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Syntheses, structures and catalytic activity of copper(II) complexes with hydroxyindanimine ligands

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Abstract

A series of new hydroxyindanimine ligands [ArN=CC$_2$H$_3$(CH$_3$)C$_6$H$_2$(R)OH] (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$, R = H (**HL^1**), R = Cl (**HL^2**), and R = Me (**HL^3**)) were synthesized and characterized. Reaction of hydroxyindanimine with Cu(OAc)$_2$ · H$_2$O results in the formation of the mononuclear bis(hydroxyindaniminato)copper(II) complexes Cu[ArN=CC$_2$H$_3$(CH$_3$)C$_6$H$_2$(R)O]$_2$ (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$, R = H (**1**), R = Cl (**2**), and R = Me (**3**)). The complex **2′** was obtained from the chlorobenzene solution of the complex **2**, which has the same molecule formula with the complex **2** but it is a polymorph. All copper(II) complexes were characterized by their IR and elemental analyses. In addition, X-ray structure analyses were performed for complexes **1**, **2**, and **2′**. After being activated with methylaluminoxane (MAO), complexes **1**–**3** can be used as catalysts for the vinyl polymerization of norbornene with moderate catalytic activities. Catalytic activities and the molecular weight of polynorbornene have been investigated for various reaction conditions.

Keywords: Copper complex; Hydroxyindanimine ligands; Polymerization; Norbornene; Structures

1. Introduction

In the past decade, there has been considerable activity in the area of late transition metal olefin polymerization catalysis [1]. However, with the exclusion of the Cu catalysts systems for the atom transfer radical polymerization (ATRP) [2], olefin polymerization catalysts based on copper are considerably rare. Cu complexes with benzamidinate ligands can catalyze ethylene homo-polymerization with low catalytic activities [3]. The benzimidazolyl-ligated Cu complexes reported by Stibrany et al. can catalyze not only the homo-polymerization of ethylene and acrylates, but also the co-polymerization of ethylene and acrylates with high incorporation of acrylates [4]. Cu catalysts based on α-diimine ligands produce very high-molecular-weight polyethylenes with moderate activity [5], which are probably the first such olefin polymerization catalyst reported in the academic literature, although some catalysts have been described in patents [3,4]. Since the past year, a few groups have been reported some series of Cu complexes containing ligands of N,O-chelate which can produce the vinyl-type polynorbornene. After activation by methylaluminoxane (MAO), both β-ketoamino Cu complexes [6] and bis(salicyldiminate) Cu complexes [7] can catalyze vinyl polymerization of norbornene with moderate activities. And the β-ketoamino Cu complexes can also produce the random co-polymer of norbornene and styrene [6b]. Recently, our group also reported a novel Cu complex with phenoxy-imidazole ligand which can catalyze vinyl polymerization of norbornene with good activities [8].

It is well established that norbornene can be polymerized by three different routes, affording polymeric products that are very different in structure, properties and applications (Scheme 1) [9]. The polynorbornene (PNB) produced by vinyl-type polymerization is a special polymer, for its heat resistivity, high glass transition temperature, low dielectric constant, transparency, and good solubility in polar organic solvents. PNB has been deeply investigated for many optical and microelectronic applications, such

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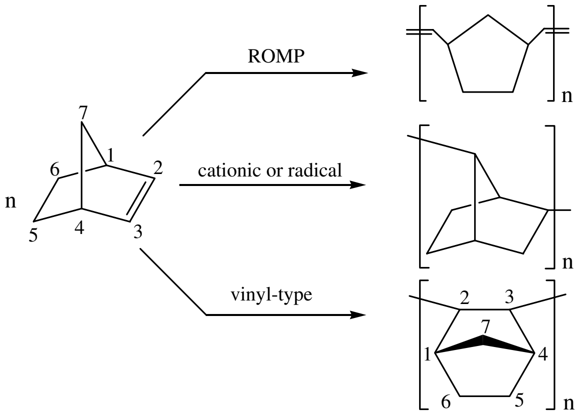


Scheme 1. Schematic representation of the three different types of polymerization for norbornene.

as components for condensers, data storage and telecommunication waveguides [10]. Up to now, catalytic systems based on early [11], middle [12], and late transition metal [13] have been mainly reported for the vinyl polymerization of norbornene.

Our group has designed and synthesized various nickel(II) catalysts with [O, N], [N, N], [C, N] and [N, P] ligands for vinyl polymerization for norbornene [14]. Herein, a series of copper complexes bearing hydroxyindanimine ligands have been synthesized, characterized, and their catalytic activities have been investigated. In fact, these air-stable, inexpensive and very ease to prepare copper complexes appear good candidates for the vinyl polymerization of norbornene.

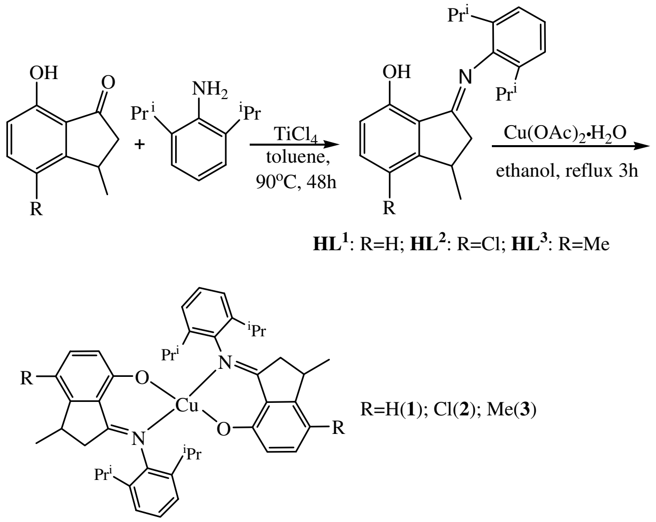
2. Results and discussion

2.1. Synthesis of hydroxyindanimine compounds and copper complexes

The three new hydroxyindanimine ligands **HL**^{n} ($n = 1,2,3$) were synthesized in moderate yields by condensation of the corresponding indanone with 2,6-diisopropylaniline in toluene using $TiCl_4$ as a Lewis acid catalyst (Scheme 2) [15]. Ligands **HL**^{n} ($n = 1,2,3$) are readily soluble in ethanol and other common solvents such as toluene, THF, Et_2O, CH_2Cl_2. IR, ^1H NMR and ^{13}C NMR spectroscopic data are consistent with the expected hydroxyindanimine structure.

When the ligands **HL**^{n} ($n = 1,2,3$) were allowed to react with $Cu(OAc)_2 \cdot H_2O$ in 2:1 molar ratio, the red-brown Cu(II) complexes $[CuL^n_2]$ ($n = 1,2,3$) **1–3** were obtained in ca. 80% yields, respectively (Scheme 2) [16]. All complexes are stable in dry air. They are very soluble in toluene, THF, CH_2Cl_2, and chlorobenzene, but sparingly soluble in ethanol and methanol.

Crystal suitable for X-ray crystallography of complexes **1–2** were obtained by slow diffusion of ethanol into toluene solution of the corresponding complexes. The crystallographic data and processing parameters are given in Table 1.



Scheme 2. Synthesis of compounds **HL**^{n} ($n = 1,2,3$) and Cu complexes **1–3**.

Table 1
Crystallographic data and structure refinement details for **1**, **2**, and **2′**

Complex	1	2	2′
Formula	$C_{44}H_{52}CuN_2O_2$	$C_{44}H_{50}Cl_2CuN_2O_2$	$C_{44}H_{50}Cl_2CuN_2O_2$
F_w	704.42	773.30	773.30
T (K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2(1)/n$	$P2(1)/c$	$P\bar{1}$
Crystal size (mm)	0.25 × 0.15 × 0.10	0.20 × 0.15 × 0.10	0.25 × 0.15 × 0.10
a (Å)	11.716(9)	9.557(6)	11.88(11)
b (Å)	21.357(16)	19.591(12)	16.7(2)
c (Å)	16.257(12)	11.295(7)	21.7(2)
α (°)	90	90	88.8(2)
β (°)	105.382(12)	107.259(10)	89.05(15)
γ (°)	90	90	71.13(14)
V (Å^3)	3922(5)	2020(2)	4065(74)
Z	4	2	4
ρ_{calc} (g cm^{-3})	1.193	1.272	1.264
μ (mm^{-1})	0.594	0.711	0.706
θ Range (°)	1.61–27.16	2.08–27.19	0.94–27.88
Reflections collected	16992	8579	16750
Independent reflections	8137	4454	15639
R_{int}	0.0698	0.0777	0.0449
Goodness-of-fit on F^2	0.765	0.785	0.831
R_1 [$I > 2\sigma(I)$]	0.0470	0.0546	0.0589
wR_2	0.0810	0.1040	0.1206

$R_1 = \sum(\|F_o| - |F_c\|)/\sum|F_o|$, $wR_2 = [\sum(|F_o|^2 - |F_c|^2)^2/\sum(F_o^2)]^{1/2}$.

The ORTEP diagrams of Cu(II) complexes **1** and **2** were shown in Figs. 1 and 2, respectively. The structure analysis shows that the molecule of complex **1** has approximate non-crystallographic C_2 symmetry, and the molecule of complex **2** has C_i symmetry. Both complexes show the same four-coordinate environment around the copper atom where the two L ligands act as bidentate N,O-chelators and lie in the *trans* conformation to create two

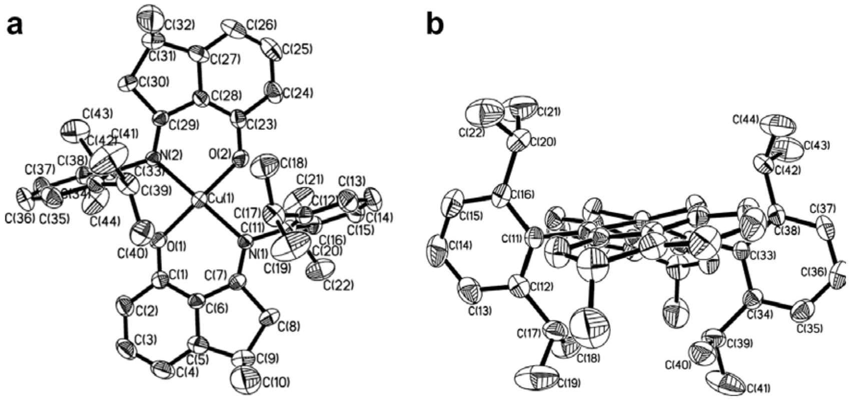


Fig. 1. Two views of the molecular structure of complex **1** (the hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.884(2), Cu(1)–O(2) 1.883(2), Cu(1)–N(1) 2.005(3), Cu(1)–N(2) 2.002(3); O(1)–Cu(1)–N(1) 95.09(9), O(2)–Cu(1)–N(2) 95.16(9), O(1)–Cu(1)–O(2) 160.83(9), N(1)–Cu(1)–N(2) 156.45(8), O(1)–Cu(1)–N(2) 88.97(9), O(2)–Cu(1)–N(1) 88.58(9).

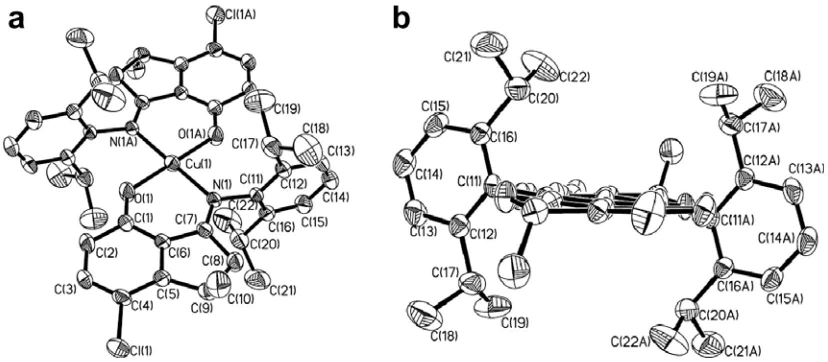
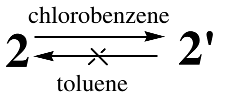


Fig. 2. Two views of the molecular structure of complex **2** (the hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.876(2), Cu(1)–N(1) 2.014(3); O(1)–Cu(1)–N(1) 93.31(10), O(1)–Cu(1)–O(1A) 180.0, N(1)–Cu(1)–N(1A) 180.0, O(1)–Cu(1)–N(1A) 86.69(10).

six-membered chelate rings (Cu–O–C–C–C–N). However, the geometry of copper atom in complexes **1** and **2** is different. In complex **1**, the dihedral angel of the two coordination planes (O–Cu–N) is 29.3°, suggesting a distorted square-planar geometry. In complex **2**, the copper atom is arranged in a square-planar geometry like that observed in the α-form of bis(*N*-methylsalicylaldiminato)copper complex [17]. The bond lengths and angels are normal in both complexes. And the presence of *N*-2,6-diisopropylphenyl group has caused an increase in the length of the Cu–N bond than that of the Cu–O bond. That this increase is due to the steric effect of the *N*-2,6-diisopropylphenyl group is supported by the equality of the Cu–N and Cu–O bond lengths in bis(salicylaldiminato)copper complex [18]. The *N*-2,6-diisopropylphenyl groups are roughly perpendicular to the remainder of the ligand L, making an angle of 86.1° or 85.9° with the two hydroxyindanimine-residues in complex **1** and an angle of 83.2° in complex **2** [19].

Polymorphism is a feature of a number of coordination compounds which has long been recognized [20]. Like bis(*N*-methylsalicylaldiminato)copper complex, which has three different isomers—α-, β-, and γ-form [17,21], there are two different isomers in the copper complex [CuL^2_2]: complex **2** and complex **2′**. The complex **2′** was obtained from the slow diffusion of ethanol into chlorobenzene solution of the complex **2** (Scheme 3). However, the complex **2** was not obtained from the toluene solution of the complex **2′**.

The crystallographic data and processing parameters of the complex **2′** are summarized in Table 1. The ORTEP diagrams of Cu(II) complexes **2′** was shown in Fig. 3. For complex **2′**, there are two independent molecules in a crystal cell. The geometry of each molecule is similar to that of the complex **1**. The two copper atoms are arranged in a distorted square-planar geometry with a dihedral angel 31.6° (Cu(1)) and 31.9° (Cu(2)) of the two coordination planes (O–Cu–N), respectively. The *N*-2,6-diisopropylphenyl groups are also roughly perpendicular to the remainder of the ligand L, making an angle of 89.8° or 89.3° (Cu(1)) and 88.9° or 89.2° (Cu(2)) with the two hydroxyindanimine-residues, respectively. Those angles are about 3°



Scheme 3. Two isomers of complex [CuL^2_2].

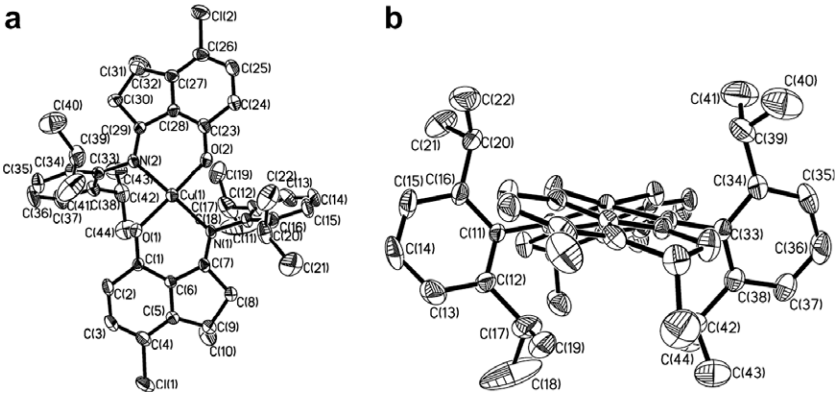


Fig. 3. Two views of the molecular structure of complex **2**′ (the hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.864(16), Cu(1)–O(2) 1.886(16), Cu(1)–N(1) 2.017(18), Cu(1)–N(2) 2.02(2); O(1)–Cu(1)–N(1) 94.5(3), O(2)–Cu(1)–N(2) 95.6(2), O(1)–Cu(1)–O(2) 158.38(19), N(1)–Cu(1)–N(2) 155.4(3), O(1)–Cu(1)–N(2) 88.8(2), O(2)–Cu(1)–N(1) 90.3(4).

greater than that in complex **1**. The distance of Cl(1) atom and Cl(4) atom of the another molecule is 3.541 Å, and that of Cl(2) atom and Cl(3) atom of the another molecule is 3.466 Å. That distances indicated the presence of the weak Cl···Cl interaction between two chlorine atoms. Similarly, there are the presence of the weak Cl···H–C interaction between the chlorine atom and the methyl group of the isopropyl group, supported by the distance 3.466 Å between Cl(2) atom and C(62) of the another molecule and the distance 3.479 Å between Cl(4) atom and C(18) of the another molecule.

3. Norbornene polymerization

The norbornene polymerization results using the copper complexes **1**–**3**/MAO as catalytic systems are summarized in Tables 2 and 3.

Chlorobenzene was chosen as the reaction medium for norbornene polymerization because it can improve the catalytic performances due to its polarity [9].

No catalytic activity was observed for complex **1**–**3** in the absence of MAO. Therefore, the co-catalyst MAO is essential for the norbornene polymerization catalyzed by complex **1**–**3**. After activation with MAO, Cu (II) complexes **1**–**3** can catalyze norbornene (NB) polymerization (Table 1, runs 1–8; Table 2, runs 1–3).

Preliminary experiments on norbornene polymerization were performed in the presence of complex **1** as catalytic precursor. Variation of the Al/Cu ratio shows a significant effect on the catalytic activities and molecular weight (Table 1, runs 1–5). The catalytic activities of **1** increase first and then slowly decrease with the increase of the Al/Cu ratio under the experimental conditions. The highest activity of 9.5 × 10^4 g PNB mol^{-1} Cu h^{-1} is observed at Al/Cu ratio of 750/1 (Table 1, run 3). All polymers display high molecular weights (M_v up to 10^6 g mol^{-1}). The effect of Al/Cu ratio on molecular weight of polymers is similar to that effect on catalytic activities. M_v increases first and then decreases with the increase of Al/Cu ratio. The highest M_v of 1.36 × 10^6 g mol^{-1} is also observed at Al/Cu ratio of 750/1 (Table 1, run 3). The reaction temperature also affects considerably the catalytic activities and molecular weight (Table 1, runs 3, 6–8). With an increase of reaction temperature, the catalytic activities and M_v's of polymers first increase and then decrease. The maximum value of activities is obtained at 30 °C (Table 1, run 3), while that of M_v of polymer (up to 1.38 × 10^6 g mol^{-1}) is observed at 45 °C (Table 1, run 7).

Table 2
Norbornene Polymerization for the **1**/MAO catalytic system[a]

Run	Al/Cu	T (°C)	Yield (mg)	Activity[b]	M_v[c]
1	300	30	10	1.0	–
2	550	30	78	7.8	1.22
3	750	30	95	9.5	1.36
4	1050	30	84	8.4	1.20
5	1500	30	78	7.8	1.04
6	750	16	77	7.7	0.50[d]
7	750	45	74	7.4	1.38
8	750	60	67	6.7	1.31

[a] Polymerization conditions: Cu = 1.0 μmol; NB = 0.952 g; time = 1 h; V_{total} = 10.0 mL; solvent: chlorobenzene.
[b] 10^4 g PNB mol^{-1} Cu h^{-1}.
[c] 10^6 g mol^{-1}.
[d] Not completely dissolved.

Table 3
Norbornene polymerization with different complexes[a]

Run	Cat	Yield (mg)	Activity[b]	M_v[c]
1	**1**	95	9.5	1.36
2 [d]	**2**	47	4.7	1.58
3	**3**	110	11.0	1.76
4	**2**′	–	–	–

[a] Polymerization conditions: Cu = 1.0 μmol; NB = 0.952 g; Al/Cu = 750; T = 30 °C; time = 1 h; V_{total} = 10 mL; solvent, chlorobenzene.
[b] 10^4 g PNB mol^{-1} Cu h^{-1}.
[c] 10^6 g mol^{-1}.
[d] Freshly dissolved in chlorobenzene.

The structures of the copper complexes also affect considerably the catalytic activities and molecular weights (Table 2, runs 1–4). When **1** was replaced by **2** containing a chlorine atom, the activity is 4.7×10^4 g PNB mol^{-1} Cu h^{-1}, which is half of that of complex **1** under the same experimental conditions (Table 2, run 2). When complex **3** bearing a methyl group was used as catalyst, the highest activity up to 11.0×10^4 g PNB mol^{-1} Cu h^{-1} is obtained in all experiment on norbornene polymerization (Table 2, run 3). The difference of activities resulting from the difference of molecular structure may be due to the different electronic effect of R group of ligands **HL**^{n} ($n = 1,2,3$). The M_v of polynorbornene obtained varies from 1.36×10^6 g mol^{-1} to 1.76×10^6 g mol^{-1}. To our surprised, the complex **2**′ can not catalyze norbornene polymerization to produce polynorbornene under our experimental conditions (Table 2, run 4). The reason is indistinct.

The microstructure of the obtained polynorbornene is characterized by FTIR spectra and ^{1}H NMR and ^{13}C NMR spectra. Those spectra are typical of a vinyl-type structure. In FTIR spectra, there are no absorptions at 1680–1620 cm^{-1}, especially about 960 cm^{-1} and 735 cm^{-1}, assigned to the *trans* and *cis* form of double bonds, respectively, which are characteristic of the ROMP structure of polynorbornenes [22]. On the contrary, these absorption peaks at about 942 cm^{-1}, which can be assigned to the ring system of bicycle [2.2.1] heptane as Kenndy noted, are observed [23].

^{1}H NMR and ^{13}C NMR spectra confirmed the above conclusions. ^{1}H NMR spectra show signals in the 0.9–3.0 ppm range, where no resonances are displayed at about δ 5.1 and 5.3 ppm in the ^{1}H NMR spectrum of the polynorbornene, assigned to the *cis* and *trans* form of double bonds [24], which generally indicates the presence of the ring-opening metathesis polymerization (ROMP) structure. The ^{13}C NMR spectrum shows the main four groups of resonances: δ (51.3, 50.4, 49.2, 47.0, 46.3, 45.9), (41.0, 40.3, 39.4, 38.3), (37.8, 36.8, 35.7, 34.8), (32.0, 30.3, 28.9, 28.4) ppm, attributed to the carbons 2 and 3, carbons 1 and 4, carbon 7, carbons 5 and 6, respectively (Scheme 1) [25]. The ^{13}C NMR spectrum is similar to that reported by Patil et al. [26]. These data indicate that the polynorbornene obtained with the aforementioned catalysts was a vinyl-type (2,3-linked) product.

All the polynorbornenes synthesized here are easily soluble in cyclohexane, chlorbenzene and *o*-dichlorobenzene, which indicated the low stereoregularity. Indeed, analysis by wide-angle X-ray diffractometry shows no indication of crystallinity. Our attempts to determine the glass transition temperature (T_g) of polynorbornenes failed, DSC studies not giving an endothermic signal upon heating to 450 °C [14].

4. Conclusion

In this work, a series of copper(II) complexes containing hydroxyindanimine ligand were synthesized and characterized, which were air-stable, inexpensive, and very easy to prepare. After activation with MAO, the resulting copper(II) complexes show moderate catalytic activities for the vinyl polymerization of norbornene. The investigations on the mechanism of polymerization are under way.

5. Experimental

5.1. General procedures

All air-sensitive experiments were carried out under nitrogen using standard Schenk techniques. Chlorobenzene was dried over CaH_2 and distilled under nitrogen prior to use. Norbornene was purchased from ACROS and purified by distillation over sodium. Methylaluminoxane (MAO) was purchased from Aldrich as 10% weight of a toluene solution and used without further purification. 2,6-Diisopropylaniline (90%) was purchased from Lancaster. Other chemicals were of analytical grade and were used as received. FTIR spectra were recorded on a Niclolet FTIR spectrometer. Element analyses were performed on an Elementar vario EL III Analyzer. ^{1}H and ^{13}C NMR spectra were carried out on a Bruker AC 500 spectrometer instrument at room temperature in $CDCl_3$ solution for ligands, and *o*-dichlorobenzene-d_4 solution for polymers using TMS as internal standard. The intrinsic viscosity $[\eta]$ was measured in chlorobenzene at 25 °C using an Ubbelohde viscometer. Viscosity average molecular weight (M_v) values of polymer were calculated by the following equation: $[\eta] = 5.97 \times 10^{-4} M_v^{0.56}$ [27]. Differential scanning calorimetric (DSC) measurements were performed on a Perkin–Elmer Pyris 1 DSC. The wide-angle X-ray diffraction (WAXD) diagram of the polymer powders was obtained using a Bruker D4 Endeavor X-ray diffractometer. Scanning was performed with 2θ ranging from 5° to 60°. 7-Hydroxy-3-methylindan-1-one, 7-hydroxy-3,4-dimethylindan-1-one and 4-chloro-7-hydroxy-3-methylindan-1-one were prepared according to literature procedures [28].

*5.2. Synthesis of 7-hydroxy-3-methylindan-1-(N-2, 6-diisopropylphenylimine) (**HL**^{1})*

To a stirred solution of 2,6-diisopropylaniline (8.6 mL, 45.4 mmol) in toluene (40 mL) was added $TiCl_4$ (1.3 mL, 11.4 mmol) in toluene (30 mL) at room temperature during 30 min. The resulting mixture was stirred at 90 °C for 30 min followed by the addition of 7-hydroxy-3-methylindan-1-one (1.84 g, 11.4 mmol). The mixture was stirred for 48 h at 90 °C, poured into saturated Na_2CO_3 solution, and extracted with ethyl ether. The organic phase was dried over anhydrous Mg_2SO_4. Evaporating the solvent, purification by column chromatography on silica gel using hexane/ethyl acetate (200/1) as eluent gave compound **HL**^{1} (1.58 g, 4.9 mmol) as an orange-red oil in 43% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13–1.30 (m, 15H), 2.05 (dd, 1H), 2.67 (dd, 1H), 2.89 (m, 2H), 3.41 (m, 1H), 6.84–7.40 (m, 6H), 11.78 (br, 1H); ^{13}C NMR (125 MHz,

$CDCl_3$): δ 22.8, 23.2, 24.2, 28.7, 35.9, 39.7, 113.9, 115.4, 118.8, 122.8, 123.1, 123.6, 125.1, 132.5, 134.6, 137.6, 145.7, 156.2, 158.3, 178.8; IR (KBr): ν 3062 (w), 2962 (s), 2927 (m), 2869 (m), 1640 (s), 1596 (m), 1471 (m), 1437 (w), 1382 (w), 1362 (m), 1318 (w), 1290 (m), 1263 (m), 1216 (m), 1184 (m), 1158 (w), 1106 (w), 1051 (w), 955 (w), 879 (w), 835 (w), 796 (m), 741 (m), 690 cm^{-1} (w); Anal. Calc. for $C_{22}H_{27}NO$: C, 82.20; H, 8.46; N, 4.36. Found: C, 81.92; H, 8.41; N 4.40%.

*5.3. Synthesis of 4-chloro-7-hydroxy-3-methylindan-1-(N-2,6-diisopropylphenylimine) (**HL**^{2})*

Analogous synthesis to **HL**^{1}, except that 4-chloro-7-hydroxy-3-methylindan-1-one instead of 7-hydroxy-3-methylindan-1-one was used. Purification by column chromatography on silica gel using hexane/ethyl acetate (200/1) as eluent gave compound **HL**^{2} as a red-yellow solid in 40% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.12–1.35 (m, 15H), 2.14 (dd, 1H), 2.69 (dd, 1H), 2.80 (m, 1H), 2.91 (m, 1H), 3.50 (m, 1H), 6.82 (d, 1H), 7.14–7.31 (m, 4H), 11.76 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.7, 22.9, 23.1, 23.8, 23.9, 28.5, 35.7, 39.4, 115.8, 120.9, 123.5, 125.0, 134.3, 137.4, 144.9, 151.9, 156.8, 178.3; IR (KBr): ν 3062 (w), 2962 (s), 2927 (m), 2869 (m), 1640 (s), 1596 (m), 1471 (m), 1437 (w), 1382 (w), 1362 (m), 1318 (w), 1290 (m), 1263 (m), 1216 (m), 1184 (m), 1158 (w), 1106 (w), 1051 (w), 955 (w), 879 (w), 835 (w), 796 (m), 741 (m), 690 cm^{-1} (w); Anal. Calc. for $C_{22}H_{26}ClNO$: C, 74.24; H, 7.36; N, 3.94. Found: C, 74.11; H, 7.28; N 3.87%.

*5.4. Synthesis of 7-hydroxy-3,4-dimethylindan-1-(N-2,6-diisopropylphenylimine) (**HL**^{3})*

Analogous synthesis to **HL**^{1}, except that 7-hydroxy-3,4-dimethylindan-1-one instead of 7-hydroxy-3-methylindan-1-one was used. Purification by column chromatography on silica gel using hexane/ethyl acetate (200/1) as eluent gave compound **HL**^{3} as a red-yellow solid in 40% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.11–1.28 (m, 15H), 2.08 (dd, 1H), 2.30 (s, 3H), 2.67 (dd, 1H), 2.84 (m, 1H), 2.96 (m, 1H), 3.43 (m, 1H), 6.77 (d, 1H), 7.14–7.18 (m, 4H), 11.78 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.4, 21.4, 22.6, 22.9, 23.1, 23.7, 23.9, 28.0, 28.4, 35.1, 39.7, 113.8, 118.6, 122.9, 123.3, 124.7, 132.5, 137.4, 145.4, 153.5, 156.1, 178.9; IR (KBr): ν 3060 (w), 2961 (s), 2868 (m), 1634 (s), 1594(m), 1461 (m), 1381 (w), 1361 (w), 1319 (w), 1287 (m), 1253 (m), 1221 (m), 1184 (w), 1107 (w), 1050 (w), 933 (w), 900 (w), 823 (m), 764 (w), 733 (m), 691 cm^{-1} (w); Anal. Calc. for $C_{23}H_{29}NO$: C, 82.34; H, 8.71; N, 4.18. Found: C, 82.19; H, 8.78; N, 4.22%.

*5.5. Synthesis of copper(II) complexes (**1–3**)*

7-Hydroxy-3-methylindan-1-(*N*-2,6-diisopropylphenylimine) (0.356 g, 1.14 mmol) was allowed to react with $Cu(OAc)_2 \cdot H_2O$ (0.114 g, 0.57 mmol) in anhydrous ethanol (20 mL) at the refluxing temperature for 3 h. After cooling, the solid was filtered and recrystallized from a toluene/ethanol solution at room temperature to give complex **1** (0.321 g, 0.456 mmol) as red-brown crystals in 80% yield. The other copper(II) complexes **2–3** were prepared by the same procedure.

Complex **1**: IR (KBr, cm^{-1}): ν 3056 (w), 2958 (s), 2922 (m), 2865 (m), 1605 (vs), 1557(s), 1468 (s), 1437 (w), 1411 (w), 1354 (m), 1288 (w), 1236 (m), 1181 (w), 1153 (w), 1049 (w), 967 (w), 795 (m), 763 (w), 744 (w); Anal. Calc. for $C_{44}H_{52}CuN_2O_2$: C, 75.07; H, 7.45; N, 3.98. Found: C, 74.75; H, 7.28; N, 3.91%.

Complex **2**: IR (KBr, cm^{-1}): ν 3060 (w), 2958 (s), 2924 (m), 2866 (m), 1612 (vs), 1550 (s), 1466 (s), 1398 (w), 1356 (s), 1322 (w), 1235 (s), 1172 (m), 1116 (w), 1062 (w), 935 (w), 869 (w), 823 (m), 797 (m), 770 (m), 730 (m); Anal. Calc. for $C_{44}H_{50}Cl_2CuN_2O_2$: C, 68.46; H, 6.53; N, 3.63. Found: C, 68.32; H, 6.49; N, 3.58%.

Complex **3**: IR (KBr, cm^{-1}): ν 3053 (w), 2956 (s), 2922 (m), 2866 (m), 1609 (vs), 1553 (s), 1481 (s), 1398 (w), 1350 (m), 1235 (m), 1184 (w), 1160 (w), 1100 (w), 1073 (w), 906 (w), 867 (w), 824 (m), 803 (m), 773(m); Anal. Calc. for $C_{46}H_{56}CuN_2O_2$: C, 75.48; H, 7.72; N, 3.83. Found: C, 75.32; H, 7.68; N, 3.81%.

*5.6. Synthesis of copper(II) complex **2′***

The complex **2** was added to the stirred chlorobenzene solvent. The stirring procedure lasted five days. And complex **2′** was obtained by the slow diffusion of ethanol into the chlorobenzene solution at room temperature.

5.7. X-ray crystallography

Diffraction data of complexes **1**, **2**, and **2′** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL) [29], absorption corrections were applied to the data. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions.

5.8. Norbornene polymerization

In a typical procedure (Table 1, run 3), 1.0 μmol of copper(II) complex **1** in 1.0 mL of chlorobenzene, 0.952 g of norbornene in 2.0 mL of chlorobenzene and another fresh chlorobenzene were added into a polymerization bottle with a strong stirred under a nitrogen atmosphere. After the mixture was kept at 30 °C for 5 min, 0.5 mL of MAO was charged into the polymerization system by means of a syringe and the reaction was initiated. Ten minutes later, acidic methanol ($V_{ethanol}:V_{concd.HCl} = 20:1$) was added to terminate the reaction. The polymer was isolated by filtration, washed with methanol and dried at 80 °C for 48 h under vacuum. For all polymerization procedures, the total reaction volume was 10.0 mL, which can be achieved by varying the amount of chlorobenzene when necessary. IR (KBr, cm^{-1}): ν 2947 (s), 2869 (s), 1476 (m), 1451 (s), 1380 (m), 1296 (m), 1259 (m), 1223 (m), 1148 (w), 1108 (m), 942 (m), 892 (m), 806 (w), 753 (w); ^1H NMR (500 MHz, *o*-dichlorobenzene-d_4): δ 0.9–3.0 ppm (m, maxima at 1.21, 1.56, 2.29 ppm).

6. Supplementary material

CCDC 644803, 644804 and 644805 contain the supplementary crystallographic data for **1**, **2** and **2′**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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