High-Pressure NMR Studies on the Alternating Copolymerization of Propene with Carbon Monoxide Catalyzed by a Palladium(II) Complex of an Unsymmetrical Phosphine−Phosphite Ligand

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When high-pressure NMR techniques are employed, the following two facts are revealed. (1) The cis/trans isomerization from (*SP*-4-4)-[Pt(CH_3)(CO)(L^1)][BAr_4] (**8a**; L^1 = (*R*,*S*)-BINAPHOS; Ar = 3,5-$(CF_3)_2C_6H_3$) to the more stable *SP*-4-3 isomer (**8b**) is faster than CO insertion into either **8a** or **8b**, the CO insertion being reversible. (2) For the Pd^{II}−L^1-catalyzed copolymerization of propene and CO, there exist at least two major resting states, most probably acylpalladium, (*SP*-4-3)-[Pd(COR)(L^2)(L^1)][BAr_4] (**3**; L^2 = CH_3CN, CO), and alkylpalladium, [Pd{$CH_2CH(CH_3)C(=O)R$}(L^1)][BAr_4] (**5a**).

Introduction

Alternating copolymerization of olefins with CO has attracted much attention from both academia and industry due to the easy availability of starting materials and the engineering plastic type novel properties of the product.[1] The polymerization process includes two of the representative reactions of a palladium complex: (1) CO insertion into an alkyl−Pd bond and (2) an olefin insertion into an acyl−Pd bond; thus, intensive efforts have been devoted to mechanistic studies of the reaction by both experimental[2] and theoretical approaches.[3]

We previously reported a cationic Pd(II) complex with the unsymmetrical chiral phosphine−phosphite (*R*,*S*)-BINAPHOS to be an efficient catalyst for the asymmetric copolymerization of propene (3 atm) with carbon monoxide (20 atm). Highly isotactic polyketone with high enantioselectivity was obtained using [Pd(CH_3)(CH_3-CN){(*R*,*S*)-BINAPHOS}][B{3,5-$(CF_3)_2C_6H_3$}$_4$] (**1**).[4] The ligand is an unsymmetrical *cis*-bidentate phosphine−phosphite, and accordingly, two nonequivalent coordination sites are available for reactions on the tetracoordinated palladium species. Mechanistic aspects of the copolymerization were studied in detail, and the complexes marked "observed" in Scheme 1 were detected by stepwise NMR studies under ambient pressure. Namely, treatment of the methylpalladium compound **1** with CO in the absence of propene gave the acylpalladium species **3-I**, and exposure of **3-I** to propene afforded a 4:1 mixture of alkylpalladium complexes **5a-I** and **5b-I**. Further, formation of the second-generation acyl complex **3-II** was detected after pressurize−depressurize treatment of a mixture of **5a-I** and **5b-I** with 20 atm of CO, and the second-generation acyl complex **5a-II** was given as an exclusive product by exposure of **3-II** to propene.

The work was then focused on the reaction pathways between the observed complexes, such as **1** → **3-I** and **3-I** → **5-I** in Scheme 1. The platinum complex [Pt(CH_3)(CH_3CN){(*R*,*S*)-BINAPHOS}][B{3,5-$(CF_3)_2C_6H_3$}$_4$] (**7**) was studied as an analogue of palladium complex **1**. Methylplatinum carbonyl **8a** was obtained under 1 atm of CO as a result of CO−acetonitrile exchange. After a pressurize−depressurize cycle with 20 atm of CO, **8a** was transformed into **8b**, the cis/trans isomer of **8a**

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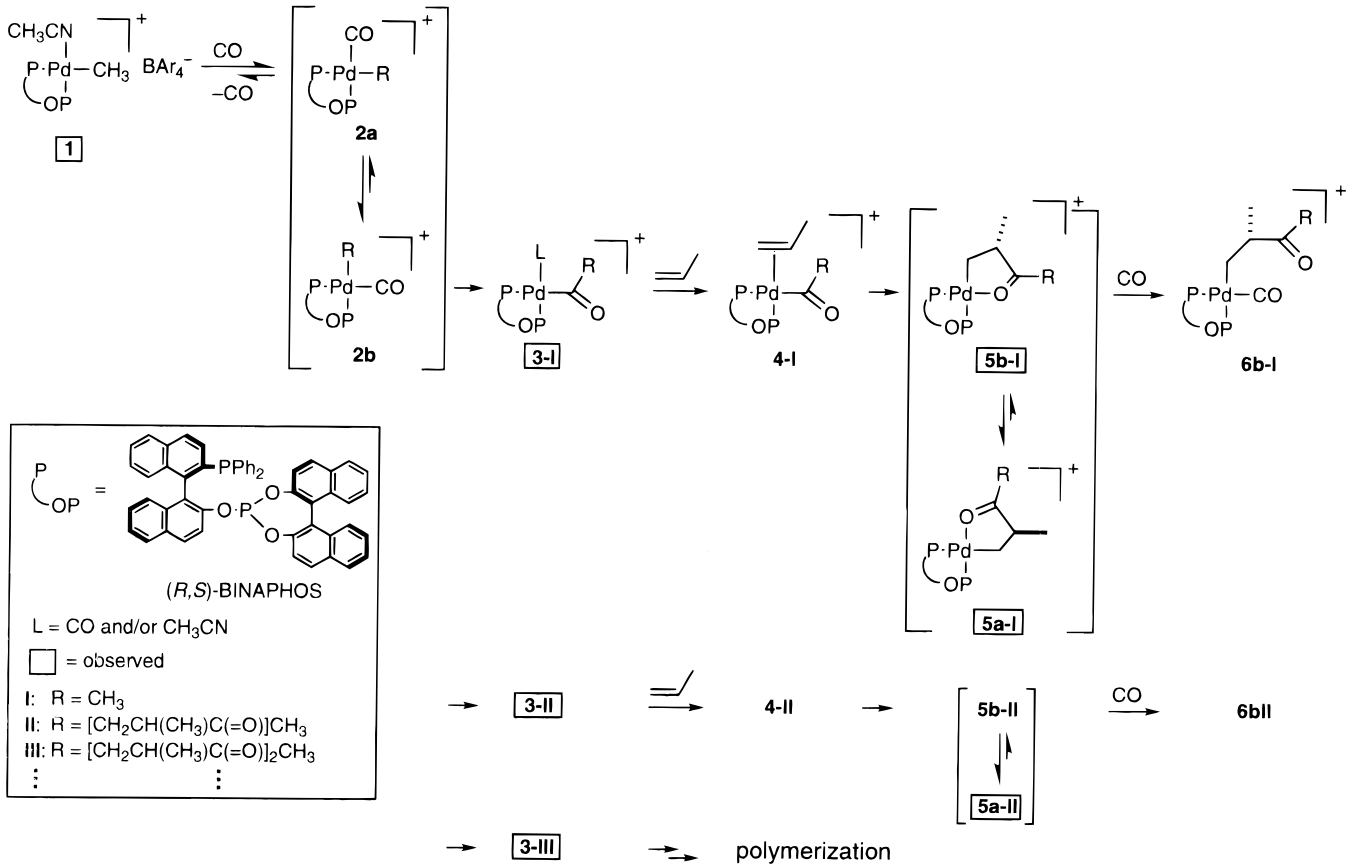
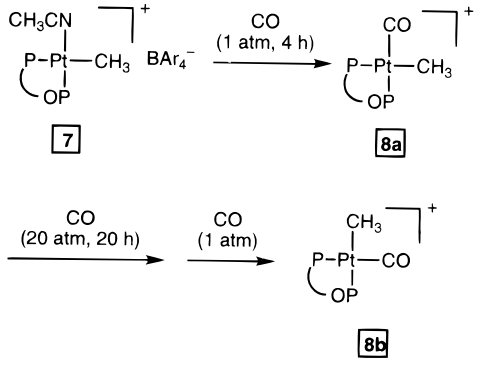
Scheme 1



(Scheme 2). On the basis of the isomerization, the process **1** → **2a** → **2b** → **3-I** was proposed. Theoretical approaches cleared the **3-I** → **5-I** process. In the previous study, however, success at determining the structures of complexes has been limited due to the difficulty in detecting in situ species which may exist only under high pressures. Hence, here we report further studies on the Pt and Pd complexes related to the copolymerization, employing high-pressure NMR techniques.[5] Two subjects will be presented: (1) the reaction of alkylplatinum **7** with CO and (2) observation of the chain growth of propene−CO copolymer initiated by cationic palladium **1**.

Scheme 2



Results and Discussion

Reaction of Alkylplatinum Complex 7 with Carbon Monoxide. As we previously reported,[4a] treatment of methylpalladium complex **1** with 1 atm of CO resulted in an immediate transformation to acyl complex **3-I** and no intermediate complexes were detectable (Scheme 1). In contrast, when methylplatinum **7** was treated with 1 atm of CO, only a ligand displacement was observed from acetonitrile to CO to give **8a** (Scheme 2). After a pressurize (up to 20 atm)−depressurize (down to 1 atm) cycle, the predominant product was **8b**, in which the methyl group and the coordinated carbonyl isomerized. Acyl complex (**9** in Scheme 3) was not detected. Here, in this work, the reaction of **7** with CO was carried out in a sapphire tube under 22 atm of CO pressure and was followed by ^{31}P NMR. When the reaction was allowed to start at −50 °C, peaks were detected at δ 122.5 for the phosphite and δ 15.4 for the phosphine, showing **8a** to be essentially the single product (part i of Figure 1). No change was observed below −25 °C. When the mixture was warmed to 25 °C, peaks due to isomer **8b** appeared at δ 148.6 for the phosphite and δ 15.0 for the phosphine (part ii of Figure 1). After 4 h at 25 °C, another set of peaks appeared at δ 112.8 for the phosphite and δ 6.9 for the phosphine (part iii of Figure 1).

To determine the structure of this new species, the same experiment was repeated using ^{13}CO. Broad peaks were detected by ^{31}P NMR for the new species, and the existence of an acyl group attached to the platinum was confirmed by the peak at δ 215.0 in ^{13}C NMR. To get a better resolution, the solution was cooled to −50 °C. At

(5) For examples of high-pressure NMR studies on homogeneous carbonylation process, see: (a) Roe, D. C. *Organometallics* **1987**, *6*, 942. (b) Horváth, I. T.; Millar, J. M. *Chem. Rev.* **1991**, *91*, 1339. (c) Horváth, I. T.; Kiss, G.; Cook, R. A.; Bond, J. E.; Stevens, P. A.; Rábai, J.; Mozeleski, E. J. *J. Am. Chem. Soc.* **1998**, *120*, 3133. See also ref 2f,j−n.

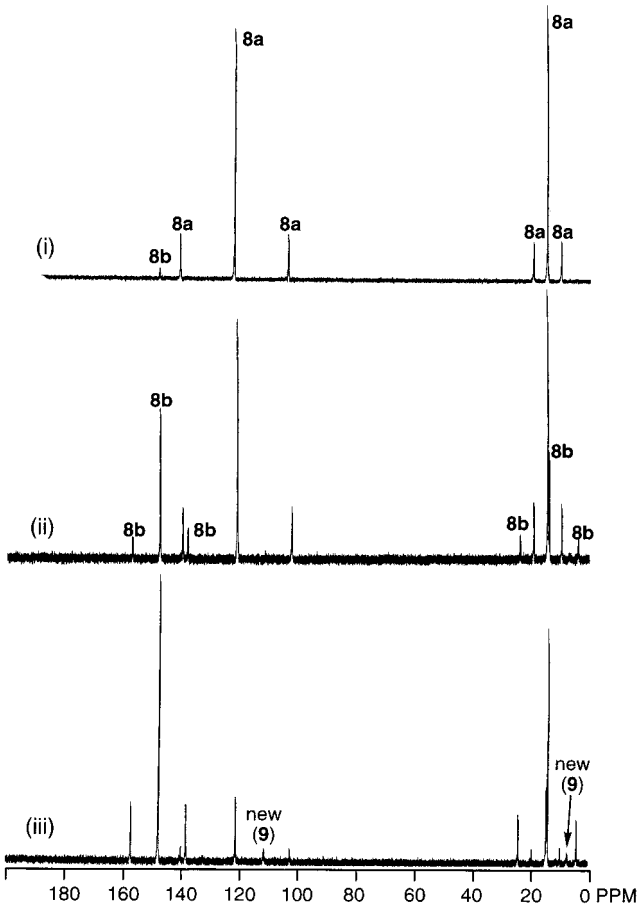
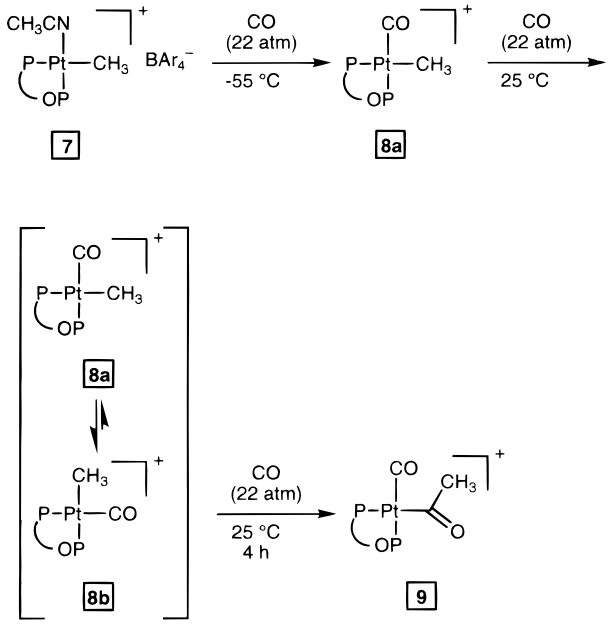


Figure 1. Treatment of alkylplatinum **7** in CD_2Cl_2 with CO in a sapphire NMR tube, followed by ^{31}P NMR: (i) at −50 °C and 22 atm of CO pressure, alkylplatinum **8a** being formed via immediate replacement of CH_3CN of **7** by CO; (ii) after the sample in (i) was warmed to 25 °C, the *cis*−*trans* isomerization **8a** → **8b** taking place to some extent; (iii) after 4 h at 25 °C, a new set of peaks appearing at δ 112.8 (phosphite) and δ 6.9 (phosphine) (the peaks will be assigned as acylplatinum **9** in Figure 2).

Scheme 3



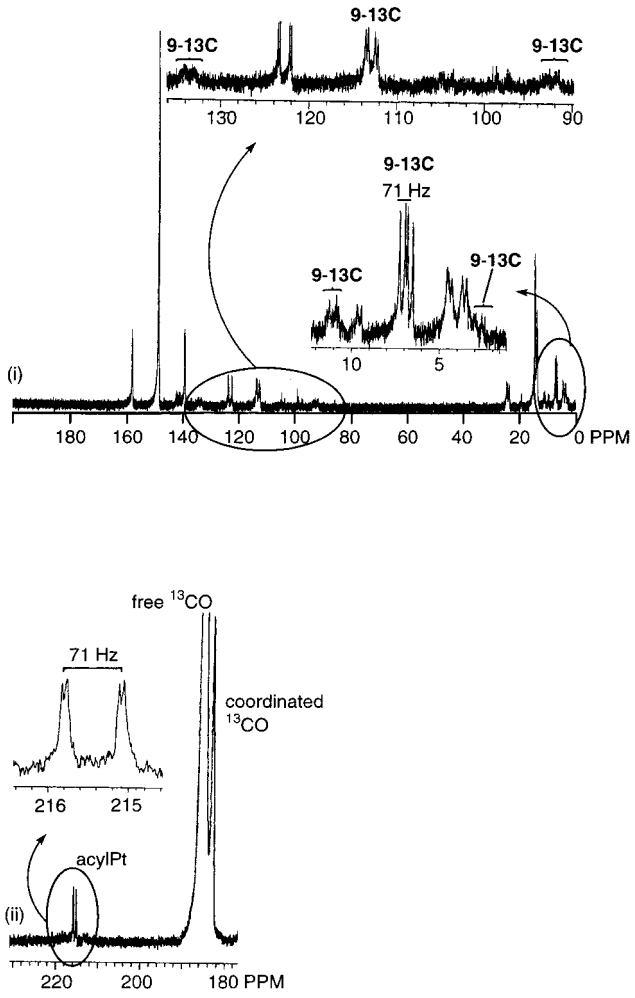


Figure 2. Reaction of alkylplatinum **7** with CO carried out using ^{13}CO in CD_2Cl_2: (i) ^{31}P NMR under 22 atm of ^{13}CO at −50 °C, the three species [Pt(CH_3)(^{13}CO){(*R*,*S*)-BINAPHOS}][B{3,5-$(CF_3)_2C_6H_3$}$_4$] (**8a-13C** and **8b-13C**) and [Pt($^{13}COCH_3$)(^{13}CO){(*R*,*S*)-BINAPHOS}][B{3,5-$(CF_3)_2$-C_6H_3}$_4$] (**9-13C**) being shown (in **9-13C**, J_{P-C} is 172 Hz for the phosphite (δ 112.8) and 71 Hz for the phosphine (δ 6.9)); (ii) ^{13}C NMR under 56 atm of ^{13}CO at −50 °C. In the carbonyl region, the sp^2 carbon of the acylplatinum exhibits a peak at δ 215.0 with J_{P-C} = 71 Hz. Next to the large peak of free ^{13}CO, a broad peak is found at δ 182.8 due to the coordinated ^{13}CO. Putting all the observations together, acylplatinum **9** in which acyl is trans to the phosphine is suggested as the new species.

this temperature, the new species exhibited P−C coupling constants in ^{31}P NMR of 172 Hz for the phosphite and 71 Hz for the phosphine (part i of Figure 2). Elevation of the ^{13}CO pressure to 56 atm increased the concentration of the new species. Again at −50 °C, one of the J_{P-C} couplings, 71 Hz, was detected in ^{13}C NMR for the sp^2 carbon of the acetylplatinum at δ 215.0, as can be seen in part ii of Figure 2. In addition, there is a broad peak at δ 182.8 due to the coordinated ^{13}CO. When all the observations are put together, acylplatinum **9** in which acyl is trans to the phosphine is suggested as the new species.

The formation of acylplatinum **9** from **7** is a reversible process. When CO was removed from the sample of part iii of Figure 1 by freeze−thaw cycles, **9** and **8a** disappeared and two new sets of peaks appeared at δ 114

and 24 and at δ 115 and 10.[6] The former set of peaks are attributed to the decarbonylated complex **7**. The latter could not be characterized. When the NMR tube is charged with CO again, the equilibrium between **8a** and **8b** is established and the cycles of events described above can be repeated.

The studies may be summarized as follows. (1) High-pressure NMR showed the appearance of **8b** followed by that of acyl complex **9**. Thus, the cis/trans isomerization from **8a** to **8b** is a faster process than the CO insertion.[7] (2) Considering that the isomerization of **8a** to **8b** is reversible, the increasing content of **8b** compared to **8a** (Figure 1: (i) → (ii) → (iii)) suggests the thermally more stable nature of **8b** than **8a**. The energy difference arises most probably from the stabilization of the coordinated CO in **8b** than in **8a**, as was shown by the IR spectra in our previous study.[4a] The energy gain at the carbonyl−Pt bond in **8b** overcomes the energy loss at the methyl−Pt bond, which is less stable in **8b** than in **8a**. Thus, in **8b**, the methyl was suggested to be more activated for a nucleophilic migration to the carbonyl and the carbonyl is less active toward the electrophilic attack to the methyl. Here, we may say safely that the present study gives no information about the origin of **9**, either/both from **8a** or/and **8b** but that, at least, the **8a** → **8b** isomerization is a faster process than the CO insertion. The chemistry presented here is valid only for the Pt(II)−(*R,S*)-BINAPHOS system. Nevertheless, it is of interest to compare the result with the recent work by Luinstra et al., who showed the cis/trans isomerization was slower than the CO insertion in their alkylpalladium−(phosphine−amine) complexes.[8,9] The difference might be attributed to the metal, either Pt or Pd, or the ligand, phosphine−phosphite or phosphine−amine.

Alternating Copolymerization of Propene with CO Initiated by 1. The palladium-catalyzed alternating copolymerization involves two major steps: namely the propene insertion into acylpalladium **3-I** and the CO insertion into alkylpalladium **5-I**. To investigate the rate-determining step, the reaction rates **3-I** → **5-I** and **5-I** → **3-II** were measured in our previous study.[4a] Unfortunately, however, both rates were close to each other, and the difference was buried in the range of experimental errors. Here in this study, the polymerization process was followed by NMR, with the expectation that the species right before the rate-determining step might be observable. First, the cationic acylpalladium species **3-I** was treated under ambient pressure (propene, 0.5 atm; CO, 0.5 atm). In this case, only alkyl complexes **1**, **5a-I**, and **5b-I** were observed in a 4:4:1 ratio by ^{31}P NMR. No polymeric or oligomeric products were observed by ^{1}H and ^{13}C NMR. The results can be interpreted as follows. (1) The decarbonylation from **3-I** to **1** could not be suppressed under 0.5 atm of CO. (2) The insertion of CO into cyclic alkyl complexes **5-I** does not proceed under these conditions. Next, we examined the same process under high pressure (propene, 3 atm; CO, 20 atm), which was employed for the real copolymerization. Polymer formation was observed by ^{13}C NMR. By ^{31}P NMR, three pairs of peaks were observed in the region of δ 138.3−139.4 (phosphite) and 7.0−7.3 (phosphine) with J_{P-P} = 104−105 Hz (Figure 3). The fact that the chemical shifts and coupling constants resemble those of acyl complexes **3-I** and **3-II** allows us to assign the peaks to **3-I**, **3-II**, **3-III**, ... In addition, peaks observed at δ 140.3 (phosphite) and 12.9 (phosphine) with J_{P-P} = 67 Hz were in the region of and alkyl complexes **5a-I**, **5a-II**, **5a-III**, ... One more set of peaks at δ 131.3 and 25.2 (broad) were unassignable.

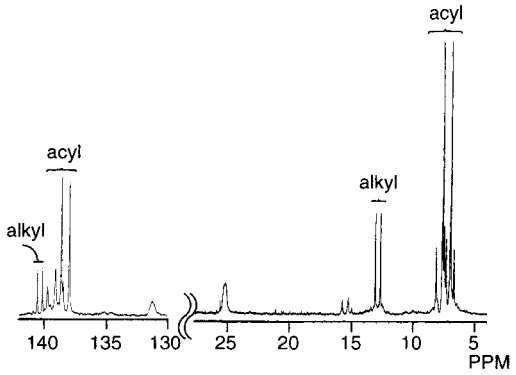


Figure 3. ^{31}P NMR of the copolymerization of propene (3 atm) with CO (20 atm) initiated by palladium complex **3-I** (CD_2Cl_2, 25 °C). Three pairs of peaks are observed in the region of δ 138.3−139.4 (phosphite) and 7.0−7.3 (phosphine) with J_{P-P} = 104−105 Hz, which may be assigned as **3-I**, **3-II**, **3-III**, ... The peaks at δ 140.3 (phosphite) and 12.9 (phosphine) with J_{P-P} = 67 Hz are characterized as alkyl complexes **5a**−**I**, **5a-II**, **5a-III**, ... One more set of peaks at δ 131.3 and 25.2 (broad) are unassignable.

Apparently, the acyl complexes **3-I**, **3-II**, **3-III**, ... (L = CH_3CN, CO) are waiting for the olefin insertion. Thus, it is suggested that either the replacement of CO by propene or the transition state for the propene insertion **ts**(**4**−**5b**) is one of the highest energy barriers to go over. Alkyl complexes **5a-I**, **5a-II**, **5a-III**, ... are another resting state of the catalytic cycle. This implies that the ring opening of cyclic alkyl complex **5a** to open alkyl complex **6b** is another high-barrier step, regardless to the pathway from **5a** to **6b**, either ring opening−isomerization or isomerization−ring opening. Thus, the present observation does not allow us to determine the rate-determining step unambiguously. Nevertheless, it seems that there are two major energy barriers in the catalytic cycle instead of simply just one. The results agree with the comparable activation energies for **3-I** → **5-I** and **5-I** → **3-II** reported in our previous study.

Conclusion

By employing high-pressure NMR techniques, we studied two subjects as described above. Acylplatinum **9**, which was invisible under 1 atm of CO, was detected. The cis/trans isomerization from **8a** to the more stable isomer **8b** is proven to be a faster process than the CO insertion to give **9**. The whole process from **7** to **9** is reversible. For the palladium-catalyzed copolymerization of propene with CO, the existence of at least two major resting states, most probably acylpalladium **3-I**,

(6) ^{31}P NMR spectra for the experiments described in this paragraph are attached as Supporting Information.

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(8) Luinstra, G. A.; Brinkmann, P. H. P. *Organometallics* **1998**, *17*, 5160. See also ref 2e.

(9) With unsymmetrical bisphosphine ligands: van Leeuwen, P. W. N. M.; Roobeek, K. F. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 73. See also ref 2h.

3-II, **3-III**, ... (L = CH_3CN or CO) and alkylpalladium **5a**−**I**, **5a-II**, **5a-III**, ..., was suggested by high-pressure NMR. The results are in sharp contrast to the observation under low pressure of CO; alkyl complexes **1**, **5a-I**, and **5b-I** were the predominant species.

Experimental Section

General Considerations. All NMR experiments were performed with an Oxford Instruments 400 MHz magnet with a Varian Associates Unity 400 system and VNMR version 5.3 software for data collection and analysis and a Varian Associates 10 mm multinuclear broad-band probe: ^{13}C, 100 MHz; ^{1}H, 400 MHz; ^{31}P, 160 MHz. High-pressure NMR was carried out in sapphire tubes. Tetramethylsilane and H_3PO_4 were used as internal and external standards. Dichloromethane, acetonitrile, and CD_2Cl_2 were obtained from Aldrich and purified by distillation under argon after drying over CaH_2. ^{13}CO (99%) was obtained from CIL and propene, and ^{12}CO was obtained from MG Industries (research grade).

Studies on the Reaction of (*SP*-4-3)-[Pt(CH_3)(CH_3CN)-{(*R,S*)-BINAPHOS}][{3,5-$(CF_3)_2C_6H_3$}$_4$B] (7) with CO. As in our previous report, a solution of Pt(CH_3)(Cl){(*R,S*)-BINAPHOS} (0.020 mmol) in dichloromethane (3 mL) and a solution of NaB{3,5-$(CF_3)_2C_6H_3$}$_4$ (0.020 mmol) in acetonitrile (2 mL) were mixed at 25 °C and stirred to form **7**.[4a] After 1 h, the solvents were removed under reduced pressure, and the remaining solids were dissolved in 2.2 mL of CD_2Cl_2. This solution was transferred to a sapphire tube, which was placed in the NMR probe and cooled to −50 °C. It was then taken out of the probe, charged with 22 atm of CO, and placed back into the probe immediately. This was done so that the solution was at 25 °C for a very brief time period and the isomerization could be slowed considerably. At this temperature, the ^{31}P NMR spectra showed the presence of mostly **8a**: δ 122.5 (phosphite, J_{P-P} = 36 Hz, J_{Pt-P} = 6022 Hz), 15.4 (phosphine, J_{Pt-P} = 1564 Hz). There was a trace amount of **8b** present, evident by a peak at δ 148.6 (J_{P-P} = 40 Hz; J_{Pt-P} could not be read). The assignments of **8a** and **8b** were previously reported.[4a] Warming the solution to −25 °C did not change the nature of the species. The solution was warmed to 25 °C and was followed by ^{31}P NMR. Isomerization of **8a** to **8b** resulted in increasing the concentration of **8b** without showing any intermediate species. **8b**: δ 148.6 (phosphite, J_{P-P} = 40 Hz, J_{Pt-P} 3029 Hz), 15.0 (phosphine, J_{Pt-P} 3265 Hz). After about 4 h, a third species, which will be assigned as **9** in the next paragraph, appeared at δ 112.8 (phosphite) and 6.9 (phosphine) with J_{P-P} = 50 Hz. At this point, the pressure was released. Disappearance of **8a** was observed and two new sets of peaks appeared at δ 114 and 24 and at δ 115 and 10. The former can be assigned as the decarbonylated complex **7**, but the latter was unassignable. The concentration of both sets of peaks increased on repeated freeze−thaw degassing cycles. When the NMR tube is charged with CO again, the equilibrium between **8a** and **8b** is established and the cycles of events described above can be repeated.

Characterization of (*SP*-4-4)-[Pt($^{13}COCH_3$)(^{13}CO){(*R,S*)-BINAPHOS}][{3,5-$(CF_3)_2C_6H_3$}$_4$B] (9-13C). Methylplatinum **7** was prepared as mentioned above and dissolved in 2.2 mL of CD_2Cl_2. In a sapphire NMR tube, the solution was charged with 21 atm of ^{13}CO at 25 °C. The peaks corresponding to **8a-13C**, **8b-13C**, and **9-13C** (not yet characterized) were detected by ^{31}P NMR. Differing from nonlabeled peaks, the phosphite peak of **8a-13C** and the phosphine peak of **8b-13C** were broadened due to the P−C couplings. Probably, the exchange between the coordinated ^{13}CO and free ^{13}CO caused the broadenings. Although the full characterization of **9-13C** should wait for the next step, the existence of an acylpalladium species was suggested by the ^{13}C NMR peak at δ 215.0 (J_{P-C} = 71 Hz) at this moment. The peaks were sharpened at −50 °C, and the couplings were read as J_{P-C} = 162 Hz for the phosphite of **8a-13C** and 132 Hz for the phosphine of **8b-13C**.

The sample was warmed again to 25 °C, and the ^{13}CO pressure was raised to 58 atm. The sample was kept at 25 °C for 12 h. To get a better resolution, the solution was then cooled to −50 °C in the NMR probe. Finally, ^{31}P and ^{13}C NMR of **9-13C** clearly showed the following peaks which enabled the characterization. **9-13C**: ^{31}P NMR δ 112.8 (phosphite, J_{P-P} = 49 Hz, J_{P-C} = 172 Hz, J_{Pt-P} = 6714 Hz) and 6.9 (phosphine, J_{P-C} = 71 Hz, J_{Pt-P} = 1342 Hz); ^{13}C NMR δ 215.0 (sp^2 carbon of the acetyl−Pt, J_{P-C} = 71 Hz, J_{Pt-C} = 509 Hz), 182.8 (broad, the coordinated ^{13}CO to Pt). The fact that J_{P-C} = 71 Hz was observed for the acyl carbon and the phosphine suggests that these two groups are trans to each other.

Alternating Copolymerization of Propene with CO Initiated by (*SP*-4-3)-[Pd($COCH_3$)(CH_3CN){(*R,S*)-BINAPHOS}][{3,5-$(CF_3)_2C_6H_3$}$_4$B] (3-I). Methylpalladium **1** was prepared from Pd(CH_3)(Cl){(*R,S*)-BINAPHOS} (0.020 mmol) and NaB{3,5-$(CF_3)_2C_6H_3$}$_4$ (0.020 mmol) and then transformed into cationic acylpalladium species **3-I** in $CDCl_3$ (1.0 mL) by treatment with CO (1 atm).[4a] The atmosphere was replaced by a mixture of propene (0.5 atm) and CO (0.5 atm) and kept for 12 h at 25 °C. Only alkyl complexes **1**, **5a-I**, and **5b-I** were observed at δ 143.0 and 13.1 (J_{P-P} = 64 Hz), δ 141.0 and 13.5 (J_{P-P} = 66 Hz), and δ 150.3 and 30.3 (J_{P-P} = 66 Hz), respectively, by ^{31}P NMR (see ref 4a for the full characterization of these species). No polymeric or oligomeric products were observed by ^{1}H and ^{13}C NMR. Next, **3-I** (0.020 mmol) in CD_2Cl_2 (1.5 mL) was treated under pressures of propene (3 atm) and CO (21 atm) at 25 °C. After a short time, three pairs of peaks were observed by ^{31}P NMR at δ 138.3 and 7.3 (J_{P-P} = 104 Hz), δ 138.8 and 7.0 (J_{P-P} = 104), and δ 139.4 and 7.8 (J_{P-P} = 105), which resemble the reported values of acyl complexes **3-I** (when X = CH_3CN: δ 133.8, 10.3, J_{P-P} = 113 Hz, in $CDCl_3$) and **3-II** (when X = CH_3CN: δ 137.0, 9.7, J_{P-P} = 108 Hz, in $CDCl_3$). In addition, peaks were observed at δ 140.3 and 12.9 (J_{P-P} = 67 Hz), which correspond to the reported data for alkyl complex **5a-I** (δ 142.4, 13.0, J_{P-P} = 66 Hz, in $CDCl_3$) and **5a-II** (δ 142.0, 13.1, J_{P-P} = 67 Hz, in $CDCl_3$). A set of peaks at δ 25.2 and 131.3 (broad) was unassignable.

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Supporting Information Available: ^{31}P NMR spectra of the sample in part iii of Figure 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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