Syntheses of Ester-Substituted Norbornyl Palladium Complexes Ligated with ^{t}Bu$_3$P: Studies on the Insertion of *exo*- and *endo*-Monomers in the Ester-Substituted Norbornene Polymerization

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Exo- and *endo*-isomers of an ester-substituted norbornene derivative [5-norbornene carboxylic acid methyl ester (NBE)] are compared in the addition polymerization using ^{t}Bu$_3$P-ligated palladium complex **1**. The polymerization rate of *endo*-NBE is slower than that of the corresponding *exo*-NBE. Each of *exo*- and *endo*-NBE inserted complexes was synthesized and the insertion rate constant was determined for *exo*-NBE and *endo*-NBE. These experiments revealed that the consecutive *exo*-NBE insertion was faster than the consecutive *endo*-NBE insertion by 2-fold. On the other hand, in polymerization of an *exo*-NBE/*endo*-NBE (1:1) mixture, consumption rates of *exo*-NBE and *endo*-NBE were almost equal and the production rate of the poly-NBE from this mixture was almost the same as that of homopolymerization of *exo*-NBE.

Introduction

Polynorbornene is equipped with a great deal of attractive properties, such as high thermal stability, very high glass transition temperature, high optical transparency, and low birefringence.[1−3] Polymerization of functionalized norbornene is of additional interest because the introduction of functionalities to nonpolar polynorbornene can enhance its properties, such as solubility and adhesive ability. The use of transition metal catalysts for polymerization of functionalized monomers sometimes faces a problem because coordination of functional groups to the metal center often poisons the catalytic activity. In contrast, late transition metal catalysts have been reported to tolerate ester functionalities in the polymerization of ester-functionalized norbornene probably due to their low oxophilicity.[4−14] Recently, we have reported the synthesis of a low-coordinated palladium complex, (^{t}Bu$_3$P)Pd(Me)Cl (**1**), which was used in combination with NaB[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$ (NaBAr$_4$) as a catalyst for polymerization of norbornene and copolymerization of norbornene with 5-norbornenecarboxylic acid methyl ester (NBE).[15] The most efficient incorporation of NBE ever reported was realized in its copolymerization with norbornene.

Since NBE is synthesized by Diels−Alder reaction, it consists of *exo*- and *endo*-isomers, the latter being the major species.[16] Using several catalyst systems, it was reported that the polymerization rate of the *endo*-isomer was slower than that of the *exo*-isomer in the polymerization of an *endo*/*exo* mixture.[4,5,8−10,17] One of the possible explanations for this deceleration for *endo*-isomer polymerization was suggested to be the formation of a chelate by the coordination of the *endo*-NBE through π-electrons of the C=C double bond and a lone pair of the ester group.[10] The bulky ^{t}Bu$_3$P in the **1**/NaBAr$_4$ system may inhibit this chelation by its steric hindrance. In order to shed light on this subject, the polymerization rates for the *exo*- and *endo*-isomers of NBE and for a mixture of *exo*/*endo* (1:1) were studied using **1**/NaBAr$_4$ as a catalyst. In addition, both *exo*- and *endo*-NBE-inserted alkylpalladium complexes were synthesized and the rate constants for NBE insertion were determined (Scheme 1).

Results and Discussion

Homopolymerization of *exo*- and *endo*-NBE Monomers. A commercially available mixture of *exo*- and *endo*-NBE was separated by silica gel column chromatography. Homopolymerization of *exo*-NBE and *endo*-NBE was performed using a **1**/NaBAr$_4$ system. When *exo*-NBE was used as a monomer, poly(*exo*-NBE) was obtained in 74% yield by reprecipitation

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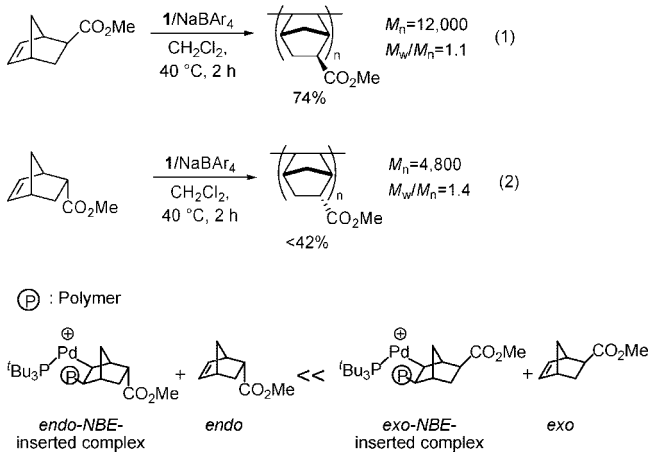


Figure 1. Proposed relative rates for monomer insertion into alkylpalladium complexes based on eqs 1 and 2.

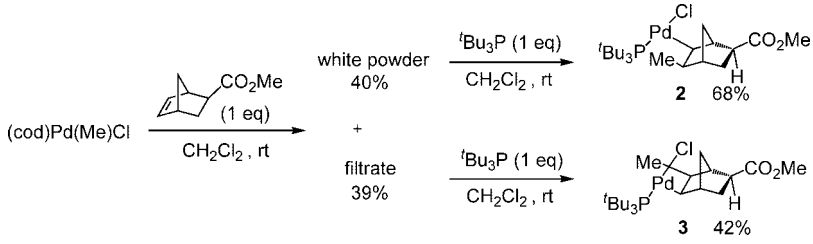
with methanol, and its molecular weight was estimated to be $M_n = 12\,000$ (eq 1). On the other hand, from *endo*-NBE, only methanol-soluble oligomers were obtained in less than 42% yield with lower molecular weight of $M_n = 4800$ (eq 2). These results indicate that the polymerization of *endo*-NBE was slower than that of *exo*-NBE. This should be interpreted that an insertion of *endo*-NBE monomer into the *endo*-NBE-inserted complex is slower than an insertion of *exo*-NBE into the *exo*-NBE-inserted complex (Figure 1).

Syntheses of NBE-Inserted Complexes. The *exo*- and *endo*-NBE-inserted complexes **2**−**5** were synthesized as described in Schemes 1 and 2. Reaction of (cod)Pd(Me)Cl with *exo*-NBE afforded a mixture of two complexes, which could be separated by recrystallization from CH_2Cl_2−pentane as a white powder and a gray filtrate.[13] Reaction of the white powder with ^{t}Bu$_3$P gave an orange powder of the *exo*-NBE-inserted complex **2**. The gray filtrate was exposed to the same conditions to form an orange powder of another *exo*-NBE-inserted complex, **3**, which is a regioisomer of **2**. Similar procedures were applied to synthesize the *endo*-NBE-inserted products **4** and **5** (Scheme 2).

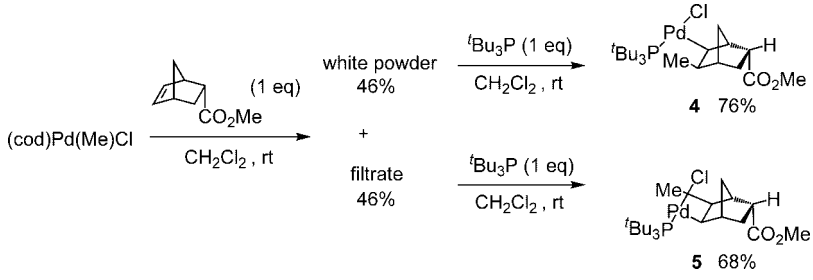
X-ray crystallographic analysis revealed the structures of **2**−**5** as follows. The palladium atom is located on the γ-carbon of the ester group in **2** and **4**, while it is attached to the δ-carbon in **3** and **5** (Figure 2). In **3**, the H44* hydrogen atom of a cocrystallized CH_2Cl_2 molecule interacted with the O1 carbonyl oxygen of the ester group via a hydrogen bond. In all of the isolated complexes **2**−**5**, addition of Me−Pd to the C−C double bond took place from the *exo*-face of norbornene but not from the *endo*-face. Selected bond lengths of the four obtained complexes are shown in Table 1 with those of reference compounds, cyclooctadiene-coordinated norbornyl complexes **6** and **7** having an ethyl ester group.[13] In all ^{t}Bu$_3$P-ligated complexes **2**−**5**, the central palladium atom had a T-shape and three-coordinate structure where the open coordination site was located at the *trans* position to the Pd(1)−C(1) bond. The vacant site induced shorter Pd(1)−C(1) bonds in **2**−**5** than those in **6** and **7**, whereas Pd(1)−Cl(1) bonds in **2**−**5** are longer than those in **6** and **7**, because the order of *trans* influence is vacant site < C=C double bond in cod ligand < ^{t}Bu$_3$P. Steric repulsion between ^{t}Bu$_3$P and the norbornyl group in **2**−**5** made the C(1)−Pd(1)−Cl(1) angle larger than those in **6** and **7**.

Monitoring Reactions of 2 and 4 with NBE Monomer. We can consider many relative stereochemical relationships for the NBE polymerization using the *exo*/*endo* mixture. During polymerization, each propagation step has eight possibilities because of insertion of *exo*/*endo* monomers, orientation of carbopalladation (regioisomers corresponding to **2** and **3** or **4** and **5**), and chain end of the polymer (*exo*/*endo*). To avoid the complexity of monitoring the reaction, we have chosen two combinations: complex **2** with *exo*-NBE and complex **4** with *endo*-NBE. In the presence of $NaBAr_4$, complex **2** was allowed to react with 1 equiv of *exo*-NBE at 0 °C, and the integral ratio of vinylic protons of *exo*-NBE to an internal standard phenanthrene was monitored by ^{1}H NMR (Scheme 3). Complete consumption of complex **2** was revealed by ^{1}H NMR spectroscopy with the disappearance of a singlet at δ_H 1.66, which is assigned to the methyl group on the norbornyl moiety in **2**/$NaBAr_4$ (Figure 3). The decay obeyed first-order kinetics, and an insertion rate constant of $k = 4.09 \times 10^{-4}$ s^{-1} was obtained. In the reaction of *endo*-NBE with **4**, a smaller insertion rate constant of $k = 1.78 \times 10^{-4}$ s^{-1} was obtained. Thus, there is an approximately 2-fold difference in rate constant for the *exo*-NBE insertion into the *exo*-NBE-inserted complex **2** and *endo*-NBE insertion into the *endo*-NBE inserted complex **4**. The results are consistent with our prediction based on the polymerization rate (Figure 1).

Scheme 1. Syntheses of *exo*-NBE-Inserted Complexes 2 and 3



Scheme 2. Syntheses of *endo*-NBE-Inserted Complexes 4 and 5



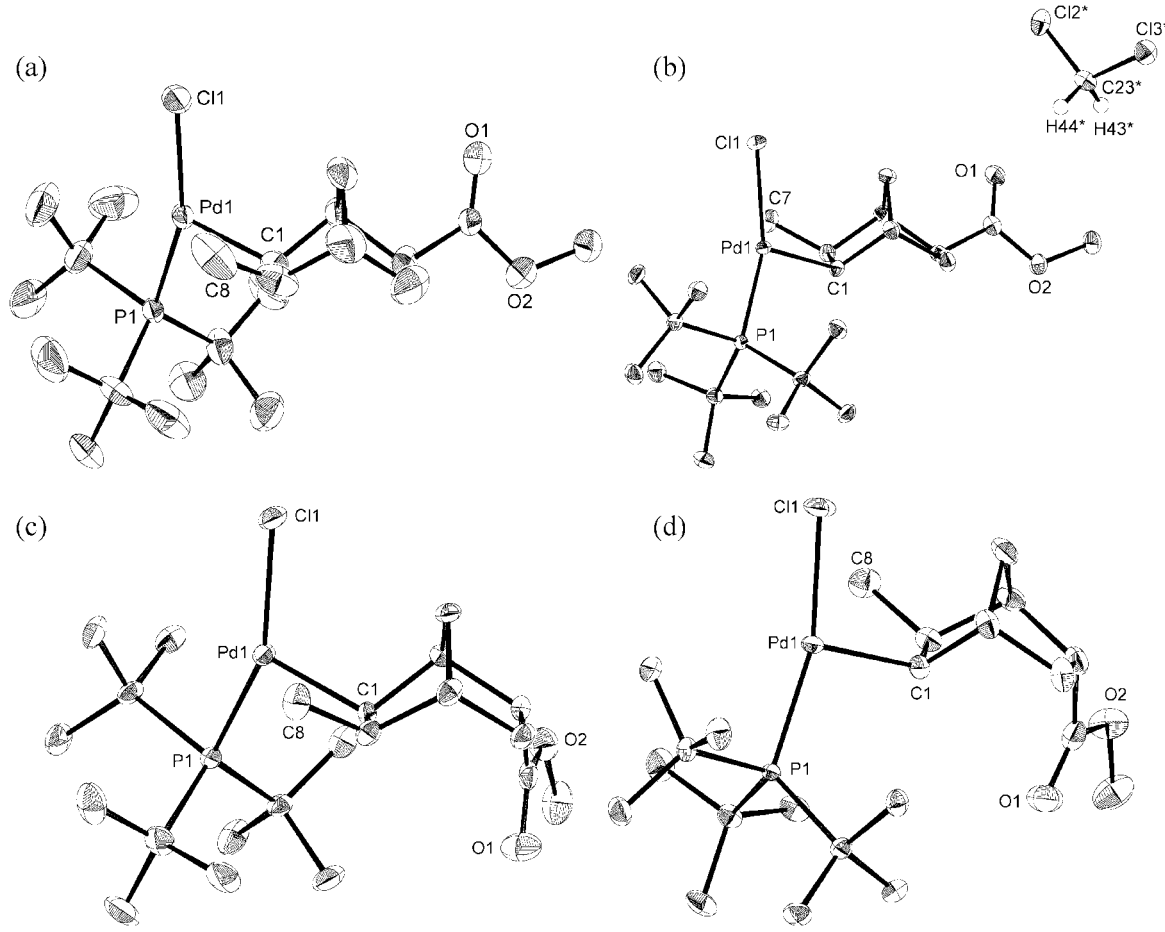
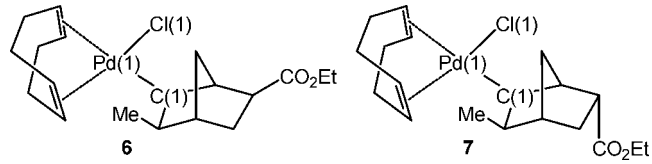


Figure 2. ORTEP drawings of **2**−**5** (**2** (a), **3** (b), **4** (c), **5** (d)). Hydrogen atoms and a minor part of disordered ester groups are omitted for clarity. In **3**, the cocrystallized CH_2Cl_2 molecule interacted with the ester group via a hydrogen bond.

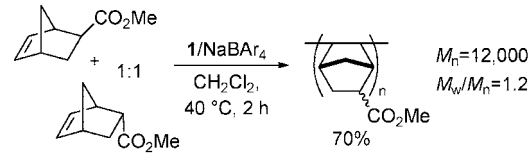
Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 2−5 and Reference Compounds 6 and 7



	2	6	3	4	7	5
Pd(1)−C(1)	2.058(5)	2.0717(19)	2.047(2)	2.051(4)	2.064(2)	2.037(2)
Pd(1)−P(1)	2.2473(14)		2.2537(17)	2.2681(11)		2.2663(13)
Pd(1)−Cl(1)	2.3570(14)	2.3486(7)	2.3669(14)	2.3776(11)	2.3426(7)	2.3511(12)
C(1)−Pd(1)−Cl(1)	106.29(14)	94.67(7)	108.65(7)	107.25(11)	98.05(6)	102.38(6)

It should be noted that polymerization of a 1:1 mixture of NBE monomer afforded a 70% yield at 40 °C in 2 h (eq 3), which was almost the same reaction rate as that for polymerization of *exo*-NBE (74% yield in 2 h, eq 1) but much higher than that for polymerization of *endo*-NBE (<42% in 2 h, eq 2). If bidentate chelation of *endo*-NBE affected the reaction rate, the polymerization of a 1:1 mixture would have also been retarded by the existence of *endo*-NBE. The similar yields for the polymerization of a 1:1 mixture and for the polymerization of *exo*-NBE imply that the chelate from the coordination of the *endo*-NBE through the C═C double bond and the ester group is less significant in the **1**/$NaBAr_4$ system bearing a bulky ligand.

In order to estimate the relative reaction rate of the two monomers, the consumption rate of each monomer was monitored by gas chromatography. Under the reaction conditions described in eq 3, the consumptions of *exo*-NBE and *endo*-NBE were almost equal (Figure 4), indicating the **1**/$NaBAr_4$ system could polymerize both *exo*-NBE and *endo*-NBE with a similar rate. Accordingly, it seems that the *endo-endo* consecutive insertion took place less often compared to the other sequences.



(3)

Conclusion

It was found that the polymerization of *endo*-NBE was slower than that of *exo*-NBE using the **1**/$NaBAr_4$ system. Four monomer-inserted palladium complexes, **2**−**5**, were independently synthesized for both *exo*- and *endo*-NBE. Monitoring

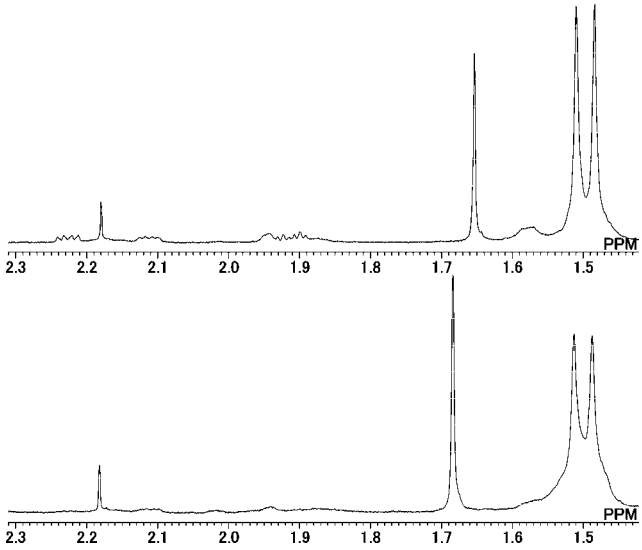
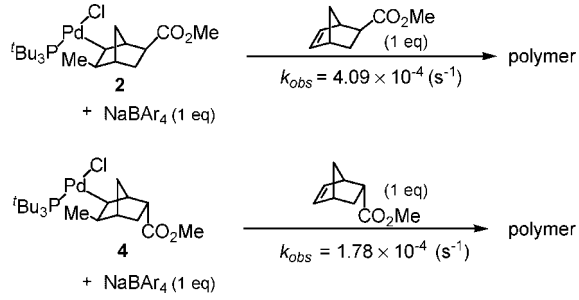


Figure 3. Aliphatic region of ^{1}H NMR before (top) and after (bottom) the reaction of **2** with *exo*-NBE.

Scheme 3. Monitoring Insertion Reactions



the consumption of *exo*- and *endo*-NBE in a reaction with the corresponding monomer-inserted palladium complex revealed that there was a 2-fold difference between the two insertion rate constants. In the polymerization of an *exo*/*endo* mixture (1:1), however, the **1**/NaBAr$_4$ system could polymerize both *exo*-NBE and *endo*-NBE at a similar rate. The similar rates for the *exo*/*endo* mixture (1:1) and for *exo*-NBE may indicate that there is no chelate from the coordination of the *endo*-NBE through the C═C double bond and the ester group in the **1**/NaBAr$_4$ system.

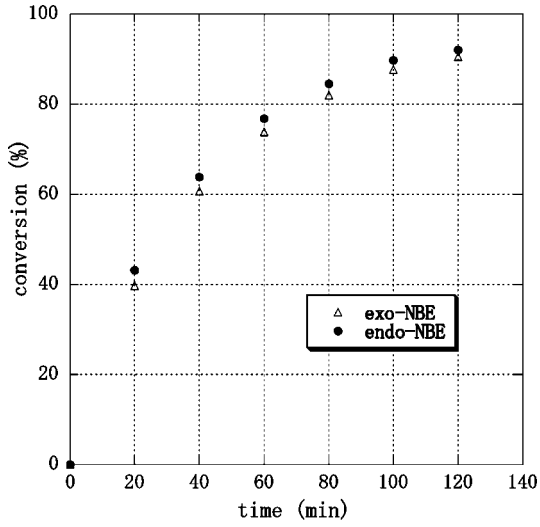


Figure 4. Monitoring the conversion of *exo*-NBE and *endo*-NBE.

Experimental Section

General Methods. Unless otherwise noted, all reactions and manipulations were conducted by using standard Schlenk or vacuum line techniques under argon except for the filtration procedures through filtering papers. ^{1}H (500 MHz), ^{13}C{^{1}H} (125 MHz), and ^{31}P{^{1}H} (202 MHz) NMR spectra were recorded on a JNM-ECP500 spectrometer with shifts relative to residual protiated solvent, deuterated solvent, and an external 85% H_3PO_4 standard. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Graduate School of Science, The University of Tokyo. X-ray crystallographic analyses were recorded on a Rigaku Mercury CCD diffractometer. Gel permeation chromatography (GPC) analyses were carried out using a GL Sciences instrument (HPLC pump PU610, LC columns oven model 556) equipped with a Shodex SE-61 RI detector, SIV GPC board, and two columns (Shodex KF-804 L). The GPC columns were eluted with tetrahydrofuran at 40 °C at 1 mL/min. Dichloromethane was purified by passing through a solvent purification system (Grass Contour). The other chemicals were used as received. Pd(cod)-MeCl[18] and NaB(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$[19,20] were prepared as previously reported. A commercially available *exo*/*endo* mixture of NBE was separated by column chromatography (silica gel; hexane−AcOEt = 30:1 as an eluent, detected by I_2).

Syntheses of 2. In a glovebox, to (cod)Pd(Me)Cl (200 mg, 0.754 mmol) in CH_2Cl_2 (2 mL) was added a solution of *exo*-NBE (114.8 mg, 0.754 mmol) in CH_2Cl_2 (2 mL) dropwise. The solution was stirred at room temperature for 2 h. After filtration to remove any metallic palladium, the solvent was removed at reduced pressure. Slow diffusion of pentane into a concentrated solution of residue in CH_2Cl_2 at −40 °C gave a white powder. The resulting solid was separated by filtration, washed with hexane several times, and dried under vacuum to give a white powder (144.1 mg 46%). The collected filtrate was evaporated at reduced pressure to form a gray, amorphous solid (145.6 mg, 46%). (This gray, amorphous solid was used as reagents for the synthesis of **3**.) In a glovebox, to a solution of a gray powder (120 mg, 0.288 mmol) in CH_2Cl_2 (2 mL) was added ^{t}Bu$_3$P (64.1 mg, 0.317 mmol) in CH_2Cl_2 (1.5 mL) solution at room temperature. The solution was stirred at room temperature for 30 min. After filtration to remove any metallic palladium, the solution was poured into hexane. Half the amount of solvent was evaporated to precipitate an orange powder. Upon filtering and washing with hexane, the desired product **2** was obtained as an orange powder (99.7 mg, 68%). Slow diffusion of pentane into a concentrated solution of **2** in ether at −40 °C gave an orange crystalline solid, which was suitable for X-ray crystallographic analysis. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.27−1.30 (m, 2H), 1.36−1.41 (m, 1H), 1.53 (d, J = 12 Hz, 27H), 1.64 (d, J = 7.3 Hz, 3H), 1.91−1.96 (m, 2H), 2.09 (m, 1H), 2.57 (d, J = 11 Hz, 1H), 2.80 (s, 1H), 3.62 (s, 3H), 4.26 (dd, J = 7.3 Hz, J = 16.3 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 24.3 (d, J = 6.7 Hz), 32.2, 32.4, 32.6, 39.4 (d, J = 9.6 Hz), 45.8, 46.0 (d, J = 6.7 Hz), 47.5 (d, J = 2.9 Hz), 49.7 (d, J = 2.9 Hz), 51.8, 54.0 (d, J = 5.8 Hz), 173.7; ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz) δ 71.4 (s). Anal. Calcd for $C_{22}H_{42}ClO_2PPd$: C, 51.67; H, 8.28. Found: C, 51.52; H, 8.18.

Synthesis of 3. In a glovebox, to a solution of the gray, amorphous solid (199.5 mg, 0.478 mmol) obtained in the previous section in CH_2Cl_2 (2 mL) was added ^{t}Bu$_3$P (106.5 mg, 0.526 mmol) in CH_2Cl_2 (1.5 mL) solution dropwise at room temperature. The solution was stirred at room temperature for 30 min. After filtration to remove any metallic palladium, the filtrate was poured into hexane. Half the amount of solvent was evaporated to precipitate

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Table 2. Crystallographic Data and Structure Refinement Details for 2, 3·CH_2Cl_2, 4, and 5

	2	**3**·CH_2Cl_2	**4**	**5**
formula	$C_{22}H_{42}ClO_2PPd$	$C_{22}H_{42}ClO_2PPd \cdot CH_2Cl_2$	$C_{22}H_{42}ClO_2PPd$	$C_{22}H_{42}ClO_2PPd$
fw	511.38	596.30	511.38	511.38
T (K)	103(2)	103(2)	103(2)	103(2)
λ (Å)	0.71070	0.71070	0.71070	0.71070
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	13.573(5)	12.052(9)	16.081(6)	8.592(5)
b (Å)	14.203(5)	10.073(7)	8.681(3)	10.019(5)
c (Å)	14.125(5)	22.418(17)	17.306(6)	15.068(8)
α (deg)	90	90	90	100.372(6)
β (deg)	116.3130(13)	104.159(3)	99.2080(17)	100.796(6)
γ (deg)	90	90	90	104.467(6)
V (Å^3)	2440.9(15)	2639(3)	2384.7(14)	1198.0(11)
Z	4	4	4	2
D_{calc} (g/cm^3)	1.392	1.501	1.424	1.418
μ (mm^{-1})	0.949	1.085	0.972	0.967
F(000)	1072	1240	1072	536
cryst size (mm)	0.25 × 0.20 × 0.10	0.30 × 0.30 × 0.10	0.45 × 0.15 × 0.05	0.35 × 0.35 × 0.05
2θ range (deg)	3.14−25.00	3.01−27.48	3.01−25.00	3.09−25.00
reflns collected	15 319	20 235	15 028	11 621
indep reflns/R_{int}	4154/0.0402	5928 /0.0306	4192/0.0423	4206/0.0282
params	291	282	266	255
GOF on F^2	1.111	1.088	1.181	1.093
R_1, wR_2 [$I > 2\sigma(I)$]	0.0525, 0.1235	0.0274, 0.0577	0.0433, 0.0805	0.0236, 0.0598
R_1, wR_2 (all data)	0.0598, 0.1283	0.0329, 0.0600	0.0511, 0.0834	0.0250, 0.0606

an orange powder. Upon filtering and washing with hexane, the desired product **3** was obtained as an orange powder (103.1 mg, 42%). Slow diffusion of pentane into a concentrated solution of **3** in CH_2Cl_2 at −40 °C gave an orange crystalline solid, which was suitable for X-ray crystallographic analysis. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.23−1.34 (m, 2H), 1.52 (d, J = 12.6 Hz, 27H), 1.68 (d, J = 7.3 Hz, 3H), 1.83 (d, J = 14.7 Hz, 1H), 1.93 (d, J = 18.1 Hz, 1H), 2.15 (s, 1H), 2.20−2.27 (m, 1H), 2.56 (d, J = 10.1 Hz, 1H), 2.62 (s, 1H), 3.64 (s, 3H), 4.19 (dd, J = 7.2 Hz, J = 16.7 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 24.0 (d, J = 7.7 Hz), 32.2, 33.1, 33.4 (d, J = 6.7 Hz), 39.4 (d, J = 9.6 Hz), 45.3 (d, J = 2.9 Hz), 46.5, 47.9 (d, J = 2.9 Hz), 50.4, 51.7, 54.6 (d, J = 4.8 Hz), 175.9; ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz) δ 71.6 (s). Anal. Calcd for $C_{23}H_{44}Cl_3O_2PPd$: C, 46.32; H, 7.44. Found: C, 46.08; H, 7.37.

Syntheses of 4. In a glovebox, to (cod)Pd(Me)Cl (200 mg, 0.754 mmol) in CH_2Cl_2 (2 mL) was added a solution of *endo*-NBE (114.8 mg, 0.754 mmol) in CH_2Cl_2 (2 mL) at room temperature. The solution was stirred at room temperature for 2 h. After filtration to remove any metallic palladium, the solvent was removed at reduced pressure. Slow diffusion of pentane into a concentrated solution of residue in CH_2Cl_2 at −40 °C gave a white powder. The resulting solid was separated by filtration, washed with hexane several times, and dried under vacuum to give a white powder (127.4 mg, 40%). The collected filtrate was evaporated at reduced pressure to form a gray, amorphous solid (122.0 mg, 39%). (This gray, amorphous solid was used as reagents for the synthesis of **5**.) In a glovebox, to the white powder (150 mg, 0.359 mmol) in CH_2Cl_2 (2 mL) was added ^{t}Bu$_3$P (79.9 mg, 0.395 mmol) in CH_2Cl_2 (1.5 mL) solution at room temperature. The solution was stirred at room temperature for 30 min. After filtration to remove any metallic palladium, the solution was poured into hexane. Half the amount of solvent was evaporated to precipitate an orange powder. Upon filtering and washing with hexane, the desired product **4** was obtained as a yellow powder (139.5 mg, 76%). Slow diffusion of pentane into a concentrated solution of **4** in ether at −40 °C gave an orange crystalline solid, which was suitable for X-ray crystallographic analysis. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.27 (d, J = 9.9 Hz, 1H), 1.50 (d, J = 13 Hz, 29H), 1.67−1.72 (m, 1H), 1.76 (d, J = 7.1 Hz, 3H), 1.92 (s, 1H), 2.48−2.52 (m, 1H), 2.88 (s, 1H), 3.58 (s, 3H), 4.48 (dd, J = 7.1 Hz, J = 15.3 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 24.5 (d, J = 7.7 Hz), 32.1, 38.5, 39.3 (d, J = 9.6 Hz), 45.3 (d, J = 4.8 Hz), 47.1, 49.5, 49.8 (d, J = 2.9 Hz), 50.7 (d, J = 5.8 Hz), 51.5, 175.3; ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz) δ 71.7(s). Anal. Calcd for $C_{22}H_{42}ClO_2PPd$: C, 51.67; H, 8.28. Found: C, 51.41; H, 8.24.

Synthesis of 5. In a glovebox, to the gray, amorphous solid (92.0 mg, 0.220 mmol) obtained in the previous section in CH_2Cl_2 (1 mL) was added ^{t}Bu$_3$P (49.0 mg, 0.242 mmol) in CH_2Cl_2 (1.5 mL) solution at room temperature. The solution was stirred at room temperature for 30 min. After filtration to remove any metallic palladium, the solution was poured into hexane. Half the amount of solvent was evaporated to precipitate a yellow powder. Upon filtering and washing with hexane, the desired product **5** was obtained as a yellow powder (76.4 mg, 68%). Slow diffusion of pentane into a concentrated solution of **5** in ether at −40 °C gave an orange crystalline solid, which was suitable for X-ray crystallographic analysis. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.20−1.47 (m, 4H), 1.53 (d, J = 12.4 Hz, 27H), 1.62 (d, J = 7.6 Hz, 3H), 2.17−2.21 (m, 1H), 2.56−2.60 (m, 1H), 2.70 (d, J = 10.3 Hz, 1H), 2.74−2.79 (m, 1H), 3.62 (s, 3H), 4.27 (ddd, J = 7.3 Hz, J = 17.3 Hz, J = 1.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 24.1 (d, J = 6.7 Hz), 32.0 (d, J = 5.8 Hz), 32.1, 37.0, 39.2 (d, J = 9.6 Hz), 43.2 (d, J = 1.9 Hz), 45.1, 46.5 (d, J = 2.9 Hz), 50.0, 51.4, 53.8 (d, J = 4.8 Hz), 175.5; ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz) δ 71.9 (s). Anal. Calcd for $C_{22}H_{42}ClO_2PPd$: C, 51.67; H, 8.28. Found: C, 51.47; H, 8.23.

X-ray Crystallography. Details of the crystal data and a summary of the intensity data collection parameters for **2**, **3**, **4**, and **5** are listed in Table 2. In each case a suitable crystal was mounted with mineral oil to the glass fiber and transferred to the goniometer of a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). The structures were solved by direct methods with (SIR97[21] or SHELXS[22]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97). The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically in the difference Fourier maps or placed using AFIX instructions.

Procedure for Homopolymerization of *exo*- and *endo*-NBE. A 20 mL Schlenk flask was charged with **1** (18.0 mg, 0.050 mmol) and NaB(3,5-$(CF_3)_2C_6H_3)_4$ (44.5 mg, 0.050 mmol), and this mixture

(21) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

(22) Sheldrick, G. M *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

was dissolved in CH_2Cl_2 (4.0 mL). The solution was degassed by three cycles of freeze−pump−thaw. Another 20 mL Schlenk flask was charged with NBE (*exo* or *endo*, 0.89 mL, 5.8 mmol) and CH_2Cl_2 (1.0 mL), and the solution was degassed by three cycles of freeze−pump−thaw. To this flask was added the solution of the palladium complex at room temperature. The Schlenk flask was then placed in a temperature-controlled silicone oil bath at 40 °C. After being stirred for 2 h, the reaction mixture was poured into methanol. The resulting polymer was separated by filtration, washed with methanol several times, and dried under vacuum at 60 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82−3.07 (br, CH, CH_2), 3.38−4.00 (br, $COOCH_3$).

Procedure for Kinetic Measurements (Scheme 3). Preparation of Stock Solutions. Preparation of Solution A. The *exo*-NBE inserted complex **2** (10.2 mg, 0.0200 mmol) and NaB(3,5-$(CF_3)_2C_6H_3)_4$ (17.8 mg, 0.0200 mmol) were placed into a 2.00 mL volumetric flask, and the flask was purged with Ar. The mixture was dissolved in $CDCl_3$, and the resulting solution was then diluted to 2.00 mL. The final concentrations were [**2**] = [NaB(3,5-$(CF_3)_2C_6H_3)_4$] = 0.0100 M.

Preparation of Solution B. In a glovebox, *exo*-NBE (15.2 mg, 0.100 mmol) and phenanthrene (10.0 mg, 0.0560 mmol) were placed into a 5.00 mL volumetric flask and were dissolved in $CDCl_3$. The resulting solution was diluted to 5.00 mL. The final concentrations were [*exo*-NBE] = 0.0200 M, [phenanthrene] = 0.0112 M.

Preparation of Solution C. The *endo*-NBE-inserted complex **4** (10.2 mg, 0.0200 mmol) and NaB(3,5-$(CF_3)_2C_6H_3)_4$ (17.8 mg, 0.0200 mmol) were placed into a 2.00 mL volumetric flask, and the flask was purged with Ar. The mixture was dissolved in $CDCl_3$, and the resulting solution was then diluted to 2.00 mL. The final concentrations were [**4**] = [NaB(3,5-$(CF_3)_2C_6H_3)_4$] = 0.0100 M.

Preparation of Solution D. In a glovebox, *endo*-NBE (15.2 mg, 0.100 mmol) and phenanthrene (10.0 mg, 0.0560 mmol) were placed into a 5.00 mL volumetric flask and were dissolved in $CDCl_3$. The resulting solution was diluted to 5.00 mL. The final concentrations were [*endo*-NBE] = 0.00200 M, [phenanthrene] = 0.0112 M.

Reaction of 2 with *exo*-NBE. Solution A was filtered through a membrane filter and an aliquot (0.500 mL) of the resulting solution was placed into a screw-capped NMR tube. The tube was cooled to −60 °C. To this tube was then added 0.250 mL of solution B, and the resulting solution was mixed in the NMR tube at −60 °C. The final concentrations were [**2**] = [NaB(3,5-$(CF_3)_2C_6H_3)_4$] = [*exo*-NBE] = 0.00500 M, [phenanthrene] = 0.00280 M. The tube was inserted into a precooled NMR probe at 0 °C. After locking and shimming, automated data acquisition was then started. The integral ratio between the internal standard, phenanthrene, and the vinylic proton of **2** was monitored and fitted with first-order kinetics to give a rate constant of $k = 4.09 \times 10^{-4}$ (s^{-1}).

Reaction of 4 with *endo*-NBE. Solution C was filtered by a membrane filter, and into a screw-capped NMR tube was added 0.500 mL of this solution by syringe. This tube was then cooled to −60 °C. To this tube was then added 0.250 mL of solution D, and the resulting solution was mixed. The final concentrations were [**4**/NaB(3,5-$(CF_3)_2C_6H_3)_4$] = 0.00500 M, [*endo*-NBE] = 0.00500 M, [phenanthrene] = 0.00280 M. The tube was inserted into the NMR probe, which had been pre-equilibrated to 0 °C. Automated data acquisition was then started. The integral ratio between the internal standard, phenanthrene, and the vinylic proton of **4** was monitored and fitted with first-order kinetics to give a rate constant of $k = 1.78 \times 10^{-4}$ (s^{-1}).

Monitoring of Polymerization of the *exo*/*endo* Mixture (1:1) (Figure 6). The consumption of *exo*-NBE and *endo*-NBE isomers was quantified using gas chromatography (GC) with 1,1,2,2-tetrachloroethane (TCE) as an internal standard. GC data were obtained on a Shimazu GC-14B gas chromatograph. A 20 mL Schlenk flask was charged with **1** (18.0 mg, 0.050 mmol) and NaB(3,5-$(CF_3)_2C_6H_3)_4$ (44.5 mg, 0.050 mmol), and this mixture was dissolved in CH_2Cl_2 (4.0 mL). The solution was degassed by three cycles of freeze−pump−thaw. Another 20 mL Schlenk flask was charged with *exo*-NBE (441.4 mg, 2.90 mmol), *endo*-NBE (441.4 mg, 2.90 mmol), CH_2Cl_2 (1.0 mL), and TCE (122 μL, 1.16 mmol), and the solution was degassed by three cycles of freeze−pump−thaw. To this flask was added the solution of the palladium complex at room temperature. The initial sample (50 μL) of the solution was diluted in 1 mL of acetone for GC analysis. The Schlenk flask was then placed in a temperature-controlled silicone oil bath at 40 °C. An aliquot (50 μL) was removed from the reaction mixture at 20 min and was diluted with 1 mL of acetone for GC analysis.

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Supporting Information Available: CIF files of **2**−**5** are available free of charge via the Internet at http://pubs.acs.org.

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