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Triazolecarboxamidate Donors as Supporting Ligands for Nickel **Olefin Polymerization Catalysts**

Dawei Xiao and Loi H. Do*

Department of Chemistry, University of Houston, 4800 Calhoun Road, Houston, Texas 77004, United States

Supporting Information

ABSTRACT: To increase the structural diversity of dinucleating platforms that are used in the construction of olefin polymerization catalysts, we are exploring new ligand designs that feature non-alkoxide/phenoxide bridging groups. In the current study, we demonstrate that 1,2,3-triazole-4-carboxamidate donors are excellent N,N-chelators for nickel and can readily bind secondary metal ions. We found that sterically bulky nickel triazolecarboxamidate complexes are active as ethylene homopolymerization catalysts and can afford low molecular weight polyethylene with about 80-130 branches per 1000 carbon atoms. The addition of zinc salts to our nickel complexes led to catalyst inhibition in



some cases, which we have attributed to the formation of catalytically inactive mixed-metal species. To circumvent this problem, we anticipate that further elaboration of the triazolecarboxamidate ligand could provide discrete heterobimetallic complexes that will be useful as single-site catalysts with unique reactivity patterns.

■ INTRODUCTION

One of the major advantages of coordination-insertion over other olefin polymerization processes is that it provides precise control over the continuous enchainment of olefin monomers.¹⁻⁴ Nickel and palladium complexes that promote coordination-insertion catalysis have even been shown to copolymerize ethylene and polar vinyl olefins such as acrylic acid, acrylic ester, acrylamide, and vinyl halide.^{5–8} Despite their broader olefin substrate scope compared to early transition metal complexes, late transition metal complexes are still far too slow in the copolymerization of ethylene and polar monomers to be practical for commercial polymer synthesis. Their poor performance is believed to be due to the preferential σ coordination of heteroatoms to the metal catalyst and the tendency to form metallacyclic intermediates upon polar monomer insertion. It has been suggested that these problems could be circumvented by using bimetallic catalysts that take advantage of metal-metal cooperativity. $^{9-11}$ As shown in Scheme 1A, it is proposed that the binding of monomers such as methyl acrylate to a bimetallic complex would engage both metal centers to yield a metal- π -olefin adduct at the active site (1). Upon olefin insertion, the resulting chelated species 2 could then convert to an open structure 3, which is poised to accept additional olefins and facilitate more rapid chain growth compared to 2. This approach appears to be promising based on work reported by several research groups, including Takeuchi and Osakada^{10,11} and Agapie.⁹

A wide range of bimetallic motifs has been explored as olefin polymerization catalysts, including the use of both symmetric and asymmetric ligands (Chart 1).¹⁰⁻¹⁶ We favor the type II over the type III/IV dinucleating platforms because they give Scheme 1. (A) Proposed Reaction of Methyl Acrylate (MA) with Bimetallic Catalysts and (B) Our Motivation for the Study of Nickel Triazolecarboxamidate Complexes To **Prepare Heterobimetallic Catalysts**

A) Proposed M–M Cooperativity in Olefin Copolymerization



complexes with the shortest metal-metal bond distances, which may help to promote cooperative interactions between both metal centers. To access novel families of type II catalysts, we are focusing on new ligand frameworks that feature Nheterocyclic rather than alkoxide/phenoxide bridging do-nors.¹⁷⁻¹⁹ Expanding the diversity of dinucleating ligands

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Chart 1. Depiction of (A) Common Bimetallic Structural Motifs and (B) Examples of Bimetallic Olefin Polymerization Catalysts Reported in the Literature

A) Common Bimetallic Structural Motifs



available to assemble bimetallic structures provides us with the opportunity to fine-tune various catalyst design parameters such as metal—metal bond distance, metal geometry, and electronic environment. In the following report, we demonstrate for the first time that 1,2,3-triazole-4-carboxamidate can be metalated with nickel to yield discrete mononuclear species that are active as catalysts for ethylene homopolymerization. We also show that the nickel triazolecarboxamidate complexes can coordinate to external zinc ions in solution, suggesting that further elaboration of the triazolecarboxamidate framework might afford discrete type II complexes. We anticipate that the introduction of secondary metal ions to our nickel catalysts could significantly enhance their polymerization rates as well as provide access to unique reactivity patterns.

RESULTS AND DISCUSSION

Nickel Triazolecarboxamidate Catalyst Design. Because most type II ligands used to prepare olefin polymerization catalyst have either anionic alkoxide or phenoxide bridges (Chart 1B), we sought to explore other donor groups such as N-heterocycles that are electronically and geometrically distinct.^{20,21} The 1,2,3-triazole-4-carboxamidate group²² is an attractive ligand because it can adopt multiple coordination modes and has the potential to accommodate more than one metal ions (Scheme 1B). Furthermore, because the triazole ring can be assembled using click chemistry,²³ accessing the triazolecarboxamidate scaffold should be synthetically straightforward.

Compounds 2a-2c were prepared starting from the coppercatalyzed cycloaddition reaction between benzyl azide and propiolic acid to give compound 1 (Scheme 2).²⁴ Activation of 1 using PCl₅, followed by the addition of an arylamine, yielded 2 in high purity after a simple workup procedure. We synthesized three ligand variants that differ in their N_{amide} -aryl substituents, including 2,6-bis(isopropyl)phenyl (2a), 2,6bis(3,5-bis(trifluoromethyl)phenyl) (2b),²⁵ and 8-pheScheme 2. Synthesis of Triazolecarboxamide Ligands 2 and Their Corresponding Nickel Complexes 3



nylnaphthyl (2c).^{26,27} To obtain the corresponding nickel complexes 3a-3c, ligand 2 was deprotonated by the addition of sodium hexamethyldisilazane (NaHMDS) and then reacted with Ni(Br)(Ph)(PPh₃)2²⁸ to afford the desired products as yellow solids in moderate yields (55–68%).

To elucidate the structure of $Ni(2a)(Ph)(PPh_3)$ (3a), we analyzed its single crystal by X-ray crystallography. As shown in Figure 1, complex 3a adopts a square planar arrangement, in



Figure 1. X-ray crystal structure of Ni(2a)(Ph)(PPh₃) (3a, ORTEP view, displacement ellipsoids drawn at 50% probably level). Hydrogen atoms and solvent molecules have been omitted for clarity. Bond lengths (Å): Ni(1)–N(1) = 1.973(3), Ni(1)–N(2) = 1.930(3), Ni(1)–C(22) = 1.891(4), and Ni(1)–P(1) = 2.165(1). Bond angles (deg): N(1)–Ni(1)–C(22) = 94.48(13), C(22)–Ni(1)–P(1) = 86.91(11), P(1)–Ni(1)–N(2) = 95.91(9), and N(1)–Ni(1)–N(2) = 82.60(12).

which the nickel center is ligated by the carbon donor of the phenyl group (Ni–C = 1.89 Å), the phosphorus donor of triphenylphosphine (Ni–P = 2.16 Å), and the *N*,*N* donors of the triazolecarboxamidate ligand (Ni–N_{amide} = 1.97 Å, Ni–N_{triazole} = 1.93 Å). Similar to the structures of related nickel complexes,²⁹ the phosphine group is coordinated *trans* relative to the anionic carboxamidate moiety. The β -nitrogen atom of

the triazole ring is sterically unhindered and should be capable of binding external metal ions.^{30–32} We did not observe the formation of any 1,3-N,O-carboxamidate³³ or 1,4-N,O-triazole-carboxamidate³⁴ coordination isomers (Chart S1).

Secondary Metal Ion Binding. Given the propensity of triazole donors to coordinate to transition metal ions,³⁵ we expected that our nickel triazolecarboxamidate complexes would have a high affinity for zinc. When $Zn(SO_3CF_3)_2$ was combined with either **3a** or **3c** in the noncoordinating solvent CDCl₃, however, the zinc salt did not dissolve. In fact, the ¹H NMR spectra of **3a** (Figure S25) and **3c** (Figure S26) remained unchanged after the addition of up to 5 equiv of zinc. In contrast, when **3b** was mixed with up to 10 equiv of $Zn(SO_3CF_3)_2$ in CDCl₃ (Figure 2), the **3b**/Zn²⁺ mixtures



Figure 2. (A) Reaction of complex 3b with $Zn(SO_3CF_3)_2$. (B) ¹H NMR spectra (CDCl₃, 600 MHz) of 3b with various equivalents of zinc salt. A tentative structure of the nickel–zinc complex is proposed. The disappearance of the triazole hydrogen at 7.63 ppm has been attributed to peak broadening rather than loss of the hydrogen atom.

were completely homogeneous and showed clear changes in their ¹H NMR spectra. For example, the singlet at 7.63 ppm, which has been assigned to the hydrogen atom of the triazole ring, broadened upon successive addition of Zn^{2+} ions and became nearly undetectable in the presence of 10 equiv of external salt. The peaks at 7.90 and 8.08 ppm, which correspond to resonances from the hydrogen atoms of the 2,6-bis(trifluoromethyl)phenyl rings, also showed significant broadening in the presence of zinc. These spectral changes suggest that there are dynamic processes occurring in solution, perhaps due to the interconversion between multiple nickelzinc clusters or oligomers on the NMR time scale. The primary coordination sphere of the nickel center is unaffected by zinc binding based on the ³¹P NMR data, which showed only a single peak at 31.3 ppm assigned to the nickel-bound triphenylphosphine ligand. When the $3b/Zn^{2+}$ mixture (1:5) was treated with excess 12-crown-4 ether to remove zinc, further changes in the ¹H NMR spectra were observed (Figure 2B, bottom trace). However, this spectrum did not match that of 3b (top trace), suggesting that 12-crown-4-ether cannot reverse zinc binding. Similar results were obtained when NMR studies were performed using 3b and $ZnCl_2$ (Figure S24).

Although we could not obtain single crystals of the $3b/Zn^{2+}$ species for X-ray structural analysis, further spectroscopic studies were performed to interrogate the binding of zinc to 3b. We hypothesize that the most likely sites for Zn²⁺ complexation are either the β -triazole nitrogen or carbonyl oxygen donors (Chart S2). We cannot determine at this time the nuclearity of the nickel-zinc species in solution. When the infrared (IR) spectrum of solid 3b was measured, a prominent $\nu_{C=0}$ stretch was observed at 1600 cm⁻¹, which was shifted by ~ 68 cm⁻¹ lower in frequency compared to that of the free ligand 2b (Figure S27). Upon the addition of 1-10 equiv of Zn- $(SO_3CF_3)_2$ to **3b**, the signal centered at 1600 cm⁻¹ appeared to split into multiple peaks. Based on a report on the study of nickel tetraazamacrocycle complexes, the $\nu_{C=0}$ frequency is expected to undergo a bathochromic shift of about 60 cm⁻¹ upon coordination of ZnCl₂ to the diketo moiety.³⁶ Because the IR features at $\sim 1600 \text{ cm}^{-1}$ are still observed in the presence of excess zinc salt, we speculate that Zn²⁺ binding to the carbonyl group of 3b is either weak (i.e., exchanges with solvent in solution) or does not occur. Thus, we propose that the β triazole nitrogen donor is the preferred site of coordination, although further investigations are needed to fully elucidate the structure of this nickel-zinc adduct.

Ethylene Polymerization with Ni. Next, compounds 3a-3c were tested as possible catalysts for ethylene homopolymerization (Table 1). The nickel complexes were dissolved in 5 mL of toluene, treated with 2 equiv of the activator $Ni(COD)_2$ (COD = 1,5-cyclooctadiene), and then stirred under 100 psi of ethylene at room temperature (RT) for 1 h (entries 2, 5, and 7). Analysis of the reaction products revealed that 3a-3cafforded polyethylene (PE) with different morphologies. Both 3a and 3b gave polymers with \sim 100 branches per 1000 carbon atoms. The presence of sec-butyl groups in their ¹³C NMR spectra (Figure 3A,B) indicated that they have hyperbranched microstructures.³⁷ Complex 3c, on the other hand, yielded polymers with 86 branches per 1000 carbon atoms and showed no detectable hyperbranching (Figure 3C). The tendency of nickel catalysts to furnish branched polyethylene is typically attributed to facile chain-walking processes and has been well documented.^{38,39} In terms of their polymer molecular weights, **3a** and **3c** afforded PE with greater M_n (4.47 × 10³ and 3.15 × 10³, respectively) than 3b (0.55 \times 10³). This result was surprising because the 2,6-bis(3,5-bis(trifluoromethyl)phenyl)phenyl substituent in 3b is more sterically encumbered than the 2,6-bis(isopropyl)phenyl substituent in 3a, which usually gives rise to PEs with higher M_n in conventional catalyst systems.^{40,41}

The PEs from **3a** and **3b** display relatively narrow polydispersities, yielding M_w/M_n values ranging from about 1.1 to 2.5. In contrast, the gel permeation chromatogram (GPC) of PE from **3c** $(M_w/M_n = 3.2-3.8)$ is bimodal (Figure S30). Although we have not yet identified the reason for this bimodal distribution, it is possible that the activated **3c** complex

| Table 1. Ethylene Polymeri | zation Data for 3a–3c" |
|----------------------------|------------------------|
|----------------------------|------------------------|

| entry | cat. | time (h) | polymer yield (mg) | TOF ($\times 10^3$ g/mol·h) | branches ^b (/1000 C) | $C_1\%$ | $C_2\%$ | $C_3\%$ | $C_{4+}\%$ | M_{n}^{c} (×10 ³) | $M_{\rm w}/M_{\rm n}^{\ c}$ |
|-------|------|----------|--------------------|------------------------------|---------------------------------|---------|---------|---------|------------|---------------------------------|-----------------------------|
| 1 | 3a | 0.5 | 138 | 11.0 | 102 | 68 | 6 | 4 | 22 | 5.81 | 2.0 |
| 2 | 3a | 1 | 266 | 10.6 | 99 | 69 | 6 | 3 | 22 | 4.47 | 2.5 |
| 3 | 3a | 2 | 464 | 9.3 | 113 | 67 | 7 | 4 | 22 | 4.11 | 2.2 |
| 4 | 3a | 3 | 497 | 6.6 | 108 | 67 | 6 | 3 | 24 | 6.16 | 1.6 |
| 5 | 3b | 1 | 158 | 6.3 | 103 | 78 | 5 | 2 | 15 | 0.55 | 1.5 |
| 6 | 3b | 3 | 276 | 3.7 | 127 | 72 | 6 | 3 | 19 | 0.46 | 1.1 |
| 7 | 3c | 1 | 49 | 2.0 | 86 | 69 | 5 | 4 | 22 | 3.15 | 3.8 ^d |
| 8 | 3c | 3 | 125 | 1.7 | 77 | 84 | 3 | 0 | 13 | 7.01 | 3.2 ^d |

^{*a*}Polymerization conditions: nickel precatalyst (25 μ mol), Ni(COD)₂ (50 μ mol), ethylene (100 psi), 5 mL of toluene, 1 h at RT. ^{*b*}The total number of branches per 1000 carbons was determined by ¹H NMR spectroscopy. ^{*c*}Determined by GPC in trichlorobenzene at 150 °C. ^{*d*}GPC trace shows two overlapping peaks, suggesting that there are two active catalyst species.



Figure 3. Representative examples of quantitative ¹³C NMR spectra (TCE- d_2 , 125 MHz, 120 °C) of polymers obtained from the reaction of ethylene/Ni(COD)₂ with catalysts (A) 3a, (B) 3b, and (C) 3c. The peak assignments were based on ref 37.

Table 2. Homopolymerization Data for 3a-3c with $Zn(SO_3CF_3)_2^a$

| entry | cat. | Zn ²⁺ (equiv) | polymer yield (mg) | TOF ($\times 10^3$ g/mol·h) | branches ^b (/1000 C) | C_1 % | $C_2\%$ | $C_{3}\%$ | $C_{4+}\%$ | $M_{\rm n}^{\ c}~(\times 10^3)$ | $M_{\rm w}/M_{\rm n}^{\ c}$ |
|-------|------|--------------------------|--------------------|------------------------------|---------------------------------|---------|---------|-----------|------------|---------------------------------|-----------------------------|
| 1 | 3a | 0 | 203 | 8.1 | 101 | 79 | 7 | 3 | 11 | 4.82 | 2.3 |
| 2 | 3a | 1 | 180 | 7.2 | 113 | 67 | 9 | 6 | 18 | 0.95 | 2.0 |
| 3 | 3a | 5 | 222 | 8.9 | 104 | 75 | 6 | 3 | 16 | 0.52 | 1.9 |
| 4 | 3b | 0 | 157 | 6.3 | 131 | 80 | 5 | 2 | 13 | 0.32 | 1.7 |
| 5 | 3b | 1 | 22 | 0.9 | | | | | | | |
| 6 | 3b | 5 | 4 | 0.2 | | | | | | | |
| 7 | 3c | 0 | 51 | 2.0 | | | | | | 3.06 | 4.1 ^d |
| 8 | 3c | 1 | 55 | 2.2 | | | | | | 3.14 | 3.4 ^d |
| 9 | 3c | 5 | 79 | 3.1 | | | | | | 1.81 | 3.4 ^d |

^{*a*}Polymerization conditions: nickel precatalyst (25 μ mol), Ni(COD)₂ (50 μ mol), Zn(SO₃CF₃)₂ (various), ethylene (100 psi), 5 mL toluene, 1 mL THF, 1 h at RT. ^{*b*}The total number of branches per 1000 carbons was determined by ¹H NMR spectroscopy. ^{*c*}Determined by GPC in trichlorobenzene at 140 °C. ^{*d*}GPC trace shows two overlapping peaks, suggesting that there are two active catalyst species.

can undergo coordination isomerization to generate multiple catalytically active constitutional isomers during catalysis.

The polymerization data showed that the activity of our nickel complexes decreased in the order 3a > 3b > 3c. Their turnover frequencies (TOFs) are approximately 10.6×10^3 , 6.3×10^3 , and 2.0×10^3 g/mol Ni·h for 3a, 3b, and 3c, respectively (Table 1). It has been shown that Pd diimine complexes featuring 8-phenylnaphthyl groups exhibit reduced catalyst

activity in favor of higher molecular weight polymers compared to those with 2,6-bis(isopropyl)phenyl groups.⁴¹ In our case, however, both the TOF and M_n decreased for 3c compared to 3a (Table 1, cf. entry 2 vs 7). On the basis of their catalytic performance, 3a-3c are considerably less active than conventional nickel phenoxyimine (TOF = $\sim 0.1-6 \times 10^6$ g/mol Ni·h)⁴² and nickel diimine (TOF = $\sim 0.8-11 \times 10^6$ g/mol Ni·h)⁴³ catalysts, although the direct comparison of TOFs in some

cases are not possible because the data reported were obtained under different polymerization conditions. Despite the moderate activity of the nickel triazolecarboxamidate complexes, we anticipate that further molecular optimization in future studies might furnish more robust catalysts.

To evaluate the stability of the nickel catalysts, polymerization studies were conducted from 0.5 to 3 h (Table 1, entries 1-8). For all three catalysts 3a-3c, there was a gradual decrease in the TOF values with increasing reaction time, which suggests that the catalysts undergo slow decomposition over time.⁴⁴ Complex 3c appeared to be the most stable, showing ~85% activity after 3 h compared to that at 1 h. Since the polymer morphology and M_n do not change as a function of polymerization time, 3a-3c are nonliving catalysts.

Ethylene Polymerization with Ni/Zn. To study the effects of external cations on ethylene polymerization, we carried out reactions under 100 psi of ethylene using 3/ $Ni(COD)_2$ (1:2) and various equivalents of $Zn(SO_3CF_3)_2$ salts (Table 2) in toluene/THF (5:1). The use of THF cosolvent enhances the solubility of the zinc salt in the reaction mixture. For catalysts 3a and 3c, the addition of Zn^{2+} did not significantly change their TOFs or PE branching microstructures compared to that in the absence of Zn²⁺ (entries 1-3 and 7-9). However, their polymer molecular weights decreased with increasing amounts of $Zn(SO_3CF_3)_2$ added. Because our metal titration studies showed that 3a and 3c do not form adducts with zinc salts (Figures S25 and S26), it is not surprising that their catalytic properties are largely unaffected by the presence of Zn^{2+} . We believe that the reduction in M_n observed is due to the zinc cation acting as a chain transfer agent.³ Interestingly, when similar studies were conducted using 3b/Ni(COD)₂/ethylene, the presence of added Zn- $(SO_3CF_3)_2$ led to significant catalyst inhibition. For example, combining 10 equiv of Zn²⁺ with 3b led to about a 30-fold decrease in TOF (cf. entry 4 vs 6). Since our NMR studies showed that the nickel center of **3b** is preserved in the presence of zinc, we propose that the most likely cause of catalyst deactivation is the self-assembly of inactive higher nuclearity structures (Chart S2). These results suggest that the use of dinucleating ligands that provide well-defined nickel-zinc species is necessary to form active olefin polymerization catalysts.

CONCLUSIONS

Toward our ultimate goal of creating cooperative bimetallic catalysts for olefin polymerization, we sought to design new type II dinucleating ligands that feature non-oxygen bridging donors. Although the 1,2,3-triazole-4-carboxamidate unit has largely been overlooked in coordination chemistry, we have demonstrated that it serves as an excellent anionic N,N-chelator for nickel. We successfully synthesized a new family of nickel triazolecarboxamidate complexes that have sterically bulky Ncarboxamidate substituents. Upon activation by treatment with $Ni(COD)_{2}$, the nickel complexes are active as catalysts for ethylene polymerization. Analysis of the polymer products revealed that their morphologies are highly dependent on the structures of the nickel catalysts. Interestingly, we showed that complex 3b binds readily to external zinc ions, most likely via coordination by the basic β -nitrogen of its triazole ring. We propose that further modification of the 1,2,3-triazole-4carboxamidate framework, such as attachment of a second metal binding moiety at the γ position of the triazole unit, would enable the construction of structurally stable bimetallic

complexes. Future work will explore the feasibly of this approach and test further the homo- and copolymerization behavior of this new class of nickel triazolecarboxamidate catalysts.

EXPERIMENTAL SECTION

General Procedures. Commercial reagents were used as received. All air- and water-sensitive manipulations were performed using standard Schlenk techniques or under a nitrogen atmosphere using a glovebox. Anhydrous solvents were obtained from an Innovative Technology solvent drying system saturated with argon. High-purity polymer-grade ethylene was obtained from Matheson TriGas without further purification. The precursor Ni(Br)(Ph)(PPh₃)₂ was prepared according to a literature procedure.²⁸ The syntheses of compound **1** and ligands **2a**-**2c** are provided in the Supporting Information.

Characterization Methods. Elemental analyses were performed by Atlantic Microlab. Trace levels of solvents in elemental analysis samples were quantified by ¹H NMR spectroscopy. NMR spectra were acquired using JEOL spectrometers (ECA-400, -500, and -600) and referenced using residual solvent peaks. ¹⁹F NMR spectra were referenced to CFCl₃, whereas ³¹P NMR spectra were referenced to phosphoric acid. IR spectra were measured using a Thermo Nicolet Avatar FT-IR spectrometer with diamond ATR. High-resolution mass spectra were obtained from the mass spectral facility at the University of Texas at Austin.

Preparation of Complex 3a. Inside the glovebox, a solution containing 2a (50 mg, 0.14 mmol, 1.0 equiv) and NaHMDS (38 mg, 0.21 mmol, 1.5 equiv) in 10 mL of CH_2Cl_2 was stirred for 2 h at RT. Solid Ni(Br)(Ph)(PPh₃)₂ (102 mg, 0.14 mmol, 1.0 equiv) was added in small portions. The reaction mixture was stirred for an additional 3 h. The resulting red mixture was filtered through a pipet plug and then dried under vacuum to give a dark red oil. Upon the addition of pentane and after being stirred for \sim 5 min, a yellow solid formed. The product was recrystallized by dissolving in CH2Cl2 and then layered with pentane to afford the final product as yellow crystals (72 mg, 0.09 mmol, 68%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 7.68 (s, 1H), 7.45 (t, $J_{\rm HH}$ = 9.2 Hz, 6H), 7.34 (m, 6H), 7.22 (m, 6H), 6.90 (d, $J_{\rm HH}$ = 7.0 Hz, 2H), 6.84 (t, $J_{\rm HH}$ = 7.4 Hz, 1H), 6.76 (d, $J_{\rm HH}$ = 7.4 Hz, 2H), 6.58 (d, J_{HH} = 7.3 Hz, 2H), 6.24 (t, J_{HH} = 6.9 Hz, 1H), 6.12 (d, J_{HH} = 7.1 Hz, 2H), 5.0 (s, 2H), 3.69 (m, 2H), 1.14 (dd, J_{HH} = 34.7 Hz, J_{HH} = 6.4 Hz, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 163.92, 149.88, 149.42, 148.83, 143.62, 142.73, 135.61 (d, $J_{CP} = 2.7$ Hz), 134.32 (d, $J_{\rm CP}$ = 10.7 Hz), 133.04, 131.58 (d, $J_{\rm CP}$ = 45.4 Hz), 129.89, 129.22, 128.46, 127.89 (d, $J_{\rm CP}$ = 10.0 Hz), 125.18, 124.15, 122.28, 121.84, 121.10, 55.27, 29.10, 25.42, 23.28. ³¹P NMR (CDCl₃, 161 MHz): δ (ppm) = 30.03. UV-vis (DCM): $\lambda_{max}/nm (\epsilon/cm^{-1} M^{-1}) =$ 332 (3906), 415 (516). FT-IR: 3056 ($\nu_{\rm NH}$), 1606 ($\nu_{\rm CO}$) cm⁻¹. Mp (decomp.) = ~166 °C. Anal. Calcd for $C_{46}H_{45}N_4NiOP \cdot (CH_2Cl_2)_{0.35}$: C, 70.53; H, 5.84; N, 7.10. Found: C, 70.61; H, 5.97; N, 7.30.

Preparation of Complex 3b. A similar procedure was used as described for 3a. Instead of 2a, ligand 2b (100 mg, 0.14 mmol, 1.0 equiv) was used. Complex 3b was obtained as a yellow solid (89.4 mg, 0.08 mmol, 58%). ¹H NMR (CDCl₃, 500 MHz): δ (ppm) = 8.09 (s, 4H), 7.91 (s, 2H), 7.64 (s, 1H), 7.30 (m, 5H), 7.06 (m, 16H), 6.73 (d, $J_{\rm HH} = 6.9$ Hz, 2H), 6.29 (t, $J_{\rm HH} = 7.0$ Hz, 1H), 6.18 (d, $J_{\rm HH} = 7.0$ Hz, 2H), 6.14 (t, $J_{\rm HH} = 7.6$ Hz, 2H), 4.94 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 166.14, 149.62, 149.16, 147.41, 144.17, 143.67, 137.01, 135.21 (d, $J_{\rm CP} = 1.6$ Hz), 133.93 (d, $J_{\rm CP} = 10.7$ Hz), 132.95, 131.07, 130.59, 130.53, 130.48 (q, $J_{\rm CF} = 32.7$ Hz), 130.39, 129.98, 129.14, 127.82 (d, $J_{\rm CP} = 10.8$ Hz), 125.43, 124.80, 123.84 (q, $J_{\rm CF} = 272.0$ Hz), 122.53, 121.43, 120.07, 552.1. ³¹P NMR (CDCl₃, 16 MHz): δ (ppm) = 31.30. ¹⁹F NMR (CDCl₃, 376 MHz): δ (ppm) = -62.34. UV-vis (DCM): $\lambda_{\rm max}/nm (ε/cm^{-1} M^{-1}) = 331 (4093), 410 (574).$ FT-IR: 3083 ($\nu_{\rm NH}$), 1600 ($\nu_{\rm CO}$) cm⁻¹. Mp (decomp.) = ~225 °C. Anal. Calcd for C₅₆H₃₇F₁₂N₄NiOP·(C₅H₁₂)_{0.2}(CH₂Cl₂)_{1.15}: C, 57.64; H, 3.47; N, 4.62. Found: C, 57.52; H, 3.73; N, 4.89.

Preparation of Complex 3c. A similar procedure was used as described above for **3a**. Instead of **2a**, ligand **2c** (50 mg, 0.12 mmol, 1.0 equiv) was used. Complex **3c** was obtained as a yellow solid (53

mg, 0.07 mmol, 55%). ¹H NMR (CDCl₃, 500 MHz): δ (ppm) = 8.28 (s, 1H), 7.5 (m, 2H), 7.35 (m, 13H), 7.18 (m, 9H), 7.03 (m, 3H), 6.92 (d, J_{HH} = 6.8 Hz, 2H), 6.73 (t, J_{HH} = 7.4 Hz, 1H), 6.48 (t, J_{HH} = 7.2 Hz, 1H), 6.37 (m, 2H), 5.86 (s, 2H), 5.56 (s, 1H), 4.85 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 163.08, 151.69, 151.22, 149.28, 146.78, 144.50, 139.76, 136.35, 135.56, 135.12, 134.37 (d, J_{CP} = 10.8 Hz), 133.65, 131.70 (d, J_{CP} = 45.6 Hz), 130.19, 129.73, 129.23, 129.11, 129.00, 128.61, 128.22, 127.87, 127.70 (d, J_{CP} = 9.8 Hz), 127.58, 126.99, 126.54, 125.05, 124.64, 124.30, 124.06, 123.44, 123.20, 121.52, 120.46, 54.99. ³¹P NMR (CDCl₃, 161 MHz): δ (ppm) = 32.05. UV-vis (DCM): $\lambda_{\text{max}}/\text{nm}$ ($\varepsilon/\text{cm}^{-1}$ M⁻¹) = 327 (9717), 410 (867). FT-IR: 3049 (ν_{NH}), 1594 (ν_{CO}) cm⁻¹. Mp (decomp.) = ~195 °C. Anal. Calcd for C₅₀H₃₉N₄NiOP·(CH₂Cl₂)_{0.5}: C, 71.86; H, 4.78; N, 6.64. Found: C, 71.80; H, 4.77; N, 6.84.

Ethylene Polymerization. Inside the glovebox, the nickel catalyst $(25 \ \mu mol)$ was dissolved in 5 mL of toluene in a scintillation vial. Solid Ni(COD)₂ $(50 \ \mu mol)$ was added, and the solution was transferred to a Fischer–Porter glass vessel. A magnetic stir bar was placed inside, and then the reactor was sealed. The high-pressure apparatus was removed from the glovebox and then securely fastened on top of a stir plate. The ethylene line was attached, and the reactor was purged with ethylene three times by pressurizing with ethylene and then releasing the pressure. The reactor was then pressurized to 100 psi of ethylene and stirred at RT for a specified amount of time. The ethylene line was closed, and the vessel was slowly vented. About 1 mL of HCl(aq) was added, followed by the addition of 2 mL of MeOH. The aqueous layer was removed by pipetting, and the organic layer was evaporated to dryness under vacuum. The resulting material was washed with MeOH and CH₂Cl₂ and then dried under vacuum.

Polymer Characterization. ¹*H NMR Spectroscopy.* Each NMR sample contained ~10–20 wt % of polymer in 0.5 mL of 1,1,2,2-tetrachlorethane- d_2 (TCE- d_2) and was recorded at 500 MHz using standard acquisition parameters at 120 °C.

Quantitative ¹³C NMR Spectroscopy. Each NMR sample contained ~10-20 wt % of polymer and 50 mM chromium acetylacetonate $Cr(acac)_3$ in 0.5 mL of TCE- d_2 and was recorded at 125 MHz (120 °C). The samples were acquired using a 90° pulse of 11.7 μ s, a relaxation delay of 2.4 s, an acquisition time of 0.67 s, and inverse gated decoupling. The T_1 values of the carbon atoms were measured to be 0.7 s. The samples were preheated for 30 min prior to data acquisition. The carbon spectra were assigned based on the chemical shift values reported in the literature. The branch ratios were determined by dividing the integrated value for a type of branch end over the total number of branches and corrected for chain end groups.¹⁷

Gel Permeation Chromatography. GPC analyses were performed using a Malvern high-temperature GPC instrument equipped with refractive index, viscometer, and light scattering detectors. Polyethylene samples were prepared with a concentration of ~30 mg of polymer in 10 mL of solvent. The polymers were predissolved in 1,2,4trichlorobenzene (TCB) at 150 °C for at least 1 h before injection. The samples were acquired at 150 °C using TCB as the mobile phase. A calibration curve was established using polystyrene standards.

Zinc Binding Studies by NMR Spectroscopy. Complex 3b (5 mg) and $Zn(SO_3CF_3)_2$ (0–10 equiv relative to Ni) were combined with 0.5 mL of chloroform-*d*. The mixtures were sonicated until the zinc salt had dissolved, providing clear yellow solutions. These samples were then transferred to NMR tubes, and their ¹H NMR spectra were recorded. A drop of 12-crown-4 ether was added to the 1:5 Ni/Zn sample, mixed, and then measured by ¹H NMR spectroscopy to determine whether Zn binding is reversible. As a control, the addition of excess 12-crown-4 ether to 3b did not result in changes to the spectrum of the nickel complex.

Zinc Binding Studies by IR Spectroscopy. Complex 3b (5 mg) and $Zn(SO_3CF_3)_2$ (0–10 equiv relative to Ni) were combined in 5 mL of dichloromethane and stirred for 20 min until the solids had completely dissolved. The solvent was removed under vacuum, and the resulting solid was measured directly using attenuated total reflectance (ATR) IR spectroscopy.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00807.

Synthetic procedures, NMR spectra, and X-ray data (PDF)

Accession Codes

CCDC 1566241 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: loido@uh.edu.

ORCID [®]

Loi H. Do: 0000-0002-8859-141X

Notes

The authors declare no competing financial interest.

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