

# Investigations into the Mechanism of Activation and Initiation of Ethylene Polymerization by Bis(imino)pyridine Cobalt Catalysts: Synthesis, Structures, and Deuterium Labeling Studies

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The activation of bis(imino)pyridine cobalt(II) precatalysts by MAO leads initially to a bis(imino)pyridine cobalt(I) cationic species with no cobalt–C(alkyl) bond into which insertion can occur. Mechanistic studies have shown that the initiation of polymerization from this species involves incorporation of alkyl groups from the cocatalyst, most likely involving attack of methide anion (from the counteranion) on a cobalt–ethylene species.

## Introduction

In recent years there has been much interest in the discovery and development of olefin polymerization catalysts based on the late transition metals.<sup>1</sup> Following the recognition of the potential of nickel complexes in olefin polymerization,<sup>2</sup> the subsequent discovery of highly active catalysts based on iron and cobalt<sup>3</sup> signposted the way forward for further advances in the design and applications of late transition metal systems. While much is now known about the influence of ligand substituents on the performance of iron- and cobalt-based systems,<sup>3,4</sup> there remains much to be understood about the mechanism of activation and initiation of polymerization.

In general, there are a number of common links between late and early transition metal systems, both in their activation pathways and the nature of the propagating species. For example, catalyst activation can usually be accomplished by treatment of a dihalide metal precursor complex with an activator such as MAO, leading initially to dialkylation of the metal center, followed by methide group abstraction to afford a cationic alkyl which, in the presence of a suitably noncoordinating counteranion, functions as the propagating species.<sup>5</sup> It has also been shown for both late and early transition metal species that a low-valent precursor route can be used to generate the active site. This involves attack by a strong Lewis acid, for example, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, MAO, or Al<sub>2</sub>Me<sub>6</sub>, on a coordinated olefin or,

more commonly, a diene.<sup>6</sup> In the iron-based polymerization system, there is good evidence for the binding of trialkylaluminum reagents at the active center,<sup>7</sup> which explains the tendency for these systems to engage in “chain transfer to metal” processes, although the oxidation state of the metal center in the active species is still open to debate.<sup>8</sup>

For cobalt, it would be tempting to expect that the dihalide precursor would follow a “traditional” activation pathway, leading to a cationic alkyl propagating species.

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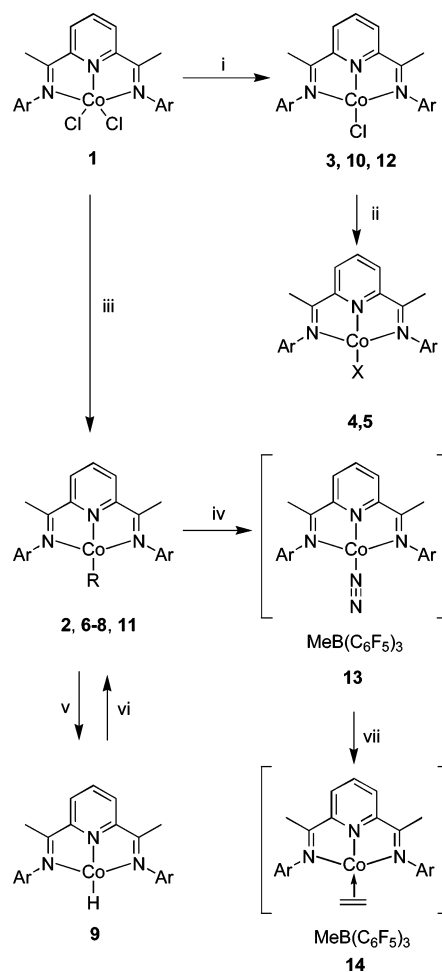
However, it has been shown in preliminary studies that the  $\text{LCoCl}_2$  precursors, rather than undergoing dialkylation to give  $\text{LCoR}_2$ , are first reduced by the alkylating agent to  $\text{LCoCl}$  and then alkylated by the same reagent to give cobalt(I) alkyl species.<sup>9</sup> These, however, do not insert olefins. Rather, in the presence of a strong Lewis acid, the alkyl group is abstracted to afford cationic cobalt(I) species that are capable of binding ethylene<sup>9a</sup> and that are the direct precursors to the propagating species. In this paper we describe the synthesis and characterization of the key intermediates in the activation process and describe studies directed toward obtaining an improved understanding of the mechanism by which cationic cobalt(I) complexes convert to an active propagating species.

## Results

**Synthesis and Characterization.** Our initial investigations into the cobalt system commenced with attempts to synthesize a cobalt(II) dimethyl complex, with the anticipation of studying reactions of this complex with well-defined activating agents. The synthesis of the cobalt(II) species was attempted by the reaction of  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}]\text{CoCl}_2$  (**1**) with 2 equiv of alkylating agents such as MeLi, MeMgX, and Me<sub>2</sub>Mg. In no case was the anticipated dimethyl complex isolated. Rather, a diamagnetic Co(I) complex was isolated and characterized as  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}]\text{CoMe}$  (**2**). The syntheses of this and other cobalt species in this work are summarized in Scheme 1. If the reaction with Grignard reagents ( $\text{X} = \text{Cl}, \text{Br}$ ) did not go to completion, NMR spectra of the crude products showed the presence of the cobalt halides  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}]\text{CoCl}$  (**3**) or  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}]\text{CoBr}$  (**4**) as intermediates, implying that the first step in this reaction is reduction to the cobalt(I) halide, followed by alkylation. The cobalt(I) chloride **3** can be accessed directly via the reduction of **1** by excess zinc in toluene at 50 °C. Upon treatment of **3** with trimethylsilylhalides, halogen exchange occurs to afford the bromo (**4**) and iodo (**5**) derivatives; these were not isolated but characterized in situ by NMR spectroscopy.

Other cobalt alkyl species can also be accessed using Grignard reagents, including  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}]\text{CoEt}^{10}$  (**6**),  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}]\text{Co}^n\text{Pr}^{10}$  (**7**), and  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}]\text{CoCH}_2\text{Ph}$  (**8**); the latter complex has also been described by Gal and co-workers.<sup>9b</sup> The resonances of the protons in the  $\beta$ -positions of the alkyl chains show unusually high-field chemical shifts ( $\delta$   $-1.18$  to  $-0.73$ ) with  $^1\text{J}_{\text{C-H}}$  coupling constants in the range expected for nonagostic alkyl groups (123–125 Hz). That the  $^1\text{J}_{\text{C-H}}$  coupling constants are virtually the same for **6** and **7** also indicates that there is no fluxional agostic interaction; a shift to a lower value would be expected on exchanging ethyl for propyl due to averaging over two rather than three  $\beta$ -hydrogens.<sup>11</sup> Addition-

**Scheme 1.** Summary of the Syntheses of Cobalt(I) Complexes<sup>a</sup>



<sup>a</sup> (i) Zn, toluene, 50 °C ( $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$  **3**;  $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$  **10**) or  $\text{C}_8\text{K}$ , toluene,  $-78$  °C ( $\text{Ar} = 2\text{-EtC}_6\text{H}_4$  **12**); (ii)  $\text{SiMe}_3\text{X}$ , 25 °C ( $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ,  $\text{X} = \text{Br}$  **4**, **5**); (iii)  $\text{RMgX}$ ,  $\text{Et}_2\text{O}$ ,  $-78$  °C ( $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ,  $\text{R} = \text{Me}$  **2**, **Et** **6**,  $^n\text{Pr}$  **7**,  $\text{CH}_2\text{Ph}$  **8**;  $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ,  $\text{R} = \text{Me}$  **11**); (iv)  $\text{B}(\text{C}_6\text{F}_5)_3$ , 25 °C ( $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ); (v)  $\text{H}_2$ , 25 °C ( $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ); (vi)  $\text{C}_2\text{H}_4$  or  $\text{C}_3\text{H}_6$ , 25 °C ( $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ) to afford **6** or **7**, respectively; (vii)  $\text{C}_2\text{H}_4$ , 25 °C ( $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ).

ally, no change in chemical shift was observed upon cooling a sample in toluene- $d_8$  to 193 K, nor upon the addition of a donor solvent such as THF or diethyl ether. It can reasonably be concluded that these unusual chemical shifts are due to ring current effects arising from the ligand aryl substituents, rather than due to the presence of  $\beta$ -agostic interactions.

The cobalt(I) alkyl complexes containing hydrogen atoms in the  $\beta$ -position of the chain are not stable over long periods, decomposing to unidentified diamagnetic products. The only volatile species isolable from these decomposition reactions are the corresponding alkanes, presumably arising via ligand cyclometalation reactions. The decomposition is slowed significantly in the presence of ethers and alkenes. A full description of the chemistry of these longer chain cobalt alkyl species has been reported elsewhere.<sup>10</sup>

The cobalt(I) hydride  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}]\text{CoH}$  (**9**) can be prepared via the reaction of **2**

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**Table 1. Variation in the Chemical Shifts of the Protons of the Ketimine Methyl Group and the *para*-Position of the Pyridine Ring with Substitution at the Cobalt Center**

complex	$\delta$ (ketimine)	$\delta$ ( <i>para</i> -H, py)
[2,6-{MeC=N(2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> N}]CoH, <sup>a</sup> <b>9</b>	-1.66	10.82
[2,6-{MeC=N(2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> N}]CoEt, <sup>a</sup> <b>6</b>	-1.33	10.25
[2,6-{MeC=N(2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> N}]CoCH <sub>2</sub> Ph, <sup>a</sup> <b>8</b>	-1.17	10.26
[2,6-{MeC=N(2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> N}]CoMe, <sup>a</sup> <b>2</b>	-1.14	10.19
[2,6-{MeC=N(2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> N}]CoI, <sup>a</sup> <b>5</b>	-0.37	10.15
[2,6-{MeC=N(2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> N}]CoBr, <sup>a</sup> <b>4</b>	-0.08	9.79
[2,6-{MeC=N(2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> N}]CoCl, <sup>a</sup> <b>3</b>	0.05	9.54
[{2,6-{MeC=N(2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> N}]Co(C <sub>2</sub> H <sub>4</sub> )}{MeB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> }] <sup>b</sup> , <b>14</b>	0.75	8.00
[{2,6-{MeC=N(2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> N}]Co(N <sub>2</sub> )}{MeB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> }] <sup>b</sup> , <b>13</b>	1.11	7.55

<sup>a</sup> In benzene-*d*<sub>6</sub>. <sup>b</sup> In toluene-*d*<sub>8</sub>.

with dihydrogen, producing methane as a byproduct.<sup>10,12</sup> **9** is insufficiently stable to allow its isolation, and so characterizing data have been obtained on samples prepared in situ. Attempts to synthesize the deuteride analogue via the reaction of **2** with <sup>2</sup>H<sub>2</sub> were unsuccessful due to scrambling of the deuterium into the isopropyl substituents of the ligand, providing a further indication that reversible ligand cyclometalation processes occur in these cobalt(I) bis(imino)pyridine complexes.

The chemistry outlined above is not unique to the di-(isopropyl)phenyl-substituted ligand. Analogous complexes containing the *N*-mesityl ligand, [2,6-{MeC=N(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N}]CoCl (**10**) and [2,6-{MeC=N(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N}]CoMe (**11**), and, for reasons that will become clear shortly, the *N*-2-EtC<sub>6</sub>H<sub>4</sub> derivative, [2,6-{MeC=N(2-EtC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N}]CoCl (**12**), have also been prepared and characterized.

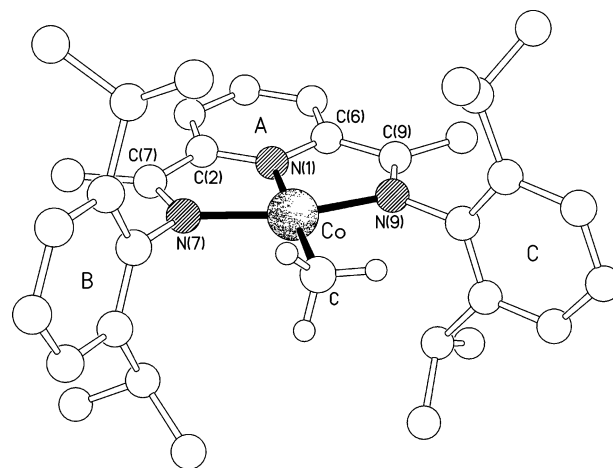
Certain features of the <sup>1</sup>H NMR spectra of the cobalt(I) complexes are worthy of note. The chemical shifts of certain ligand resonances are highly dependent upon the nature of the substitution at the cobalt center, with the singlet resonance of the ketimine methyl group and the triplet resonance of the proton in the *para*-position of the pyridine ring being particularly sensitive. The shift of the ketimine resonance correlates with the electrophilicity of the cobalt center (Table 1). Thus, the ketimine resonance of the cation **13** (vide infra), at  $\delta$  +1.11, compares with shifts of  $\delta$  0.05 to -0.37 for the halide derivatives **3**–**5**,  $\delta$  -1.14 to -1.33 for alkyl derivatives **2**, **6**, and **8**, and  $\delta$  -1.66 for complex **9**. The resonance of the proton in the *para*-position of the pyridine ring shows the opposite trend, being  $\delta$  7.55 and 10.19 for **13** and **2**, respectively. The variation in the chemical shifts has been explained by the presence of a low-lying triplet state that can be thermally populated from the singlet ground state.<sup>12,13</sup>

In our earlier communication<sup>9a</sup> we reported the solid state structures of **3** and **13** (see Supporting Information, Figures S3 and S4), and we have now also determined the X-ray structures of crystals of **2** and **10** (comparative selected bond lengths and angles for all four complexes are given in Table 2). The core structures of **2** (Figure 1) and **10** (Figure 2) are very similar to those of **3** and **13**, having approximate C<sub>2v</sub> symmetry about the Co–N(py) bond. In both **2** and **10** the metal

**Table 2. Comparative Selected Bond Lengths (Å) and Angles (deg) for **2**, **3**, **10**, and **13****

	<b>2</b> [X = Me]	<b>3</b> [X = Cl]	<b>10</b> [X = Cl]	<b>13</b> [X = N <sub>2</sub> ]
Co–X	1.960(4)	2.1807(10)	2.1672(13)	1.841(3)
Co–N(1)	1.833(3)	1.797(3)	1.793(3)	1.812(3)
Co–N(7)	1.907(3)	1.916(3)	1.914(3)	1.915(3)
Co–N(9)	1.903(3)	1.912(3)	1.914(3)	1.908(3)
C(7)–N(7)	1.335(4)	1.317(5)	1.328(5)	1.303(5)
C(9)–N(9)	1.329(5)	1.322(5)	1.325(4)	1.303(5)
C(2)–C(7)	1.443(5)	1.444(5)	1.432(5)	1.465(5)
C(6)–C(9)	1.434(5)	1.435(5)	1.442(5)	1.459(5)
N(7)–Ar	1.445(4)	1.449(5)	1.437(4)	1.452(4)
N(9)–Ar	1.441(5)	1.440(5)	1.443(4)	1.444(4)
N(1)–C(2)	1.366(4)	1.373(5)	1.365(4)	1.356(4)
N(1)–C(6)	1.365(4)	1.370(5)	1.375(4)	1.354(4)
N(1)–Co–X	178.94(17)	179.15(10)	176.65(11)	178.3(2)
N(7)–Co–X	98.95(14)	98.89(9)	99.40(9)	98.23(14)
N(9)–Co–X	98.70(15)	98.17(9)	97.25(9)	98.44(14)
N(1)–Co–N(7)	81.22(12)	81.35(14)	81.46(12)	81.67(12)
N(1)–Co–N(9)	81.11(12)	81.58(14)	81.96(12)	81.68(12)
N(7)–Co–N(9)	162.32(12)	162.92(12)	163.35(12)	163.31(12)
C(7)–N(7)–Ar	118.4(3)	118.6(3)	118.2(3)	119.9(3)
C(9)–N(9)–Ar	119.1(3)	119.5(3)	118.2(3)	119.5(3)

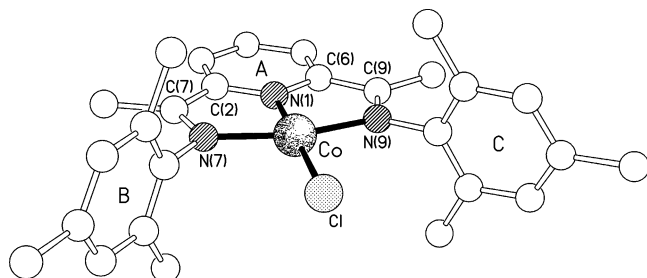
coordination plane extends to include the ligand backbone, the maximum deviations from planarity for the (C<sub>5</sub>H<sub>3</sub>N)(MeC=N–C<sub>i</sub>)<sub>2</sub>Co units being ca. 0.12 and 0.08 Å, respectively, cf. 0.03 and 0.08 Å in **3** and **13**, respectively. The pendant aryl rings are, as usual for bis(imino)pyridine ligands, inclined almost orthogonally to the planes of their parent nitrogen atoms, the N(7)–Ar, N(9)–Ar torsion angles being ca. 85°, 87° and 89°, 86° in **2** and **10**, respectively. (The geometries at these nitrogen centers are all trigonal planar, the central nitrogen lying in each case no more than ca. 0.04 Å out of its associated {C<sub>2</sub>Co} plane.) Inspection of the

**Figure 1. Molecular structure of **2**.**

(12) Knijnenburg, Q.; Hetterscheid, D.; Kooistra, T. M.; Budzelaar, P. H. M. *Eur. J. Inorg. Chem.* **2004**, 1204.

(13) While this description of the systems as cobalt(II) bound to a ligand radical may be correct, we will continue to refer to these systems as Co(I) in this article in order to avoid confusion with cobalt(II) complexes such as **1**. The distribution of electrons within the cobalt(I) complexes does not affect our later mechanistic experiments and conclusions.





**Figure 2.** Molecular structure of **10**.

comparative table of bond lengths and angles reveals that there are few instances where statistically significant differences of comparable parameters can be seen. In particular, there is no obvious variation in the angle of the aryl rings to the imine bond with variation of the bulk of the fourth substituent at the cobalt center (see the C(7)–N(7)–Ar and C(9)–N(9)–Ar angles). For the Co–N(1) bond to the central pyridyl ring, however, the distance seen in **2** is markedly longer than those seen in **3**, **10**, and **13**. The Co–N(imine) bonds are all statistically the same, although the imine bonds themselves in **13** are noticeably (though not significantly) shorter than in the other three species. For the bond angles, the only feature of note is a slight lateral displacement of the X ligand in **10** [where X = Cl]; in the other three structures the two N(imine)–Co–X angles are the same to within ca. 0.72°, but in **10** they are different by ca. 2.15°. Associated with this is a markedly more distorted N(1)–Co–X *trans* angle of 176.65(11)°, cf. 178.94(17)°, 179.15(10)°, and 178.3(2)° for **2**, **3**, and **13**, respectively.

The packing of molecules in the crystals of **2** is dominated by intermolecular C–H··· $\pi$  contacts. One of the *meta* protons on ring B in one molecule approaches the centroid of ring A in another (H···A 2.84 Å, C–H···A 136°, vector inclined by ca. 76° to the ring plane), the *para* proton of ring C approaches ring B (H···B 3.01 Å, C–H···B 165°, vector inclined by ca. 70° to the ring plane), and one of the C(7)–Me protons approaches ring C (H···C 2.96 Å, C–H···C 166°, vector inclined by ca. 75° to the ring plane). The effect of these interactions is to form a two-dimensional sheet of molecules in the 101 plane. The most notable intermolecular interactions in the structure of **10** involve the pyridyl ring A. There is a weak  $\pi$ – $\pi$  contact between this ring in one molecule and ring B in a glide related counterpart (centroid···centroid and mean interplanar separations of ca. 4.25 and 3.42 Å, respectively, rings inclined by ca. 5°), and the disposition of the two rings is such that one of the *para* methyl protons on ring B comes closest to the centroid of ring A (H···A 3.00 Å, C–H···A 124°, vector inclined by ca. 73° to the ring plane). The opposite face of ring A is approached by one of the *meta* methyl protons on ring C of a lattice translated molecule (H···A 3.09 Å, C–H···A 123°, vector inclined by ca. 73° to the ring plane), the two C–H··· $\pi$  contacts subtending an angle of ca. 147° at the centroid of ring A. As was seen in **2**, the combined effect of these intermolecular interactions is the formation of a two-dimensional sheet.

**Mechanism of Catalyst Activation and Initiation of Polymerization. Catalyst Activation.** The polyethylene produced by the cobalt system is linear, with

one vinyl and one methyl end group per chain.<sup>3</sup> This is consistent with the major termination process being  $\beta$ -hydrogen transfer, either via the metal center or directly to monomer. It is thus clear that significant amounts of chain-transfer to the aluminum cocatalyst do not occur for cobalt, unlike for closely related iron systems.<sup>3</sup>

The well-established mode of activation for both early and late transition metal complexes involves the transformation of a catalyst precursor  $L_nMX_2$  into an electron-deficient metal alkyl species  $[L_nM-R]^+$  by the action of MAO.<sup>5</sup> If this mode of activation were followed by the cobalt system, the formation of a 15-electron cobalt(II) species  $[LCo-R]^+$  would be anticipated. However, as described in the previous section, attempts to synthesize this putative species led to cobalt(I) products. Indeed, activation of the cobalt(I) chloride complex **3** with MAO affords a catalytically active species that displays the same activity as **1**/MAO; the resultant polymer also has identical properties (microstructure, molecular weight, PDI, end groups; see Figure S5 for GPC traces). The same catalytically active species thus appears to be present in each case, and in view of the reduction chemistry, the first species formed in the activation process is presumed to be  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}\}\text{CoCl}(\mathbf{3})]$ , which is then alkylated to form  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{C}_5\text{H}_3\text{N}\}\text{CoMe}(\mathbf{2})]$ ; subsequent transformations then form the active species. Similar conclusions were reached upon studying the reaction between **1** with small amounts of MAO.<sup>9b</sup>

Addition of ethylene to a solution of **2** in toluene does not lead to the formation of polymer, nor are any changes observed in the NMR spectrum of **2** under an atmosphere of ethylene. It is clear, therefore, that **2** is not the active species. Those alkyl compounds that have protons in the  $\beta$ -position of the chain (**6** and **7**) undergo exchange reactions with ethylene, but not insertion. Studies of this process have been reported separately.<sup>10</sup> The cobalt(I) hydride  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}\}\text{CoH}(\mathbf{9})]$  does react with ethylene, but only undergoes a single insertion to afford **6**.<sup>10</sup> It is thus clear that the Co(I) alkyl complexes are not the chain-propagating species in ethylene polymerization.

**Reactions of Cobalt(I) Alkyls with Lewis Acids.** Treatment of **2** with  $\text{Al}_2\text{Me}_6$  does not activate it toward ethylene polymerization. However, in situ NMR studies reveal that alkyl group exchange occurs between the aluminum and the cobalt centers. Although slow on the NMR time scale, addition of  $\text{Al}_2\text{Me}_6\text{-}d_{18}$  to a sample of **2** afforded a statistical distribution of protio- and deuterio-methyl groups between the two metals. Similarly, addition of  $\text{AlEt}_3$  afforded a mixture of **2** and **6**. It would thus appear that  $\text{Al}_2\text{Me}_6$  is not a sufficiently strong Lewis acid to activate **2** toward ethylene polymerization, and a stronger Lewis acid (e.g., MAO) is needed. We therefore decided to investigate the reaction of **2** with the strong Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$ . Upon mixing, an immediate color change occurred from claret to royal blue; the product of this reaction was identified as  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}\}\text{Co}(\text{N}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$ , **13-MeBAr**<sup>f</sup>.<sup>14</sup> The molecular structure of this compound has been reported previously and shows the

(14) This nomenclature is used so as to be able to refer to the cationic cobalt fragment as **13**, whether synthesized by the use of  $\text{B}(\text{C}_6\text{F}_5)_3$  or MAO; the MAO-activated cation will be referred to as **13-MAO**.

presence of an end-on bonded dinitrogen ligand.<sup>9a</sup> The [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> anion does not show any close interaction with the cobalt center in the solid state. This also appears to be the case in solution, where the <sup>19</sup>F NMR data are indicative of an anion that is not coordinated to the metal center.<sup>15</sup>

#### Reactions of Cobalt(I) Cations with Ethylene.

Exposure of a dark blue solution of 18 μmol of **13-MeBARf<sub>3</sub>** in toluene to ethylene resulted in a color change to aquamarine, concomitant with the onset of polymerization. Over a 20 min run 130 mg of polyethylene was produced, corresponding to an activity of 11 g/mmol bar h. Repeating this reaction in the presence of 5 equiv of Al<sub>2</sub>Me<sub>6</sub> as co-activator resulted in the formation of 1.12 g of polymer (96 g/mmol bar h), an order of magnitude increase in activity. The polymer formed has properties identical to that produced by **1/MAO**.

NMR spectroscopy is a useful tool for the study of these cobalt(I) species due to their diamagnetic nature and especially due to the aforementioned sensitivity of certain ligand proton resonances to groups attached to the cobalt center. The chemical shift of the ketimine methyl group is particularly useful in this respect, allowing even very closely related species to be distinguished. Addition of 1.0 equiv of ethylene to a solution of the cation afforded a species identifiable from its <sup>1</sup>H NMR spectrum as [{2,6-{MeC=N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N}-Co(η-C<sub>2</sub>H<sub>4</sub>)}][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> (**14-MeBARf<sub>3</sub>**). The ketimine resonance is now found at δ 0.75 (cf. δ 1.11 for the dinitrogen adduct), with the resonance attributable to bound ethylene occurring as a sharp singlet at δ 4.65 (cf. δ 5.24 for free ethylene). The small shift in the ethylene resonance upon binding to the cobalt center implies that the ethylene is only weakly bound; indeed, it can be removed by degassing the NMR sample. Addition of further equivalents of ethylene resulted in a rapid exchange between free and bound ethylene, affording an averaged chemical shift for all of the ethylene present in the system. The excess ethylene was consumed over time, resulting in the formation of polyethylene on the walls of the NMR tube. Once all excess ethylene had been consumed, the ethylene-adduct **14-MeBARf<sub>3</sub>** remained. No other organometallic species were discernible in the <sup>1</sup>H NMR spectrum during the polymerization.

The direct study of MAO-activated systems by NMR spectroscopy is generally complicated by the presence of an intense, broad resonance in the high-field region of the spectrum attributable to a variety of averaging Me-Al environments. Taking advantage of the highly sensitive nature of the chemical shifts of the ketimine methyl resonances, we decided to use ligands labeled with deuterium at their ketimine positions. These ligands are readily accessible from diacetylpyridine-*d*<sub>6</sub>,<sup>16</sup> and **1-d<sub>6</sub>**, **2-d<sub>6</sub>**, and **3-d<sub>6</sub>**, have been synthesized by routes described for their nonlabeled analogues. The activation of these compounds with MAO and the subsequent interaction of the activated species with ethylene can thus be conveniently studied using <sup>2</sup>H NMR spectroscopy, since only the ketimine resonance is observed for each species formed.

The reaction between **2-d<sub>6</sub>** and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in 2-chlorotoluene<sup>17</sup> afforded **13-d<sub>6</sub>-MeBARf<sub>3</sub>**, for which the <sup>2</sup>H NMR spectrum contained a sharp resonance at δ 1.2, consistent with the <sup>1</sup>H NMR spectrum of its per-protio analogue. Introduction of an atmosphere of ethylene to the NMR tube caused the resonance to shift to δ 0.83, a shift indicative of the ethylene adduct **14-d<sub>6</sub>-MeBARf<sub>3</sub>**.

The activation of **3-d<sub>6</sub>** in 2-chlorotoluene using dry MAO/Al<sub>2</sub>Me<sub>6</sub><sup>18</sup> (Al:Co = 14:1) afforded a species that displayed a ketimine methyl resonance at δ 0.2. A slightly broader resonance but at a similar chemical shift was also obtained upon activation of **1-d<sub>6</sub>** with the same MAO solution and the same Al:Co ratio. A ketimine methyl resonance at this chemical shift, partway between that of the cobalt(I) chloride **3-d<sub>6</sub>** and the cobalt(I) cation **13-d<sub>6</sub>-MeBARf<sub>3</sub>**, is likely to be the result of the interaction of the anion ([Cl-MAO]<sup>-</sup> or [Me-MAO]<sup>-</sup> formed during the activation process) with a cationic cobalt center. Addition of ethylene to the NMR tube gave rise to a ketimine resonance at ca. δ 0.9, a chemical shift very close to that observed for **14-d<sub>6</sub>-MeBARf<sub>3</sub>**. Thus, it can be reasonably concluded that addition of ethylene to the MAO-activated catalyst also results in the formation of the cationic ethylene species [{2,6-{MeC=N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N}-Co(η-C<sub>2</sub>H<sub>4</sub>)}]<sup>+</sup>, **14**. These observations are summarized in Scheme 2.

Unlike the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-activated system, once the ethylene in the MAO-activated system is consumed, the initial species is regenerated; that is, the resonance at δ 0.2 replaces the resonance at δ 0.9. This reflects the stronger coordinating ability of [Cl-MAO]<sup>-</sup> or [Me-MAO]<sup>-</sup> over [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup>, the anions derived from MAO being able to displace the bound ethylene, whereas the more weakly coordinating [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> counteranion cannot.

There are some initial conclusions that can be drawn from these results. First, the species that is initially formed upon activation, and thus the species from which the initiation of polymerization must occur, is a cobalt(I) cation, a species that contains *no* cobalt-C(alkyl) σ-bond. Second, the MAO cocatalyst appears to perform a number of important functions: (i) reduction of the cobalt(II) precatalyst to cobalt(I), (ii) alkylation of the cobalt(I) halide to cobalt(I) methyl, (iii) abstraction of a chloride or methide unit to give a cobalt-(I) cation, and (iv) stabilization of the active catalyst, most likely through the scavenging of impurities. It is also possible that the Al<sub>2</sub>Me<sub>6</sub> present in the MAO may enhance the rate of polymerization, as evidenced by the greater activity found upon addition of Al<sub>2</sub>Me<sub>6</sub> to **13-MeBARf<sub>3</sub>**.

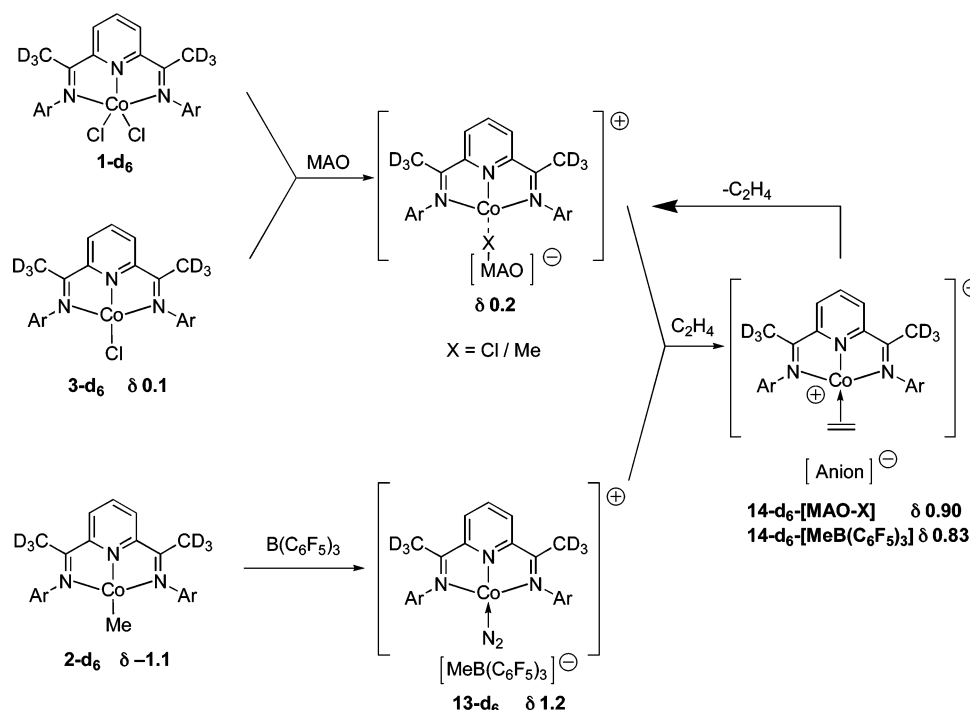
**Mechanism of Initiation.** Plausible pathways for transforming a cobalt cation with a bound ethylene into a complex with a Co-C(alkyl) bond are shown in Scheme 3. Pathway I involves nucleophilic attack by methide on the cobalt-bonded ethylene to give a cobalt-(I) alkyl species. The methide may be derived from the

(17) The MAO-activated system was insufficiently soluble in toluene to allow <sup>2</sup>H NMR data to be obtained. Although the cobalt(I) complexes are generally unstable in chlorinated and brominated solvents, leading to unidentified paramagnetic products, no decomposition is seen in the sterically protected 2-chlorotoluene over a period of at least 5 h.

(18) Dry MAO is the white solid obtained by removal of solvent and trialkylaluminums from a solution of MAO, followed by repeated slurring in heptane and removal of the volatile components.

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(16) Clentsmith, G. K. B.; Gibson, V. C.; Hitchcock, P. B.; Kimberley, B. C.; Rees, C. W. *Chem. Commun.* **2002**, 1498.

Scheme 2. Summary of  $^2\text{H}$  NMR Study of the Active System

[MeBar<sup>f</sup><sub>3</sub>]<sup>−</sup> or [Me-MAO]<sup>−</sup> counteranion, or another Al–Me bond. II is a closely related transformation, but here the Lewis acid remains associated with the alkyl group to form a bimetallic Co–Al/B complex, similar to the active species originally proposed by Natta.<sup>19</sup> A species of this type has recently been proposed to explain the activity of cationic zirconium complexes with no apparent Zr–alkyl bond.<sup>20</sup> III involves electrophilic attack of a Lewis acid on the bound ethylene in a fashion analogous to Erker's activation of zirconocene and nickel butadiene complexes, leading to a cobalt(III) center.<sup>6</sup> This Lewis acid may be the cocatalyst, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or MAO, or possibly another cobalt cation; the latter would lead initially to a bimetallic Co(I)/Co(III) species. In IV, oxidative coupling of two molecules of ethylene occurs to afford a cobaltacyclopentane species, where the metal center is now in the +3 oxidation state. Such a pathway would be analogous to the commonly postulated initial step of the Phillips and other chromium-based polymerization systems.<sup>21</sup> V involves the transfer of a methide group to the cobalt center, concomitant with electrophilic attack of the Lewis acid on the bound ethylene, leading to a net oxidation to cobalt(III). Insertion could potentially occur into either, or both, of the cobalt–carbon bonds. In VI, C–H activation of the bound ethylene molecule occurs to afford a cobalt(III) vinyl hydride species, a reaction that has precedence in the chemistry of the group 9 metals<sup>22</sup> and that has been proposed previously as an activation step in the dimerization of ethylene by a Co(I) tris(triphenylphosphine) cation.<sup>23</sup>

**Studies to Distinguish among Pathways I–VI.** Nucleophilic attack by methide on the bound ethylene, as shown in pathway I, leads to the formation of the

cobalt(I) propyl complex **7**. It is already known that cobalt(I) alkyls such as **7** do not polymerize ethylene. Pathway I can thus be ruled out. In II, the active site would effectively be a cobalt(I) alkyl interacting with a Lewis acid. But, we already know that the cobalt(I) alkyls are not active for ethylene polymerization in the presence of Al<sub>2</sub>Me<sub>6</sub>. Rather, alkyl group exchange is observed. Additionally, in the presence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or MAO, the cobalt-bonded alkyl group is abstracted to afford cationic cobalt(I) products rather than engaging in an interaction of the type found in II, and so this pathway can also be excluded.

In addressing pathway III, separate solutions of **13-MeBar<sup>f</sup><sub>3</sub>** were prepared via reactions of 18 μmol of **2** with 0.98 and 5.0 equiv of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, respectively; these were then exposed to 1 atm of ethylene. No difference in activity was observed between the two; both afforded 130 mg of polymer over a 20 min run, corresponding to activities of 11 g/mmol bar h. It is thus clear that the presence of excess Lewis acid is not required to initiate polymerization, implying that route III can be discounted as a mechanism for the initiation of polymerization. The low activities obtained may be due to the lack of any scavenger to remove impurities in the ethylene feed; the order of magnitude increase in activity upon adding small amounts of alkyl aluminums (vide supra) is consistent with this. A second cobalt center acting as a Lewis acid is highly unlikely due to the steric hindrance of the ligand system, the very low concentrations of the cobalt species in solution, and the

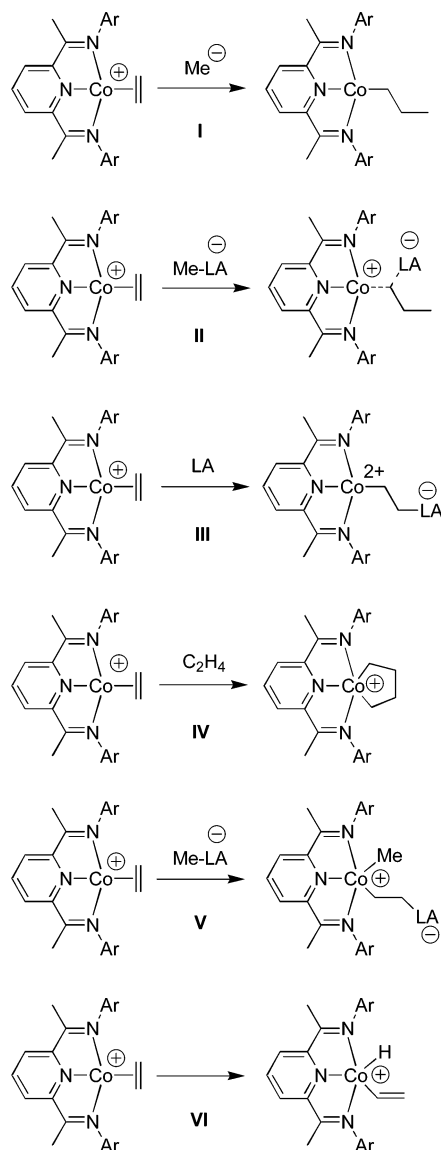
(19) Natta, G.; Mazzanti, G. *Tetrahedron* **1960**, *8*, 86.  
 (20) (a) Jin, J.; Wilson, D. R.; Chen, E. X.-Y. *Chem. Commun.* **2002**, 708. (b) Cano, J.; Royo, P.; Lanfranchi, M.; Pellinghelli, M. A.; Tiripicchio, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2495.  
 (21) McDaniel, M. P. *Adv. Catal.* **1985**, *33*, 47.

(22) See, for example: (a) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581. (b) Bely, S. T.; Duckett, S. B. *Organometallics* **1989**, *8*, 748. (c) Ghosh, C. K.; Hoyano, J. K.; Krentz, R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 5480. (d) Tanke, R. S.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3444. (e) Papenfuhs, B.; Mahr, N.; Werner, H. *Organometallics* **1993**, *12*, 4244. (f) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Rey, L.; Ruiz, C.; Carmona, E. *Inorg. Chem.* **1998**, *37*, 4538.

(23) Kawakami, K.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 21.



**Scheme 3.** Possible Mechanisms for the Initiation of Polymerization from the Cobalt(I) Cation **14** (LA represents a Lewis acid)



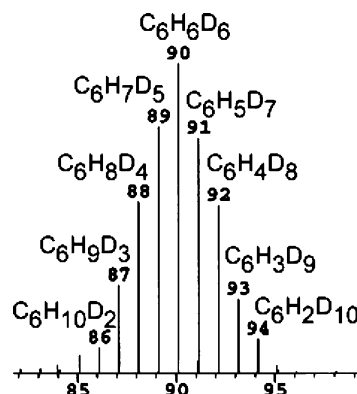
repulsive electrostatic interactions associated with bringing together positively charged cobalt centers.

We also examined the reaction of 59  $\mu\text{mol}$  of **2-d<sub>3</sub>** with 1 equiv of  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ , i.e., a Lewis acid-free system. Exposure of this mixture to an atmosphere of ethylene gave 42 mg of polymer, corresponding to an activity of 0.5 g/mmol bar h.<sup>24</sup> A similar activity was observed by Erker and co-workers upon treatment of **3** with  $\text{Li}[\text{B}\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4]$ .<sup>25</sup>

To probe pathway IV, we turned to the oligomerization precatalyst **12**, since this would generate liquid products more readily analyzed for end groups and

(24) The lower activity is not due to the presence of dimethylaniline competing with ethylene for the metal center; the  $^1\text{H}$  NMR spectra of **13-MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** and **13-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>** are identical, whereas differences would be apparent due to the sensitivity of the ligand chemical shifts to the environment at the cobalt center. In addition, it is possible to make the ethylene adduct **14-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>** by the addition of 1 equiv of ethylene to **13-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>**; no equilibrium is observed. It thus appears that the tertiary amine is too bulky to interact with the sterically protected cobalt center.

(25) Steffen, W.; Blömker, T.; Kleigrew, N.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem. Commun.* **2004**, 1188.



**Figure 3.** Mass spectrum of the 1-hexene fraction obtained from the co-oligomerization of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$  using **12**/dry MAO.

deuterium labels. **12**/MAO was treated with a 50:50 mixture of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$ , and the reaction terminated after 75 s by vacuum transfer of all the volatile species. The  $^1\text{H}$  NMR spectrum of the product mixture showed the presence of  $\alpha$ -olefins and unreacted ethylene, both with complex coupling patterns consistent with H/D coupling. Analysis of the solution by GC-MS confirmed that the oligomers were  $\alpha$ -olefins and showed that all possible H/D isotopomers were present, with the distribution approaching the statistical ratios expected for a 1:1 ratio of H and D. The mass spectrum of the C6 fraction is shown in Figure 3.

GC-MS analysis of the ethylene gas remaining above the polymerization mixture (prior to transfer of the volatiles) revealed peaks at  $m/z$  29, 30, and 31 corresponding to  $\text{C}_2\text{H}_3\text{D}$ ,  $\text{C}_2\text{H}_2\text{D}_2$ , and  $\text{C}_2\text{HD}_3$ , respectively. This indicates that H/D scrambling between the protio and deuterio ethylene had occurred. Two control experiments were undertaken, one using pure  $\text{C}_2\text{H}_4$ , and the other using pure  $\text{C}_2\text{D}_4$ . In neither of these experiments were isotopic mixtures observed, ruling out the possible incorporation of hydrogen isotopes from other sources, e.g., from ligand C–H activation processes or from contamination of the feedstock.

The presence of all possible isotopomers in the reaction products, at first sight, seems to rule out the possibility of initiation via the oxidative coupling route (IV, Scheme 3) since oligomers generated via this route should contain only even-numbered isotopomers.<sup>26</sup> Isotopic scrambling on the other hand is readily accounted for in a Cossee–Arman-type mechanism. However, the isotopic scrambling in the free ethylenes complicates matters somewhat since oligomers generated from isotopically scrambled ethylene would lead to all possible oligomer isotopomers. If isotopic scrambling in the monomer was arising in a predominantly metallacyclic mechanism, it would mean that a second process must be occurring that serves to scramble H and D between molecules of ethylene. In oligomerization systems with low  $\alpha$ -values, the rate of chain transfer is high relative to the rate of propagation, meaning that the likelihood of  $\beta$ -elimination from a Co–Et species is high. We therefore carried out a similar experiment using the polymerization system **13-MeBarf<sub>3</sub>** as the catalyst. In this case no scrambling was observed in the free

(26) Agapie, T.; Schofer, S. J.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 1304.

ethylene, consistent with the much lower rate of  $\beta$ -H elimination from a Co-Et species for a polymerization catalyst compared to an oligomerization catalyst. This observation favors a Cossee–Arlman-type propagation mechanism over the oxidative olefin coupling route since a secondary process that causes isotopic scrambling between the free ethylenes independent of the polymerization mechanism would be expected to operate in both oligomerizations and polymerizations catalyzed by these cobalt systems.

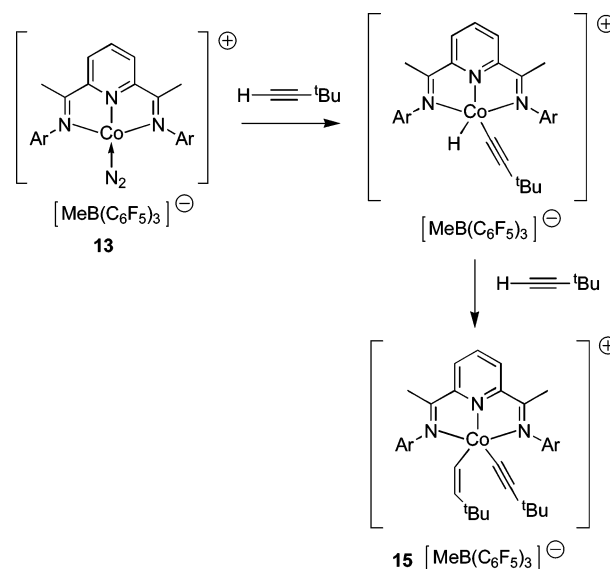
Having ruled out pathways I–IV, pathways V and VI are left as possibilities. V involves attack of an abstracted methide group on the cobalt center with concomitant electrophilic attack by the Lewis acid on the bound ethylene to afford a zwitterionic cobalt(III) dialkyl. The final, and substantially different, possibility is a vinylic C–H activation to afford a cobalt(III) vinyl hydride species (VI, Scheme 3).

To probe pathway V, we turned to deuterium labeling studies involving (separately) the precatalyst and activator. A polymerization using  $[2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}]\text{CoCD}_3$  (**2-d**<sub>3</sub>) activated by  $\text{B}(\text{C}_6\text{F}_5)_3$  gave an activity of 22 g/mmol bar h over a 1 h run. The polymer produced was analyzed by both  $^1\text{H}$  and  $^2\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectrum showed the polymer to be linear with methyl and vinyl chain ends in an approximately 1:1 ratio, as observed for all polymerizations using bis(imino)pyridine cobalt systems. Moreover, the  $^2\text{H}$  NMR spectrum showed the methyl end groups of the polymer to be deuterium enriched. From the  $M_n$  and yield of the polymer produced, it can be calculated that 5% of the polymer chains contain a  $\text{CD}_3$  end group.<sup>27,28</sup> If these arise from the initiation process, it would mean that 6% of the cobalt centers were active, producing an average of 20 chains per active center. A similar experiment undertaken using **2-d**<sub>3</sub> activated by  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  gave an activity of 0.5 g/mmol bar h. In this case neither  $\text{CD}_3$  nor  $\text{C}_6\text{F}_5$  end groups were observable in  $^2\text{H}$  or  $^{19}\text{F}$  NMR spectra of the polymer.

In another series of polymerizations, **1** was activated with perdeuterated MAO (synthesized by the controlled hydrolysis of  $\text{Al}_2\text{Me}_6\text{-d}_{18}$ ), followed by termination of the polymerization by the addition of  $\text{MeOH}/\text{HCl}$ . These also yielded polymers that contained  $\text{CD}_3$  end groups, confirming that the abstracted methide is reincorporated into the polymer in both the MAO- and  $\text{B}(\text{C}_6\text{F}_5)_3$ -activated systems, consistent with pathway V and providing additional evidence that pathways III and IV do not operate.<sup>29</sup>

Since it is not possible to observe the organocobalt product of vinylic C–H activation (VI, Scheme 3) nor to readily distinguish the polymer products of such a pathway (except in certain specific instances),<sup>30</sup> we have probed the viability of obtaining Co(III) from Co(I) via a C–H activation process through the reaction of **13-MeBARf**<sub>3</sub> with 3,3-dimethylbutyne. An immediate

**Scheme 4.** Hypothesized Route for the Formation of **15** ( $\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ )



color change from dark blue to brown-green is observed, and the NMR spectrum of the product was consistent with the formation of  $[\{2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}\}\text{Co}(\text{CC}^t\text{Bu})(\text{C}(\text{H})=\text{C}(\text{H})^t\text{Bu})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**15**) (Scheme 4). The  $^1\text{H}$  NMR spectrum contains two doublet resonances each integrating for one proton and with a  $^3J_{\text{H-H}}$  coupling constant of 5.6 Hz; this is at the low end of the range for a *cis* arrangement about a double bond. One of these doublets has a chemical shift of  $\delta$  3.12; the other is shifted greatly to the high-field end of the spectrum, at  $\delta$  -0.83. The latter is reminiscent of the chemical shift of the protons in the  $\beta$ -position of the alkyl chains in complexes **6–8** and is similarly presumed to be due to the ring current of the aryl substituents on the imine groups, particularly as the vinyl group is too rigidly constrained to adopt an agostic conformation. We were unable to obtain further characterizing data for **15**, as its high solubility and the presence of byproducts have precluded its purification.

The formation of **15** is presumed to proceed via C–H activation of the alkyne to afford a Co(III) alkynyl hydride, followed by the insertion of a second equivalent of alkyne into the Co–H bond (Scheme 4). It is thus clear that it is possible for Co(III) species to be derived from the Co(I) precursor **13** via the oxidative addition of a C–H bond to the cobalt(I) center. A similar reaction was observed for  $[\text{Co}(\text{PMe}_3)_3][\text{BPh}_4]$ , where the reaction product,  $[\text{Co}(\text{PMe}_3)_3(\text{CPh})(\text{C}(\text{H})=\text{C}(\text{H})\text{Ph})][\text{BPh}_4]$ , was fully characterized.<sup>31</sup>

## Discussion

The observation of  $\text{CD}_3$  end groups in all of the PE samples prepared using either  $\text{CD}_3$ -labeled cobalt pre-

(27) No  $\text{C}_6\text{F}_5$  groups were detectable in the polymer.

(28) Errors in all quantitative measurements obtained by NMR spectroscopy are estimated to be  $\pm 20\%$ , arising mainly from errors in the integration of NMR signals.

(29) It should be noted that it is possible that some of these  $\text{CD}_3$  chain end groups arise through small amounts of chain transfer to aluminum. While chain transfer to aluminum does not occur on a large scale in the cobalt system, as shown by the 1:1 ratio of methyl:vinyl chain ends in the  $^1\text{H}$  NMR spectrum, the presence of very low amounts of chain transfer cannot be ruled out completely.

(30) Insertion into the Co–H bond that results from a vinylic C–H activation (the less sterically demanding bond into which insertion could occur) would result in a polymer or oligomer with one methyl and one vinyl bond (as observed) whether the polymer was terminated by  $\beta$ -hydrogen elimination or reductive elimination. Insertion into the Co–vinyl bond would afford chains with one methyl and one vinyl chain end only if termination occurred via reductive elimination. If termination occurred by  $\beta$ -hydrogen elimination, dienes would result, which would be detectable among the oligomeric products.

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**Table 3. Summary of Activities and Polymerization Data Using Different Activators<sup>a</sup>**

catalytic system	polymer yield (g)	activity (g/mol bar h)	$M_n$	$M_w/M_n$
1 <sup>a</sup> /100 MAO	6.12	350	6800	2.8
3 <sup>a</sup> /100 MAO	6.14	350	8300	2.3
2 <sup>b</sup> /1 B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	0.13	11	14000	2.4
2 <sup>b</sup> /5 B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	0.13	11	9600	2.3
2 <sup>b</sup> /1 B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> + 5 Al <sub>2</sub> Me <sub>6</sub>	1.12	96	8100	2.5
2-d <sub>3</sub> /1 [HNMe <sub>2</sub> Ph][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	0.042	0.5	<i>d</i>	<i>d</i>

<sup>a</sup> 8.8  $\mu$ mol of precatalyst, 100 mL of toluene, 2 bar of ethylene, 1 h, 298 K. <sup>b</sup> 18  $\mu$ mol of precatalyst, 15 mL of toluene, 2 bar of ethylene, 20 min, 298 K. <sup>c</sup> 59  $\mu$ mol of precatalyst, 10 mL of toluene, 1.5 bar of ethylene, 1 h, 298 K. <sup>d</sup> Not analyzed.

catalysts or CD<sub>3</sub>-labeled activators points to the mechanism proceeding via either (or possibly both) pathway II or V. The C–H activation of alkyne to afford a cobalt(III) species suggests that the vinylic C–H activation reaction pathway VI is a possibility, but it does not prove that the related reaction occurs for ethylene. A key difference between the postulated pathways lies in the involvement of the cocatalyst. The productivities of the catalyst/cocatalyst combinations lie in the order **13/MAO**  $\gg$  **13/MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>**  $\gg$  **13/B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>**, with order of magnitude differences between each system. The oxidative addition of a vinylic C–H bond to the cobalt center would be expected to be largely independent of the nature of the cocatalyst, while the nucleophilic attack of a methide group is clearly dependent on the nature of the cocatalyst. When these observations are combined with the appearance of CD<sub>3</sub> end groups in the resultant polymers, a pathway involving nucleophilic attack of a methide anion on **14**, i.e., pathways II and V, seems the most plausible of the various possibilities. However, II can be ruled out since the cobalt(I) alkyls undergo alkyl group abstraction in the presence of strong Lewis acids such as MAO or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and are inactive for ethylene polymerization in the presence of Al<sub>2</sub>Me<sub>6</sub>. This leaves pathway V, in which the Lewis acid is attached to a carbon terminus, and therefore can be more readily accommodated sterically. It also involves a cobalt(III) center as opposed to cobalt(I), in common with other known cobalt ethylene polymerization systems.<sup>32</sup> Chain growth could occur via either of the cobalt–carbon bonds, polymerization then being terminated by  $\beta$ -H transfer.

On a final point, it should be noted that it is not possible to explain the activity (albeit very low) observed for **2**/[HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] on the basis of the above observations, where there are no nucleophilic alkyl groups present, and the polymer does not contain C<sub>6</sub>F<sub>5</sub> end groups. That the activity in this system is far lower than in the systems where nucleophilic alkyl groups are present (see Table 3 for a summary of activities using different activators) may indicate that a different mechanism is operating, possibly involving vinylic C–H activation or the formation of metallacycles. However, the difficulties of assessing the intricacies of what may be a side reaction, with little net contribution to the overall catalyst productivity, preclude conclusions on the possible involvement of this process at this time.

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## Summary

Cobalt bis(imino)pyridine/MAO ethylene polymerization catalysts have been shown to operate by initial reduction of a cobalt(II) precatalyst to a cobalt(I) halide, followed by conversion to a cobalt(I) methyl, and ultimately to a cobalt(I) cationic species. Addition of ethylene to this system affords an ethylene adduct, which is the immediate precursor to the active species. Deuterium labeling studies show that the methyl groups of “noncoordinating” [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] or [Me-MAO] anions are incorporated at the saturated ends of the polyethylene chains, consistent with an activation mechanism that involves nucleophilic attack by an abstracted alkyl group on the cationic ethylene species.

## Experimental Details

All reactions were carried out under an atmosphere of dinitrogen gas. Standard Schlenk-line and associated techniques were employed for the manipulation of air-sensitive compounds. Conventional inert atmosphere dryboxes were used for the preparation of the analytical and spectroscopic samples, as well as for weighing and storage of air-sensitive compounds. With the exception of pentane, heptane, and toluene, all solvents were dried by refluxing over an appropriate drying agent,<sup>33</sup> distilled, and degassed prior to use. Pentane, heptane, and toluene were dried and deoxygenated according to a published procedure.<sup>34</sup> <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded at ambient temperature on a Bruker AC-250 at 250.133, 62.896, and 235.318 MHz, respectively, unless otherwise stated. Spectra at higher fields were recorded on a Bruker DRX-400 (<sup>1</sup>H and <sup>13</sup>C resonances at 400.129 and 100.613 MHz, respectively). Low-temperature <sup>1</sup>H NMR and <sup>2</sup>H NMR were recorded on a Bruker AM-500 at 500.133 and 76.774 MHz, respectively. Chemical shifts were referenced internally to the residual protio impurity of the deuterated solvents (<sup>1</sup>H), the solvent resonance (<sup>13</sup>C), or *d*<sub>6</sub>-benzene at 7.15 ppm (<sup>2</sup>H) and are quoted in ppm relative to tetramethylsilane. Coupling constants are quoted in Hz. Chemical shifts for <sup>19</sup>F were referenced externally to CFCl<sub>3</sub> at 0 ppm. Mass spectra were recorded on either a VG Autospec or a VG Platform II spectrometer. Microanalyses (C, H, N) were performed at London Metropolitan University. GPC and NMR analyses of polymers were carried out by BP Chemicals. The compounds **1**,<sup>3</sup> **6**,<sup>10</sup> **7**,<sup>10</sup> [2,6-{(CD<sub>3</sub>)C=N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N}]<sub>2</sub>,<sup>16</sup> and tris-(pentafluorophenyl)borane<sup>35</sup> were prepared as described in the literature. The compound Al<sub>2</sub>Me<sub>6</sub>-*d*<sub>18</sub> was prepared from CD<sub>3</sub>I and Al by a published procedure.<sup>36</sup>

**Preparation of [2,6-{MeC=N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N}]CoMe, **2**.** A suspension of **1** (612 mg, 1.00 mmol) in diethyl ether (30 mL) at –78 °C was treated dropwise with methylmagnesium bromide (0.84 mL of a 3.0 M solution in diethyl ether, 2.52 mmol) and allowed to slowly warm to ambient temperature, during which time a color change to red-purple was observed. After stirring for 24 h at room temperature, the volatiles were removed under reduced pressure and the red-purple residue was extracted with toluene (30 cm<sup>3</sup>). Filtration and removal of the volatile components under reduced pressure afforded the crude product as a claret-colored powder. Yield: 465 mg, 81% based on **1**. Crystals suitable for an X-ray

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structure determination were grown via slow solvent evaporation from a concentrated solution of **2** in diethyl ether.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 10.19 (1H, t; *p-H*, py), 7.86 (2H, d; *m-H*, py), 7.49 (2H, distorted triplet; *p-H*, Ar), 7.37 (4H, distorted doublet; *m-H*, Ar), 3.13 (4H, septet;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 1.19 (12H, d;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 0.62 (12H, d;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 0.58 (3H, s;  $\text{CoCH}_3$ ), -1.14 ppm (6H, s;  $\text{ArN}=\text{CCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 62.9 MHz): 166.1 ( $\text{ArN}=\text{CCH}_3$ ), 157.1 (*o-C*, py), 154.7 (*i-C*, Ar), 140.6 (*o-C*, Ar), 126.5 (*p-C*, Ar), 123.9 (*m-C*, Ar), 122.7 (*m-C*, py), 117.4 (*p-C*, py), 28.4 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 25.3 ( $\text{ArN}=\text{CCH}_3$ ), 24.1 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 23.2 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), -15.5 ppm ( $\text{CoCH}_3$ ). EI-MS ( $m/z$ ): 555 [ $\text{M}^+$ ], 28%; 540 [ $\text{M} - \text{Me}^+$ ], 100%. Anal. Calcd (%) for  $\text{C}_{34}\text{H}_{46}\text{N}_3\text{Co}$ : C 73.49, H 8.34, N 7.56. Found: C 73.56, H 8.25, N 7.44.

[2,6-{ $\text{MeC}=\text{N}(\text{2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoCD $_3$  (**2-d<sub>3</sub>**) was prepared in similar fashion using  $\text{MgMe}_2\text{-d}_6$ .

**Preparation of [2,6-{ $\text{MeC}=\text{N}(\text{2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoCl, **3**.** A suspension of **1** (917 mg, 1.50 mmol) and an excess of zinc powder (3 g, 45 mmol) in toluene (75 cm $^3$ ) were heated to 50 °C for 15 h. During this time, the initial ochre slurry became an intense red-purple-colored solution. The suspended solids were allowed to settle, and the solution was then filtered. The volatile components were removed under reduced pressure to afford **3** as a red-purple solid, which was recrystallized from toluene/pentane. Yield: 664 mg, 78% based on **1**.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 9.54 (1H, t; *p-H*, py), 7.41 (2H, distorted triplet; *p-H*, Ar), 7.27 (4H, distorted doublet; *m-H*, Ar), 6.91 (2H, d; *m-H*, py), 3.33 (4H, septet;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 1.18 (12H, d;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 1.06 (12H, d;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 0.05 ppm (6H, s;  $\text{ArN}=\text{CCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz): 167.3 ( $\text{ArN}=\text{CCH}_3$ ), 152.7 (*o-C*, py), 150.8 (*i-C*, Ar), 140.7 (*o-C*, Ar), 127.0 (*p-C*, Ar), 125.5 (*m-C*, py), 123.7 (*m-C*, Ar), 114.9 (*p-C*, py), 29.3 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 24.0 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 23.8 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 21.2 ppm ( $\text{ArN}=\text{CCH}_3$ ). EI-MS ( $m/z$ ): 575 [ $\text{M}^+$ ], 100%. Anal. Calcd (%) for  $\text{C}_{33}\text{H}_{43}\text{N}_3\text{CoCl}$ : C 68.80, H 7.52, N 7.29. Found: C 68.82, H 7.57, N 7.22.

[2,6-{ $(\text{CD}_3)\text{C}=\text{N}(\text{2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoCl (**3-d<sub>6</sub>**) was prepared similarly.

**Preparation of [2,6-{ $\text{MeC}=\text{N}(\text{2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoBr, **4**.** A solution **3** (14.8 mg, 25.7  $\mu\text{mol}$ ) in benzene- $d_6$  (0.7 cm $^3$ ) was treated in situ with trimethylsilylbromide (3.4 mm $^3$ , 25.8  $\mu\text{mol}$ ) at room temperature. Following inspection by  $^1\text{H}$  NMR spectroscopy, a further 4.0 equiv of trimethylsilylbromide (13.6 mm $^3$ , 103  $\mu\text{mol}$ ) was added to the solution in order to drive the reaction to completion.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 9.79 (1H, t; *p-H*, py), 7.45 (2H, distorted triplet; *p-H*, Ar), 7.30 (4H, distorted doublet; *m-H*, Ar), 6.88 (2H, d; *m-H*, py), 3.37 (4H, septet;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 1.18 (12H, d;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 1.10 (12H, d;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), -0.08 ppm (6H, s;  $\text{ArN}=\text{CCH}_3$ ).

**Preparation of [2,6-{ $\text{MeC}=\text{N}(\text{2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoI, **5**.** The procedure was as for **4** above. Approximately 5.0 equiv of trimethylsilylbromide was required to drive the equilibrium over to **5** +  $\text{Me}_3\text{SiCl}$ .

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 10.15 (1H, t; *p-H*, py), 7.44 (2H, distorted triplet; *p-H*, Ar), 7.30 (4H, distorted doublet; *m-H*, Ar), 6.81 (2H, d; *m-H*, py), 3.37 (4H, septet;  $\text{CH}(\text{CH}_3)_2$ ), 1.13 (24H, d;  $\text{CH}(\text{CH}_3)_2$ ), -0.37 ppm (6H, s;  $\text{ArN}=\text{CCH}_3$ ).

**Preparation of [2,6-{ $\text{MeC}=\text{N}(\text{2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoCH $_2\text{Ph}$ , **8**.** The synthesis was as for **2**, using **1** (520 mg, 0.850 mmol) and benzylmagnesium bromide (2.8 cm $^3$  of a 1.0 M solution in Et $_2\text{O}$ , 2.8 mmol). Yield: 310 mg, 54% based on **1**.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 10.26 (1H, t; *p-H*, py), 7.68 (2H, t; *m-H*, py), 7.61 (2H, distorted triplet; *p-H*, Ar), 7.44 (4H, distorted doublet; *m-H*, Ar), 6.79 (1H, t; *p-H*, CH $_2\text{Ph}$ ), 6.56 (2H, d; *m-H*, CH $_2\text{Ph}$ ), 5.59 (2H, d; *o-H*, CH $_2\text{Ph}$ ), 3.22 (4H, septet;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 2.50 (2H, s;  $\text{CoCH}_2\text{Ph}$ ), 1.14 (12H, d;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 0.63 (12H, d;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), -1.17 ppm (6H, s;  $\text{ArN}=\text{CCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz): 165.9 ( $\text{ArN}=\text{CCH}_3$ ), 157.4 (*i-C*, CH $_2\text{Ph}$ ), 155.5 (*o-C*, py), 154.8 (*i-C*,

Ar), 141.3 (*o-C*, Ar), 127.8 (*m-C*, CH $_2\text{Ph}$ ; signal buried beneath solvent resonance), 127.5 (*o-C*, CH $_2\text{Ph}$ ), 126.9 (*p-C*, Ar), 124.8 (*m-C*, Ar), 124.0 (*m-C*, py), 119.9 (*p-C*, CH $_2\text{Ph}$ ), 116.4 (*p-C*, py), 28.8 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 25.9 ( $\text{ArN}=\text{CCH}_3$ ), 24.6 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 23.5 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), -3.4 ppm ( $\text{CoCH}_2\text{Ph}$ ). EI-MS ( $m/z$ ): 555 [ $\text{M} - \text{C}_6\text{H}_5^+$ ], 12%; 482 [ $\text{M} - \text{Co} - \text{CH}_2\text{Ph}^+$ ], 26%; [ $\text{M} - \text{Co} - \text{CH}_2\text{Ph} - \text{Me}^+$ ], 24%. Anal. Calcd (%) for  $\text{C}_{40}\text{H}_{50}\text{N}_3\text{Co}$ : C 76.04, H 7.98, N 6.65. Found: C 75.89, H 7.60, N 6.61.

**Preparation of [2,6-{ $\text{MeC}=\text{N}(\text{2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoH, **9**.** In a typical procedure, a solution of **2** (5.6 mg, 0.010 mmol) in benzene- $d_6$  (0.7 cm $^3$ ) was degassed by two freeze-pump-thaw cycles. A stoichiometric quantity of room-temperature hydrogen gas was then admitted into the vacuum above the solution, frozen at 77 K. The solution was allowed to thaw and mixed with the gas by repeated shaking. Yield > 98% by NMR.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz): 10.83 (1H, t,  $^3J_{\text{H-H}} = 7.6$  Hz; *p-H*, py), 7.60 (2H, distorted triplet,  $^3J_{\text{H-H}} = 7.7$  Hz; *p-H*, Ar), 7.59 (2H, d,  $^3J_{\text{H-H}} = 7.6$  Hz; *m-H*, py), 7.46 (4H, distorted doublet,  $^3J_{\text{H-H}} = 7.7$  Hz; *m-H*, Ar), 3.42 (4H, septet,  $^3J_{\text{H-H}} = 6.8$  Hz;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 1.31 (12H, d,  $^3J_{\text{H-H}} = 6.8$  Hz;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 0.28 (12H, d,  $^3J_{\text{H-H}} = 6.8$  Hz;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), -1.66 ppm (6H, s;  $\text{ArN}=\text{CCH}_3$ ). No resonance for  $\text{Co-H}$  is detectable over the range +100 to -150 ppm [ $I(^{59}\text{Co}) = 7/2$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz): 168.6 ( $\text{ArN}=\text{CCH}_3$ ), 160.1 (*i-C*, Ar), 156.5 (*o-C*, py), 140.2 (*o-C*, Ar), 126.3 (*p-C*, Ar), 124.2 (*m-C*, Ar), 123.7 (*m-C*, py), 118.0 (*p-C*, py), 28.9 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 25.6 ( $\text{ArN}=\text{CCH}_3$ ), 23.6 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 22.7 ppm ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ). Infrared (Nujol):  $\nu(\text{Co-H})$  2092 cm $^{-1}$ . The sensitivity of this complex precluded its isolation.

**Preparation of [2,6-{ $\text{MeC}=\text{N}(\text{2,4,6-Me}_3\text{C}_6\text{H}_2)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoCl, **10**.** The synthesis was as for **3**, starting from [2,6-{ $\text{MeC}=\text{N}(\text{2,4,6-Me}_3\text{C}_6\text{H}_2)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoCl $_2$ . Yield: 56%.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz): 9.49 (1H, t,  $^3J_{\text{H-H}} = 7.7$  Hz; *p-H*, py), 6.93 (4H, s; *m-H*, Ar), 6.90 (2H, d,  $^3J_{\text{H-H}} = 7.7$  Hz; *m-H*, py), 2.19 (12H, s; *o-CH}\_3*, Ar), 2.18 (6H, s; *p-CH}\_3*, Ar), -0.06 ppm (6H, s;  $\text{ArN}=\text{CCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz): 167.0 ( $\text{ArN}=\text{CCH}_3$ ), 152.9 (*o-C*, py), 151.8 (*i-C*, Ar), 135.0 (*p-C*, Ar), 129.8 (*o-C*, Ar), 129.4 (*m-C*, Ar), 125.1 (*m-C*, py), 114.8 (*p-C*, py), 21.3 (*p-CH}\_3*, Ar), 20.2 ( $\text{ArN}=\text{CCH}_3$ ), 19.4 ppm (*o-CH}\_3*, Ar). EI-MS ( $m/z$ ): 491 [ $\text{M}^+$ ], 72%. Anal. Calcd (%) for  $\text{C}_{27}\text{H}_{31}\text{N}_3\text{CoCl}$ : C 65.92, H 6.35, N 8.54. Found: C 66.06, H 6.19, N 8.43.

**Preparation of [2,6-{ $\text{MeC}=\text{N}(\text{2,4,6-Me}_3\text{C}_6\text{H}_2)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoMe, **11**.** The synthesis was as for **2**, using [2,6-{ $\text{MeC}=\text{N}(\text{2,4,6-Me}_3\text{C}_6\text{H}_2)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoCl $_2$  (580 mg, 1.10 mmol) and methylmagnesium chloride (1.00 cm $^3$  of a 3.0 M solution in THF, 3.0 mmol) in diethyl ether (35 cm $^3$ ). Yield: 397 mg, 77%.

$^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ , 400 MHz): 10.08 (1H, t; *p-H*, py), 7.88 (2H, d; *m-H*, py), 6.99 (4H, s; *m-H*, Ar), 2.28 (6H, s; *p-CH}\_3*, Ar), 1.93 (12H, s; *o-CH}\_3*, Ar), 0.46 (3H, s;  $\text{CoCH}_3$ ), -1.21 ppm (6H, s;  $\text{ArN}=\text{CCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ , 100 MHz): 165.2 ( $\text{ArN}=\text{CCH}_3$ ), 157.1 (*o-C*, py), 155.2 (*i-C*, Ar), 134.2 (*p-C*, Ar), 129.5 (*o-C*, Ar), 129.3 (*m-C*, Ar), 121.9 (*m-C*, py), 117.4 (*p-C*, py), 24.1 ( $\text{ArN}=\text{CCH}_3$ ), 21.2 (*p-CH}\_3*, Ar), 19.0 (*o-CH}\_3*, Ar), -17.3 ppm (br,  $\text{CoCH}_3$ ). EI-MS ( $m/z$ ): 471  $\text{M}^+$ , 34%; 456 [ $\text{M} - \text{Me}^+$ ], 100%. Anal. Calcd (%) for  $\text{C}_{28}\text{H}_{34}\text{N}_3\text{Co}$ : C 71.32, H 7.27, N 8.91. Found: C 71.11, H 7.08, N 8.81.

**Preparation of [2,6-{ $\text{MeC}=\text{N}(\text{2-EtC}_6\text{H}_4)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoCl, **12**.** To a mixture of [2,6-{ $\text{MeC}=\text{N}(\text{2-EtC}_6\text{H}_4)$ }] $_2\text{C}_5\text{H}_3\text{N}$ ]CoCl $_2$  (153 mg, 0.250 mmol) and potassium graphite (35.3 mg, 0.263 mmol) in a Schlenk tube at -78 °C was added precooled toluene (15 cm $^3$ ). Within seconds, the color of the mixture changed to deep purple, and the solution was then allowed to warm to room temperature slowly. After stirring for 16 h the supernatant was separated by filtration. Removal of all volatiles under reduced pressure afforded the title compound as a claret solid. Yield: 102 mg, 71% based on **1**.

$^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ ), 388 K: 9.72 (1H, br; *p-H*, py), 7.67 (2H, m; Ar), 7.3-6.8 (8H; Ar and *m-H*, py), 2.55 (4H, q; *o-CH}\_2\text{CH}\_3*), 0.92 (6H, t; *o-CH}\_2\text{CH}\_3*), -0.01 ppm (6H, br s;  $\text{ArN}=\text{CCH}_3$ ). The



low solubility of **11** in hydrocarbons, combined with its instability in other solvents, precluded acquisition of a resolved low-temperature  $^1\text{H}$  NMR spectrum. EI-MS ( $m/z$ ): 463  $\text{M}^+$ , 100%; 369, 46%; 354, 88%; 77, 60%. Anal. Calcd (%) for  $\text{C}_{25}\text{H}_{27}\text{N}_3\text{CoCl}$ : C 64.73, H 5.87, N 9.06. Found: C 64.60, H 5.71, N 8.93.

**Preparation of**  $[\{\{2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}\}\text{-Co}(\eta^1\text{-N}_2)\}\{\text{MeB}(\text{C}_6\text{F}_5)_3\}]$ , **13-MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>**. A solution of  $\text{B}(\text{C}_6\text{F}_5)_3$  (184 mg, 0.36 mmol) in pentane (10  $\text{cm}^3$ ) was allowed to diffuse slowly into a claret solution of **2** (200 mg, 0.36 mmol) in benzene (5  $\text{cm}^3$ ) at room temperature. After 4 days the resulting blue solution was decanted, and the crystals were washed with pentane ( $2 \times 5 \text{ cm}^3$ ). Yield: 310 mg, 81% based on **2**.

$^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ ): 7.55 (1H, t; *p*-H, py), 7.00 (2H, t, *p*-H, Ar), 6.87 (4H, d; *m*-H, Ar), 6.69 (2H, pseudo-doublet; *m*-H, py), 2.85 (4H, septet;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 1.11 (6H, s;  $\text{ArN}=\text{CCH}_3$ ), 1.05 (12H, d;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 0.98 (12H, d;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), -2.00 ppm ( $\sim 3\text{H}$ , br s;  $\text{H}_3\text{C}-\text{B}(\text{C}_6\text{F}_5)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ , 125 MHz): 173.8 ( $\text{ArN}=\text{CCH}_3$ ), 155.9 (*o*-C, py), 143.2 (*i*-C, Ar), 139.8 (*o*-C, Ar), 136.6 (*p*-C, py), 124.6 (*m*-C, Ar), 123.4 (*m*-C, py), 29.1 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 23.6 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 23.3 ( $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 17.1 ( $\text{ArN}=\text{CCH}_3$ ), 13.0 ppm ( $\text{H}_3\text{C}-\text{B}(\text{C}_6\text{F}_5)_3$ ). The  $^{13}\text{C}$  resonance signal for the *para*-C, Ar—although obscured by solvent peaks—may be located through the HSQC spectrum and has a chemical shift in the region 128.0–128.5 ppm. The  $^{13}\text{C}$  signals of the pentafluorophenyl groups are too broad to be observed.  $^{19}\text{F}$  NMR ( $\text{C}_7\text{D}_8$ ): -130.8 (2F, m; *o*-F), -163.2 (1F, m; *p*-F), -164.1 ppm (2F, m; *m*-F). Infrared (Nujol):  $\nu(\text{NN})$  2197  $\text{cm}^{-1}$ . Anal. Calcd (%) for  $\text{C}_{52}\text{H}_{46}\text{BCoF}_{15}\text{N}_5$ : C 57.00, H 4.23, N 6.39. Found: C 56.90, H 4.17, N 6.29.

**Preparation in situ.** Solutions of **2** (5.0 mg, 9  $\mu\text{mol}$ ) in toluene- $d_8$  (0.35  $\text{cm}^3$ ) and  $\text{B}(\text{C}_6\text{F}_5)_3$  (4.6 mg, 9  $\mu\text{mol}$ ) in toluene- $d_8$  (0.35  $\text{cm}^3$ ) were mixed to give a blue solution. This was then transferred to an NMR tube fitted with a Young's tap. NMR spectral data were the same as those given above.

**Preparation of**  $[\{\{2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}\}\text{-Co}(\eta\text{-C}_2\text{H}_4)\}\{\text{MeB}(\text{C}_6\text{F}_5)_3\}]$ , **14-MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>**. A solution of **13-MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** prepared as described above was degassed by two freeze–pump–thaw cycles, after which ethylene ( $V = 5.0 \text{ cm}^3$ ,  $p = 41 \text{ mbar}$ , 1.1 equiv) was condensed into the NMR tube. Warming of the mixture to room temperature was accompanied by a color change to aquamarine. Yield: quantitative by NMR spectroscopy.

$^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ ): 8.00 (1H, t,  $^3J_{\text{H-H}} = 7.8 \text{ Hz}$ ; *p*-H, py), ca. 7.0 (obscured by solvent resonance) (2H, t; *p*-H, Ar), ca. 7.0 (2H, d; *m*-H, py), 6.77 (4H, d,  $^3J_{\text{H-H}} = 7.5 \text{ Hz}$ ; *m*-H, Ar), 4.65 (4H, s;  $\text{C}_2\text{H}_4$ ), 3.02 (4H, septet,  $^3J_{\text{H-H}} = 6.5$ ;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 1.09 (12H, d,  $^3J_{\text{H-H}} = 6.5 \text{ Hz}$ ;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 0.76 (12H, d,  $^3J_{\text{H-H}} = 6.5 \text{ Hz}$ ;  $(\text{CH}_3)\text{CH}(\text{CH}_3)$ ), 0.75 (6H, s;  $\text{ArN}=\text{CCH}_3$ ) 0.36 ppm (3H, br;  $\text{B}-\text{CH}_3$ ).  $^{19}\text{F}$  NMR ( $\text{C}_7\text{D}_8$ ): -130.8 (2F, m; *o*-F), -163.2 (1F, m; *p*-F), -163.8 ppm (2F, m; *m*-F). Low solubility in noncoordinating solvents precluded the collection of  $^{13}\text{C}$  NMR data.

Further equivalents of ethylene were added in similar fashion. The only change to the NMR spectra was in the position of the resonance attributable to the ethylene protons which moved to an averaged position of 5.24 ppm.

**Preparation of**  $[\{\{2,6\text{-}\{\text{MeC}=\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}_2\text{C}_5\text{H}_3\text{N}\}\text{-Co}(\text{CC}^i\text{Bu})(\text{C}(\text{H})=\text{C}(\text{H})^i\text{Bu})\}\{\text{MeB}(\text{C}_6\text{F}_5)_3\}]$ , **15**. To a solution of **13-MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** prepared as described above was added 3,3-dimethylbutyne (2.2  $\mu\text{L}$ , 18  $\mu\text{mol}$ ). An instant color change from blue to dark green-brown occurred. The solution was transferred to a NMR tube and the spectrum recorded.

**Deuterium NMR Spectroscopy. Preparation of MAO Solutions in 2-Chlorotoluene.** All volatiles were removed from a sample of commercial MAO. The resulting white solid (146 mg, about 2.0–2.5 mmol) and trimethylaluminum (146 mg, 2.0 mmol) were dissolved in 2-chlorotoluene (5.0  $\text{cm}^3$ ) to

afford a viscous solution. The solution was then spiked with a small amount of benzene- $d_6$  as a reference.

**$^2\text{H}$  NMR Study of MAO-Activated Systems.** Either **1-d<sub>6</sub>** or **3-d<sub>6</sub>** (0.035 mmol) was dissolved in a solution of MAO (0.6  $\text{cm}^3$ , Al:Co = 14:1) in 2-chlorotoluene to give a purple solution. A  $^2\text{H}$  NMR spectrum of each activated complex was recorded. The sample was then freeze–pump–thaw degassed twice and ethylene condensed into the tube. The sample was allowed to warm to room temperature and shaken, and the spectrum recorded.

**$^2\text{H}$  NMR Study of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-Activated System.** A sample of **13-MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** in 2-chlorotoluene was prepared via the reaction of **2-d<sub>6</sub>** (19.4 mg, 0.035 mmol) and  $\text{B}(\text{C}_6\text{F}_5)_3$  (18.0 mg, 0.035 mmol) as described above.

**Ethylene Polymerizations. Polymerizations Using MAO as Cocatalyst.** To a magnetically stirred solution of a pre-catalyst (0.0088 mmol) in toluene (100  $\text{cm}^3$ ) was added MAO (0.55  $\text{cm}^3$  of a 1.6 M solution in toluene, Al:Co = 100:1) at room temperature. The solution first turned claret, then blue within a few minutes. The solution was degassed, and ethylene admitted (2.0 bar), the pressure being maintained for the full duration of the polymerization run. Polymerizations were terminated (typically after 60 min) by addition of MeOH/1 M HCl (about 9:1). The precipitated polyethylene was filtered, washed with methanol, and dried in vacuo at 60  $^\circ\text{C}$  overnight.

**Polymerizations Using B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as Cocatalyst.** Inside a glovebox, freshly prepared solutions of **2** or **2-d<sub>3</sub>** (10.0 mg, 0.018 mmol) in toluene (10  $\text{cm}^3$ ) and  $\text{B}(\text{C}_6\text{F}_5)_3$  (9.2 mg, 0.018 mmol) in toluene (15  $\text{cm}^3$ ) were mixed at room temperature, leading to a color change from claret to blue. Trimethylaluminum (13 mg, 0.18 mmol, 10 equiv) was added if required. This solution was transferred into a Schlenk tube, diluted with toluene (to 50  $\text{cm}^3$  total volume), sealed, and removed from the glovebox. The solution was degassed and subsequently exposed to ethylene (2.0 bar). Runs were typically terminated after 20 min because no further ethylene uptake was observed. The polymer was isolated as described for the runs using MAO as cocatalyst.

**Polymerization Using [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as Cocatalyst.** The general procedure was as described for the  $\text{B}(\text{C}_6\text{F}_5)_3$ -activated systems. A claret solution of **2-d<sub>3</sub>** (5.2 mg, 0.0094 mmol) in toluene (10  $\text{cm}^3$ ) was added to  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$  (7.5 mg, 0.0094 mmol) at room temperature. The mixture was agitated for several minutes, during which the anilinium salt slowly reacted to afford a deep blue solution. This solution was transferred into a Schlenk tube, diluted with toluene (to 50  $\text{cm}^3$  total volume), sealed, degassed, and exposed to ethylene (1.5 bar). The run was terminated after 60 min. Polymer yield: 7 mg (activity = 0.5 g  $\text{mmol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ ). Repeating this run on a larger scale (0.059 mmol) afforded sufficient polymer (42 mg, activity = 0.5 g  $\text{mmol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ ) for characterization by NMR.

**Preparation of Deuterated MAO.** *Caution:* care must be taken to avoid the release of large volumes of methane and potential explosion. A precooled ( $-20 \text{ }^\circ\text{C}$ ) suspension of  $\text{LiOH}\cdot\text{H}_2\text{O}$  (147 mg, 3.50 mmol) in toluene (4.0  $\text{cm}^3$ ) was transferred in several portions onto a cold solution ( $-20 \text{ }^\circ\text{C}$ ) of either  $\text{Al}_2\text{Me}_6\text{-d}_{18}$  (505 mg, 3.50 mmol) in toluene (3.0  $\text{cm}^3$ ). The mixture was slowly allowed to warm to room temperature and then left to stir overnight. The supernatant was separated by filtration.  $[\text{Al}] = 1.0 \text{ M}$ .

**X-ray Crystallography.** *Crystal data for 2:*  $\text{C}_{34}\text{H}_{46}\text{CoN}_3$ ,  $M = 555.67$ , monoclinic,  $P2_1/n$  (no. 14),  $a = 13.882(2) \text{ \AA}$ ,  $b = 14.823(2) \text{ \AA}$ ,  $c = 15.492(6) \text{ \AA}$ ,  $\beta = 90.92(2)^\circ$ ,  $V = 3187.4(14) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.158 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo K}\alpha) = 0.563 \text{ mm}^{-1}$ ,  $T = 203 \text{ K}$ , very dark green platy blocks; 5600 independent measured reflections,  $F^2$  refinement,  $R_1 = 0.054$ ,  $wR_2 = 0.103$ , 3750 independent observed reflections  $[\text{I}(\text{F}_o) > 4\sigma(\text{I}(\text{F}_o))]$ ,  $2\theta_{\text{max}} = 50^\circ$ , 346 parameters. CCDC 256785.



**Crystal data for 10:**  $C_{27}H_{31}ClCoN_3$ ,  $M = 491.93$ , monoclinic,  $C2/c$  (no. 15),  $a = 36.945(11)$  Å,  $b = 8.062(3)$  Å,  $c = 17.718(5)$  Å,  $\beta = 101.91(5)^\circ$ ,  $V = 5164(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.265$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 0.786$  mm<sup>-1</sup>,  $T = 203$  K, claret platy needles; 4500 independent measured reflections,  $F^2$  refinement,  $R_1 = 0.044$ ,  $wR_2 = 0.094$ , 3089 independent observed absorption-corrected reflections [ $|F_o| > 4\sigma(|F_o|)$ ,  $2\theta_{\text{max}} = 50^\circ$ ], 298 parameters. CCDC 256786.

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**Supporting Information Available:** Molecular structures of **2**, **3**, **10**, and **13**; CIF files for **2** and **10**; <sup>1</sup>H NMR and <sup>2</sup>H NMR spectra for key reactions and products, and GPC traces are available free of charge via the Internet at <http://pubs.acs.org>.

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