High-Pressure NMR Studies on the Alternating Copolymerization of Styrene with Carbon Monoxide Catalyzed by a Palladium(II)−(*R*,*S*)-BINAPHOS Complex

Jonathan A. Iggo,*,[†] Yasutoyo Kawashima,[‡] Jianke Liu,[†] Tamejiro Hiyama,[‡] and Kyoko Nozaki*,[§]

Department of Chemistry, Donnan and Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 7ZD, U.K., Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan, Conversion and Control by Advanced Chemistry, PRESTO, Japan Science and Technology Corporation (JST), Department of Chemistry & Biotechnology, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

The asymmetric copolymerization of styrene with CO catalyzed by Pd−(*R*,*S*)-BINAPHOS complexes has been studied using in situ NMR spectroscopy under both diffusion- and reaction-controlled conditions. While a study conducted in a conventional zirconia tube suffered from gas diffusion limitation, use of a high-pressure NMR flow cell allows the observation of potential catalytic intermediates. The formation of Pd−alkyl complexes via 1,2-insertion of styrene into Pd−acyl complexes is confirmed to be the most active catalytic pathway. The 2,1-insertion complexes were found to be quite inactive to further insertion and remarkably stable toward β-hydride elimination, in contrast to our previous expectations.

Introduction

Palladium-catalyzed alternating copolymerization of olefins with carbon monoxide[1−4] proceeds through alternating insertion of an olefin into a Pd−acyl bond and of carbon monoxide into a Pd−alkyl bond.[5−10] When an α-olefin such as propene or styrene inserts into a Pd−acyl bond, regioisomers and stereoisomers of the resulting Pd−alkyl complexes may be formed, depending on the sense (1,2 or 2,1) of the olefin insertion.[10] The stereoregularity of the polymer affects the physical properties of the polyketone;[11,12] thus, it is essential to control, and to understand the factors that control, the regio- and enantioselectivity of the olefin insertion in order to obtain stereocontrolled polyketones. There are several reports of the successful asymmetric copolym-

erization of α-olefins with CO.[13−25] For palladium-catalyzed copolymerization of styrene, or its derivatives, with CO, nitrogen-based bidentate ligands are usually the most effective,[17−25] and in such a case, styrene or its derivative usually inserts with high 2,1-insertion regioselectivity.[26−29] There are many fewer examples of styrene−CO copolymerization using palladium complexes bearing phosphorus-based ligands. Two possible reasons for this have been suggested: (i) rapid β-hydride

* To whom correspondence should be addressed. J.A.I.: fax, 44 151 794 3588; tel, 44 151 794 3538; e-mail, iggo@liv.ac.uk. K.N.: tel, 81 3 5841 7261; fax, 81 3 5841 7261; e-mail, nozaki@chembio.t.u-tokyo.ac.jp.
† University of Liverpool.
‡ Kyoto University.
§ The University of Tokyo.

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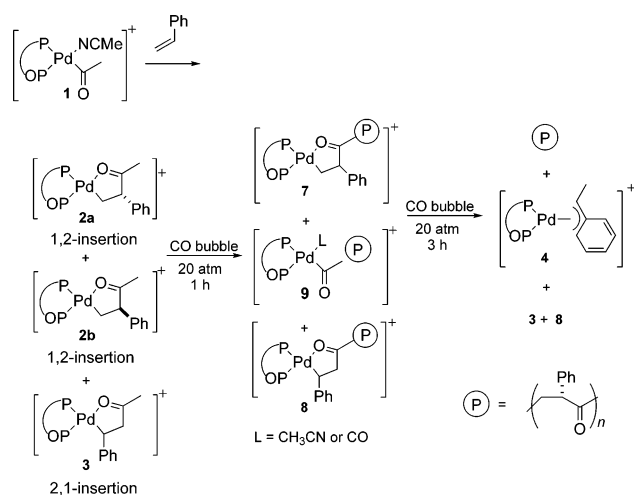(28) Bionotti, B.; Carfagna, C.; Gatti, G.; Martini, D.; Mosca, L.; Pettinari, C. *Organometallics* **2003**, *22*, 1115.
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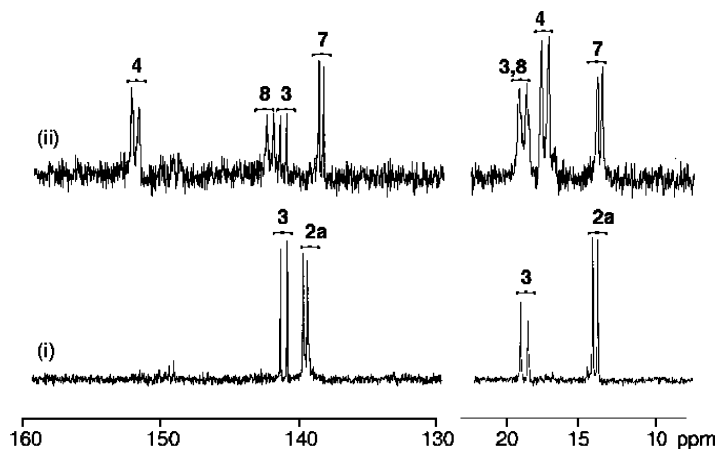
Figure 1. High-pressure $^{31}P\{^1H\}$ NMR studies (Θ = 202.5 MHz) under diffusion-controlled conditions: (i) on treatment of Pd−acetyl complex **1** (0.02 mmol) with styrene (1.0 mmol) in 0.6 mL of CDCl$_3$ at 23 °C; (ii) after 7 h under 20 atm of CO.

Scheme 1

elimination from Pd(phosphorus ligand)−alkyl species[6−8] might be expected and/or (ii) slow reinitiation of polymerization from the Pd−benzyl complex which results from the β-hydride elimination followed by styrene insertion into the resulting Pd−H bond.[30]

(*R*,*S*)-BINAPHOS provides an exception to this general observation and is reported to give an effective palladium-based catalyst for the copolymerization of styrene, or its derivatives, with CO.[15,31,32] We have previously reported an ex situ NMR study to elucidate the unique behavior of the Pd/(*R*,*S*)-BINAPHOS catalyst system for the alternating copolymerization of α-olefins such as propene and styrene with carbon monoxide and have shown the following, under 1 atm of CO.[15,31−33]

(i) The *stoichiometric* reaction of styrene with the Pd−acetyl complex **1** gives both 1,2- and 2,1-insertion products (**2** and **3**; Scheme 1. Two diastereomers, **2a** and **2b**, were observed for the 1,2-complex, and β-hydride elimination followed by styrene insertion took place from both **2a,b** and **3** to give the Pd−π-benzyl complex **4** (see the Supporting Information, Scheme 1).

(ii) Poly(propene-*alt*-CO)-attached alkyl−Pd complex **5**, a mimic of the real polymerization intermediate, underwent exclusive 1,2-insertion of styrene to give **6** (see the Supporting Information, Scheme 2).[33]

Although a Pd−acyl intermediate must be involved in alkene−CO copolymerization and such species have been widely observed in stoichiometric studies of alkene−CO copolymerization[10,11,34−41] and of propene−CO copolymerization using this catalyst system,[42] we had been unable to observe such a species in our ex situ studies of styrene−CO copolymerization. We were thus interested in discovering whether the mechanism outlined above was viable under conditions more closely resembling copolymerization conditions (23 °C, 20 atm of CO) and whether the "missing" acyl intermediate could be observed under these conditions. We have studied the reaction both in a conventional zirconia high-pressure NMR tube (diffusion-controlled conditions) and in a new high-pressure NMR flow cell that completely eliminates the gas diffusion problem by bubbling the reacting gases at pressure through the reacting catalyst solution (see the Supporting Information, Figure 1).[43] An acyl intermediate can be observed only in the flow cell, an observation that can be attributed to gas starvation in the zirconia tube.

Results and Discussion

Diffusion-Controlled Conditions. A 50-fold excess of styrene was added to a CDCl$_3$ solution of the Pd−acetyl complex **1** in a commercially available zirconia

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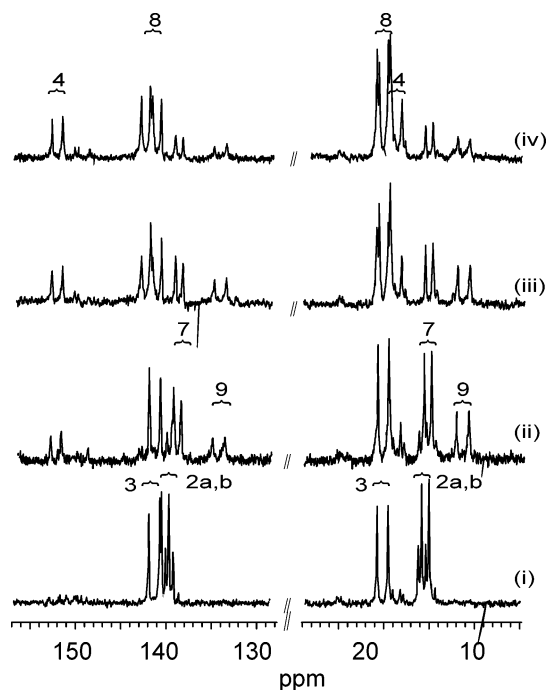
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high-pressure NMR tube and the progress of the copolymerization monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy (Figure 1). The spectra in Figure 1 show peaks in the ranges 8−23 and 130−160 ppm which are attributable to the phosphine and phosphite ends of (*R,S*)-BINAPHOS, respectively. At this stage, traces of the Pd−acetyl starting complex **1** and the styrene insertion complexes resulting from 1,2-insertion (**2a**) and 2,1-insertion (**3**) were observed (Figure 1(i) and the Supporting Information, Scheme 3).[33]

The tube was then pressurized to 20 atm with CO and placed in an NMR probe without spinning at 23 °C. After 7 h under CO pressure the reaction was quenched; conversion of styrene had reached 10%, a value corresponding to a turnover number of 5 and turnover frequency of ca. 0.7 h^{-1}. Four pairs of doublets were observed by ^{31}P{^{1}H} NMR spectroscopy (Figure 1(ii)). The chemical shifts and the coupling constants[33] suggest the presence of the new 1,2-complex **7** (δ 138.9 and 14.3) and the new 2,1-insertion complex **8** (δ 142.6 and 19.4), resulting from multiple insertions of CO and styrene into either **2a** or **3**, and the known initial 2,1-complex **3** (δ 141.7 and 19.4), and π-benzyl complex **4** (δ 152.4 and 17.9). At the end of the reaction some initial 2,1-complex **3** remained, although all of the initial 1,2-complex **2a** had been consumed. It should be noted, however, that no peaks assignable to the polymer-attached Pd−acyl complex **9** were observed. It is likely that, in this study, the reaction proceeded under diffusion control because, in the unmixed zirconia tube, it was impossible to maintain a sufficient supply of CO to the reaction. Thus, Whyman has shown that, in high-pressure IR experiments, gas diffusion is extremely slow and critically dependent on breaking the interface between the gas and liquid phases,[44] something not achieved in the sapphire tube, while Garland has modeled the behavior of gas diffusion in sapphire NMR tubes and shown that reactions performed in this way must be limited by gas diffusion.[45] Furthermore, we have recently shown that, in in situ NMR studies, gas diffusion has a major impact on the concentration of dissolved gases[43] and consequently on the rate of reaction.[46] Accordingly, we next examined the reaction under reaction controlled conditions in our high-pressure NMR flow cell.[43]

Reaction-Controlled Conditions. The ability, using our high-pressure NMR flow cell system, to bubble gas through the reacting catalytic solution eliminates the gas diffusion problem associated with the use of sapphire tubes ensuring that gas starvation of the reaction does not occur. Good mixing of the reaction is also achieved.[43,46] We have thus been able to observe directly, by ^{31}P{^{1}H} NMR spectroscopy, the catalytic species under real copolymerization conditions.

At the beginning of the reaction (i.e. under 1 atm of CO), formation of the 1,2-insertion complexes **2a** and **2b**, a diastereomer of **2a**, and the 2,1-insertion complex **3** was observed as before (Figure 2(i)). **2b** is formed as a result of isomerization of the initially formed **2a**.[33] The apparent difference between Figure 1(i) and Figure 2(i)

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Figure 2. High-pressure ^{31}P{^{1}H} NMR studies ($\Theta = 81.0$ MHz) under reaction-controlled conditions, where Pd−acetyl complex **1** (0.2 mmol) was treated with styrene (10 mmol) in 5.2 mL of CDCl$_3$: (i) 19 °C, 1 atm of CO, $t = 0$ min; (ii) 19 °C, 10−14 atm of CO, $t = 55$ min; (iii) 23 °C, 20 atm of CO, $t = 98$ min; (iv) 23 °C, 20 atm of CO, $t = 127$ min.

and Figure 3(i) reflects differences in the time between addition of styrene and recording of the NMR spectrum. On pressurization with CO to 20 atm, the previously observed 1,2-insertion complexes **2a,b** are rapidly consumed to give the new 1,2-insertion and 2,1-insertion complexes **7** and **8** (Figure 2(ii,iii)). The initial 2,1-insertion complex **3** is consumed at a much slower rate, if at all (Figure 2(ii−iv)). The resonances of the new complex **9** can also be seen in Figure 2(ii−iv). The appearance of **9** is associated with the admission of CO to the reaction. Purging the solution containing **9** with N$_2$ (20 atm, 6 L$_n$ h^{-1}, 30 min) (L$_n$ = normal liter, i.e. the volume that would be occupied by a compressed gas if expanded to STP) to remove dissolved CO results in the complete disappearance of **9** (Figure 3(ii,iii)). It is therefore reasonable to assume that **9** results from reaction with CO and is most likely either a Pd−acyl or Pd−carbonyl complex. A ^{13}C labeling experiment at high pressure in a flow cell is not viable; however, **9** can confidently be assigned as the polymer-attached Pd−acyl complex, via a comparison of its NMR chemical shifts and P−P coupling constant (**9**: δ 134.3 (d, J_{P-P} = 110 Hz), 10.3 d) with those of **1** (δ 133.8 (d, J_{P-P} = 113 Hz), 10.3 d) and with those of the fully characterized analogous ion [Pd(COCH$_2$CH(CH$_3$)COCH$_3$)(CD$_3$CN)-{(*R,S*)-BINAPHOS}]$^+$ (δ 137.0 (d, J_{P-P} = 108 Hz), 9.7 d).[15] After ca. 1 h, under CO pressure (Figure 2(ii,iii)), the initial 1,2-insertion complexes **2a,b** had disappeared completely to be replaced by **7**, the multiple 1,2-insertion complex, and the Pd−acyl complex **9**. The amount of the initial 2,1-insertion complex **3**, however, remains essentially unchanged. After 2 h (Figure 2(iv)), the two 2,1-insertion complexes **3** and **8** dominate the ^{31}P{^{1}H} NMR spectrum. The resonances of the Pd−π-benzyl
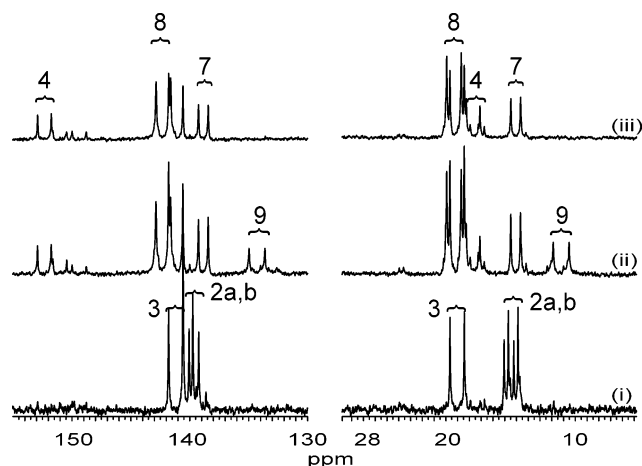
Figure 3. High-pressure $^{31}P\{^1H\}$ NMR studies ($\Theta = 81.0$ MHz) under reaction-controlled conditions, where Pd−acetyl complex **1** (0.08 mmol) was treated with styrene (16 mmol) in 5.2 mL of CDCl$_3$: (i) 23 °C, 1 atm of CO, $t = 0$ min; (ii) 23 °C, 20 atm of CO, $t = 15$ min; (iii) 23 °C, 20 atm of N$_2$, $t = 45$ min.

complex **4** can also be seen growing in intensity throughout the experiment (Figure 2(ii−iv)). After 2 h, the copolymerization was quenched. Conversion of styrene had reached ca. 20%, corresponding to a TON and TOF of 10 and ca. 7 h^{-1}, respectively.

The above observations may be interpreted as follows: styrene−CO copolymerization is initiated by insertion of CO into **2a** and **2b** to give the Pd−acyl complex **9**. Subsequent insertion of styrene into the Pd−acyl bond gives the new 1,2-complex **7** or the new 2,1-complex **8** (Scheme 1).

Gas diffusion limitation of the reaction is evident in the experiment performed in the zirconia tube, resulting in both a TOF that is an order of magnitude lower than that observed in the flow cell and the failure to observe the acyl intermediate **9**. Thus, on the basis of the intermediates observed, in the zirconia tube, the reaction *appears* to have a single, high-energy barrier, formation of the acyl intermediate, which is consumed immediately in the presence of a large excess of styrene. However, the simultaneous observation of both the acyl and alkyl intermediates in the working catalyst solution in the flow cell indicates that both intermediates are relatively long-lived species and have comparable lifetimes in the presence of *both* CO and styrene, in agreement with the result from our previous study of propene−CO copolymerization that there are two major energy barriers in the alkene−CO copolymerization reaction using this catalyst.[42] The experiments in the zirconia tube and flow cell were conducted under as close to identical as feasible conditions of substrate and catalyst concentration in order to minimize effects other than gas diffusion. The failure to observe **9** in the ex situ and diffusion control experiments must therefore be ascribed to starvation of the reaction of CO. The ca. 10-fold increase in rate observed in the flow cell when compared with that observed in the zirconia tube provides further evidence for diffusion limitation of the reaction in the zirconia NMR tube. The observation of **9** in the flow cell and not in the zirconia tube therefore does not reflect the *intrinsic* kinetics and/or thermodynamics of the reaction; rather, it has to do with the slow

dissolution of CO in the zirconia tube, which ensures that the *effective* standing dissolved concentration of CO in that experiment approaches zero. In such a case, and in the presence of even a small excess concentration of styrene, the acyl will not be observed.

Insertion of CO into the 2,1-insertion complexes **3** and **8** is much slower than that into **2** and **7**, as evidenced by (i) the rapid consumption of **2a,b**, whereas the initial 2,1-complex **3** remains until the end of the reaction, and (ii) by the buildup of complex **8**, as would be expected if 2,1-insertion represents a "dead end" in the reaction. During the reaction the Pd−acyl complex **9** and 1,2-insertion complexes **2a,b** and **7** are consumed, leaving the 2,1-insertion complexes **3** and **8** and the Pd−π-benzyl complex **4**, the concentrations of which build up throughout the reaction, indicating that, under the relatively mild operating conditions required by this catalyst, the 2,1-insertion complexes **3** and **8** are less active in the copolymerization and/or more stable with respect to the expected rapid β-hydride elimination than had been anticipated.[6−8,30,33] That CO insertion into the Pd−alkyl bond seems to have taken place much faster in **2a** than in **3** is in contrast to the situation found for palladium catalysts containing nitrogen-based bidentate ligands[17−25] and supports our hypothesis that the productive route to copolymer in our system is via 1,2- and not 2,1-insertion.[33] The 2,1-complexes **3** and **8** are relatively inert against CO insertion; however, β-hydride elimination from **3** and **8** does occur, albeit slowly, to give **4**. We have previously shown that **4** can initiate catalysis;[33] however, the present work indicates that this is much less efficient than 1,2-insertion of styrene following CO insertion into a Pd-alkyl species.

Conclusions

In situ NMR studies have been used to reveal the catalytic pathway in the Pd−(R,S)-BINAPHOS catalyzed asymmetric copolymerization of styrene and CO. The Pd−acyl complex **9** and the 1,2-insertion complex **7** are proposed to be intermediates in the chain propagation using a Pd−(R,S)-BINAPHOS catalyst. Both species can be observed under reaction control conditions; however, only the 1,2-insertion complex is observed under diffusion control. In agreement with our previous report,[33] and in contrast to the situation found using bidentate nitrogen ligands, 1,2-insertion of styrene is suggested as the chain-propagation step. Thus, insertion of CO into the 1,2-insertion product is rapid, whereas CO insertion into the 2,1-insertion product appears to be slow or negligible.[30] We also find that the 2,1-insertion complexes are relatively unreactive toward β-hydride elimination under the reaction conditions, although it had previously been proposed that rapid β-hydride elimination from 2,1-complexes would occur.[30,33]

Experimental Section

General Considerations. All experiments were carried out using standard Schlenk techniques under an atmosphere of argon or nitrogen. High-pressure NMR spectra in a sealed cell were recorded on a JEOL ECP-500 spectrometer (^1H NMR 500 MHz and $^{31}P\{^1H\}$ NMR 202.5 MHz) equipped with a 10 mm zirconia tube, using tetramethylsilane as an internal standard (^1H) or 85% phosphoric acid (^{31}P) as an external standard.

High-pressure gas flow NMR was performed on a Bruker AM200 SWB (^{31}P{^{1}H} NMR 81 MHz) spectrometer equipped with a home-built in situ high-pressure NMR flow cell (see the Supporting Information Figure 1). Solvents were purified by distillation under argon after drying over suitable drying reagents. Styrene was stabilized by *tert*-butylcatechol and used as received.

Observation of Alternating Copolymerization of Styrene and CO Using High-Pressure NMR in a Sealed Cell. A solution of 18.5 mg (0.02 mmol) of [Pd(CH$_3$)(Cl){(*R,S*)-BINAPHOS}] in CH$_2$Cl$_2$ (1.5 mL) was added to a solution of 20 mg (0.0225 mmol) of Na[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] in CD$_3$CN (0.5 mL), and the solution was stirred at 20 °C for 1 h. The reaction mixture was taken to dryness, and the reaction solids, principally [Pd(CH$_3$)(CD$_3$CN){(*R,S*)-BINAPHOS}][BAr$_4$], were dissolved in CDCl$_3$ (0.6 mL) and treated with 1 atm of CO for 30 min at 23 °C to form [Pd(COCH$_3$)(CD$_3$CN){(*R,S*)-BINA-PHOS}][BAr$_4$] (**1**).[15] The resulting solution and a 50-fold excess of styrene (115 μL, 1.0 mmol) were transferred into a 10 mm zirconia high-pressure NMR tube. A 50 mL autoclave was connected to the zirconia tube to maintain the constant pressure. After the tube/autoclave system was pressurized with 20 atm of CO, the tube was placed into an NMR probe at 23 °C. The reaction was followed by ^{1}H NMR and ^{31}P{^{1}H} NMR. After 7 h, the reaction was quenched when the conversion of styrene was shown to be 10% by ^{1}H NMR, corresponding to a turnover number of 5. At this stage, four Pd complexes were observed by ^{31}P{^{1}H} NMR spectroscopy. ^{31}P NMR (CDCl$_3$): initial 1,2-complex **2a**, δ 139.9 (d, $J_{P-P} = 64$ Hz), 14.6 (d, $J_{P-P} = 64$ Hz); initial 2,1-complex **3**:, δ 141.6 (d, $J_{P-P} = 98$ Hz), 19.1 (d, $J_{P-P} = 98$ Hz); π-benzyl complex **4**, δ 152.4 (d, $J_{P-P} = 101$ Hz), 17.9 (d, $J_{P-P} = 92$ Hz); the new 1,2-complex **7**, δ 138.9 (d, $J_{P-P} = 64$ Hz), 14.3 (d, $J_{P-P} = 64$ Hz); the new 2,1-complex **8**, δ 142.6 (d, $J_{P-P} = 100$ Hz), 19.4 (d, $J_{P-P} = 96$ Hz). For characterization data, see ref 33.

Observation of Alternating Copolymerization of Styrene and CO Using a High-Pressure NMR Flow Cell. Method 1. In an experiment analogous to that above, 185 mg (0.2 mmol) of [Pd(CH$_3$)(Cl){(*R,S*)-BINAPHOS}], CH$_2$Cl$_2$ (15 mL), 200 mg (0.225 mmol) of Na[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$], CD$_3$CN (5 mL), and a 50-fold excess of styrene (1.15 mL, 10.0 mmol) were used, and the final solution was placed in the HPNMR

flow cell against a counter stream of CO. The NMR probe was shimmed, a ^{31}P{^{1}H} NMR spectrum recorded, and the probe pressurized to 20 ($\pm$2) atm of CO at 23 °C. During and after the pressurization, the reaction was monitored by ^{31}P{^{1}H} and ^{1}H NMR (Figure 2). In addition to resonances of **2a**,**b**, **3**, **4**, **7**, and **8**, the new acyl complex **9** was observed. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 134.3 (d, $J_{P-P} = 110$ Hz), 10.3 (d, $J_{P-P} = 110$ Hz). After 2 h, the reaction was quenched when the conversion of styrene was 20% in ^{1}H NMR, corresponding to a turnover number of 10.

Method 2. In an experiment analogous to that above, a solution of 144 mg (0.080 mmol) of [Pd(CH$_3$)(CH$_3$CN){(*R,S*)-BINAPHOS}][BAr$_4$] in CDCl$_3$ (5.2 mL) was prepared and treated with CO (1 atm) at 23 °C for 30 min, styrene (1.8 mL, 16 mmol) was added, and the resulting solution was placed in the flow cell. The probe was pressurized to 20 ($\pm$2) atm of CO at 23 °C and the reaction monitored by ^{31}P{^{1}H} NMR spectroscopy. After 30 min the gas flow was changed to N$_2$ and a ^{31}P{^{1}H} NMR spectrum recorded. Under 1 atm of CO, ^{31}P{^{1}H} NMR (CDCl$_3$) showed the presence of **2a**,**b**, **3**, **4**, **7**, and **8**, under 20 atm of CO **2**, **3**, **4**, **7**, **8**, and the new acyl complex **9** were observed, and under 20 atm of N$_2$ the results were as above, except that resonances of **9** were no longer present.

Supporting Information Available: Text giving full experimental details for the flow cell experiments and figures giving an assembled view of the high-pressure NMR flow cell and reaction schemes summarizing previous ex situ stoichiometric work, the reaction of the poly(propene-*alt*-CO)-attached alkyl−Pd complex, a mimic of the real polymerization intermediate, with 1,2-insertion of styrene, and the reaction as observed under diffusion-controlled conditions in a zirconia HPNMR tube. This material is available free of charge via the Internet at http://pubs.acs.org.

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