

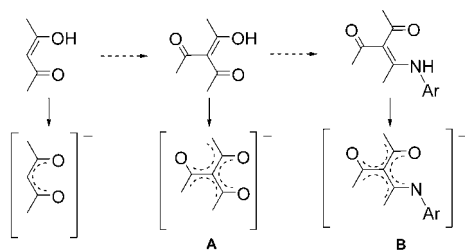
Remote Activation of Nickel Catalysts for Ethylene Oligomerization**

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An important consideration in the design of homogenous transition-metal initiators for the oligomerization and polymerization of olefins concerns the mode of activation. While neutral initiators are becoming increasingly available,^[1] the majority are cationic species generated upon addition of a strong Lewis acid, in the presence or absence of an alkylating agent, to a neutral organometallic precursor. The most typical activators are alkylaluminoxanes^[2] and well-defined Lewis acids, such as $B(C_6F_5)_3$.^[3] For example, $B(C_6F_5)_3$ reacts with $[Cp_2ZrMe_2]$ ($Cp = C_5H_5$) to give $[Cp_2ZrMe(MeB(C_6F_5)_3)]$.^[4] The dynamics of the resulting cation/anion pair, such as dissociation equilibria or the ability of the olefin to displace the anion, are important in determining the availability of the active site and the overall reactivity towards the unsaturated organic substrate.^[3,5]

Zwitterionic initiators, which provide an intermediate choice between cationic and neutral species for specifying reactivity and functionality tolerance, are fewer in number.^[6–10] In the case of $[(H_3C)C[N(C_6H_5)]C[O-B(C_6F_5)_3]-[N(C_6H_5)]-\kappa^2N,N']Ni(\eta^3-CH_2C_6H_5)]$, the Lewis acid attaches to a site removed from the trajectory of the incoming substrate and no dissociative process is required for initiation or propagation of oligomerization or polymerization reactions.^[11] This complex has found utility in the design of tandem copolymerization reactions for producing branched polyethylene from ethylene alone.^[12]

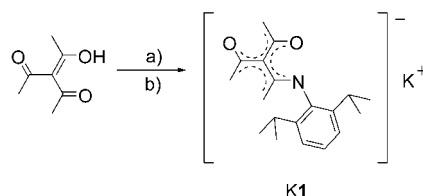
Herein we provide a design for a ligand with an electronically delocalized conduit that extends the distance between the metal and the site of Lewis acid attachment. Our rationale begins with the well-known bidentate acetylacetonate (acac) ligand, which forms readily from 4-hydroxypent-3-ene-2-one. Extension of the framework by addition of an acetyl group at the internal carbon atom yields commercially available triacetyl methane (3-(1-hydroxyethylidene)-2,4-pentanedione), which, upon deprotonation, is anticipated to yield the delocalized structure **A** in Scheme 1. Replacement of one of the oxygen atoms by an aryl-substituted nitrogen group provides 3-[1-(arylamino)ethylidene]pentane-2,4-dione derivatives and anionic structures, such as **B** (Scheme 1). On the basis of additional steric bulk from the aromatic unit, we anticipated π coordination to nickel complexes. However, it also seemed plausible that a strong and large Lewis acid



Scheme 1. General ligand design.

would prefer binding to an O site and force π coordination to the nickel.

Condensation of 2,6-diisopropylaniline with triacetyl methane in toluene using a catalytic amount of *p*-toluenesulfonic acid provides 3-[1-(2,6-diisopropylphenylamino)ethylidene]pentane-2,4-dione. The 2,6-diisopropylphenyl group was chosen for its stabilization of reactive nickel centers and tendency to increase the molecular weight of the products of ethylene addition reactions.^[13] Subsequent deprotonation with KH in THF provides the potassium salt of the ligand (**K1**) in 46% overall yield starting from triacetyl methane (Scheme 2).



Scheme 2. Synthesis of the potassium salt of the ligand (**K1**); a) 2,6-diisopropylaniline, *p*-toluenesulfonic acid monohydrate, toluene; b) KH, THF.

1H and ^{31}P NMR spectroscopy show that the reaction of **K1** with $[Ni(\eta^1-CH_2C_6H_5)Cl(PMe_3)_2]$ ^[14] provides an organometallic compound which contains the organic fragment in **K1**, an η^1 -benzyl group (1H NMR: $\delta = 7.68$ ppm), and a coordinated trimethylphosphine ligand. These data do not allow for unambiguous determination of the ligand coordination mode. Single crystals of the product suitable for X-ray diffraction studies were obtained from a solution of pentane (Figure 1).^[15] The product is therefore **2**, as shown in Scheme 3. The nickel center has a distorted square-planar coordination geometry with the 3-[1-(2,6-diisopropylphenyl-imino)ethyl]acetylacetonate ligand bound through the two oxygen atoms at nearly equal Ni–O separations (1.889(2) and 1.8982(19) Å). The bond lengths, C1–O1 (1.269(3) Å), C3–O2 (1.276(3) Å), C1–C2 (1.411(4) Å), and C2–C3 (1.399(4) Å), are intermediate between those of typical single and double bonds. The coplanar disposition of C1, C2, C3, O1, and O2 atoms is consistent with a delocalized electronic structure.

The addition of one equivalent $B(C_6F_5)_3$ to **2** was monitored by NMR spectroscopy in C_6D_6 . Quick formation of a new organometallic product is detected, which contains a coordinated trimethylphosphine ligand (1H NMR: $\delta =$

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[**] This work was supported by the US Department of Energy (Grant Number: DE-FG03098ER14910).

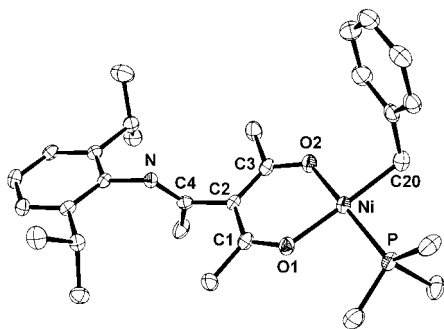
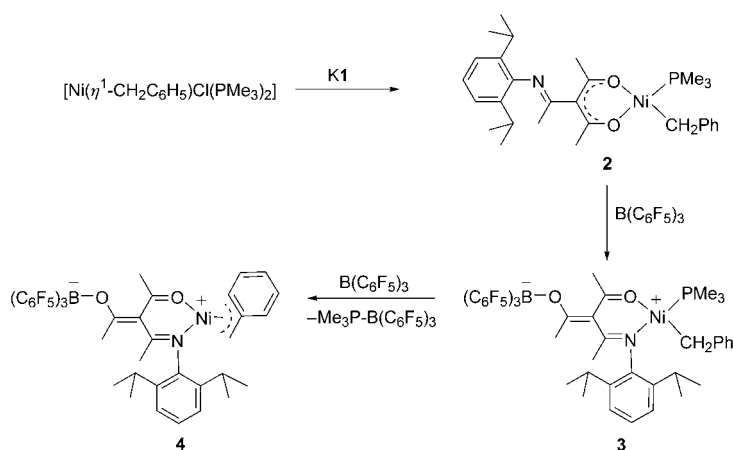


Figure 1. ORTEP drawing of **2**; thermal ellipsoids set at 50% probability, hydrogen atoms are omitted for clarity.



Scheme 3. Synthesis of compounds **2**, **3**, and **4**.

0.46 ppm; ^{31}P NMR: $\delta = -7.92$ ppm), $\text{B}(\text{C}_6\text{F}_5)_3$ (^{11}B NMR: $\delta = -12.55$ ppm), and an $\eta^1\text{-CH}_2\text{C}_6\text{H}_5$ fragment (^1H NMR: $\delta = 7.40$ ppm). Single crystals formed directly from the C_6D_6 solution and the solid-state structure was determined by crystallographic methods (Figure 2).^[15] These data indicate that the molecular structure of **3** is as shown in Scheme 3, where one of the carbonyl groups binds $\text{B}(\text{C}_6\text{F}_5)_3$. The transformation from **2** to **3** requires for the ligand to change its binding mode. Our current thinking is that this process is likely from a small amount of the NO bound regioisomer of **2**, which is in equilibrium with the OO bound counterpart. Coordination of the oxygen center to boron drives the equilibrium to the NO isomer. Although the product may be a mixture of *E*- and *Z*-isomers, only the isomer that minimizes steric interactions between the bulky 2,6-diisopropylphenyl substituent and $\text{B}(\text{C}_6\text{F}_5)_3$ is observed.

The structural parameters in **3** offer insight into bond localization and charge distribution. The C2–C3 separation (1.371(5) Å) is consistent with a double bond, whereas the C2–C1 (1.466(5) Å) and C2–C4 (1.486(5) Å) separations reveal substantial single-bond character. This localized bonding in the chelating ring forces C2 away from the O1–C1–C4–N plane. The nickel center is also removed from this plane (0.95 Å) and the overall six-member cyclic structure adopts a boat-like conformation (Figure 2b).^[16] These observations are consistent with the bond order of **3** shown in Scheme 3 and

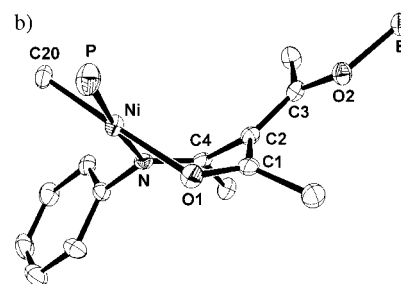
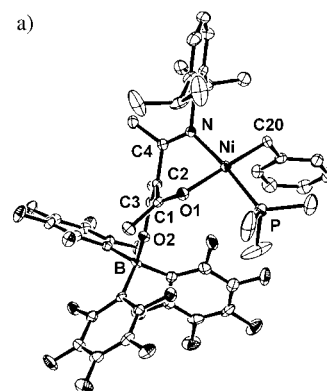
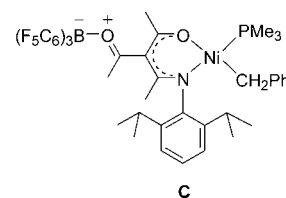


Figure 2. ORTEP diagrams of the molecular structure of compound **3**. a) Complete structure and b) the environment close to the nickel center. Thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity.

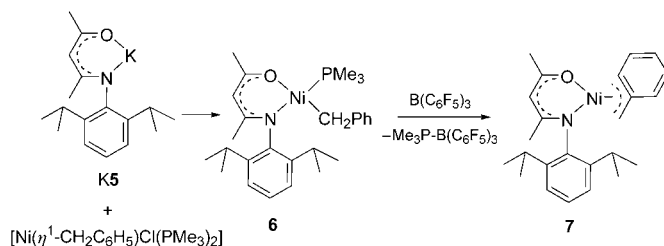
indicate that a contribution from structure **C** is not significant. As a result, we expect a zwitterionic structure for **3** with a large partial positive charge on the nickel center.



A new complex is formed on addition of one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ to **3** along with a white precipitate which corresponds to $\text{Me}_3\text{P-B}(\text{C}_6\text{F}_5)_3$. The same products are formed by addition of two equivalents $\text{B}(\text{C}_6\text{F}_5)_3$ to **2**. Characterization by ^1H , ^{13}C , ^{11}B and ^{19}F NMR spectroscopy shows that the nickel-containing product forms nearly quantitatively and contains the fragment corresponding to ligand **1**, $\text{B}(\text{C}_6\text{F}_5)_3$ (^{11}B NMR: $\delta = -13.25$ ppm) and an $\eta^3\text{-benzyl}$ ligand (^1H NMR: $\delta = 6.26$ ppm). Based on these data we propose that the reaction removes the trimethylphosphine from the coordination sphere of nickel and yields **4** (see Scheme 3). Repeated efforts to structurally characterize **4** were not successful.

Two ketoaryliminato compounds (**6** and **7**) were prepared to provide a baseline measure for reactivity towards ethylene and to provide a comparison of ligand structures. As shown in

Scheme 4, the reaction of potassium 4-(2,6-diisopropylphenylimino)acetylacetonate (**K5**) with $[\text{Ni}(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)\text{Cl}(\text{PMe}_3)_2]$ provides a new compound, **6**. NMR spectroscopy indicates that the compound contains the organic fragment in



Scheme 4. Synthesis of compounds **6** and **7**.

K5, an η^1 -benzyl group (^1H : NMR $\delta = 7.90$ ppm) and a coordinated trimethylphosphine ligand.^[17] Single crystals of **6** were grown from a pentane solution (Figure 3).^[15] A distorted

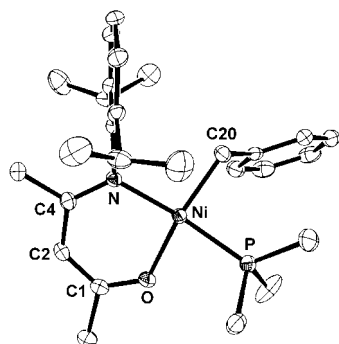


Figure 3. ORTEP diagram of the molecular structure of compound **6**, thermal ellipsoids are set at 50% probability, hydrogen atoms are omitted for clarity.

square-planar coordination geometry is observed, with the 4-(2,6-diisopropylphenylimino)acetylacetonate ligand coordinating by the nitrogen and oxygen atoms. The Ni–O and Ni–N bond lengths are 1.907(2) and 1.954(2), respectively. As in the case of **2**, the ligand fragment coordinated to Ni in **6** displays a delocalized electronic framework. For example, the bond lengths, C1–O (1.288(3) Å), C4–N (1.329(4) Å), C1–C2 (1.373(4) Å), and C2–C4 (1.410(4) Å), are intermediate between those of typical single and double bonds, and the C1, C2, C4, O, and N atoms are coplanar.

Comparison of the structures of **3** and **6** shows the influence of $\text{B}(\text{C}_6\text{F}_5)_3$ –carbonyl coordination on the ligand electronic structure. Compared with **6**, compound **3** contains longer C1–C2 and C2–C4 bonds and shorter C1–O1 and C4–N bonds (for **3**, C1–O1 1.241(4) Å, C4–N 1.288(5) Å). By this remote attachment of the Lewis acid, the bonding in the ligand becomes considerably more localized. It is also of note that the Ni–O bond (1.974(3) Å) in **3** is about 0.07 Å longer than that in **6** (1.907(2) Å), which reveals that the borated ligand in **3** is a poorer donor.

The addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to **6** in toluene results in the formation of $\text{Me}_3\text{P-B}(\text{C}_6\text{F}_5)_3$ and a new product **7**, which ^1H and ^{13}C NMR spectroscopy show contains the fragment in ligand **5** and an η^3 -benzyl ligand (^1H NMR: 6.68 ppm). Based on these results we propose that the net reaction involves borane–phosphine complexation and a hapticity increase by the benzyl ligand to fill the vacant coordination site. The final product is thus compound **7** in Scheme 4.

Addition of 100 psi (689.476 kPa) ethylene above a solution of **4** in toluene at 30°C results in the quick consumption of the ethylene, with an activity of 1450 kg product/mol Ni h. When 2 equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ are added as a “scrubbing agent”, the activity increases to 5450 kg product/mol Ni h. The products are a distribution of ethylene oligomers with an internal olefin structure. Similar products and activities are found by addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to **2** under ethylene. For example, the catalytic system produced by **2** and 3 equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ displays an activity of 3130 kg product/mol Ni h. No reaction occurs with **2** alone since the trimethylphosphine blocks coordination of ethylene. The activity of compound **7** towards ethylene under similar reaction conditions is only 51 kg product/mol Ni h. Therefore, the decreased electron density at the nickel center in **3**, relative to **7**, results in a substantial increase of reactivity.

In summary, addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to **2** results in a change of the binding mode of ligand **1** and in the coordination of a carbonyl functionality to boron. Direct attachment of $\text{B}(\text{C}_6\text{F}_5)_3$ to the “pendant” imino nitrogen in **2** is discouraged by the steric bulk of the diisopropylphenyl substituent. The conversion from **2** into **3** changes the binding mode of ligand **1** from LX (L = neutral two-electron donor, X = one-electron ligand in the covalent model)^[18] to L_2 , thereby removing electron density from the nickel center. The bonding parameters of **3** are consistent with little electron delocalization within the ligand framework. Removing the PMe_3 in **3** with $\text{B}(\text{C}_6\text{F}_5)_3$ induces an η^1 to η^3 hapticity change in the benzyl ligand to provide **4**, which is an effective ethylene oligomerization initiator. While we recognize that there are structural differences, the much higher reactivity of **4**, relative to **7**, highlights the effect of the reduced electron density at nickel. It is noteworthy that the Lewis acid makes its influence across the Ni–N–C–C–O structural unit.

Experimental Section

All manipulations were performed under a nitrogen atmosphere. Toluene and THF were distilled from benzophenone ketyl, and pentane was dried over Na/K alloy. The toluene for reactions with ethylene use was purchased from Aldrich (anhydrous grade) and purified further over Na/K alloy. Tris(pentafluorophenyl)boron was provided by Boulder Scientific Company, and purified further by sublimation. Ethylene (99.99%) was purchased from Matheson Trigas and purified by passing through Agilent moisture and oxygen/moisture traps. Triacetylmethane (3-(1-hydroxyethylidene)-2,4-pentanedione) and 2,6-diisopropylaniline were purchased from Aldrich and used without further purification. 4-(2,6-Diisopropylphenylimino)acetylacetone (**5**) was prepared from condensation of 2,6-diisopropylaniline with acetylacetone in benzene using a catalytic amount of *p*-toluenesulfonic acid.^[19] NMR spectra were recorded on a Varian 200, 400, or Bruker 200 spectrometers. ^1H NMR spectra were calibrated using signals from the solvent and are reported downfield

from tetramethylsilane (TMS) referenced to residual solvent ^1H signals. ^{11}B NMR, ^{19}F NMR, and ^{31}P NMR spectra were calibrated and reported downfield from external $\text{BF}_3\cdot\text{OEt}_2$, CFC_3 , and H_3PO_4 , respectively. Mass spectrometric analyses were obtained using a VG70 magnetic sector instrument. Elemental analyses were performed by Analytic Lab, Marine Science Institute, University of California, Santa Barbara.

1: 3-(1-hydroxyethylidene)-2,4-pentanedione (1.02 g, 7.2 mmol), 2,6-diisopropylaniline (1.06 g, 6.0 mmol), *p*-toluenesulfonic acid monohydrate (200 mg), and toluene (25 mL) were placed in a 50-mL flask equipped with Dean–Stark apparatus. After refluxing overnight, the solvent was removed under vacuum, and the residue was extracted with hexane (60 mL). The volume of the solution was then concentrated to approximately 5 mL, and cooled to -20°C to give a white solid (0.95 g, 53% yield, m.p. 103°C); ^1H NMR (200 MHz, C_6D_6 , 25°C): $\delta = 14.23$ (br s, 1H; NH), 7.15–6.95 (m, 3H; imine-ph-H), 2.98 (septet, $J = 6.8$ Hz, 2H; *i*Pr-CH), 2.19 (br s, 3H; CH_3 in acetyl), 2.10 (br s, 3H; CH_3 in acetyl), 1.75 (s, 3H; CH_3), 1.01 (d, $J = 6.6$ Hz, 6H; *i*Pr- CH_3), 0.99 ppm (d, $J = 6.6$ Hz, 6H; *i*Pr- CH_3); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): $\delta = 199.59$ (br s, carbonyl), 166.21 (imine), 145.67, 132.77, 128.87, 123.98 (ph-C), 114.57 (ethylene), 31.67 (br s, CH_3 in acetyl), 28.77 (*i*Pr-CH), 24.66 (*i*Pr- CH_3), 22.75 (*i*Pr- CH_3), 18.06 ppm (CH_3); HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_2$, 301.2042; found, 301.2047; Elemental analysis calcd (%) for $\text{C}_{19}\text{H}_{27}\text{NO}_2$: C 75.71, H 9.03, N 4.65; found: C 75.60, H 8.87, N 4.79.

K1: KH (64 mg, 1.6 mmol) was added to 3-[1-(2,6-diisopropylphenylamino)ethylidene]pentane-2,4-dione (452 mg, 1.5 mmol) in THF (5 g). After stirring for 3 h at room temperature, the reaction mixture was filtered, and the solvent was removed under vacuum. Trituration with pentane for 1 h gave the potassium salt (**K1**) as a white solid (441 mg, in 87% yield). ^1H NMR (200 MHz, $\text{C}_6\text{D}_6/\text{THF}$ (10/1), 25°C): $\delta = 7.13$ –6.98 (m, 3H; imine-ph-H), 2.22 (s, 6H; CH_3 in acetyl), 1.98 (s, 3H; CH_3), 1.80 (septet, $J = 7.2$ Hz, 2H; *i*Pr-CH), 1.24 (d, $J = 6.8$ Hz, 6H; *i*Pr- CH_3), 1.13 ppm (d, $J = 6.8$ Hz, 6H; *i*Pr- CH_3).

2: **K1** (290 mg, 0.85 mmol) and $[\text{Ni}(\eta^1\text{-CH}_2\text{C}_6\text{H}_5)\text{Cl}(\text{PMe}_3)_2]$ (288 mg, 0.85 mmol) were stirred in THF (5 g) for 3 h at room temperature. The reaction mixture was then filtered, the filtrate collected, and the THF removed under vacuum. The residue was extracted with pentane (25 g). The solution was concentrated to approximately 4 mL and cooled to -35°C to yield a yellow solid (360 mg, 80% yield). ^1H NMR (400 MHz, C_6D_6 , 25°C): $\delta = 7.68$ (d, $J = 7.2$ Hz, 2H; benzyl-ph- $\text{H}^{2,6}$), 7.25–7.11 (m, 6H; imine-ph-H and benzyl-ph- $\text{H}^{3,4,5}$), 3.06 (septet, $J = 6.8$ Hz, 2H; *i*Pr-CH), 2.18 (s, 3H; CH_3 in acetyl), 2.07 (d, $J = 6.8$ Hz, 2H; benzyl- CH_2), 1.92 (s, 3H; CH_3 in acetyl), 1.62 (s, 3H; CH_3), 1.16 (d, $J = 6.8$ Hz, 6H; *i*Pr- CH_3), 1.15 (d, $J = 6.8$ Hz, 6H; *i*Pr- CH_3), 0.76 ppm (d, $J = 10.0$ Hz, 9H; PCH_3); ^{13}C NMR (100 MHz, C_6D_6 , 25°C): $\delta = 184.96$, 183.98 (carbonyl), 169.87 (imine), 149.97, 147.14, 136.89, 129.13, 128.82, 124.41, 123.97, 123.44 (ph-C), 118.63 (ethylene), 28.46 (*i*Pr-CH), 27.88 (CH_3 in acetyl), 27.25 (CH_3 in acetyl), 24.56 (CH_3), 24.45 (*i*Pr- CH_3), 23.79 (*i*Pr- CH_3), 12.92 (d, $J = 28$ Hz, PCH_3), 12.28 ppm (d, $J = 26$ Hz, benzyl- CH_2); ^{31}P NMR (162 MHz, C_6D_6 , 25°C): $\delta = -6.79$ ppm; Elemental analysis calcd (%) for $\text{C}_{29}\text{H}_{42}\text{NO}_2\text{P}_2\text{Ni}$: C 66.18, H 8.04, N 2.66; found: C 66.11, H 7.40, N 2.82.

3: Compound **2** (10.5 mg, 0.02 mmol) and one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ (10.2 mg, 0.02 mmol) were mixed in C_6D_6 (0.9 mL). After 1 h, the solution was filtered, and ^1H , ^{19}F , ^{11}B and ^{31}P NMR spectra of the filtrate were recorded. The spectra indicated the nearly quantitative formation of complex **3**. ^1H NMR (400 MHz, C_6D_6 , 25°C): $\delta = 7.40$ (d, $J = 8.0$ Hz, 2H; benzyl-ph- $\text{H}^{2,6}$), 7.18–7.05 (m, 6H; imine-ph-H and benzyl-ph- $\text{H}^{3,4,5}$), 2.46 (s, 3H; CH_3 in acetyl), 2.12 (s, 3H; CH_3), 1.47 (s, 3H; $\text{CH}_3\text{-CO-B}(\text{C}_6\text{F}_5)_3$), 0.94 (br d, $J = 4.8$ Hz, 6H; *i*Pr- CH_3), 0.46 ppm (d, $J = 10.0$ Hz, 9H; PCH_3), *i*Pr-CH, benzyl- CH_2 and one of *i*Pr- CH_3 not observed; ^{19}F NMR (376 MHz, C_6D_6 , 25°C): $\delta = -133.83$, -157.97 , -163.91 ppm; ^{31}P NMR (162 MHz, C_6D_6 , 25°C): $\delta = -7.92$ ppm; ^{11}B NMR (161 MHz, C_6D_6 , 25°C): $\delta = -12.55$ ppm. Single crystals suitable for X-ray analysis formed after three days.

4: Compound **2** (52.6 mg, 0.10 mmol) and two equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ (102 mg, 0.20 mmol) were mixed in C_6H_6 (4.0 g). The color of the solution changed from orange to red immediately along with the formation of white precipitate. After stirring for 1 h, hexane (1.0 g) was added to the mixture and the reaction mixture was filtered after 15 min. The C_6H_6 and hexane were removed from the filtrate under vacuum, which gave a red solid product (91 mg, 94% yield). ^1H NMR (400 MHz, C_6D_6 , 25°C): $\delta = 7.27$ (t, $J = 7.6$ Hz, 1H; benzyl-ph- H^4), 7.00 (t, $J = 7.6$ Hz, 1H; imine-ph- H^4), 6.96 (d, $J = 7.4$ Hz, 2H; imine-ph- $\text{H}^{3,5}$), 6.90 (t, $J = 7.6$, 2H; benzyl-ph- $\text{H}^{3,5}$), 6.26 (d, $J = 7.0$ Hz, 2H; benzyl-ph- $\text{H}^{2,6}$), 2.88 (septet, $J = 6.8$ Hz, 2H; *i*Pr-CH), 2.01 (br s, 3H; CH_3 in acetyl), 1.80 (s, 3H; CH_3), 1.48 (br s, 3H; $\text{CH}_3\text{-CO-B}(\text{C}_6\text{F}_5)_3$), 1.31 (d, $J = 6.8$ Hz, 6H; *i*Pr- CH_3), 0.96 (s, 2H; benzyl- CH_2), 0.85 ppm (d, $J = 6.8$ Hz, 6H; *i*Pr- CH_3); ^{13}C NMR (50 MHz, C_6D_6 , 25°C): $\delta = 184.93$, 174.46, 151.30, 146.48, 140.41, 138.76, 138.05, 135.41, 129.59, 125.05 and 116.25 (carbonyl, imine and ph-C), 107.94 (ethylene), 31.06, 29.27 and 25.07 (CH_3 in acetyl, $\text{CH}_3\text{-CO-B}(\text{C}_6\text{F}_5)_3$ and CH_3), 28.61 (*i*Pr-CH), 24.89 (*i*Pr- CH_3), 24.09 (*i*Pr- CH_3), 23.46 ppm (benzyl- CH_2); ^{19}F NMR (C_6D_6 , 376 MHz, 25°C): $\delta = -133.79$, -158.13 , -164.29 ppm; ^{11}B NMR (C_6D_6 , 161 MHz, 25°C): $\delta = -13.25$ ppm; Elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{33}\text{NO}_2\text{BF}_{15}\text{Ni}$: C 54.92, H 3.46, N 1.46; found: C 53.71, H 3.51, N 1.45.

6: Compound **6** was prepared in 90% yield from potassium 4-(2,6-diisopropylphenylimino)acetylacetonate by the same method for preparing **2**. ^1H NMR (400 MHz, C_6D_6 , 25°C): $\delta = 7.90$ (d, $J = 7.2$ Hz, 2H; benzyl-ph- $\text{H}^{2,6}$), 7.08–6.97 (m, 6H; imine-ph-H and benzyl-ph- $\text{H}^{3,4,5}$), 5.13 (s, 1H; CH), 4.07 (septet, $J = 6.8$ Hz, 2H; *i*Pr-CH), 1.81 (s, 3H; CH_3), 1.59 (s, 3H; CH_3), 1.40 (d, $J = 6.8$ Hz, 6H; *i*Pr- CH_3), 1.21 (d, $J = 7.2$ Hz, 6H; *i*Pr- CH_3), 0.81 (s, 2H; benzyl- CH_2), 0.66 ppm (d, $J = 9.6$ Hz, 9H; PCH_3); ^{13}C NMR (100 MHz, C_6D_6 , 25°C): $\delta = 176.42$ (carbonyl), 166.02 (imine), 147.79, 142.16, 130.36, 127.99, 126.01, 124.02, 123.60, 123.60 (ph-C), 98.29 (ethylene), 28.63 (*i*Pr-CH), 26.64 (CH_3), 26.02 (CH_3), 25.07 (*i*Pr- CH_3), 24.86 (*i*Pr- CH_3), 12.55 (d, $J = 26$ Hz, PCH_3), 10.04 ppm (d, $J = 24$ Hz, benzyl- CH_2); ^{31}P NMR (162 MHz, C_6D_6 , 25°C): $\delta = -13.26$ ppm; Elemental analysis calcd (%) for $\text{C}_{27}\text{H}_{40}\text{NOPNi}$: C 66.96, H 8.33, N 2.89; found: C 67.56, H 8.51, N 3.02.

7: $\text{B}(\text{C}_6\text{F}_5)_3$ (153 mg, 0.30 mmol) in toluene (2 g) was added to **6** (145 mg, 0.30 mmol) in toluene (2 g). The color of solution changed from orange to dark red, and a white precipitate formed after several minutes. After stirring for 1 h, 1 g hexane was added to the mixture and the reaction mixture was filtered after 15 min. Solvents were removed from the filtrate under vacuum and the residue was extracted with hexane (1 g). The hexane was removed under vacuum to afford 114 mg of **7** in 93% yield. ^1H NMR (400 MHz, C_6D_6 , 25°C): $\delta = 7.46$ (t, $J = 7.6$ Hz, 1H; benzyl-ph- H^4), 7.08–7.05 (m, 5H; imine-ph-H and benzyl-ph- $\text{H}^{3,5}$), 6.68 (dd, $J = 8.0$ Hz, 2H; benzyl-ph- $\text{H}^{2,6}$), 4.85 (s, 1H; CH), 3.85 (septet, $J = 6.8$ Hz, 2H; *i*Pr-CH), 1.70 (s, 3H; CH_3), 1.42 (d, $J = 6.8$ Hz, 6H; *i*Pr- CH_3), 1.41 (s, 3H; CH_3), 1.13 (d, $J = 6.8$ Hz, 6H; *i*Pr- CH_3), 0.70 ppm (s, 2H; benzyl- CH_2); ^{13}C NMR (100 MHz, C_6D_6 , 25°C): $\delta = 178.30$ (carbonyl), 165.22 (imine), 151.91, 140.10, 134.91, 127.62, 125.67, 124.05, 116.92, 107.65 (ph-C), 97.71 (ethylene), 28.88 (CH_3), 28.56 (*i*Pr-CH), 27.09 (CH_3), 24.68 (*i*Pr- CH_3), 24.53 (*i*Pr- CH_3), 23.06 ppm (benzyl- CH_2); Elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{31}\text{NONi}$: C 70.62, H 7.65, N 3.43; found: C 70.42, H 7.53, N 3.48.

Typical reaction with ethylene: Compound **4** (5 μmol) in toluene (0.50 g) was added to a 70-mL glass reactor charged with toluene (27.50 g). The reactor was assembled and brought out of the glove box. After stirring the solution at 30°C for 2 min, ethylene was fed continuously for 20 min under a pressure of 100 psi (689.476 kPa). The reaction was quenched by release of ethylene pressure and addition of acetone (1 mL). The solvent was removed to afford a viscous oil, which was further dried under high vacuum overnight. The yield was measured by weighing the viscous oil or by weighing the

entire reaction assembly before and after reaction; the two techniques are in agreement to within $\pm 5\%$.

Received: August 12, 2004

Published online: January 12, 2005

Keywords: ethylene oligomerization · homogeneous catalysis · Lewis acids · nickel · zwitterionic compounds

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- [15] a) Crystal data for **2**: $C_{29}H_{42}NO_2PNi$, $M_r = 526.32$, monoclinic, space group $P2_1/c$, $a = 13.270(2)$, $b = 26.931(4)$, $c = 7.9511(13)$ Å, $\beta = 99.479(3)^\circ$, $V = 2802.7(8)$ Å³, $Z = 4$, orange, crystal size $0.3 \times 0.15 \times 0.1$ mm³, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $T = 117(1)$ K, $R = 5.57\%$, $wR = 12.78\%$ for 4582 unique reflections with $I > 2\sigma(I)$. Crystal data for **3**: $C_{53}H_{42}D_6BF_{15}NO_2PNi$, $M_r = 1122.42$, triclinic, space group $P\bar{1}$, $a = 10.7104(11)$, $b = 17.4223(17)$, $c = 27.722(3)$ Å, $\alpha = 94.128(2)$, $\beta = 91.465(2)$, $\gamma = 101.601(2)^\circ$, $V = 5049.9(9)$ Å³, $Z = 4$, yellow, crystal size $0.25 \times 0.2 \times 0.1$ mm³, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $T = 117(1)$ K, $R = 6.68\%$, $wR = 15.45\%$ for 14927 unique reflections with $I > 2\sigma(I)$. Crystal data for **6**: $C_{27}H_{40}NOPNi$, $M_r = 484.28$, triclinic, space group $P\bar{1}$, $a = 9.5913(8)$, $b = 11.4579(10)$, $c = 13.7938(12)$ Å, $\alpha = 108.936(2)$, $\beta = 90.072(3)$, $\gamma = 111.424(2)^\circ$, $V = 1322.4(2)$ Å³, $Z = 2$, orange, crystal size $0.25 \times 0.2 \times 0.15$ mm³, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $T = 117(1)$ K, $R = 4.19\%$, $wR = 10.00\%$ for 5050 unique reflections with $I > 2\sigma(I)$. b) CCDC-245971 (**2**), CCDC-245972 (**3**), and CCDC-245973 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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