α-Iminocarboxamidato Nickel Complexes

BRYCELYN M. BOARDMAN AND GUILLERMO C. BAZAN*

Center for Polymers and Organic Solids, Departments of Chemistry & Biochemistry and Materials, University of California, Santa Barbara, California 93106

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CONSPECTUS

Polyolefins constitute a vast class of macromolecules that range from everyday plastics to sophisticated materials used as hip-replacement joints and in bullet-proof vests. By tailoring the molecular structure of the backbone, researchers can tune the bulk properties of these materials for specific product applications.

Transition-metal complexes that mediate the polymerization of ethylene, 1-alkenes, and related monomers provide an important tool for industrial preparation. Although commercially viable options exist for large-scale manufacturing, it is not possible to achieve all desirable polymer targets using these methods. For example, the copolymerization of ethylene with co-monomers bearing polar functionalities under living conditions, where there is high activity and minimum chain transfer and termination, is not available at this scale. Also, given the magnitude of polyolefin production, we anticipate a need to more efficiently manage chemical resources. For these reasons, new metal/catalyst combinations and methods for their applications continue to be an active area of research in both academic and industrial laboratories.

This Account focuses on the chemistry of α-iminocarboxamidato complexes of nickel carried out in our laboratories. Such complexes can serve as precursors to zwitterionic or neutral active species, depending upon the mode of activation. We have successfully applied the zwitterionic systems in the tandem action of multiple active sites to yield branched polyethylene from ethylene alone; a coordinated effort of catalysts that is reminiscent of metabolic pathways. These polymerizations show many of the characteristics of living polymerizations. The neutral initiators allow for the controlled preparation of copolymers containing ethylene and functionalized co-monomers and can be used to access higher order polymer architectures, such as block, tapered, and pseudo-tetrablock copolymers. Many of these polymers are not readily available using other catalytic methods.

In this Account, we first provide a historical narrative of developments leading to ligands derived from the α-iminocarboxamide framework. Second, we explore how structural variations of this ligand system are readily obtained and how they can be used to provide insight into the mechanism of activation and for controlling polymerization reactions. We conclude by describing emerging applications, particularly in the area of graft copolymers.
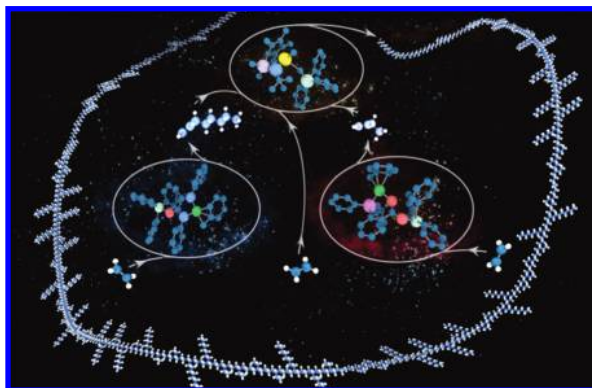
Introduction

Pioneering work by Ziegler and Natta revealed that certain transition-metal catalysts facilitate the polymerization of olefins under mild reaction conditions.[1] While under certain circumstances "initiators" may be a more technically precise term to describe the active polymerization sites, the term "catalyst" will be used throughout this Account.

Subsequent work performed on homogeneous bent metallocenes of early transition metals was of fundamental importance for teaching how to rationally predict the structure of the polymer products via the steric and electronic properties of ligands on the precursor complexes.[2] New polymers with unique properties were successfully designed using these catalysts, and some of these

are now commercialized. Interest on late transition-metal complexes rejuvenated in the mid 1990s principally because of their higher tolerance toward co-monomers bearing polar substituents and their ability to yield branched polyethylene via "chain walking" reactions. This collective effort has yielded catalyst types that are capable of excellent control over the stereochemistry of the backbone, show living characteristics, and display tolerance of polar functional groups.[3] The overall scientific and commercial effort on the design of polyolefin catalysts has been immense and encompasses polymer science, organometallic chemistry, theoretical insight, and chemical engineering considerations. Recent literature examples highlight how innovative new ligand metal combinations and methods of polymerization continue to emerge with the goal of expanding the range of properties and possible uses of the polymer products.[4]

In this Account, we detail our rationale for the development of nickel complexes supported by α-iminocarboxamidato ligands. Our goal is to provide a broad general perspective that illustrates a continuum of ideas starting from an interest in the use of aromatic heterocycles as ligands for early transition metals to the generation of macroinitiators capable of yielding graft copolymers with a polyolefin backbone and pendant branches derived from free-radical-mediated reactions.

Zwitterionic Nickel Catalysts

Interest on boron heterocycles that are isoelectronic to all-carbon π-aromatic rings traces its roots to fundamental questions associated with the concept of aromaticity.[5] For example, the anionic boratabenzene or the dianionic borollide[6] are 6-π electron donors analogous to the cyclopentadienyl fragment.[7,8] These electronic relationships make the preparation and study of early metal bent metallocene analogues compelling for understanding how differences in metal–ligand binding can modify polymerization reactions. In collaboration with Professor A. Ashe, our group described the synthesis and reactivity of a series of boratabenzene complexes of general structure $(C_5H_5B–R)_2ZrCl_2$ that are isoelectronic to $(C_5H_5)_2ZrCl_2$, an archetypal precursor for sites capable of ethylene polymerization. Indeed, activation of the $(C_5H_5B–R)_2ZrCl_2$ complexes with methylaluminoxane (MAO) led to fast ethylene consumption.[9] A significant observation was that, under similar reaction conditions, the exocyclic substituent on boron modifies the product properties. When $R = N(CH(CH_3)_2)_2$, one obtains polyethylene (PE); changing to $R = OCH_2CH_3$, the product is a distribution of 1-alkenes. These observations, in conjunction with examination of the structural parameters in different
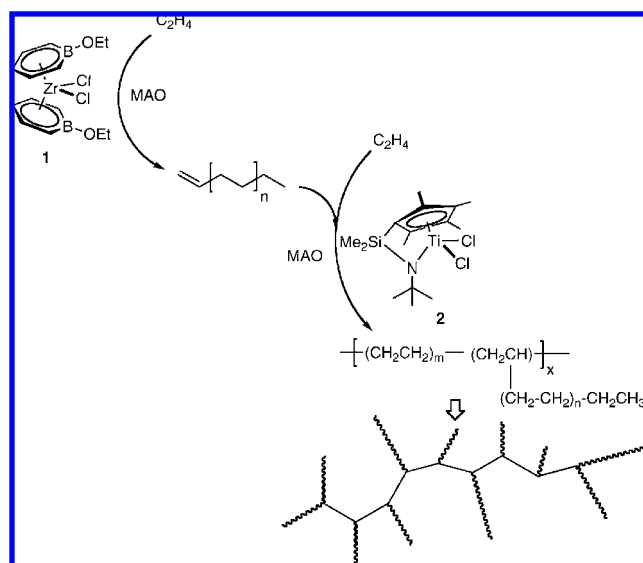
$(C_5H_5B–R)_2ZrCl_2$ derivatives, indicate that reactivity is modified by changes of the electron density at the metal center by virtue of the π-overlap between boron and the exocyclic group.

It occurred to us that the product selectivity observed with $(C_5H_5B–OCH_2CH_3)_2ZrCl_2$ (**1**)/MAO complemented the propensity of "constrained geometry catalysts",[10] such as $[(\eta^5-C_5(CH_3)_4)SiMe_2(\eta^1-NC(CH_3)_3)]TiCl_2$ (**2**),[11] to effectively incorporate 1-hexene and 1-octene into a growing PE chain.[12] A combination of compounds **1** and **2** in the presence of MAO was anticipated to form branched PE from ethylene alone via the tandem catalyst approach in Scheme 1. In this strategy, 1-alkenes produced by compound **1**/MAO remain in solution, and as their concentration increases, they become incorporated into the PE grown by compound **2**/MAO. It was found that the PE products display low melting temperatures (T_m) and ^{13}C nuclear magnetic resonance (NMR) spectroscopy reveals signatures because of the branched structure. However, it was not possible to elucidate the exact polymer structure because of the distribution of branch lengths and also because some of the branches are sufficiently long that their internal methylene carbons overlap with those in the backbone.

While successful, the **1**/**2**/MAO combination suffers from an important limitation. Namely, the activities of **1**/MAO and **2**/MAO depend upon MAO/transition metal ratios,[9a,b] a situation that results in the inability to obtain a linear relationship between the molar ratio of the precatalysts and the incorporation of branches into the backbone. Catalysts based on better defined coactivators seemed a reasonable way to alleviate these problems.[13] Inspired by Piers' work on the

SCHEME 2. Formation of Poly(ethylene-co-butene) Using Compounds **4/5**
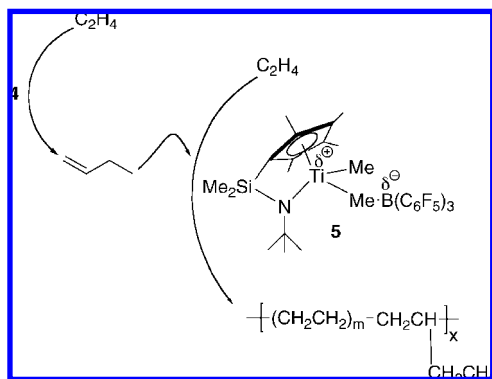
action of B(C6F5)3 on carbonyl Lewis bases,[14] a new method of activating SHOP-type catalysts was explored. It was found that **3**[15] and B(C6F5)3 produce **4**, as shown in eq 1. Of particular importance is the resonance description of **4** that places a positive charge on Ni and highlights the removal of electron density from the metal by attachment of a Lewis acid on a ligand site removed from the monomer insertion trajectory.
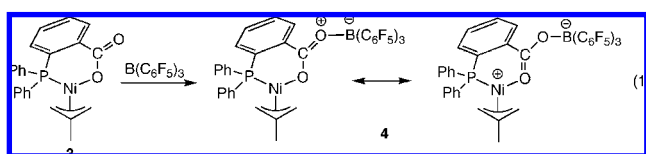
Compound **4** is considerably more active toward ethylene than **3**.[16] Furthermore, it is possible to find reaction conditions where the majority of the product (>99%) is 1-butene, i.e., ethylene dimers. Such features are a good complement to the reactivity of **5** (see Scheme 2), which, as in the case of **2**/MAO, can copolymerize ethylene with 1-alkenes.[17] Indeed, it is possible to combine **4** and **5** to produce poly(ethylene-co-1-butene) from ethylene alone, as shown in Scheme 2. NMR spectroscopy showed a linear relationship between the frequency of ethyl branches in the backbone and the Ni/Ti ratio. Such features indicate that the overall process behaves predictably and showed that well-defined homogeneous catalysts can be coordinated to generate polymer architectures from a single monomer feedstock that are not readily obtained by the action of a single catalyst.

The methallyl ligand in **4** is tightly bound and less reactive than the catalytic species, leading to incomplete participation of Ni sites. To obtain more control, [(C6H5)2PC6H4C-(O−B(C6F5)3)O-$\kappa^2 P,O$]Ni(η^3-CH2C6H5) (**6**) was introduced, in which the methallyl ligand in **4** is replaced by the isoelectronic but more weakly bound η^3-benzyl counterpart.[18] Figure 1 shows the molecular structure of **6**, as determined by single-crystal X-ray diffraction studies. Compound **6** consumes more
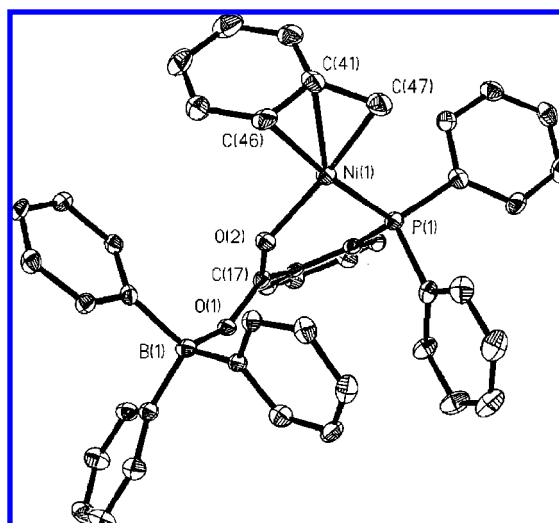
FIGURE 1. ORTEP view of compound **6**. Thermal ellipsoids at 30% probability level. Hydrogen and fluorine atoms have been omitted for clarity.

ethylene in an hour than **4** without influencing the 1-butene/1-hexene ratio, consistent with the presence of the same catalytic species and a more efficient initiation step.[19] Tandem catalysis with **6/5** produces PE with more branching than **4/5**. Examination of the product distribution under conditions where higher 1-alkene products are obtained revealed unexpected features. Specifically, the K factor, defined by

$$K = (\text{mol of } C_{n+2} \text{ olefin})/(\text{mol of } C_n \text{ olefin}) = R_p/(R_p + R_{CT})$$

where R_p and R_{CT} are the rates of propagation and chain transfer, respectively, is independent of ethylene pressure ($P_{C_2H_4}$) yet shifts toward higher molecular-weight products with increasing temperature. From the plot of ln[ratio of 1-butene to all higher α-olefins] against $1/T$, the difference in activation enthalpies for propagation and chain transfer [$\Delta H_p^{\ddagger} - \Delta H_{CT}^{\ddagger} = 4.8(2)$ kcal/mol] and the difference in activation entropies [$\Delta S_{CT}^{\ddagger} - \Delta S_p^{\ddagger} = -11(1)$ eu] can be obtained. These values imply that, while propagation and chain transfer are second-order processes, the transition state for chain transfer is more organized.

α-Iminocarboxamidato Ligand

Compound **4** showed how to increase the activity of a metal center by Lewis acid attachment to a basic site removed from the trajectory of the incoming substrate, and unlike the majority of other activation processes, no dissociative process is required for initiation or propagation of the oligomerization reactions.[13] On the basis of experimental and theoretical studies of nickel α-diimine complexes, it was expected that an increase of steric interference at the pseudo-axial sites around the metal center would enable this new activation strategy to

SCHEME 3. Synthesis of α-Iminocarboxamide Derivatives
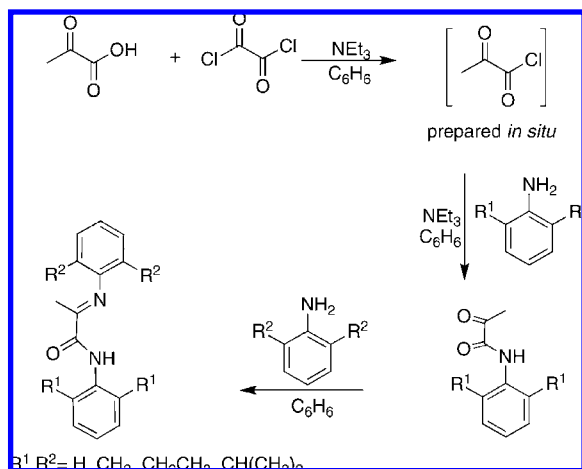
yield complexes capable of forming high-molecular-weight PE.[3] Such considerations led us to consider the α-iminocarboxamide framework, which affords flexibility of substituents on nitrogen and an exocyclic carbonyl when attached to a metal in a *N,N* fashion.[20] The initial synthesis begins by the reaction of oxalyl chloride and pyruvic acid to generate the acid chloride *in situ* (Scheme 3). The addition of an equivalent of aniline in the presence of triethylamine results in the reaction at the acid chloride site. An additional equivalent of the same aniline may be added at this stage to yield similar N substituents. Alternatively, one can access unequally substituted variations by the addition of a different aniline to the initially formed *N*-aryl pyruvamide.

Deprotonation of the α-iminocarboxamides by KH in THF, followed by their addition to Ni(η^1-CH$_2$Ph)Cl(PMe$_3$)$_2$,[18] yields the target complexes (Scheme 4). The binding mode of the α-iminocarboxamidato fragment depends upon the bulk of the *N*-aryl groups. *N,N* binding is observed with smaller substituents, as seen in **7**, whereas larger molecules, such as **11**, prefer *N,O* binding.[20b] The addition of 2 equiv of B(C$_6$F$_5$)$_3$ to **7**, **9**, and **11** results in the precipitation of Me$_3$P—B(C$_6$F$_5$)$_3$ and the desired zwitterionic complexes. It is interesting to note that the affinity of the borane for the carbonyl gives rise to a ligand rearrangement in the case of **11**, ultimately leading to **11′** (Scheme 4). Furthermore, the products from reactions with ethylene show similar trends as those observed with nickel α-diimine complexes; high-molecular-weight PE is obtained with **9′** and **11′** and a mixture of oligomers with **7′**.[20a] These studies establish the use of α-iminocarboxamidato ligands and demonstrate their flexibility in modulating the reactivity of catalytically active nickel complexes.
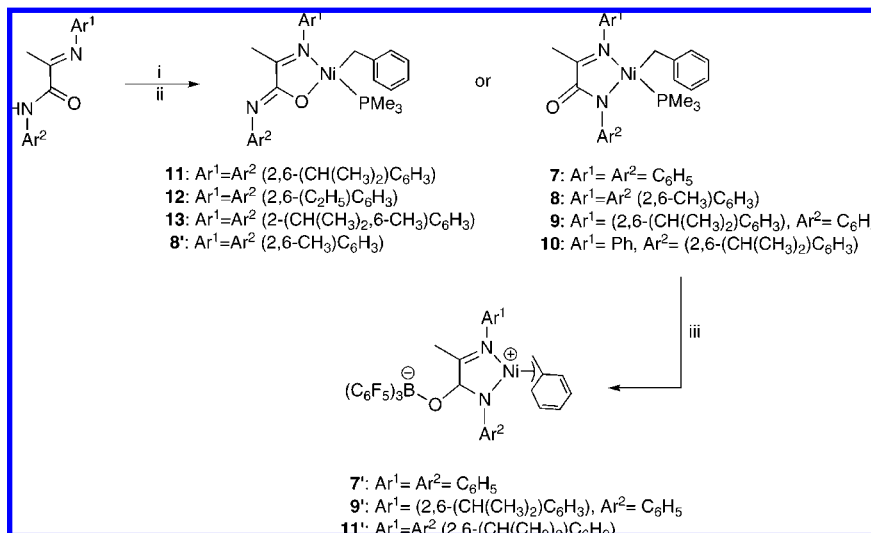
Compounds **7**, **9**, and **11** led to the consideration of other ligand classes for generating zwitterionic complexes.[21−27] As

seen in Figure 2, **14** is a molecule that was specifically designed to extend the distance between Ni and the site of Lewis acid attachment.[21] A comparison against a neutral ketoaryliminato analogue showed that **14** is more active toward ethylene oligomerization by approximately 2 orders of magnitude. The higher activity highlights the effect of the reduced electron density at nickel and that the Lewis acid makes its influence across the Ni−N−C−C−O structural unit.

Three-Component Tandem Polymerization

Similar ethylene consumption rates are observed with **6** and **7′**. However, their products are different, with **6** producing predominantly 1-butene and **7′** giving rise to a distribution of 1-alkenes with a larger average number of repeat units. As shown in Scheme 5, it is conceptually feasible to combine **6** and **7′** with **5** in a triple tandem catalysis scheme to provide a branched PE structure that is not readily attainable using tandem cooperation of two catalysts.[29a] Controlling the action of **5**, **6**, and **7′**, such that the 1-butene generated by **6** (shown in blue) and the distribution of 1-alkenes from **7′** (shown in green) are efficiently incorporated by the titanium site of **5** into a PE backbone, provides polymers with varying ratios of ethyl branches and longer branches. The challenge in reducing these ideas to practice resides in the large matrix of reaction variables that need to be concurrently optimized, so that the majority of 1-alkenes are introduced in the product. Furthermore, characterization of molecular-weight distributions by gel-permeation chromatography (GPC) and polymer structures by ^{13}C NMR spectroscopy are time-consuming but necessary to obtain insight into the success of the reactions. A different approach, one that would generate a large number of polymerization experiments in a short time was required to attain optimum conditions. Successful execution of Scheme 5 was achieved using high-throughput parallel reactor technology and computer control of reaction conditions.[35] The resultant polymer materials were examined with techniques that take advantage of robotic assistance. By examination of polymerization reaction libraries, it was possible to find the appropriate catalyst ratios, temperatures, concentrations, and reaction times, so that the products were described by monomodal molecular-weight distributions. These studies show that three catalysts can be coordinated to produce a single product and that it should be possible to generate branched PEs with properties tailored for specific applications by simply adjusting the composition of catalyst mixtures.

SCHEME 4. Synthesis of *N,N-* or *N,O*-Bound α-Iminocarboxamidato Nickel Complexes[a]

11: Ar^1=Ar^2 (2,6-(CH(CH$_3$)$_2$)C$_6$H$_3$)
12: Ar^1=Ar^2 (2,6-(C$_2$H$_5$)C$_6$H$_3$)
13: Ar^1=Ar^2 (2-(CH(CH$_3$)$_2$,6-CH$_3$)C$_6$H$_3$)
8': Ar^1=Ar^2 (2,6-CH$_3$)C$_6$H$_3$)

7: Ar^1=Ar^2= C$_6$H$_5$
8: Ar^1=Ar^2 (2,6-CH$_3$)C$_6$H$_3$)
9: Ar^1= (2,6-(CH(CH$_3$)$_2$)C$_6$H$_3$), Ar^2= C$_6$H
10: Ar^1= Ph, Ar^2= (2,6-(CH(CH$_3$)$_2$)C$_6$H$_3$)

7': Ar^1= Ar^2= C$_6$H$_5$
9': Ar^1= (2,6-(CH(CH$_3$)$_2$)C$_6$H$_3$), Ar^2= C$_6$H$_5$
11': Ar^1=Ar^2 (2,6-(CH(CH$_3$)$_2$)C$_6$H$_3$)

[a] (i) KH/THF/−H$_2$, (ii) Ni(η^1-CH$_2$Ph)Cl(PMe$_3$)$_2$/toluene/−KCl, and (iii) B(C$_6$F$_5$)$_3$/toluene/−Me$_3$P−B(C$_6$F$_5$)$_3$.
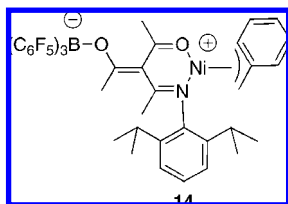

FIGURE 2. Example of remote activation across a Ni−N−C−C−C−O unit.

Neutral α-Iminocarboxamidato Complexes: Polymer Synthesis

The addition of bis(1,5-cyclooctadiene)Ni (Ni(COD)$_2$) to **11** generates a catalytic species capable of polymerizing ethylene, albeit with lower activities than those observed with zwitteri-onic **11'**.[20a,29] The reactivity is higher when 2.5 equiv of Ni(COD)$_2$ are used instead of 1 equiv. NMR spectroscopy experiments showed no reaction over a period of 1.5 h when **11** and Ni(COD)$_2$ are mixed together. Furthermore, no PE forms upon the addition of ethylene to either **11** or Ni(COD)$_2$. Thus, the formation of the catalytic species requires the presence of the three reactants and suggests displacement of COD by ethylene as the first step in the initiation process. The PE formed by **11**/Ni(COD)$_2$ at 20 °C and $P_{C_2H_4}$ = 100 psi shows relatively narrow polydispersities (PDIs = 1.3−1.5). Moreover, a plot of M_n against the polymerization time is linear, which is a typical feature of living polymerization systems. Because the PDIs of these polymers are not as narrow as one would

SCHEME 5. Triple Tandem Catalysis for the Synthesis of Branched PE Using Compounds **5**, **6**, and **7'**
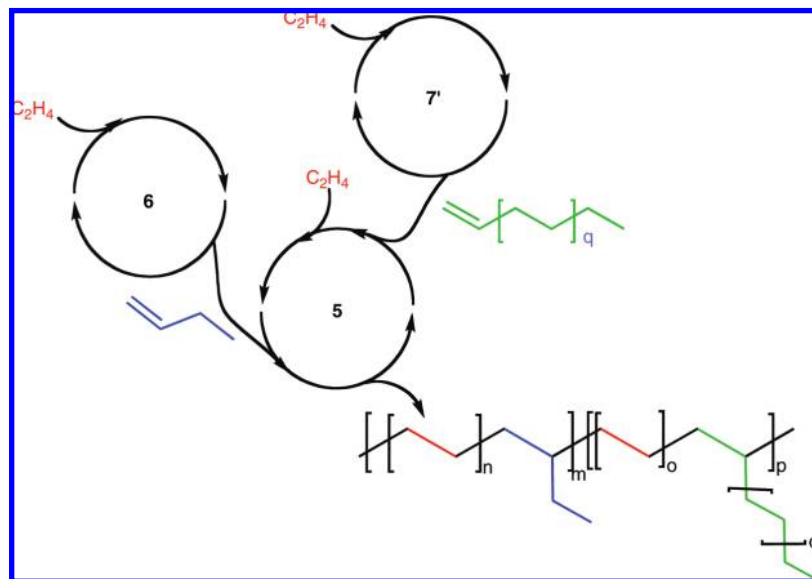
expect for a truly living polymerization, the polymerization was classified as quasi-living.[30]

It is also possible with **11**/Ni(COD)$_2$ to copolymerize ethylene with functionalized norbornenes, such as 5-norbornen-2-ol and 5-norbornen-2-yl acetate (NBA) and to obtain high-molecular-weight PE bearing hydroxy and acetate functionalities, respectively, as shown in eq 2. For the NBA copolymerizations, one also observes quasi-living characteristics; linear growth of M_n versus time is possible up to 120 min. These reactions are carried out by first mixing **11**/Ni(COD)$_2$ and NBA in toluene inside an autoclave reactor. Examination of these mixtures by NMR spectroscopy reveals no reaction under these conditions. Subsequent addition of ethylene results in copolymers with 5−25% molar incorporation of NBA within a PE backbone, depending upon $P_{C_2H_4}$, [NBA], and reaction time. Higher incorporation occurs with shorter reaction times because [NBA] decreases as the reaction proceeds. Additionally, a decrease in copolymer molecular weight occurs with increasing [NBA], suggesting competition between the acetate functionality and ethylene for the active metal site. A diversity of acetate-functionalized PEs with excellent control over polymer structure can thus be accessed.[29]
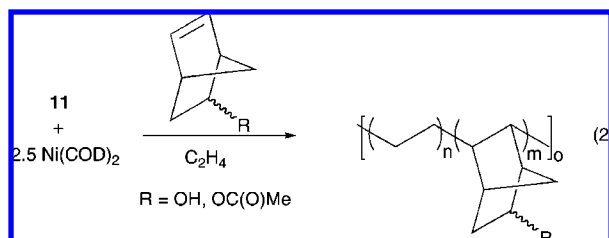
Under $P_{C_2H_4}$ = 50 psi and [NBA]$_0$ = 0.15 M, **11**/Ni(COD)$_2$ produces an amorphous copolymer with ∼25 mol % NBA, while under $P_{C_2H_4}$ = 1100 psi, one obtains semi-crystalline copolymers that contain 1−2 mol % NBA. This ability to control polymer structure by pressure variations under quasi-living conditions allows for the synthesis of block copolymers with segments containing different ethylene/NBA ratios. The approach is illustrated in Scheme 6[30a] and, in practice, can be demonstrated by first carrying out the copolymerization at $P_{C_2H_4}$ = 50 psi for a set period of time (t_1). A pressure jump to $P_{C_2H_4}$ = 1100 psi is then applied, and the reaction is allowed to proceed for another predetermined interval (t_2). The products after t_1 + t_2 are described by monomodal molecular-weight distributions with PDIs between 1.3 and 1.6, and there is excellent conversion of the product at the end of t_1 into the block copolymer structure. Analysis by NMR spectroscopy of the final product shows higher ethylene incorporation, relative to the copolymer obtained after t_1. Thermal characteriza-

SCHEME 6. Block Copolymers Obtained by Increasing $P_{C_2H_4}$
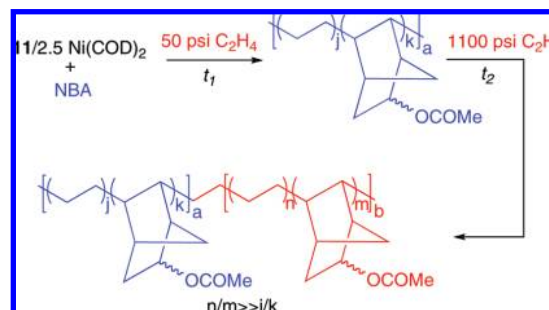
tion provides an indication that two segments with different physical properties are obtained. Glass transition temperature (T_g) values are observed for the amorphous segments from 25 to 28 °C, together with melting transitions (T_ms) in the 108−121 °C range for the ethylene-rich portions. Finally, transmission electron microscopy (TEM) revealed microphase separation between the two different types of domains, as shown in Figure 3.

The sudden differential in $P_{C_2H_4}$ for changing the [C$_2$H$_4$]/[NBA] ratio in Scheme 6 is difficult to carry out effectively in a large reactor, as would be required for scale up. However, on the basis of the fact that one starts with a set [NBA]$_0$ but [C$_2$H$_4$] can be maintained constant and that termination and chain transfer are not significant, it seemed reasonable that allowing the reaction to proceed at a constant $P_{C_2H_4}$ would yield a tapered block copolymer (TBC). TBCs are characterized by a chemical structure with a gradual change of composition along the chain, from one co-monomer to the other. If the average chain length is sufficiently long, the degree of incompatibility between the two co-monomers is high, and the gradient profile provides chain ends that contain mainly one
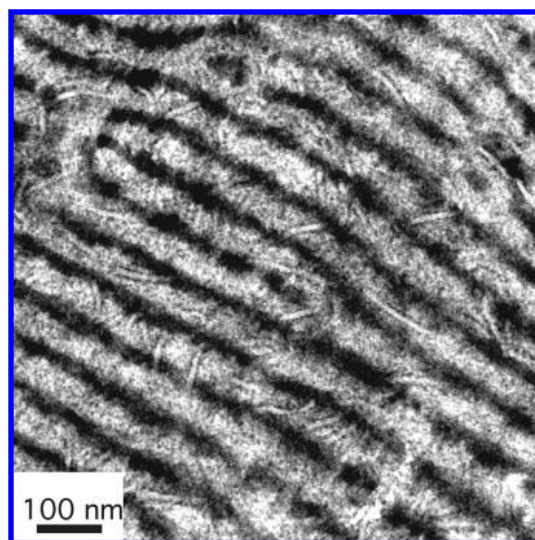

FIGURE 3. TEM image of a block copolymer obtained via the process in Scheme 6. The morphology is lamellar, where semi-crystalline PE layers (white) alternate with amorphous copolymer layers (dark).

type of monomer, then microphase-separated structures similar to those observed in traditional block copolymers can be observed.[32] Equation 3 shows how these ideas can be reduced to practice for C_2H_4/NBA.[37] For example, with: $[NBA]_0$ = 0.15 M, [**11**] = 0.67 mM, $[Ni(COD)_2]$ = 1.67 mM, $P_{C_2H_4}$ = 200 psi, after 4 min of reaction, one obtains a copolymer with M_n = 10 kg/mol (PDI = 1.3) and a mol % NBA of 18 ± 1. Increasing the reaction time to 120 min yields M_n = 170 kg/mol (PDI = 1.5) and 4 ± 1 mol % NBA. The fact that the overall fraction of NBA decreases with longer reaction times is consistent with the polymer chains containing the highest mol % NBA at the beginning, i.e., when [NBA] is at its maximum. Copolymers with larger NBA content are soluble in toluene, whereas the ethylene-rich segments formed at later stages of the reaction are not. No indication of phase separation was observed by TEM in films with reaction times <45 min (M_n < 63 kg/mol). With longer reaction times, the polar and nonpolar portions of the polymer chain are sufficiently different to result in microphase-separated structures with lamellar or cylindrical morphologies.
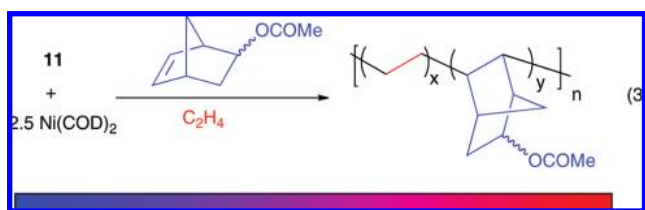

The fact that the gradient profile in TBCs obtained by eq 3 leads to chains with amorphous and crystalline end points prompted targeting multiblock copolymers. By combining the product characteristics obtained from Scheme 6, i.e., a change in the polymer composition because of sudden changes in monomer concentration, and eq 3, i.e., a gradual change in polymer structure because of NBA depletion, one can obtain a process for obtaining pseudo-tetrablock copolymers, as illustrated in Scheme 7. One begins the polymerization with a set $[NBA]_0$ under a constant $P_{C_2H_4}$. The reaction continues for a time t_1, during which [NBA] decreases in the reaction medium, leading to an increase of C_2H_4 incorporation relative to NBA. After t_1, a second batch of NBA is added to the reactor, and the reaction is then allowed to proceed for a time t_2. The end result is a backbone containing two similar TBC structures covalently joined in a head to tail fashion; each chain contains four distinct regions, similar to a tetrablock copolymer.[34a]

Structural Diversity

Studies to understand the active sites responsible for the quasi-living polymerizations previously discussed were initially
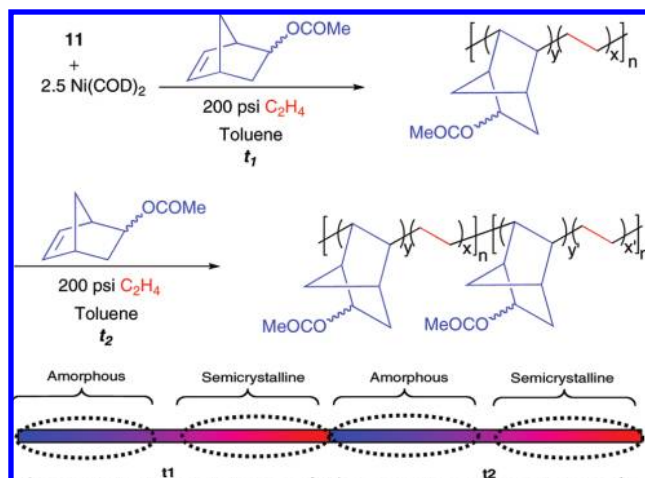
centered on a comparison of the reactivity of complexes **7**−**13** in Scheme 4. The most important reactivity trend is that only *N,O*-bound precursors give rise to catalytic action when in the presence of $Ni(COD)_2$. Compound **8** is noteworthy in that the *N,O*-bound isomer **8′** is kinetically preferred, probably because of easier displacement by the sterically unencumbered oxygen. However, the *N,N* isomer **8** is ultimately the thermodynamic product, which reflects an electronic preference for nickel to bind nitrogen over oxygen. Further examination of reactions with compound **8′** and $Ni(COD)_2$ by ^{1}H NMR spectroscopy gives an indication of η^3-benzyl formation and PMe_3 loss. This information supports that the loss of phosphine is a prerequisite for the initiation of ethylene polymerization. Relevant to the discussion here is the synthesis of the neutral η^3-benzyl complex **15**, as shown in eq 4, which proved unreactive toward ethylene. Putting together the structural and reactivity observations provided in this study suggests that the species responsible for initiating polymerizations are neutral [*N,O*-α-iminocarboxamidato](η^3-benzyl)Ni complexes. It is also interesting to note that the polymerization reactions show no decrease in activity, even after 30 min. Perhaps *N,O* → *N,N* rearrangement is slower for the phosphine-free species, or the resting state of the active site is an olefin adduct, in which isomerization is restricted. Alternatively, it may be that *N,N*-bound species are incapable of initiation but can insert ethylene once the polymerization is underway.
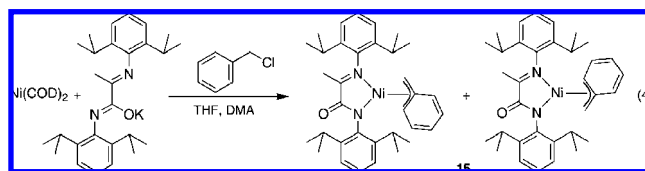

Better insight into the catalytic species led to the synthesis of phosphine-free complexes that eliminate the need for

co-activation with Ni(COD)$_2$. A typical example is shown in eq 5 for **16**, where 2,6-Lu is 2,6-lutidine.[34] A similar reaction is successful with pyridine but fails when 2,6-di(*tert*-butyl)pyridine is used. Ethylene polymerization or copolymerization with NBA can be achieved with **16**, but it is necessary to heat the reaction to at least 40 °C. Higher temperatures are required when using the pyridine analogue of **16**, presumably as a result of the more tightly bound nitrogen ligand. It is not possible with **16** to obtain quasi-living C$_2$H$_4$/NBA copolymerization; however, these complexes may be advantageous for situations where there is a need to circumvent using Ni(COD)$_2$.[34]
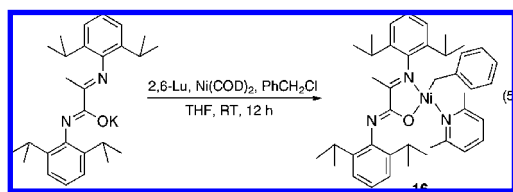
The most recently reported α-iminocarboxamidato ligands involve variations with additional steric bulk at the site adjacent to the imine functionality (eq 6). An important improvement in ligand synthesis involves using TiCl$_4$ and trimethylamine during the condensation of the second aniline equivalent. Ethylene homopolymerization reactions show that as the bulk on the ligand framework increases so does the activity and the molecular weight of the products, i.e., **17** < **18** < **19** < **20**. Copolymerization reactions show that the reactivity of NBA relative to ethylene decreases with increasing steric constraints. Compound **19**, however, exhibits high levels of activity and NBA enchainment, while **21** yields the narrowest PDIs. Indeed, as described below, the success of macroinitiator synthesis rests on the improved reactivity of **19** relative to **11**.[35]
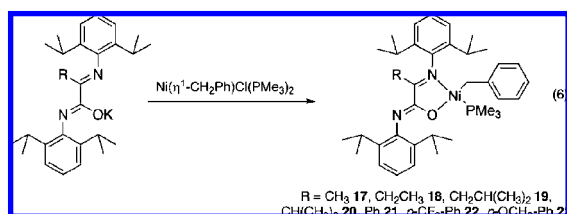
Synthesis of Macroinitiators

As a final example on the flexibility of α-iminocarboxamidato Ni complexes for attaining functionalized PE with higher order architectures, we describe the synthesis of macroinitiators and their subsequent grafting by atom transfer radical polymerization (ATRP), as shown in Scheme 8.[36] In the first step, **19**/Ni(COD)$_2$ are used to copolymerize ethylene with **24**. The isobutyl variant, **19**, was chosen because increased bulk adja-
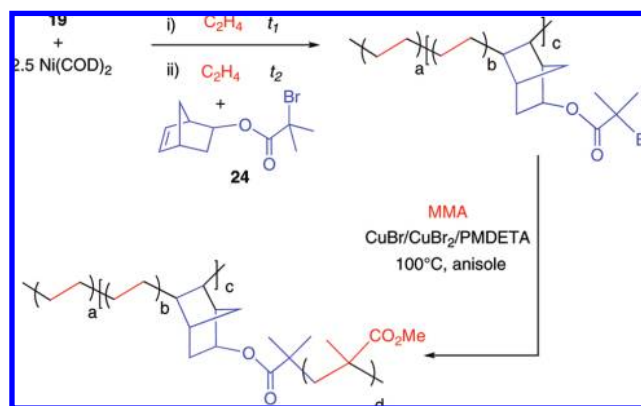
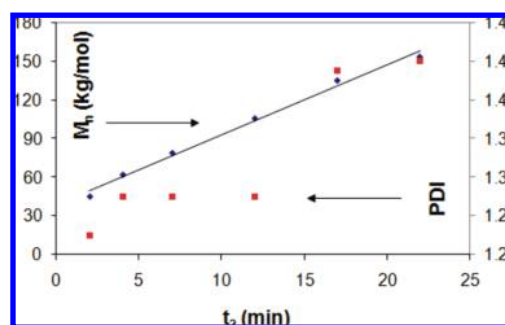[a] PMDETA is *N,N,N',N'',N''*-pentamethyldiethylenetriamine.

FIGURE 4. Plot of macroinitiator M_n and PDI versus t_2 (t_1 = 3 min).

cent to the imine leads to faster initiation and weaker interactions with polar groups (*vide supra*). Compound **24**, which provides the functionality for initiating ATRP reactions in the second step of Scheme 8, is easily prepared from 5-norbornen-2-ol and bromoisobutyryl bromide.

Initial efforts to carry out Scheme 8 showed that, while **19** is inert, Ni(COD)$_2$ immediately yields a metallic precipitate in the presence of **24**. A modified procedure was thus developed, where the **19**/Ni(COD)$_2$ mixture is exposed to ethylene for a time t_1, after which **24** is added via a pre-pressurized addition funnel and the polymerization is allowed to proceed for another period of time, t_2. It is possible with this approach to find conditions where the M_n of the product increases linearly with t_2. This dependence, together with the relatively low PDI values, illustrated by the plot in Figure 4, confirms that the copolymerization takes place in a controlled manner. As in the case illustrated in Scheme 6, changes in $P_{C_2H_4}$ result in the tuning of the molar incorporation of **24** into the polymer backbone. The control in product properties afforded by Scheme 8 is noteworthy in light of the intrinsic instability of Ni(COD)$_2$ toward **24**.

ATRP reactions were performed as shown in the second step of Scheme 8.[37] Typically, 50 mg of macroinitiator was

treated with methyl methacrylate (MMA) and a solution of a copper salt in anisole at 100 °C, such that the ratio of reactants was [**19**]/[MMA]/[Cu^{I}Br]/[Cu^{II}Br$_2$]/[PMDETA] = 1:200:1:0.05:2. After an hour of reaction, M_n increases from 45 to 58 K. While the T_m of this material is 126 °C, similar as the starting macroinitiator, the degree of crystallinity (X_c) decreases from 43 to 16%. The products have low PDIs and increased PMMA content at longer reaction times, indicating control over the grafting process. As secondary characterization, the PMMA side chains were hydrolyzed using sodium methoxide in methanol.[37a] GPC analysis confirms that the M_n of the detached chains increases with longer reaction times, while the PDIs remain at ~1.2. Therefore, the method in Scheme 8 provides access to PE-*graft*-PMMA with excellent control over the structural properties of the macroinitiator and the resulting graft copolymers.[36] A key element is the initiation in the absence of **24**, which decomposes Ni(COD)$_2$. Once the active species is generated, the copolymerization of ethylene and **24** proceeds in a controlled fashion.

Conclusions

Ligands derived from the α-iminocarboxamidato framework provide multiple structural handles for tailoring the reactivity of metal centers. Nickel precursor complexes can be synthesized that yield zwitterionic or neutral catalyst types. The zwitterionic systems have found application in the development of tandem polymerization reactions and are relevant model systems for understanding how depletion of electron density at nickel leads to differences in reactivity toward olefins. Neutral catalysts show higher tolerance to polar functionalities. The fact that the polymerizations show many features characteristic of living systems allows for the preparation of higher order polymer architectures, including block, tapered, pseudotetrablock, and graft copolymers. Indeed, some of these polymers are not readily obtained by any other catalytic means. Whether the α-iminocarboxamidato-based systems become incorporated into commercial processes requires increases in monomer consumption rates and will also be dictated by the cost analysis of the functionalized monomers and the market value of specialty materials.

BIOGRAPHICAL INFORMATION

Brycelyn M. Boardman obtained her B.Sc. in 2003 from James Madison University, where she did undergraduate research with Professors Donna S. Amenta and John W. Gilje. She then studied nickel-based catalysts for olefin polymerization with Guillermo C. Bazan at the University of California, Santa Barbara (UCSB), where she obtained her Ph.D. in 2008. She is currently a postdoctoral research associate with Professor Colin Nuckolls at Columbia University, where she is studying the synthesis and electronic properties of metal chalcogenide clusters.

Guillermo C. Bazan is Professor in the Departments of Materials and Chemistry & Biochemistry and is co-director of the Center for Polymers and Organic Solids at the University of California, Santa Barbara (UCSB). He obtained his B.Sc. in 1986 from the University of Ottawa. His Ph.D. thesis was performed with Professor Richard R. Schrock at Massachusetts Institute of Technology (MIT). After a postdoctoral appointment at Caltech with Professor John Bercaw, he began his independent career in 1992 at the University of Rochester. He moved to UCSB in 1998. His research interests concern the synthesis and applications of organic molecules with delocalized electronic structures and the design of homogeneous catalysts for the polymerization of olefins.

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