

Evidence for Ligand-Dependent Mechanistic Changes in Nickel-Catalyzed Chain-Growth Polymerizations

Erica L. Lanni and Anne J. McNeil*

Department of Chemistry and Macromolecular Science and Engineering Program, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109-1055

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ABSTRACT: The mechanisms for Ni(dppp)Cl₂-catalyzed chain-growth polymerization of 4-bromo-2,5-bis(hexyloxy)phenylmagnesium chloride and 5-bromo-4-hexylthiophen-2-ylmagnesium chloride were investigated. A combination of rate and spectroscopic studies revealed that transmetalation is the rate-determining step of the catalytic cycle for both monomers. ³¹P NMR spectroscopic studies revealed that a Ni(II)–aryl halide and a Ni(II)–thienyl halide are the catalyst resting states. In addition, LiCl was found to alter the arene polymerization rates. These results are different than those previously obtained with an alternative catalyst (Ni(dppe)Cl₂) and suggest that the ligand has a strong mechanistic influence on the polymerization.

Introduction

Organic π -conjugated polymers are promising materials for thin-film solar cells,¹ light-emitting diodes,² and transistors³ because they exhibit tunable optical and electrical properties and can be solution-processed onto large, flexible substrates. However, these materials have several limitations that prevent their widespread application. For example, homopolymers are the most synthetically accessible but often lack one or more properties that are necessary for device operation. To advance the field, synthetic methods that provide access to new polymers are needed. In 2004, Yokozawa⁴ and McCullough⁵ reported the first chain-growth synthesis of poly(3-hexylthiophene). This initial result garnered much interest^{6,7} because living, chain-growth methods can be used to synthesize polymers with sequence control⁸ and end-functionalization.⁹ However, efforts toward expanding the scope and utility of this method have been hindered by the highly monomer-specific reaction conditions necessary to achieve chain growth. As a result, even simple block copolymers have been difficult to synthesize.¹⁰ To develop a general synthetic method, a mechanistic understanding of the role of monomer, ligand, and additives on the chain-growth pathway is needed.

Yokozawa^{4,11,12} and McCullough^{5,13,14} independently proposed a new mechanism to account for the unexpected chain-growth behavior wherein the key difference from conventional cross-coupling mechanisms is formation of a π -complex^{15,16} between the polymer chain and Ni⁰ following reductive elimination.¹⁷ Subsequent intramolecular oxidative addition leads to chain growth. Indirect evidence supporting this mechanism has been provided.¹⁸ Most significantly, MALDI-TOF MS data on polymer samples revealed end-groups consistent with the structure of the initiating and propagating species, which is characteristic of chain-growth polymerizations.¹¹ In addition, aryl and thienyl halides that can undergo competitive oxidative addition with Ni⁰ were shown to be unreactive during polymerization, consistent with Ni⁰–polymer π -complex formation and intramolecular oxidative addition.^{12b,18b} Nevertheless, the sensitivity of this synthetic method to changes in monomer, ligand, and additives suggests that the chain-growth mechanism is competing with other reaction pathways like chain transfer and termination.

As a result, a detailed mechanistic understanding of each reaction pathway will be necessary to guide the rational development of an improved synthetic method.

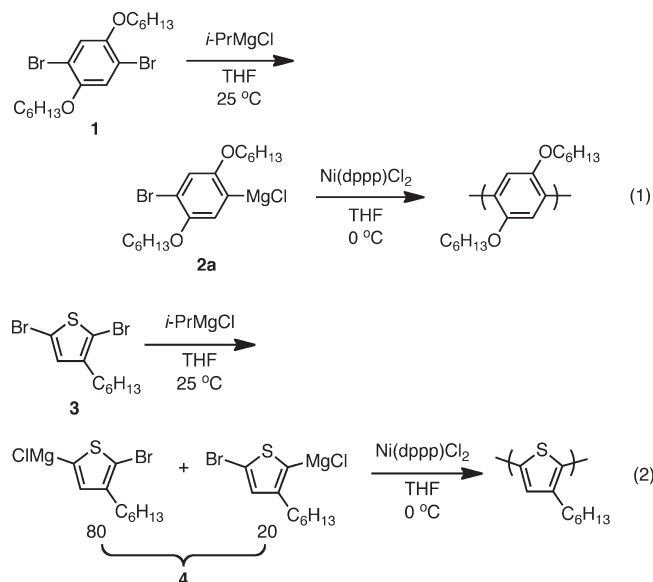
In 2009, we reported the influence of monomer structure and additives on the mechanism of Ni(dppe)Cl₂-catalyzed syntheses of poly(*p*-(2,5-bis(hexyloxy)phenylene) and poly(3-hexylthiophene).¹⁹ Rate and spectroscopic studies were consistent with rate-limiting reductive elimination for both monomers. Further studies showed that although LiCl forms a mixed aggregate with the arene monomer, the salt did not affect the propagation rate or mechanism. Because McCullough reported that an alternative catalyst (Ni(dppp)Cl₂) led to different rate behavior,^{10a,13} we anticipated that the ligand might be a key mechanistic determinant. In this report, we provide detailed rate and spectroscopic evidence for a ligand-dependent change in the rate-determining step. Specifically, we demonstrate that Ni(dppp)Cl₂-catalyzed syntheses of both poly(*p*-(2,5-bis(hexyloxy)phenylene) and poly(3-hexylthiophene) proceed through a rate-determining transmetalation. Moreover, we show that LiCl influences the reaction order in monomer and, consequently, the polymerization rate. Given the important mechanistic influence of ligand, these results suggest that modifying the ligand structure may lead to new catalysts that are effective for a broader range of monomers.

Results and Discussion

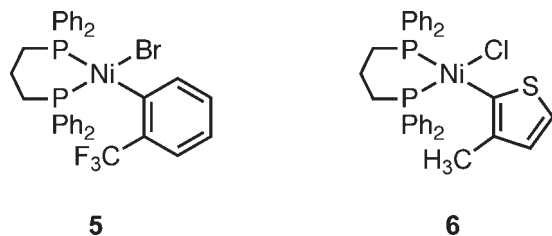
Rate Studies. Monomers **2a** and **4** were generated in situ from **1** and **3** via Grignard metathesis (GRIM) with *i*-PrMgCl (eqs 1 and 2).²⁰ Although **4** is an approximately 80:20 mixture of regioisomers, the minor regioisomer is not significantly consumed during polymerization (see Figure S18 in Supporting Information). To generate a soluble catalyst species, the Ni(dppp)Cl₂ was preinitiated with 5–7 equiv of monomer prior to starting the rate studies. Initial rates of polymerization were measured by in situ IR spectroscopy²¹ or GC analysis of aliquots at varying concentrations of monomer and catalyst (Supporting Information). For the Ni(dppp)Cl₂-catalyzed polymerization of both **2a** and **4**, an approximate first-order dependence of the initial rate on both [catalyst] and [monomer] was observed (Figures 1 and 2).²² These monomer reaction orders are different than those obtained with Ni(dppe)Cl₂,¹⁹ suggesting a ligand-dependent change in rate-determining step. Indeed, the rate data obtained with

*Corresponding author. E-mail: ajmcneil@umich.edu.

Ni(dppp)Cl_2 are consistent with either rate-determining transmetalation or intermolecular oxidative addition because both steps involve the monomer and catalyst. To distinguish between these two scenarios, in situ NMR spectroscopic studies were used to characterize the catalyst resting state during polymerization.



NMR Spectroscopic Studies. The polymerizations were followed by ^1H and ^{31}P NMR spectroscopy to identify the catalyst resting states. During the polymerization of both **2a** and **4**, two doublets with similar intensities were observed in each ^{31}P NMR spectrum (**2a**: $J_{\text{PP}} = 52$ Hz; **4**: $J_{\text{PP}} = 66$ Hz; Figure 3A,B). This result, coupled with the relatively large $\Delta\delta$, is consistent with complexes **II** and **V** as the polymerization resting states (Scheme 1). Because the catalytic cycle will stall at complexes **II** and **V** when the monomer is depleted, further support for this assignment was provided by the fact that the spectra remain unchanged even after the monomer was consumed (see Figures S26 and S28 in Supporting Information). However, the coupling constants for these dppp-based Ni^{II} complexes were significantly larger than those observed for the related dppe-based Ni^{II} complexes.¹⁹ Therefore, two model complexes (**5** and **6**) were synthesized and characterized by ^{31}P NMR spectroscopy. Complexes **5** and **6** exhibited similar chemical shifts and coupling constants to the polymerization resting states (**5**: $J_{\text{PP}} = 59$ Hz; **6**: $J_{\text{PP}} = 64$ Hz; see Figures S6 and S7 in Supporting Information), supporting these assignments. These resting states are different than those observed with Ni(dppe)Cl_2 ,¹⁹ consistent with a ligand-dependent change in rate-determining step. Overall, the observed first-order rate dependence on both [catalyst] and [monomer], and the identification of complexes **II** and **V** as the catalyst resting states, support transmetalation as the rate-determining step in the Ni(dppp)Cl_2 -catalyzed polymerization of **2a** and **4**.



Role of Ligand. The change in rate-determining step from reductive elimination (dppe) to transmetalation (dppp)

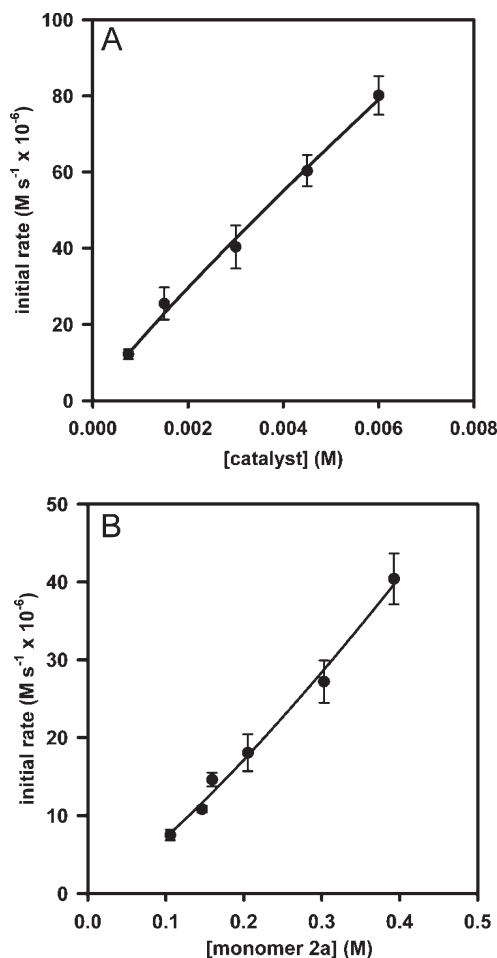


Figure 1. (A) Plot of initial rate versus [catalyst] for the polymerization of **2a** in THF at 0 °C ($[\text{2a}] = 0.20$ M). The curve depicts an unweighted least-squares fit to the expression $\text{initial rate} = a[\text{catalyst}]^n$ that gave $a = (8 \pm 2) \times 10^3$ and $n = 0.89 \pm 0.05$. (B) Plot of initial rate versus [monomer] for the polymerization of **2a** in THF at 0 °C ($[\text{Ni(dppp)Cl}_2] = 0.0015$ M). The curve depicts an unweighted least-squares fit to the expression $\text{initial rate} = a[\text{monomer}]^n$ that gave $a = (1.3 \pm 0.1) \times 10^2$ and $n = 1.24 \pm 0.07$.

points to a significant mechanistic role of the ligand in the polymerization. The principal differences between the two ligands are the bite angle, with dppp (91°) exhibiting a larger bite angle than dppe (85°), and the size of the chelate rings. As a result, differences in reactivity may be observed due to changes in the sterics, electronics, and geometry of the nickel complex. These ligand effects are well documented in the small-molecule cross-coupling literature.²³ For example, Yamamoto observed faster rates for reductive elimination from $(\text{P-P})\text{NiMe}_2$ when using dppp versus dppe.²⁴ Similarly, the chain-growth polymerizations are known to be highly sensitive to ligand structure.²⁵ However, the interpretation of these effects is often ambiguous because the elementary steps in the catalytic cycle can be affected differently by changes in the ligand. For example, in the Ni-catalyzed polymerizations reported herein, it is difficult to pinpoint the affect of ligand on either the rate of transmetalation or reductive elimination because the rate-determining step changes with the different ligands. Therefore, future studies are needed to elucidate the affect of ligand structure on the elementary steps of both the chain-growth and competing reaction pathways.

Role of LiCl. In our previous studies with Ni(dppe)Cl_2 , LiCl had no effect on the polymerization rate of **2** even

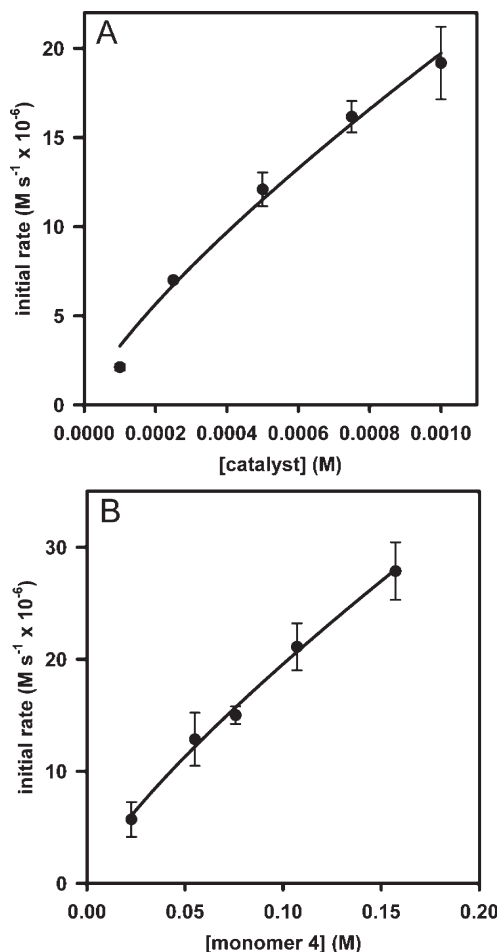


Figure 2. (A) Plot of initial rate versus [catalyst] for the polymerization of **4** in THF at 0 °C ([**4**] = 0.05 M). The curve depicts an unweighted least-squares fit to the expression $\text{initial rate} = a[\text{catalyst}]^n$ that gave $a = (4 \pm 2) \times 10^3$ and $n = 0.78 \pm 0.07$. (B) Plot of initial rate versus [monomer] for the polymerization of **4** in THF at 0 °C ([Ni(dppp)Cl₂] = 0.000 25 M). The curve depicts an unweighted least-squares fit to the expression $\text{initial rate} = a[\text{monomer}]^n$ that gave $a = (12 \pm 1) \times 10^1$ and $n = 0.79 \pm 0.04$.

though ¹H NMR spectroscopic studies revealed that LiCl aggregates with the monomer.¹⁹ These results are consistent with the observed rate-determining reductive elimination since the monomer is not involved in this step. In contrast, because transmetalation involves the monomer, a rate dependence on LiCl was anticipated in the Ni(dppp)Cl₂-catalyzed polymerization of **2b**. Indeed, rate studies in the presence of 1 equiv of LiCl revealed an approximate first-order dependence on [catalyst] and half-order dependence on [monomer] (eq 3 and Figure 4). Noninteger reaction orders are common for aggregated species, and a half-order dependence suggests a higher order aggregate (e.g., a mixed tetramer, (ArMgCl)₂(LiCl)₂). However, ¹H NMR spectroscopic studies provided evidence that multiple aggregates may be equilibrating in solution: the aromatic protons of monomer **2** shifted downfield with increasing either [**2b**] or [LiCl] (see Figures S31 and S32 in Supporting Information). Polymerization rate studies performed with excess LiCl revealed slower rates with higher [LiCl], consistent with [LiCl]-dependent changes in aggregate structure (see Figure S23 in Supporting Information). Because solution-based characterization techniques for Grignard reagents remain limited,^{26,27} no further insight into the structure of **2b** was obtained. One interesting consequence of the change in monomer reaction order is that

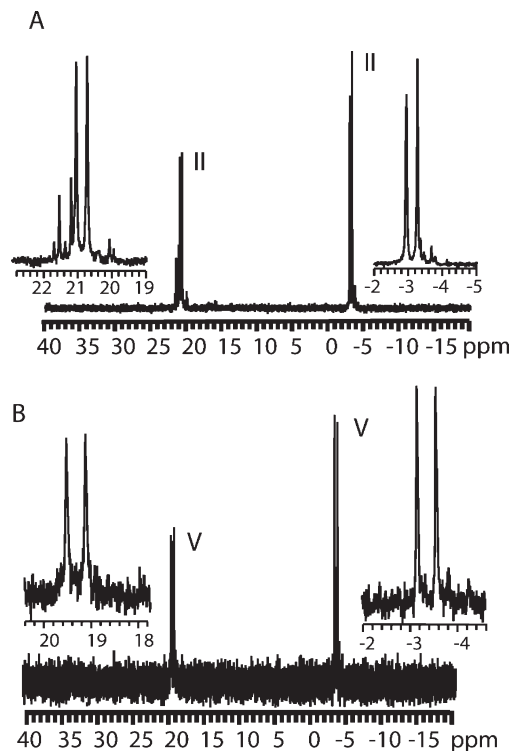
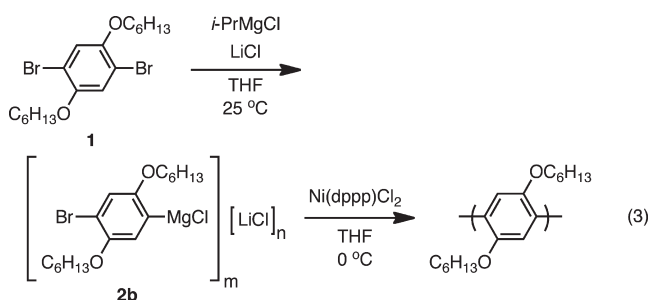


Figure 3. ³¹P NMR spectra for the resting state during polymerization of (A) **2a** and (B) **4**.

the rate effect of LiCl will depend on [monomer] (Figure 5). For example, the polymerization of **2b** will be faster than **2a** at low monomer concentrations (< 0.4 M) and slower at high monomer concentrations (> 0.4 M).



In contrast to data reported by Yokozawa,^{7c} plots of the M_n and PDI versus conversion revealed that adding 1 equiv of LiCl resulted in small changes to the M_n and PDI (see Table S1 in Supporting Information). We previously reported a similar result with Ni(dppe)Cl₂¹⁹ and ascribed this discrepancy to differences in catalyst preparation: Yokozawa used Ni(dppp)Cl₂ and Ni(dppe)Cl₂ as initiators, which are both insoluble in THF and must react with the monomer to enter the catalytic cycle. The relative rates of these heterogeneous initiation reactions²⁸ to propagation may depend on LiCl since it is aggregated with the monomer. We avoided this relative rate issue by preinitiating these insoluble complexes with 5–7 equiv of monomer before beginning the polymerizations.

Conclusion

Our finding that the rate-determining step changes from reductive elimination to transmetalation when the ligand is varied from dppe to dppp points to a strong mechanistic influence of the

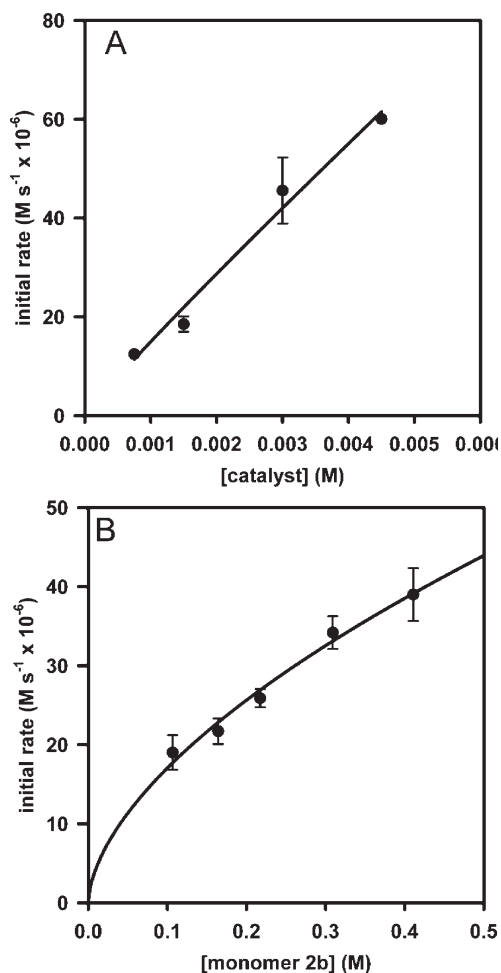


Figure 4. (A) Plot of initial rate versus [catalyst] for the polymerization of **2b** in THF at 0 °C ([**2b**] = 0.20 M). The curve depicts an unweighted least-squares fit to the expression $\text{initial rate} = a[\text{catalyst}]^n$ that gave $a = (1.0 \pm 0.7) \times 10^{-4}$ and $n = 0.9 \pm 0.1$. (B) Plot of initial rate versus [monomer] for the polymerization of **2b** in THF at 0 °C ([Ni(dppp)Cl₂] = 0.0015 M). The curve depicts an unweighted least-squares fit to the expression $\text{initial rate} = a[\text{monomer}]^n$ that gave $a = 66 \pm 4$ and $n = 0.59 \pm 0.05$.

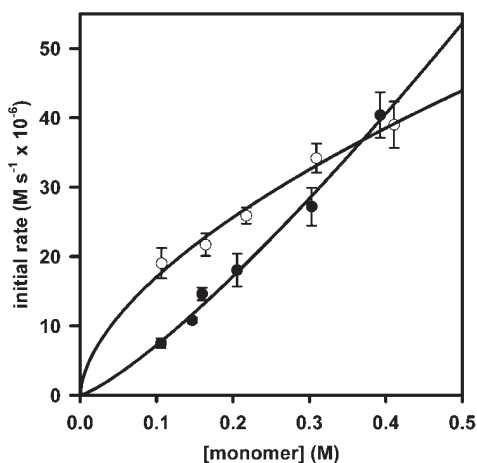
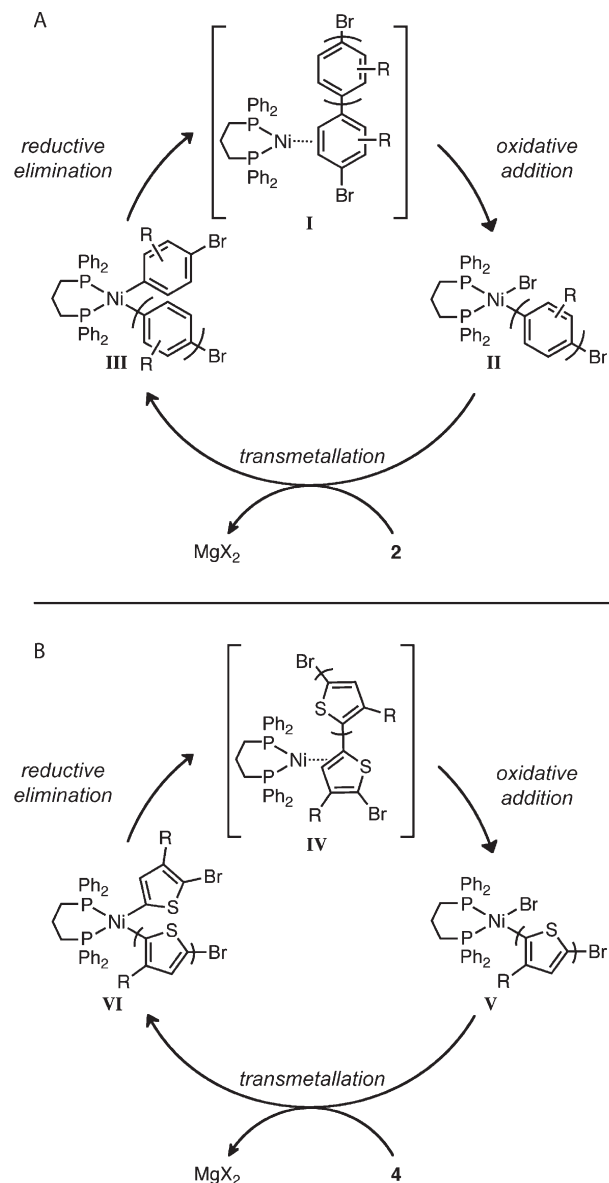


Figure 5. Plot of initial rate versus [monomer] for the polymerization of **2a** (●) and **2b** (○) in THF at 0 °C ([Ni(dppp)Cl₂] = 0.0015 M).

ligand on the polymerization. As a result, substantial improvements in the synthetic method may be possible through advances in ligand design. However, to rationally select new ligands, it will be necessary to understand the influence of ligand structure

Scheme 1. Proposed Mechanism for the Chain-Growth Polymerizations of (A) **2** and (B) **4**



on the rate-determining steps, the stability and reactivity of key intermediates—including the hypothesized Ni⁰-polymer π-complexes²⁹—and the competing reaction pathways. Future studies are aimed at addressing these issues.

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Supporting Information Available: Experimental details as well as rate and spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Note Added after ASAP Publication. This article posted ASAP on September 1, 2010. Structures 5 and 6 have been added which are located in the Results and Discussion section. The correct version posted on September 8, 2010.

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