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Boron trifluoride activation of ethylene oligomerization and polymerization catalysts

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Dedicated in honor of Professor Richard R. Schrock

Abstract

Addition of $BF_3 \cdot Et_2O$ to {[(C_6H_5)_2 $PC_6H_4(\mu-CO_2$)- $\kappa^3 P$, *O*, *O*']Ni(η^1 -CH_2C_6H_5)} gives [(C_6H_5)_2 $PC_6H_4C(O-BF_3)O-\kappa^2 P$, *O*]Ni(η^3 -CH_2C_6H_5) (4). The single crystal structure of **4** is consistent with substantial positive charge at the nickel atom. Addition of ethylene to solutions of **4** in toluene provides ethylene oligomers. The average molecular weight of the products is larger than that of the oligomers obtained using [(C_6H_5)_2 $PC_6H_4C(OB(C_6F_5)_3)O-\kappa^2 P$, *O*]Ni(η^3 -CH_2C_6H_5) (1). When 2 equiv. of Et₂O·BF₃ are added to {(H_3C)C[N(2,6-(CHMe_2)_2-C_6H_3)]C(O)[N(2,6-(CHMe_2)_2-C_6H_3)]- $\kappa^2 N$, *O*}Ni(η^1 -CH_2C_6H_5) (7). Two isomers of **7** are observed by NMR spectroscopy and are incorporated into the crystal lattice, as shown by X-ray diffraction studies. Polyethylene is obtained upon exposure of a solution of **7** to ethylene. Active species can also be generated in situ by addition of BF₃ gas, Et₂O·BF₃ or [†]BuMeO·BF₃ to **5**.

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1. Introduction

Transition metal-mediated ethylene polymerization and oligomerization catalysts are under intense investigation in academic and industrial laboratories [1]. Metallocenes and other single-site catalysts provide access to new manufacturing opportunities and to materials with properties not obtained using the more established heterogeneous processes [2]. Oligomerization catalysts have also recently appeared with extremely high reactivity toward ethylene and with remarkable specificity toward 1-alkenes [3]. A *general* feature of these reactions is the generation of highly active species by combination of a transition metal precatalyst with a suitable co-catalyst.

The importance of co-catalysts has coupled their design and performance to new ligand-metal combina-

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tions available for precatalyst development [4]. An important consideration in metallocene chemistry is that the final cost of the activator frequently exceeds that of the transition metal reagent. The majority of cocatalysts are derived from aluminum alkyls, alkylaluminoxanes or perfluoroaryl boranes. An interplay between several kinetic and thermodynamic factors determines the utility of a co-catalyst but, after activation, the cocatalyst is transformed into an anion which is loosely associated with the electrophilic metal center [5]. Because the structure and dynamics of alkylaluminoxanes are complex and they must be used in large excess, the highly Lewis acidic perfluoroaryl borane reagents, such as $B(C_6F_5)_3$, provide better defined catalysts. In a typical reaction, $B(C_6F_5)_3$ reacts with a neutral metallocene of general type Cp_2ZrMe_2 (Cp = cyclopentadienylderivative) to give $Cp_2ZrMe(MeB(C_6F_5)_3)$ [6]. It is widely accepted that anion-cation separation or displacement of the borate anion $(MeB(C_6F_5)_3)$ by the olefin is required for the insertion reaction to take place [5].

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We recently reported that attachment of $B(C_6F_5)_3$ to a site *removed* from the monomer trajectory can be used to activate nickel-based oligomerization and polymerization catalysts [7]. For example, $[(C_6H_5)_2PC_6H_4C_ (OB(C_6F_5)_3)O-\kappa^2 P, O]Ni(\eta^3-CH_2CMeCH_2)$ displays an activity toward ethylene orders of magnitude greater than the precursor $[(C_6H_5)_2PC_6H_4C(O)O-\kappa^2P,O]Ni(\eta^3-$ CH₂CMeCH₂) [8]. Faster initiation occurs by use of the isoelectronic n³-CH₂C₆H₅ ligand in [(C₆H₅)₂PC₆H₄C- $(OB(C_6F_5)_3)O-\kappa^2 P, O]Ni(\eta^3-CH_2C_6H_5)$ (1), relative to the methallyl counterpart. The two resonances shown for 1 (Scheme 1) show the net withdrawal of electron density from the metal atom. Conceptually, this mode of activation is different from other reactions where the counteranion needs to decoordinate in order to offer a vacant site for the monomer or be displaced by the incoming substrate [9]. Compound $\{(H_3C)C[N(2,6 (CHMe_2)_2 - C_6H_3)$]C[O-B(C₆F₅)₃][N(2,6-(CHMe_2)_2- C_6H_3]- $\kappa^2 N, N'$ }Ni(η^3 -CH₂C₆H₅) (2) is highly active and produces high molecular weight polyethylene.

The Lewis acidity of the activator, $B(C_6F_5)_3$ is comparable to that of BF_3 [10–12], therefore it seemed plausible that the action of the simple trihaloborane reagent could be used in generating initiators analogous to 1 and 2. Despite this competitive acidity, the use of BF₃ in metallocene chemistry is prevented by facile fluoride transfer to the transition metal [13]. In 1 and 2, charge buildup at boron and the metal are not as extreme as in the prototypical case of Cp₂ZrMe(MeB- $(C_6F_5)_3$). This feature, coupled to the greater tolerance toward functional groups displayed by late metals, is expected to make fluoride transfer less pronounced. Ethylene olgomerization catalysts have been prepared by addition of BF₃ to allyl-nickel alkoxides, though the activated species were not clearly defined [14]. We note also that certain cationic nickel olefin polymerization catalysts have been shown to be inert towards anions such as BF_4^- and PF_6^- [1d,1e].

In this contribution we show that, indeed, the above considerations are appropriate and that BF_3 can be used to generate complexes analogous to 1 and 2. These

complexes are useful precatalysts for the oligomerization and polymerization of ethylene.

2. Experimental

2.1. General remarks

All manipulations were carried out in an inert atmosphere of Ar or nitrogen using standard glovebox and Schlenk techniques [15]. $[(C_6H_5)_2PC_6H_4C(O B(C_6F_5)_3)O-\kappa^2 P, O]Ni(\eta^3-CH_2C_6H_5)$ (1)[7b], {[(C_6H_5)₂ PC_6H_4 (μ -CO₂)- $\kappa^3 P, O, O'$]Ni(η^1 -CH₂ C_6H_5)} [7b] and $\{(H_3C)C[N(2,6-(CHMe_2)_2-C_6H_3)]C(O)[N(2,6-(CHMe_2)_2-C_6H_3)]C(O)]N(2,6-(CHMe_2)_2-C_6H_3)]C(O)[N(2,CHMe_2)]C(O)[N(2,CHMe_2)]C(O)[N(2,CHMe_2)]$ $(CHMe_2)_2 - C_6H_3$]- $\kappa^2 N, O$ } Ni $(\eta^1 - CH_2C_6H_5)(PMe_3)$ (5) [7a] were prepared according to literature procedures. BF₃·Et₂O and BF₃·MeO^tBu were obtained from Aldrich and used as received. Tris(pentafluorophenyl)borane was obtained from Boulder Scientific Company, Mead, Colorado and was sublimed under high vacuum prior to use. Benzene-d₆ and C₅H₁₂ were distilled from sodium benzophenone ketyl. Toluene was distilled from Na-K alloy. ¹H, ¹⁹F and ³¹P{¹H} NMR spectra were acquired using a Varian Unity 400 spectrometer at ambient temperature. ¹H spectra are referenced internally to the solvent resonances, while 19 F and 31 P{ 1 H} are referenced externally to α, α, α -trifluorotoluene (0.0 ppm) and 85% H₃PO₄ (0.0 ppm), respectively. ${}^{13}C{}^{1}H{}$ and ¹¹B{¹H} spectra were recorded on a Varian Unity 500 spectrometer and are referenced internally to solvent resonances and externally to BF₃·Et₂O, respectively. IR data were collected on a Shimadzu FTIR-8300 spectrometer. GPC analyses were carried out by Equistar Chemicals, Cincinnati, OH. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

2.2. Preparation of $[(C_6H_5)_2PC_6H_4C(O-BF_3)O-\kappa^2P,O]Ni(\eta^3-CH_2C_6H_5)$ (4)

Boron trifluoride diethyl etherate (70 mg, 490 μ mol) was added with rapid stirring to a slurry of **3** (172 mg,



Scheme 1. Ethylene oligomerization and polymerization initiators.

378 μ mol) in 3 ml CH₂Cl₂. The reaction mixture quickly turned dark red and homogeneous and was stirred for an additional hour. The solvent was removed in vacuo. The residue was redissolved in a few drops of CH₂Cl₂, precipitated by addition of $C_6H_5CH_3$ (approximately 5) ml) and was triturated overnight. The solid was collected by filtration, washed once with $C_6H_5CH_3$ and twice with C₅H₁₂. Drying in vacuo yields 126 mg (64%) of an orange powder. The structure of 4 was confirmed by X-ray crystallography [16]. Anal. Calc. for C₂₆H₂₁BF₃NiO₂P: C, 59.72; H, 4.05. Found: C, 59.50; H, 3.98%; ¹H NMR (CD₂Cl₂, 400 MHz): δ 8.38 (ddd, 1H, ${}^{3}J(H,H) = 7.9$, ${}^{4}J(H,P) = 4.8$, ${}^{4}J(H,H) = 1.0$ Hz; oto carboxylate), 7.88–7.20 (m, 16H; Ph and η^3 -benzyl-(m,p), 7.14 (d, 2H, ${}^{3}J(H,H) = 7.7$ Hz; η^{3} -benzyl-o), 1.63 (d, 2H, ${}^{3}J(H,P) = 3.8$ Hz; $CH_{2}Ph$); ${}^{13}C{}^{1}H$ NMR (CD₂Cl₂, 125 MHz): δ 170.3 (COO), 135.8–128.8 (m; C-arom.), 116.6 (d, ${}^{2}J(C,P) = 5.5$ Hz; η^{3} -benzyl-*o*), 27.9 $(d, {}^{2}J(C,P) = 5.5 \text{ Hz}; CH_{2}Ph); {}^{19}F \text{ NMR} (CD_{2}Cl_{2}, 376)$ MHz, CF₃Ph): $\delta = -87.4$; ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz, H_3PO_4): δ 22.1; ¹¹B{¹H} NMR (CD₂Cl₂, 160 MHz, BF₃·OEt₂): δ -0.82.

2.3. Preparation of $\{(H_3C)C[N(2,6-(CHMe_2)_2-C_6H_3)]C[O-BF_3][N(2,6-(CHMe_2)_2-C_6H_3)]-\kappa^2N,N'\}Ni(\eta^3-CH_2C_6H_5)$ (7)

Boron trifluoride diethyl etherate (37 mg, 260 µmol) in 250 μ l C₆H₆ was added to compound 5 (80 mg, 130 μ mol) in 1 ml C₆H₆ and mixed thoroughly. The solution color changed from orange-red to dark red. This solution was allowed to stand for 2 additional hours, during which a colorless solid precipitates and the solution becomes less intensely colored. Filtration through oven-dried glass wool and removal of volatiles in vacuo gave an orange powder which was redissolved in approximately 1 ml of C₆H₅CH₃ and placed in a C_5H_{12} filled chamber at -35 °C for 2 days. Red crystals were isolated, after removal of the mother liquor and drying in vacuo to yield 20 mg (25%) of 7. A second crop obtained in the same manner gave 12 mg (15%) of the desired product. The structure of 7 was confirmed by Xray crystallography [17] Anal. Calc. for C₃₄H₄₄BF₃-NiN₂O: C, 65.53; H, 7.12; N, 4.49. Found: C, 65.47; H, 7.21; N, 4.49; two pseudo-rotamers in a 1:1 ratio are observable in the NMR spectra. ¹H NMR (C_6D_6 , 400 MHz): δ 7.20–6.82 (m, 12H; both rotamers ⁱPr₂C₆H₃), 6.63 (t, 1H, ${}^{3}J(H,H) = 7.5$ Hz; η^{3} -benzyl-p), 6.57 (t, 1H, ${}^{3}J(H,H) = 7.6$ Hz; η^{3} -benzyl-*p*), 6.19 (pst, 2H, ${}^{3}J(H,H) = 7.8$ Hz; η^{3} -benzyl-m), 6.13 (pst, 2H. ${}^{3}J(H,H) = 7.7$ Hz, η^{3} -benzyl-*p*), 5.86 (d, 4H, ${}^{3}J(H,H) = 7.3$ Hz; both rotamers η^{3} -benzyl-o), 3.65 (sept, 2H, ${}^{3}J(H,H) = 6.9$ Hz; CHMe₂), 3.23 (sept, 2H, ${}^{3}J(H,H) = 6.9$ Hz; CHMe₂), 3.18 (sept, 2H, ${}^{3}J(H,H) =$ 6.8 Hz; CHMe₂), 2.81 (sept, 2H, ${}^{3}J(H,H) = 6.8$ Hz; CHMe₂), 2.28 (s, 3H; Me), 2.24 (s, 3H, Me), 1.50 (d, 6H,

 ${}^{3}J(H,H) = 6.7$ Hz; MeCHCH₃), 1.50 (s, 2H; CH₂Ph), 1.38 (d, 6H, ${}^{3}J(H,H) = 6.7$ Hz; MeCHCH₃), 1.37 (d, 6H, ${}^{3}J(H,H) = 6.9$ Hz; MeCHCH₃), 1.37 (s, 2H; CH₂Ph), 1.20 (d, 6H, ${}^{3}J(H,H) = 6.7$ Hz; MeCHCH₃), 1.09 (d, 6H, ${}^{3}J(H,H) = 6.7$ Hz; MeCHCH₃), 0.96 (d, 6H, ${}^{3}J(H,H) =$ 6.9 Hz; MeCHCH₃), 0.94 (d, 6H; ${}^{3}J(H,H) = 6.9$ Hz; $^{3}J(H,H) = 6.7$ $MeCHCH_3$), 0.85 (d, 6H, Hz: MeCHCH₃); ${}^{13}C{}^{1}H$ NMR (C₆D₆, 125 MHz): δ 180.3, 177.6, 141.0, 140.8, 138.52, 138.47, 136.0, 135.4, 129.2, 127.8, 127.5, 124.6, 124.3, 124.1, 123.7, 104.3, 104.0, 39.7, 38.8, 29.8, 29.7, 29.4, 29.3, 24.8, 24.5, 24.3, 24.1, 23.93, 23.85, 23.5, 21.0, 14.6; ¹⁹F NMR (C₆D₆, 376 MHz, CF_3Ph): δ -81.7, -82.0; ¹¹B{¹H} NMR (C₆D₆, 160 MHz, BF₃·OEt₂): δ -0.71 (br).

2.4. Exchange reaction with 4 and $B(C_6F_5)_3$

Inside the glovebox, a resealable NMR tube was charged with 14.0 mg (26.8 μ mol) **4** and approximately 500 μ l CD₂Cl₂. ¹H, ³¹P, ¹⁹F and ¹¹B NMR spectra were obtained as references for the starting material. The tube was then brought back into the box and a solution of 13.7 mg (26.9 μ mol) B(C₆F₅)₃ in approximately 100 μ l CD₂Cl₂ was added to the solution of **4** with no observable changes in color. ¹H, ³¹P, ¹⁹F and ¹¹B NMR spectra were recollected and showed only compound **1**. The solution was then degassed on a high vacuum line at -78 °C and backfilled with BF₃ gas. Reacquisition of **4**; only **1** was observed.

2.5. Ethylene oligomerization procedure

Inside the glovebox, the appropriate mass of a stock solution (1.00 μ mol g⁻¹) of **4** or powder form of **1** was weighed into a 5 ml vial, transferred to a Fisher-Porter bottle and diluted with 30 ml (25.8 g) of $C_6H_5CH_3$. Once the apparatus was assembled, it was brought out of the box and placed in a room temperature (r.t.) water bath. Ethylene was introduced at the desired pressure and the oligomerization was allowed to proceed for 15 min monitoring the monomer consumption with a mass flow controller to determine the activity of the catalyst. At the end of the reaction time, the vessel was vented and the reaction quenched by addition of 5 ml H₂O and stirring rapidly for approximately 5 min. The $C_6H_5CH_3$ layer was then collected and analyzed by gas chromatography to determine the distribution of oligomers, as well as by proton NMR to determine the composition of α -olefins, internal olefins and dimers [18].

2.6. Ethylene polymerization procedure

Inside the glovebox, a Fisher–Porter bottle was charged with 14 μ mol of 7 or 5 with the appropriate amount of BF₃ and diluted with 30 ml of C₆H₅CH₃. A

stainless steel reactor head was assembled and the system brought out of the glove box. Ethylene was fed continuously for 15 min under 100 psig pressure with a r.t. external water bath to control the reaction temperature. The ethylene flow rate was monitored by a mass flow controller. The reaction was quenched by release of ethylene pressure and addition of C_3H_6O (30 ml). Polyethylene powder was collected by filtration and dried in vacuo. The activity of the catalyst was determined by the mass of the polymer obtained and correlated against the amount of ethylene measured by the mass flow controller. Branch numbers were calculated from the integration values of methyl, methylene and methine proton regions in ¹H NMR spectra collected at 115 °C in C₆H₆-d₆ and 1,2,4-trichlorobenzene (v/v, 1:4). The polymers were further characterized by GPC and DSC.

3. Results and discussion

3.1. Synthesis and characterization of $[(C_6H_5)_2 - PC_6H_4C(O-BF_3)O-\kappa^2P, O]Ni(\eta^3-CH_2C_6H_5)$ (4)

Addition of excess $BF_3 \cdot Et_2O$ (approximately 1.5 equiv.) to a slurry of {[(C_6H_5)_2PC_6H_4(μ -CO₂)- $\kappa^3 P, O, O'$]Ni(η^1 -CH₂C₆H₅)}₂ (**3**) in dichloromethane results in the formation of a red homogeneous solution. Addition of toluene to this solution precipitates an orange powder that can be isolated by filtration. The ¹H NMR spectrum of this solid in CD₂Cl₂ is consistent with the structure [(C_6H_5)₂PC₆H₄C(O-BF₃)O- $\kappa^2 P, O$]Ni(η^3 -CH₂C₆H₅) (**4**) as shown in Eq. (1).



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): Ni(1)–O(2), 1.905(2); Ni(1)–P(1), 2.1270(7); Ni(1)–C(37), 1.957(3); Ni(1)–C(31), 2.029(2); Ni(1)–C(36), 2.228(2); O(2)–C(47), 1.241(3); O(1)–C(47), 1.291(2). Selected bond angles (°): O(2)–Ni(1)–P(1), 94.92(5); P(1)–Ni(1)–C(37), 100.18(8); C(37)–Ni(1)–C(36), 70.73(10); C(36)–Ni(1)–O(2), 95.93(8).

isometric to that of 1. The only statistically significant difference lies within the C–O bond distances. In 1, the two C–O distances are equal in length within statistical error (2.7 σ). In 4, the C(47)–O(2) length (1.241(3) Å) is shorter than the C(47)–O(1) distance (1.291(2) Å) which *suggests* a stronger contribution from resonance structure of type A in Scheme 1 and a more cationic nickel center in 4 relative to 1.

IR spectroscopy in CH₂Cl₂ can be used to gauge



Single crystals of **4** suitable for X-ray diffraction studies were obtained by layering pentane on top of a CD_2Cl_2 solution, and allowing the mixture to slowly diffuse overnight. The results of this study, shown in Fig. 1, show a pseudo square planar arrangement of ligands around nickel. With the exception of the boron substituents, the solid state structure of **4** is nearly differences in C–O bond strengths. For 4, v(C=O) is 1617 cm⁻¹, which is higher than the v(C=O) for 1, 1602 cm⁻¹. However, the relative C=O bond strengths determined by IR spectroscopy do not indicate which of the two possible resonance structures dominates, only that 4 lies further towards one of the resonance extremes than 1. If the bond order observed in the solid structure

Table 1							
Oligomerization	of	C_2H_4	by	1	and	4	a

Entry	Precatalyst	P (psig)	[Ni] (µM)	Activity ^b	K ^c	$\%$ α-Olefin d	% 2-Alkyl-1-alkene ^d	% Internal ^d
1	4	100	470	1066	0.26 ^e	60	22	18
2	4	100	220	1210	0.21	98	2	
3	4	100	90	1290	0.18	100		
4	4	50	220	590	0.19	99	1	
5	1	100	90	4500	0.07	79	14	7

^a Reaction conditions: toluene, 15 min, 20 °C.

^b Kg ethylene consumed per mole *pre* catalyst per hour.

^c Determined by GC.

^d Mole percent determined by ¹H NMR spectroscopy.

^e The exothermicity of the reaction prevented temperature control.

is maintained in solution, then the higher stretching frequency observed in 4 supports the notion of a more positively charged nickel atom.

A competition experiment was set up by adding 1 equiv. of $B(C_6F_5)_3$ to a solution of 4 in CD_2Cl_2 . ¹H NMR spectroscopy showed quantitative formation of 1. Formation of 4 was not reestablished, even after addition of excess (approximately 5 equiv.) of BF₃ gas to the solution. Therefore, the borane adduct is stronger in 1, relative to 4 and $B(C_6F_5)_3$ is a stronger Lewis acid towards 3 than BF₃. This observation coupled with the higher activity of 1 vis-à-vis 4 is the strongest evidence that the nickel center in 1 is more positively charged than in 4.

3.2. Ethylene oligomerization by $[(C_6H_5)_2PC_6H_4C(O-BF_3)O-\kappa^2P,O]Ni(\eta^3-CH_2C_6H_5)$ (4)

Rapid consumption of ethylene is observed upon exposure to a toluene solution of **4**. The results of these experiments are summarized in Table 1. Entries 1-3show the effect of concentration. Comparison against entry 4 shows that reducing ethylene pressure by a factor of two decreases the activity by a half. The activity of **4** towards ethylene is lower than for **1** (entries 3 and 5). The activity versus time profiles of the two catalysts measured by use of a mass flow controller are similar in shape, with the activity dropping with reaction time. The selectivity for α -olefins is enhanced by lowering the concentration of nickel (entries 1-3) or by increasing the ethylene pressure (entries 2-4). Similar trends are observed for **1** [7b].

The K factor, defined by $K = (\text{moles } C_{n+2} \text{ olefin})/(\text{moles } C_n \text{ olefin}) = R_P/(R_P + R_{CT})$, where R_P and R_{CT} are the rates of propagation and chain termination, respectively, is readily determined by GC analysis of the oligomer products and can be used to probe how structural variations on the active species influence the propagation and insertion processes. Entries 2, 3, and 5 show that the K factor remains constant within experimental certainty. Thus, both propagation and chain

transfer are first order in monomer. Similar dependence of rates on monomer concentration occurs for the catalyst derived from 1 [7b]. Because the reaction is highly exothermic, it is not possible to control temperature at higher nickel concentrations and a higher Kfactor is observed (entry 1). Interestingly, reactions with $4/C_2H_4$ have a higher K factor than the $1/C_2H_4$ system, indicating that they produce products with larger average molecular mass. That 1 and 4 are nearly isostructural near the vicinity of the nickel atom indicates that the difference in activity and chain length selectivity is largely electronic in origin.

3.3. Synthesis and characterization of $\{(H_3C)C[N(2,6-(CHMe_2)_2-C_6H_3)]C[O-BF_3][N(2,6-(CHMe_2)_2-C_6H_3)]-\kappa^2N,N'\}Ni(\eta^3-CH_2C_6H_5)$ (7)

Addition of 2 equiv. BF₃·OEt₂ to {(H₃C)C[N(2,6- $(CHMe_2)_2 - C_6H_3)$]C(O)[N(2,6-(CHMe_2)_2 - C_6H_3)]- $\kappa^2 N, O$ Ni(η^1 -CH₂C₆H₅)(PMe₃) (5) in C₆D₆ intensifies the red color of the solution. ¹H NMR spectroscopy shows complete consumption of 5 and the clean formation of a product. Since ³¹P NMR signals are observed which do not correspond to F_3B-PMe_3 , we suspect that this initial product is compound 6 in Eq. (2). An alternative coordination of BF3 to amide nitrogen cannot be ruled out at this stage. After 45 min, a fine dispersion of F₃B–PMe₃ forms. The new organometallic product exhibits resonances indicative of an η^3 -benzyl ligand in the range of 5.8-6.7 ppm, significantly upfield from the η^1 -benzyl species 5 (7–8 ppm). Two species form and are assigned to coordination isomers of the benzyl ligand about nickel. The product does not contain a coordinated phosphine, as determined by ³¹P NMR spectroscopy. These data are consistent with the formation of $\{(H_3C)C[N(2,6-(CHMe_2)_2-C_6H_3)]C[O BF_3$][N(2,6-(CHMe_2)_2-C_6H_3)]- $\kappa^2 N, N'$ }Ni(η^3 - $CH_2C_6H_5$ (7), as shown in Eq. (2). Compound 7 exists as a mixture of interconverting isomers.

X-ray quality crystals were obtained by dissolving the product in a small amount of toluene, layering pentane



on top and letting the solvents diffuse at -35 °C. The structure of this compound is shown in Fig. 2. The two possible coordination isomers of the η^3 -benzyl ligand are incorporated into the lattice, resulting in a disor-



Fig. 2. ORTEP view of 7 showing the average structure of the two isomers. Thermal ellipsoids are shown at 20% probability level. Hydrogen atoms have been omitted for clarity.

Table 2 Activity of 7 towards C_2H_4 ^a

dered benzyl fragment. The error associated with the structural model prevents a detailed analysis of metrical parameters. Nonetheless, the connectivity is unambiguous and clearly shows that the BF_3 has been coordinated by the carbonyl functionality and that the two isomers are due to benzyl ligand orientation, rather than N,O bonding variations from the carboxamide functionality.

3.4. Ethylene polymerization by $\{(H_3C)C[N(2,6-(CHMe_2)_2-C_6H_3)]C[O-BF_3][N(2,6-(CHMe_2)_2-C_6H_3)]-\kappa^2N,N'\}Ni(\eta^3-CH_2C_6H_5)$ (7)

A series of polymerization reactions were studied in which compound 7 was isolated and used or generated directly from 5 by addition of a suitable BF₃ source. This study is summarized in Table 2. Entry 1 demonstrates that 7 is an active initiator for ethylene polymerization. Generation of 7 in situ, either by addition of BF₃ gas or an etherate adduct, prior to introduction of ethylene also yields active polymerization systems (entries 2–5). This procedure allows one to save the time and effort required to isolate and purify 7. Highest activity is obtained when 10 equiv. of BF₃ gas is added to 5 (entry 2). A branched structure is observed for all

Entry	Source	[B]/[Ni]	Activity ^b	$M_{\rm w}/1000$	PDI	Branches ^c	$T_{\rm m}$ (°C)
1	7		200	769	22 ^d	20	129
2	5 /BF ₃ ^e	10	270	45.7	7.76	32	115
3	5/BF ₃ ^e	f	170	343	18.6	22	126
4	$5/Et_2O \cdot BF_3$	13	140	259	4.25	16	114
5	$5/^{t}BuMeO \cdot BF_{3}$	13	150	82.2	4.22	31	106
6	$5/B(C_6F_5)_3$	13	350	302	4.60	20	123

^a Polymerization conditions: [Ni] = 0.47 mM in toluene, 100 psig ethylene, 15 min.

^b Kg product (mol Ni h) $^{-1}$.

^c Determined by ¹H NMR and corresponds to the number of branches/1000 carbons.

^d Bimodal distribution with centers at 31.6 and 631×10^3 g mol⁻¹.

^e Obtained from aliquots of a saturated solution of the gas in toluene.

^f Saturated solution of BF₃ in toluene (approximately 27 mM) was used as reaction solvent.

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polymers and the amount of branching is controlled to a slight extent by the source of BF₃. For example, higher branching occurs when using ^tBuMeO·BF₃ instead of Et₂O·BF₃ (entries 4 and 5). In comparison to $2/C_2H_4$ in which **2** is generated in situ (entry 6), the polymerization system produced by $7/C_2H_4$ under these conditions exhibits a decreased activity towards ethylene.

4. Conclusions

In summary, we have shown that it is possible to activate single site oligomerization and polymerization catalysts by use of the inexpensive reagent BF_3 [14,19]. This co-activator may be used directly as a gas or in the form of etherate adducts. The activated precatalysts have been fully characterized by NMR spectroscopy and X-ray crystallography. The key reactivity design consists of attaching the Lewis acid at a site away from monomer approach and the absence of a counteranion, which must dissociate to allow monomer insertion.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 169902–169903 for compounds 4 and 7. Copies of the data may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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[17] (a) Crystal data for 7: $C_{34}H_{44}BF_3N_2NiO$, $M_r = 623.23$, crystal dimensions = $0.20 \times 0.20 \times 0.02 \text{ mm}^3$, monoclinic, space group P_{2_1}/n , a = 10.614(5), b = 20.812(9), c = 15.025(6) Å, $\beta = 99.627(9)^\circ$, V = 3272(2) Å³, Z = 4, $\rho_{calc} = 1.265$ Mg m⁻³, T = 165 K, absorption coefficient $\mu = 0.638 \text{ mm}^{-1}$. Data were collected on a Bruker SMART CCD diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å), 10 399 reflections collected, 3060 independent ($R_{int} = 0.1137$). Refinement on F^2 with SHELXTL.

Final indices $R_1 = 0.0967$, $wR_2 = 0.2266$ with $I > 2\sigma(I)$. The largest peak and hole in a final difference electron density map were 0.578 and -0.310 e Å⁻³.

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