APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; 20: 181–186

Materials, Nanoscience and Catalysis AOC

Nickel (II) complexes supported by a fluorinated β-diketiminate backbone ligand: synthesis, catalytic activity toward norbornene polymerization, and the oxygenated species

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Received 3 July 2005; Revised 28 November 2005; Accepted 28 November 2005

The reaction of the lithium salt of backbone fluorinated β-diketiminate ligands, ArNC(CF_3)CHC(CF_3)NArLi, with *trans*-[NiCl(Ph)(PPh_3)$_2$] gives nickel (II) complexes, ArNC(CF_3)CHC(CF_3)NAr(Ph)(PPh_3)Ni (Ar = 2, 6-$Me_2C_6H_3$: 1; 2, 6-$^iPr_2C_6H_3$: 2). When activated by methylaluminoxane (MAO), both complexes polymerize norbornene rapidly via a vinyl-type polymerization mechanism. Treatment of nickel complex 1 with oxygen gives rise to intramolecular aerobic hydroxylation. The oxygenated species 3 was characterized by X-ray crystallography. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: β-diketiminate; nickel; norbornene; vinyl polymerization; hydroxylation

INTRODUCTION

The discovery by Brookhart and coworkers of highly active nickel and palladium α-diimine catalysts[1,2] has attracted great interest in developing new late transition metal catalysts for olefin polymerization. Compared with catalysts containing early transition metals, late transition metal catalysts exhibit lower oxophilicity and therefore heteroatom tolerance, which permits catalytic copolymerization of olefins with polar monomers.[3–6] Additionally, they provide the possibility of making polymers with versatile topologies and thereby new materials with special properties.

Norbornene(bicycle[2,2,1]hept-2-ene) has been used widely as a monomer for homo- and co-polymerization to prepare new types of polyolefin materials over the past decades.[7] Generally, norbornene polymerizes via three different modes: ring-opening metathesis polymerization (ROMP),[8,9] cationic or radical polymerization[10–13] and vinyl (or addition) polymerization.[14–16] Each polymerization mechanism results in polynorbornene with a different framework. Homopolymerization of norbornene and the co-polymerization of norbornene with other olefins, such as ethylene, styrene and polar monomers via vinyl polymerization, are popular polymer materials.[7,17] Their superior properties include high glass transition temperatures, excellent optical transparency, low birefringence and good solubility in common organic solvents and serve as reasons for the increased interest.[7,17]

Many transition metal complexes including titanium,[18,19] zirconium,[20,21] iron,[22] nickel,[23–25] palladium[26,27] and cobalt[28] have been used as precursors for vinyl polymerization of norbornene. In recent years, our efforts have focused on devising new late transition metal complexes bearing simple ancillary ligands for catalytic homo-polymerization and the co-polymerization of norbornene with other monomers. Prior to this work, we described the use of a series of complexes supported by [N,N] and [N,O] chelating ligands for norbornene polymerization. All nickel (II) complexes bearing anilido-imine ligands[29] and β-diimine ligands,[30] nickel (II) and cobalt (II) complexes of β-ketoamine ligands[31–33] exhibit characteristic vinyl polymerization of norbornene. The bis(β-ketoamino)nickel (II) complex can catalyze copolymerization

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Contract/grant sponsor: NSFC.
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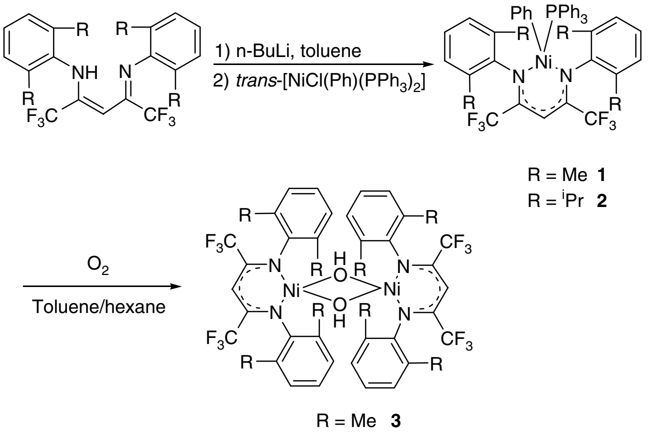
of norbornene with polar monomers.[31] We report herein the preparation of new nickel (II) complexes bearing a fluorinated β-diketiminate backbone ligands. The catalytic polymerization of norbornene was investigated when activated by MAO. Moreover, the stability of the prepared complexes to air and moisture was examined. The oxygenated species was successfully isolated on treatment of the complex with air, and the structure was determined by single crystal X-ray crystallography.



Scheme 1. Synthesis and oxidation of nickel (II) complexes.

RESULTS AND DISCUSSION

Synthesis and ^{1}H NMR spectroscopy of nickel(II) complexes

β-Diketiminate ligands were synthesized by condensation of 1,1,1,5,5,5-hexafluoroacetylacetone with the corresponding aniline by literature methods.[34] Reaction of the ligands with 1 molar equiv. of *n*-BuLi gave lithium salts of the β-diketiminate ligands. Without further treatment of the reaction system, 1 molar equiv. of *trans*-[NiCl(Ph)(PPh$_3$)$_2$] was added, resulting in immediate color change from orange/yellow to dark black. Green/purple complex **1** or green complex **2** was obtained by filtration and hexane precipitation (Scheme 1).

It is difficult to obtain single crystal structures of **1** and **2** due to the lability of β-diketiminato nickel complexes, but they were successfully characterized by NMR spectroscopy and elemental analyses (see Experimental section).

Similar to nickel complexes bearing β-diketiminate ligands,[35–37] both nickel complexes **1** and **2** also exhibit strongly broadened ^{1}H NMR spectra due to their paramagnetic nature. As an example, Fig. 1 shows the ^{1}H NMR spectrum of complex **1** in C_6D_6 at 25 °C. Signals at −2.57, 15.25 and 14.12 ppm are assigned to protons of the aryl substituent at nitrogen by its integration in a 1 : 2 : 6 ratio. The upfield signal at −35.52 is assigned to a backbone proton according to the intensity ratio.[35–37] Other signals at 2.66, 2.36 and 1.30–0.87 ppm are assigned to aromatic protons of PPh$_3$ and Ph. The assignments of signals in the range 12–5 and 2.14 ppm are free ligands and solvent signals due to the lability of complex **1** in solution.

Norbornene polymerization behavior

Complexes **1** and **2** can catalyze polymerization of norbornene when activated by MAO. The results are summarized in Table 1. Both complexes exhibit high activity (>10^6 g PNB mol^{-1} Ni h^{-1}) for norbornene polymerization.

The reaction temperature and Al : Ni molar ratio greatly influence the activity and the molecular weight of the obtained polymers. With increases in reaction temperature from 30 to 90 °C, activity increases, but the molecular weight decreases

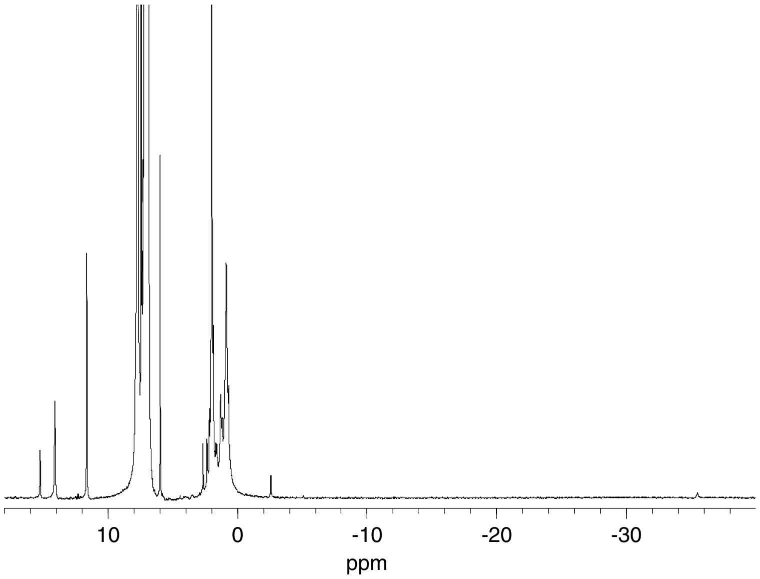


Figure 1. ^{1}H NMR spectrum of complex **1** in C_6D_6 at 25 °C.

strikingly, and the polydispersity ($M_w : M_n$) broadens. The activity increases first then decreases with increases in the Al : Ni molar ratio. In contrast, the molecular weights (M_w) of the polymers decreased with an increasing Al : Ni ratio, which suggests that excess MAO gives rise to easy chain transfer.[29–32]

Under the same conditions, complex **2** exhibited higher catalytic activity and produced higher molecular weights of polynorbornene than complex **1**. The bulky *o*-aryl substituents at nitrogen stabilize the active center and inhibit β-hydride elimination.[38]

Table 1. Results of norbornene polymerizations with **1**– and **2**–MAO systems[a]

Entry	Complex	T (°C)	Al : Ni	Yield (%)	Activity[b]	M_w[c]	M_w/M_n
1	**1**	60	200	30.82	2.05	60.33	2.21
2	**1**	60	400	41.14	2.74	59.28	2.20
3	**1**	60	800	45.23	3.02	48.36	2.38
4	**1**	60	1200	40.11	2.68	36.45	2.58
5	**1**	30	800	43.62	2.91	61.79	2.09
6	**1**	70	800	48.18	3.21	35.82	3.23
7	**1**	90	800	51.29	3.42	31.65	4.07
8[d]	**1**	60	800	60.41	2.01	33.11	2.59
9	**2**	60	400	41.97	2.80	68.33	2.12
10	**2**	60	800	47.51	3.17	64.26	2.26
11	**2**	60	1200	43.49	2.90	44.33	2.65
12	**2**	30	800	45.34	3.02	87.46	1.84
13	**2**	90	800	52.27	3.48	35.82	3.55
14[e]	**2**	60	800	32.88	4.39	53.84	2.18

[a] Polymerization conditions: solvent, toluene; total volume, 30 ml; nickel complex, 1.2 µmol; norbornene, 4 g; reaction time, 30 min.
[b] 10^6 g PNB mol^{-1} Ni h^{-1}.
[c] 10^{-4} g mol^{-1}.
[d] Nickel complex, 2.4 µmol.
[e] Reaction time, 15 min.

The microstructure of the polynorbornene was characterized by ^{1}H NMR and IR. In the ^{1}H NMR spectra (Fig. 2), no proton signals were observed from 3.0 to 6.0 ppm, which usually indicates ROMP of norbornene.[39] In the IR spectra (Fig. 3), the absorption at 941 cm^{-1} is assigned to the bicyclo[2,2,1]heptane system.[40] The absence of absorption at 1620–1680 cm^{-1} and near 960 cm^{-1} in IR spectra also supports vinyl polymerization of norbornene.[41]

Intramolecular aerobic hydroxylation and X-ray structure of oxygenated species

Nickel(II) complexes prepared in this work are exceedingly air- and moisture-sensitive. Exposure of the complexes in air causes rapid decomposition, while traces of air give rise to intramolecular aerobic hydroxylation. Copper complexes of β-diketiminate ligand have been reported to be

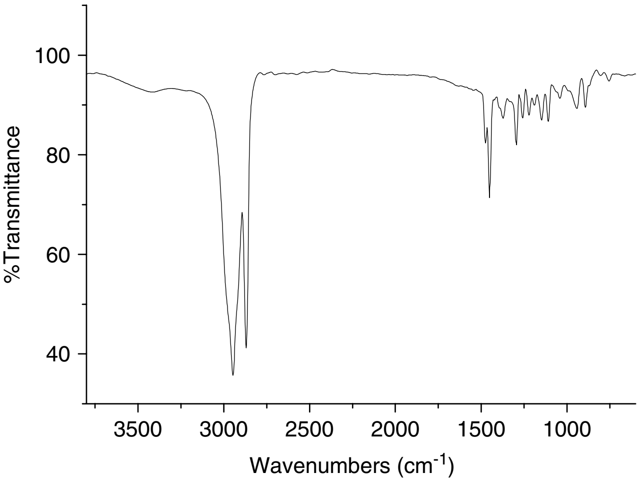


Figure 3. IR spectrum of polynorbornene obtained by **2**–MAO (entry 13 in Table 1).

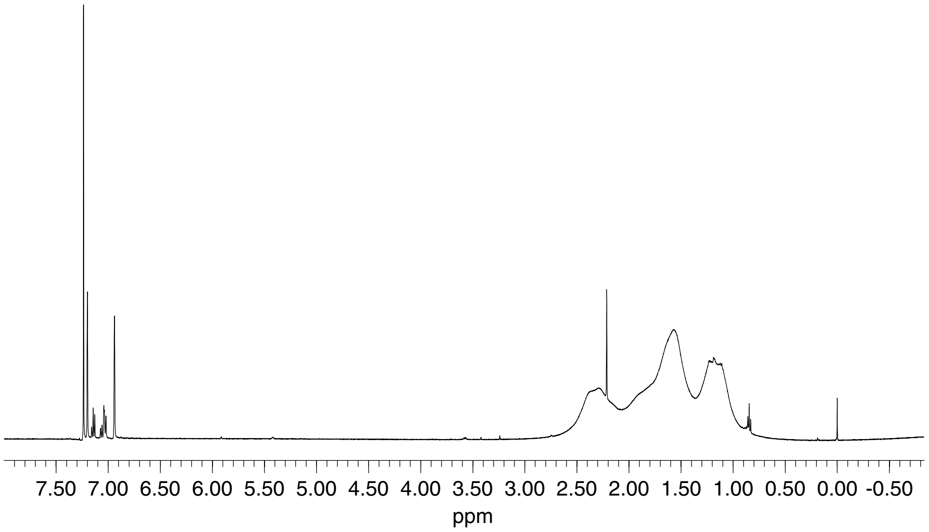


Figure 2. ^{1}H NMR spectrum of polynorbornene obtained by **1**/MAO (entry 3 in Table 1. solvent, *o*-dichlorobenzene-d_4).

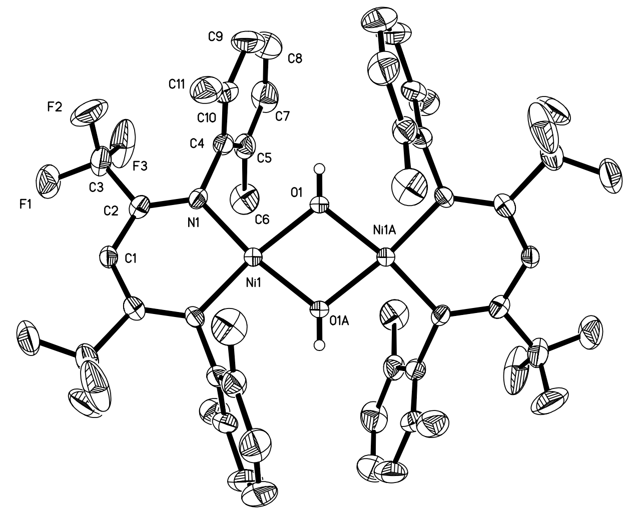


Figure 4. Molecular structure of complex **3**.

easily oxidized with ligands bearing electron-withdrawing substituents.[42,43] Our experiments indicate that these nickel complexes offer similar behavior. X-ray analyses indicates the oxygenated species is indeed the bis(μ-OH)dinickel (II, II) of complex **3** (Fig. 4).

Copper complexes with fluorinated β-diketiminate ligands have been structurally characterized.[42,43] To our knowledge, this is the first report of this type of nickel complex supported by a β-diketiminate ligand. Nickel complexes bearing nonfluorinated β-diketiminate ligands have been reported as bis(μ-Cl)dinickel (II, II) structures.[44] In bis(μ-OH)dinickel (II, II), there is a small distortion of the coordination ring (NCCCN) to the O–Ni–O–Ni plane (with a dihedral of 20.5°), while in bis(μ-Cl)dinickel (II, II) complex, both planes are approximately vertical.[44] The Ni–N bond length is 1.869(3) Å. The N–Ni–N bite angle is 96.00(17)° (Table 2). In the bis(μ-Cl)dinickel (II, II) complex, bond lengths for Ni–N are 1.913(3) and 1.915(3) Å, and the bite angle is 94.69(11)°.[44] These indicate that the electron-withdrawing groups increase the bite angle and force the metal center deeper into coordination ring (Table 3).

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

Empirical formula	$C_{42}H_{40}F_{12}N_4Ni_2O_2$
Formula weight	978.20
Temperature (K)	293(2)
Crystal system	Orthorhombic
Space group	Ccca
a (Å)	14.044(3)
b (Å)	22.663(3)
c (Å)	13.326(2)
α (deg)	90
β (deg)	90
γ (deg)	90
Volume (Å^3)	4241.3(13)
Z	4
D_t (mg/m^3)	1.532
Absorption coefficient (mm^{-1})	0.982
F(000)	2000
Crystal size (mm)	0.23 × 0.18 × 0.08
θ range (deg)	2.29–26.07
Index ranges	$-17 \leq h \leq 17, -27 \leq k \leq 27, -16 \leq l \leq 11$
Maximum and minimum transmission	0.9256 and 0.8057
Reflections collected/unique	12399/2109
Goodness-of-fit on F^2	1.002
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0452, wR_2 = 0.1099$
R indices (all data)	$R_1 = 0.0952, wR_2 = 0.1323$
Largest difference peak and hole (e/Å^{-3})	0.403 and −0.353

CONCLUSIONS

Nickel (II) complexes bearing fluorinated β-diketiminate backbone ligands were successfully synthesized. Both complexes exhibit high activity for vinyl polymerization of norbornene when activated by MAO. All polynorbornenes obtained have high molecular weights and good solubility in

Table 2. Selected bond lengths (Å) and angles (°) of complex **3**

Bond lengths			
Ni(1)–O(1),	1.863(2)	Ni(1)–O(1)#1	1.863(2)
Ni(1)–N(1)	1.869(3)	Ni(1)–N(1)#2	1.869(3)
Ni(1)–Ni(1)#1	2.9254(13)	O(1)–Ni(1)#1	1.863(2)
Bond angles			
O(1)–Ni(1)–O(1)#1	76.54(15)	O(1)#1–Ni(1)–N(1)#2	95.38(12)
O(1)#1–Ni(1)–N(1)	163.12(10)	O(1)–Ni(1)–N(1)#2	163.12(10)
O(1)#1–Ni(1)–Ni(1)#1	38.27(8)	O(1)–Ni(1)–Ni(1)#1	38.27(8)
O(1) #1–Ni(1)–N(1) #2	95.38(12)	O(1)–Ni(1)–N(1)	95.38(12)
N(1)#2–Ni(1)–N(1)	96.00(17)	N(1)#2–Ni(1)–Ni(1)#1	132.00(9)
N(1)–Ni(1)–Ni(1)#1	132.00(9)	Ni(1)–O(1)–Ni(1)#1	103.46(15)

ordinary solvents, such as cyclohexane, chlorobenzene and *o*-dichlorobenzene. The complexes are exceedingly air- and moisture-sensitive; traces of air cause oxidation of the nickel complexes. An X-ray structural analysis indicated that the oxygenated species of complex **1** is bis(μ-OH)dinickel (II, II) complex.

EXPERIMENTAL

General procedures and materials

All air- and/or moisture-sensitive manipulations were performed under a dry, deoxygenated nitrogen atmosphere using standard high vacuum or Schlenk techniques, using anhydrous, air-free reagents and solvents. Toluene and *n*-hexane were used freshly distilled under nitrogen from sodium/benzophenone. Dichloromethane was distilled from calcium hydride. 2,6-Diisopropylaniline and 2,6-dimethylaniline were distilled from potassium hydroxide prior to use. Norbornene (bicycle[2,2,1]hept-2-ene, Fluka) was purified by distillation over potassium and used as a solution in toluene. Solid methylaluminoxane (MAO)[45] and *trans*-chloro(phenyl)bis(triphenylphosphane)nickel(II) [*trans*-NiCl(Ph)$(PPh_3)_2$][46] were prepared according to the literature procedures. *n*-Butyllithium in *n*-hexane solution (2.2 M) and 1,1,1,5,5,5-hexafluoroacetylacetone were purchased from Aldrich Chemical Co. Other commercially available reagents were purchased and used as received.

Elemental analysis were performed on a Vario EL microanalyzer. The metal complexes were analyzed within a few hours of being taken out of the freezer of the glovebox. ^{1}H NMR spectra were carried out on Mercury-plus 300 MHz NMR spectrometers at room temperature in $CDCl_3$ solution for ligands, and *o*-dichlorobenzene solution for polymer using tetramethylsilane (TMS) as internal standard. ^{1}H NMR spectra of complexes were recorded on Varian INOVA 500 MHz NMR spectrometers at room temperature in dry C_6D_6 solution using C_6D_6 as internal standard. Ten milligrams of complexes were dissolved in 0.5 ml of dried C_6D_6 and sealed in a 5 mm tube for NMR determination. IR spectra were measured with a Nicolet/Nexus 670 FT-IR Analyzer using KBr disks. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of the polymers were performed on a Waters 150C instrument using standard polystyrene as the reference with chlorobenzene as the eluent at a flow rate of 1.00 ml/min at 40 °C.

Synthesis of ArNHC(CF_3)CHC(CF_3)NAr (Ar = 2, *6-Me$_2$C$_6$H$_3$*) (***L1***)

β-Diketiminate ligands were synthesized by literature methods.[34] Yellow crystalline **L1** was obtained after recrystallization from methanol. Yield: 22%. ^{1}H NMR (300 MHz; $CDCl_3$): δ2.14 (12H, s, *Me*); 5.87 (1H, s, NC(CF_3)C*H*C(CF_3)N); 7.04–7.26 (6H, aromatic protons); 11.83 ppm (1H, br s, N*H*). Elemental analysis calcd for $C_{21}H_{20}F_6N_2$: C, 60.86; H, 4.87; N, 6.76. Found: C, 60.80; H, 4.95; N, 6.62.

Synthesis of ArNHC(CF_3)CHC(CF_3)NAr (Ar = 2, *6-^{i}Pr$_2$C$_6$H$_3$*) (***L2***)

Bright yellow ligand **L2** was prepared using methods similar to **L1**. Yield: 32%. ^{1}H NMR (300 MHz, $CDCl_3$): δ1.13 (12H, d, *Me*CH*Me*); 1.25 (12H, d, *Me*CH*Me*); 2.95 (4H, septet, MeC*H*Me); 5.80 (1H, s, NC(CF_3)C*H*C(CF_3)N); 7.10–7.20 (6H, aromatic protons); 11.20 ppm (1H, br s, N*H*). Elemental analysis calcd for $C_{29}H_{36}F_6N_2$: C, 66.13; H, 6.90; N, 5.32. Found: C, 66.03; H, 7.07; N, 5.18.

Synthesis of ArNC(CF_3)CHC(CF_3) NAr(Ph_3)(Ph)Ni (Ar = 2, 6-$Me_2C_6H_3$) (1)

n-BuLi (1.0 ml, 2.2 M, 2.2 mmol) in a solution of hexane was added slowly to a solution of the ligand **L1** (0.87 g, 2.1 mmol) in toluene (40 ml) at −78 °C. The mixture was allowed to warm to room temperature and stirred for another 2 h. The orange/yellow solution thus obtained was added to *trans*-[NiCl(Ph)$(PPh_3)_2$] (1.53 g, 2.2 mmol) with stirring, resulting in a immediate color change to black. The reaction mixture was stirred overnight at 50 °C. Evaporation of the solvent *in vacuo* yielded a crude product. To the crude product, dry, deoxygenated dichloromethane (20 ml) was added, and the mixture was stirred for 10 min and filtered, the filtrates were concentrated to about 5 ml and 30 ml of hexane were added. The mixture was filtered, and the solid was washed with hexane (5 ml × 3). Complex **1** was obtained as a green/purple solid. Yield: 0.82 g (48%). ^{1}H NMR (500 MHz, C_6D_6): δ_H 15.25 (s, 4H, *m*-Ar), 14.12 (s, 12H, *o*-CH_3Ar), 2.66 (s), 2.36 (s) and 1.30–0.70 (m), (20H, Ph + PPh_3), −2.57 (s, 2H, *p*-Ar), −35.52 (s, C*H*, backbone) ppm. Elemental analysis calcd for $C_{45}H_{39}F_6N_2NiP$: C, 66.61; H, 4.81; N, 3.45. Found: C, 66.67; H, 5.08; N, 3.10.

Synthesis of ArNC(CF_3)CHC(CF_3) NAr(Ph_3)(Ph)Ni (Ar = 2, 6-^{i}Pr$_2$C$_6$H$_3$) (2)

Complex **2** was prepared using a procedure similar to that for complex **1** giving a green solid. Yield: 0.78 g (40%). ^{1}H NMR (500 MHz, C_6D_6): δ_H 36.08 [s, 4H, C*H*$(CH_3)_2$], 18.87 (s, 4H, *m*-Ar), 12.55 [s, 12H, CH$(CH_3)_2$], 4.05–3.56 (m), 2.84 (s), 2.58 (s), (20H, Ph + PPh_3), −15.95 (2H, *p*-Ar), −83.36 (C*H*, backbone) ppm. Elemental analysis calcd for $C_{53}H_{55}F_6N_2NiP$: C, 68.93; H, 5.96; N, 3.03. Found: C, 68.67; H, 5.68; N, 3.32.

Procedure for norbornene polymerization

In a typical experiment, solid MAO (55.7 mg, 0.96 mmol) was added to a 50 ml glass vessel, and then 10 ml of a toluene solution of norbornene (0.4 g/ml) were added via a syringe. Toluene (19 ml) and 1 ml of nickel complex (1.2 mmol/L) in toluene solution were syringed into the well-stirred solution to keep the total volume of solution at 30 ml. The reaction system was continuously stirred for 30 min at 60 °C. The reaction was quenched by adding HCl/ethanol solution. The polymer was filtered, washed with ethanol several times, and dried at 60 °C in vacuum to a constant weight. ^{1}H NMR (*o*-dichlorobenzene-d_4, 500 MHz): δ_H 0.86–2.71(m) ppm. IR (KBr): 2943, 2869, 1477, 1450, 1260, 1220, 1190, 1152, 1109, 1043, 941, 893 cm^{-1}.

Oxygenation of complex **1**

To get a further proof of the air-sensitive complexes, dry air was bubbled via a syringe to a sealed nitrogen-filled saturated toluene–hexane solution of complex **1** for 5 s, the vessel was resealed quickly and kept refrigerated at −30 °C; brown crystals were obtained after a week. One crystal was selected for X-ray crystallography analysis. The result of X-ray analysis is summarized in Table 3.

X-ray structural determination of complex **3**

A crystal was manipulated and mounted in a glass capillary, and the data were collected on a Bruker SMART 1000 CCD diffractometer. All determinations of unit cell and intensity data were performed on a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K by employing the ω-scan technique. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL software. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Supplementary materials

Crystallographic data for structural analysis of complex **3** has been deposited with Cambridge Crystallographic Data Centre, CCDC 278405. Copies of this information may be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336063; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Acknowledgements

The finacial supports by NSFC and SINOPEC (Joint-Project 20334030), the Science Foundation of Guangdong Province (Project 039184), and the Ministry of Education of China (Project 20030558017) are gratefully acknowledged.

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