N-(2-Benzoylphenyl)benzamido nickel(II) complexes and polymerization reactivity

Chang Bo Shim [a], Young Heui Kim [a], Bun Yeoul Lee [a,*], Dong Mok Shin [b], Young Keun Chung [b]

[a] Department of Molecular Science and Technology, Ajou University, San 5 Wonchondong, Suwon 442-749, Republic of Korea
[b] Department of Chemistry and the Center for Molecular Catalysis, College of Natural Sciences, Seoul National University, Seoul 151-742, Republic of Korea

Abstract

[N-(2-Benzoylphenyl)benzamido-$\kappa^2 N,O$](η^1-benzyl)(trimethylphosphine)Ni(II) (**3**) is prepared by the reaction of potassium N-(2-benzoylphenyl)benzamide and Ni(η^3-CH$_2$C$_6$H$_5$)Cl(PMe$_3$). When **3** is treated with one equivalent of B(C$_6$F$_5$)$_3$, one obtains a zwitterionic complex, [PhC(O)–C$_6$H$_4$–N=C(Ph)OB(C$_6$F$_5$)$_3$-$\kappa^2 N,O$]Ni(η^1-CH$_2$C$_6$H$_5$)(PMe$_3$) (**4**). When two equivalents of B(C$_6$F$_5$)$_3$ is added, PMe$_3$ is abstracted to give a η^3-benzyl zwitterionic complex, [PhC(O)–C$_6$H$_4$–N=C(Ph)OB(C$_6$F$_5$)$_3$-$\kappa^2 N,O$]Ni(η^3-CH$_2$C$_6$H$_5$) (**5**). Solid structures of **4** and **5** were determined by X-ray crystallography. When ethylene is added to **5**, low molecular weight polyethylene is obtained.
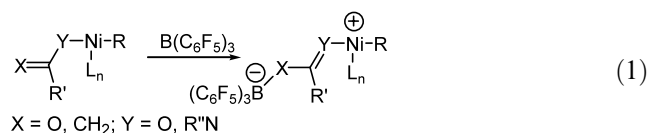© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Nickel catalyst; Ethylene; Tris(pentafluorophenyl)borane; Zwitterionic complexes

1. Introduction

Recently, Bazan and I have reported that nickel complexes containing carboxylato [1,2], carboxamidato [3], or enamido ligand [4] could be activated by electrophilic addition reaction of B(C$_6$F$_5$)$_3$ or Al(C$_6$F$_5$)$_3$. In those cases, B(C$_6$F$_5$)$_3$ or Al(C$_6$F$_5$)$_3$ is added to the electron-rich oxygen on carbonyl functionality or carbon on methylene functionality to afford a zwitterionic active complex (Eq. 1) [5]. It is significant that the partially negative boron or aluminium atom is situated on the side opposite from monomer insertion. The traditional active species is the presence of a loosely coordinated base, which competes with the incoming monomer molecule for the vacant site of lowest energy. Polyethylene was produced with the carboxamidato and enamido complexes having bulky substituents on the ligand frame. However, mainly butene was obtained, when ethylene was added to the carboxylato complexes. The activity and selectivity depend deeply on the nature of ligand. For example, [(C$_6$H$_5$)$_2$PC$_6$H$_4$C(OB(C$_6$F$_5$)$_3$)O-$\kappa^2 P,O$]Ni(η^3-CH$_2$CMeCH$_2$) gives 1-butene with high efficiency but the complex, [(C$_6$H$_5$)$_2$NC$_6$H$_4$C-(OB(C$_6$F$_5$)$_3$)O-$\kappa^2 N,O$]Ni(η^3-CH$_2$CMeCH$_2$), where only the phosphorus is replaced with nitrogen, is sluggish to the ethylene and the product is a mixture of 1- and 2-butene.

$$X = \underset{R'}{\overset{Y-Ni-R}{\diagdown}} \xrightarrow[(C_6F_5)_3B]{B(C_6F_5)_3} \underset{R'}{\overset{\oplus}{\diagdown}} \overset{Y-Ni-R}{\underset{L_n}{\diagup}} \quad (1)$$

X = O, CH$_2$; Y = O, R''N

We were interested in a complex having imine donor, [(C$_6$H$_5$)$_2$C=NC$_6$H$_4$C(OB(C$_6$F$_5$)$_3$)O-$\kappa^2 N,O$]Ni(η^3-CH$_2$-C$_6$H$_5$) because imine functionality has been successfully used for the nickel complexes which is active to the ethylene polymerisation [6]. The synthesis of the ligand for the imine complex was reported (Eq. 2) [7]. Nucleophilic attack of phenyllithium to 2-phenyl-1,2-dihydro-4H-3,1-benzoxazin-4-one, which is commercially available, affords two compounds. One of them

* Corresponding author. Tel.: +82-31-2191844; fax: +82-31-2191592.
E-mail address: bunyeoul@ajou.ac.kr (B. Lee).

is soluble in diethyl ether, which was assigned to the imine compound **1** in the literature, and the other is not soluble in diethyl ether, which was assigned to amide compound **2**. We first tried the metallation with the ligand assigned to be an imine compound **1** but X-ray crystallography studies of the resulting complexes revealed that the assignment between two compounds is not correct. The structure is the one synthesized from amide compound **2**. Herein, we report the synthesis of the nickel complexes derived from **2** and their reactivities to ethylene. Metallation to **1** was not successful.

$$\text{(2)}$$
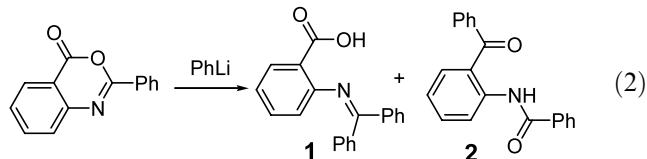
2. Results and discussion

2.1. Synthesis and characterization

Deprotonation of the amide compound **2** is successfully carried out with 1.0 equivalent of KH in toluene for 2 days. Addition of Ni(η^3-CH$_2$C$_6$H$_5$)Cl(PMe$_3$) [8] to the resulting potassium salt affords red crystalline solid in 77% yield (Eq. 3). Proton signal of PMe$_3$ is observed at 0.42 ppm as doublet ($^2J_{H-P}$ = 9.6 Hz) and very broad signal is observed at 1.8–1.6 ppm for methylene protons on benzyl ligand in ^{1}H-NMR (C$_6$D$_6$). In ^{13}C{^{1}H}-NMR spectrum (C$_6$D$_6$), one observes signals at 199.08 and 173.58 ppm which can be assigned to the carbonyl carbon on ketone and amide. Signals of methylene carbon on benzyl and methyl carbons on PMe$_3$ are split as doublet at 15.62 ($^2J_{C-P}$ = 34.2 Hz) and 13.03 ppm ($^1J_{C-P}$ = 29.6 Hz). Although complete assignment of the carbon signals is not achieved, the number of inequivalent carbons and the number of signals are coincided each other. A single signal is observed in ^{31}P{^{1}H}-NMR at −10.55 ppm. The exact structure cannot be argued with the NMR spectra but it is probably amido–ketone chelated one depicted in Eq. 3 [9].

$$\text{(3)}$$
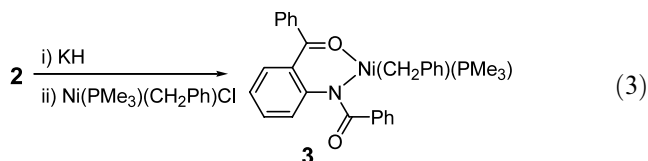
Addition of one equivalent of B(C$_6$F$_5$)$_3$ to **2** in C$_6$D$_6$ results in clean formation of a complex (Eq. 4) in contrast with the cases of pyridinecarboxamidato-Ni(II) and α-iminocarboxamidato-Ni(II) complexes [3], in which addition of one equivalent of B(C$_6$F$_5$)$_3$ did not

afford a clean complex. Signal of protons on PMe$_3$ at 0.18 ppm as doublet ($^2J_{H-P}$ = 10 Hz) and very broad signal at 1.2–1.4 ppm for methylene protons on benzyl ligand are observed in ^{1}H-NMR (C$_6$D$_6$). Single signal is also observed in ^{31}P{^{1}H}-NMR at −10.82 ppm. In ^{19}F-NMR, characteristic signals of pentafluorophenyl group are observed at −40.30, −66.77 and −72.60 ppm.

$$\text{(4)}$$
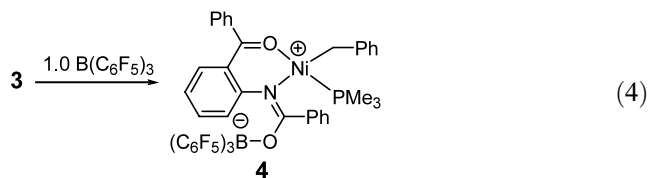
Single crystals suitable for X-ray crystallography was obtained by vapor phase addition of pentane to a benzene solution at room temperature overnight. Fig. 1 shows the structure with selected bond lengths and angles. It is a N–O chelated square planar complex. The phosphine ligand is situated opposite to the ketone ligand and the benzyl is to nitrogen atom. The metrical parameters within the Ni–N–C–O–B fragment are in agreement with previously characterized pyridinecarboxamidoato-Ni(II) and α-iminocarboxamidato-Ni(II) complexes [3] (distances in Å: Ni–N = 1.954(5), N–C(24) = 1.310(7), C(24)–O(2) = 1.295(7), O(2)–B = 1.518(8)) strongly supporting the zwitterionic structure depicted in Eq. 4. The distances of Ni–C(1) and Ni–P are 1.977(6) and 2.129(2) Å which are comparable with those observed for neutral carboxamido complex, {(H$_3$C)C[NC$_6$H$_5$]C(O)[NC$_6$H$_5$]}Ni(η^1-CH$_2$C$_6$H$_5$)(PMe$_3$) (1.947(3) and 2.1238(11) Å, respectively) [3].
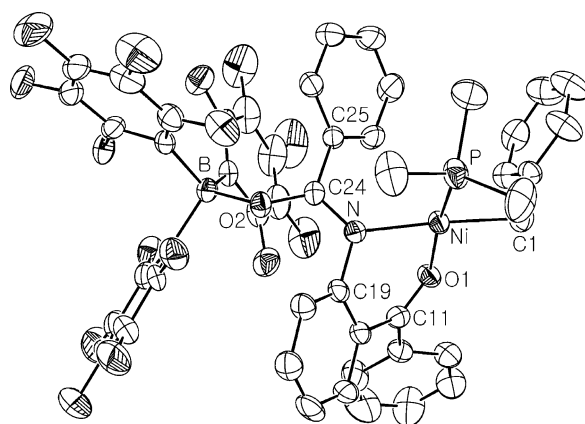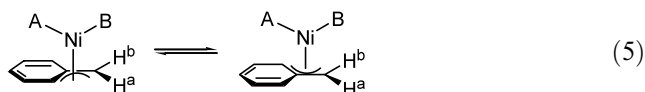

Fig. 1. ORTEP view of **4**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni–N, 1.954(5); Ni–O(1), 1.968(4); Ni–C(1), 1.977(6); Ni–P, 2.129(2); N–C(24), 1.310(7); O(2)–C(24), 1.295(7); B–O(2), 1.518(8); O(1)–C(11), 1.237(7); N–C(19), 1.442(7); N–Ni–O(1), 84.58(18); O(1)–Ni–C(1), 88.1(2); C(1)–Ni–P, 90.3(2); N–Ni–P, 97.09(15); C(24)–N–C(19), 119.1(5); C(19)–N–Ni, 112.2(4); C(24)–O(2)–B, 131.5(5).

Addition of two equivalents of $B(C_6F_5)_3$ affords η^3-benzyl complexes (Eq. 5). PMe_3 signals are disappeared in ^{1}H-NMR spectrum and one observes the appearance of characteristic signals for *ortho*-protons on η^3-benzyl ligand at 5–6 ppm. In the cases of pyridinecarboxamidoato-Ni(II) and α-iminocarboxamidato-Ni(II) complexes, the two *ortho*-protons and two methylene protons on the benzyl ligand are equivalent, respectively, and hence a relatively sharp doublet signal for *ortho*-protons and a singlet signal for methylene protons are observed in ^{1}H-NMR spectra. The equivalency results from not only the rapid suprafacial shift [10] as shown below but also equivalency of two faces bisected by the square plane. In this case, two *ortho*-protons are separately observed at 5.81 and 5.59 ppm and the signals are broad. The two methylene protons are also separately observed at 1.07 and 0.34 ppm as broad singlet. These observations indicate, if the rapid suprafacial shift is underway still, that the two faces bisected by the square plane are not equivalent.

$$(5)$$

Single crystals suitable for X-ray crystallography were grown from toluene/pentane solution in a freezer and Fig. 2 shows the results. Structural characterization reveals a square planar geometry with a trans relationship between the ketone oxygen and the benzyl CH_2 carbon. Two faces bisected by the square plane are not equivalent as expected by its ^{1}H-NMR spectrum. The $Ph(OB(C_6F_5)_3)C=$ fragment is directed to one face and the other face is relatively open. Metrical changes compared with **4** are a contraction of N–Ni distance (1.954(5) and 1.905(13) Å for **4** and **5**, respectively), an elongation of C–O distance in ketone (1.237(7) and 1.266(18) Å for **4** and **5**, respectively) and an elongation of B–O distance (1.518(8) and 1.531(19) Å for **4** and **5**, respectively). Bite angle (O–Ni–N) is enlarged by removing PMe_3 ligand (84.58(18) and 87.1(5)° for **4** and **5**, respectively). The other parameters are almost identical to **4**.
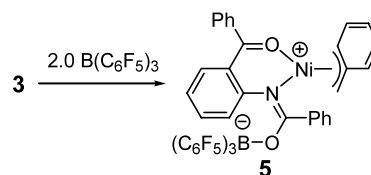
2.2. Polymerization studies

Neither **3** nor **4** is active to ethylene. However, rapid ethylene consumption is observed when ethylene gas is added to a NMR tube containing **5** in C_6D_6 but polyethylene precipitates are not observed. ^{1}H-NMR spectrum indicates that oligomers are produced. Signals of internal vinyl protons are observed at 5.1–5.6 ppm but the signals characteristic for the terminal olefins are not detected. When the ethylene gas is added under the pressure of 100 psig at room temperature, low molecular weight polyethylene is obtained. The oligomers are readily soluble in benzene and the vinyl-end group signals are observed in ^{1}H-NMR spectrum. M_n is calculated to be 1200 by using the integration value of the vinyl and the aliphatic signals in the ^{1}H-NMR spectrum. ^{1}H-NMR spectrum also indicates that the polymer is branched one (the branch number, 37/1000C). The averaged activity for 100 min is 244 kg mol^{-1} h^{-1}. The complex **5** is also active to the norbornene polymerization and 850 kg mol^{-1} h^{-1} activity is observed which is rather lower than that of $[(C_6H_5)_2NC_6H_4C(OB(C_6F_5)_3)O\text{-}\kappa^2N,O]Ni(\eta^3\text{-}CH_2CMeCH_2)$ [2].
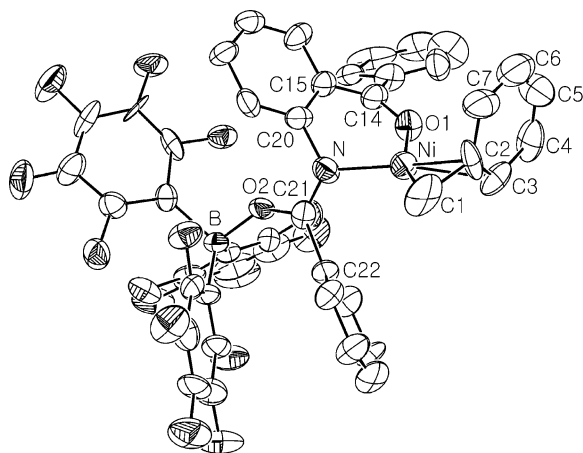
Fig. 2. ORTEP view of **5**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni–C(1), 1.887(17); Ni–C(2), 2.050(17); Ni–C(3), 2.20(2); Ni–O(1), 1.966(11); Ni–N, 1.905(13); N–C(21), 1.312(18); N–C(20), 1.455(18); O(2)–C(21), 1.314(17); O(2)–B, 1.531(19); O(1)–C(14), 1.266(18); C(1)–C(2), 1.43(2); C(2)–C(3), 1.49(3); C(2)–C(7), 1.38(3); C(3)–C(4), 1.39(3); N–Ni–O(1), 87.1(5); C(20)–N–Ni, 115.4(11); C(21)–N–C(20), 118.1(13); C(21)–O(2)–B, 137.6(13).

3. Experimental

3.1. General considerations

All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. Toluene, pentane, and C_6D_6 were distilled from benzophenone ketyl. Toluene used for polymerization reaction was purchased from Aldrich (anhydrous grade) and purified further over Na/K alloy. Ethylene was purchased from Conley Gas (99.9%) and purified by

contacting with molecular sieves and copper overnight under the pressure of 150 psig. Starting material, 2-phenyl-1,2-dihydro-4H-3,1-benzoxazin-4-one was phased from Aldrich. NMR spectra were recorded on a Varian Mercury plus 400. ^{19}F-, ^{11}B-, ^{31}P-NMR spectra were calibrated and reported downfield from external α,α,α-trifluorotoluene, BF$_3$·OEt$_2$ and PPh$_3$, respectively. Elemental analyses were carried out on a Fisons EA1108 microanalyzer.

3.2. [N-(2-Benzoylphenyl)benzamido-κ^2N,O](η^1-benzyl)(trimethylphosphine)Ni(II) (3)

KH (22.9 mg, 0.571 mmol) and **2** (172 mg, 0.571 mmol) were weighed in a vial and toluene (4 ml) was added. The mixture was stirred for 2 days, upon which the hydrogen gas was evolved. Ni(η^3-CH$_2$C$_6$H$_5$)-Cl(PMe$_3$) (149 mg, 0.571 mmol) in toluene (1 ml) was added. The solution was stirred for 4 h and filtered over celite. The solvent was removed by vacuum. The residue was triturated with pentane for 30 min to yield red solid which is pure by NMR spectra (230 mg, 77%). Analytically pure crystals were obtained by vapor phase addition of pentane to a benzene solution. ^{1}H-NMR (400 MHz, C$_6$D$_6$): δ 9.44 (d, $J = 7.2$ Hz, 2H), 8.54 (d, $J = 8.4$ Hz, 1H), 7.70 (d, $J = 5.6$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 1H), 7.26–7.05 (m, 8H), 6.94 (t, $J = 7.6$ Hz, 2H), 6.65 (t, $J = 7.6$ Hz, 1H), 1.8–1.6 (br, 2 H, Ni–CH_2), 0.42 (d, $J = 9.6$ Hz, 9H) ppm. ^{13}C{^{1}H}-NMR (100 MHz, C$_6$D$_6$): δ 199.08 (carbonyl), 173.58 (carbonyl), 152.32, 149.38, 143.09, 137.22, 134.17, 133.40, 133.14, 131.78, 131.51, 129.87, 129.77, 128.96, 128.90, 128.79, 128.39, 128.16, 123.44, 119.93, 15.62 (d, $^2J_{PC} = 34.2$ Hz, Ni–CH$_2$), 13.03(d, $^1J_{PC} = 29.6$ Hz, PCH$_3$) ppm. ^{31}P{^{1}H}-NMR (162 MHz, C$_6$D$_6$): δ −10.55 ppm. Anal. Calc. (C$_{30}$H$_{30}$NO$_2$PNi): C, 68.5; H, 5.76. Found: C, 68.8; H, 6.04%.

3.3. [PhC(O)−C$_6$H$_4$−N=C(Ph)OB(C$_6$F$_5$)$_3$-κ^2N,O]Ni(η^1-CH$_2$C$_6$H$_5$)(PMe$_3$) (4)

Equimolar amount of B(C$_6$F$_5$)$_3$ and **3** (0.010 mmol) were dissolved in C$_6$D$_6$. The NMR spectra indicated that a single complex was formed cleanly. Single crystals suitable for X-ray crystallography and elemental analysis were obtained by vapor phase addition of pentane to a benzene solution. ^{13}C-NMR spectrum was not obtained due to its low solubility in benzene and decomposition in polar solvent as CD$_2$Cl$_2$. ^{1}H-NMR (400 MHz, C$_6$D$_6$): d 8.42 (d, $J = 7.2$ Hz, 2H), 7.46 (d, $J = 6.8$ Hz, 2H), 7.52–7.38 (br, 4H), 7.14–7.06 (m, 3H), 7.01 (d, $J = 8.4$ Hz, 2H), 7.00 (t, $J = 6.8$ Hz, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 6.79 (t, $J = 7.2$ Hz, 1H), 6.72 (t, $J = 8.0$ Hz, 2H), 6.69 (d, $J = 8.4$ Hz, 1H), 1.2–1.4 (br, 2 H, Ni–CH_2), 0.18 (d, $J = 10$ Hz, 9H, PCH_3) ppm. ^{19}F{^{1}H}-NMR (C$_6$D$_6$, 376 MHz): δ −40.3 (br s), −69.77 (t,

$^3J_{FF} = 19$ Hz), −72.60 (t, $^3J_{FF} = 19$ Hz) ppm. ^{31}P{^{1}H}-NMR (162 MHz, C$_6$D$_6$): δ −10.82 ppm.

3.4. [PhC(O)−C$_6$H$_4$−N=C(Ph)OB(C$_6$F$_5$)$_3$-κ^2N,O]Ni(η^3-CH$_2$C$_6$H$_5$) (5)

B(C$_6$F$_5$)$_3$ (0.020 mmol) and **3** (0.010 mmol) were dissolved in C$_6$D$_6$ and ^{1}H-NMR study was carried out with the solution. Three sets of signals are observed in ^{1}H-NMR. The major signals were tentatively assigned to the desired complex **5** (ca. 60%). One of the minors was **4** (ca. 20%). Pure complex **5** was synthesized and isolated according to the following method. Thus, **3** (0.53 mg, 0.10 mmol) and B(C$_6$F$_5$)$_3$ (0.103 mg, 0.200 mmol) were weighed in a vial and toluene (12 ml) was added. The red solution was stirred for 4 h. The solid was removed by filtration over celite. The solvent was removed by vacuum and the residue was dissolved again in toluene (ca. 1.0 ml). The solid was removed by filtration over celite again. Pentane (ca. 6 ml) was added to the filtrate and the solid was removed by filtration over celite once again. The red crystals suitable for X-ray crystallography were deposited by storing the filtrate in a freezer (0.035 g, 36%). ^{1}H-NMR (400 MHz, C$_6$D$_6$): δ 8.01 (d, $J = 7.6$ Hz, 1H), 7.69 (d, $J = 7.6$ Hz, 2H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 7.6$ Hz, 2H), 7.24 (t, $J = 6.8$ Hz, 1H), 6.92–6.78 (m, 7H), 6.73 (t, $J = 7.6$ Hz, 1H), 6.62 (br, 1H), 5.81 (br, 1H), 5.59 (br, 1H), 1.07 (br s, 1H, Ni–CH_2), 0.34 (br s, 1H, Ni–CH_2) ppm. ^{13}C{^{1}H}-NMR (100 MHz, C$_6$D$_6$): δ 202.19, 172.04 (carbonyl), 148.1 (dm, $^1J_{FC} = 240$ Hz), 144.84, 139.8 (dm, $^1J_{FC} = 250$ Hz), 137.57, 137.3 (dm, $^1J_{FC} = 250$ Hz), 135.27, 135.07, 134.98, 134.38, 133.29, 131.48, 130.47, 130.38, 129.28, 128.71, 128.66, 127.52, 125.07, 121.40 (br, C−B), 114.10, 108.81, 103.25 (br), 27.80 ppm. ^{19}F{^{1}H}-NMR (C$_6$D$_6$, 376 MHz): δ −40.76 (d, $^3J_{FF} = 20$ Hz), −66.57, −72.55 (t, $^3J_{FF} = 20$ Hz) ppm. ^{11}B{^{1}H}-NMR (C$_6$D$_6$, 128 MHz): δ −2.2 ppm.

3.5. Polymerization

Complex **3** (10 μmol) and B(C$_6$F$_5$)$_3$ (45 μmol) were weighed inside a glove box in a 70 ml glass reactor containing stirring bar. Thirty milliliter of toluene was added. The reactor was assembled and brought out of the glove box. The reactor was immersed in a water bath. The ethylene was fed continuously for 100 min under the pressure of 100 psig. Ethylene pressure was released. The volatiles were removed by evacuation to give waxy solid. Branch numbers were calculated from the integration value of methyl, methylene, methine proton regions in ^{1}H-NMR spectra.

Norbornene polymerization was carried out by the same method and condition reported previously in the literature [2].

3.6. Crystallographic studies

Crystals coated with grease (Apiezon N) were mounted inside a thin glass tube with epoxy glue and placed on an Enraf–Nonius CCD single crystal X-ray diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$Å). The structures were solved by direct methods (SHELXS-97) [11] and refined against all F^2 data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions.

3.6.1. Crystal data for 4

C$_{48}$H$_{30}$BF$_{15}$NNiO$_2$P, $M = 1038.22$, red crystals, crystal size $0.3 \times 0.3 \times 0.2$ mm, orthorhombic, space group *Pbca*, temperature 293(2) K, $a = 13.0699(2)$, $b = 19.8973(3)$, $c = 34.8018(6)$ Å, $V = 9050.4(2)$ Å^3, $Z = 8$, $D_{calcd} = 1.524$ Mg m^{-3}, $F(000) = 4192$, 9877 reflections collected in $h(-13/13)$, $k(-20/20)$, $l(-36/36)$, measured in the range $1.17° < \theta < 21.72°$, $R_{int} = 0.0408$, 625 parameters, 0 restraints, $R_1 = 0.0549$, $wR_2 = 0.1633$ (for reflections with $I > 2\sigma(I)$), $R_1 = 0.0945$, $wR_2 = 0.2027$, Goodness-of fit $= 1.084$, largest difference peak and hole: $0.589/-0.660$ e Å^{-3}.

3.6.2. Crystal data for 5

C$_{45}$H$_{21}$BF$_{15}$NNiO$_2$, $M = 962.15$, light yellow crystals, crystal size $0.3 \times 0.2 \times 0.15$ mm, triclinic, space group $P\bar{1}$, temperature 293(2) K, $a = 13.083(2)$, $b = 13.416(2)$, $c = 13.397(2)$ Å, $\alpha = 80.321(8)$, $\beta = 68.169(11)$, $\gamma = 71.599(10)°$, $V = 2067.8(5)$ Å^3, $Z = 2$, $D_{calcd} = 1.545$ Mg m^{-3}, $F(000) = 964$, 6664 reflections collected in $h(-12/12)$, $k(-12/12)$, $l(-12/12)$, measured in the range $1.60° < \theta < 19.96°$, $R_{int} = 0.0951$, 586 parameters, 0 restraints, $R_1 = 0.0734$, $wR_2 = 0.1780$ (for reflections with $I > 2\sigma(I)$), $R_1 = 0.1871$, $wR_2 = 0.2812$, Goodness-of-fit $= 0.950$, largest difference peak and hole: $0.460/-0.645$ e Å^{-3}.

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 199002 and 199003 for compounds **4** and **5**). Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033: e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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