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Nickel and cobalt complexes bearing β-ketoamine ligands: syntheses, structures and catalytic behavior for norbornene polymerization

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Late transition metal (nickel, cobalt) complexes (1, 2) with β-ketoamine ligand (L) based on the pyrazolone derivative are synthesized by condensing 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone with *p*-fluoroaniline, and then treating the β-ketoamine (L) produced with the respective metal halide. The bis(β-ketoamine)metal complexes can act as catalyst precursors for norbornene polymerization with activation by methylaluminoxane. The effects of the central metal variation in the complex on catalyst activities and polymer microstructure are described. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: β-ketoamine; late transition metal complexes; norbornene; vinylic polymerization

INTRODUCTION

In recent years there has been a great deal of effort on the use of late transition metal catalysts for homo- and co-polymerization of olefins.[1–8] The large tolerance of heteroatom functionalities leads to reduced poison sensitivity and offers the prospect of incorporating polar monomers into olefin copolymers.[9–15] The late transition metals can be stabilized by heterodonor ligands with multiple coordination modes and give mono- and di-nuclear complexes. In particular, the use of such ligands is of fundamental importance to the development of late transition metal complexes bearing N,O mixed ligands.[16–22]

Complexes of pyrazolone derivatives have been used in many fields.[23] These compounds are relatively convenient to obtain and can be tolerant of polar substances. In addition, the luminescence effects and biological activities of these complexes have been studied widely.[24–28] Norbornene can be polymerized in three different ways, leading to different polymer structures.[29–31] The processes studied most are ring-opening metathesis polymerization (ROMP) and vinyl addition polymerization. With the aim of studying the catalytic properties of complexes with different central metals for norbornene polymerization, two late transition metal pyrazolone complexes were prepared and used as catalyst precursors for the polymerization of norbornene after activation by methylaluminoxane (MAO).

EXPERIMENTAL

Materials

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk techniques. Solvents were purified using standard procedures. Reagents 1-phenyl-3-methyl-4- benzoyl-5-pyrazolone and *p*-fluoroaniline (AR) were obtained from China National Medicine Group, Shanghai Chemical Reagent Company, and used without further purification. Norbornene from Aldrich was dried with potassium and distilled, and then dissolved in toluene to make a 0.4 g ml^{-1} solution. Anhydrous toluene was obtained by distillation over sodium. MAO was prepared by the hydrolysis of trimethylaluminum with $Al_2(SO_4)_3 \cdot 18H_2O$ in toluene with an H_2O/Al molar ratio of 1.3 : 1.

Measurements

Elemental analyses (carbon, hydrogen, and nitrogen) of the ligand and complexes were performed on a Vario

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EL microanalyzer. IR spectra were recorded on a Bruker EQUINOX55 FT-IR spectrophotometer in the region 4000 – 400 cm^{-1} in KBr pellets. ^1H NMR spectra were obtained using an INOVA 500 Hz spectrometer at room temperature in $CDCl_3$ (for ligand and complex) or *o*-$C_6D_4Cl_2$ (for polynorbornene) solution using tetramethylsilane as internal standard. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distributions of the polymers were performed on a Waters Breeze system with chlorobenzene as the eluent at 40 °C using standard polystyrene as the reference.

Crystal structure determination

Single-crystal X-ray diffraction data of the ligand (**L**) and complexes **1** and **2** were collected on a Bruker SMART 1000 CCD diffractometer at room temperature using Mo Kα radiation, 2θ range 3.6–56.0° (Table 1). The structures were solved by direct methods, followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques against F^2 using SHELXTL[32] with anisotropic thermal parameters for all the non-hydrogen atoms. Absorption corrections were applied using SADABS.[33]

Syntheses

*5-Methyl-2-phenyl-4-[(2-p-fluorophenylamino)-phenylmethylene]pyrazol-3(2H)-one (**L**)*

1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (2.50 g, 9.0 mmol) and *p*-fluoroaniline (1.04 g, 9.35 mmol) were mixed in acetic acid (30 ml) and the solution heated to reflux for 6 h. The solvent was removed in vacuum and the pure product obtained by recrystallization from a 1 : 1 ethanol/*n*-heptane mixture (35 ml); yield: 2.35 g, 70.38%. Anal. Found: C, 74.62; H, 4.78; N, 11.34. Calc.: $C_{23}H_{18}FN_3O$: C, 74.38; H, 4.88; N, 11.31%. IR (KBr, cm^{-1}): 1623.5 (vs), 1504.7 (vs), 1384.0 (vs), 1210.3 (vs), 1055.4 (m), 1010.2 (s), 912.4 (w), 838.7 (s), 766.8 (s), 697.4 (m), 652.8 (m), 603.7 (w), 542.3 (w), 507.5 (m). ^1H NMR ($CDCl_3$), δ (ppm): 12.869 (1H, –N*H*); 7.314 (2H, *p*-fluorophenyl); 6.793 (2H, *p*-fluorophenyl); 1.568 (3H, –CH_3).

*Complex **1** [Ni(L)$_2$(CH$_3$CH$_2$OH)$_2$]*

A CH_2Cl_2 solution (5 ml) containing **L** (37 mg, 0.1 mmol) and Et_3N (14 µ*l*, 0.1.mmol) was stirred for 10 min at room temperature, then a solution of $NiCl_2$ (6.5 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 products in 70% yield. Anal. Found: C, 67.52; H, 5.34; N, 9.89. Calc.: $C_{50}H_{46}F_2N_6NiO_4$: C, 67.34; H, 5.20; N, 9.43%. IR (KBr, cm^{-1}): 1581.9 (vs), 1493.9 (vs), 1388.5 (m), 1203.4 (vs), 1055.9 (m), 1016.3 (m), 907.8 (w), 846.1 (s), 768.1 (s), 698.5 (m), 612.9 (w), 565.1 (w), 511.8 (m). ^1H NMR ($CDCl_3$), δ (ppm): 7.174 (2H, *p*-fluorophenyl); 6.586 (2H, *p*-fluorophenyl); 4.049 (1H, –CH_2), 1.531 (3H, –CH_3), 1.333 (3H, –CH_3).

*Complex **2** [Co(L)$_2$CH$_3$CH$_2$OH)$_2$]*

Complex **2** was prepared by a similar procedure to complex **1**. Yield: 76%. Anal. Found: C, 67.16; H, 5.47; N, 9.53. Calc.: $C_{50}H_{46}CoF_2N_6O_4$: C, 67.34; H, 5.20; N, 9.42%. IR (KBr, cm^{-1}): 1558.8 (vs), 1496.9 (vs), 1386.4 (m), 1205.6 (vs), 1056.6 (m), 1017.8 (m), 908.7 (w), 855.2 (s), 767.6 (s), 697.6 (m), 613.3 (w),

Table 1. Crystallographic data for ligand (**L**) and complexes **1** and **2**

	L	1	2
Empirical formula	$C_{23}H_{18}FN_3O$	$C_{50}H_{46}NiF_2N_6O_4$	$C_{50}H_{46}CoF_2N_6O_4$
Formula weight	371.40	891.64	891.86
Crystal size (mm^3)	0.50 × 0.37 × 0.21	0.41 × 0.32 × 0.24	0.50 × 0.41 × 0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$
a (Å)	9.879(16)	24.731(7)	24.729(9)
b (Å)	9.193(16)	10.850(3)	10.848(4)
c (Å)	20.77(3)	17.185(3)	17.259(6)
β (°)	98.18(4)	106.602(5)	106.121(6)
V (Å^3)	1867(5)	4419(2)	4448(3)
Z	4	4	4
D_{calcd}/g cm^{-3}	1.321	1.340	1.332
μ(Mo Kα)/mm^{-1}	0.09	0.500	0.446
T/K	293(2)	293(2)	293(2)
θ range (°)	1.98–27.93	2.06–27.08	2.06–27.07
Reflections collected	15 053	12 254	12 898
Unique reflections	4190	4800	4865
R_1 ($I > 2\sigma$)	0.0418	0.0455	0.0474
wR_2 (all data)	0.1408	0.1381	0.1459
Largest diff. peak and hole (e^- Å^{-3})	0.132 and −0.176	0.628 and −0.420	0.569 and −0.361

567.7 (w), 513.1 (m). ^{1}H NMR (CDCl$_3$), δ (ppm): 7.658 (2H, *p*-fluorophenyl); 6.993 (2H, *p*-fluorophenyl); 3.724 (1H, $-CH_2$), 1.554 (3H, $-CH_3$), 1.224 (3H, $-CH_3$).

Typical polymerization procedure

MAO (0.5 mmol) was added to a Schlenk flask under an inert atmosphere with 10 ml solution of norbornene (53.19 mmol, 5.0 g) in toluene, and 9 ml of toluene. The reaction was started by the addition of 1 ml of a fresh catalyst solution (toluene, 1×10^{-6} mol catalyst) at 60 °C. After 1 h the reaction mixture was poured into an excess of ethanol acidified with 5% HCl (molar ratio), which was washed with ethanol, filtered, dried under vacuum at 80 °C for 48 h, weighed, and finally characterized by ^{1}H NMR and GPC. The whole reaction volume is 20 ml unless stated otherwise.

RESULTS AND DISCUSSION

Syntheses and structures of complexes

The new ligand is very soluble in CH$_2$Cl$_2$ and CHCl$_3$, but moderately soluble in hot EtOH and MeOH. When the deprotonated (by triethylamine) ligand was allowed to react with MtCl$_2$ or Mt(NO$_3$)$_2$ (Mt = Ni or Co) in either 2 : 1 or 1 : 1 molar ratio (Scheme 1), the crystalline products obtained were identified by IR and X-ray diffraction studies, which suggests that the composition of the products is not sensitive to the anion type or the ligand-to-metal ratio under these reaction conditions.

Crystal structure of the ligand L

As shown in Fig. 1, the N1, C7, C14, C15 and O1 atoms have a good coplanarity (the largest deviation is 0.0373 Å), where the least-squares plane forms a dihedral angle of 4.8° with the pyrazolyl ring (N3–C16–C14–C15–N2). The bond length of C7–C14 (1.381(3) Å) between the usual C–C and C=C bond lengths indicates delocalization of the electrons, aided by the fact that a proton added to N1 is more favorable in the Fourier map than to O1. The ligand tautomerizes, as determined by the bond lengths for N1=C7 and C7–C14, leading to formation of the enamine configuration NH–C7=C14, as proven by the ^{1}H NMR of the ligand (in the ^{1}H NMR spectrum, a signal was observed at 12.869 ppm). The conjugated system has large dihedral angles of 60.1° and 68.1° with the two phenyl rings (C1–C2–C3–C4–C5–C6 and C8–C9–C10–C11–C12–C13 respectively), which must be due to the effects of steric hindrance and the electron withdrawing character of the *p*-fluorobenzyl group of the ligand **L**.

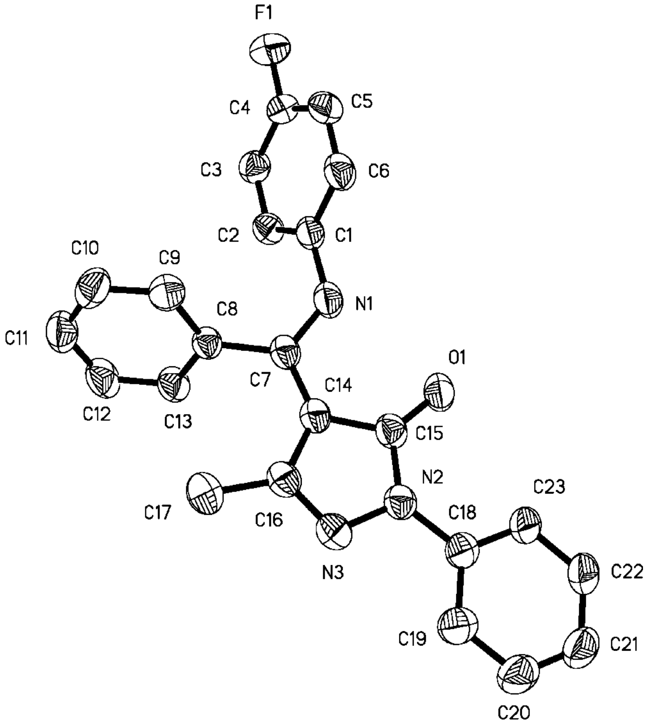
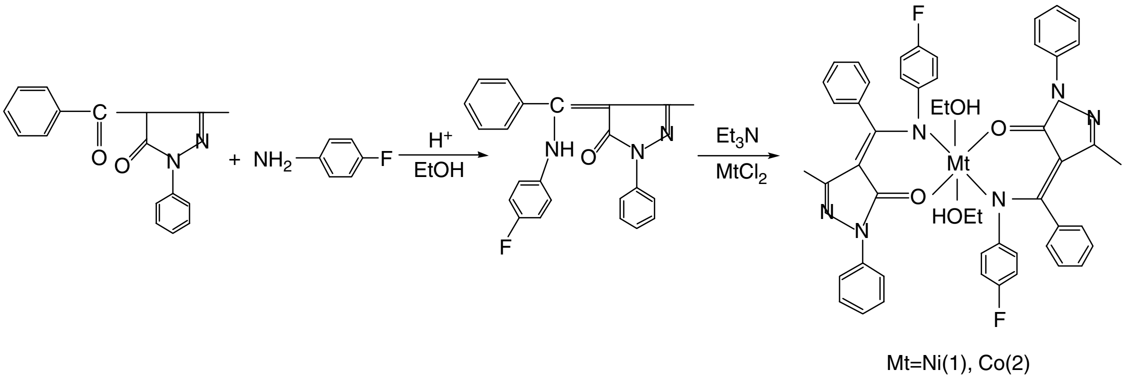


Figure 1. X-ray structure of ligand. ORTEP representation with 40% ellipsoid probability. Hydrogen atoms are omitted for clarity.



Scheme 1. Syntheses of complexes.

Crystal structure of [Ni($C_{23}H_{17}N_3OF$)$_2$(CH_3CH_2OH)$_2$] (1)

Figure 2 shows the coordination geometry of complex **1**, in which the distorted octahedral environment of Ni1 is composed of two oxygen and nitrogen atoms of two trans-conformationally monoanionic **L** ligands and two oxygen atoms of two coordinated EtOH solvates. The metal–ligand bond length of Ni–O (1.993(2) Å) is significantly less than the metal–solvate bond length of Ni–O (2.190(2) Å) and slightly less than the metal–ligand bond length of Ni–N (2.081(2) Å). The six-membered chelate ring defined by Ni1–O1–C7–C14–C15–N1 has a better coplanarity (largest deviation of 0.0079 Å) than the least-squares plane from the N1, C7, C14, C15 and O1 atoms in **L** ligand due to the formation of metal complex such that the distance of the nickel(II) ion to the plane defined by O1–C7–C14–C15–N1 is just 0.005 Å, and the conjugation system (Ni1–O1–C7–C14–C15–N1 ring) has significantly larger dihedral angles of 94.2° and 100.2° with the two phenyl rings (C1–C2–C3–C4–C5–C6 and C8–C9–C10–C11–C12–C13 respectively). Interestingly enough, there is the same weak intramolecular π–π stacking as that in the solid structure of ligand **L**. Although there are several aromatic face to face interactions, the shortest $\pi \cdots \pi$ contact having a centroid to centroid distance is 3.583(2) Å in **1**.

Crystal structure of [Co($C_{23}H_{17}N_3OF$)$_2$(CH_3CH_2OH)$_2$] (2)

X-ray structural analysis indicated that complex**2** is isostructural with complex **1**, although they contain different metal ions. As shown in Fig. 3, the distorted octahedral environment and the two monoanionic ligands′ trans conformation are the same, although the metal–ligand bond lengths of Co–O (2.006(2) Å) and Co–N (2.131 (2) Å), the metal–solvate bond length of Co–O (2.336 (2) Å), the coplanarity of the six-membered chelate ring defined by Co1–O1–C7–C14–C15–N1 (largest deviation of 0.0094 Å), distance of the cobalt(II) ion to the plane defined by O1–C7–C14–C15–N1 (0.015 Å) and the shortest centroid to centroid $\pi \cdots \pi$ contact distance (3.587(2) Å) are different, which is most likely due to the bigger size of cobalt(II) compared with nickel(II).

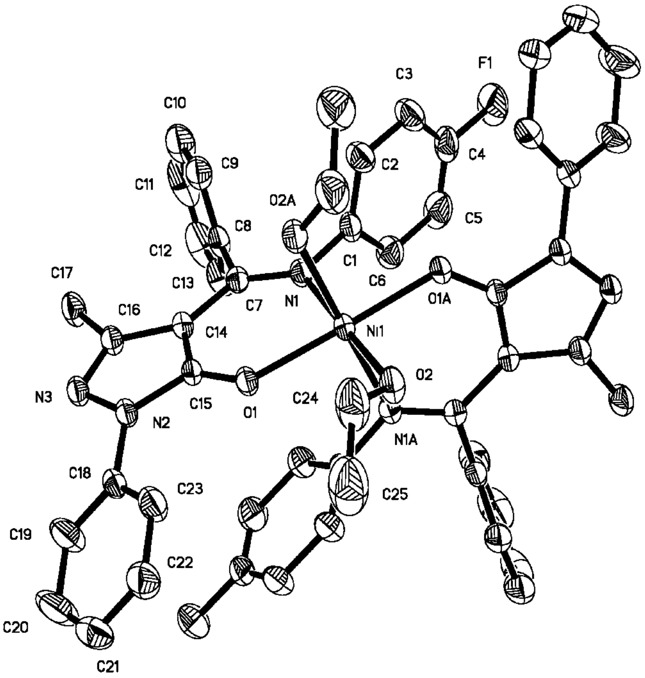


Figure 2. X-ray structure of complex **1**. ORTEP representation with 30% ellipsoid probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–N1=2.329, Ni1–O1=2.319, Ni1–O2=2.345, N1–Ni1–O1=93.21, N1–Ni1–O2=92.37, N1–Ni1–N1a=174.19, N1–Ni1–O1a=52.49, N1–Ni1–O2a= 52.24.

Norbornene polymerization

Norbornene polymerization in the presence of nickel and cobalt complexes activated with MAO was studied, with the results summarized in Table 2. It was assumed that the ethanol molecules in the complexes were consumed by MAO in the first step. Then, the complexes were activated with MAO to form catalytic species for norbornene polymerization. Pretty good activities were obtained with complex **1**–MAO. Its activity could be up to 1.56×10^7 g h^{-1} (polymer/mole of nickel). The catalytic activities obtained for complex **1**–MAO are currently higher than those of the nickel complexes obtained by Gui *et al.*[34] In contrast,

Table 2. Norbornene polymerization with different catalysts[a]

Run	Complex	Al/Mt (mole ratio)	Reaction time/h	[Mt]/10^{-6} mol	Polymer yield/g	Activity[b]	$M_n^c/10^5$	$M_w/10^5$	M_w/M_n
1	**1**	800	1	1	1.450	145.0	4.16	9.37	2.25
2	**1**	1200	1	6	3.852	64.2	4.53	9.87	2.18
3	**1**	800	0.05	1	0.780	1560	4.41	9.96	2.26
4	**2**	800	1	1	Trace	–	–	–	–
5	**2**	1200	1	6	0.178	2.97	3.36	8.78	2.61

[a] Conditions: 20 ml toluene, 60 °C, 5 g norbornene, reaction for 1 h.

[b] Activity in 10^4 g h^{-1} (polymer/mole of Mt).

[c] Molecular weights of the polymers were determined by a Waters Breeze system at 40 °C in chlorobenzene with polystyrene as standard.

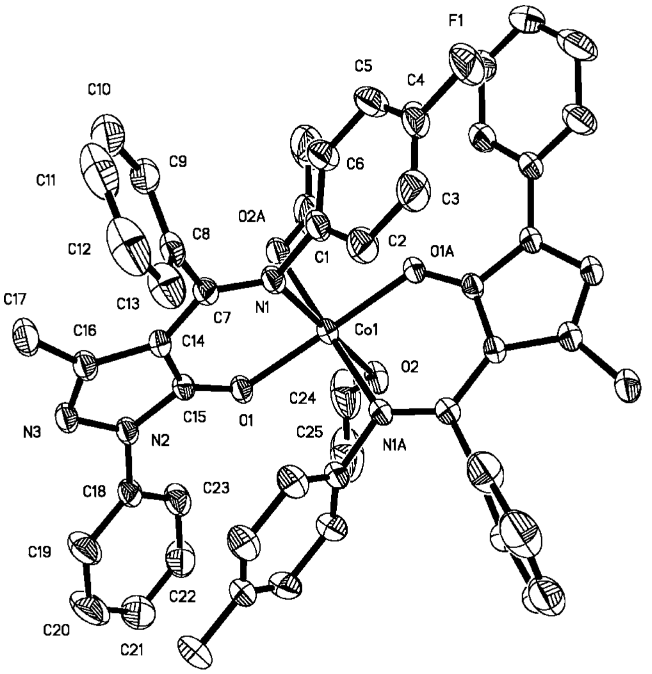


Figure 3. X-ray structure of complex **2**. ORTEP representation with 30% ellipsoid probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co1–N1=2.164, Co1–O1=2.103, Co1–O2=2.191, N1–Co1–O1=94.09, N1–Co1–O2=94.20, N1–Co1–N1a=171.68, N1–Co1–O1a=54.60, N1–Co1–O2a =127.03.

the activity of complex**2**–MAO is much lower than that of complex **1**–MAO under the same conditions (its activity being only up to 10^4g h^{-1} (polymer/mole of cobalt)). The distinct differences between the catalytic activities of nickel and cobalt complexes bearing the same ligand can be attributed to the different metals. The nickel complex appears to be more easily activated than the cobalt complex. Thus, the nickel system produces a more active center for norbornene polymerization.

During the past few years, several series of cobalt complexes bearing β-diketone ligands (abbreviated [**O, O**]), bidentate phosphine ligands (abbreviated [**P, P**]) and tridentate bis(imino)pyridine ligands (abbreviated [**N, N, N**]) for MAO-promoted vinyl-addition-type polymerization of norbornene have been reported.[35–39] However, the nature of the cobalt(II) complex bearing an **N,O**-chelate ligand used for the polymerization of norbornene is still unknown.

We are interested in comparing our results with other series of cobalt complexes. Complex **2** was used for comparison purposes as follows. The activity for norbornene polymerization by the series [**O, O**] can be up to 10^7 g h^{-1} (polymer/mole of cobalt).[35,36] However, the activities of the series [**P, P**] and [**N, N, N**] are around 10^4 g h^{-1} (polymer/mole of cobalt).[37–39] Similarly, the activity of the cobalt(II) complexes bearing the β-ketoamine ligands [**N, O**] in this manuscript is about 10^4 g h^{-1} (polymer/mole of cobalt). These results can be attributed to the non-planar framework of the former ligands. The series [**O, O**] are drawn in a simplified square-planar coordination environment and they have less-rigid ligand frameworks. Therefore, the norbornene molecular inserts into the Co–C bond more easily after the precatalyst is activated with MAO to afford an empty site.[40]

The reaction parameters can also affect the catalytic activity, polymer yield and polymer molecular weight remarkably. As shown in Fig. 4, the polymerization temperature can affect the catalytic activities and the M_w of the polymers greatly. With an increase in the reaction temperature from 0 to 80 °C, a prominent increase in activity was observed, but with a significant decrease in molecular weight.

Finally, the evolution of the polymerization yield with time was examined. Results are reported in Fig. 5. The polymer yield should increase monotonically with increasing time. However, the polymerization activities reach their highest values at an early stage and then decrease rapidly with time. This indicates that the character of the catalytic system changed rapidly. Besides the monomer consumption, the reason for the activity decreasing with time is that a part of the catalytic species is deactivated gradually. The results from norbornene polymerizations using complexes **1** and **2** at different molar ratios of MAO/Ni (Al/Ni) and MAO/Co (Al/Co) complexes are shown in Fig. 6. The monomer conversion and catalytic activity increase monotonously with an increase in Al/Mt from 600 to 2400.

The polynorbornenes obtained with these catalysts show high molecular weights ($M_n > 3.36 \times 10^5$ g mol^{-1}, $M_w > 8.78 \times 10^5$ g mol^{-1}) and molecular weight distributions of $M_w/M_n = 2.18 - 2.61$. As shown in Fig. 7, the ^{1}H NMR spectra do not show vinyl protons in the polymers, indicating polymerization through a vinyl-type mechanism. Similarly, the IR spectra of the polymers also support a vinyl-type polymerization rather than ROMP, which would

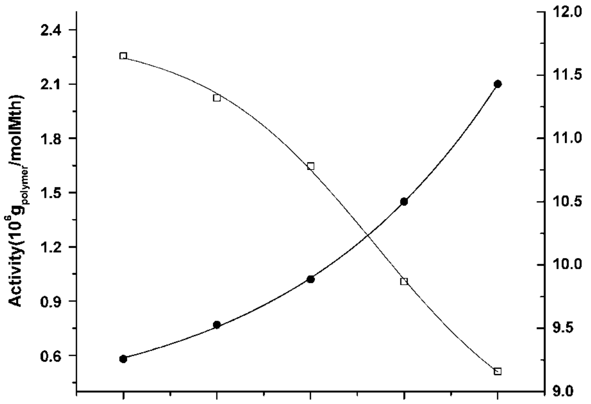


Figure 4. Plot of activity (●) and M_w (□) versus polymerization temperature (complex **1**): $M_{Ni} = 1 \times 10^{-6}$ mol; 60 °C; $V_{total} = 20$ ml; reaction time, 1 h.

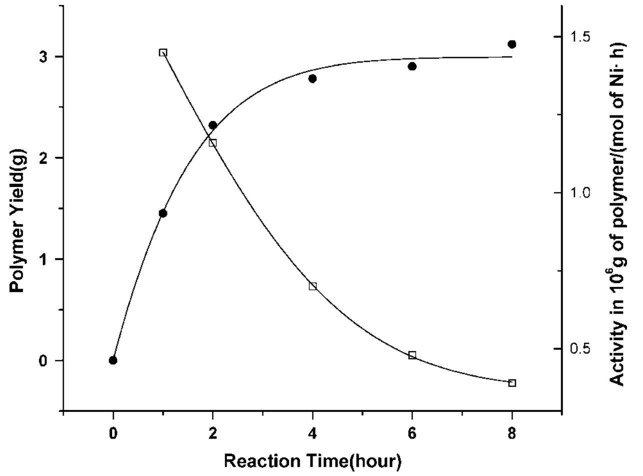


Figure 5. Plot of activity (●) and polymer yield (□) versus polymerization time (complex **1**). [Ni]/[Al]/[norbornene] = 1/1200/53 000 (molar ratio); $M_{Ni} = 1 \times 10^{-6}$ mol; 60 °C; V_{total} = 20ml.

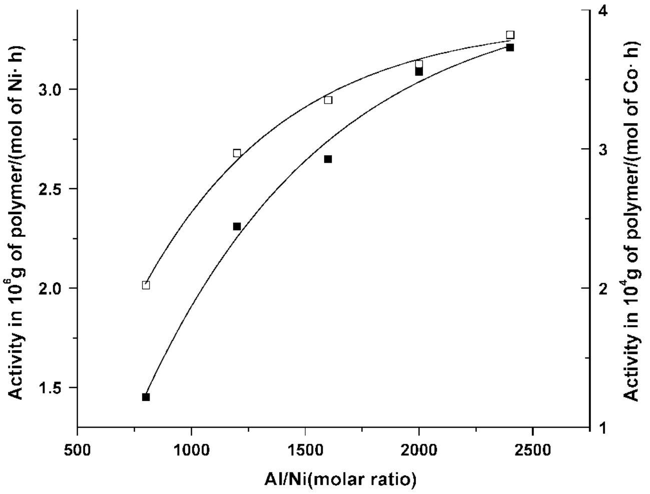


Figure 6. Plot of activity (■) versus Al/Ni molar ratio (complex **1**): $M_{Ni} = 1 \times 10^{-6}$ mol; 60 °C; V_{total} = 20ml; reaction time, 1 h. Plot of activity (□) versus Al/Co molar ratio (complex **2**): $M_{Co} = 6 \times 10^{-6}$ mol; 60 °C; V_{total} = 20 ml; reaction time, 1 h.

afford a double-bond-containing polymer showing peaks at 996 and 735 cm^{-1}.[41] All the polynorbornenes obtained here are readily soluble in cyclohexane, chlorobenzene and *o*-dichlorobenzene, which indicates low stereoregularity.

CONCLUSIONS

Bis(β-ketoamine) nickel and cobalt complexes based on pyrazolone derivatives can be activated by MAO to catalyze norbornene polymerization via a vinyl addition mechanism. The catalysts afford polynorbornenes with high molecular weight and molecular weight distributions (M_w/M_n = 2.18 – 2.61). The catalytic activity of the cobalt–MAO complex is much lower than that of the nickel–MAO complex under the same reaction conditions. This is attributed to the easier activation of the nickel complex. The catalytic activity, polymer yield and the polymer molecular weight can be controlled over a wide range by variation of the reaction parameters. Studies on polar and nonpolar monomer polymerization are currently under investigation.

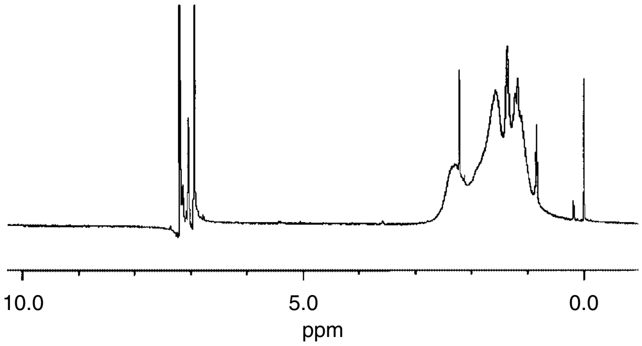


Figure 7. ^{1}H NMR spectrum of polynorbornene prepared by complex **1**–MAO at 60 °C.

SUPPLEMENTARY MATERIALS

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; CCDC reference numbers for **L, 1** and **2** are 261 163, 261 164 and 261 165 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 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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