two L'' ligands acting as monoanionic bidentate N,O -chelators lie in the *trans*-conformation to create two stable delocalized six-membered chelate rings (CuOCCCN), with O–Cu–O and N–Cu–N angles in the range 136–149° and 141–152°, respectively. Weak axial Cu···H–C_{edge} intramolecular interaction was observed in the complexes with Cu to the nearest C_{phenyl} distances in the range 3.2–4.0 Å.

The distances of the Cu(II) ion in **1** to the two least square chelate planes defined by O1–C7–C8–C11–N3 and O2–C30–C31–C34–N6 are 0.407 and 0.077 Å, respectively. Similar distances are 0.439 and 0.254 Å in **3**. The Cu(II) to chelate-ring distance is increased to 0.481 Å in **4** where the alkyl substituent is *p*-nitrophenyl (L^4). A sequence can be observed within the series **1**, **3** and **4**, where the R group is phenyl, *o*-methylphenyl, and *p*-nitrophenyl, respectively, and the aforementioned Cu-to-chelate-plane distances are in the order of **1** < **3** < **4**. Besides that, the dihedral angles (127.9°, 121.0° and 47.0° for **1**, **3** and **4**, respectively) of the two six-membered chelate rings are in the order of **1** > **3** > **4**, which showed a reverse trend. On correlation of the crystal structure versus catalytic activity (see next section), a fact is disclosed that with larger and more electron withdrawing substituent for the R group of the ligand, such as in **4**, higher activity is observed (next section), which is accompanied by larger Cu-to-chelate distance and smaller dihedral angle. These results imply that both steric and electronic effects are important for good catalytic activity. Although the structure of **2** [16] was not studied, it can be assumed that **2** will have similar molecular framework by comparison of its spectral data with those of known structures as discussed in the previous section, and also shown in Section 3.

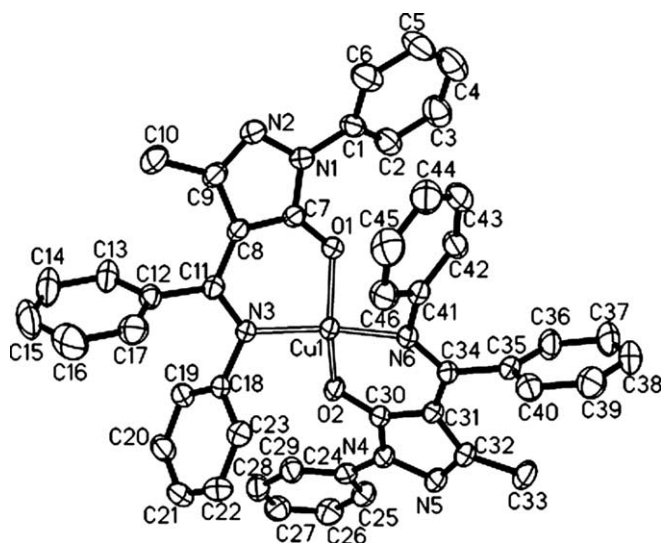


Fig. 1. Structure of complex **1** with atomic-labeling scheme. Hydrogen atoms and the solvate molecule are omitted for clarity.

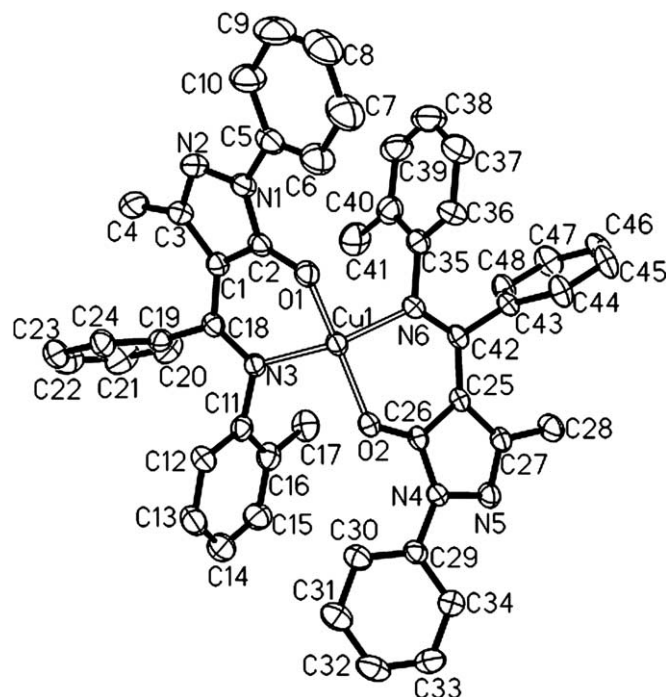


Fig. 2. Structure of complex **3** with atomic-labeling scheme. Hydrogen atoms are omitted for clarity.

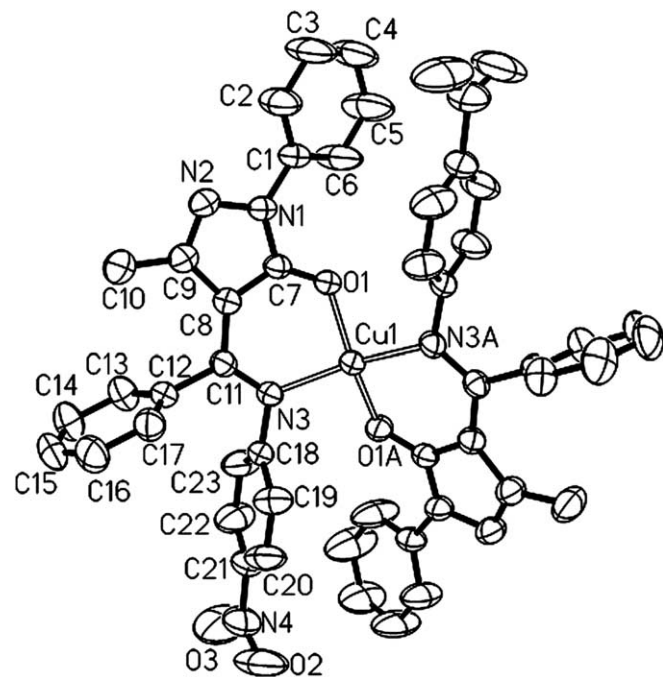


Fig. 3. Structure of complex **4** with atomic-labeling scheme. Hydrogen atoms are omitted for clarity.

There is only weak intramolecular π – π interaction although there are several aromatic planes present, the shortest π ··· π centroid-to-centroid distances are 4.36, 4.01, and 4.19 Å for complexes **1**, **3**, and **4**, respectively. No intermolecular interaction can be observed for any of the complexes (see Table 2).

Table 1
Selected atomic distances (Å) and bond angles (°) for complexes **1** · EtOH, **3** and **4**

1 · EtOH		3		4	
<i>Atomic distance (Å)</i>					
Cu(1)–O(1)	1.910(2)	Cu(1)–O(1)	1.905(2)	Cu(1)–O(1)	1.9015(15)
Cu(1)–O(2)	1.890(2)	Cu(1)–O(2)	1.906(2)		
Cu(1)–N(3)	1.971(2)	Cu(1)–N(3)	1.984(2)	Cu(1)–N(3)	1.9914(18)
Cu(1)–N(6)	1.946(2)	Cu(1)–N(6)	1.978(2)		
O(1)–C(7)	1.275(4)	O(1)–C(2)	1.280(4)	O(1)–C(7)	1.278(2)
O(2)–C(30)	1.285(4)	O(2)–C(26)	1.286(3)		
C(7)–C(8)	1.407(4)	C(1)–C(2)	1.413(4)	C(7)–C(8)	1.415(3)
C(30)–C(31)	1.415(4)	C(25)–C(26)	1.421(4)		
C(8)–C(11)	1.432(4)	C(1)–C(18)	1.418(4)	C(8)–C(11)	1.411(3)
C(31)–C(34)	1.408(4)	C(25)–C(42)	1.415(4)		
N(1)–N(2)	1.395(3)	N(1)–N(2)	1.388(4)	N(1)–N(2)	1.392(2)
N(4)–N(5)	1.396(3)	N(4)–N(5)	1.401(3)		
N(1)–C(7)	1.358(3)	N(1)–C(2)	1.356(4)	N(1)–C(7)	1.356(2)
N(4)–C(30)	1.355(4)	N(4)–C(26)	1.343(4)		
N(2)–C(9)	1.316(4)	N(2)–C(3)	1.313(4)	N(2)–C(9)	1.309(3)
N(5)–C(32)	1.315(4)	N(5)–C(27)	1.310(4)		
N(3)–C(11)	1.320(3)	N(3)–C(18)	1.315(4)	N(3)–C(11)	1.318(3)
N(6)–C(34)	1.317(3)	N(6)–C(42)	1.309(4)		
C(8)–C(9)	1.433(4)	C(1)–C(3)	1.422(4)	C(8)–C(9)	1.436(3)
C(31)–C(34)	1.408(4)	C(25)–C(27)	1.434(4)		
<i>Bond angle (°)</i>					
O(1)–Cu(1)–O(2)	136.25(10)	O(1)–Cu(1)–O(2)	145.01(10)	O(1)–Cu(1)–O(1) ^a	149.03(9)
N(3)–Cu(1)–N(6)	144.20(11)	N(3)–Cu(1)–N(6)	141.43(10)	N(3)–Cu(1)–N(3) ^a	151.67(10)
O(1)–Cu(1)–N(3)	95.01(8)	O(1)–Cu(1)–N(3)	93.25(10)	O(1)–Cu(1)–N(3)	93.74(6)
O(1)–Cu(1)–N(6)	94.86(9)	O(1)–Cu(1)–N(6)	97.04(9)	O(1) ^a –Cu(1)–N(3)	93.75(6)
O(2)–Cu(1)–N(3)	99.97(9)	O(2)–Cu(1)–N(3)	97.90(9)		
O(2)–Cu(1)–N(6)	96.33(9)	O(2)–Cu(1)–N(6)	94.62(9)		

Equivalent position for a: $-x + 1, y, -z + 3/2$.

2.3. Catalytic studies

Complexes **1–4** showed medium catalytic activities towards the polymerization of norbornene (NBE) in the presence of co-catalyst MAO (methylaluminoxane) [17] as compared to the reported Ni catalysts [13]. However, this could be the first report of Cu(II) complexes with β -keto-amine ligands to show fair activities. A summary of the catalytic data are listed in Table 3.

Assisted by the co-catalyst MAO, the catalytic activity of the complexes could reach the highest to 6.35×10^4 g polymer/(mol Cu h) for **2** among the four complexes, and the activity sequence is in the order of $\mathbf{2} > \mathbf{4} > \mathbf{3} > \mathbf{1}$, with R groups (as shown in Scheme 2) of α -naphthyl (**2**), *p*-nitrophenyl (**4**), *o*-methylphenyl (**3**) and phenyl (**1**). A plausible preliminary interpretation for the activity sequence can be given to the bulkiness of the R-substituents, since the size of R is in the same order as that of the activities. In addition to that, the nearly 5-fold increase of activity of **2** as compared to **1** could be attributed to the large π -system of the naphthyl ring. Furthermore, complex **4** with an *p*-nitro-substituent on the phenyl ring in R is more active than **1** by 3.5-fold, which could be caused by the electron-withdrawing *p*-NO₂ group affording the active Cu(II) center more deficient in electron density. Such electronic effect was also observed by Grubbs [8a] for the salicylaldiminato Ni(II) complexes in the poly-

merization of ethylene. These results imply that both steric and electronic effects of the ligands play important roles in catalysis [8b]. Such effects have been discussed in Section 2.2.

EPR measurements were performed in toluene in which the polymerization reactions were run. Complexes **1** and **3** were chosen as examples to check on the oxidation state of the active species – the copper atom. Signals at $g_{\parallel} = 2.110$ and $g_{\perp} = 2.065$ were observed for the complexes, which are very similar to the literature values for Cu(II) complexes [18]. These signals persist for both **1** and **3** after the solution was added with an excess amount of the co-catalyst MAO, although the intensity is weaker due to dilution of the solution by the large amount of MAO (400 molar excess). These experimental facts indicate that the copper ions in these complexes were in the divalent state and remained to be Cu(II) after the co-catalyst MAO was added, no reduction can be observed as that occurred for the Co catalysts [19].

All the four copper catalysts afforded the polynorbornenes with narrow molecular weight distributions ($M_w/M_n = 2.48–2.70$), indicating the presence of a single active species in the polymerization process [20]. The DSC measurement of the polynorbornenes did not give any endothermic signal in a heating range of 20–400 °C and the TGA data indicated that these polymers are stable up to 400 °C. No olefinic bonds in the polymers formed can be

Table 2
Crystallographic data and structure refinement details for **1** · EtOH, **3** and **4**

Complex	1 · EtOH	3	4
Formula	C ₄₈ H ₄₂ CuN ₆ O ₃	C ₄₈ H ₄₀ CuN ₆ O ₂	C ₄₆ H ₃₄ CuN ₈ O ₆
Formula weight	814.42	796.40	858.35
<i>T</i> (K)	298(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> /2 <i>c</i>
Crystal size (mm)	0.46 × 0.26 × 0.25	0.47 × 0.46 × 0.07	0.46 × 0.39 × 0.21
<i>a</i> (Å)	10.673(1)	10.252(4)	21.990(9)
<i>b</i> (Å)	13.552(2)	14.207(5)	15.551(7)
<i>c</i> (Å)	15.106(2)	14.323(5)	15.181(6)
α (°)	104.858(2)	76.604(6)	90
β (°)	90.029(2)	78.247(6)	129.021(6)
γ (°)	97.165(2)	79.582(6)	90
<i>V</i> (Å ³)	2094.1(5)	1967.0(13)	4033(3)
<i>Z</i>	2	2	4
<i>D</i> _{calc} (g cm ⁻³)	1.292	1.345	1.414
μ (mm ⁻¹)	0.570	0.604	0.603
Reflections collected	18038	15748	12429
Reflections observed <i>I</i> > 2 σ (<i>I</i>)	9063	7858	4371
Maximum 2 θ (°)	54.22	52.72	54.08
<i>R</i> _{int}	0.0199	0.0257	0.0194
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0495	0.0482	0.0375
<i>wR</i> ₂	0.1384	0.1208	0.0935

Table 3
Catalytic data in the polymerization of norbornene by the pyrazolone-based Cu(II) complexes **1–4**^a

No.	Complex	Polymer yield (g)	Acitivity (10 ⁴ g mol ⁻¹ h ⁻¹)	<i>M</i> _n ^b (10 ⁵)	<i>M</i> _w ^c (10 ⁵)	<i>M</i> _w / <i>M</i> _n
1	1	0.3250	1.31	2.86	7.32	2.56
2	2	1.5746	6.35	2.24	5.55	2.48
3	3	0.4734	2.19	3.20	8.46	2.64
4	4	0.9673	4.48	2.84	7.52	2.65

^a Reaction conditions: toluene: 20 ml, 60 °C, norbornene: 5 g, Cu complex: 5.4 μmol, MAO as auxiliary catalyst, Al/Cu = 400 (molar ratio) and 4 h.

^b *M*_n is the relative number-average molecular weight.

^c *M*_w is the relative weight-average molecular weight.

identified by IR and ¹H NMR spectroscopic measurements: the presence of bridging methylene group at 1296 cm⁻¹, the absence of bands for C=C absorption in range 1620–1680 cm⁻¹ in IR [12,13b], and the absence of vinyl proton at ~5.3 ppm in the ¹H NMR spectra [12]. These results showed that the vinylic-type polymerization process of NBE has occurred when catalyzed by the MAO/Cu(II) complexes **1–4**.

3. Experimental

All chemicals of reagent grade were commercially available and used without further purification. Element analyses were performed on a Perkin–Elmer 240C element analyzer. Infrared spectra were recorded on a Bruker EQUINOX55 FT-IR spectrophotometer in the region 4000–400 cm⁻¹ in KBr pellets. ES-MS was performed on a Finnigan LCQ^{DECA}XP HPLC-MSⁿ mass spectrometer with a mass to charge (*m/z*) range of 2000 using a standard electrospray ion source and toluene as solvent. ¹H NMR spectra were measured on a Varian Unity INOVA 400NB instrument using CDCl₃ as solvent and TMS as

internal standard at room temperature. Thermogravimetric analyses were carried out on a NETZSCH TG 209 Instrument under flowing nitrogen by heating the samples from 25 to 600 °C. EPR spectra were performed on a Bruker ER-420 spectrometer in toluene at room temperature with frequency of 9.65 GHz and scan range of 100 mT and centered at 330 mT.

3.1. Syntheses

3.1.1. Ligands HL¹–HL⁴

Ligands HL¹–HL⁴ were obtained by similar procedures by condensation of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (2.50 g, 9.0 mmol) and a suitable amine (9.4–9.7 mmol) in 35 ml of EtOH under reflux for 6 h. Pure products were obtained on removal of solvent and recrystallization from 1:1 mixture of ethanol/*n*-heptane.

3.1.1.1. 5-Methyl-2-phenyl-4-[(2-phenylamino)-phenylmethylene]pyrazol-3(2*H*)-one (HL¹). Aniline (0.9 g) was used to give HL¹ in 60% yield (1.92 g). Anal. Calc. for C₂₃H₁₉N₃O: C, 78.19; H, 5.38; N, 11.90. Found: C,

78.10; H, 5.56; N, 11.92%. Mp: 142–143 °C. IR (KBr, cm^{-1}): 1629 (vs), 1584 (s), 1535 (m), 1498 (s), 1385 (vs), 1365 (s), 1227 (w), 1139 (w), 1006 (w), 778 (w), 758 (m), 699 (m), 573 (w), 509 (w). ES–MS (m/z): 354 (M^+). ^1H NMR (CDCl_3), δ (ppm): 12.99 (s, 1H, $-\text{NH}$); 8.04 (d, 2H), 7.41 (m, 7H), 7.14 (t, 3H), 7.06 (t, 1H), 6.81 (d, 2H), 1.56 (s, 3H).

3.1.1.2. 5-Methyl-2-phenyl-4-[(2-naphthylamino)-phenylmethylene]pyrazol-3(2H)-one (HL^2). Ligand HL^2 was obtained by using α -naphthylamine (1.36 g), in 62% (2.24 g) yield. Anal. Calc. for $\text{C}_{27}\text{H}_{21}\text{N}_3\text{O}$: C, 80.37; H, 5.25; N, 10.41. Found: C, 80.34; H, 5.34; N, 10.29%. Mp: 175–176 °C. IR (KBr, cm^{-1}): 1620 (vs), 1587 (s), 1535 (m), 1489 (s), 1460 (w), 1439 (w), 1393 (vs), 1321 (w), 1272 (w), 1250 (w), 1174 (w), 1145 (m), 1004 (w), 797 (m), 764 (m), 698 (w), 588 (w), 561 (w), 511 (w). ES–MS (m/z): 404.3 (M^+). ^1H NMR (CDCl_3), δ (ppm): 13.32 (s, $-\text{NH}$); 8.25 (d, 1H), 8.08 (d, 2H), 7.82 (d, 1H), 7.60 (m, 2H), 7.53 (m, 1H), 7.43 (t, 2H), 7.35 (m, 1H), 7.28 (m, 4H), 7.18 (t, 1H), 7.12 (t, 1H), 6.84 (d, 1H), 1.62 (s, 3H).

3.1.1.3. 5-Methyl-2-phenyl-4-[(2-*o*-tolyl)-phenylmethylene]pyrazol-3(2H)-one (HL^3). Ligand HL^3 was obtained by using *o*-toluidine (1.29 g), Yield: 65% (2.15 g). Anal. Calc. for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}$: C, 78.45; H, 5.76; N, 11.44. Found: C, 78.23; H, 6.06; N, 11.14%. Mp: 173–174 °C. IR (KBr, cm^{-1}): 1626 (vs), 1585 (vs), 1537 (m), 1498 (s), 1463 (m), 1385 (vs), 1237 (w), 1188 (w), 1143 (m), 1051 (w), 1007 (m), 831 (w), 756 (s), 708 (w), 654 (w), 589 (w). ES–MS (m/z): 368 (M^+). ^1H NMR (CDCl_3), δ (ppm): 12.88 (s, $-\text{NH}$); 8.06 (d, 2H), 7.43 (m, 6H), 7.29 (t, 1H), 7.19 (t, 2H), 7.03 (t, 1H), 6.88 (t, 1H), 6.62 (d, 1H), 2.46 (s, 3H), 1.63 (s, 3H).

3.1.1.4. 5-Methyl-2-phenyl-4-[(2-*p*-nitrophenylamino)-phenylmethylene]pyrazol-3(2H)-one (HL^4). Ligand HL^4 was obtained by using *p*-nitroaniline (1.30 g) and formic acid (1 ml), the latter was added to ensure acidity of the solution. Yield: 2.10 g (60%). Anal. Calc. for $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_3$: C, 69.35; H, 4.52; N, 14.07. Found: C, 69.50; H, 4.68; N, 14.14%. Mp: 202–203 °C. IR (KBr, cm^{-1}): 1644 (vs), 1581 (vs), 1522 (s), 1497 (vs), 1399 (s), 1372 (s), 1340 (vs), 1312 (s), 1235 (m), 1194 (w), 1141 (m), 1109 (m), 1051 (w), 1008 (w), 933 (w), 858 (w), 830 (s), 779 (m), 754 (s), 726 (m), 709 (m), 689 (m), 647 (w), 610 (m), 554 (w), 498 (w). ES–MS (m/z): 399 (M^+). ^1H NMR (CDCl_3), δ (ppm): 13.31 (s, 1H, $-\text{NH}$); 7.99 (m, 4H), 7.55 (m, 4H), 7.42 (m, 4H), 6.82 (d, 2H), 1.61 (s, 3H, $-\text{CH}_3$).

3.1.2. Complexes 1–4

Complexes 1–4 were prepared by a similar procedure as depicted by the synthesis of 1.

3.1.2.1. $[\text{Cu}(\text{L}^1)_2]$ (1). The CH_2Cl_2 solution (5 ml) containing HL^1 (36 mg, 0.1 mmol) and Et_3N (14 μl , 0.1 mmol) was stirred for 10 min at room temperature, then the solu-

tion of CuCl_2 (9 mg, 0.05 mmol) in EtOH (5 ml) was added and the mixture kept stirring for 20 min. The resultant clear brown solution was filtered and left to stand at room temperature for several days to give black crystalline product of 1 in 70% yield. Anal. Calc. for $\text{C}_{46}\text{H}_{36}\text{N}_6\text{O}_2\text{Cu}$: C, 71.91; H, 4.72; N, 10.94. Found: C, 72.22; H, 5.04; N, 10.79%. IR (KBr, cm^{-1}): 1595 (s), 1561 (vs), 1526 (s), 1475 (vs), 1435 (s), 1398 (m), 1377 (s), 1246 (w), 1212 (m), 1153 (w), 1064 (w), 1026 (w), 1006 (w), 980 (w), 850 (w), 791 (w), 757 (m), 706 (m), 659 (w), 589 (m), 513 (w), 481 (w). ES–MS (m/z): 769 ($\text{M}^+ - \text{H}$).

3.1.2.2. $[\text{Cu}(\text{L}^2)_2]$ (2). 2 was prepared using HL^2 (41 mg, 0.1 mmol). Yield: 71%. Anal. Calc. for $\text{C}_{54}\text{H}_{40}\text{N}_6\text{O}_2\text{Cu}$: C, 74.68; H, 4.64; N, 9.68. Found: C, 74.62; H, 5.14; N, 9.79%. IR (KBr, cm^{-1}): 1595 (m), 1560 (vs), 1526 (s), 1480 (vs), 1435 (s), 1380 (m), 1261 (w), 1225 (w), 1156 (w), 1084 (w), 1025 (w), 805 (w), 763 (m), 693 (m), 658 (w), 631 (w), 595 (w), 511 (w). ES–MS (m/z): 869 ($\text{M}^+ - \text{H}$).

3.1.2.3. $[\text{Cu}(\text{L}^3)_2]$ (3). 3 was prepared using HL^3 (37 mg, 0.1 mmol). Yield: 67%. Anal. Calc. for $\text{C}_{48}\text{H}_{40}\text{N}_6\text{O}_2\text{Cu}$: C, 72.39; H, 5.06; N, 10.55. Found: C, 72.52; H, 5.44; N, 10.79%. IR (KBr, cm^{-1}): 1595 (m), 1560 (vs), 1526 (s), 1477 (vs), 1438 (s), 1375 (m), 1220 (w), 1188 (w), 1064 (w), 1028 (w), 843 (w), 758 (m), 722 (w), 704 (w), 658 (w), 598 (w), 511 (w). ES–MS (m/z): 797 ($\text{M}^+ - \text{H}$).

3.1.2.4. $[\text{Cu}(\text{L}^4)_2]$ (4). 4 was prepared using HL^4 (40 mg, 0.1 mmol) with 80% yield (0.78 g). Anal. Calc. for $\text{C}_{46}\text{H}_{34}\text{N}_8\text{O}_6\text{Cu}$: C, 64.37; H, 3.99; N, 13.05. Found: C, 64.82; H, 4.34; N, 12.79%. IR (KBr, cm^{-1}): 1597 (m), 1563 (vs), 1519 (s), 1479 (vs), 1436 (s), 1381 (m), 1340 (s), 1251 (w), 1217 (m), 1168 (w), 1107 (w), 1063 (w), 1011 (w), 983 (w), 867 (m), 784 (w), 758 (m), 714 (m), 655 (w), 609 (w), 573 (w), 435 (w). ES–MS (m/z): 859 ($\text{M}^+ - \text{H}$).

3.2. X-ray crystallography

Single crystals of 1·EtOH, 3 and 4, obtained from recrystallization in CH_2Cl_2 –EtOH (v/v, 1/2), of suitable dimensions were mounted onto glass fibers for crystallographic analyses. All the intensity data were collected on a Bruker SMART CCD diffractometer (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) in Φ and ω scan modes. Structures were solved by Patterson methods followed by difference Fourier syntheses, and refined by full-matrix least-squares techniques against F^2 using SHELXTL [21a]. Except for atoms belonging to disordered solvate molecules, all the non-hydrogen atoms were refined with anisotropic thermal parameters. The solvate EtOH molecule in 1·EtOH was disordered over two positions and were refined with fractional site occupancy. Absorption corrections were applied using SADABS [21b]. All hydrogen atoms were placed in calculated positions and refined isotropically using a riding

model. Crystallographic data and refinement parameters for the complexes are presented in Table 2.

3.3. Catalytic activity measurement

Catalytic polymerization of norbornene has been carried out in a Fisher–Porter glass reactor and protected by nitrogen. All the copper catalyst precursors can be activated with MAO. The resultant polynorbornenes were filtered, washed with acidified ethanol and dried under reduced pressure at 60 °C for 48 h. The results were reproduced several times and gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of the polymers were performed on a Waters 150C instrument in chlorobenzene using polystyrene as standard.

4. Summary

By varying the substituents on the amines, a series of β -ketoamine ligands can be obtained by condensation reactions with benzoylpyrazolones. The resulting Cu(II) complexes have been found active in the vinyl polymerization of NBE in the presence of MAO. The structure–activity relationship showed by the complexes was that bulky and/or electron withdrawing substituents in R are favorable for high activities. With these in mind, the quest for Cu(II)-catalysts containing ligands with different substituents for the homo- and copolymerization of norbornene/olefin is now under way.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers for **1** · EtOH, **3** and **4** are 238374, 244299 and 244300, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). The DSC, IR and NMR of the measurement of the polynorbornene are shown within.

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