APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 436–442
Published online 14 June 2006 in Wiley InterScience
(www.interscience.wiley.com) DOI:10.1002/aoc.1097

Novel nickel (II) complexes chelating β-diketiminate ligands: synthesis and simultaneous polymerization and oligomerization of ethylene

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Received 7 March 2006; Revised 17 April 2006; Accepted 24 April 2006

Two novel nickel (II) complexes, $CH\{C(CF_3)NAr\}_2NiBr$ (1, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ and 2, 2,6-Me$_2$C$_6$H$_3$), were synthesized by the reaction of the lithium salt of fluorinated β-diketiminate backbone ligands with (1,2-dimethoxyethane) nickel (II) bromide [(DME)NiBr$_2$]. The solid-state structure of nickel (II) complex 2 as a dimer reveals four-coordination and a tetrahedral geometry with bromide bridged by single crystal X-ray measurement. Both complexes catalyze simultaneous polymerization and oligomerization of ethylene when activated by methylaluminoxane (MAO). It was found that the reaction temperature has a pronounced effect on the activity of ethylene polymerization and the molecular weight of obtained polyethylene. In addition, the nickel catalytic systems predominantly produce linear polyethylene with unsaturated end groups. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: nickel complex; fluorinated β-diketiminate ligand; ethylene; polymerization; oligomerization

INTRODUCTION

β-Diketiminate ligands have attracted great attention in organometallic chemistry in the past few years. Besides the facile synthesis of β-diketiminate ligands with a variety of coordinated metals, the wide application of these complexes for small molecule activation and catalysis is the reason for this growing interest.[1] In addition, easy modification of both substituents at nitrogen and the backbone of β-diketiminate ligand is convenient for investigating the electronic and steric effects on the character of the complexes. The chemistry of β-diketimines was reviewed by Lappert.[2]

The application of transition metal β-diketiminate complexes in olefin polymerization catalysis is an attractive field. Many early transition metal complexes bearing β-diketiminate ligand have proved to be interesting olefin polymerization catalyst precursors.[3–10] Nickel and palladium complexes bearing netural β-diketimine ligand have been reported as precursors of olefin polymerization catalysts,[11,12] but have not been widely studied, perhaps due to their relative low activity compared with cationic α-dimine system reported by Brookhart and coworkers.[13–20]

The chemistry of unsaturated three-coordinate late transition metal complexes of monoanionic β-diketiminate ligand was studied by Holland[21–28] and Warren.[29–33] Three-coordinate β-diketiminate alkyl complexes of Fe and Co adopt a tetrahedral structure. Recently, the lutidine-free Ni (II) β-agostic alkyl complexes were successfully isolated and characterized.[30] A three-coordinated nickel (I) complex of β-diketiminate ligands bearing a triphenylphosphine was reported with high activity for norbornene polymerization; however, this complex did not catalyze ethylene polymerization when activated by modified methylalumoxane (MMAO).[34]

In recent years, our efforts have focused on devising new nickel complexes of β-diketiminate ligands as olefin polymerization catalyst precursors. We have reported the synthesis and oligomerization of 1-hexene using β-diketiminate nickel (II) complexes when activated by MAO.[35] Studies on ethylene polymerization and copolymerization using these catalyst systems are in progress (we have screened a number of nickel complexes reported here in olefin polymerization and copolymerization, and the results

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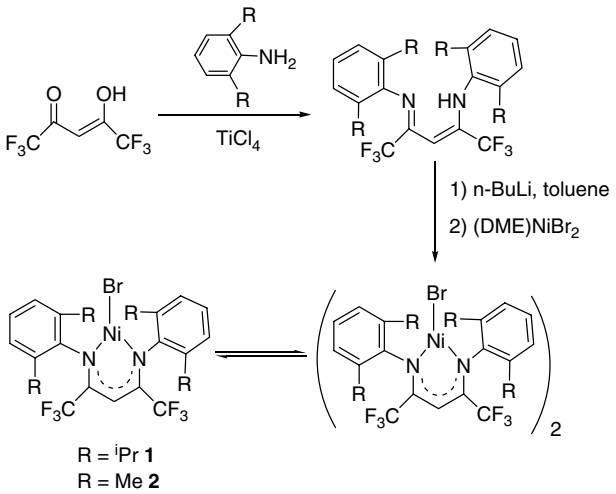
Contract/grant sponsor: NSFC.
Contract/grant sponsor: SINOPEC.
Contract/grant sponsor: Science Foundation of Guangdong Province.
Contract/grant sponsor: Ministry of Education of China.

will be reported elsewhere; Zhang J, Wu Q *et al*., manuscript in preparation). Bulky anilido-imino nickel (II) complexes have also been reported. They show low activities for ethylene oligomerization with MAO as cocatalyst, but high activities for norbornene polymerization in the presence of MAO.[36,37] Herein, the preparation and catalytic behavior of novel nickel (II) complexes supported by fluorinated β-diketiminate backbone ligands are reported. The complexes have different *o*-aryl substituents on nitrogen, particularly, with electron withdrawing groups on the ligand backbone. Our studies provide insight into the effect of ligand steric environments at nickel with β-diketiminate ligands on ethylene polymerization behavior.



Scheme 1. Synthesis of nickel complexes.

RESULTS AND DISCUSSION

Synthesis and molecular structure of nickel (II) complexes

β-Diketiminate ligands were prepared by condensation of 1,1,1,5,5,5-hexafluoroacetylacetone with the corresponding aniline according to literature methods.[38] After treating the ligands with *n*-butyllithium in toluene at −78 C, one equivalent of (1,2-dimethoxyethane) nickel (II) bromide [(DME)$NiBr_2$] was added carefully to the reaction system. A dark green complex **1** or dark purple complexes **2** were obtained by hexane precipitation from CH_2Cl_2 solution (Scheme 1).

Complex **2** is suitable for single crystal X-ray studies after recrystallization from toluene–hexane. The molecular structure is show in Fig. 1. Significant bond distances and angles, and crystallographic data are summarized in Tables 1 and 2.

The previously reported β-diimine Ni (II) adopts a pseudotetrahedral coordination geometry, and the six-membered chelate nickel complex sits in a boat conformation,[11] while the bulky backbone-substituted (^{t}Bu) nickel (II) complex of the β-diketiminate ligand favors a trigonal planar geometry

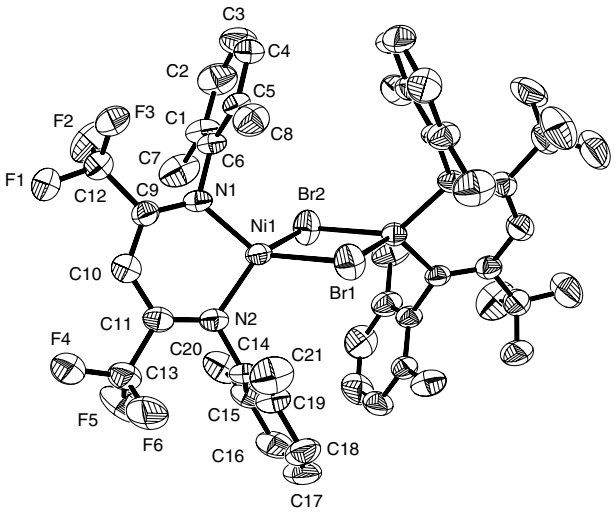


Figure 1. Molecular structure of complex **2**. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (deg) of complex **2**[a]

Bond lengths			
Ni(1)–N(1)	1.921(4)	Br(1)–Ni(1)#1	2.4041(10)
Ni(1)–N(2)	1.926(4)	Br(2)–Ni(1)#1	2.4184(10)
Ni(1)–Br(1)	2.4040(10)	C(9)–N(1)	1.316(7)
Ni(1)–Br(2)	2.4184(10)	C(11)–N(2)	1.334(7)
Bond angles			
N(1)–Ni(1)–N(2)	94.82(19)	Ni(1)–Br(2)–Ni(1)#1	90.02(5)
N(1)–Ni(1)–Br(1)	129.44(13)	C(9)–N(1)–C(6)	121.0(4)
N(2)–Ni(1)–Br(1)	106.72(13)	C(9)–N(1)–Ni(1)	124.6(3)
N(1)–Ni(1)–Br(2)	107.27(13)	C(6)–N(1)–Ni(1)	114.4(3)
N(2)–Ni(1)–Br(2)	134.23(13)	C(11)–N(2)–C(14)	120.8(4)
Br(1)–Ni(1)–Br(2)	89.64(3)	C(11)–N(2)–Ni(1)	125.0(4)
Ni(1)–Br(1)–Ni(1)#1	90.71(5)	C(14)–N(2)–Ni(1)	114.3(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z + 1/2$.

DOI: 10.1002/aoc

Table 2. Crystal data and structure refinements of complex **2**

Empirical formula	$C_{42}\ H_{38}\ Br_2\ F_{12}\ N_4\ Ni_2$
Formula weight	1104.00
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	C2/c
a (Å)	24.556(3)
b (Å)	8.3321(11)
c (Å)	24.329(3)
α (deg)	90
β (deg)	118.075(2)
γ (deg)	90
Volume (Å^3)	4392.2(10)
Z	4
Density (calculated) (mg cm^{-3})	1.670
Absorption coefficient, μ (mm^{-1})	2.763
F(000)	2208
Crystal size (mm^3)	0.50 × 0.33 × 0.12
θ range (deg)	1.88–27.05
Limiting indices	$-29 \le h \le 31$ $-10 \le k \le 10$ $-30 \le l \le 18$
Reflections collected/unique	11 959/4777 ($R_{int} = 0.0294$)
Data/restraints/parameters	4777/0/285
GOF on F^2	1.044
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0565$, $wR2 = 0.1740$
R indices (all data)	$R1 = 0.0999$, $wR2 = 0.2084$
Largest diff. peak and hole (e Å^{-3})	1.246 and −1.372

at Ni.[26] Complex **2** exhibits a structure similar to nickel complexes of β-diketiminate ligands,[23,32] and exists as a dimer in solid state with a tetrahedral geometry at Ni. The nickel atom lies 0.103 Å out of the coordination plane, which is much shorter than the nonfluorinated analogue (0.353 Å[32]). The slightly longer Ni–N bond distances in complex **2** [1.921(4) and 1.926(4) Å] and the slightly larger bite angle (N–Ni–N) of 94.82(19)° than the nonflourorinated analogue [1.913(3), 1.915(3) Å and 94.69(11)°, respectively[32]] may be the result of the strong electron-withdrawing character of the ligand backbone of complex **2**. However, the electronic effects of fluoro-substituents on Ni–N bond distances and bite angles are not so great as compared with the stereo effects in the three coordinate nickel β-diketiminate complexes in which the Ni complex with bulky *tert*-butyl backbone substituents has an Ni–N bond distance of 1.815(3) and N–Ni–N angle of 97.3(2),[26] but that with methyl backbone substituents has Ni–N bond distances of 1.938(3) and 1.946(3) Å and N–Ni–N angle 93.7(1)°.[23] The Ni–Br distances are 2.4040(10) and 2.4184(10) Å in complex **2**.

Similar to nickel complex of β-diketiminate ligands[23,35] and anilido-imine ligands,[36] two sets of proton signals, respectively, for monomer and dimer could be detected in the ^{1}H NMR spectra of complexes **1** and **2** in benzene-d_6 solution. The molar ratio of monomer to dimer could be calculated by hydrogen integration in the ^{1}H NMR spectra. For example, at room temperature in benzene-d_6, the ratio of monomer : dimer is ~10 : 1 for complex **1** and ~3 : 2 for complex **2**. It is seen that complex **2** has a greater tendency to dimerize in solution than complex **1**. This can be attributed to the steric effects of the *ortho*-aryl substitution.

Polymerization and oligomerization behaviors of ethylene

The Ni complexes activated by MAO catalyze ethylene polymerization to produce simultaneously ethylene polymer and short chain oligomers (C_4–C_8). The results of ethylene polymerization experiments with the nickel complexes are summarized in Table 3. The simultaneous formation of ethylene polymer and oligomer indicates that there are at

Table 3. Results from ethylene polymerizations with **1** and **2**–MAO[a]

			Solid product		Activity[b]		Polymer characters			Oligomer distribution[c]		
Entry	Precatalyst	Temperature (°C)	Yield (g)	Share (%)	Polymer	Oligomer	M_n[d]	M_w/M_n[d]	T_m[e] (°C)	C_4 (%)	C_6 (%)	C_8 (%)
1	**1**	60	0.03	41.2	3.1	4.3	1.3	21.3	121	58.7	19.3	22.0
2	**1**	30	0.45	85.5	45.2	7.6	1.4	33.7	125	50.3	23.4	26.3
3	**1**	0	3.49	98.7	348.7	4.6	30.7	1.9	130	47.8	24.2	28.0
4	**1**	−10	3.86	100	385.9		31.1	2.1	132			
5	**2**	60	0.01	32.5	1.1	5.2	nd	nd	nd	65.1	20.8	14.1
6	**2**	30	0.30	72.1	29.8	11.6	nd	nd	112	56.9	23.2	19.9
7	**2**	0	2.37	97.2	237.1	6.8	0.6	2.5	118	52.1	23.6	24.3
8	**2**	−10	3.24	100	324.5		nd	nd	109			

[a] Polymerization conditions: 10 atm of ethylene pressure; precatalyst, 10 μmol; 100 ml stainless steel autoclave; solvent, toluene; total volume, 30 ml; reaction time, 1 h; MAO, 4 mmol. [b] 10^3 g mol^{-1} Ni h^{-1}. [c] Determined by GC. [d] Measured by GPC. M_n, 10^3 g mol^{-1}. [e] Measured by DSC. nd, not determined.

DOI: 10.1002/aoc

least two kinds of catalytically active species in the reaction systems.

The activity for ethylene polymerization increases with increases in steric bulk of the substituents on the aryl rings, similar to the α-diimine nicke complexes where less bulky ligands favor oligomerization of ethylene.[15,16] The reaction temperature significantly affected the catalytic activity, and the highest ethylene polymerization activity was observed at −10 C. With increases in reaction temperature from −10 to 60 C, the catalytic activity decreases drastically. On the contrary, the activity for ethylene oligomerization increases with increasing reaction temperature, but decreases near 60 C. This may be ascribed to decomposition of the active species at high temperature.[16,39,40]

The oligomers obtained from these catalytic systems are exclusively dimers, trimers and tetramers of ethylene, no odd carbon number oligomers and other higher carbon olefins were detected by GC and GC-MS analysis. The proposed active species for producing oligomeric olefins are electrophilic cationic intermediates produced by the interaction of complexes with MAO. Studies by Talsi *et al*. with 2,6-bis(imino)pyridiyl iron complexes[41,42] and Zargarian with Ni–indenyl complexes[43–45] revealed that the interaction of the precatalysts with MAO (or PMAO) produces both neutral and cationic species. Similar species have also been detected in the reaction of Ti and Zr metallocenes with MAO.[46–51]

The oligomers produced herein by the fluorinated β-diketiminate Ni complex systems consist of α-olefins and internal olefins. For example, as determined by GC-MS for the oligomers obtained from the **1**–MAO system, the C_4 distribution is 1-butene (major) and 2-butene (minor), while the C_6 distribution is 1-hexene (major), 4-methyl-2-pentene, 2-hexene and 3-hexene. The distribution of oligomers shifts to low carbon olefins with increases in temperature. This can be understood by increases in the rate of chain transfer relative to the rate of chain propagation with increases in temperature.

The polyethylene samples obtained with these catalytic systems are white powders, and GPC analyses indicate that the obtained polyethylene has a relatively low molecular weight with M_n values in the range 600–31 000 (see Table 3). The M_n values of polyethylenes produced by **1**–MAO are much higher than those obtained from **2**–MAO under similar polymerization conditions, which suggests that, the greater steric bulk of the Ni complex, the higher the molecular weight of polyethylene produced.

The polyethylene molecular weight decreases greatly with increases in reaction temperature. As shown by the GPC traces in Fig. 2, the polyethylene samples obtained from **1**–MAO at low reaction temperatures show higher molecular weight (M_n) and narrower molecular weight distributions ($M_w/M_n \approx 2$), while samples obtained at 30 C display a bimodal distribution. The bimodal molecular weight distribution might arise from formation of different types of active species due to partial decomposition of the Ni (II) complex at high temperature.

The ^{13}C NMR spectra for the polyethylene samples are shown in Figs 3 and 4. For the relatively low molecular weight polymer obtained from **2**–MAO at 0 °C, no branching was detectable in the ^{13}C NMR spectrum besides the end-group peaks at 33.94, 32.20, 29.60, 22.91 and 14.15 ppm (Fig. 3). The single peaks in the ^{13}C NMR spectrum at 139.21 and 114.28 ppm indicate mainly vinyl-type unsaturated chain ends.[52] Similarly, linear polyethylene was obtained from the **1**–MAO system at 0 °C [Fig. 4(A)]. However, for the polyethylene obtained from the **1**–MAO system at 30 C [Fig. 4(B)], methyl branches (signals at 20.15, 27.48, 30.81, 33.30 and 37.61 ppm) and minor ethyl (signals at 11.26, 26.78, 27.38, 30.47, 34.12 and 39.73 ppm) besides the signals of end-group were observed in the ^{13}C NMR.[53–56] DSC measurements of T_m for PE obtained from **1**–MAO are 132–121 C (Table 3).

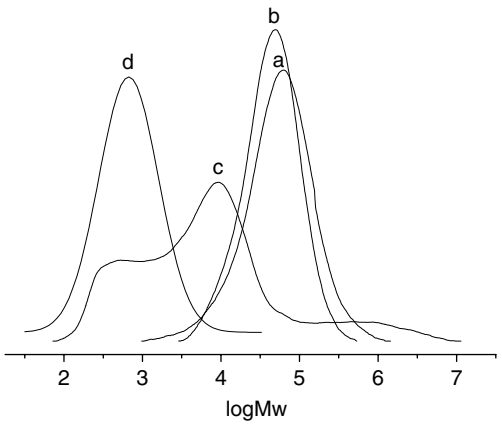


Figure 2. GPC profiles of polyethylene samples obtained from **1**–MAO (a, 0 °C; b, −10 °C; c, 30 °C) and **2**–MAO (d, 0 °C).

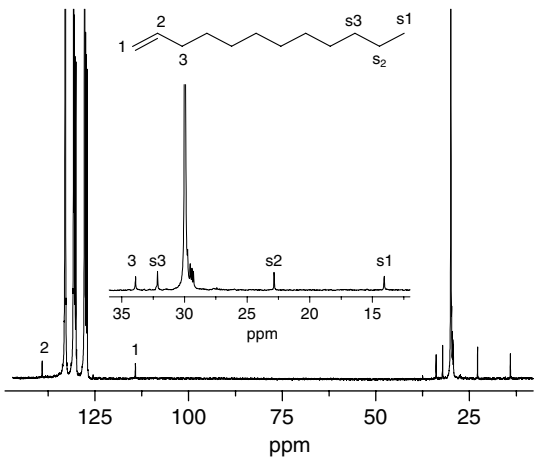


Figure 3. ^{13}C NMR spectrum of polyethylene obtained by **2**–MAO at 0 °C.

DOI: 10.1002/aoc

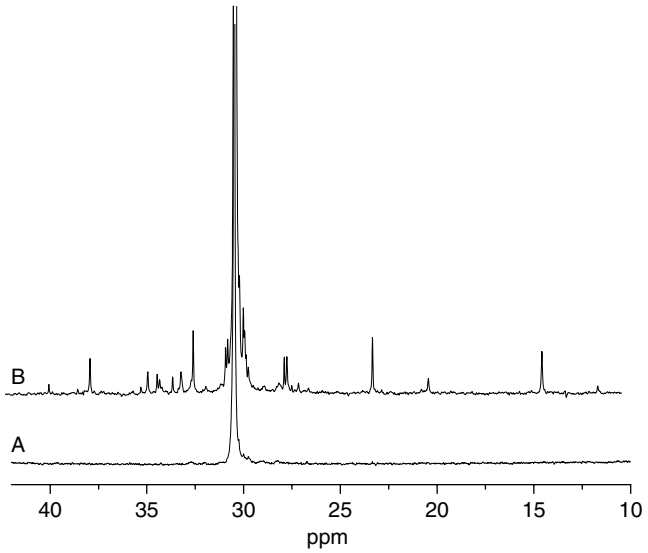


Figure 4. ^{13}C NMR spectra of polyethylenes obtained by **1**–MAO at 0 °C (A) and 30 °C (B).

CONCLUSIONS

Novel nickel (II) complexes with fluorinated β-diketiminate ligand can be synthesized by the reaction of lithium salt of fluorinated β-diketiminate backbone ligands with (DME)$NiBr_2$. The solid-state structure of the nickel (II) complex dimers reveals four-coordination and a tetrahedral geometry with bridging bromides. The Ni complexes can be used as catalyst precursors for ethylene polymerization in the presence of MAO. The catalyst systems simultaneously polymerize and oligomerize ethylene. β-Diketiminate ligands with greater steric bulk afford catalysts that give higher molecular weight polymer and higher ratios of polymer to oligomer under the same conditions. The polymer produced at temperatures below 0 C is linear polyethylene, while that obtained at higher temperatures is branched.

EXPERIMENTAL

All manipulations that are air and/or moisture-sensitive were performed under dry, deoxygenated nitrogen atmosphere using standard high vacuum or Schlenk techniques.

Materials

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. Solid methylaluminoxane (MAO)[36] and (1,2-dimethoxyethane) nickel (II) bromide [(DME)$NiBr_2$][57] were prepared according to 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 used as received.

Elemental analyses

All elemental analysis was performed on a Vario EL microanalyzer. The metal complexes were analyzed within a few hours of being taken out of the nitrogen glovebox.

NMR analyses

^1H NMR spectra of ligands were recorded on Mercury-plus 300 MHz NMR at room temperature in $CDCl_3$ solution. Chemical shifts were reported in ppm and referenced to tetramethylsilane (TMS). ^1H NMR spectra of complexes were performed in dry C_6D_6 and recorded on Varian INOVA 500 MHz spectrometers at room temperature. A spectral width of 150 000 Hz, a pulse width of 4.0 ms, an acquisition time of 1.0 s, and a relaxation delay of 3.0 s were used for each spectrum. Chemical shifts were reported in ppm and referenced to residual H solvent shifts (7.2 ppm). ^{19}F NMR spectra were recorded on Varian INOVA 500 MHz spectrometers at room temperature in C_6D_6. Chemical shifts were referenced to CF_3COOH ($\delta_F = -78.5$ ppm, CF_3COOH in sealed capillary). ^{13}C NMR spectra of polymer samples were recorded on a Varian INOVA 500 MHz spectrometer in a 5:1 mixture of *o*-Cl_2-C_6H_4 and *o*-Cl_2-C_6D_4 (3.0 ml) at 110 C. A spectral width of 27 000 Hz, a pulse width of 4.0 ms, an acquisition time of 1.0 s, and no relaxation delay were used for each spectrum. Chemical shifts were referenced to *o*-Cl_2-C_6D_4 (127.3 ppm).

Gel permeation chromatography

All GPC were determined using a PL-GPC210 gel permeation chromatography with a mixed 3× (PLgel 10 μm) column and refractive index (RI) detector at 150 C. 1,2,4-Trichlorobenzene was used as a solvent at a flow rate of 1.0 ml min^{-1}. The system was calibrated using polystyrene stands.

Differential scanning calorimetry

Melting points of the polymers were obtained on a Perkin–Elmer DSC-7 instrument under a nitrogen atmosphere. The polymer sample was first equilibrated at 0 °C and then heated to 200 °C at a rate of 10 °C min^{-1} to remove thermal history. The sample was then cooled to 0 °C at a rate of 10 °C min^{-1}. A second heating scan was run from 0 to 200 °C at a rate of 10 °C min^{-1}, and the data are reported for this second heating scan.

Gas chromatography and gas chromatography-mass spectrometry

GC analysis was performed on a Varian CP3800 Series GC System with a HP-5MS GC column (30 m × 0.25 mm × 0.25 μm) with a FID detector. The temperature program used was: initial temperature 35 C (isothermal for 5 min), 35–280 C at 10 C min^{-1}. GC–MS analysis was performed on a Finnigan Voyager GC-8000Top Series GC–MS System with DB-5MS GC column (60 m × 0.25 mm × 0.25 μm). Temperatures: 35 C

DOI: 10.1002/aoc

(isothermal for 5 min), 35–280 C at 10 C min^{-1}; injector temperature, 220 C; column head pressure, 20 psig He; Split flow, 60 cm^3 min^{-1}.

Synthesis of ArNHC(CF_3)CHC(CF_3)NAr (Ar = 2, 6-^{i}Pr$_2$C$_6$H$_3$) (L1)

β-Diketiminate ligands were synthesized by literature methods.[38] Bright yellow crystalline **L1** was obtained after recrystallization from methanol; yield, 32%. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm, 1.13 (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 (1H, br s, N*H*). ^{19}F NMR (500 MHz, C_6D_6): δ_F ppm, −66.36 (6F, s, CF_3). 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 ArNHC(CF_3)CHC(CF_3)NAr (Ar = 2, 6-Me$_2$C$_6$H$_3$) (L2)

Yellow ligand **L2** was prepared using a method similar to **L1**; yield, 22%. ^{1}H NMR (300 MHz; $CDCl_3$): δ ppm, 2.14 (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 (1H, br s, N*H*). ^{19}F NMR (500 MHz, C_6D_6): δ_F ppm, −68.51 (6F, s, CF_3). 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 CH{C(CF_3)NAr}$_2$NiBr (Ar = 2, 6-^{i}Pr$_2$C$_6$H$_3$) (1)

To a stirred solution of **L1** (1.11 g, 2.11 mmol) in toluene (40 mL) at −78 C, an *n*-BuLi hexane solution (1.0 ml, 2.2 M, 2.20 mmol) was added slowly. The mixture was allowed to warm to room temperature and stirred for another 2 h. The orange/yellow solution thus obtained was added to (DME)$NiBr_2$ (0.62 g, 2.26 mmol) with stirring, resulting in a immediate color change to black, and then 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 *in vacuo*, and 30 ml of *n*-hexane were added. Solvent was removed from the precipitate via cannula filtration, and the residual dark green solid was washed with *n*-hexane (3 × 5 ml). Drying *in vacuo* produced the desired nickel complex **1** as dark green solid; yield, 0.59 g (42%). ^{1}H NMR (500 MHz, C_6D_6): dimer, δ_H ppm, 52.97 (8H, *m*-Ar), 40.05 [8H, C*H*(CH_3)$_2$], 8.46 [24H, CH(C*H*$_3$)$_2$], 7.65 [24H, CH(C*H*$_3$)$_2$], −27.13 (4H, *p*-Ar), −140.24 (2H, C*H*, backbone); monomer, δ_H ppm, 55.05 (4H, *m*-Ar), 31.24 [4H, C*H*(CH_3)$_2$], 37.42 [12H, CH(C*H*$_3$)$_2$], 17.35 [12H, CH(C*H*$_3$)$_2$], −25.61 (2H, *p*-Ar), −132.50 (1H, C*H*, backbone); monomer/dimer ≈ 10 : 1. ^{19}F NMR (500 MHz, C_6D_6): dimer, δ_F ppm, −70.66 (12F, s, CF_3); monomer, δ_F ppm, −72.74 (6F, s, CF_3). Elemental analysis calcd for C_{58} H_{70} Br_2 F_{12} N_4 Ni_2: C, 52.41; H, 5.27; N, 4.22. Found: C, 52.68; H, 5.65; N, 4.01.

Synthesis of CH{C(CF_3)NAr}$_2$NiBr (Ar = 2, 6-Me$_2$C$_6$H$_3$) (2)

Complex **2** was prepared using a similar procedure as a dark purple solid; yield, 0.74 g (46%). ^{1}H NMR (500 MHz, C_6D_6): dimer, δ_H ppm, 15.10 (8H, *m*-Ar), 13.94 (24H, *o*-C*H*$_3$Ar), −2.43 (4H, *p*-Ar), −34.87 (2H, C*H*, backbone); monomer, δ_H ppm, 44.48 (4H, *m*-Ar), 51.74 (12H, *o*-C*H*$_3$Ar), −26.40 (2H, *p*-Ar), −174.26 (1H, C*H*, backbone); monomer/dimer ≈ 3 : 2. ^{19}F NMR (500 MHz, C_6D_6): dimer, δ_F ppm, −79.62 (12F, s, CF_3); monomer, δ_F ppm, −82.65 (6F, s, CF_3). Elemental analysis calcd for C_{42} H_{38} Br_2 F_{12} N_4 Ni_2: C, 45.65; H, 3.44; N, 5.07. Found: C, 45.80; H, 3.65; N, 4.82.

Procedure for ethylene polymerization

Ethylene polymerizations were performed in a 100 ml stainless steel autoclave equipped with a heat jacket and a magnetic stirrer. In a typical experiment, the fully dried reactor was charged with a solution of solid MAO (232 mg, 4 mmol) in toluene (20 ml), and toluene (5 ml) up to a total volume of 25 ml. This was pressurized with ethylene with stirring (900 rpm) for 10 min at the reaction temperature. The polymerization was started by injection of Ni complexes (10 μmol) in toluene (5 ml), and the reactor was pressurized to 10 atm quickly. After 60 min, the reaction was quenched by addition of 30 ml dilute hydrochloric acid. About 2 ml of organic solution were dried with anhydrous Na_2SO_4 for GC and GC-MS analysis. The polymer was precipitated with 100 ml of ethanol, filtered off with a fritted glass filter, and dried *in vacuo* at 60 C until the weight remained constant.

X-ray structural determination of complex 2

A crystals was mounted on a glass fiber using the oil drop scan method.[58] Data obtained with the $\omega - 2\theta$ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved using direct methods, while further refinement with full-matrix least squares on F^2 were obtained with the SHELXTL program package.[59,60] 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 **2** has been deposited with Cambridge Crystallographic Data Centre, CCDC 600760. 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).

Acknowledgments

The financial support 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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