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Remote Activation of Nickel Complexes by Coordination of $B(C_6F_5)_3$ to an Exocyclic Carbonitrile Functionality

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*Summary: The synthesis of two new organometallic species, compounds **1** and **2**, allows for the investigation of remote activation through an exocyclic CN functionality. The in situ generation of **2** from **1** plus excess $B(C_6F_5)_3$ yields polyethylene possessing a bimodal distribution.*

Activation of nickel complexes by $B(C_6F_5)_3$ attachment onto an exocyclic carbonitrile basic site on a bidentate *N*,*O* ligand is demonstrated. The synthesis of the ligand 2-acetyl-3-(2,6-diisopropylphenylimino)butyronitrile allows access to the investigation of remote activation through an exocyclic CN functionality. The potassium salt of the ligand is obtained by deprotonation with KH in ether. Potassium 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olate can then be reacted with $Ni(PMe_3)_2(\eta^1\text{-}CH_2C_6H_5)Cl$ to yield 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olato-κ^2N,O](η^1-CH_2Ph)(PMe_3)Ni (**1**). The addition of 2 equiv. of $B(C_6F_5)_3$ to **1** yields 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olato)tris(pentafluorophenyl)borato-κ^2N,O]](η^3-CH_2Ph)Ni (**2**). Compound **2** is an active single component for the homopolymerization of ethylene. The resulting polymers are described by a single molecular weight distribution, consistent with the presence of a single active metal site. The in situ generation of **2** from **1** plus excess $B(C_6F_5)_3$ yields polyethylene possessing a bimodal distribution.

A variety of early and late transition metal complexes, the majority being neutral or cationic, are available for the preparation of polyolefins.[1] In addition considerable efforts have been focused on understanding the role of coactivators on mediating these polymerization processes.[2] There have also been substantial efforts directed at the development of single site initiators for the preparation of polyolefins.[3] Much of the motivation stems from the potential of fabricating new materials with previously unattained properties.

Zwitterionic complexes, where a partial positive charge formally resides at the metal center, constitute a smaller class of initiators.[4] In some examples, Lewis acids are used to activate the metal center upon coordination to a basic functionality on the ligand framework at a site removed from the metal center.[5] This type of activation places the Lewis acid away from the trajectory of monomer insertion and eliminates the complexities associated with the use of methylaluminoxane derivatives and the equilibria of complexes where anion decoordination or displacement is required for monomer insertion. Structural variations based on the α-iminocarboxamide ligand have led to the use of zwitterionic initiators in the tandem synthesis of branched polyethylene from ethylene alone.[6]

In this contribution, we report on nickel complexes supported by the 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olate ligand. Of particular importance is the synthetic control over the coordination mode of this ligand. The exocyclic carbonitrile functionality in 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-

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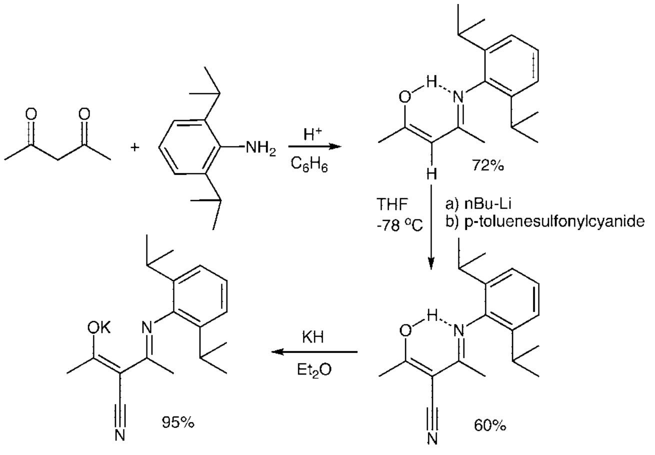
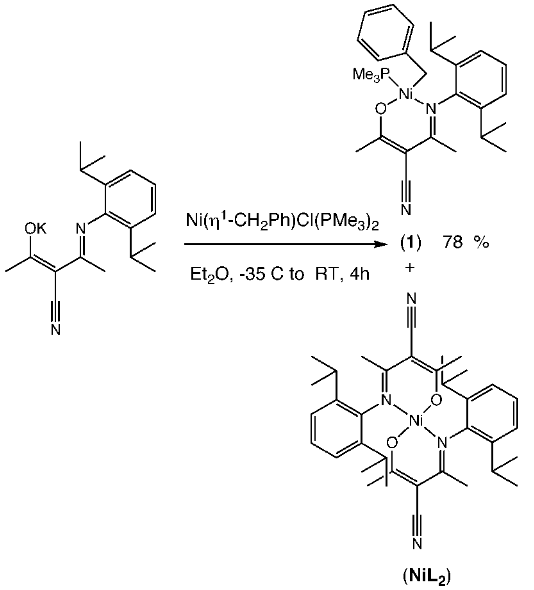
Scheme 1. Synthesis of Potassium 3-Cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olate



Scheme 2. Synthesis of 3-Cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olato-κ^2N,O](η^1-CH$_2$Ph)(PMe$_3$)Ni (1)



en-2-olato-κ^2N,O](η^1-CH$_2$Ph)(PMe$_3$)Ni (**1**) is sufficiently basic to coordinate to B(C$_6$F$_5$)$_3$ and form 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olato)tris(penta-fluorophenyl)borato-κ^2N,O]](η^3-CH$_2$Ph)Ni (**2**). The activity of **1** and **2** toward the homopolymerization of ethylene is also described along with the characterization of the products.

Scheme 1 shows the synthetic pathway to the potassium 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olate ligand salt. The reaction sequence begins with condensation of 3,3-dimethyl-pentane-2,4 dione with 2,6-diisopropylphenylaniline at 110 °C in the presence of catalytic p-toluenesulfonic acid in benzene. The product was purified via crystallization in 72% yield and the ^{1}H NMR spectrum is consistent with the exclusive formation of the enolate form of the product (12.1 ppm, 1H, O*H*-CCH$_3$; 5.25 ppm, 1H, C*H*-COHCH$_3$). The CN functionality is then installed by deprotonation with n-BuLi followed by the addition of p-toluenesulfonylcyanide at −78 °C. Purification of the product can be achieved either by chromatography or crystallization, in 60% yield. The ^{1}H and ^{13}C NMR spectra are consistent with the formation of a single isomer. FT-IR spectroscopy shows the presence of a band at 2200 cm^{-1}, due to the −CN functionality. The potassium salt of ligand is obtained by deprotonation of 2-acetyl-3-(2,6-diisopropylphenylimino)butyronitrile with KH in diethyl ether. The suspension was filtered and the solvent was removed to provide potassium 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olate as a beige powder in 95% yield.

Scheme 2 depicts the synthesis of **1** by the addition of potassium 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olate to Ni(η^1-CH$_2$Ph)Cl(PMe$_3$)$_2$ in diethyl ether at room temperature. The product is obtained as a mixture of **1** and bis[3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olate-κ^2*N,O*-]Ni (**NiL$_2$**). **NiL$_2$** was structurally characterized and the details have been deposited in the Supporting Information. **NiL$_2$** contamination can be minimized by slow addition of the ligand salt at decreased reaction temperatures. Successive crystallization from pentane allows isolation of **1** as air and thermally sensitive dark orange crystals in 78% yield. The ^{31}P NMR spectrum in C$_6$D$_6$ exhibits a single resonance at −12.31 ppm.

Single crystals of **1** suitable for X-ray diffraction studies were obtained by diffusion of pentane into a toluene solution at room temperature. The results of this study are shown in Figure 1. The molecular structure shows an *N,O*-binding mode for the 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olate ligand and a trans-orientation between PMe$_3$ and the imine nitrogen. The square-planar geometry around nickel is slightly distorted. For example, the N(1)−Ni−P and C(19)−Ni−O angles project 16° and 15.5°, respectively, out of the plane in opposite directions. The PMe$_3$ is located cis to the oxygen with an O−Ni−P angle of 84.24(9)°. The Ni−N(1), Ni−O, Ni−P and Ni−C(19) bond distances are 1.962(3), 1.912(3), 2.1535(12) and 1.947(4), respectively. The C(1)−O and C(5)−N(2) bond distances of 1.268(5) and 1.140(5) indicate double and triple bond character, respectively.[7]

Adding 2 equiv. of B(C$_6$F$_5$)$_3$ to **1** in toluene (scheme 3) results in the precipitation of Me$_3$P−B(C$_6$F$_5$)$_3$ and the formation of a new organometallic species, which was purified via crystallization from a pentane/diethyl ether mixture, orange plates were isolated in 80% yield.

The ^{1}H NMR spectrum of the product shows the presence of a single isomer. The upfield shift of the benzyl aromatic signals from 7.7 to 6.5 ppm is consistent with η^3-coordination. Three signals in the ^{19}F NMR spectrum at −134, −156, and −163 ppm indicate the presence of bound B(C$_6$F$_5$)$_3$. These data are consistent with the formation of 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olato)tris(pentafluorophenyl)borato-κ^2N,O]](η^3- CH$_2$Ph)Ni (**2**).

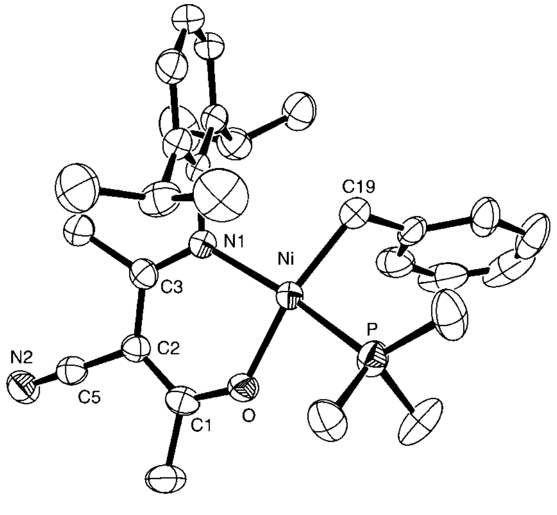
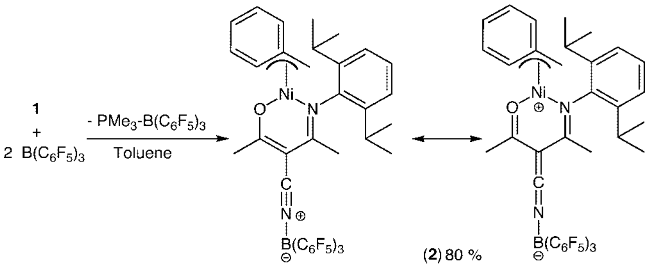


Figure 1. ORTEP drawing of **1** drawn at 50% probability. Hydrogen atoms were omitted for clarity.

Scheme 3. Synthesis of 3-Cyano-4-(2, 6-diisopropylphenylimino)pent-2-en-2-olato)tris(pentafluorophenyl)borato-κ^2N,O]](η^3-CH$_2$Ph)Ni (2)



Single crystals of **2** were obtained from a diethyl ether/pentane mixture and the resulting molecular structure is shown in Figure 2. Most significant is the binding of B(C$_6$F$_5$)$_3$ to the carbonitrile nitrogen and the η^3-coordination of the benzyl ligand. There is a noticeable rearrangement of the metrical parameters on the bidentate ligand. Note the lengthening of the C(5)−N(2) distance from 1.140(5) Å in **1** to 1.156(6) Å in **2**, whereas the C(5)−C(2) distance is reduced from 1.434(6) Å in **1** to 1.408(7) Å in **2** indicating the presence of double bond character. A slight contraction in the C(1)−O distance from 1.268(5) Å in **1** to 1.261(5) Å in **2** and a lengthening of the C(1)−C(2) from 1.394(6) Å in **1** to 1.422(6) Å in **2** was also observed. These changes in bond distance result from the two resonance structures in Scheme 3. The benzyl group is coordinated in a trans orientation relative to the imine nitrogen atom. A square planar arrangement surrounds the nickel center. The Ni−N(1) and Ni−O distances (1.911(4) Å and 1.879(3) Å, respectively) are slightly shorter compared to the corresponding distances in **1** (1.962(3) Å and 1.912(3) Å, respectively).

A study of the homopolymerization of ethylene using compound **1** activated with 5 equivalents of B(C$_6$F$_5$)$_3$ and compound **2** were carried out and the results are summarized in Table 1. These polymerization reactions were performed in a 100 mL autoclave reactor in 30 mL of toluene. Entries 1–5 show that the in situ addition of B(C$_6$F$_5$)$_3$ provides an active initiator species. Entry 7 shows that compound **2** can serve as a single component initiator. Comparison of entries 2 and 7 shows that under similar conditions **1**/5 B(C$_6$F$_5$)$_3$ provides polyethylene of similar molecular weight as that obtained by **2** alone, which suggests that the initiating species of **1**/5 B(C$_6$F$_5$)$_3$ is **2**. Some differences are apparent.

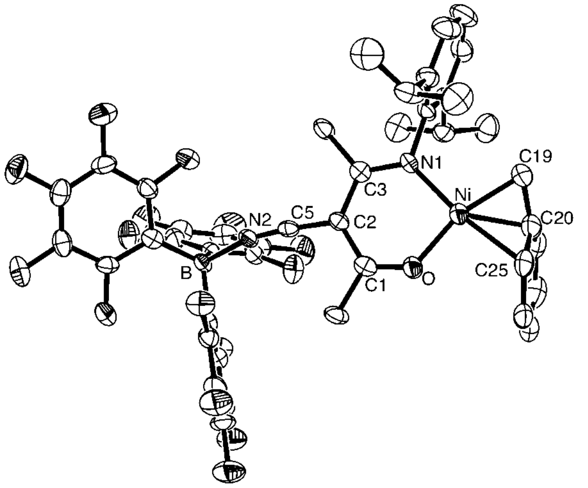


Figure 2. ORTEP drawing of **2** drawn at 50% probability. Hydrogen atoms were omitted for clarity.

Table 1. Summary of Polymerization Reactions[a]

entry	catalyst[a]	time[c]	P[d]	yield[e]	A[f]	M_w[g]	PDI	T_m[h]
1	**1/5**[b]	15	100	2.28	1.14	13.9	1.7	83
2	**1/5**[b]	40	100	5.72	1.07	14.9	1.8	80
3	**1/5**[b]	15	200	3.76	1.88	14.5	1.8	82
4	**1*/5**[b]	15	280	3.88	2.67	15.4	1.8	83
5	**1*/5**[b]	15	400	6.02	3.01	14.6	1.9	76
6	**2/3**[b]	40	100	4.08	0.728	14.6	1.9	82
7	**2**	40	100	1.70	0.320	14.5	1.8	76
8	**2**	40	200	2.82	0.530	15.9	1.9	77
9	**2**	40	300	3.17	0.595	17.2	2.0	79
10	**2***	40	400	2.51	0.674	14.7	2.0	76

[a] Polymerizations were carried out in 100 mL autoclave reactors with 8 μmol (5.6 μmol when indicated with an asterisk (*)) of Ni in 30 mL of toluene at 20 °C; the internal temperature was measured by using a thermocouple and controlled using an external cooling bath. [b] Equivalence of B(C$_6$F$_5$)$_3$ used. [c] Time in minutes. [d] Ethylene pressure in psi. [e] Grams. [f] Activity in kg polymer/(mmol Ni h). [g] $\times 10^3$g/mol. [h] °C.

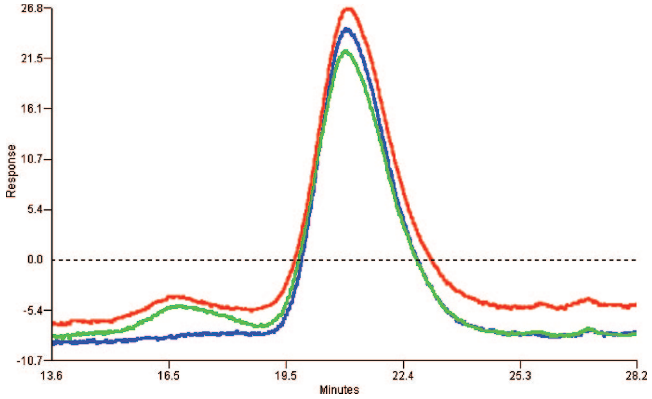


Figure 3. GPC analysis of the polyethylene isolated from entries 2 (red), 5 (green), and 7 (blue) in Table 1 relative to polystyrene standards at 135 °C.

In particular, the activity with **1**/5 B(C$_6$F$_5$)$_3$ is higher than that obtained with **2** alone; our current thinking is that B(C$_6$F$_5$)$_3$ acts as a scrubbing agent that removes impurities in the reaction medium, which may interfere with the propagating sites. Entries 1 and 2 show little loss in the reactivity of **1**/5 B(C$_6$F$_5$)$_3$ when the reaction time is extended from 15 to 40 min. In addition, increasing the ethylene pressure gives rise to an increase in the total consumption of monomer but does not significantly impact the molecular weight of the products. Although the specific branch content of these polymers has not been analyzed, a slight increase in the melting point of the polymer was observed suggesting a decrease in branching with increased pressure. An important difference between the polymer products obtained with **1**/5 B(C$_6$F$_5$)$_3$ compared to those obtained with **2** is the presence of a small fraction of high molecular weight polymer with a M$_w$ of approximately 700 000. The lack of bulk around the metal center facilitates chain transfer, which is responsible for the major fraction of polymer isolated to be low molecular weight.

Figure 3 shows gel permeation chomatography (GPC) results of entries 2, 5, and 7. A monomodal distribution is only observed with **2**. Entries 2 and 5 show a bimodal distribution. In addition as shown by entry 6, **2**/3 B(C$_6$F$_5$)$_3$ shows increased activities compared to those with **2** alone and yields PE with a bimodal molecular weight distribution similar to entries 1–5 (see the Supporting Information). Because the small high molecular

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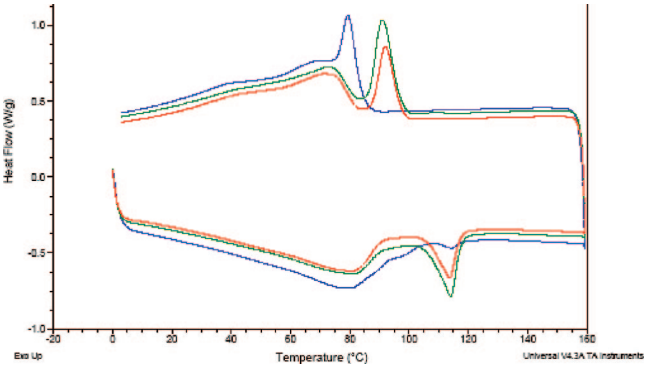

Figure 4. DSC trace of PE isolated from: entries 2 (red), 5 (green), and 7(blue).

weight fraction is present when excess $B(C_6F_5)_3$ is added to **2**, it is our current thinking that a second species maybe generated in low concentrations. The species responsible for this high molecular weight fraction is currently under investigation, but may involve the coordination of another $B(C_6F_5)_3$ to the oxygen on the ligand framework. This coordination could increase the steric bulk around the metal center resulting in PE with increased molecular weight.

Thermal analysis was performed using differential scanning calorimetry (DSC). Typical results are shown in Figure 4. Samples were scanned from 0 to 160 °C at 10 °C /min. Two broad thermal transitions are observed for the PE obtained from compound **1**, as shown by the red and green curves corresponding to entries 2 and 5, respectively. Analysis of the polymer isolated from entry 7 (blue curve) shows a single broad melting transition. Thus, the DSC data correlate with the molecular weight characterization. This allows for the assignment of the major fraction produced by the zwitterionic species to be a branched low molecular weight polymer with a melting point of 80 °C.

In summary, we demonstrated the synthesis of the 2-acetyl-3-(2,6-diisopropylphenylimino)butyronitrile ligand. In addition two new organometallic complexes have been isolated and characterized. The first from the reaction of potassium 3-cyano-4-(2,6-diisopropylphenylimino)pent-2-en-2-olate and $Ni(\eta^1\text{-}CH_2C_6H_5)Cl(PMe_3)_2$ to yield **1** and the reaction of **1** with 2 equiv. of $B(C_6F_5)_3$ yields **2**. The binding of $B(C_6F_5)_3$ to the carbonitrile nitrogen results in a redistribution of electron density within the electronically delocalized ligand framework. The net result is a removal of electron density from Ni, as shown by the two resonance structures in Scheme 3. Compound **2** is a single component initiator for the homopolymerization of ethylene. The resulting polymers are described by monomodal molecular weight distributions, consistent with the presence of a single active metal site. The in situ generation of **2** from **1** plus excess $B(C_6F_5)_3$ yields polyethylene possessing a bimodal molecular distribution. The major fraction is consistent with that produced by **2**. The ratio of the high to low molecular weight is unaffected by pressure or reaction time. Activation via an exocyclic CN functionality opens new possibilities for design of ligands appropriate for zwitterionic ethylene polymerization initiators.

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Supporting Information Available: Synthetic details (PDF) and crystallographic studies (CIF) for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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