Single-Component α-Iminocarboxamide Nickel Ethylene Polymerization and Copolymerization Initiators

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The reaction of $Ni(COD)_2$, benzyl chloride, potassium *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidate, and pyridine or 2,6-lutidine yields *N*,*O*-bound α-iminocarboxamide complexes that can be used as single-component initiators for the homopolymerization of ethylene or the copolymerization of ethylene with functionalized norbornene monomers. Comparison of the Py versus 2,6-lutidine complexes highlights how the nitrogen ligand lability influences polymerization activity. It is also possible to synthesize η^1-CH_2COPh complexes via these procedures, which are less stable to the presence of monomer functionalities.

Introduction

Interest in late transition metal initiators for the copolymerization of ethylene with functionalized monomers stems from the opportunity to access new commodity plastics and specialty materials with unique properties.[1] The ultimate utility of such initiators is determined in part by whether preparative methods are amenable for scale-up and incorporation into large-scale manufacturing processes and by the potential applications and cost of the resulting materials. Despite substantial progress in the control of coactivator species,[2] single-component systems should provide better control over the polymerization reaction conditions.[3] Initiators that incorporate functionalities, are single component, and provide living polymerization characteristics are relatively rare and provide optimum control over polymer chain composition and architecture.[4]

α-Iminocarboxamide-Ni(η^1-CH_2Ph)(PMe_3) complexes have been used for concurrent tandem polymerization of branched polyethylene from ethylene alone.[5] Additionally, upon activation with $Ni(COD)_2$, these complexes provide sites that show quasi-living characteristics for the polymerization of ethylene with 5-norbornen-2-yl-acetate (NBA).[6] Significantly, activation with $Ni(COD)_2$ occurs only in the presence of ethylene. This feature of the reaction allows for the synthesis of tapered, or gradient, copolymer structures, although the mechanistic details of how the $Ni(COD)_2$/ethylene mixture activates the α-iminocarboxamide complex remain uncertain at this stage. Structure−reactivity relationship studies have shown that only *N*,*O*-bound species (see Scheme 1) are useful in quasi-living polymerizations; negligible reactivity is seen with *N*,*N*-isomers under

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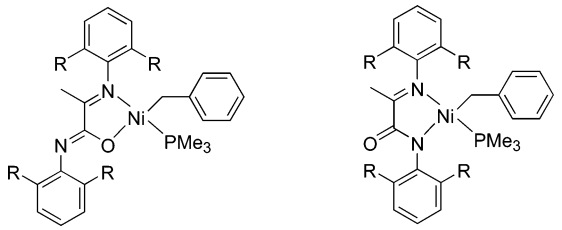
Scheme 1 . The Two Binding Modes of α-Iminocarboxamide Ligands

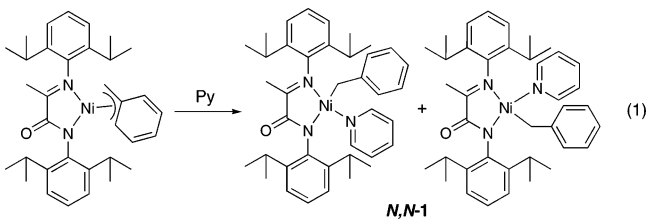


reaction conditions where there is control over polymer structure.[7] *N,N*-Binding appears to be favored by electronic reasons. *N,O*-Binding is observed when bulky substituents are present on the aryl groups. Additional isomers not shown in Scheme 1 arise from the position of PMe_3 within the square plane, i.e., *cis* or *trans* to the imine coordination site. These observations are consistent with an activation process that generates a phosphine-free *N,O*-bound initiator species.

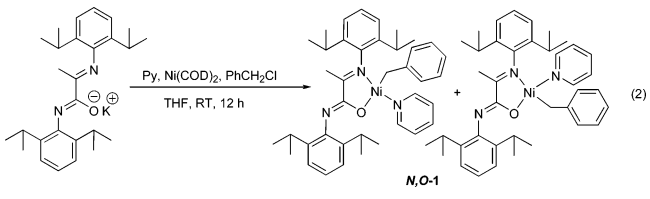
In this contribution we disclose α-iminocarboxamide species that are isoelectronic and isostructural adducts to the structures in Scheme 1 but that take advantage of nitrogen ligands instead of PMe_3. These complexes can initiate ethylene homopolymerization and ethylene/NBA or 5-norbornen-2-ol NBO copolymerization without the need to use $Ni(COD)_2$, thereby simplifying the polymerization procedures. Of particular interest is the control required over the synthetic entry into these new complexes to favor the *N,O*-bound isomers over the less reactive *N,N*-bound species. We also show that these synthetic methods are also suitable for making analogous complexes with η^1-CH_2-COPh.

Results and Discussion

Synthesis, Characterization, and Reactivity of η^1-Benzyl Complexes. Initial efforts involved direct addition of excess pyridine (Py) to the base-free compound [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,N*]-Ni(η^3-CH_2Ph),[7] as shown in eq 1. The strategy here was to force dissociation of the benzyl π-component by Py, with a concomitant rearrangement to the *N,O*-bound species. NMR spectroscopy revealed that the product of the reaction contained two isomers in a 1:1 ratio. Single crystals suitable for X-ray crystallography studies were obtained by slow evaporation of a benzene solution. As seen in Figure 1, the results show a square-planar arrangement around the nickel center with an *N,N*-bound α-iminocarboxamide ligand, and Py *trans* to the imine nitrogen. The products of the reaction are thus *cis*- and *trans*-[*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,N*]Ni(η^1-CH_2Ph)(Py) (***N,N*-1** in eq 1). We assign the second isomer as the *N,N*-bound α-iminocarboxamide complex with Py *trans* to the carboxamide nitrogen. On the basis of the previously observed lack of reactivity from *N,N*-isomers, we sought a different synthetic method.



A more direct approach involved the reaction of potassium *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidate, $Ni(COD)_2$, benzyl chloride, and Py in THF. Running the reaction at 22 °C in the absence of light yields two isomers in a 3:1 ratio, which, as determined by ^{1}H and ^{13}C NMR spectroscopies, do not correspond to the products in eq 1. Single crystals were obtained after workup by slow evaporation of a benzene solution, and the results of subsequent X-ray diffraction studies are shown in Figure 2. The room-temperature reaction thus yields the desired *N,O*-bound structure, [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,O*]Ni(η^1-CH_2Ph)(Py) (***N,O*-1**), as shown in eq 2. The two isomers observed in solution are assigned to *cis*- versus *trans*-binding of Py relative to the imine nitrogen.



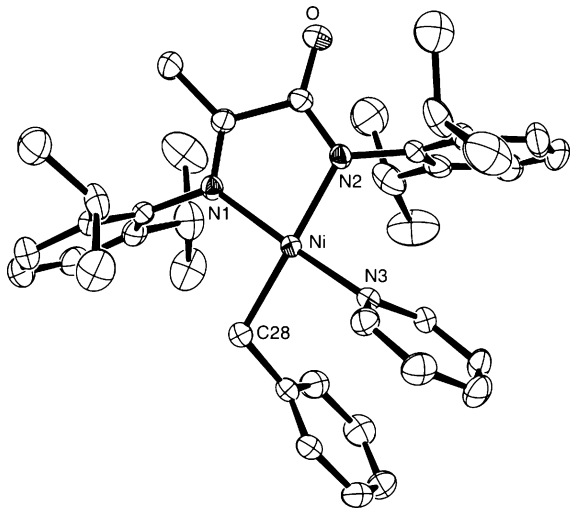


Figure 1. ORTEP drawing of ***N,N*-1** (50% probability). Hydrogen atoms were omitted for clarity.

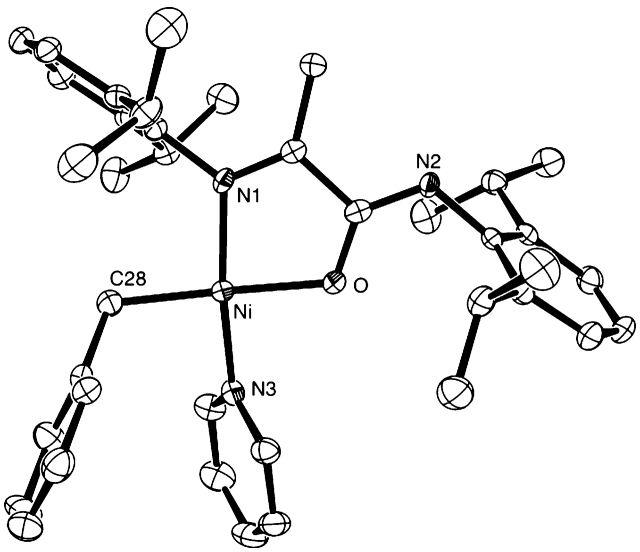


Figure 2. ORTEP drawing of ***N,O*-1** (50% probability). Hydrogen atoms were omitted for clarity.

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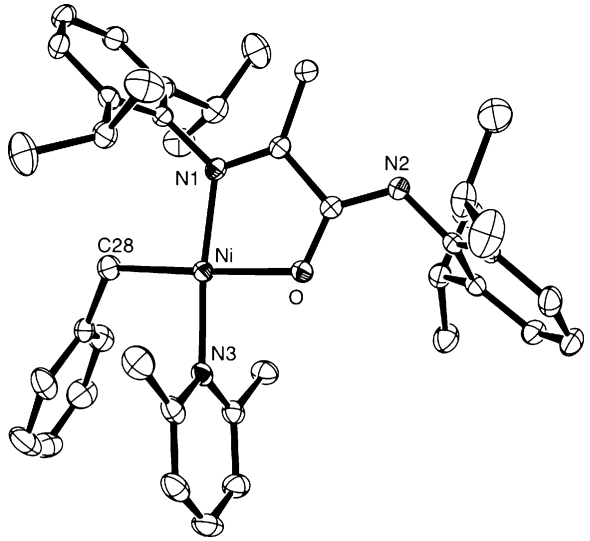
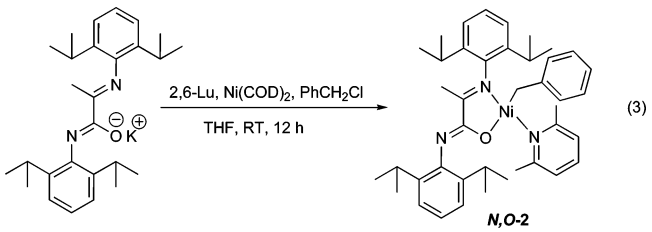


Figure 3. ORTEP drawing of ***N,O*-2** (50% probability). Hydrogen atoms were omitted for clarity.

Comparison of ^{1}H NMR spectra shows that heating a solution of ***N,O*-1** in C_6D_6 at 60 °C for 14 h produces ***N,N*-1** in nearly quantitative yield. The transformation is irreversible. Thus, ***N,O*-1** is a kinetic product, formed presumably because the oxygen in the carboxamidate functionality is more open than the nitrogen site and therefore more likely to participate in displacement reactions.

A reaction similar to that in eq 2 using 2,6-lutidine (2,6-Lu) instead of Py yields, after purification by recrystallization from a 1:4 ether−pentane mixture, a single organometallic product in higher than 85% yield. The composition of the product is [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,O*]Ni(η^1-CH_2Ph)(2,6-Lu) (***N,O*-2** in eq 3), as determined by NMR spectroscopy and single-crystal diffraction studies (Figure 3). Reactions analogous to those in eqs 1 and 2, with the bulkier 2,6-di(*tert*-butyl)pyridine, did not yield the desired benzyl complexes. Instead, one obtains the base-free compound [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,N*](η^3-CH_2Ph)nickel complex, i.e., the starting material in eq 1.



(3)

Statistically significant differences are observed in the structures of ***N,O*-1** and ***N,O*-2**. Table 1 contains a summary of relevant metrical data. As a result of the increased bulk of 2,6-Lu compared to Py, the coordination sphere around Ni is more crowded in ***N,O*-2**. For example, when comparing ***N,O*-2** with ***N,O*-1**, longer Ni−ligand distances are found: Ni−C(28) (1.9647(17) vs 1.943(3) Å), Ni−N(3) (1.9132(13) vs 1.888(2) Å), Ni−O (1.9453(11) vs 1.9267(19) Å), and Ni−N(1) (1.9253(13) vs 1.915(2) Å). On the basis of these distances, it is reasonable to expect that 2,6-Lu is more weakly bound than Py.

Polymerization Activity with η^1-Benzyl Complexes. A series of ethylene homopolymerization and copolymerization reactions were conducted, and the summary of the results is given in Table 2. Reactions were performed in a 100 mL autoclave reactor in toluene at an ethylene pressure of 100 psi with [Ni] = 3.33×10^{-4} M. Temperatures were controlled by either an external water bath or an internal heater and were monitored by using an internal thermocouple. No reaction occurred when using ***N,N*-1** at either 20 or 40 °C (entries 1 and 2). In the case of ***N,O*-1**, negligible monomer consumption occurs at 20 °C (entry 3); however polyethylene forms at 40 °C with an activity of 60 kg/(mol Ni)(h) (entry 4). Increasing the ethylene pressure to 500 or 1000 psi results in no activity for ***N,N*-1** or change in the consumption of ethylene by ***N,O*-1**. Higher activities are observed when the nitrogen ligand is changed from Py to 2,6-Lu, at both 20 and 40 °C (compare entries 3 and 4 vs 5 and 6). Gel permeation chromatography measurements calibrated against polystyrene standards show that the weight average molecular weights of the resulting polyethylenes are in the range 63 000 to 183 000 with polydispersities centered around 2.

Table 1. Selected Bond Distances (Å) and Angles (deg)

	***N,N*-1**	***N,O*-1**	***N,O*-2**	***N,O*-3**
Ni(1)−N(1)	1.9223(15)	1.915(2)	1.9253(13)	1.912(3)
Ni(1)−O(1)		1.9267(19)	1.9453(11)	1.939(2)
Ni(1)−C(28)	1.966(2)	1.943(3)	1.9647(17)	1.860(4)
Ni(1)−N(2)	1.9403(16)			
Ni(1)−N(3)	1.9060(16)	1.888(2)	1.9132(13)	1.913(3)
O(1)−C(8)	1.251(2)	1.295(3)	1.2961(19)	1.298(4)
C(28)−O(2)				1.231(5)
N(1)−Ni(1)−N(2)	82.53(7)			
N(1)−Ni(1)−O(1)		83.89(8)	83.47(5)	83.70(1)
C(28)−Ni(1)−N(1)	94.88(8)	96.39(11)	94.20(7)	94.52(14)
N(1)−Ni(1)−N(3)	167.28(7)	169.87(10)	171.51(5)	174.37(12)
N(2)−Ni(1)−C(28)	171.83(10)			
O(1)−Ni(1)−C(28)		172.85(11)	175.80(7)	177.45(14)
N(3)−Ni(1)−C(28)	89.54(8)	90.13(12)	93.93(7)	91.04(14)
N(3)−Ni(1)-N(2)	94.62(7)			
N(3)−Ni(1)−O(1)		90.60(9)	88.57(5)	90.71(11)
Ni(1)−C(28)−O(2)				120.1(3)

The differences in reactivity and structure between ***N,O*-1** and ***N,O*-2** suggest that the rate of Py or 2,6-Lu dissociation influences the rate of initiation. Addition of an equivalent of 2,6-Lu shuts down the polymerization activity. The choice of 2,6-Lu over Py thus may be useful in two ways: it provides for a faster initiation step (more labile) and it has a lower tendency to bind to the propagating species and block ethylene coordination (see Figure S-2 in the Supporting Information). ^{1}H NMR spectroscopy analysis in C_6D_6 at 60 °C of ***N,O*-1** and ***N,O*-2** up to 1 h shows no evidence of Py or 2,6-Lut loss; the formation of only a small fraction of the η^3-complex takes place. These observations are consistent with an equilibrium constant that favors the Py or 2,6-Lut adducts. Two possibilities ensue. The first involves ethylene coordination/insertion on the small fraction of unbound species, the concentration of which increases at higher temperatures. Alternatively, ethylene displaces the nitrogen ligand via an associative mechanism. Under these circumstances, the more important factor is that lutidine is more weakly bound instead of its increased ability to sterically protect the nickel center.

The last four entries in Table 2 show that ***N,O*-2** can initiate the copolymerization of ethylene with NBA or 5-norbornen-2-ol (NBO). Similar efforts using ***N,O*-1** were not as successful. In these reactions fixed concentrations of the comonomer and the initiator source are mixed inside the glovebox, placed in the reactor, and subsequently attached to an ethylene feed line. The percent incorporation of the comonomers into the polymer chain is controlled by the initial concentration in the reaction medium prior to polymerization. For example, when the

Table 2. Summary of Polymerization Reactions with *N,O*-1 and *N,O*-2[a]

entry	initiator	comonomer	T (°C)	activity[b]	M_w	M_w/M_n	% inc.
		[M]					
1	***N,N*-1**		20				
2	***N,N*-1**		40				
3	***N,O*-1**		20				
4	***N,O*-1**		40	60	63 000	1.8	
5	***N,O*-2**		20	43	125 000	1.8	
6	***N,O*-2**		40	304	143 000	2.2	
7	***N,O*-2**	NBA (0.075)	40	160	96 000	1.9	9
8	***N,O*-2**	NBA (0.150)	40	170	93 000	1.8	13
9	***N,O*-2**	NBO (0.075)	40	147	88 000	2.0	8
10	***N,O*-2**	NBO (0.150)	40	48	183 000	5.7	14

[a]Polymerizations were carried out in a 100 mL autoclave reactor with 10 μmol of Ni in 30 mL of toluene ([Ni] = 3.33×10^{-4} M); reaction time 20 min; P_{C2H4} = 100 psi; temperature controlled by using a water bath. [b]kg polymer/(mol Ni)(h), as determined by the mass of the polymer product. Yield = activity × mol Ni × 0.333 h.

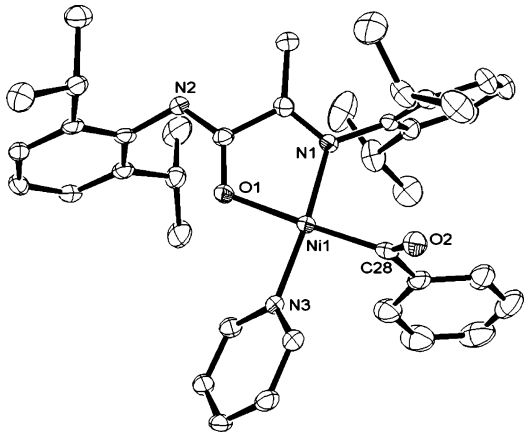


Figure 4. ORTEP drawing of ***N,O*-3** (50% probability). Hydrogen atoms were omitted for clarity.

concentration of NBA is increased from 0.075 to 0.15 M and the reaction is allowed to proceed for 20 min, the molar incorporation increases from 9% to 13%, as determined by ^{1}H NMR spectroscopy of the isolated products. A qualitatively similar increase is also observed with NBO. However, higher initial concentrations of NBO result in a decrease of net activity and a broadening of molecular weight (compare entries 6 and 9 vs 10), possibly as a result of deactivation or competitive binding by the hydroxyl functionalities.

Microstructure characterization of the products in Table 2 by ^{13}C NMR spectroscopy reveals that the ethylene homopolymers contain only methyl branches. The copolymers also contained only methyl branches, and there is no evidence that the functionalized monomers are found adjacent to each other along the polymer backbone (see Supporting Information).

Synthesis, Characterization, and Reactivity of an η^1-Benzoyl Complex. Previous studies demonstrated that, compared to η^3-benzyl, the stronger binding to nickel of the η^3-methallyl fragment results in a decrease of initiation rates for ethylene oligomerization reactions.[8] On the basis of these observations, we sought to synthesize an isostructural analogue of ***N,O*-1** with η^1-benzoyl instead of η^1-benzyl. The η^1-benzoyl fragment was chosen, in part, because of the expected ease of oxidative addition to Ni(COD)$_2$, a primary requirement for the synthetic entry into α-iminocarboxamide complexes and because of the electron-withdrawing ability of the carbonyl group. The synthesis of [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,O*]Ni(η^1-COPh)(Py) (***N,O*-3**) was carried out by adapting the procedures developed for ***N,O*-1** and ***N,O*-2**, as shown in eq 4. Under minimal exposure to light, benzoyl chloride and Py were mixed and added to a solution of Ni(COD)$_2$ in THF at −35 °C. The reaction was allowed to warm to room temperature, and after 20−30 min of stirring the originally clear reaction mixture turned slightly cloudy. At this stage, potassium *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidate in THF was added dropwise to the reaction mixture over a 45 min period and the mixture was stirred overnight. After workup by filtration, the product of the first crystallization effort contained ***N,O*-3** with an impurity corresponding to bis[*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,O*]Ni (see Supporting Information). Successive crystallizations from pentane−ether solvent mixtures allowed the isolation of ***N,O*-3** as dark orange crystals in 54% yield. ^{1}H NMR and ^{13}C NMR spectra are consistent with the presence of a single isomer.

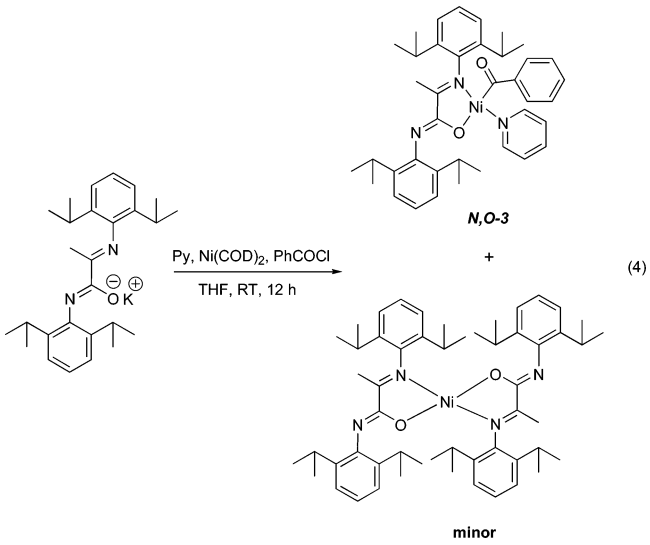


Figure 4 provides the results of X-ray diffraction studies from single crystals of ***N,O*-3** obtained by slow evaporation of an ether solution. The desired *N,O*-bonding mode is observed with the benzoyl ligand coordinated in an η^1-fashion *trans* to the amide nitrogen (similar orientation as in ***N,O*-1**). Note that the benzoyl carbonyl is "perpendicular" to the nickel square plane. The C(28)−O(2) bond distance (1.231(5) Å) and the O(2)−C(28)−Ni angle (120.1(3)°) (Table 1) indicate sp^2 hybridization and that no strong interaction between the benzoyl carbonyl and nickel occurs. The two aryl rings on the α-iminocarboxamide are also perpendicular to the square plane. The bond distances for Ni−N(1) and Ni−O(1) (1.912(3) and 1.939(2) Å, respectively) are similar to those in compound ***N,O*-1** (Table

(8) Komon, Z. J. A.; Bu, X. H.; Bazan, G. C. *J. Am. Chem. Soc*. **2000**, *122*, 12379.

Table 3. Summary of Polymerization Reactions with *N,O*-3[a]

entry	initiator	comonomer [M]	T (°C)	activity[b]	M_w	M_w/M_n	% inc.
1	***N,O*-3**		20				
2	***N,O*-3**		40	270	145 000	1.7	
3	***N,O*-3**		50	301	160 000	2.0	
4	***N,O*-3**		60	131	183 000	2.4	
5	***N,O*-3**[c]	NBA (0.075)[c]	50				
6	***N,O*-3**[c]	NBO (0.075)[c]	40, 50				
7	***N,O*-3**	NBA (0.075)	50	261	125 000	2.5	2.5
8	***N,O*-3**	NBO (0.075)	50	323	112 000	2.6	3.0

[a]Polymerizations were carried out in a 100 mL autoclave reactor with 10 μmol of Ni in 30 mL of toluene; [Ni] = 3.33×10^{-4} M; reaction time, 20 min; ethylene pressure 400 psi; temperature controlled by using a water bath. [b]kg polymer/(mol Ni)(h). Yield = activity × mol Ni × 0.333 h. [c]Method 1: *initial addition of comonomer*. In these reactions fixed concentrations of the comonomer and the initiator source are mixed inside the glovebox, placed in the reactor, and subsequently attached to an ethylene feed line. Method 2: *Addition of comonomer after initiation with ethylene.* Initiator solutions (***N,O*-3**) and toluene are placed in the reactor, subsequently attached to an ethylene feed line, and the polymerization is run for 5 min. After this time the comonomer was added via an addition funnel and the copolymerization reaction was allowed to run for an additional 15 min.

1). The Ni−N(3) bond distance for ***N,O*-1** is slightly shorter than that in ***N,O*-3** (1.888(2) vs 1.913(3) Å), while the Ni−C(28) (η^1-benzoyl) is 0.083(4) Å shorter than Ni−C28 (η^1-benzyl).

Table 3 provides the results for a series of polymerization reactions at ethylene pressures of 400 psi when carried out with ***N,O*-3**. No reaction occurs at 20 °C (entry 1). However, at 40 °C (entry 2) an ethylene consumption activity of 270 kg/(mol Ni)(h) is observed. Increasing the temperature from 40 to 50 °C (entry 3), without changing reaction time or ethylene pressure, results in a slight increase of activity. However, increasing the temperature to 60 °C (entry 4) decreases the activity, perhaps as a result of thermal decomposition. An increase in the molecular weight and PDIs of the resulting polyethylene was also seen with increasing temperature.

Copolymerization tests with ***N,O*-3** are contained in entries 5 to 8 in Table 3. For the results in entries 5 and 6, where no reactivity was observed, the same technique as for the polymerization reactions using ***N,O*-2** were used. That is, ***N,O*-3** was mixed in the presence of comonomer prior to ethylene addition. Separate tests, where ***N,O*-3** and NBA were mixed in C_6D_6, revealed by ^{1}H NMR spectroscopy that quick decomposition took place, leading to the formation of a complex mixture of unassignable products. A different copolymerization method was thus explored. Here NBA or NBO was added via a pressurized addition funnel after 5 min of exposing ***N,O*-3** to ethylene and the temperature was increased to 50 °C. Entries 7 and 8 show that this post-initiation addition method leads to a high molecular weight polymer that incorporates the desired functionalized norbornenes. The lower incorporation under these conditions, relative to those in Table 2, may be attributed to the higher ethylene pressures.[9] Polymer microstructures are similar to those observed for the products in Table 2 (Supporting Information).

Conclusions

In summary, we report on the synthetic access to compounds ***N,O*-1** and ***N,O*-2**, which are single-component initiators for the polymerization of ethylene and copolymerization of ethylene with NBA or NBO. There is no need to use $Ni(COD)_2$ for activation, as is the case for the PMe_3 analogues. Thermal activation is required, possibly for dissociation of Py or 2,6-Lu, which reduces the control over the polymer structure; that is, it was not possible to find polymerization conditions with quasi-living characteristics. The syntheses of ***N,O*-1** and ***N,O*-2** require the methods shown in eqs 2 and 3, which are simple and of high yield and can be extended to the preparation of the η^1-benzoyl complex ***N,O*-3**. We anticipate similar success with other α-iminocarboxamide frameworks that have sufficiently bulky aryl substituents to inhibit *N,N*-binding and with pyridine derivatives that can bind tightly to nickel. Structural analysis shows that the 2,6-Lu ligand in ***N,O*-2** is more weakly bound than Py in ***N,O*-1**. Consistent with a more weakly bound 2,6-Lu ligand, we find that polymerizations with ***N,O*-2** can be accomplished milder reaction conditions, relative to ***N,O*-1**. We find that ***N,O*-3** is unstable to the presence of NBA or NBO. Successful copolymerizations with ethylene can be achieved only when the functionalized norbornenes are added after initiation with ethylene.

Experimental Section

General Remarks. All manipulations were performed in an inert atmosphere using standard glovebox and Schlenk-line techniques. Unless otherwise specified, all reagents were used as received from Aldrich. Ethylene was purchased from Matheson Tri-Gas (research grade, 99.99% pure) and was further purified by passing through an oxygen/moisture trap (Matheson model 6427-4S). Toluene, THF, hexane, and pentane were distilled from benzophenone ketyl. All polymerization reactions were carried out in a Parr autoclave reactor as described below. Toluene for polymerization was distilled from sodium/potassium alloy. Compound ***N,N*-1** was prepared by the addition of Py to the previously reported compound [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,N*]Ni(η^3-CH_2Ph).[7] Compounds ***N,O*-1** and ***N,O*-2** were prepared by direct reaction of potassium *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidate with $Ni(COD)_2$, benzyl chloride, and pyridine or 2,6-lutidine in THF. NMR spectra were run on Varian Unity 400 and 500 spectrometers. Polymers were dried overnight under vacuum, and the polymerization activities were calculated from the mass of product obtained. These values were within 5% of the mass calculated by measuring the ethylene consumed using a mass flow controller. The polymers were characterized by GPC at 135 °C in *o*-dichlorobenzene (in a Polymer Laboratories high-temperature chromatograph, Pl-GPC 200). ^{1}H NMR spectra of the polymers were obtained in a mixed solvent (C_6D_6/1,2,4-trichlorobenzene in a 1:4 ratio by volume) at 115 °C. Elemental analysis was performed on a Leeman Labs Inc. CE440 elemental analyzer and a Control Equipment Corporation 440 elemental analyzer.

X-ray Crystallography. The monocrystal was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[10] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using

(9) Chen, G.; Ma, X. S.; Guan, Z. *J. Am. Chem. Soc*. **2003**, *125* (22), 6697.

(10) *SMART Software Users Guide*, Version 5.1; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999.

Table 4. Crystal Data and Structure Refinement for Phosphine-Free α-Iminocarboxamide Nickel Complexes

	N,N-1	N,O-1	N,O-2	N,O-3
empirical formula	$C_{39}H_{49}N_3ONi$	$C_{39}H_{49}N_3ONi$	$C_{41}H_{53}N_3ONi$	$C_{39}H_{47}N_3O_2Ni$
fw	634.52	634.52	662.58	648.51
temperature (K)	118 (1)	119(1)	118 (1)	117 (1)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/c$
unit cell dimensions (Å, deg)	$a = 9.1867(7)$	$a = 12.3182(13)$	$a = 12.8214(9)$	$a = 37.976(3)$
	$b = 16.0857(11)$	$b = 17.9079(19)$	$b = 18.6216(13)$	$b = 14.4551(12)$
	$c = 23.3613(18)$	$c = 17.6910(19)$	$c = 17.7596(13)$	$c = 14.8230(12)$
	$\alpha = 90$	$\alpha = 90$	$\alpha = 90$	$\alpha = 90$
	$\beta = 90$	$\beta = 93.588(3)$	$\beta = 101.519(2)$	$\beta = 98.536(2)$
	$\gamma = 90$	$\gamma = 90$	$\gamma = 90$	$\gamma = 90$
volume (Å^3)	3452.2(4)	3894.9(7)	4154.8(5)	8046.9(12)
Z	4	4	4	4
density (calcd) (Mg/m^3)	1.221	1.215	1.184	1.147
absorp coeff (mm^{-1})	0.596	0.535	0.504	0.518
$F(000)$	1360	1528	1592	2968
cryst size (mm^3)	0.3 × 0.15 × 0.08	0.2 × 0.1 × 0.06	0.3 × 0.3 × 0.20	0.35 × 0.3 × 0.15
θ range (deg)	1.54 to 28.57	1.62 to 26.48	1.60 to 28.52	5.10 to 26.37
index ranges	$-12 \le h \le 9$	$-15 \le h \le 15$	$-17 \le h \le 17$	$-29 \le h \le 47$
	$-21 \le k \le 20$	$-20 \le k \le 22$	$-23 \le k \le 24$	$-17 \le k \le 17$
	$-30 \le l \le 30$	$-22 \le l \le 21$	$-21 \le l \le 22$	$-17 \le l \le 15$
no. of reflns collected	30 092	30 670	36 086	60 995
no. of indep reflns	8123 [R(int) = 0.0430]	7976 [R(int) = 0.0787]	9768 [R(int) = 0.0386]	15 837 [R(int) = 0.0618]
completeness to the respective θ	95.2	99.0	92.6	96.2
no. of data/restraints/params	8123/0/593	7976/0/672	9768/0/705	15 837/25/889
goodness-of-fit on F^2	0.978	1.012	1.039	1.063
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0353, wR2 = 0.0722	R1 = 0.0533, wR2 = 0.1191	R1 = 0.0381, wR2 = 0.0902	R1 = 0.0613, wR2 = 0.1474
R indices (all data)[a]	R1 = 0.0482, wR2 = 0.0753	R1 = 0.0873, wR2 = 0.1348	R1 = 0.0580, wR2 = 0.0974	R1 = 0.1021, wR2 = 0.1660
largest diff peak and hole (e Å^{-3})	0.448 and −0.205	0.854 and −0.489	0.419 and −0.323	1.297 and −0.533

[a] $R1 = \sum||F_o| - |F_c||]/\sum[|F_o|$; $wR2 = [\sum(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n is the number of reflections and p is the total number of refined parameters.

SAINT[11] and SADABS[12] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[13] program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Analytical scattering factors[14] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference Fourier map and refined (x,y,z and U_{iso}).[15] Single crystals of ***N,N*-1**, ***N,O*-1**, ***N,O*-2**, and ***N,O*-3** suitable for X-ray diffraction studies were obtained by evaporation of benzene or diffusion of pentane into a benzene or toluene solution. The crystal data and refinement are summarized in Table 4.

Synthesis and Characterization of Compounds. [*N*-(2,6-Diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,N*](η^1-CH$_2$Ph)nickel(pyridine) (*N,N*-1). The synthesis of ***N,N*-1** was carried out by addition of 4 equiv of pyridine to a [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2N,N](η^3-CH$_2$Ph)nickel toluene solution (50 mg, 0.09 mmol in 5 mL of toluene). The reaction mixture was stirred for 1 h; volatiles were then removed under vacuum. The solid was extracted with a 1:2 ether−pentane mixture (5 mL), and crystallization took place at room temperature overnight. Compound ***N,N*-1** was isolated as red crystals in 95% yield. ^{1}H NMR spectroscopy revealed two isomers in a 1:1 ratio.

^{1}H NMR (399.95 MHz, [d_6]-benzene, 298 K): δ 8.02−7.99 (m, 4H, H_o-Bn), 7.36 (t, 2H, Bn), 7.09−7.00 (m, 12H, *H*-Ph, Bn), 6.92−6.79 (m, 4H, *H*-Ph), 6.76−6.63 (m, 4H, *H*-Ph), 6,24−6.12 (m, 2H, H_p-Py), 5.85−5.80 (m, 4H, $^3J_{HH}$ = 6.4 Hz, H_0-Py), 4.70 (sep 2H, $^3J_{HH}$ = 6.8 Hz, *CH*-i-Pr), 4.21 (sep 2H, $^3J_{HH}$ = 6.8 Hz, *CH*-i-Pr), 3.97 (sep 2H, $^3J_{HH}$ = 6.8 Hz, *CH*-i-Pr), 3.48 (sep 2H, $^3J_{HH}$ = 6.8 Hz, *CH*-i-Pr), 1.98 (s, 2H, CH_2-Bn), 1.92 (s, 3.0, CH_3), 1.88 (s, 3.0, CH_3), 1.77 (d, 6H, $^3J_{HH}$ = 7.2 Hz, CH_3-i-Pr), 1.67 (s, 2H, CH_2-Bn), 1.67 (d, 6H, $^3J_{HH}$ = 7.2 Hz, CH_3-i-Pr), 1.63 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3-i-Pr), 1.54 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3-i-Pr), 1.27 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3-i-Pr), 1.11 (d, 6H, $^3J_{HH}$ = 7.2 Hz, CH_3-i-Pr), 1.05 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3-i-Pr), 0.92 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH_3-i-Pr).

[*N*-(2,6-Diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-propanamidato-κ^2*N,O*](η^1-CH$_2$Ph)nickel(pyridine)(*N,O*-1). The synthesis of ***N,O*-1** was carried out under minimal light exposure. A Ni(COD)$_2$ solution (68 mg, 0.25 mmol in 5 mL of THF) was treated with a mixture of benzyl chloride (63 mg, 0.49 mmol) and pyridine (234 mg, 2.96 mmol) in 2 mL of THF at −35 °C. The potassium salt of the ligand (105 mg, 0.23 mmol dissolved in 3 mL of THF) was added after 10 min of reaction. The reaction mixture was allowed to warm to room temperature and was stirred overnight. Volatiles were then removed under vacuum. The resulting oil was extracted with ether (15 mL) and filtered through Celite. The solvent volume was reduced, and crystallization took place at room temperature overnight. Compound ***N,O*-1** was isolated from the first crystallization as dark orange crystals in 62% yield. ^{1}H NMR spectroscopy showed two isomers in a 3:1 ratio.

Anal. Calcd for $C_{39}H_{49}N_3ONi$: C, 73.82; H, 7.78; N, 6.62. Found: C, 72.05; H, 7.80; N, 6.62. ^{1}H NMR (399.95 MHz, [d_6]-benzene, 298 K): δ 8.24 (br), 7.91 (d, $^3J_{HH}$ = 5.6 Hz), 7.24 (t, $^3J_{HH}$ = 7.6 Hz), 7.08−6.96 (m), 6.80−6.63 (m), 6.25 (dd, 2H, $^3J_{HH}$ = 7.8 Hz, H_0-Py$_{minor}$), 5.83 (dd, 2H, $^3J_{HH}$ = 6.8 Hz, H_0-Py$_{major}$); *Major isomers*, δ 3.90 (sep 2H, $^3J_{HH}$ = 6.8 Hz, *CH*-i-Pr), 3.54 (sep

(11) *SAINT Software Users Guide*, Version 6.0; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999.
(12) Sheldrick, G. M. *SADABS*, Version 2.05; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2001.
(13) Sheldrick, G. M. *SHELXTL* Version 6.12; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2001.
(14) *International Tables for X-Ray Crystallography*, Vol. C; Kluwer Academic Publishers: Dordrecht, 1992.
(15) Flack, H. D. *Acta Crystallogr.* **1983** *A39*, 876.

2H, $^3J_{HH}$ = 6.8 Hz, *CH*-i-Pr), 2.09 (s, 3H, CH_3), 2.07 (s, 2H, CH_2-Bn), 1.58 (dd 12H, $^3J_{HH}$ = 6.8 Hz, CH_3-i-Pr), 1.39 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH_3-i-Pr); *Minor isomers*, 3.64 (sep 2H, $^3J_{HH}$ = 6.8 Hz, *CH*-i-Pr), 3.31 (sep 2H, $^3J_{HH}$ = 6.8 Hz, *CH*-i-Pr), 2.53 (s, 3H, CH_3), 1.17 (d, 12H, $^3J_{HH}$ = 6.4 Hz, CH_3-i-Pr), 0.98 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3-i-Pr), 0.92(d, 6H, $^3J_{HH}$ = 6.4 Hz, CH_3-i-Pr). ^{13}C NMR (125.7 MHz, [d_6]-benzene, 298 K): δ 182.35 (carbonyl$_{major}$), 178.35 (carbonyl$_{minor}$), 165.05 (C=N$_{minor}$), 163.76 (C=N$_{major}$), 152.27, 152.04, 151.29, 150.89, 146.87, 141.97, 140,26, 139.26, 139.01, 138.77, 135.74, 135.25, 129.24, 127.94, 127.28, 124.60, 123.72, 123.29, 123.10, 123.01, 122.95, 122.29, 122.09, 29.90, 29.77, 29.27, 28.74, 24.71, 24.56, 24.31, 24.12, 23.51, 21.00, 15.12.

[*N*-(2,6-Diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-propanamidato-κ^2*N,O*](η^1-benzyl)nickel(lutidine) (*N,O*-2). The synthesis of ***N,O*-2** was carried out under minimal light exposure. A Ni(COD)$_2$ solution (68 mg, 0.25 mmol in 5 mL of THF) was treated with a mixture of benzyl chloride (63 mg, 0.5 mmol) and 2,6-lutidine (156 mg, 1.45 mmol) in 2 mL of THF at −35 °C. Potassium salt (105 mg, 0.25 mmol dissolved in 3 mL of THF) was added after 10 min. The reaction mixture was allowed to warm to room temperature and was stirred overnight. Volatiles were removed under vacuum. The resulting oil was extracted with ether (15 mL) and filtered through Celite. The solvent volume was reduced, pentane was added, and crystallization took place at room temperature overnight. Compound ***N,O*-2** was isolated from the first crystallization as dark orange crystals in 85% yield. ^{1}H NMR spectroscopy showed a single isomer.

Anal. Calcd for $C_{41}H_{53}N_3ONi$: C, 74.32; H, 8.06; N, 6.34. Found: C, 74.10; H, 8.01; N, 6.38. ^{1}H NMR (399.95 MHz, [d_6]-benzene, 298 K): δ 7.11−7.04 (m, 5H, *Bn*), 6.90 (t, 1H, $^3J_{HH}$ = 7.2 Hz, H_p-Ph), 6.75 (t, 1H, $^3J_{HH}$ = 7.2 Hz, H_p-Ph), 6.58−6.50 (m, 4H, H_m-Ph), 6,23 (t, 1H, $^3J_{HH}$ = 7.6 Hz, H_p-Lu), 5.84 (d, 2H, $^3J_{HH}$ = 7.6 Hz, H_m-Lu), 3.89 (sep 2H, $^3J_{HH}$ = 6.8 Hz, *CH*-i-Pr), 3.66 (s, 6H, *Me*-Lu), 3.49 (sep 2H, $^3J_{HH}$ = 7.2 Hz, *CH*-i-Pr), 2.09 (s, 3.0, CH_3), 1.61 (d, 6H, $^3J_{HH}$ = 7.2 Hz, CH_3-i-Pr), 1.42 (s, 2H, CH_2-Bn), 1.40 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH_3-i-Pr), 1.17(d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3-i-Pr). ^{13}C NMR (125.7 MHz, [d_6]-benzene, 298 K): δ 182.34 (carbonyl), 158.79 (C=N), 152.24, 141.93, 140.13, 138.64, 136.29, 127.86, 127.04, 124.52, 122.96, 122.88, 122.07, 29.73, 29.20 (*CH*-i-Pr), 26.67 (CH_3-Lut), 24.67, 24.34, 24.11 (CH_3-i-Pr), 21.09 (CH_2-Ph), 11.66 (CH_3).

[*N*-(2,6-Diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-propanamidato-κ^2*N,O*](η^1-COPh)nickel(pyridine) (*N,O*-3). The synthesis of ***N,O*-3** was carried out under an inert atmosphere with minimum exposure to light. A Ni(COD)$_2$ solution (112 mg, 0.41 mmol in 5 mL of THF) was treated with a mixture of benzoyl chloride (58 mg, 0.41 mmol) and pyridine (130 mg, 1,65 mmol) in 2 mL of THF at room temperature. After 15 min, the potassium salt of the ligand (140 mg, 0.31 mmol dissolved in 3 mL of THF) was added over 45 min. The reaction mixture was stirred overnight, and volatiles were removed under vacuum. The resulting oil was extracted with ether (15 mL) and filtered. The solvent volume was reduced, and crystallization took place at room temperature overnight. The product of the first crystallization batch contained ***N,O*-3** with an impurity. Successive crystallizations from pentane−ether allowed the isolation of ***N,O*-3** as dark orange crystals in 54% yield. ^{1}H NMR spectroscopy showed one isomer.

^{1}H NMR (399.95 MHz, [d_6]-benzene, 298 K): δ 8.58 (d, 2H), 8.39−8.36 (tt, 2H) 7.29 (d, 2H), 7.02 (t, 1H), 6.96−6.89 (m, 6H), 6,24 (t, 1H), 5.85 (t, 2H), 3.86 (broad-sep 2H), 3.61 (sep 2H), 2.12 (s, 3.0), 1.46 (d, 12H), 1.25 (m, 6H), 1.11(d, 6H). ^{13}C NMR (125.7 MHz, [d_6]-benzene, 298 K): δ 250.98, 184.67, 162.60, 152.58, 151.35, 147.13, 143.45, 140.22, 139.18, 137.17, 131.29, 127.71, 125.67, 124.41, 124.19, 123.09, 29.90, 29.56, 25.21, 24.14, 23.59, 21.20.

Typical Homopolymerization of Ethylene. Polymerizations were conducted in the following manner using the initiators ***N,N*-1**, ***N,O*-1**, ***N,O*-2**, or ***N,O*-3**. An autoclave reactor (100 mL) was loaded inside a glovebox with an appropriate amount (10 μmol) of a neutral nickel(II) α-iminocarboxamide initiator with toluene, for a final volume of 30 mL of toluene solution. The reactor was sealed inside the glovebox, and it was attached to an ethylene line. The gas was fed continuously into the reactor at a pressure of 100 psi (in specifics tests also to 400, 500, and 1000 psi). The pressurized reaction mixture was stirred at variable temperatures ranging from 20 to 40 °C. After a specific reaction time, the ethylene was vented and acetone was added to quench the polymerization. The precipitated polymer was collected by filtration and dried overnight under vacuum. (The molecular weight average and PDIs were determined by GPC analysis in dichlorobenzene at 135 °C and are relative to polystyrene standards.)

Copolymerization of Ethylene with Norbornene Derivatives. Method 1: Initial Addition of Comonomer. A steel reactor was loaded inside a glovebox with an appropriate amount (10 μmol) of a neutral nickel(II) α-iminocarboxamide initiator (compound ***N,O*-2**), 5-norbornen-2-yl acetate (NBA) or 5-norbornen-2-ol (NBO) (0.075 to 0.15 M), and toluene (26 g) for a final volume of 30 mL of toluene solution. The steel reactor was sealed inside the glovebox and was attached to the ethylene line. Ethylene was fed continuously into the reactor at 100 psi, and the pressurized reaction mixture was stirred at 40 °C. Ethylene was vented after 20 min, and acetone and methanol were added to quench the polymerization. The precipitated polymer was collected by filtration and dried under high vacuum for 12 h. The molecular weight of the polyethylene polymer was calculated by refractive index GPC analysis (*o*-dichlorobenzene, 135 °C) relative to universal calibration from polystyrene standards. Mol % incorporation of the norbornenyl group was calculated from ^{1}H NMR spectroscopy (C_6D_6−*o*-dichlorobenzene, 120 °C).

Method 2: Addition of Comonomer after Initiation with Ethylene. Initiator solutions (***N,O*-3**) were prepared as described above; however the comonomer was added via an addition funnel after the polymerization of ethylene was allowed to run for 5 min. Polymerization was quenched as described in method 1.

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