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(CH₃)(CO)(L¹)][BAr₄] (**8a**; L¹ = (*R*,*S*)-BINAPHOS; Ar = 3,5-(CF₃)₂C₆H₃) 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}-L¹-catalyzed copolymerization of propene and CO, there exist at least two major resting states, most probably acylpalladium, (SP-4-3)-[Pd(COR)(L²)(L¹)][BAr₄] (**3**; L² = CH₃CN, CO), and alkylpalladium, [Pd{CH₂CH(CH₃)C(=O)R}(L¹)][BAr₄] (**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 experimental² and theoretical approaches.³

We previously reported a cationic Pd(II) complex with the unsymmetrical chiral phosphine–phosphite (R,S)-

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The work was then focused on the reaction pathways between the observed complexes, such as $1 \rightarrow 3$ -I and **3-I** \rightarrow **5-I** in Scheme 1. The platinum complex [Pt(CH₃)-(CH₃CN){(*R*,*S*)-BINAPHOS}][B{3,5-(CF₃)₂C₆H₃}] (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 $\mathbf{1} \rightarrow \mathbf{2a} \rightarrow \mathbf{2b} \rightarrow \mathbf{3}$ -I was proposed. Theoretical approaches cleared the $\mathbf{3}$ -I $\rightarrow \mathbf{5}$ -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.



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 ³¹P 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 ¹³CO. Broad peaks were detected by ³¹P 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 ¹³C 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 ³¹P NMR: (i) at -50 °C and 22 atm of CO pressure, alkylplatinum **8a** being formed via immediate replacement of CH₃CN of **7** by CO; (ii) after the sample in (i) was warmed to 25 °C, the *cis*-*trans* isomerization **8a** \rightarrow **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 со CO (22 atm) (22 atm) BAr₄ 25 °C 7 8a 8a со (22 atm) CO 25 °C 4 h 8b 9



Figure 2. Reaction of alkylplatinum **7** with CO carried out using ¹³CO in CD₂Cl₂: (i) ³¹P NMR under 22 atm of ¹³CO at -50 °C, the three species [Pt(CH₃)(¹³CO){(*R*,*S*)-BINAPHOS}][B{3,5-(CF₃)₂C₆H₃}] (**8a-13C** and **8b-13C**) and [Pt(¹³COCH₃)(¹³CO){(*R*,*S*)-BINAPHOS}][B{3,5-(CF₃)₂-C₆H₃}] (**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) ¹³C NMR under 56 atm of ¹³CO at -50 °C. In the carbonyl region, the sp² carbon of the acylplatinum exhibits a peak at δ 215.0 with *J*_{P-C} = 71 Hz. Next to the large peak of free ¹³CO, a broad peak is found at δ 182.8 due to the coordinated ¹³CO. 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 ³¹P NMR of 172 Hz for the phosphite and 71 Hz for the phosphine (part i of Figure 2). Elevation of the ¹³CO 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 ¹³C NMR for the sp² 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 ¹³CO. 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) Highpressure 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) \rightarrow (ii) \rightarrow (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 $8a \rightarrow 8b$ 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 $3 \cdot I \rightarrow 5 \cdot I$ and **5-I** \rightarrow **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 ³¹P NMR. No polymeric or oligomeric products were observed by ¹H and ¹³C 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



Figure 3. ³¹P NMR of the copolymerization of propene (3 atm) with CO (20 atm) initiated by palladium complex **3-I** (CD₂Cl₂, 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.

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 ¹³C NMR. By ³¹P 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.

Apparently, the acyl complexes 3-I, 3-III, 3-III, ... (L = CH₃CN, 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 openingisomerization 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 \rightarrow 5-I and 5-I \rightarrow 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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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: ¹³C, 100 MHz; ¹H, 400 MHz; ³¹P, 160 MHz. High-pressure NMR was carried out in sapphire tubes. Tetramethylsilane and H₃PO₄ were used as internal and external standards. Dichloromethane, acetonitrile, and CD₂Cl₂ were obtained from Aldrich and purified by distillation under argon after drying over CaH₂. ¹³CO (99%) was obtained from CIL and propene, and ¹²CO was obtained from MG Industries (research grade).

Studies on the Reaction of (SP-4-3)-[Pt(CH₃)(CH₃CN)-{(*R,S*)-BINAPHOS}][{3,5-(CF₃)₂C₆H₃}₄B] (7) with CO. As in our previous report, a solution of Pt(CH₃)(Cl){(R,S)-BINA-PHOS} (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 CD₂Cl₂. 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 ³¹P 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 ³¹P 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 $(\hat{SP}$ -4-4)-[Pt(¹³COCH₃)(¹³CO){(*R*,*S*)-BINAPHOS}][{3,5-(CF₃)₂C₆H₃}₄B] (9-13C). Methylplatinum 7 was prepared as mentioned above and dissolved in 2.2 mL of CD₂Cl₂. In a sapphire NMR tube, the solution was charged

with 21 atm of ¹³CO at 25 °C. The peaks corresponding to **8a-13C**, **8b-13C**, and **9-13C** (not yet characterized) were detected by ³¹P 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 ¹³CO and free ¹³CO 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 ¹³C 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 ¹³CO 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, ³¹P and ¹³C NMR of **9-13C** clearly showed the following peaks which enabled the characterization. **9-13C**: ³¹P 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); ¹³C NMR δ 215.0 (sp² carbon of the acetyl–Pt, $J_{P-C} = 71$ Hz, $J_{Pt-C} = 509$ Hz), 182.8 (broad, the coordinated ¹³CO 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(COCH₃)(CH₃CN){(R,S)-BINA-**PHOS**}][{3,5-(**CF**₃)₂**C**₆**H**₃}₄**B**] (3-I). Methylpalladium 1 was prepared from Pd(CH₃)(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 CDCl₃ (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 $(J_{\rm P-P} = 66 \text{ Hz})$, and δ 150.3 and 30.3 $(J_{\rm P-P} = 66 \text{ Hz})$, respectively, by ³¹P NMR (see ref 4a for the full characterization of these species). No polymeric or oligomeric products were observed by ¹H and ¹³C NMR. Next, 3-I (0.020 mmol) in CD₂-Cl₂ (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 ³¹P 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 CDCl₃) and **3-II** (when $X = CH_3CN$: δ 137.0, 9.7, J_{P-P} = 108 Hz, in CDCl₃). 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 CDCl₃) and **5a-II** (δ 142.0, 13.1, $J_{P-P} = 67$ Hz, in CDCl₃). A set of peaks at δ 25.2 and 131.3 (broad) was unassignable.

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Supporting Information Available: ³¹P 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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