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Synthesis and characterization of new bis(1-aryliminomethylenylnaphthalen-2-oxy)nickel complexes and their catalytic behavior for vinyl polymerization of norbornene ☆

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Abstract

The synthesized 1-aryliminomethylenylnaphthalen-2-ol derivatives reacted with nickel chloride to form bis(1-aryliminomethylenylnaphthalen-2-oxy)nickel complexes. All resultant compounds were structurally characterized by elemental analyses, IR and H NMR, and the structures of the formed complexes were elucidated by X-ray crystal structure analysis. The complexes show high catalytic activities for the vinyl polymerization of norbornene in the presence of methylaluminoxane. The catalytic activity variations have been followed by gas chromatography through monitoring the conversion of norbornene.

Keywords: Nickel complex; Norbornene; Vinyl polymerization; Crystal structure

1. Introduction

The polymerization of norbornene found its root in the 1950s when Andersen and Merckling first reported polynorbornenes prepared by means of ring-opening metathesis polymerization (ROMP) [1]. Nowadays, norbornene polymerization is commonly achieved by using various transition metal-containing catalysts via three typical routes: ROMP [2,3], cationic or radical polymerization [4], and vinyl polymerization (addition polymerization) [5,6]. Vinyl-type polymerization was first described in the early 1960s. By employing classical $TiCl_4$-based Ziegler catalyst [5], cycloaliphatic polymers that contained bicyclic structural units intact without any double bond were generated. With constrained rings in each unit, these polymers possess interesting and unique properties [7], such as high chemical resistance, good UV resistance, low dielectric constant and excellent transparency, showing some advantages over related materials [8].

There have been numerous reports about transition metal complexes that serve as catalysts for norbornene polymerization, e.g., Ni complexes [9–13], Co complexes [14] and Pd complexes [15,16], of which nickel complexes have drawn great attention [11,17,18]. It was reported that nickel complexes bearing ethylhexanoate with $HSbF_6$ system exhibited high catalytic activities for the homo-polymerization of norbornene, from which high polymers were generated [19]. In addition, nickel acetylacetonate complexes were employed with MAO as the catalytic system to catalyze norbornene polymerization [20]. Furthermore, highly active phosphoraneiminide-containing nickel complexes in the presence of MAO as well as salen nickel complexes [21] were reported [22]. In general, these complexes are activated by MAO or

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weakly coordinating counter ions like BF_4^- or PF_6^- (Ni, Pd). We have been engaging in the research of Schiff base-containing nickel complex-catalyzed ethylene polymerization, and we have extensively investigated the vinyl polymerization of norbornene catalyzed by nickel complexes liganded by 8-(diphenylphosphino)quinoline [23] and salicylideneimide [24]. In this paper, we describe the design and synthesis of a series of new bis(1-aryliminomethylenylnaphthalen-2-oxy)nickel complexes and the examination of their catalytic activities for norbornene polymerization. These complexes prove to be highly active catalysts for norbornene polymerization.

2. Experimental

2.1. General procedures

All manipulations involving air- or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were refluxed over the appropriate drying reagents and distilled under nitrogen prior to use. NaH (Beijing Chemical Regent Company) was washed with petroleum ether before use to remove contained mineral oil. Elemental analyses were performed by using Flash-EA 1112 microanalyzer. NMR experiments were performed with a Brucker DMX-300 Spectrometer and the chemical shifts were recorded with respect to TMS. The IR experiments were conducted on a FTIR-spectrometer (Perkin–Elmer type 2000). Melting points were determined with a digital electrothermal apparatus without further correction. Gel permeation chromatography analysis was performed on a Waters Alliance GPCV 2000 system (USA) at 135 °C eluting with 1,2,4-trichlorobenzene, the molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene. Gas chromatography VISTA 6000 was used to monitor the progress of the reactions. TGA data were measured on a Perkin–Elmer 7 series thermal analysis system instrument. All chemicals for synthesizing the ligands were purchased from Aldrich or Acros Chemicals except for MAO (1.4 mol/L in toluene) which was obtained from Albemarle Corp (USA); all other chemicals were obtained from commercial sources unless stated otherwise.

3. Preparation of ligands and complexes

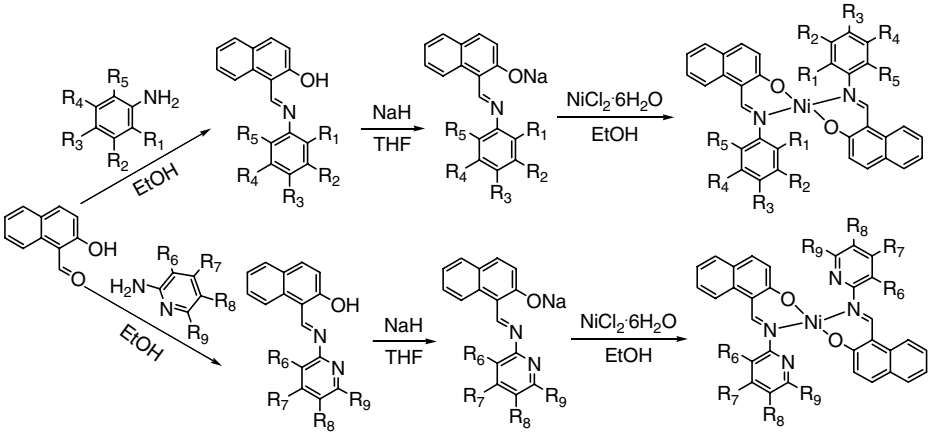
The typical procedure for the synthesis of the ligands and nickel complexes are outlined in Scheme 1.

3.1. Synthesis of ligands

All ligands were synthesized via the condensation of 2-hydroxy-1-naphthaldehyde with phenylamines or pyridinylamines with protocols reported in the literatures [23–33].

3.1.1. 1-[[(2-Isopropylphenyl)imino]methylenyl]-2-naphthalenol (*L1*)

Typical procedure is as follows: 2-isopropylaniline (0.34 g, 2.5 mmol) in ethanol (10 mL) was added slowly



1. R_1= iPr, R_2=R_3=R_4=R_5=H
2. R_1=Ethyl, R_2=R_3=R_4=R_5=H
3. R_1=R_4=Me, R_2=R_3=R_5=H
4. R_1=R_5=Me, R_2=R_3=R_4=H
5. R_1=R_2=Me, R_3=Br, R_2=R_4=H
6. R_1=R_5=iPr, R_2=R_3=R_4=H
7. R_1=R_3=R_5=Me, R_2=R_4=H
8. R_1=F, R_2=R_3=R_4=R_5=H
9. R_1=R_5=F, R_2=R_3=R_4=H
10. R_1=R_2=R_3=F, R_4=R_5=H
11. R_1=R_2=R_5=F, R_3=R_4=H
12. R_1=R_3=R_4=Cl, R_2=R_5=H
13. R_1=R_3=R_5=Cl, R_2=R_4=H
14. R_6=Benzyloxy, R_7=R_8=R_9=H
15. R_6=R_7=R_8=R_9=H
16. R_7=Me,R_6=R_8=R_9=H
17. R_7=R_9=Me, R_6=R_8=H
18. R_6=R_8=Br, R_9=Me, R_7=H
19. R_8=NO_2, R_6=R_7=R_9=H

Scheme 1. Synthesis of ligands and their complexes.

over 30 min into a stirred solution of 2-hydroxy-1-naphthaldehyde (0.43 g, 2.5 mmol) in ethanol (10 mL) at ambient temperature. The solution was heated at reflux for 4 h. Upon cooling to room temperature, the solution was concentrated in vacuum, and the chilled (0 °C) ethanol solution gave yellow microcrystals. Yield 0.60 g (83.2%), m.p. 129–131 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (d, $J = 6.8$ Hz, 6H), 3.46–3.51 (m, 1H), 7.13–8.14 (m, 10H), 9.33 (d, $J = 4.3$ Hz, 1H), 15.77 (d, $J = 4.2$ Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.9, 28.2, 109.0, 118.2, 118.8, 121.9, 123.4, 126.0, 126.9, 127.2, 128.0, 129.3, 133.1, 136.4, 141.3, 143.4, 155.5, 169.5 ppm. IR (KBr): 3462, 3034, 1618, 1589, 1542, 1485, 1343, 1318 cm^{-1}. *Anal.* Calc. for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.70; H, 6.58; N, 4.64%.

3.1.2. 1-[[(2-Ethylphenyl)imino]methylenyl]-2-naphthalenol (*L2*)

Ligand **L2** was prepared with a protocol described in the literature [26], and was obtained as yellow microcrystals. Yield 0.58 g (84.1%).

3.1.3. 1-[[(2,5-Dimethylphenyl)imino]methylenyl]-2-naphthalenol (*L3*)

Ligand **L3** was prepared by using the above protocol for **L1** except that 2,5-dimethylaniline was used in place of 2-isopropylaniline, and was obtained as yellow solid. Yield 0.56 g (81.9%), m.p. 110–112 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.42 (s, 3H), 2.44 (s, 3H), 7.00–8.12 (m, 9H), 9.28 (d, $J = 5.7$ Hz, 1H), 15.80 (d, $J = 5.4$ Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 17.6, 21.1, 108.5, 117.3, 118.6, 123.0, 123.3, 126.9, 127.1, 127.4, 127.9, 129.2, 130.8, 133.3, 136.8, 136.9, 142.3, 152.4, 172.7 ppm. IR (KBr): 3415, 3023, 1612, 1545, 1491, 1381, 1313 cm^{-1}. *Anal.* Calc. for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.94; H, 6.30; N, 5.06%.

3.1.4. 1-[[(2,6-Dimethylphenyl)imino]methylenyl]-2-naphthalenol (*L4*)

Ligand **L4** was prepared with a previously described protocol [27], and was obtained as yellow solid. Yield 0.56 g (82.1%).

3.1.5. 1-[[(4-Bromo-2,6-dimethylphenyl)imino]methylenyl]-2-naphthalenol (*L5*)

Ligand **L5** was prepared by using the above protocol for **L1** except that 4-bromo-2,6-dimethylaniline was used in place of 2-isopropylaniline, and was obtained as yellow microcrystals. Yield 0.56 g (65.5%), m.p. 165–167 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.25 (s, 6H), 7.18–8.02 (m, 8H), 9.13 (s, 1H), 14.93 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.5, 108.6, 118.2, 118.8, 120.7, 123.6, 127.5, 128.1, 129.3, 131.1, 131.4, 132.9, 135.8, 145.9, 162.1, 166.0 ppm. IR (KBr): 3452, 3062, 1624, 1582, 1486, 1421, 1323 cm^{-1}. *Anal.* Calc. for $C_{19}H_{16}BrNO$: C, 64.42; H, 4.55; N, 3.95. Found: C, 64.25; H, 4.54; N, 3.84%.

3.1.6. 1-[[(2,6-Diisopropylphenyl)imino]methylenyl]-2-naphthalenol (*L6*)

Ligand **L6** was prepared with a protocol reported in the literature [27], and was obtained as yellow microcrystals. Yield 0.61 g (74.2%).

3.1.7. 1-[[(2,4,6-Trimethylphenyl)imino]methylenyl]-2-naphthalenol (*L7*)

Ligand **L7** was prepared from the condensation of 2-hydroxy-1-naphthaldehyde with 2,4,6-trimethylaniline using the above protocol for **L1**, and was obtained as yellow solid. Yield (83.5%), m.p. 86–87 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.13 (s, 3H), 2.18 (s, 6H), 6.83–7.81 (m, 8H), 8.90 (d, $J = 3.9$ Hz, 1H), 15.14 (d, $J = 3.8$ Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.6, 20.8, 108.2, 118.6, 122.0, 123.3, 127.1, 128.0, 129.3, 129.6, 133.2, 135.3, 136.1, 142.5, 160.7, 169.2 ppm. IR (KBr): 3443, 1622, 1575, 1476, 1328 cm^{-1}. *Anal.* Calc. for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.89; H, 6.69; N, 4.69%.

3.1.8. 1-[[(2-Fluorophenyl)imino]methylenyl]-2-naphthalenol (*L8*)

Ligand **L8** was prepared with a protocol described in the literature [28], and was obtained as yellow solid. Yield 71.1%.

3.1.9. 1-[[(2,6-Difluorophenyl)imino]methylenyl]-2-naphthalenol (*L9*)

Ligand **L9** was obtained as yellow microcrystals from the condensation of 2-hydroxy-1-naphthaldehyde with 2,6-difluoroaniline by using the above protocol for **L1**. Yield 90.9%, m.p. 135–137 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.91–8.12 (m, 9H), 9.75 (s, 1H), 15.13 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 109.5, 112.0, 112.2, 112.3, 119.2, 120.6, 123.7, 124.3, 126.0, 126.1, 126.2, 127.6, 128.1, 129.2, 132.9, 136.3, 154.3, 157.7, 162.5, 166.1 ppm. IR (KBr): 3443, 3059, 1620, 1576, 1474, 1391, 1332 cm^{-1}. *Anal.* Calc. for $C_{17}H_{11}F_2NO$: C, 72.08; H, 3.91; N, 4.94. Found: C, 72.10; H, 3.84; N, 4.93%.

3.1.10. 1-[[(2,3,4-Trifluorophenyl)imino]methylenyl]-2-naphthalenol (*L10*)

Ligand **L10** was prepared with the above protocol for **L1** except that 2,3,4-trifluoroaniline was used in place of 2-isopropylaniline, and was obtained as yellow solid. Yield 0.62 g (82.4%), m.p. 178–180 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.04–8.16 (m, 8H), 9.53 (s, 1H), 14.84 (d, $J = 1.2$ Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 109.3, 111.8, 112.0, 114.6, 119.1, 120.2, 123.9, 127.7, 128.2, 129.4, 132.8, 136.3, 159.9, 165.2 ppm. IR (KBr): 3446, 3070, 1623, 1575, 1502, 1425, 1393, 1331 cm^{-1}. *Anal.* Calc. for $C_{17}H_{10}F_3NO$: C, 67.78; H, 3.35; N, 4.65. Found: C, 67.94; H, 3.19; N, 4.38%.

*3.1.11. 1-[[(2,3,6-Trifluorophenyl)imino]methylenyl]-2-naphthalenol (**L11**)*

Ligand **L11** was prepared with the above protocol for **L1** except that 2,3,6-trifluoroaniline was used in place of 2-isopropylaniline, and was obtained as yellow microcrystals. Yield 0.66 g (87.8%), m.p. 164–165 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.97–8.12 (m, 8H), 9.77 (s, 1H), 14.79 (d, $J = 1.2$ Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 109.5, 110.6, 110.7, 110.8, 111.0, 111.1, 112.7, 112.9, 113.0, 113.1, 119.2, 120.2, 123.9, 126.4, 127.7, 128.3, 129.3, 132.8, 136.6, 146.0, 149.4, 149.9, 153.1, 163.9, 165.2 ppm. IR (KBr): 3443, 3067, 1620, 1570, 1498, 1475, 1423, 1391, 1331 cm^{-1}. *Anal.* Calc. for $C_{17}H_{10}F_3NO$: C, 67.78; H, 3.35; N, 4.65. Found: C, 67.60; H, 3.30; N, 4.38%.

*3.1.12. 1-[[(2,4,5-Trichlorophenyl)imino]methylenyl]-2-naphthalenol (**L12**)*

Ligand **L12** was prepared from the condensation of 2,4,5-trichloroaniline with 2-hydroxy-1-naphthaldehyde using the protocol described for **L1** and was obtained as yellow crystals. Yield 0.58 g (66.5%), m.p. 204–206 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.16–8.19 (m, 8H), 9.43 (d, $J = 1.8$ Hz, 1H), 14.96 (d, $J = 1.5$ Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 108.9, 118.7, 119.6, 120.1, 123.4, 123.5, 127.2, 127.9, 129.0, 129.8, 130.8, 131.5, 132.3, 136.5, 143.3, 157.3, 166.1, 200.2 ppm. IR (KBr): 3481, 3059, 1603, 1584, 1559, 1453, 1422, 1393, 1349, 1322 cm^{-1}. *Anal.* Calc. for $C_{17}H_{10}Cl_3NO$: C, 58.23; H, 2.87; N, 3.99. Found: C, 58.20; H, 2.86; N, 3.84%.

*3.1.13. 1-[[(2,4,6-Trichlorophenyl)imino]methylenyl]-2-naphthalenol (**L13**)*

Ligand **L13** was prepared from the condensation of 2,4,6-trichloroaniline with 2-hydroxy-1-naphthaldehyde using the protocol described for **L1**, and was obtained as yellow microcrystals. Yield 0.49 g (56.2%), m.p. 158–160 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.23–8.09 (m, 8H), 9.49 (s, 1H), 14.20 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 108.9, 118.5, 119.1, 119.3, 119.8, 123.9, 124.4, 127.8, 128.1, 128.3, 128.6, 129.1, 129.3, 129.4, 130.6, 132.9, 136.3, 139.1, 142.9, 163.8, 165.7, 193.2 ppm. IR (KBr): 3424, 3072, 1608, 1583, 1450, 1321 cm^{-1}. *Anal.* Calc. for $C_{17}H_{10}Cl_3NO$: C, 58.23; H, 2.87; N, 3.99. Found: C, 57.93; H, 2.79; N, 3.74%.

*3.1.14. 1-[[(3-Benzyloxy-2-pyridinyl)imino]methylenyl]-2-naphthalenol (**L14**)*

An ethanol (20 mL) solution of 2-amino-3-benzyloxypyridine (0.50 g, 2.5 mmol) was added slowly over 30 min into a solution of 2-hydroxy-1-naphthaldehyde (0.43 g, 2.5 mmol) in ethanol (10 mL) at room temperature. The reaction mixture was stirred for 5 h at 40–45 °C, and the solution was then evaporated into 10 mL under vacuum. The product was recrystallized from ethanol, and, after filtration, the yellow crystals were collected, washed with cold ethanol and dried. Yield 0.81 g (91.6%), m.p. 190–191 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.34 (s, 2H), 6.82–8.10 (m, 14H), 9.78 (d, $J = 10.5$ Hz, 1H), 15.38 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 70.5, 109.0, 119.1, 120.0, 120.5, 123.8, 126.6, 126.7, 126.8, 128.2, 128.5, 128.8, 129.3, 134.4, 135.7, 139.8, 140.0, 142.4, 144.1, 145.2, 183.1 ppm. IR (KBr): 3438, 3059, 1618, 1570, 1536, 1496, 1460, 1405, 1384, 1314, 1280, 621, 430 cm^{-1}. *Anal.* Calc. for $C_{23}H_{18}N_2O_2$: C, 77.95; H, 5.12; N, 7.90. Found: C, 77.83; H, 5.09; N, 7.83%.

*3.1.15. 1-[[(2-Pyridinyl)imino]methylenyl]-2-naphthalenol (**L15**)*

Ligand **L15** was prepared from the condensation of 2-hydroxy-1-naphthaldehyde with 2-aminopyridine using the above protocol for **L14** as yellow solid. Yield 0.60 g (96.3%). Its characteristic data are consistent with reported paper [29].

*3.1.16. 1-[[(4-Methyl-2-pyridinyl)imino]methylenyl]-2-naphthalenol (**L16**)*

Ligand **L16** was prepared with a protocol described in the literature [30], and was obtained as yellow microcrystals. Yield 0.58 g (89.0%).

*3.1.17. 1-[[(4,6-Dimethyl-2-pyridinyl)imino]methylenyl]-2-naphthalenol (**L17**) [30]*

Ligand **L17** was prepared from the condensation of 2-hydroxy-1-naphthaldehyde with 2-amino-4,6-dimethylpyridine using the above protocol for **L14**, and was obtained as yellow crystals. Yield 0.58 g (83.7%), m.p. 196–198 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.36 (s, 3H), 2.55 (s, 3H), 6.77–8.12 (m, 8H), 9.91 (d, $J = 8.4$ Hz, 1H), 15.39 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.8, 24.1 108.3, 112.9, 119.1, 121.6, 123.6, 125.3, 126.6, 128.3, 129.2, 134.2, 139.1, 149.0, 150.0, 151.4, 157.8, 179.8 ppm. IR (KBr): 3438, 3036, 1617, 1541, 1451, 1404, 1294, 611, 432 cm^{-1}. *Anal.* Calc. for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found: C, 78.11; H, 5.90; N, 10.08%.

*3.1.18. 1-[[(3,5-Dibromo-6-methyl-2-pyridinyl)imino]-methylenyl]-2-naphthalenol (**L18**)*

Ligand **L18** was prepared by using the above protocol for **L14** except that 2-amino-3,5-dibromo-6-methylpyridine was used in place of 2-amino-3-benzyloxypyridine, and was obtained as yellow crystals. Yield 0.93 g (88.8%), m.p. 217–218 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.66 (s, 3H), 6.93–8.14 (m, 7H), 9.91 (d, $J = 6.6$ Hz, 1H), 15.55 (d, $J = 6.4$ Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.4, 109.4, 109.6, 116.7, 119.4, 124.0, 124.2, 127.2, 128.6, 129.4, 133.7, 139.5, 144.0, 149.2, 150.6, 155.6, 177.2 ppm. IR (KBr): 3435, 3057, 1621, 1609, 1540, 1437, 1407, 1379, 1319, 1291, 600, 435 cm^{-1}. *Anal.* Calc. for $C_{17}H_{12}Br_2N_2O$: C, 48.60; H, 2.88; N, 6.67. Found: C, 48.69; H, 2.91; N, 6.48%.

*3.1.19. 1-[[(5-Nitro-2-pyridinyl)imino]methylenyl]-2-naphthalenol (**L19**) [29]*

Ligand **L19** was prepared as yellow solid in yield 0.48 g (65.9% yield) by using the above protocol for **L14** except that 2-amino-5-nitropyridine was used in place of 2-amino-3-benzyloxypyridine, m.p. 159–160 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.83–9.31 (m, 8H), 9.85 (d, $J = 7.8$ Hz, 1H), 15.15 (d, $J = 7.3$ Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 114.8, 118.9, 119.6, 124.7, 125.0, 127.3, 129.1, 129.6, 134.0, 141.2, 143.4, 144.8, 145.7, 148.8, 155.3, 181.2 ppm. IR (KBr): 3495, 3048, 1637, 1592, 1571, 1477, 1419, 1291, 582, 448 cm^{-1}. *Anal.* Calc. for $C_{16}H_{11}N_3O_3$: C, 65.53; H, 3.78; N, 14.33. Found: C, 65.47; H, 3.60; N, 14.28%.

3.2. Syntheses of complexes

Complexes **C4** [34], **C15** [35] were prepared with previously described procedures, and all other complexes were prepared with the same protocol as for **C4** or **C15**. The typical procedure for synthesizing bis{1-[[(2-isopropylphenyl)imino]methylenyl]-2-naphthalenolato-*N, O*}-nickel (**C1**) was as follows: NaH (0.036 g, 1.5 mmol) was added into an tetrahydrofuran (THF) (20 mL) solution of 1-[[(2-isopropylphenyl)imino]methylenyl]-2-naphthalenol (0.44 g, 1.5 mmol) at room temperature. After stirring the reaction mixture for 30 min, ethanol solution (15 mL) containing $NiCl_2 \cdot 6H_2O$ (0.75 mmol, 0.18 g) was added. The mixture was then stirred for 24 h, and green precipitate was collected by filtration, and the resultant solid cake was washed with anhydrous diethyl ether, and dried in vacuum for 24 h at 50 °C. Yield 0.31 g (63.5%). After recrystallization from CH_2Cl_2, green crystals were obtained. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.20–1.26 (m, 12H), 2.36 (m, 2H), 5.57 (d, $J = 8.5$ Hz, 2H), 6.75–7.64 (m, 18H), 7.92 (d, $J = 8.1$ Hz, 2H) ppm. IR (KBr): 3033, 1606, 1581, 1451, 1432, 1398, 1362, 1319 cm^{-1}. *Anal.* Calc. for $C_{40}H_{36}N_2NiO_2$: C, 75.61; H, 5.71; N, 4.41. Found: C, 75.34; H, 5.38; N, 4.51%.

*3.2.1. Bis{1-[[(2-ehtylphenyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C2**)*

Green solid, yield 0.28 g (60.1%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.35–1.42 (m, 6H), 2.84–2.91 (m, 4H), 5.74 (d, $J = 9.1$ Hz, 2H), 7.14–7.74 (m, 18H), 8.27 (s, 2H) ppm. IR (KBr): 3053, 1603, 1580, 1484, 1451, 1401, 1361, 1315 cm^{-1}. *Anal.* Calc. for $C_{38}H_{32}N_2NiO_2$: C, 75.15; H, 5.31; N, 4.61. Found: C, 74.75; H, 5.31; N, 4.49%.

*3.2.2. Bis{1-[[(2,5-dimethylphenyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C3**)*

Green solid, 0.28 g (60.9% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.21 (s, 6H), 2.45 (s, 6H), 5.84 (d, $J = 9.2$ Hz, 2H), 7.08–7.80 (m, 16H), 8.37 (s, 2H) ppm. IR (KBr): 3033, 1602, 1581, 1451, 1432, 1398, 1362, 1319 cm^{-1}. *Anal.* Calc. for $C_{38}H_{32}N_2NiO_2 \cdot H_2O$: C, 72.98; H, 5.48; N, 4.48. Found: C, 73.33, H, 5.28; N, 4.25%.

*3.2.3. Bis{1-[[(2,6-dimethylphenyl)imino]methylenyl]-2-naphthalenolato- N,O}nickel (**C4**)*

Green solid, yield 0.30 g (65.2%). The H NMR and IR data obtained is consistent with that reported for compound **C4** [34].

*3.2.4. Bis{1-[[(4-bromo-2,6-dimethylphenyl)imino]methylenyl]-2-naphthalenolato- N,O}nickel (**C5**)*

Green solid, yield 0.33 g (59.6%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.66 (s, 12H), 5.87 (d, $J = 9.0$ Hz, 2H), 7.16–7.67 (m, 14H), 8.05 (s, 2H) ppm. IR (KBr): 3054, 1604, 1584, 1536, 1452, 1434, 1406, 1361, 1315 cm^{-1}. *Anal.* Calc. for $C_{38}H_{30}Br_2N_2\ NiO_2 \cdot 1/2H_2O$: C, 58.95; H, 4.04; N, 3.62. Found: C, 58.79; H, 3.93; N, 3.35%.

*3.2.5. Bis{1-[[(2,6-diisopropylphenyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C6**)*

Green solid, 0.33 g (62.0% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.24 (d, $J = 6.8$ Hz, 12H), 4.28–4.33 (m, 4H), 5.70 (d, $J = 9.1$ Hz, 2H), 7.15–7.66 (m, 16H), 8.16 (s, 2H) ppm. IR (KBr): 3059, 1604, 1583, 1536, 1510, 1435, 1404, 1364, 1313 cm^{-1}. *Anal.* Calc. for $C_{46}H_{48}N_2NiO_2 \cdot H_2O$: C, 74.90; H, 6.83; N, 3.80. Found: C, 74.75; H, 6.59; N, 3.82%.

*3.2.6. Bis{1-[[(2,4,6-trimethylphenyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C7**)*

Green powder, yield 0.30 g (63.4%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.33 (d, $J = 4.8$ Hz, 6H), 2.66 (s, 12H), 5.87 (d, $J = 9.0$ Hz, 2H), 6.96–7.69 (m, 14H), 8.09 (s, 2H) ppm. IR (KBr): 1603, 1582, 1535, 1478, 1433, 1402, 1360, 1315 cm^{-1}. *Anal.* Calc. for $C_{40}H_{36}N_2NiO_2$: C, 75.61; H, 5.71; N, 4.41. Found: C, 75.42; H, 5.92; N, 4.43%.

*3.2.7. Bis{1-[[(2-fluorophenyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C8**)*

Green solid, 0.30 g (67.9% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.72 (d, $J = 9.1$ Hz, 2H), 7.16–7.78 (m, 18H), 8.43 (s, 2H) ppm. IR (KBr): 1612, 1579, 1533, 1496, 1452, 1433, 1395, 1368, 1316 cm^{-1}. *Anal.* Calc. for $C_{34}H_{22}F_2N_2\ NiO_2 \cdot 1/2CH_2Cl_2$: C, 65.80; H, 3.68; N, 4.45. Found: C, 66.04; H, 3.64; N, 4.46%.

*3.2.8. Bis{1-[[(2,6-difluorophenyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C9**)*

Green crystals, yield 0.14 g (29.8%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.85 (d, $J = 9.2$ Hz, 2H), 6.95–7.86 (m, 16H), 8.33 (s, 2H) ppm. IR (KBr): 1599, 1535, 1472, 1453, 1430, 1392, 1365, 1312 cm^{-1}. *Anal.* Calc. for $C_{34}H_{20}F_4N_2NiO_2 \cdot 1/2H_2O$: C, 64.59; H, 3.35; N, 4.43. Found: C, 64.45; H, 3.14; N, 4.23%.

*3.2.9. Bis{1-[[(2,3,4-trifluorophenyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C10**)*

Green solid, yield 0.33 g (65.9%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.95 (d, $J = 9.1$ Hz, 2H), 7.24–7.77 (m, 14H), 8.36 (s, 2H) ppm. IR (KBr): 3059, 1602, 1581, 1535,1505, 1451, 1431, 1364, 1307 cm^{-1}. *Anal*. Calc. for $C_{34}H_{18}F_6N_2NiO_2$: C, 61.95; H, 2.75; N, 4.25. Found: C, 61.84; H, 2.61; N, 3.99%.

*3.2.10. Bis{1-[[(2,3,6-trifluorophenyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C11**)*

Green solid, 0.26 g (52.2% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.86 (d, $J = 9.3$ Hz, 2 H), 6.95–7.74 (m, 14H), 8.27 (s, 2H) ppm. IR (KBr): 3057, 1603, 1581, 1537, 1454, 1430, 1391, 1370, 1314 cm^{-1}. *Anal*. Calc. for $C_{34}H_{18}F_6N_2NiO_2$: C, 61.95; H, 2.75; N, 4.25. Found: C, 61.36; H, 2.61; N, 4.12%.

*3.2.11. Bis{1-[[(2,4,5-trichlorophenyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C12**)*

Green solid, yield 0.23 g (40.3%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.83 (d, $J = 8.9$ Hz, 2H), 7.16–7.79 (m, 14H), 8.20 (s, 2H) ppm. IR (KBr): 3077, 1604, 1581, 1534, 1450, 1432, 1403, 1366, 1345, 1314 cm^{-1}. *Anal*. Calc. for $C_{34}H_{18}C_{l6}N_2NiO_2$: C, 53.88; H, 2.39; N, 3.70. Found: C, 53.92; H, 2.16; N, 3.49%.

*3.2.12. Bis{1-[[(2,4,6-trichlorophenyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C13**)*

Green solid, 0.24 g (42.1% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.89 (d, $J = 9.1$ Hz, 2H), 7.23–7.76 (m, 14H), 8.10 (s, 2H) ppm. IR (KBr): 3070, 1604, 1583, 1536, 1435, 1405, 1366, 1315 cm^{-1}. *Anal*. Calc. for $C_{34}H_{18}C_{l6}N_2NiO_2$: C, 53.88; H, 2.39; N, 3.70. Found: C, 53.91; H, 2.43; N, 3.54%.

*3.2.13. Bis{1-[[(3-benzyloxy-2-pyridinyl)imino]methylenyl]- 2-naphthalenolato-N,O}nickel (**C14**)*

Brown powder, yield 0.34 g (59.6%). IR (KBr): 3059, 1613, 1562, 1534, 1458, 1423, 1383, 1363, 1312, 618, 414 cm^{-1}. *Anal*. Calc. for $C_{46}H_{34}N_4NiO_4 \cdot CH_2Cl_2$: C, 66.38; H, 4.27; N, 6.59. Found: C, 66.35; H, 4.51; N, 6.39%.

*3.2.14. Bis{1-[[(2-pyridinyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C15**)*

Brown powder, 0.25 g (61.2% yield). It was previously reported complex [35].

*3.2.15. Bis{1-[[(4-methyl-2-pyridinyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C16**)*

Purple solid, yield 0.27 g (62.5%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.38 (s, 6H), 6.97–7.99 (m, 18H), 8.10 (d, $J = 9.2$ Hz, 2H) ppm. IR (KBr): 3055, 1614, 1534, 1456, 1295, 557, 416 cm^{-1}. *Anal*. Calc. for $C_{34}H_{26}N_4NiO_2$: C, 70.25; H, 4.51; N, 9.64. Found: C, 70.02; H, 4.37; N, 9.58%.

*3.2.16. Bis{1-[[(4,6-dimethyl-2-pyridinyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C17**)*

Purple solid, yield 0.25 g (54.2%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.34 (s, 6H), 2.55 (s, 6H), 5.75 (s, 2H), 6.51–7.95 (m, 14H), 8.10 (d, $J = 8.7$ Hz, 2H) ppm. IR (KBr): 3035, 1613, 1532, 1453, 1299, 590, 413 cm^{-1}. *Anal*. Calc. for $C_{36}H_{30}N_4NiO_2 \cdot CH_2Cl_2$: C, 64.01; H, 4.65; N, 8.07. Found: C, 63.88; H, 4.47; N, 7.96%.

*3.2.17. Bis{1-[[(3,5-dibromo-6-methyl-2-pyridinyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C18**)*

Purple powder, yield 0.35 g (52.7%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.69 (s, 6H), 5.80 (d, $J = 9.0$ Hz, 2H), 6.94–8.04 (m, 14H), 8.12 (d, $J = 8.1$ Hz, 2H) ppm. IR (KBr): 3054, 1616, 1580, 1530, 1291, 635, 431 cm^{-1}. *Anal*. Calc. for $C_{34}H_{22}Br_4N_4NiO_2$: C, 45.53; H, 2.47; N, 6.25. Found: C, 45.97; H, 2.68; N, 6.30%.

*3.2.18. Bis{1-[[(5-nitro-2-pyridinyl)imino]methylenyl]-2-naphthalenolato-N,O}nickel (**C19**)*

Purple solid, 0.22 g (46.7% yield). ^{1}H NMR (DMSO, 300 MHz): δ 5.72 (d, $J = 9.9$ Hz, 2H), 6.41–7.85 (m, 16H), 8.49 (s, 2H) ppm. IR (KBr): 3061, 1620, 1585, 1539, 1460, 1293, 622, 400 cm^{-1}. *Anal*. Calc. for $C_{32}H_{20}N_6NiO_6 \cdot 2CH_2Cl_2$: C, 50.22; H, 2.98; N, 10.34. Found: C, 50.11; H, 3.04; N, 10.40%.

3.3. Polymerization of norbornene

In a typical procedure (entry 7, Table 3), the precursor **C7** (2 μmol) was dissolved in a Schlenk tube under nitrogen with 4.74 mL of new distilled toluene and appropriate *N*-nonane. Ten millimolar of norbornene in toluene (1.40 mL) was then added via syringe. The polymerization was initiated by the addition of the toluene solution of MAO (1.4 M, 2.86 mL, 4.00 mmol) via syringe. After stirring for 5 h, the polymerization was terminated by pouring the reaction mixture into 100 mL acidic ethanol (ethanol:HCl_{conc} = 95:5). The poly(norbornene) (PNB) was isolated by filtration, washed with ethanol, and dried in a vacuum at 100 °C for 100 h.

3.4. X-ray crystallography measurements

Suitable crystals for X-ray diffraction were obtained by slow evaporation of the relevant solvent from their diethyl ether/THF solution. The single-crystal X-ray diffraction for bis{1-[[(2,4,6-trimethylphenyl)imino]-methylenyl]-2-naphthalenolato-N,O}nickel (**C7**) was carried out at 293 K on a Bruker SMART 1000 CCD diffractometer with graphite monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). The structure determination of bis{1-[[(3-benzyloxy-2-pyridinyl)imino]methylenyl]-2-naphthalenolato- N,O}nickel (**C14**) was carried out at 123 K on a Rigaku RAXIS Rapid IP diffractometer with

Table 1
Crystallographic data for complexes **7** and **14**

	Complex **7**	Complex **14**
Empirical formula	$C_{40}H_{36}N_2NiO_2$	$C_{47}H_{36}N_4NiO_4 \cdot 0.5CH_3OCH_3$
Formula weight	635.42	802.54
Crystal color	Green	Red
Crystal size (mm)	$0.20 \times 0.18 \times 0.16$	$0.49 \times 0.19 \times 0.09$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a (Å)	11.164(4)	37.950(8)
b (Å)	12.511(5)	13.691(4)
c (Å)	12.093(5)	16.211(4)
α (°)	90	90
β (°)	105.440(8)	112.09(3)
γ (°)	90	90
V (Å^3)	1628.0(11)	7804(3)
Z	2	8
D_{calc} (g cm^{-3})	1.296	1.366
μ(Mo Kα) (mm^{-1})	0.633	0.551
$F(000)$	668	3352
Temperature (K)	293(2)	123(2)
λ (Å)	0.71073	0.71073
θ range (°)	2.21–26.54	1.95–27.52
Reflections collected	8334	22,554
Independent reflections	3361	8567
R_{int}	0.0739	0.1425
Goodness-of-fit on F^2	1.013	0.769
Parameters	209	506
Final R indices	$R_1 = 0.0594$	$R_1 = 0.0855$
$(I > 2\sigma(I))$	$wR_2 = 0.0945$	$wR_2 = 0.1475$
R indices (all data)	$R_1 = 0.1456$	$R_1 = 0.2463$
	$wR_2 = 0.1159$	$wR_2 = 0.1875$

graphite monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by the global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods, and refined by full-matrix least-square on F^2. Each hydrogen atom was placed in a calculated position, and refined using a riding model. All nonhydrogen atoms were refined anisotropically. Structure solution and refinement were performed using SHELXL-97 package [36]. Relevant crystal data are summarized in Table 1.

4. Results and discussion

4.1. Synthesis and characterization of ligands and complexes

The syntheses of the nickel complexes as catalytic precursors were shown in Scheme 1. Ligands **L1**–**L19** were synthesized via the condensation of 2-hydroxy-1-naphthaldehyde with appropriate aniline or 2-aminopyridine. Following the treatment with NaH in THF, the ligands then reacted with $NiCl_2 \cdot 6H_2O$ and formed nickel complexes. All ligands and their complexes were structurally characterized by IR, H NMR and elemental analyses. For further confirmation, the structures of complexes **C7** and **C14** were elucidated by crystal X-ray analysis, which are shown in Figs. 1 and 2.

As shown in Fig. 1, complex **C7** contains two ligands around the nickel center with nearly ideal parallelogram-planar coordination geometry, and both ligands are coordinated in a centro-symmetric geometry. Its selected bond distances and angles were collected in Table 2. The nickel center lies on a crystallographic inversion center and is coordinated with O(1), O(1A) of the naphthalene and N(1), N(1A) of the imino group, forming two fused five-membered rings with acute

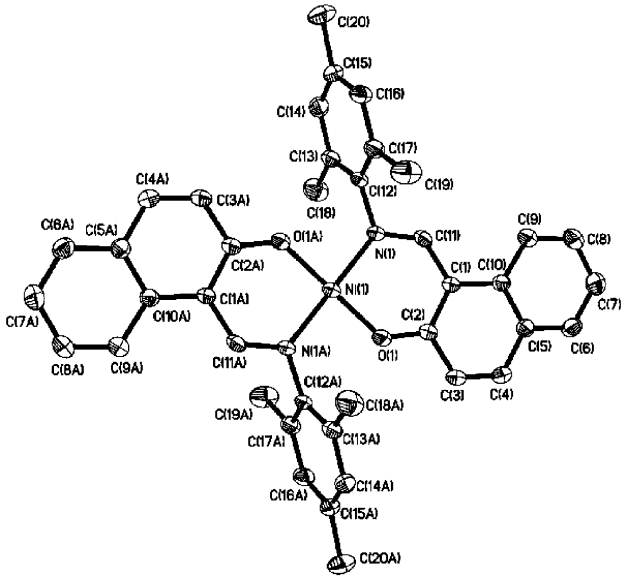


Fig. 1. Molecular structure of complex **7** in which Ni is four-coordinate, displacement ellipsoids are drawn at 30% probability level; hydrogen atoms are omitted for clarity.

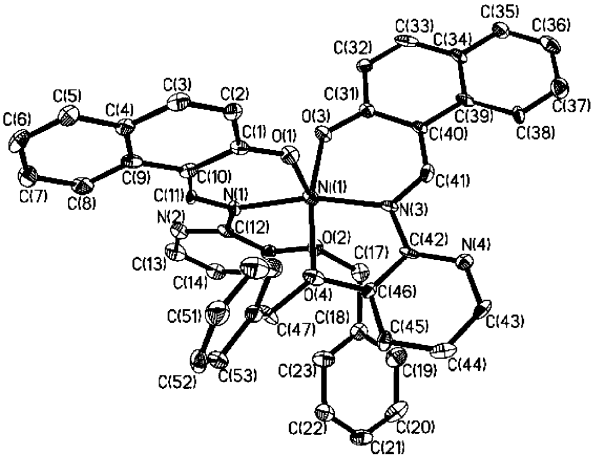


Fig. 2. Molecular structure of complex **14** in which Ni is six-coordinate, displacement ellipsoids are drawn at 30% probability level; hydrogen atoms and one molecule of diethyl ether are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for **7** and **14**

Complex **12**		Complex **14**	
Bond lengths			
Ni(1)–O(1A)	1.810(2)	Ni(1)–O(1)	1.956(4)
Ni(1)–O(1)	1.810(2)	Ni(1)–N(3)	1.959(6)
Ni(1)–N(1A)	1.898(3)	Ni(1)–O(3)	1.965(4)
Ni(1)–N(1)	1.898(3)	Ni(1)–N(1)	1.975(5)
O(1)–C(2)	1.291(4)	Ni(1)–O(2)	2.220(4)
N(1)–C(11)	1.296(4)	Ni(1)–O(4)	2.286(4)
N(1)–C(12)	1.450(4)	O(1)–C(1)	1.274(8)
C(1)–C(11)	1.414(4)	N(1)–C(11)	1.296(7)
Bond angles			
O(1A)–Ni(1)–O(1)	180.0	O(1)–Ni(1)–N(3)	98.40(19)
O(1A)–Ni(1)–N(1A)	93.15(11)	O(1)–Ni(1)–O(3)	94.39(18)
O(1)–Ni(1)–N(1A)	86.85(11)	N(3)–Ni(1)–O(3)	92.0(2)
O(1A)–Ni(1)–N(1)	86.85(11)	O(1)–Ni(1)–N(1)	91.4(2)
O(1)–Ni(1)–N(1)	93.15(11)	N(3)–Ni(1)–N(1)	165.62(19)
N(1A)–Ni(1)–N(1)	180.0	O(3)–Ni(1)–N(1)	97.76(19)
C(2)–O(1)–Ni(1)	131.0(2)	O(1)–Ni(1)–O(2)	167.86(19)
C(11)–N(1)–C(12)	114.0(3)	N(3)–Ni(1)–O(2)	92.24(18)
C(11)–N(1)–Ni(1)	124.0(2)	O(3)–Ni(1)–O(2)	91.06(16)
C(12)–N(1)–Ni(1)	121.8(2)	N(1)–Ni(1)–O(2)	77.10(17)
C(2)–C(1)–C(11)	119.3(3)	O(1)–Ni(1)–O(4)	88.73(16)
C(2)–C(1)–C(10)	119.8(3)	N(3)–Ni(1)–O(4)	76.9(2)

angles: 93.15(11)° for N(1)–Ni(1)–O(1), 86.85(11)° for N(1)–Ni(1)–O(1A). The atoms O(1)–C(11)–N(1)–Ni(1)–C(11A)–N(1A)–O(1A) fragment is planar (mean deviation 0.0037 Å) and the dihedral angle between O(1)–C(11)–N(1)–Ni(1)–C(11A)–N(1A)–O(1A) and C(1)–C(2)–C(3)–C(4)–C(5)–C(6)–C(7)–C(8)–C(9)–C(10) (naphthalene ring, mean deviation 0.0022 Å) is 5.3°. The 2,4,6-trimethylphenyl substituent C(12)–C(13)–C(14)–C(15)–C(16)–C(17) is oriented ca. orthogonal to the basal coordination plane defined by O(1)–C(11)–N(1)–Ni(1)–N(1A)–C(11A)–O(1A), with the ca 98.4° twist about the C(12)–N(1) bond.

Complex **C14** (shown in Fig. 2) shows a six-coordinated nickel core, in which the nickel is surrounded by two ligands in a greatly distorted octahedral environment with four shorter and two longer bonds. The shorter bonds [Ni(1)–O(1), Ni(1)–N(3), Ni(1)–O(3), Ni(1)–N(1)] are formed by two N atoms and two O atoms of two symmetry-related ligands, while the longer bonds [Ni(1)–O(2), Ni(1)–O(4)] are formed by two O atoms from the benzoxy group. Its selected bond distances and angles were collected in Table 2. The equatorial plane is made by O(2), N(1), O(1) and Ni(1) (mean deviation is 0.0286 Å), while the axial positions are occupied by atoms O(3), N(3), O(4). The equatorial plane and the axial plane make a dihedral angle of 89.6°. The metal center is coordinated with O(1), O(2), O(3), O(4), N(1), N(3) and their angles are 92.0(2)° for N(3)–Ni(1)–O(3), 91.4(2)° for O(1)–Ni(1)–N(1), 77.10(17)° for N(1)–Ni(1)–O(2) and 76.9(2)° for N(3)–Ni(1)–O(4). No significant shifts of pyridine ring stretching bands between 1610 and 1440 cm^{-1} and the ring deformation bands between 400 and 600 cm^{-1}in the IR spectra of **C14** are observed, which indicates the pyridine nitrogen is not involved in the coordination [35,37–39].

Table 3
Polymer yields and the catalytic activities of a variety of nickel-based complexes

Complex	Yield (%)	Activity[a]	M_w[b]	M_w/M_n
1	83.2	7.83	5.55	3.98
2	91.8	8.64	7.61	5.95
3	82.4	7.76	8.45	3.21
4	84.8	7.98	13.3	6.68
5	84.0	7.91	19.2	6.13
6	83.4	7.85	13.4	5.85
7	85.1	8.00	11.6	5.04
8	90.4	8.52	9.50	6.01
9	87.3	8.22	11.7	4.54
10	86.8	8.17	5.82	4.75
11	88.5	8.33	7.88	6.19
12	86.1	8.10	8.54	6.43
13	85.2	8.02	18.4	4.62
14	95.0	8.95	8.38	2.07
15	94.0	8.85	6.11	1.99
16	85.9	8.09	12.4	1.94
17	89.4	8.41	6.87	1.98
18	83.0	7.82	5.69	2.07
19	85.2	8.02	8.05	2.30

Conditions: [Ni]:[Al]:[norbornene] = 1:2000:5000 (molar ratio), $C_{Ni} = 2 \times 10^{-4}$ mol/L, toluene, $V_{total} = 10$ mL, 25 °C, 5 h.
[a] 10^4 g/(mol Ni · h).
[b] 10^5 (g/mol).

4.2. Polymerization of norbornene

The activities of catalysts as well as the M_w values of resultant polymers in norbornene polymerization have been demonstrated to be influenced by several parameters, including the nature of catalyst precursors, co-catalyst, reaction temperature, monomer concentration and reaction time. Therefore, GC was used to monitor the conversion of norbornene in the presence of *N*-nonane as the internal standard.

Table 3 summarizes the polymer yields and catalyst activities obtained for the norbornene polymerization catalyzed by a variety of nickel complexes. As shown in Table 3, yields of over 80% were obtained within 5 h of the reactions in all cases, and the resultant polymers possessed high molecular weights ($M_w = 5.55 \times 10^5$ to 1.92×10^6 g/mol). Interestingly, complexes **C14**–**C19**, which contain a pyridinyl group, show somewhat higher catalytic activities than the aryl analogue-substituted complexes **C1**–**C13**, and the generated polynorbornene exhibit more narrow molecular distributions. However, as is apparent, substitution on the ligand in general does not notably affect the catalytic activity of the complex.

To demonstrate what factors, and how they may affect the vinyl polymerization of norbornene, the activity of catalyst precursor **C7** was particularly investigated at varied Al/Ni molar ratio, temperature, reaction time, or

initial norbornene concentration. MAO has been known to play a role in initiating the polymerization reactions, most likely by creating an empty site on the catalyst for the insertion of a norbornene monomer. Indeed, we observed that the amount of MAO employed in the **C7**-catalyzed norbornene polymerization reaction is critical for the catalyst to exhibit high activity, and the optimal Al/Ni ratio is 2000. As shown in Fig. 3, with increased Al/Ni ratio, **C7** show enhanced catalytic activity, and, at the Al/Ni molar ratio of up to 2000, **C7** exhibit the highest activity. However, further increase of the Al/Ni ratio impairs the activity of the catalyst. The explanation for this observation is that, with the proper ratio of MAO to the nickel complex, the formation and stabilization of the active species is achieved. Based upon this observation, the Al/Ni ratio of 2000 was employed in the remaining experiments, in which other reaction parameters were varied.

Fig. 4 shows the influence of polymerization time on the polymer yield and the activity of the catalyst **C7**.

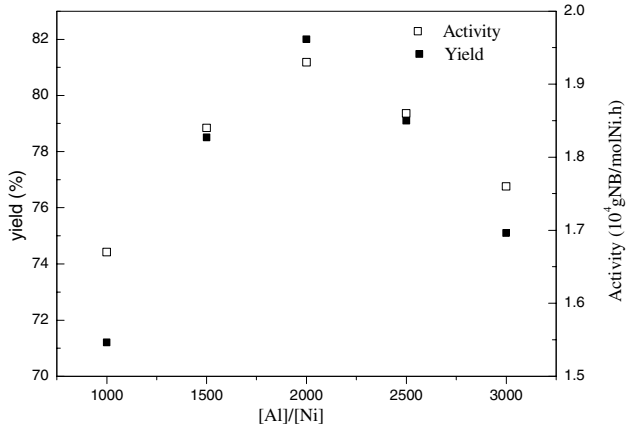


Fig. 3. Polymer yield and catalytic activity versus Al/Ni ratio [Ni]:[norbornene] = 1:6000, $C_{Ni} = 1.7 \times 10^{-4}$ mol/L, toluene, $V_{total} = 15$ mL, 25 °C, 24 h.

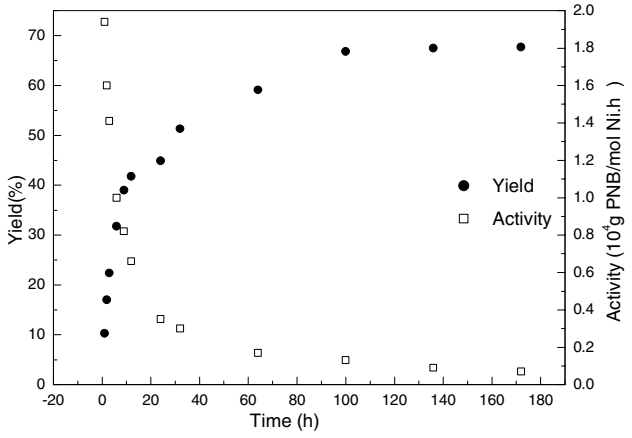


Fig. 4. Influence of polymerization time on the conversion yield and the catalyst activity [Ni]:[Al]:[norbornene] = 1:2000:2000, $C_{Ni} = 1.7 \times 10^{-4}$ mol/L, toluene, $V_{total} = 15$ mL, 25 °C.

Apparently, the polymer yield increased with longer reaction time, and two typical periods were clearly observed. In the first period, the conversion yield increased rapidly from 10.3% to 39.0%, and following this, the yield increase tended to be modest and then reach a constant value in the second period. In contrast, the activity of the catalyst decreased in this whole process with longer reaction time. This observation suggests that the active species be formed rapidly at the initial stage of the reaction, and then stabilized for a period of time.

Table 4 shows the results obtained at varied reaction temperature. A series of polymerizations catalyzed by **C7** were carried out at varied reaction temperature from 0 to 100 °C while other reaction parameters were fixed. The temperature setting was obtained with an external oil bath except for 0 °C which was obtained with an ice-water bath. As shown in Table 4, the polymer yield and the activity of the catalyst decreased with increased reaction temperature. With the temperature from 0 to 100 °C, the polymer yield decreased from 71.1% to 32.5% and the activity of **C7** from 6.70×10^5 to 3.06×10^5 g PNB/(mol Ni · h). Overall, the catalytic system displays good activity over a wide range of reaction temperature.

Shown in Fig. 5 are the yields obtained for the polymerization reaction carried out in varied reaction

Table 4
The influence of temperature on polymer yield and catalyst activity

Run	T (°C)	Yield (%)	Activity[a]
1	0	71.1	6.70
2	25	54.8	5.16
3	50	47.7	4.49
4	75	44.4	4.18
5	100	32.5	3.06

Conditions: [Ni]:[Al]:[norboenene] = 1:2000:5000, $C_{Ni} = 1.7 \times 10^{-4}$ mol/L, toluene, $V_{total} =$ 30 mL, 0.5 h.
[a] 10^5 g/(mol Ni · h).

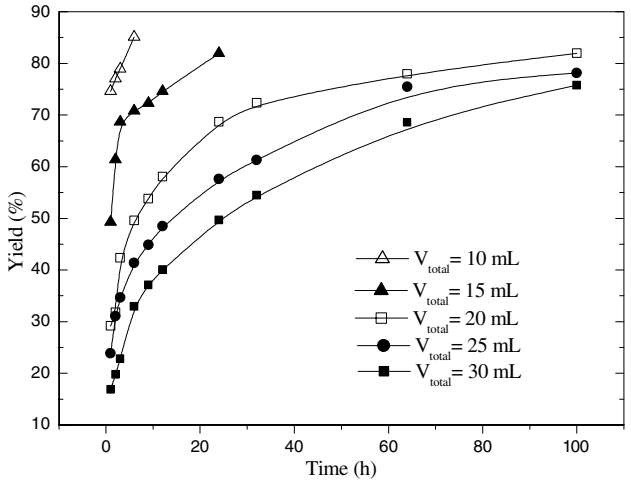


Fig. 5. Influence of total reaction volume on polymer yield [Ni]:[Al]:[norbornene] = 1:2000:6000, toluene, $V_{total} = 10$, 15, 20, 25, 30 mL, 25 °C.

Table 5
The influence of [norbornene]/[Ni] molar ratio on polymer yield and catalyst activity

Run	[M]/[Ni]	Yield (%)	Activity[a]
1	2000	17.0	1.60
2	4000	38.5	7.25
3	6000	55.0	15.5
4	8000	58.2	21.9
5	10,000	82.9	39.0

Conditions: [Ni]:[Al] = 1:2000, $C_{Ni} = 1.7 \times 10^{-4}$ mol/L, toluene, $V_{total} = 15$ mL, 25 °C, 2 h.
[a] 10^4 g/(mol Ni · h).

volume. The change of reaction volume (while other reaction parameters fixed) does actually change the concentrations of norbornene and the catalyst, and therefore, affects the polymer yield and catalyst activity. Indeed, as shown in Fig. 5, the yield decreased with increased reaction volume, and the highest yield was obtained when the total reaction volume was reduced to 10 mL.

Table 5 shows the catalytic activity of **C7** versus the monomer/Ni ratio (M/Ni). Apparently, the increase of the monomer/Ni molar ratio, which actually increased the monomer concentration while the C_{Ni} and reaction volume were kept constant, dramatically enhanced the catalyst activity and polymer yield. The catalyst activity of 1.6×10^4 g/(mol Ni · h) was obtained at a M/Ni ratio of 2000:1 while a much higher catalyst activity of 3.9×10^5 g/(mol Ni · h) achieved at a M/Ni ratio of 10,000:1. This observation imply that higher M/Ni ratio facilitate the complexation of monomers with the activated Ni complexes, and thus, render the catalyst to show higher activity.

All obtained polymer samples showed very similar IR spectra. The absence of a double band in IR spectra, which typically appears between the ranges 1620 and 1680 cm^{-1}, reveals that it is via vinyl-type polymerization, and not through ring-opening metathesis polymerization (ROMP) [40], that these nickel complexes catalyze the norbornene polymerization. TGA studies indicated that the obtained polymers were stable at up to 450 °C in the atmosphere of nitrogen and at 350 °C in the air with a 5–7% mass loss. The determination of the glass transition temperature (T_g) of vinyl homo-polymers has proved to be difficult, because the T_g of vinyl homo-polymers is apparently close to the temperature where decomposition tends to set in [5,41]. Indeed, our attempts to determine the T_g of the obtained polymers failed. The DSC studies did not show an endothermic signal upon heating the polymers up to the decomposition temperature. The obtained polynorbornene are amorphous and soluble in halogenated aromatic hydrocarbons. No indication of stereoregularity was observed, which was verified by the amorphous morphology of the products.

In summary, we synthesized a series of nickel-based catalysts, and determined their structures by X-ray analysis. We have demonstrated that all the nickel complexes exhibit high catalytic activity for the vinyl polymerization of norbornene, and the conversion yield and catalytic activity can be controlled via varying reaction parameters.

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