α-Iminocarboxamide Nickel Complexes: Synthesis and Uses in Ethylene Polymerization

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A series of nickel complexes containing α-iminocarboxamide, η^1-benzyl, and PMe_3 ligands were synthesized to identify structural features of neutral Ni complexes that are employed in ethylene polymerization and ethylene/functionalized norbornene copolymerizations. Variations in steric bulk on aryl substituents in the α-iminocarboxamide framework were used to probe *N,N*- versus *N,O*-binding modes. When the steric bulk is sufficiently large, as in [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,O*]Ni(η^1-CH_2-Ph)(PMe_3) (**1**), [*N*-(2,6-diethylphenyl)-2-(2,6-diethylphenylimino)propanamidato-κ^2*N,O*](η^1-CH_2Ph)(PMe_3)nickel (**2**), and [*N*-(2,6-methyl-isopropylphenyl)-2-(2,6-methylisopropylphenylimino)propanamidato-κ^2*N,O*](η^1-CH_2Ph)(PMe_3)nickel (**3**), one observes *N,O*-binding. In the case of [*N*-(2,6-dimethylphenyl)-2-(2,6-dimethylphenylimino)propanamidato](η^1-CH_2Ph)-(PMe_3)nickel (**4**), both, *N,O*- and *N,N*-bound modes can be obtained and isolated; the *N,N* structure is the thermodynamic product. *N,N* products are observed with smaller ligands, as in [*N*-phenyl-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,N*](η^1-CH_2Ph)(PMe_3)nickel (**5**) and [*N*-(2,6-diisopropylphenyl)-2-(phenylimino)propanamidato-κ^2*N,N*](η^1-CH_2Ph)(PMe_3)-nickel (**6**). Ethylene polymerization, upon activation with $Ni(COD)_2$, is observed only with the *N,O*-bound species. NMR spectroscopy shows that addition of $Ni(COD)_2$ to **5** and **6** results in removal of the phosphine and the formation of an η^3-benzyl fragment. Furthermore, the phosphine-free complex [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,N*](η^3-CH_2Ph)nickel (**7**) is also inactive toward ethylene polymerization. These observations suggest that ethylene polymerization is preferentially initiated by nickel complexes with *N,O*-bound α-iminocarboxamide ligands.

Introduction

Interest in metal-mediated polymerization of olefins remains unabated in academic and industrial laboratories.[1] Recent advances in stereocontrol and improved functionality tolerance, together with insight from mechanistic and theoretical studies, have considerably improved control over the final polymer structures and thereby the bulk properties of the resulting materials. High-throughput techniques for screening metal−ligand combinations and polymerization conditions[2] have led to improved initiator structures and have enabled the use of multiple catalysts in a tandem process so that branched polyethylene can be obtained from ethylene alone.[3] Initiators that provide for the living polymerization of ethylene and 1-alkenes[4] constitute a special

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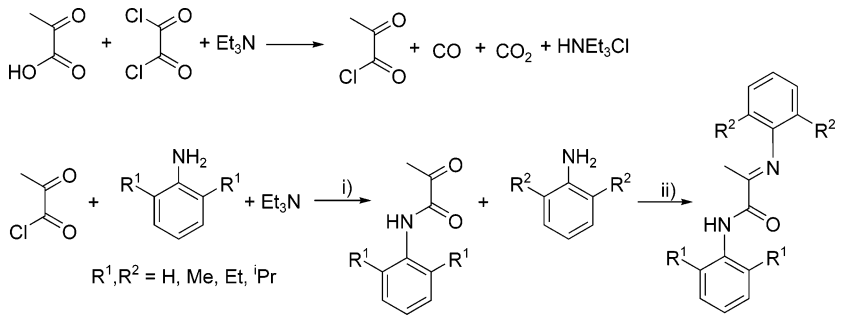
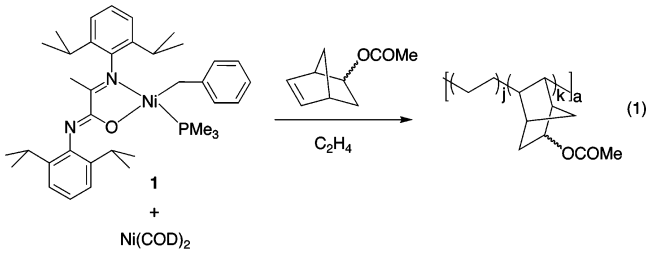
Scheme 1. General Synthesis of α-Iminocarboxamide Ligands[a]



[a] (i) Benzene, 25 °C, 2 h; (ii) toluene, *p*-toluenesulfonic acid, 24 h.

area of attention, since they allow for accessing macromolecular architectures such as block and tapered copolymers,[5] star-shaped structures,[6] end-functionalized polymers,[7] and grafted backbones.[8,9] Macromolecular structure impacts the solid state arrangement of the polymer chains and therefore physical and mechanical properties.

We recently disclosed that the activation of [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-propanamidato-κ^2*N,O*]Ni(η^1-CH_2Ph)(PMe_3) (**1**) with Ni(COD)$_2$ (Ni(COD)$_2$ = bis(1,5-cyclooctadiene)nickel) generates an active site that is capable of copolymerizing ethylene and 5-norbornen-2-yl acetate in a quasi-living fashion (eq 1).[10] The polymerization reaction shows a linear increase in molecular weight with increasing reaction time; however the molecular weight distributions of the products show polydispersities (PDIs) that are larger than the ones expected from a living system. Deviations from a living behavior are likely due to the precipitation of the product as the reaction proceeds and to inefficient initiation, as determined by NMR spectroscopy experiments. Polymerizations with **1**/Ni(COD)$_2$ are sufficiently well-behaved, and they can produce block copolymers containing segments of random sequences of ethylene and 5-norbornen-2-yl acetate with different molar compositions. These structures have been synthesized by a simple procedure that involves an ethylene pressure jump. The resulting materials show microphase separation and have the potential to reduce the interfacial energy between polyolefins and polar plastics, such as polycarbonates.



(1)

In this contribution, we report on the synthesis of nonionic structural variations of **1**, which were designed to obtain insight into the active species in the reaction shown in eq 1. We anticipated that the size of the aromatic substituents on the imine and carboxamide nitrogens would influence ligand coordination mode (i.e., *N,N* vs *N,O*). Examination of the reactivity toward ethylene, coupled with the targeted synthesis of a phosphine-free analogue of **1**, suggests that only *N,O*-coordinated compounds provide active sites at room temperature, i.e., conditions that allow the quasi-living polymerization of ethylene.

Results and Discussion

Synthesis and Characterization of α-Iminocarboxamide Nickel Complexes. α-Iminocarboxamide ligands can be synthesized following standard condensation reaction procedures.[11] An improved synthesis employs oxalyl chloride and pyruvic acid in benzene at room temperature in the presence of triethylamine to generate pyruvic acid chloride in situ (Scheme 1). Addition of 1 equiv of aniline results in reaction at the acid chloride site. This reaction takes place over a period

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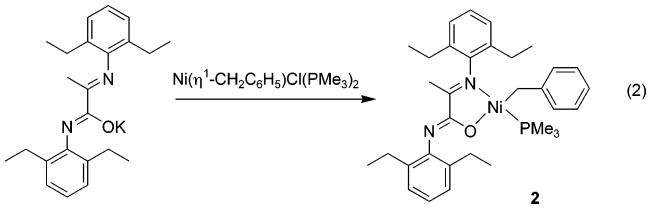
of 2 h and requires the addition of 1 equiv of triethylamine. A different aniline may be added at this stage to generate α-iminocarboxamide ligands with different substituents at the two nitrogen sites. The second step requires overnight heating to ~110 °C. Two equivalents of aniline are added to pyruvic acid chloride in cases where identical substitution is desired. Purification can be accomplished by chromatography or crystallization, depending on the aryl substituents. Deprotonation is readily accomplished using KH in THF. Addition of the potassium salts to Ni(η^1-CH_2Ph)Cl(PMe_3)$_2$[12] yields the desired complexes.

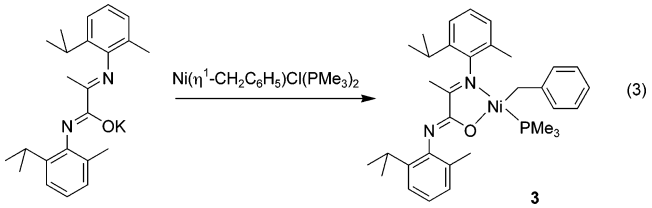
The reaction of potassium *N*-(2,6-diethylphenyl)-2-(2,6-diethylphenylimino)propanamide with Ni(η^1-CH_2-Ph)Cl(PMe_3)$_2$ yields a single organometallic product, which was characterized by NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra are consistent with the formation of a single isomer containing a nickel center ligated by α-iminocarboxamide, η^1-CH_2Ph, and PMe_3 ligands (^{1}H NMR: 1.03, CH_2-Ph; 0.53, P(CH_3)$_3$; ^{13}C NMR: 12.65, PCH_3; 8.3, CH_2-Ph). The ^{31}P NMR spectrum reveals a single peak at $\delta = -7.7$ ppm, which indicates *N,O*-coordination of the α-iminocarboxamide fragment to nickel (*N,N*-coordination gives rise to peaks in the −18 to −20 ppm range).[11] The product is therefore [*N*-(2,6-diethylphenyl)-2-(2,6-diethylphenylimino)propanamidato-κ^2*N,O*](η^1-CH_2Ph)(PMe_3) nickel (**2**), as shown in eq 2.



(2)

2

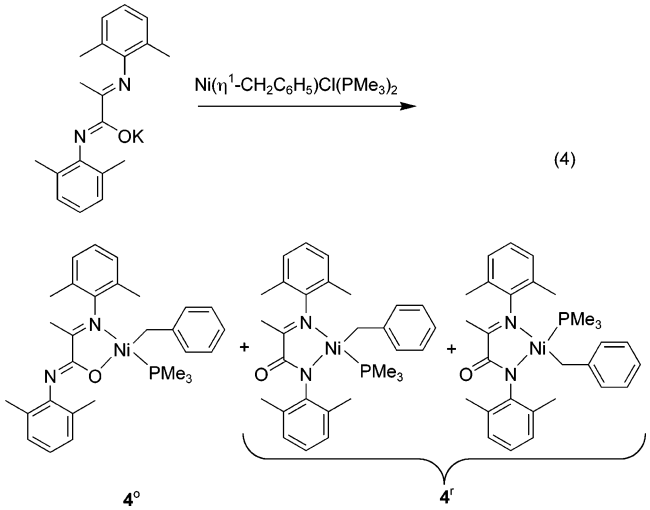
Equation 3 shows the synthesis of [*N*-(2,6-methylisopropylphenyl)-2-(2,6-methylisopropylphenylimino)propanamidato-κ^2*N,O*](η^1-CH_2Ph)(PMe_3)nickel (**3**) by addition of potassium *N*-(2,6-methylisopropylphenyl)-2-(2,6-methylisopropylphenylimino)propanamide to Ni(η^1-CH_2Ph)Cl(PMe_3)$_2$. ^{1}H and ^{31}P NMR spectroscopy and elemental analysis are consistent with the molecular structure and *N,O*-coordination of the α-iminocarboxamide ligand (^{31}P NMR: $\delta = -7.8$ pm).



(3)

3

The steric bulk of the ligand was further reduced by employing *N*-(2,6-dimethylphenyl)-2-(2,6-dimethylphenylimino)propanamide to synthesize [*N*-(2,6-dimethylphenyl)-2-(2,6-dimethylphenylimino)propanamidato]-(η^1-CH_2Ph)(PMe_3)nickel (**4**). The product is obtained as a mixture of three isomers, as determined by NMR spectroscopy. In particular, the ^{31}P NMR spectrum in C_6D_6 exhibits three PMe_3 signals (^{31}P NMR: δ −8.1, −18.6, and −19.7 ppm). Diffusion of pentane at room temperature into a toluene solution of the crude product gave a crystalline product. Optical microscopy revealed that single crystals with different colors were obtained. The majority of the crystals were red (**4**^{r}), while the second fraction was pale orange (**4**^{o}). Successive recrystallization at −35 °C provided mostly the pale orange crystals (**4**^{o}). The ^{31}P NMR shifts for the red fraction occur at −18.6 and −19.7 ppm, in a 3:1 ratio, while the orange product displays a single peak at −8.1 ppm. These data are consistent with **4**^{r} corresponding to two isomers of the *N,N*-bound product, which differ in the orientation of the η^1-benzyl and phosphine ligands, relative to the imine and carboxamide nitrogens. The structure of **4**^{o} corresponds to the *N,O*-bound structure, with the bulkier phosphine ligand opposite the imine nitrogen, as shown in eq 4.



(4)

4^o **4**^{r}

The stability of **4**^{o} was investigated by ^{1}H NMR spectroscopy starting with a sample of 90% purity. Over a period of 60 min at 40 °C, the methyl peak of PMe_3 ($\delta = 0.56$ ppm) is reduced in intensity by more than 50% with a concomitant increase of two signals at 0.34 and 0.22 ppm, which correspond to the phosphine resonances in **4**^{r}. Complete conversion from **4**^{o} to **4**^{r} takes place after 2 h at 50 °C. The rearrangement is irreversible. These studies led to fine-tuning of the reaction conditions so that each isomer could be produced directly. Compound **4**^{o} was isolated in greater than 95% purity by running the reaction at −10 °C for 4 h, while **4**^{r} was isolated by running the reaction at 50 °C for 4 h. It should be noted here that there is no change in the binding mode of the α-iminocarboxamide ligands in compounds **1**, **2**, and **3** after heating to 60 °C for 1 h.

Solid state characterization of **4**^{o} by single-crystal X-ray diffraction (Figure 1) is consistent with the structure in eq 4. Compound **4**^{o} adopts a square-planar coordination geometry around the nickel center with a *cis* relationship between PMe_3 and the carboxamide oxygen. The PMe_3 is displaced by 10° below the N−Ni−N plane, while the benzyl ligand is 4° is above the plane (Table 1).

Single crystals of **4**^{r} suitable for X-ray diffraction studies were obtained by diffusion of pentane into a toluene solution, and the resulting structure is shown in Figure 2. The molecular structure confirms the *N,N*-binding mode determined by ^{31}P NMR spectroscopy. There is a distortion of the square-planar geometry

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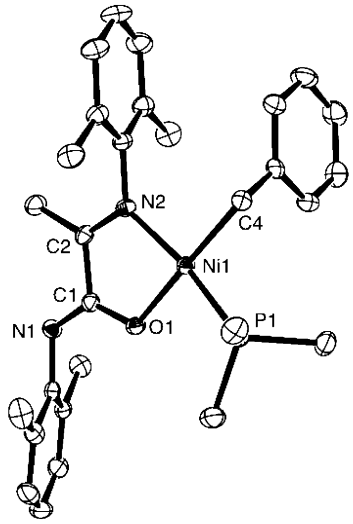


Figure 1. ORTEP drawing of **4**^{o} drawn at 50% probability. Hydrogen atoms were omitted for clarity.

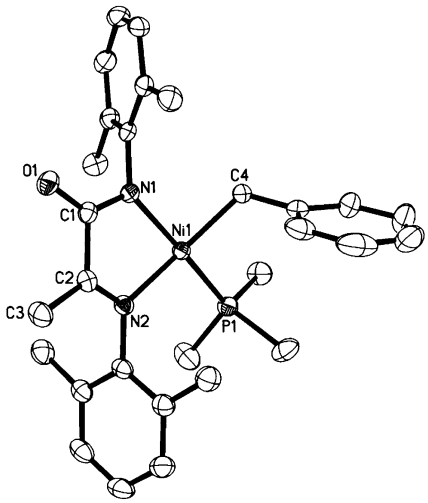
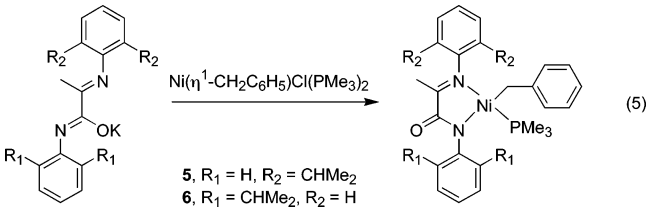


Figure 2. ORTEP drawing of **4**^{r} drawn at 50% probability. Hydrogen atoms were omitted for clarity.

around nickel (the N(1)−Ni−P(1) angle (168.56(4)°) being smaller than 180° and the P(1) atom is ∼11° out of the N(1)−Ni−N(2) plane). The benzyl group is located *cis* to the carboxamide nitrogen with a N(2)−Ni−C(4) angle of 161.56(6)° and is tilted 18.5° out of the plane. The Ni−P, Ni−N(1), and Ni−C(4) bond distances are similar in **4**^{o} and **4**^{r} (Table 1).

Equation 5 shows the synthesis of two complexes with α-iminocarboxamide ligands featuring unsubstituted and substituted aromatic rings. The two compounds are [*N*-phenyl-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N*,*N*](η^1-CH_2Ph)(PMe_3)nickel (**5**) and [*N*-(2,6-diisopropylphenyl)-2-(phenylimino)propanamidato-κ^2*N*,*N*](η^1-CH_2Ph)(PMe_3)nickel (**6**). In both compounds *N*,*N*-coordination is observed. For compound **5**, the ^{1}H and ^{31}P NMR spectra are consistent with a single isomer containing α-iminocarboxamide, η^1-benzyl, and PMe_3 ligands (^{31}P NMR: δ −20.3 ppm). Compound **6** displays three sets of signals in the ^{1}H and ^{31}P NMR spectra that can be attributed to two *N*,*N*-coordinated isomers in a 3:1 ratio, which together account for 90% of the product, and an *N*,*O*-coordinated isomer (10%) (^{31}P NMR: δ −20.4, −18.5, −7.1 ppm). There is no change in the isomeric distribution in **6** upon heating to 60 °C for 1 h.

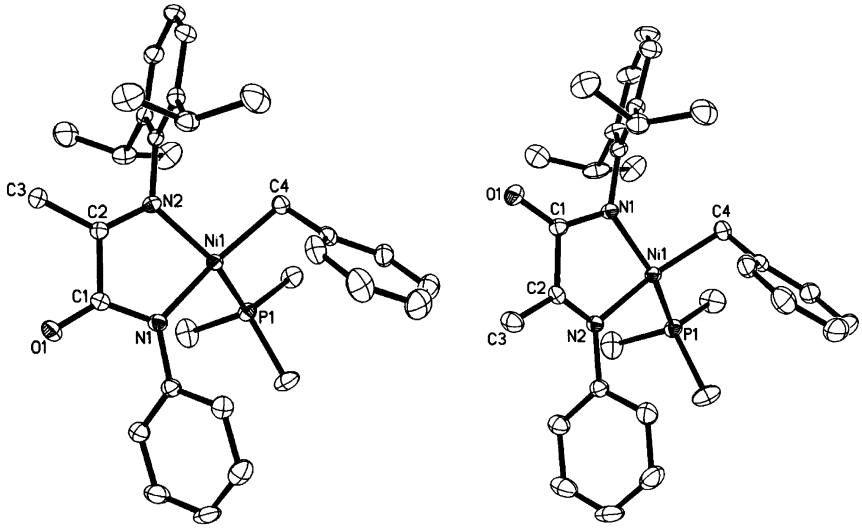


Diffusion of pentane into toluene solutions of **5** or **6** at room temperature yields single crystals suitable for X-ray studies. As shown in Figure 3, the nickel atom in both complexes is contained within a square-planar arrangement. The phosphine and benzyl groups show distortions above and below the plane. The N(2)−Ni−P(1) angles are 148.92(5)° for **5** and N(1)−Ni−P(1) 155.21(4)° for **6**. The N(1)−Ni−C(4) angles amount to 161.14(8)° and N(2)−Ni−C(4) to 156.18(7)° for **5** and **6**, respectively (Table 1). The benzyl ligand binds *trans* to the carboxamide nitrogen in **5** and *cis* to the carboxamide in **6**. The PMe_3 ligand coordinates *trans* to the substituted aromatic ring in both cases, indicating that steric demands are more important than electronic preferences. The Ni−N(1), Ni−N(2), Ni−C(4), and Ni−(P1) bond lengths are similar in both complexes.

Activation with Ni(COD)$_2$ and Reactivity toward Ethylene. A study of the polymerization of ethylene with the family of *N*,*O*- and *N*,*N*-bound nickel complexes ([Ni-α-iminocarboxamide] = 3.43×10^{-4} M) activated with 2.5 equiv of $Ni(COD)_2$ was carried out, and the results are summarized in Table 2. The [$Ni(COD)_2$]/[Ni-

Table 1. Selected Bond Distances (Å) and Angles (deg) for α-Iminocarboxamide Nickel Complexes

	4^{o}	**4**^{r}	**5**	**6**	**7**
Ni(1)−N(1)		1.9415(12)	1.9350(16)	1.9633(13)	1.888(2)
Ni(1)−O(1)	1.920(2)				
Ni(1)−C(4)	1.960(3)	1.9714(14)	1.9479(19)	1.9533(17)	1.946(3)
Ni(1)−N(2)	1.972(3)	1.9922(11)	1.9793(15)	1.9721(13)	1.950(2)
Ni(1)−P(1)	2.1429(9)	2.1885(4)	2.1555(6)	2.1607(5)	
O(1)−C(1)	1.307(4)	1.2454(17)	1.237(2)	1.2427(19)	1.237(3)
Ni(1)−C(5)					2.035(3)
Ni(1)−C(6)					2.155(2)
N(1)−Ni(1)−N(2)		81.01(5)	81.94(7)	81.87(5)	83.63(8)
N(2)−Ni(1)−O(1)	83.17(10)				
C(4)−Ni(1)−P(1)	89.10(10)	88.79(5)	92.50(6)	92.47(6)	
N(1)−Ni(1)−C(4)		91.38(6)	161.14(8)	94.64(7)	98.88(10)
N(2)−Ni(1)−P(1)	169.98(9)	101.98(4)	148.92(5)	100.52(4)	
O(1)−Ni(1)−C(4)	176.17(12)				
N(1)−Ni(1)−P(1)		168.56(4)	98.12(5)	155.21(4)	
C(4)−Ni(1)−N(2)	96.16(12)	161.56(6)	96.90(8)	156.18(7)	176.31(11)
O(1)−Ni(1)−P(1)	92.13(7)				
N(1)−Ni−C(6)					167.00(10)



(5) **(6)**

Figure 3. ORTEP drawing of **5** and **6** drawn at 50% probability.

Table 2. Ethylene Polymerization Reactions[a]

entry	precatalyst	time (min)	reaction temp (°C)	activity[b]	M_n ($\times 10^{-3}$)	M_w/M_n	T_m (°C)
1	**1**[10]	20	20	55	110	1.4	125
2	**1**	20	70	186	7	6.1	
3	**2**	10	20	35	59	2.0	130
4	**2**	20	20	28	73	1.8	130
5	**2**	30	20	31	77	2.0	130
6	**2**	40	20	21	85	1.9	130
7	**2**	20	70	112	7	5.0	
8	**3**	20	20	30	76	1.7	130
9	**3**	40	20	26	104	1.8	131
10	**4**^{o}	20	20	19	61	1.9	132
11	**4**^{o}	40	20	22	79	2.0	132
12	**4**^{r}	20	20				
13	**4**^{r}	20	70	3	oligomers		
14	**5**[c]	20	20				
15	**5**	20	70	11	oligomers		
16	**6**	20	20				
17	**6**	20	20	7		multimodal	
18	**6**	20	70	18	oligomers		

[a] Polymerizations were carried out in 100 mL autoclave reactors with 10 μmol of precatalyst, 25 μmol of Ni(COD)$_2$ in 30 mL of toluene; reaction time, 20 min; temperature controlled by using a water bath, pressure 100 psi. [b] kg polymer/(mol Ni)(h)(atm); entry 17 run with 40 μmol of **6**, 100 μmol of Ni(COD)$_2$. [c] Reaction run under the same conditions as entry 17 did not show ethylene consumption; entries 12, 14, and 16 were repeated at 500 and 1000 psi: none showed ethylene consumption.

α-iminocarboxamide] ratio of 2.5 was determined in previous studies.[10] Reactions were performed inside a 100 mL autoclave reactor in toluene at an ethylene pressure of 100 psi. The reactions used an external water bath kept constant at 20 °C. Entry 1 corresponds to the reactivity previously reported for **1**/Ni(COD)$_2$ and is provided for comparison.[10] Entries 3−6 show the results obtained at different reaction times with **2**/Ni(COD)$_2$. Comparison of these entries shows that the ethylene consumption is constant up to 30 min, with the molecular weights of the resulting polymers increasing with longer reaction times. However, the PDIs (M_w/M_n ratios) are approximately 2, while the PDI of the polyethylene obtained by using complex **1** is more narrow (entry 1). Entries 2 and 7 show that at higher temperatures compounds **1**/Ni(COD)$_2$ and **2**/Ni(COD)$_2$ provide higher activity, compared to room-temperature reactions (entries 1 and 3), but result in low molecular weight products with broad PDIs.

Entries 8 and 9 with **3**/Ni(COD)$_2$ and entries 10 and 11 with **4**^{o}/Ni(COD)$_2$ demonstrate that these combinations also yield ethylene polymerization sites. A comparison of entries 1, 4, 8, and 10 performed with **1**, **2**, **3**, and **4**^{o}, respectively, under similar reaction conditions shows that the polymerization activity decreases with a reduction of the steric bulk on the α-iminocarboxamide ligand. Entries 6, 9, and 11 show that increasing the reaction time to 40 min, while keeping the temperature at approximately 20 °C, results in a decrease in the overall integrated polymerization activity and an increase in the molecular weight of the polyethylene product; interestingly the PDIs do not change. For all precatalyst/Ni(COD)$_2$ combinations there was no change in the ethylene consumption rate when the ethylene pressure was varied between 200 and 1000 psi (Supporting Information).

Entries 12−18 show the results obtained with the *N,N*-bound complexes **4**^{r}, **5**, and **6**. Negligible reactivity was observed at 20 °C (entries 12, 14, and 16). Ethylene consumption is observed when the reactions are carried out at 70 °C (entries 13, 15, and 18), however at rates substantially lower than that obtained with the *N,O*-

bound counterparts under the same reaction conditions (entries 2 and 7).[13] At the higher temperature, compounds **5** and **6** provide low molecular weight ethylene oligomerization products. In the case of **6** (entry 17) performing the reactions at higher Ni concentrations ([**6**] $\approx 1.4 \times 10^{-3}$ M, [**6**]/[Ni(COD)$_2$] = 2.5) yields a mixture of polyethylene and oligomeric products. Additionally, there is no perturbation on the activity of any combination (either *N,O*- or *N,N*-bound) upon increasing the ethylene pressure (500 and 1000 psi) at 20 °C.

NMR Spectroscopy of Reactions with Ni(COD)$_2$. ^{1}H NMR spectroscopy was used to investigate reactivity differences between *N,O*- and *N,N*-coordinated complexes. We previously reported that the ^{1}H NMR spectra of solutions of **1** and 2.5 equiv of Ni(COD)$_2$ at room temperature over a period of 1.5 h provide no observable changes, except for the decomposition of Ni(COD)$_2$.[10a] We repeated these experiments at 40 and 60 °C and obtained similar observations using compounds **2** and **3**. The results are different when using **5** and 2.5 equiv of Ni(COD)$_2$ under similar reaction conditions. Resonances attributed to free COD (5.58, 2.21 ppm) and an η^3-benzyl complex (between 5.8 and 6.8 ppm) are observed. After 1 h at 65 °C, 75% of **5** is consumed and two η^3-benzyl isomers can be identified. Two separate doublets are observed corresponding to the *ortho*-hydrogens (6.0 and 5.9 ppm) on the benzyl ligand and two triplets for the benzyl *meta*-hydrogens (6.2 and 6.4 ppm). The set of signals is attributed to two isomers, which appear in a 3:2 ratio. Signals from the *para*-substituted hydrogens are sharp at 7.33 and 7.28 ppm. Other evidence supporting the formation of two η^3-benzyl isomers is the presence of new septets at 3.54, 3.33, and 2.86 ppm, which are associated with the C*H*Me$_2$ groups. Isolation of the product was not possible; however there is no reaction upon addition of ethylene to the mixture of isomers.

At room temperature, the reaction between **6** and Ni(COD)$_2$ provided approximately 20% of an η^3-benzyl complex, together with free COD. Signals characteristic of η^3-coordinated benzyl ligands are observed at 5.95 and 5.83 ppm (*ortho*-hydrogens) and 6.58 and 6.22 ppm (*meta*-hydrogens), indicating the formation of two isomers. Substantial amounts of starting material were converted (~75%) after increasing the temperature to 65 °C and allowing the reaction to proceed for an hour.

No ethylene polymerization was obtained with **5** or **6** in the presence of Ni(COD)$_2$ at room temperature (Table 2). This observation and the results described above from NMR spectroscopy experiments suggest that *N,N*-coordinated η^3-benzyl nickel complexes are not active species at room temperature. Instead, the data are consistent with only the *N,O*-coordinated nickel complexes being the active species.

Synthesis and Isolation of a Phosphine-Free α-Iminocarboxamide η^3-Benzyl Nickel Complex. Efforts to remove PMe$_3$ from **1** and **2** by using CuCl or (MeCN)$_3$CuCl in toluene were not successful, as determined by ^{1}H NMR spectroscopy. No reactivity was also observed when these reactions were performed in the presence of ethylene. Addition of 1 equiv of B(C$_6$F$_5$)$_3$ to **1** or **2** did not result in a neutral η^3-complex; instead a product mixture was obtained including a zwitterionic B(C$_6$F$_5$)$_3$ adduct[11] and insoluble B(C$_6$F$_5$)$_3$-PMe$_3$.

(13) Polymer formation was also observed when the ethylene polymerization was run at 50 °C.

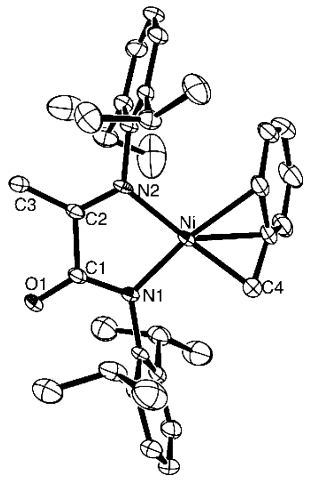
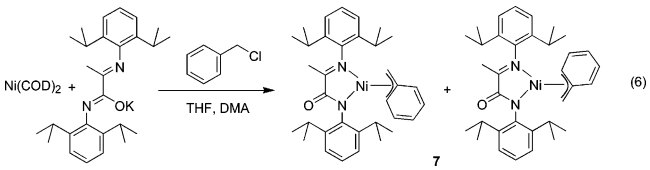


Figure 4. Molecular structure of **7** drawn at 50% probability. Hydrogen atoms were omitted for clarity.

A neutral η^3-benzyl complex, [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,N*]-(η^3-CH$_2$Ph)nickel (**7**), was successfully synthesized by direct reaction of potassium *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamide with Ni(COD)$_2$ and benzyl chloride in THF, as shown in eq 6. Best results are obtained when exposure to light is minimized and with the addition of dimethylaniline. The role of dimethylaniline is not clear at this stage; presumably it improves the product yield by stabilizing reactive intermediates. Successive crystallization from pentane allowed for isolation of **7** as thermally and air-sensitive dark orange crystals in 70% yield. While isopropyl substitution on both phenyl rings provides the desired product, similar reactions with ligand frameworks with lesser steric bulk failed.



Single crystals of **7** suitable for crystallographic studies were obtained from pentane by slow evaporation at −35 °C, and the results are shown in Figure 4. The benzyl group is coordinated in an η^3-fashion with the methylene group in a *trans* orientation relative to the imine nitrogen atom. A square-planar arrangement surrounds the nickel center. The two aryl rings are perpendicular to the square plane and are pushed slightly toward the metal. The bond distances for Ni−N(1) and Ni−N(2) (1.889(2) and 1.950(2) Å, respectively) are slightly shorter compared to the values for the η^1-benzyl *N,N*-nickel complexes (Table 1) (the bond distances for Ni−N(1) and Ni−N(2) are 1.9415(12) and 1.9922(11) Å for compound **4**^{r} and 1.9350(16) and 1.9793(15) Å for compound **5**), consistent with stronger binding of the ligand. Comparison of metrical parameters with those of a polymerization-active zwitterionic *N,N*-chelating α-iminocarboxamide nickel complex featuring an η^3-benzyl ligand and B(C$_6$F$_5$)$_3$ attached to the carbonyl functionality shows comparable bond distances

between the Ni and the two nitrogen atoms.[11] As expected, the C(1)−O(1) bond is shorter in **7** (1.238(3) Å), due to its double-bond character, while zwitterionic compounds show more single-bond character.

Two isomers of **7** in a 5:8 ratio are observed by ^{1}H NMR spectroscopy. NOESY studies were carried out to identify the structure of the isomers. Two possibilities considered were *N,N*-ligand coordination and *N,O*-ligand coordination versus η^3-benzyl positional isomers, with the CH_2 group either *cis* or *trans* to the imine site. The NOESY study is consistent with two *N,N*-coordinated structures with different orientations of the benzyl fragment. Full details for these experiments are deposited in the Supporting Information. From a reactivity perspective, it is important to note that there is no ethylene consumption when 100 to 1000 psi ethylene was added to **7**, at temperatures ranging from 20 to 70 °C. Addition of $Ni(COD)_2$ did not result in a change of activity.

Summary, Discussion, and Conclusion

As stated in the Introduction, our interest in examining a variety of nickel complexes with α-iminocarboxamide ligands stems from the ability of **1**/$Ni(COD)_2$ to generate block copolymers with ethylene and functionalized norbornenes. The exact structure corresponding to the initiating species has not been determined previously and is the main subject of this study.

Scheme 1 provides a straightforward approach to generating α-iminocarboxamide ligands in which the steric bulk on the imine and carboxamide nitrogens can be controlled by aromatic substituents. Deprotonation of the ligand with potassium hydride, followed by reaction with $Ni(\eta^1\text{-}CH_2Ph)Cl(PMe_3)_2$, yields the target compounds with general structure [α-iminocarboxamidato](η^1-CH_2Ph)(PMe_3)nickel. Structural characterization, by ^{31}P NMR spectroscopy and X-ray diffraction structure determination, shows that the *N,O*-binding mode is preferred when the steric bulk at *both* nitrogen sites is sufficiently large, for example, compounds **1**, **2**, and **3**. In the case of compound **4**, where 2,6-dimethylphenyl substituents are present, one obtains an intermediate situation. The *N,O*-mode is kinetically preferred, probably because of easier displacement by the sterically unencumbered oxygen. The *N,N* isomer is ultimately the thermodynamic product, which reflects an electronic preference for nickel to bind to nitrogen over oxygen. Examination of Figure 3 shows that the *N,N*-bound compounds **5** and **6** are nearly isostructural, in the sense that the overall molecular arrangements differ only by the location of oxygen and methyl on the ligand bridge. The PMe_3 is situated *trans* to the bulky 2,6-diisopropylphenyl fragment and is adjacent to the more accommodating phenyl fragment.

Reactions of ethylene with mixtures composed of [α-iminocarboxamidato](η^1-CH_2Ph)(PMe_3)nickel and 2.5 equiv of $Ni(COD)_2$ have been summarized in Table 2. The most important reactivity trend that can be extracted from these data is that only the *N,O*-bound precursors give rise to effective ethylene polymerization initiators. Particularly striking is the difference between compounds $\mathbf{4}^o$ (*N,O*-bound and active) and $\mathbf{4}^r$ (*N,N*-bound and inactive), which are supported by the same α-iminocarboxamidato ligand and differ in the binding mode. It is also informative that the narrowest polydispersities are obtained with **1**, which contains the largest steric bulk around nickel. Differences in reactivity within the set of active species are not sufficiently large to draw further structure/reactivity relationships.

Examination of reactions with compounds **5** and **6** and $Ni(COD)_2$ by ^{1}H NMR spectroscopy indicates η^3-benzyl ligand formation and loss of PMe_3. This information supports the idea that loss of the phosphine is a prerequisite for the initiation of ethylene polymerization. No such indication could be observed with other compounds. We note, however, that ethylene is present in the polymerization reactions. It has been previously suggested that ethylene may displace COD to form a more active species that proceeds to extract phosphine.[7a] Monitoring such reactions by NMR spectroscopy is not feasible because the rate of propagation is faster than that of initiation. Polyethylene forms and precipitates, which renders such analysis uninformative.

Compound **7** provides for a phosphine-free, η^3-benzyl structure. That it is unreactive toward ethylene is consistent with the proposal that only *N,O*-bound species are active. Putting together the structural and reactivity observations provided in this study indicates that the neutral initiators capable of quasi-living polymerization of ethylene are [*N,O*-α-iminocarboxamidato](benzyl)nickel complexes. Two situations may be further considered, one where the initiator is an η^3-benzyl complex that can be converted to $Ni(C_2H_4)(\eta^1$-benzyl) species, by dissociative or associative displacement by ethylene of the π-component of the η^3-benzyl fragment. Alternatively, the $Ni(C_2H_4)(\eta^1$-benzyl) species may form directly after PMe_3 displacement. There is insufficient information at this stage to differentiate the two possibilities. It is also interesting to note that the polymerization reactions show no decrease in activity, even after 30 min. Perhaps *N,O* → *N,N* isomerization is slower for the phosphine-free species, or the resting state of the active site is an olefin adduct in which α-iminocarboxamide 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. Having identified plausible initiating structures should allow for a more rational improvement of the polymerization activity of this class of complexes and therefore a better control of the product structures.

Experimental Section

General Remarks. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from Aldrich unless otherwise specified. Ethylene was purchased from Matheson Tri-Gas (research grade, 99.99% pure) and was further purified by passage 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. The synthesis of compounds **2**, **3**, $\mathbf{4}^o$, $\mathbf{4}^r$, **5**, and **6** used procedures similar to the literature procedure for **1**[10] and were purified by recrystallization. NMR spectra were obtained using Varian Unity 400 and 500 spectrometers. Polymers were dried overnight under vacuum, and the polymerization activities

Table 3. Crystal Data and Structure Refinement for α-Iminocarboxamide Nickel Complexes

	4^o	**4^r**	**5**	**6**	**7**
empirical formula	$C_{29}H_{37}N_2NiOP$	$C_{29}H_{37}N_2NiOP$	$C_{31}H_{41}N_2NiOP$	$C_{31}H_{41}N_2NiOP$	$C_{34}H_{44}N_2NiO$
fw	519.29	519.29	547.34	547.34	555.42
temp (K)	117 (1)	168 (2)	163 (2)	163 (2)	117(1)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	$C2/c$
unit cell dimens (Å, deg)	a = 17.3082(13)	a = 10.0245(4)	a = 10.2471(19)	a = 10.9043(9)	a = 32.086(3)
	b = 9.5254(7)	b = 24.6120(10)	b = 16.382(3)	b = 17.1985(15)	b = 9.2402(7)
	c = 16.6458(13)	c = 11.2350(5)	c = 17.047(3)	c = 15.6966(13)	c = 21.1912(17)
	α = 90	α = 90	α = 90	α = 90	α = 90
	β = 96.424(2)	β = 100.2400(10)	β = 90	β = 93.937(2)	β = 104.209(2)
	γ = 90	γ = 90	γ = 90	γ = 90	γ = 90
volume (Å^3)	2727.1(4)	2727.8(2)	2861.6(9)	2936.8(4)	6090.5(8)
Z	4	4	4	4	8
density (calcd) (Mg/m^3)	1.264	1.264	1.270	1.238	1.211
absorp coeff (mm^{-1})	0.198	0.793	0.760	0.740	0.665
F(000)	276	1104	1168	1168	2384
cryst size (mm^3)	0.2 × 0.15 × 0.1	0.37 × 0.33 × 0.31	0.40 × 0.37 × 0.30	0.25 × 0.23 × 0.15	0.25 × 0.15 × 0.08
θ range (deg)	1.18 to 29.44	1.65 to 28.28	2.32 to 28.29	1.76 to 28.31	1.31 to 26.50
index ranges	$-23 \le h \le 17$	$-12 \le h \le 13$	$-13 \le h \le 13$	$-14 \le h \le 14$	$-40 \le h \le 38$
	$-13 \le k \le 12$	$-32 \le k \le 31$	$-21 \le k \le 21$	$-22 \le k \le 22$	$-11 \le k \le 11$
	$-11 \le l \le 22$	$-14 \le l \le 14$	$-22 \le l \le 22$	$-20 \le l \le 20$	$-26 \le l \le 23$
no. of reflns collected	13 719	27 928	29 503	35 747	17 585
no. of indep reflns	6581 [R(int) = 0.0423]	6524 [R(int) = 0.0264]	6933 [R(int) = 0.0416]	7190 [R(int) = 0.0378]	5851 [R(int) = 0.0392]
completeness to θ = 28.28° (%)	87.2	96.4	98.9	98.3	92.7
max. and min. transmn	0.6922[a]	0.7911 and 0.7579	0.8042 and 0.7510	0.8971 and 0.8366	0.8482[a]
no. of data/restraints/params	6581/0/277	6524/0/455	6933/0/489	7190/0/489	5851/0/519
goodness-of-fit on F^2	0.908	1.042	1.050	1.063	1.051
final R indices	R1 = 0.0511,	R1 = 0.0287,	R1 = 0.0302,	R1 = 0.0309,	R1 = 0.0460,
[$I > 2\sigma(I)$][b]	wR2 = 0.1257	wR2 = 0.0707	wR2 = 0.0699	wR2 = 0.0726	wR2 = 0.1122
R indices (all data)[b]	R1 = 0.0894,	R1 = 0.0361,	R1 = 0.0385,	R1 = 0.0485,	R1 = 0.0625, wR2 = 0.1214
	wR2 = 0.1399	wR2 = 0.0753	wR2 = 0.0747	wR2 = 0.0819	
largest diff peak and hole (e Å^{-3})	0.715 and −0.629	0.410 and −0.293	0.606 and −0.358	0.383 and −0.295	1.126 and −0.452

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

were calculated from the mass of product obtained. These values were to within 5% of the calculated mass by measuring the ethylene consumed by use of a mass flow controller. The polymers were characterized by GPC analysis at 135 °C in *o*-dichlorobenzene (in a Polymers Laboratories, high-temperature chromatograph, Pl-GPC 200). Polymer melting points were measured on a TA Instruments differential scanning calorimeter (model DSC 2920) at a rate of 10 °C/min for two cycles using a temperature range of 0−150 °C. ^{1}H NMR spectra of the polymers were obtained in a mixed solvent (C_6D_6/1,2,4-trichlorobenzene in a 1:4 volume ratio) at 115 °C. Elemental analysis was performed on a Leeman Labs Inc. CE440 elemental analyzer and a Control Equipment Corporation 440 elemental analyzer. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets and in solution using C_6D_6 as solvent.

X-ray Crystallography. The monocrystal was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[14] 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 SAINT[15] and SADABS[16] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[17] program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[18] 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}).[19] The crystal data and refinement are summarized in Table 3.

Synthesis and Characterization of Compounds. Potassium *N*-(2,6-diethylphenyl)-2-(2,6-diethylphenylimino)propanamide. *N*-(2,6-Diethylphenyl)-2-(2,6-diethylphenylimino)propanamide (1.28 g, 3.63 mmol) and KH (145.6 mg, 3.63 mmol) were stirred in THF overnight. The reaction showed rapid gas evolution. The suspension was filtered, and the solvent was removed in a vacuum, providing a beige powder in 81% yield.

^{1}H NMR (399.95 MHz, [d$_3$]-chloroform, 298 K): δ 7.06−7.00 (m, 3H, $^3J_{HH}$ = 6.2 Hz, H-Ph), 7.86 (d, 2H, $^3J_{HH}$ = 7.5 Hz, H-Ph), 6.65 (t, 1H, $^3J_{HH}$ = 7.5 Hz, H-Ph), 2.75 (m, 2H, $^3J_{HH}$ = 7.2 Hz, CH_2), 2.62 (m, 2H, $^3J_{HH}$ = 7.2 Hz, CH_2), 2.31 (m, 4H, $^3J_{HH}$ = 7.2 Hz, CH_2), 2.34 (s, 3H, CH_3), 1.25 (t, 6H, $^3J_{HH}$ = 7.2 Hz, CH_3-Et), 1.08 (t, 6H, $^3J_{HH}$ = 7.2 Hz, CH_3-Et).

[*N*-(2,6-Diethylphenyl)-2-(2,6-diethylphenyl)propanamidato-κ^2*N,O*][η^1-CH_2Ph)(PMe$_3$)nickel (2). Potassium *N*-(2,6-diethylphenyl)-2-(2,6-diethylphenylimino)propanamide (610

(14) *SMART* Software Users Guide, Version 5.1; Bruker Analytical X-Ray Systems, Inc.; Madison, WI, 1999.
(15) *SAINT* Software Users Guide, Version 6.0; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999.
(16) Sheldrick, G. M. *SADABS*, Version 2.05; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2001.
(17) Sheldrick, G. M. *SHELXTL* Version 6.12; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2001.
(18) *International Tables for X-ray Crystallography*, Vol. C; Kluwer Academic Publishers: Dordrecht. 1992.
(19) Flack, H. D. *Acta Crystallogr*. **1983**, *A39*, 876.

mg, 1.57 mmol) in toluene was added to Ni($(\eta^1$-$CH_2Ph)Cl(PMe_3)_2$ (529 mg, 1.57 mmol) in toluene and stirred for 4 h. The suspension was filtered, and all volatiles were removed under vacuum to give a light red solid. The latter was triturated with pentane and left at −35 °C overnight. The product in the form of an orange solid (73%) was filtered and dried in a vacuum.

^{1}H NMR (399.95 MHz, [d$_6$]-benzene, 298 K): δ 7.21 (d, 2H, $^3J_{HH}$ = 7.5 Hz, H-Ph), 7.18 (m, 1H, H-Ph), 7.10 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, H-Ph), 7.03 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, H-Ph), 6.96 (m, 6H, H-Ph), 2.84 (q, 4H, $^3J_{HH}$ = 7.4 Hz, CH_2-Et), 2.71 (dq, 4H, $^3J_{HH}$ = 7.4 Hz, $^5J_{HP}$ = 2.8 Hz, CH_2-Et), 2.08 (s, 3H, CH_3), 1.40 (t, 6H, $^3J_{HH}$ = 7.4 Hz, CH_3-Et), 1.15 (t, 6H, $^3J_{HH}$ = 7.4 Hz, CH_3-Et), 1.03 (s, 2H, CH_2-Ph), 0.53 (d, 9H, $^2J_{HP}$ = 10.1 Hz, P(CH_3)$_3$). ^{13}C NMR (125.7 MHz, [d$_6$]-benzene, 298 K): δ 181.40 (carbonyl), 149.92, 148.72, 143.35, 135.19, 134.66, 129.93, 128.69, 127.09, 126.62, 126.31, 123.56, 122.73 (imine, ph-C), 26.66, 24.87 (Et-CH_2), 19.18 (CH_3), 15.27, 13.99 (Et-CH_3), 12.65 (d, J = 28 Hz, PCH_3), 8.3 (CH_2-Ph). ^{31}P{^{1}H} NMR (161.91 MHz, [d$_6$]-benzene, 298 K, H_3PO_4): δ −7.7. Anal. Calcd for $C_{33}H_{45}N_2$OPNi: C, 68.93; H, 7.89; N, 4.87. Found: C, 68.90; H, 7.72; N, 4.91.

[*N*-(2,6-Methylisopropylphenyl)-2-(2,6-methylisopropylphenylimino)propanamidato-κ^2*N,O*](η^1-CH_2Ph)(PMe_3)nickel (3). Potassium *N*-(2,6-methylisopropylphenyl)-2-(2,6-methylisopropylphenylimino)propanamide (300 mg, 0.77 mmol) in toluene was added to Ni($(\eta^1$-$CH_2Ph)Cl(PMe_3)_2$ (260 mg, 0.77 mmol) in toluene and stirred for 4 h at room temperature. The suspension was filtered, and all volatiles were removed under vacuum to give a red solid. Trituration with pentane and crystallization at −35 °C overnight gave the product as a dark orange solid in 69% yield. The product was isolated by filtration and was dried under vacuum.

^{1}H NMR (399.95 MHz, [d$_6$]-benzene, 298 K): δ 7.23 (m, 4H, H-Ph), 7.07 (m, 2H, H-Ph), 6.96 (m, 4H, H−Ph), 6.81 (d, 1H, $^3J_{HH}$ = 7.2 Hz, H-Ph), 3.92 (sep., 2H, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 3.54 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 2.44 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 1.44 (d, 3H, $^3J_{HH}$ = 6.8 Hz, ^{i}Pr-CH_3), 1.43 (d, 3H, $^3J_{HH}$ = 6.8 Hz, ^{i}Pr-CH_3), 1.34 (d, 3H, $^3J_{HH}$ = 6.8 Hz, ^{i}Pr-CH_3), 1.09 (d, 3H, $^3J_{HH}$ = 6.8 Hz, ^{i}Pr-CH_3), 1.12 (s, 2H, CH_2), 0.55 (d, 9H, $^2J_{HP}$ = 10 Hz, PMe_3). ^{31}P{^{1}H} NMR (161.91 MHz, [d$_6$]-benzene, 298 K, H_3PO_4): δ −7.8. Anal. Calcd for $C_{33}H_{45}N_2$OPNi: C, 68.93; H, 7.89; N, 4.87. Found: C, 68.58; H, 7.60; N, 4.71.

[*N*-(2,6-Dimethylphenyl)-2-(2,6-dimethylphenylimino)-propanamidato-κ^2*N,O*](η^1-CH_2Ph)(PMe_3)nickel (4^o). Potassium *N*-(2,6-dimethylphenyl)-2-(2,6-dimethylphenylimino)-propanamide (300 mg, 0.9 mmol) in toluene was added to Ni($(\eta^1$-$CH_2Ph)Cl(PMe_3)_2$ (305 mg, 0.9 mmol) in toluene and stirred for 4 h at −30 °C. The suspension was filtered, and all volatiles were removed under vacuum to give an orange solid. Trituration with pentane and crystallization at −35 °C overnight gave the product as a light orange solid in 78% yield. The product was isolated by filtration and was dried under vacuum.

^{1}H NMR (399.95 MHz, [d$_6$]-benzene, 298 K): δ 7.19 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *para*-H-Ph), 7.13 (m, 2H, H-Ph), 7.03 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, *meta*-H−Ph), 6.97 (m, 3H, H-Ph), 6.87 (m, 3H, H-Ph), 2.43 (s, 6H, Ph-CH_3), 2.11 (s, 6H, Ph-CH_3), 2.00 (s, 3H, CH_3), 0.97 (s, 2H, CH_2-Ph) 0.56 (d, 9H, $^2J_{HP}$ = 10.0 Hz, P(CH_3)$_3$). ^{13}C NMR (125.7 MHz, [d$_6$]-benzene, 298 K): δ 181.22 (carbonyl), 163.4 (C=N), 149.56, 149.18, 144.38, 134.60, 130.14, 129.98, 129.83, 129.66, 129.08, 128.82, 127.95, 126.61, 123.86, 122.34 (imine, ph-C), 19.46, 18.45 (Ph-CH_3), 18.37 (CH_3), 12.72 (d, J = 28 Hz, PCH_3), 8.27 (CH_2-Ph). ^{31}P{^{1}H} NMR (161.91 MHz, [d$_6$]-benzene, 298 K, H_3PO_4): δ −8.1. Anal. Calcd for $C_{29}H_{37}N_2$OPNi: C, 67.08; H, 7.18; N, 5.39. Found: C, 66.98; H, 7.06; N, 5.31.

[*N*-(2,6-Dimethylphenyl)-2-(2,6-dimethylphenylimino)-propanamidato-κ^2*N,N*](η^1-CH_2Ph)(PMe_3)nickel (4^r). Potassium *N*-(2,6-dimethylphenyl)-2-(2,6-dimethylphenylimino)-propanamide (200 mg, 0.6 mmol) in toluene was added to Ni($(\eta^1$-$CH_2Ph)Cl(PMe_3)_2$ (203 mg, 0.6 mmol) in toluene and stirred for 4 h at 40 °C. The suspension was filtered, and all volatiles were removed under vacuum to give a red solid. The crude material was triturated with pentane and crystallized at −35 °C overnight. The product, in the form of a dark red solid, was isolated by filtration and dried under vacuum in 84% yield. The ^{1}H NMR spectrum shows two isomers in a 3:1 ratio.

^{1}H NMR (399.95 MHz, [d$_6$]-benzene, 298 K): δ 7.50 (m, 2H, H-Ph$_{minor}$), 7.36 (m, 2H, H-Ph$_{major}$), 7.25 (d, 2H, $^3J_{HH}$ = 7.2 Hz, H-Ph$_{minor}$), 7.14−6.87 (m, 13H, H-Ph), 6.72 (dd, 1H, $^3J_{HH}$ = 6.8 Hz, H-Ph$_{minor}$), 6.64 (d, 2H, $^3J_{HH}$ = 7.6 Hz, H-Ph$_{minor}$). *Major isomers*: 2.70 (s, 6H, Ph- CH_3), 2.24 (s, 6H, Ph- CH_3), 1.86 (s, 3H, CH_3), 1.00 (d, 2H, $^3J_{HP}$ = 6.4 Hz, CH_2−Ph) 0.32 (d, 9H, $^2J_{HP}$ = 9.6 Hz, P(CH_3)$_3$). *Minor isomers*: 2.90 (s, 6H, Ph-CH_3), 2.02 (s, 6H, Ph-CH_3), 1.70 (s, 3H, CH_3), 1.52 (d, 2H, $^3J_{HP}$ = 8.4 Hz, CH_2-Ph) 0.20 (d, 9H, $^2J_{HP}$ = 8.8 Hz, P(CH_3)$_3$). ^{31}P{^{1}H} NMR (161.91 MHz, [d$_6$]-benzene, 298 K, H_3PO_4): δ −18.6, −19.7. Anal. Calcd for $C_{29}H_{37}N_2$OPNi: C, 67.08; H, 7.18; N, 5.39. Found: C, 67.20; H, 7.05; N, 5.31.

[*N*-Phenyl-2-(2,6-diisopropylphenylimino)propanamidato-κ^2*N,N*](η^1-CH_2Ph)(PMe_3)nickel (5). Potassium *N*-phenyl-2-(2,6-diisopropylphenylimino)propanamide (245 mg, 0.68 mmol) in toluene was added to Ni($(\eta^1$-$CH_2Ph)Cl(PMe_3)_2$ (230 mg, 0.68 mmol) in toluene and stirred for 4 h at room temperature. The suspension was filtered, and all volatiles were removed in a vacuum to give an orange solid. Trituration with pentane and crystallization at −35 °C overnight gave the product as a dark orange solid in 75% yield. The product was isolated by filtration and dried in a vacuum. Single crystals for X-ray crystallography were grown by layering pentane onto a toluene solution of **5** at room temperature. For NMR data see ref 11.

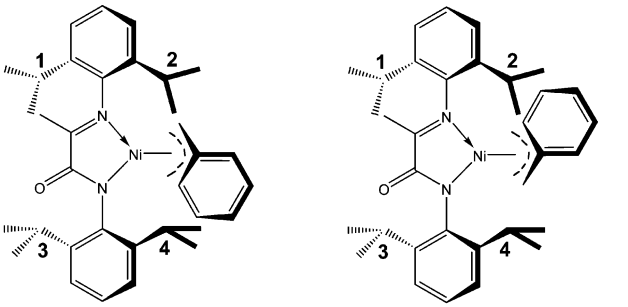
[*N*-(2,6-Diisopropylphenyl)-2-(phenylimino)propanamidato-κ^2*N,N*](η^1-CH_2Ph)(PMe_3)nickel (6). Potassium *N*-(2,6-diisopropylphenyl)-2-(phenylimino)propanamide (200 mg, 0.55 mmol) in toluene was added to Ni($(\eta^1$-$CH_2Ph)Cl(PMe_3)_2$ (187 mg, 0.55 mmol) in toluene and stirred for 4 h at room temperature. Purification similar to that for **5** gave the compound **6** in 72% yield. The product was isolated by filtration and dried in a vacuum. Single crystals for X-ray crystallography were grown by layering pentane onto a toluene solution of compound **6** at room temperature.

^{1}H NMR (399.95 MHz, [d$_6$]-benzene, 298 K): δ 7.67 (d, 2H, $^3J_{HH}$ = 6.8 Hz, H-Ph), 7.36 (m, H-Ph), 7.06 (m, H-Ph), 6.91 (m, H-Ph), 6.78 (m, H-Ph), 6.69 (m, H-Ph), 6.57 (m, H-Ph), 4.73 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 4.18 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 3.47 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 2.12 (s, 3H, CH_3), 2.93 (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 1.68 (d, 6H, $^3J_{HH}$ = 6.8 Hz, ^{i}Pr-CH_3), 1.63 (d, 6H, $^3J_{HH}$ = 6.4 Hz, ^{i}Pr-CH_3), 1.54 (s, 2H, CH_2Ph), 1.527 (d, 6H, $^3J_{HH}$ = 7.2 Hz, ^{i}Pr-CH_3), 1.46 (d, 12H, $^3J_{HH}$ = 5.6 Hz, ^{i}Pr-CH_3) 1.27 (d, 6H, $^3J_{HH}$ = 6.8 Hz, ^{i}Pr-CH_3), 1.19 (s, 2H, CH_2Ph), 0.53 (d, 9H, $^2J_{HP}$ = 10.0 Hz, PMe_3), 0.51 (d, 9H, $^2J_{HP}$ = 14.8 Hz, PMe_3), 0.30 (d, 9H, $^2J_{HP}$ = 8.8 Hz, PMe_3). ^{13}C NMR (125.7 MHz, [d$_6$]-benzene, 298 K): δ 182.04, 178.75 (carbonyl), 149.74, 149.46, 148.05, 147.61, 145.39, 144.39, 138.67, 129.71, 129.55, 129.48, 129.32, 129.05, 126.55, 126.48, 125.53, 124.04, 123.84, 123.61, 122.97. 122.90, 122.82 (imine, ph-C), 29.92, 29.61 (^{i}Pr-CH), 26.12, 24.47 (^{i}Pr-CH_3), 19.16, 18.55 (CH_3) 13.96 (d, J = 25, PCH_3), 12.45 (d, J = 27, PCH_3). ^{31}P{^{1}H} NMR (161.91 MHz, [d$_6$]-benzene, 298 K, H_3PO_4): δ −20.4, −18.46, −7.13. Anal. Calcd for $C_{31}H_{41}N_2$OPNi: C, 68.03; H, 7.55; N, 5.12. Found: C, 68.18; H, 7.30; N, 5.22.

[*N*-(2,6-Diisopropylphenyl)-2-(2,6-diisopropylphenyl)-propanamidato-κ^2*N,N*](η^3-CH_2Ph)nickel (7). The synthesis of **7** was carried out while minimizing exposure to light. A Ni(COD)$_2$ solution (124 mg, 0.46 mmol) in 5 mL of THF was treated with potassium *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamide (200 mg, 0.46 mmol, in 4 mL

of THF) and DMA (~1 g) at −35 °C. Benzyl chloride (60 mg in 5 mL of THF at −35 °C, 0.48 mmol) was added immediately after. The reaction mixture was allowed to reach room temperature and was stirred overnight. The volatiles were then removed under vacuum. The resulting oil was extracted with pentane (15 mL) and filtered. The solvent volume was reduced, and crystallization took place at −35 °C overnight. The product of the first crystallization contains **7** and unreacted $Ni(COD)_2$. Successive crystallization from pentane allows the isolation of **7** as dark orange crystals in 70% yield. ^{1}H NMR spectroscopy showed two isomers.

FTIR (KBr, cm^{-1}): ν 3058 s, 2957br, 1624s, 1584 s, 1473br, 1437 s, 1381 s, 1361s, 1323s, 1255m, 899m, 795br, 747s. FTIR (C_6D_6, cm^{-1}): ν 3061 s, 2960br, 1628s, 1586 s, 1465br, 1439 s, 1380 m, 1358s, 1255m, 899m, 790br, 745s. ^{1}H NMR and ^{1}H-{NOE} NMR, assignment according to figure below. ^{1}H NMR (499.86 MHz, [d_6]-benzene, 298 K): δ 7.30 (m, 3H, *meta*-Ph-3/4^b, *para*-Ph), 7.18 (m, 2H, *meta*-Ph-3/4^s), 7.01 (m, 3H, *meta*-Ph-1/2^s, *para*-Ph), 6.90 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *meta*-Ph-1/2^b), 6.72 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *para*-Bn^s), 6.57 (t, 1h, $^3J_{HH}$ = 7.7 Hz, *para*-Bn^b), 6.35 (t, 2H, $^3J_{HH}$ = 7.6 Hz, *meta*-Bn^s), 6.25 (t, 2H, $^3J_{HH}$ = 7.7 Hz, *meta*-Bn^b), 5.98 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *ortho*-Bn^b), 5.92 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *ortho*-Bn^s), 4.08 (p, 2H, $^3J_{HH}$ = 6.9 Hz, CH-3/4^b), 3.61 (p, 2H, $^3J_{HH}$ = 6.9 Hz, CH-3/4^s), 3.39 (p, 2H, $^3J_{HH}$ = 6.9 Hz, CH-1/2^s), 2.94 (p, 2H, $^3J_{HH}$ = 6.8 Hz, CH-1/2^b), 1.78 (s, 3H, $CH_3{}^s$), 1.75 (s, 3H, $CH_3{}^b$), 1.53 (s, 2H, $CH_2{}^b$), 1.50 (dd, 12H, $^3J_{HH}$ = 6.9 Hz, CH_3-3/4^b), 1.41 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH_3-3/4^s), 1.30 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH_3-1/2^s), 1.28 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH_3-3/4^s), 1.26 (s, 2H, $CH_2{}^s$), 1.05 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3-1/2^b), 0.96 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH_3-1/2^s), 0.84 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3-1/2^b).



s = small fraction / minor product b = big fraction / major product

^{1}H{NOE} NMR (499.86 MHz, [d_6]-benzene, 298K): $\delta_{H(ir)}$/$\delta_{H(res)}$ 5.98 (d, *ortho*-Bn^b)/6.25 (t, *meta*-Bn^b), 2.94 (p, CH-1/2^b), 1.53 (s, $CH_2{}^b$), 1.05 (d, CH_3-1/2^b); 5.92 (d, *ortho*-Bn^s)/6.35 (t, *meta*-Bn^s), 3.61 (p, 2H, CH-3/4^s), 1.26 (s, $CH_2{}^s$); 4.08 (p, CH-3/4^b)/7.30 (m, *meta*-Ph-3/4^b), 1.53 (s, $CH_2{}^b$), 1.50 (dd, CH_3-3/4^b); 3.61 (p, 2H, CH-3/4^s)/5.92 (d, *ortho*-Bn^s), 1.41 (d, CH_3-3/4^s), 1.28 (d, CH_3-3/4^s); 3.39 (p, CH-1/2^s)/1.78 (s, $CH_3{}^s$), 1.30 (d, CH_3-1/2^s), 1.26 (s, $CH_2{}^s$), 0.96 (d, CH_3-1/2^s); 2.94 (p, CH-1/2^b)/5.98 (d, *ortho*-Bn^b), 1.75 (s, $CH_3{}^b$), 1.05 (d, CH_3-1/2^b), 0.84 (d, CH_3-1/2^b); 1.53 (s, $CH_2{}^b$)/5.98 (d, *ortho*-Bn^b), 4.08 (p, CH-3/4^b); 1.50 (dd, CH_3-3/4^b)/7.30 (m, *meta*-Ph-3/4^b), 5.98 (d, *ortho*-Bn^b); 1.41 (d, CH_3-3/4^s)/7.18 (m, *meta*-Ph-3/4^s), 3.61 (p, 2H, CH-3/4^s), 1.28 (d, CH_3-3/4^s); 1.30 (d, CH_3-1/2^s), 1.28 (d, CH_3-3/4^s)/7.18 (m, *meta*-Ph-3/4^s), 7.01 (m, *meta*-Ph-1/2^s), 6.35 (t, *meta*-Bn^s), 5.92 (d, *ortho*-Bn^s), 3.61 (p, 2H, CH-3/4^s), 3.39 (p, CH-1/2^s), 1.41 (d, CH_3-3/4^s), 0.96 (d, CH_3-1/2^s); 1.05 (d, CH_3-1/2^b)/6.90 (d, *meta*-Ph-1/2^b), 6.57 (t, *para*-Bn^b), 6.25 (t, *meta*-Bn^b), 5.98 (d, *ortho*-Bn^b), 2.94 (p, CH-1/2^b), 0.84 (d, CH_3-1/2^b); 0.96 (d, CH_3-1/2^s)/7.01 (m, *meta*-Ph-1/2^s), 3.39 (p, CH-1/2^s), 1.78 (s, $CH_3{}^s$), 1.30 (d, CH_3-1/2^s); 0.84 (d, CH_3-1/2^b)/6.90 (d, *meta*-Ph-1/2^b), 2.94 (p, CH-1/2^b), 1.75 (s, $CH_3{}^b$), 1.05 (d, CH_3-1/2^b). ^{13}C NMR (125.7 MHz, [d_6]-benzene, 298 K): δ 182.04, 179.23 (carbonyl), 169.85, 168.62 (C=N), 147.74, 146.21, 145.55, 144.16, 143.87, 143.77, 138.97, 138.92, 135.79, 134.86, 127.69, 127.57, 127.26, 127.03, 125.64, 125.16, 124.55, 124.15, 123.63, 123.09 (imine, ph-C), 118.58, 118.35 (*ortho*-Bn), 103.06, 102.17 (*ortho*-Bn), 37.54, 35.90 (^{i}Pr-CH), 29.90, 29.87, 29.34, 29.18, 26.02, 25.68, 24.49, 24.33, 23.94, 23.75(^{i}Pr-CH_3), 24.36, 24.22 (CH_2−Ph), 19.89, 19.32 (CH_3). Anal. Calcd for $C_{34}H_{44}N_2ONi$: C, 73.52; H, 7.98; N, 5.04. Found: C, 73.38; H, 7.90; N, 5.02.

Typical Reaction with Ethylene. An autoclave reactor was loaded inside a glovebox with an α-iminocarboxamide complex (10 μmol) and $Ni(COD)_2$ (25 μmol) and toluene, such that the final volume of the toluene solution was 30 mL. The reactor was sealed inside the glovebox. The reactor was attached to an ethylene line, and the gas was fed continuously into the reactor at a specific pressure. The pressurized reaction mixture was stirred at a temperature controlled by an external water bath. 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.

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Supporting Information Available: Additional polymerization reaction results, summary of NOSEY ^{1}H NMR spectroscopy results for compound **7**, and the complete details for crystallographic studies of **4**^{o}, **4**^{r}, **5**, **6**, and **7**.

OM050640G