

Evidence for a preferential intramolecular oxidative addition in Ni-catalyzed cross-coupling reactions and their impact on chain-growth polymerization†

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Small molecule competition experiments were performed to determine whether Ni-catalyzed Kumada cross-coupling reactions proceed through an intramolecular oxidative addition. Indeed, preferential intramolecular oxidative addition was observed for all four complexes when stoichiometric quantities of competitive agent were present. At higher concentrations of competitive agent, the intramolecular pathway was still preferred when bidentate, electron-rich ligands were utilized, suggesting that these ligands promote the formation and reactivity of the key intermediate. To determine whether a similar pathway is involved in the polymerizations, (4-bromo-2,5-bis(hexyloxy)phenyl)magnesium bromide was polymerized in the presence and absence of competitive agent. The number-average molecular weights were lower and the molecular weight distributions were broadened substantially when competitive agent was present, consistent with the presence of competing intermolecular pathways. Because bidentate, electron-rich ligands suppressed these undesired intermolecular reactions, these ligands should lead to improved polymerization catalysts.

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Introduction

Organic π -conjugated polymers are being investigated as the active components in many optoelectronic devices due to their ability to absorb/emit light and conduct charge.¹ These properties can be tuned for specific applications based on the polymer structure (*e.g.*, monomer identity, regioregularity, and copolymer sequence). A significant advance in the field of π -conjugated polymers occurred in 2004, when Yokozawa *et al.*² and McCullough *et al.*³ independently reported the first chain-growth method for synthesizing poly(3-hexylthiophene). This method has enabled many new materials to be prepared,⁴ including all-conjugated block⁵ and gradient copolymers,⁶ as well as surface-grafted⁷ and end-functionalized polymers.⁸ Synthesizing these polymers has been challenging, however, as it requires extensive screening of catalysts and reaction conditions for each new application. Moreover, for many monomers of interest, conditions for chain-growth homo- and copolymerization have not been found.

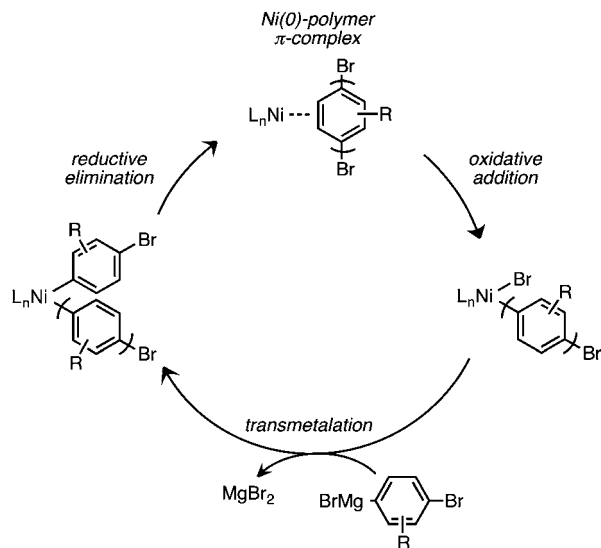
A more detailed understanding of what factors promote chain-growth polymerization over competing reaction pathways is needed to increase the utility of this method. To accomplish

this goal, the chain-growth mechanism must be elucidated. The conventional M(0)/M(II) mechanism for small molecule cross-coupling reactions does not account for the chain-growth behavior observed in the polymerizations. An alternative mechanism was therefore proposed^{2,3} wherein an associative complex forms between the Ni catalyst and the polymer chain after reductive elimination, facilitating an intramolecular oxidative addition. In principle, this associative complex could be an η^2 or η^6 Ni(0) π -complex which undergoes oxidative addition *via* a two-electron pathway, or a caged radical pair which undergoes oxidative addition through a one-electron pathway. Few definitive examples of the latter pathway exist,⁹ while many Ni(0)-arene π -complexes have been characterized¹⁰ and implicated in oxidative addition reactions.¹¹ As a consequence, we¹² and others have invoked a π -complex intermediate in the chain-growth polymerizations (Scheme 1). We further hypothesized that the formation and reactivity of the π -complex determines whether the chain-growth or undesired reaction pathways occur. Based on this hypothesis, we investigated the impact of electron-rich ligands in the polymerizations,¹³ which should both promote the formation of an associative Ni(0) π -complex¹⁴ and accelerate the intramolecular oxidative addition.¹⁵ Although this approach has led to an improved catalyst,¹³ it remains unclear whether these results were due to stabilizing the proposed π -complex or some other factor. Further studies on the formation of this intermediate, as well as the factors controlling its reactivity were warranted.

In related small molecule cross-coupling reactions, indirect evidence supporting an preferential intramolecular oxidative

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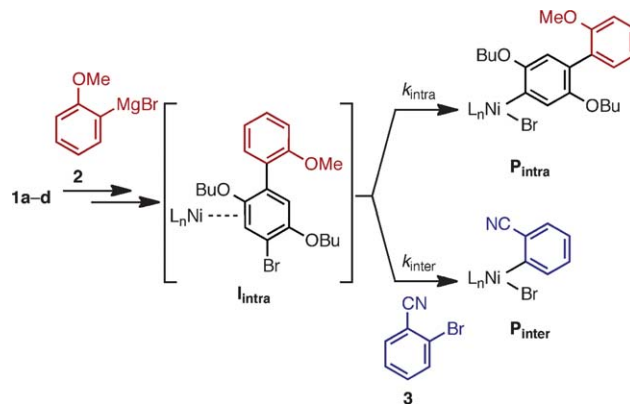
Scheme 1 Proposed chain-growth mechanism.

addition has been reported.^{16–18} For example, several groups have reported selective difunctionalization reactions of dihaloarenes when sub-stoichiometric quantities of the cross-coupling partner are used,¹⁷ which is consistent with preferential oxidative addition into the initial product *via* an associative intermediate. In a different example, van der Boom *et al.* generated a Ni(0)-olefin π -complex *in situ* and observed selective oxidative addition into the less reactive, intramolecular Ar–Br bond *versus* a more reactive, intermolecular Ar–I bond.¹⁸ We were inspired by the latter example and designed a series of competition experiments to distinguish whether the proposed Ni(0) π -complex is an intermediate in Ni-catalyzed small molecule cross-coupling reactions and chain-growth polymerizations.¹⁹

As described herein, these experiments have provided compelling evidence of an associative intermediate, with a subsequent intramolecular oxidative addition. We further revealed that bidentate, electron-rich ligands promote the formation and reactivity of this intermediate. Most significantly, we have demonstrated that the results from the small molecule studies correlate with chain-growth behavior in polymerizations, suggesting that the associative complex is the key intermediate between the desired and undesired reaction pathways. Overall, these studies indicate that the utility and scope of these chain-growth polymerizations can be improved by considering the formation and reactivity of the Ni(0) π -complex intermediate.

Results and discussion

To determine whether a Ni(0) π -complex forms after reductive elimination, we designed a competition experiment wherein the proposed intramolecular oxidative addition must outcompete an intermolecular oxidative addition involving a more reactive coupling partner. As highlighted in Scheme 2, the hypothesized^{2,3} Ni(0) π -complex (I_{intra}) is generated *in situ* *via* transmetalation of complex **1** (Chart 1) using Grignard **2**, followed by reductive elimination. Based on the observed chain-growth



Scheme 2 Competition experiment.

behavior in the polymerizations, this π -complex is expected to undergo preferential intramolecular oxidative addition to generate P_{intra} . The presence of a competitive agent (*i.e.*, aryl bromide **3**) provides an alternative pathway. The more reactive²⁰ and better π -binding²¹ **3** can intercept I_{intra} ,²² undergo intermolecular oxidative addition and generate P_{inter} .²³ If the proposed π -complex does not form at all, then the resulting “free” Ni(0) should be selectively trapped by **3** to produce P_{inter} . To verify that **3** is more reactive towards Ni(0), we measured the relative intermolecular oxidative addition rates of **3** and **4** to Ni(PPh₃)₂(cod) (eqn (1)).²⁴ A > 99 : 1 preference for oxidative addition into **3** was observed, consistent with its anticipated higher reactivity.²⁵ Due to this large difference in reactivity between **3** and **4** in the intermolecular competition, we can assume that any P_{intra} formed during the reaction stems from the proposed π -complex. The analysis proved more complicated than depicted in Scheme 2, as both P_{intra} and P_{inter} can undergo transmetalation by **2** and reductive elimination to generate additional organic and organometallic products (ESI[†]). For the sake of simplicity in the discussion, we will refer to the collection of products stemming from each pathway as P_{intra} and P_{inter} .

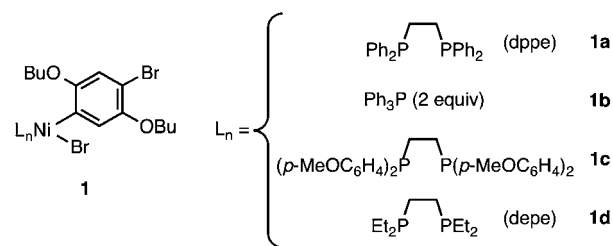
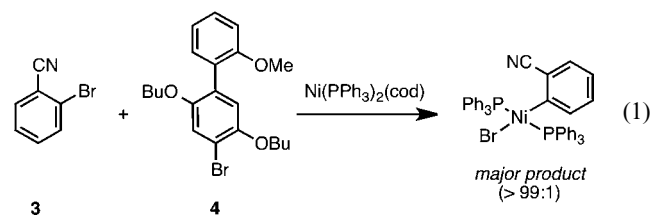


Chart 1

Competition experiments were first performed using complex **1a** because related Ni complexes containing the ligand, 1,2-bis(diphenylphosphino)ethane (dppe), mediate chain-growth polymerizations of several different monomers.²⁶ With near stoichiometric quantities of **1a**, **2** and **3**, we observed a 95 : 5 ratio of $P_{\text{intra}} : P_{\text{inter}}$ (Table 1). The observed large preference for P_{intra} is remarkable considering that P_{inter} is the favored product if the π -complex did not form. Combined, these results provide compelling evidence of an associative intermediate and intramolecular oxidative addition.²⁷ Because ligand steric and electronic properties have a dramatic influence on chain-growth polymerizations, we compared several different ligands under identical conditions to determine their impact on the π -complex. Complex **1b**, containing monodentate ligand PPh_3 , was selected for comparison because it does not mediate controlled, chain-growth polymerizations.²⁸ Consistent with this observation, at near stoichiometric quantities of **1b**, **2** and **3**, a 65 : 35 ratio of $P_{\text{intra}} : P_{\text{inter}}$ was observed. This result indicates that the π -complex is either weakly associated or that rate of dissociation is similar to the rate of intermolecular oxidative addition. Because bidentate, electron-rich ligands have been reported to yield improved chain-growth polymerizations relative to dppe,¹³ complexes **1c** and **1d** were also examined. Both **1c** and **1d** gave higher ratios of $P_{\text{intra}} : P_{\text{inter}}$ than **1a** and **1b** at the near stoichiometric conditions (Table 1), suggesting that the chain-growth behavior and π -complex formation/reactivity are related. Overall, the observed dominance of the intramolecular oxidative addition in all four cases provides strong evidence of an intermediate π -complex in these Ni-catalyzed cross-coupling reactions.



$$\frac{d[P_{\text{intra}}]}{dt} = k_{\text{intra}}[I_{\text{intra}}] \quad (4)$$

$$\frac{d[P_{\text{inter}}]}{dt} = k_{\text{inter}}[I_{\text{intra}}][3] \quad (5)$$

$$\frac{[P_{\text{intra}}]}{[P_{\text{inter}}]} = \frac{k_{\text{intra}}}{k_{\text{inter}}[3]} \quad (6)$$

Table 1 Results of the competition experiments^a

Equiv. of 3 ^b	$P_{\text{intra}} : P_{\text{inter}}$			
	1a	1b	1c	1d
1	95 : 5	65 : 35	97 : 3	98 : 2
2	91 : 9	55 : 45	94 : 6	96 : 4
10	69 : 31	28 : 72	78 : 22	87 : 13
50	40 : 60	13 : 87	49 : 51	71 : 29
100	32 : 68	11 : 89	40 : 60	64 : 36

^a The reactions were run in THF at rt for 2 h ($[\text{Ni}] = 0.02 \text{ M}$; $[2] = 0.016 \text{ M}$). The reported ratios reflect the averages of three runs, with standard deviations ranging from 0.06–2%. ^b Relative to **2**.

Further insight into the formation and reactivity of these Ni(0) π -complexes can be elucidated based on how the product ratios change as a function of $[3]$. As evident in Table 1, the products stemming from the intramolecular reaction (P_{intra}) decrease with increasing concentrations of **3** for all four complexes. Nevertheless, the magnitude of the change in these ratios is different for each ligand. Comparing the bidentate ligands, the preference for the intramolecular pathway has the following order: **1a** < **1c** < **1d**. This result parallels their electron-donating abilities, which were measured for the analogous monodentate ligands ($\text{PPh}_3 < \text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OMe})_3 < \text{PEt}_3$).²⁹ As noted above, the electron-rich ligands are expected to promote the formation of the π -complex,¹⁴ consistent with the Dewar–Chatt–Duncanson model of metal– π coordination,³⁰ and also increase the rate of oxidative addition.¹⁵ Both factors would result in larger quantities of the intramolecular oxidative addition product (P_{intra}), as observed herein. A plot of the product ratio ($[P_{\text{intra}}]/[P_{\text{inter}}]$) versus $1/[3]$ reveals the inherent preference for the intramolecular pathway for each ligand (eqn (2)–(6)).³¹ The slope provides the relative rate constants ($k_{\text{intra}}/k_{\text{inter}}$), which we can use to compare the ligands. As evident in Fig. 1, among the bidentate ligands the most electron-rich ligand (depe) exhibits the largest slope while the least electron-rich ligand (dppe) provides the smallest slope. In addition, PPh_3 , which exhibits the most uncontrolled polymerization, exhibits the smallest overall slope. These results are again consistent with the expectation that electron-donating ligands promote the formation and reactivity of the associative complex. Overall, these slopes provide a convenient and quantitative comparison between these and future ligands using this methodology.

To determine the relevance of the Ni(0) π -complex on the chain-growth nature of the polymerizations, (4-bromo-2,5-bis(hexyloxy)phenyl)magnesium bromide was polymerized with catalysts **1a–d** (ESI[†]). The molecular weight dispersity (D), which reflects the breadth of the distribution, is predicted to be 1.0 in a perfectly controlled chain-growth polymerization.³² Many

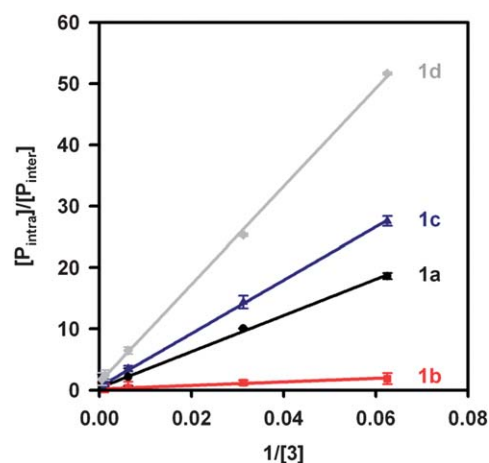


Fig. 1 Plot of the product ratio ($[P_{\text{intra}}]/[P_{\text{inter}}]$) versus $1/[3]$ for complexes **1a** (●), **1b** (■), **1c** (▲), and **1d** (◆). The lines represent nonlinear least-squares fits to the equation $[P_{\text{intra}}]/[P_{\text{inter}}] = k_{\text{intra}}/(k_{\text{inter}}[3]) + b$ where $k_{\text{intra}}/k_{\text{inter}} = 295$ (**1a**), 29 (**1b**), 435 (**1c**), and 800 (**1d**).

Table 2 Results of the polymerizations^a

Equiv. of 3 ^b	<i>D</i>			
	1a	1b	1c	1d
0	1.38	2.42	1.29	1.44
50	2.30	2.50	1.89	1.98
100	2.35	2.42	2.28	2.15

^a The reactions were run in THF at rt for 24 h ([Ni] = 0.0015 M; [2] = 0.1005 M). The reported *D* reflect the averages of two runs, with standard deviations ranging from ±0.01 to 0.03. ^b Relative to **1**.

factors, including the frequency of chain-transfer/termination events (*i.e.*, intermolecular reactions) as well as the relative rates of initiation and propagation, contribute to broaden this distribution. As a result, the *D* from the standard polymerizations cannot be compared directly to the small molecule studies. Because the intermolecular reactions are favored at high concentrations of competitive agent, the polymerizations were run with 50 and 100 equiv. of **3** (Table 2). As anticipated, the *D* broadened substantially (**1a** (1.38 → 2.35), **1c** (1.29 → 2.28), and **1d** (1.44 → 2.15)) with increasing concentrations of the competitive agent, consistent with an increase in the number of undesired intermolecular reactions. In contrast, catalyst **1b** gave polymer samples that were broad regardless of whether competitive agent was present, suggesting an uncontrolled or step-growth process. Significantly, at high concentrations of **3**, the *D* follow the same trend as observed in the small molecule studies (**1d** (2.15) < **1c** (2.28) < **1a** (2.35)), consistent with the anticipated impact of electron-donating ligands on the formation and reactivity of the π -complex. The absence of a trend at lower concentrations of **3** is likely due to the dominance of other factors on the *D*, such as a slow initiation relative to propagation.^{13,33} Note that the number-average molecular weights also decreased with increasing concentrations of **3** (ESI[†]), consistent with the initiation of new polymer chains *via* the intermolecular pathway. Overall, these results provide compelling evidence that the Ni(0) π -complex is an important intermediate in the chain-growth polymerizations.

Conclusions

In summary, both small molecule cross-coupling reactions as well as chain-growth polymerizations were found to proceed *via* an associative intermediate. By varying the ligand electronic properties, we observed that electron-rich, bidentate ligands lead to a higher preference for this intramolecular pathway. Further studies revealed that the fate of this intermediate correlates with the chain-growth behavior of the polymerizations. As a consequence, this type of competition experiment should prove valuable for expanding the scope and utility of these polymerizations, particularly in identifying catalysts for currently challenging monomers (*e.g.*, electron-deficient monomers). These studies also suggest that electron-rich, bidentate ligands can be used to achieve selective polyfunctionalizations of small molecules in related cross-coupling reactions.

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