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Alternating Copolymerization of Fluoroalkenes with Carbon Monoxide

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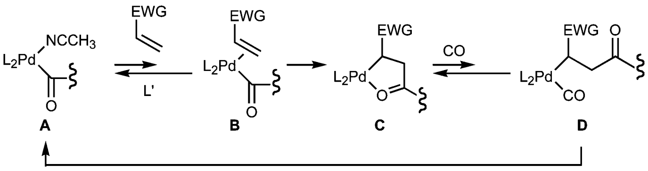
Abstract: The palladium-catalyzed alternating copolymerization of fluoroalkenes, represented as $CH_2{=}CH{-}CH_2{-}C_nF_{2n+1}$, with CO was performed using (*R*,*S*)-BINAPHOS (**2e**) as a ligand. The $CH_2{-}C_nF_{2n+1}$ group is the most electronegative substituent ever reported for the copolymerization (Taft's σ^* value of 0.90 for CH_2CF_3). The copolymer obtained from $CH_2{=}CH{-}CH_2{-}C_8F_{17}$ (**1a**) existed as a mixture of polyspiroketal and polyketone, while that from $CH_2{=}CH{-}CH_2{-}C_4F_9$ (**1b**) was a pure polyspiroketal, as was revealed by infrared and ^{13}C−CP/MAS NMR spectroscopies. The terminal structure of the polymer from **1b** was confirmed by MALDI-TOF MS spectrometry. Detailed NMR studies suggested that the much higher reactivity with (*R*,*S*)-BINAPHOS (**2e**) than that with the conventional ligand DPPP (**2a**) can be attributed to the unique 1,2-insertion of the fluoroalkene into acylpalladium species. The existence of an electronegative substituent on the α-carbon of the palladium center is successfully avoided in the 1,2-insertion mechanism.

Introduction

Electron-deficient olefins, such as methyl acrylate,[1,2] vinyl acetate,[3,4] and vinyl chloride,[5] are reported to be unfavorable for the alternating copolymerization with carbon monoxide. As shown in Scheme 1, the copolymerization would proceed via olefin coordination to acylpalladium (**A**→**B**), intramolecular olefin insertion (**B**→**C**), carbon monoxide coordination (**C**→**D**), and intramolecular CO insertion (**D**→**A**). In this scheme, there are several disadvantages of the olefins bearing electron-withdrawing groups. The coordination of electron-deficient olefins (**A**→**B**) is less favorable as compared to ethene or simple 1-alkenes.[6−9] Nevertheless, for acetylpalladium complexes, the olefin insertion (**B**→**C**) was reported to proceed for X = COOMe,[1,2] $OCOCH_3$,[3,4,7] and Cl.[5,8,10,11] The insertion undergoes via the predominant 2,1-insertion in all of the reported examples. Alkylpalladium **C** thus produced has an electron-withdrawing group on the α-carbon of palladium. The electron-withdrawing group in **C** was reported to cause the stronger five-membered chelation of the carbonyl oxygen to the metal center.[5] This chelation was anticipated to obstruct the subsequent CO insertion, which requires the replacement of the intramolecular ketone-coordination by the intermolecular CO-coordination (**C**→**D**). In addition, the electronegative substituent on the α-carbon in **D** should retard the subsequent CO insertion to the metal−carbon bond (**D**→**A**) by lowering the nucleophilicity of the migrating α-carbon atom.[5,12−15] For example, in a carbonyl complex $L_2Pd(CO)R$ where L_2 is a bidentate sp^2-nitrogen ligand, the CO insertion takes place when R is CH_2Cl[12] or CH_2-$OCOCH_3$,[7] but does not undergo when R is $CHCl_2$ or *n*-C_3F_7[12] (L_2 is dppp for the last example). As a result, all of the attempted examples for the alternating copolymerization of electron-deficient olefins with CO ended up at the stage of complex **C** when started from an acetylpalladium corresponding to **A**.

Scheme 1. Ideal Catalytic Cycle of the Alternating Copolymerization of Electron-Deficient Olefins and Carbon Monoxide



EWG = COOMe, OAc, or Cl

In contrast, palladium-catalyzed copolymerization with CO is reported for monomers represented as $CH_2{=}CH{-}EWG$,

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10.1021/ja055862k CCC: $33.50

Scheme 2. The Alternating Copolymerization of Olefins and Carbon Monoxide Catalyzed by the Palladium Complexes Bearing a Bidentate Ligand

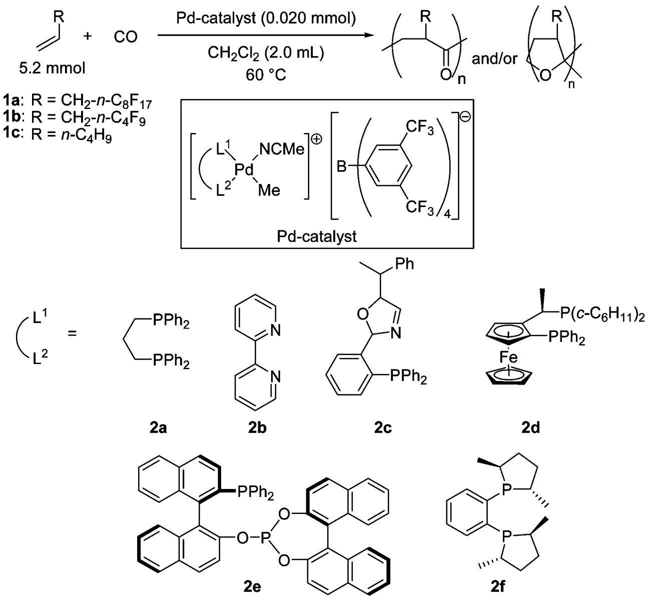

Table 1. The Alternating Copolymerization of Fluoroalkenes **1a**, **1b**, or 1-Hexene (**1c**) with CO[a]

run	fluoroalkene (R=)	ligand L^1–L^2	P_{CO} (MPa)	time	yield[b] (%)
1	CH_2–*n*-C_8F_{17} (**1a**)	**2a**	3.0	24 h	3
2	CH_2–*n*-C_8F_{17} (**1a**)	**2a**	8.0	24 h	3
3	CH_2–*n*-C_8F_{17} (**1a**)	**2b**	3.0	17 h	2
4	CH_2–*n*-C_8F_{17} (**1a**)	**2c**	3.0	40 h	0
5	CH_2–*n*-C_8F_{17} (**1a**)	**2d**	3.0	24 h	5
6	CH_2–*n*-C_8F_{17} (**1a**)	**2e**	3.0	24 h	27
7	CH_2–*n*-C_8F_{17} (**1a**)	**2e**	5.0	24 h	49
8	CH_2–*n*-C_8F_{17} (**1a**)	**2e**	8.0	24 h	54
9	CH_2–*n*-C_8F_{17} (**1a**)	**2e**	8.0	84 h	81[c]
10	CH_2–*n*-C_8F_{17} (**1a**)	**2f**	3.0	24 h	8
11	CH_2–*n*-C_8F_{17} (**1a**)	**2f**	5.0	24 h	27[d]
12	CH_2–*n*-C_8F_{17} (**1a**)	**2f**	8.0	24 h	34[d]
13	CH_2–*n*-C_4F_9 (**1b**)	**2e**	8.0	84 h	27[e]
14	*n*-C_4H_9 (**1c**)	**2e**	8.0	3 h	71
15	*n*-C_4H_9 (**1c**)	**2e**	2.0	45 min	40[f]
16	*n*-C_4H_9 (**1c**)	**2e**	5.0	45 min	58[f]

[a] Pd (0.020 mmol), alkene (5.2 mmol) in CH_2Cl_2 (2 mL) at 60 °C (palladium complexes were prepared by the reaction of (cod)PdMeCl with ligands **2a**–**2f** in toluene and then with Na[B(3,5-$(CF_3)_2C_6H_3)_4$] in MeCN/CH_2Cl_2; the resulting cationic palladium complex and alkene **1** were dissolved in CH_2Cl_2, transferred into an autoclave, and treated with CO at 60 °C). [b] Calculated by assuming the polymeric materials were poly(alkene-*alt*-CO). [c] 4 mL of CH_2Cl_2 was used for the reaction. [d] 2.6 mmol of alkene was used for the reaction. [e] Low yield may be due to the impurity of alkene. [f] 6 mmol of alkene was used for the reaction.

where EWG is CH_2CH_2OH,[16] CH_2COOH,[16] CH_2OR,[17] $CH_2C_6F_5$,[18] and $CH_2CH_2C_4F_9$.[19] It is of interest to compare the substituents based on their electronegativity. As an index to compare the electronegativity of substituents, Taft's σ^* value may be referred.[20] When the monomers did not copolymerize with CO, Taft's σ^* values of the substituents were 2.26 (−COOEt), 2.51 (−$OCOCH_3$), and 2.94 (−Cl). On the other hand, the values were 0.21 (−CH_2CH_2OH), 0.82 (−CH_2COOEt), 0.58 (−CH_2-OEt), and 0.32 (−$CH_2CH_2CF_3$) for the substituents that were applicable to the copolymerization.

Here in this paper, we report the alternating copolymerization of fluoroalkenes represented as $CH_2{=}CH{-}CH_2{-}C_nF_{2n+1}$ with CO. Taft's σ^* value of 0.90 for $-CH_2CF_3$ is the highest value ever reported for substituents of olefins that copolymerize with CO using palladium catalysts.[21] By using the Pd−(*R*,*S*)-BINAPHOS (**2e**) system as a catalyst, the alternating copolymer of $CH_2{=}CH{-}CH_2{-}C_8F_{17}$ and CO was obtained in up to 81% yield. The use of DPPP (=1,3-bis(diphenylphosphino)propane, **2a**), instead of **2e**, resulted in a much lower yield. The higher reactivity with **2e** is attributed to the unique 1,2-insertion of the fluoroalkene into acylpalladium species, producing Pd−CH_2-CH(EWG)− instead of Pd−CH(EWG)−CH_2−.[22]

Results and Discussion

The Reaction of $CH_2{=}CH{-}CH_2{-}$Rf with CO Catalyzed by Various Pd-Complexes. First, the palladium-catalyzed reaction of $CH_2{=}CHCH_2{-}$*n*-C_nF_{2n+1} with CO was carried out using several ligands under various conditions (Scheme 2). Under CO pressure, fluoroalkenes $CH_2{=}CHCH_2{-}$*n*-C_8F_{17} (**1a**) and $CH_2{=}CHCH_2{-}$*n*-C_4F_9 (**1b**) were treated with cationic palladium complexes represented as $[Pd(CH_3)(NCCH_3)(\mathbf{2})]^+[BAr^F]^-$, where $[BAr^F]^-$ is $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$. The results are summarized in Table 1. The polymer obtained from **1a** (runs 1−12 in Table 1) was not soluble in any of the common organic solvents. Thus, the materials obtained in Table 1 were characterized by solid-state IR and solid-state NMR spectroscopies and MALDI-TOF mass spectrometry, as will be discussed in the next section. It should be noted that the copolymer forms not only a polyketone structure but also a spiroketal structure, a structural isomer of the polyketone, depending on the substituents and the reprecipitation conditions (Scheme 2).[16,19]

As is shown in run 1, the weight of the residue after evaporation of the solvent and monomer corresponded to 3% yield of the polyketone using the conventional ligand 1,3-bis-(diphenylphosphino)propane (DPPP, **2a**). Elevation of the CO pressure did not affect the result (run 2). Only negligible amounts of nonvolatiles were given using nitrogen-based ligands **2b** and **2c**, both of which are effective for styrene/CO copolymerization (runs 3 and 4).[23,24] In contrast, the yield was slightly improved with **2d** (JOSIPHOS), which provides isotactic poly-(propene-*alt*-CO), effectively (run 5).[25] A higher yield of 27% was achieved with **2e** (BINAPHOS) (run 6). The yield was improved at the higher CO pressure (runs 6−8), and the highest yield of 81% was achieved under CO pressure of 8.0 MPa in 84 h (run 9). A similar pressure effect was observed with MeDuPHOS (**2f**), which was previously reported as an effective ligand for polymerization of $CH_2{=}CHCH_2C_6F_5$,[18] although the yields were slightly lower than those with **2e** (runs 10−12). Fluoroalkene $CH_2{=}CHCH_2$-*n*-C_4F_9 (**1b**) bearing a shorter fluoroalkyl-chain was similarly copolymerized with CO (run

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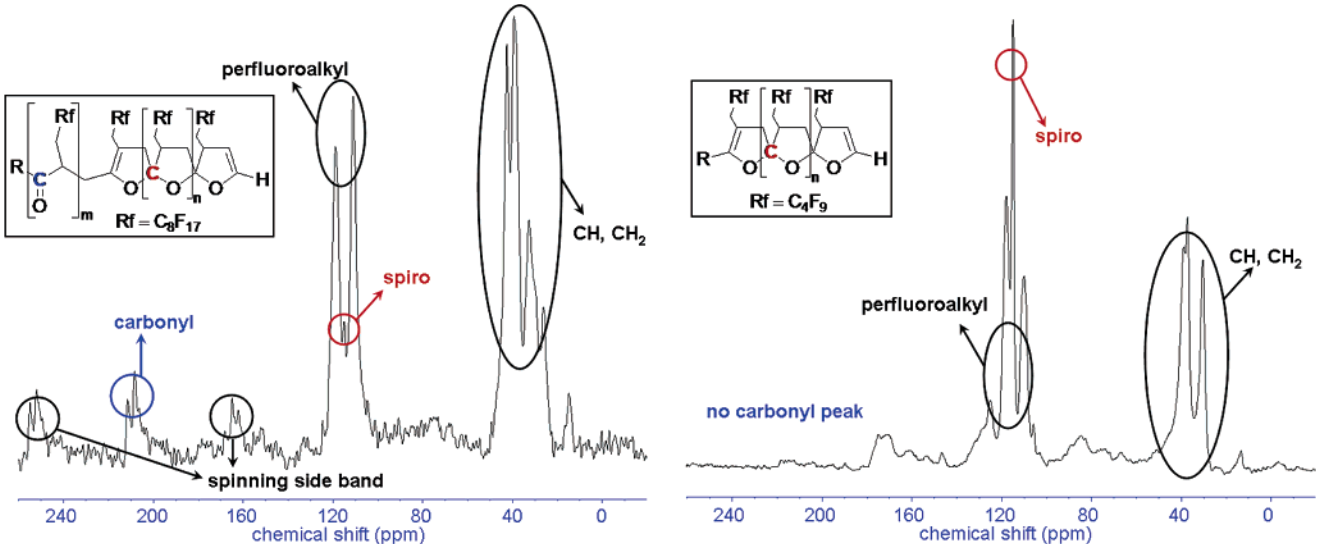

Figure 1. ^{13}C CP/MAS spectra of the polymers obtained from **1a** (run 9 in Table 1, left) and from **1b** (run 13 in Table 1, right).

13). It should be noted that the fluoroalkenes **1a** and **1b** are much less active than simple aliphatic 1-alkenes. As is shown in runs 14−16, 1-hexene (**1c**) copolymerizes with CO in a much shorter time of 45 min otherwise under the same conditions.

Characterization of the Polymeric Products. The materials obtained in Table 1 were characterized by IR and NMR spectroscopies, MALDI-TOF mass spectrometry and thermal analysis. The IR spectrum of the polymer from **1a** (Table 1, run 9, KBr pellet) showed a weak carbonyl vibration at 1718 cm^{-1}, suggesting that the copolymer is in a polyketone form or is a mixture of polyketone and polyspiroketal. Heating the copolymer at 200 °C for 10 min led to no change of IR spectrum. On the other hand, the IR spectrum of polymeric material obtained from **1b** (Table 1, run 13) showed no carbonyl vibration, indicating that the material has a complete spiroketal form. The melting point of the polymer obtained in run 9 was determined by DSC analysis to be 182−183 °C.[26] Above the melting point, loss of weight (decomposition) of the polymer started as determined by TGA.[26] It is notable that the material obtained in run 2 also exhibited a carbonyl absorption at 1716 cm^{-1} but it melted at 89−94 °C, at much lower temperature. Either higher molecular weight or higher stereoregularity for the polymer in run 9 is implied.

The low solubility of these polymers in common organic solvents, unlike the reported polymer made from CO and $CH_2{=}CHCH_2C_6F_5$,[18] prevented us from analysis of their solution state. Thus, the ^{13}C CP/MAS NMR spectra were recorded for the products obtained at runs 9 and 13 (Figure 1). The spectrum of copolymer from **1a** exhibited peaks at the carbonyl region accompanied with spinning sidebands, which were confirmed by changing rotational frequency. A peak at δ 116 overlapped with the carbons of the perfluoroalkyl group should be assigned to the quaternary carbon of the spiroketal structure. In sharp contrast, exclusive formation of the spiroketal is manifested for the copolymer obtained from **1b** by the absence of the carbonyl carbon and by the existence of a large peak of the spiroketal quaternary center. The difference between the copolymers from **1a** and that from **1b** may be explained in that the longer perfluoroalkyl group caused the aggregation of fluorous groups overcoming the demand by the main-chain to form the spiroketal structure.[19] However, there might be even further factors that control the ratio of spiroketal and ketone structures. For example, Sen reported that the alternating copolymer made from CO and $CH_2{=}CHCH_2C_6F_5$ was a pure polyketone, while that from $CH_2{=}CHCH_2C_6H_4{-}4{-}CF_3$ was a pure spiroketal.[18] Currently, no clear explanation for their difference has been given.

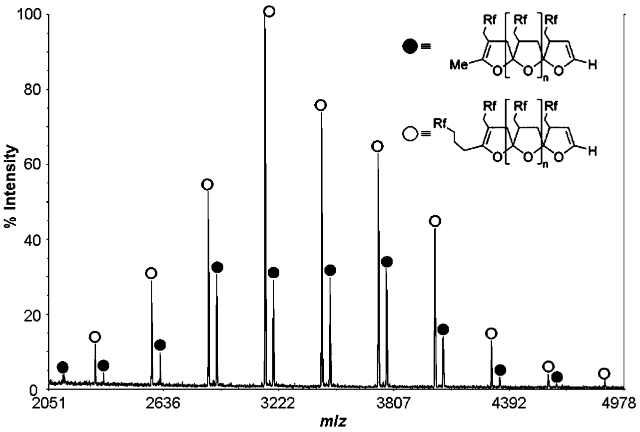

Figure 2. MALDI-TOF mass spectrum of poly(**1b**-*alt*-CO) obtained in run 13 of Table 1. Open circles (○) describe a series of $m/z = 559 + 288 \times n$ ($n = 6{-}15$). Solid circles (●) describe a series of $m/z = 314 + 288 \times n$ ($n = 6{-}15$). Both estimated structures are drawn at the top right ($\mathrm{Rf} = n\text{-}C_4F_9$).

The higher solubility of the copolymer from **1b** allowed us subject the material to MALDI-TOF mass spectrometry. As is shown in Figure 2, there were two series of polymers whose repeating units were all 288 corresponding to the unit $-CH_2-CH(CH_2C_4F_9)-C(=O)-$. The peak-series with lower intensity can be characterized as poly(spiroketal) initiated by the CO insertion to the original methylpalladium complex resulting in the formation of two dihydrofuran rings at the head and end groups. The peak-series with the higher intensity is assigned as poly(spiroketal) initiated by the olefin insertion to a Pd−H bond. The generation of these two series of polymers may be explained by the mechanism shown in Scheme 3. The catalyst precursor, a cationic methylpalladium complex $[Pd(CH_3)(NCCH_3)(\mathbf{2e})]^+$-

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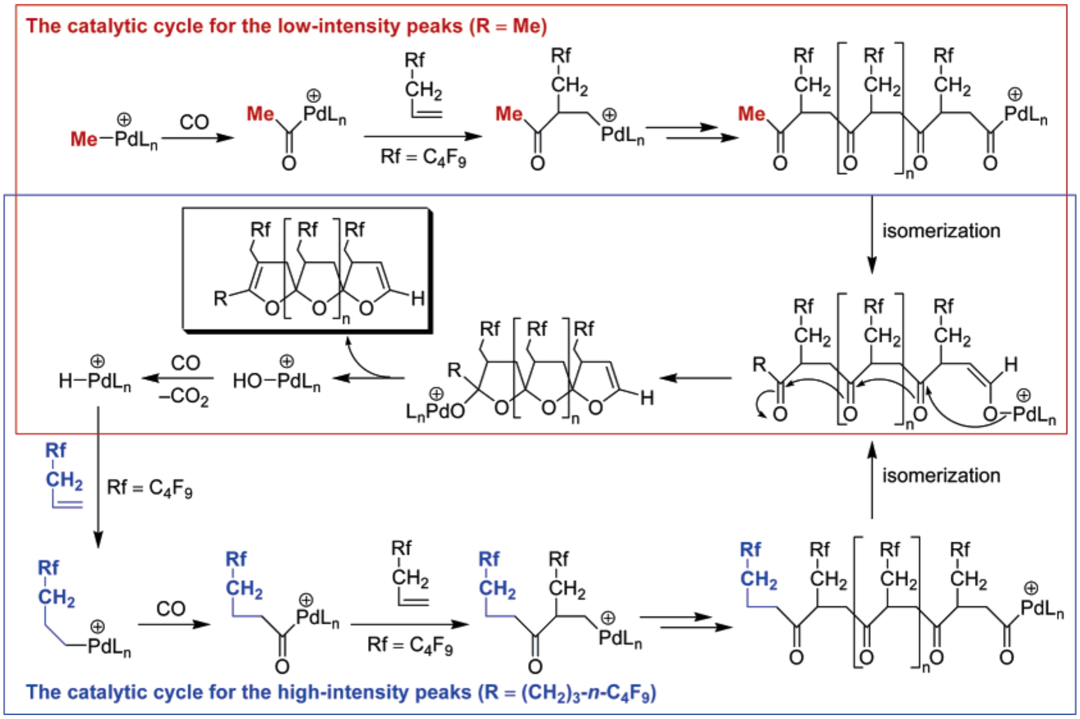
(26) See the Supporting Information.

Scheme 3. A Possible Mechanism for the Chain Propagation and Chain Transfer, Consistent with the Results of the MALDI-TOF Mass Spectrum



$[BAr^F]^-$, reacts with CO to form the corresponding acylpalladium complex, and then the insertion of the olefin into the acyl–palladium bond affords the alkyl complex. After several chain propagation cycles, the acylpalladium complex may isomerize to a palladium enolate by a hydride migration. Nucleophilic attack of the enolate oxygen atom to the neighboring carbonyl group leads to the tandem acetalization to form the spiroketal skeleton. Elimination of hydroxide gives the first series of polymer, which was detected with the lower intensities in MALDI-TOF mass spectra. The generated palladium hydroxide may be reduced to form a hydridopalladium complex, possibly via the hydroxide migration to the coordinated carbonyl to form a hydroxycarbonylpalladium and followed by a β-hydride elimination producing carbon dioxide.[27]

NMR Studies on the Reaction of Acetylpalladium with $CH_2{=}CHCH_2C_8F_{17}$ (1a). To clarify the polymerization mechanism, the reaction of acetylpalladium $[CH_3C({=}O)Pd(NCMe)(\mathbf{2})]^+[BAr^F]^-$ with $CH_2{=}CHCH_2C_8F_{17}$ (**1a**) in the absence of CO was monitored by NMR spectroscopy using DPPP (**2a**), BINAPHOS (**2e**), or MeDuPHOS (**2f**) as a ligand (Scheme 4). Characterization of the alkyl complexes **3**, which were generated by mixing acetylpalladium complexes with 10 equiv of **1a** at 0 °C, was performed by ^1H, ^{13}C, ^{19}F, and ^{31}P NMR experiments and 2D NMR techniques at 0 °C. In the case of using ligand **2a**, alkyl complex **3a**(2,1) was observed as a single product via the 2,1-insertion of **1a**. In contrast, ^{31}P NMR spectra of the alkyl complex bearing **2e** showed six pairs of doublets (six doublets for phosphine and six doublets for phosphite); three pairs of them were detected as separated peaks, and the other three pairs were overlapping each other. The ratio of the six pairs was 54%, 11%, 8% for the separated three pairs and 27% for the sum of the three overlapped pairs. The major two pairs of doublets were assigned to isomers of the 1,2-adducts; these are **3e**(1,2)OP-*trans*-CO (for the peak of 54%) and **3e**(1,2)OP-*cis*-CO (for the peak of 11%) by ^{31}P NMR[22] (OP-*trans*-CO and OP-*cis*-CO explains the stereochemistry between phosphite moiety and the carbonyl ligand). The structure of the major species **3e**(1,2)-OP-*trans*-CO was further confirmed by 2D-NMR technique (see Experimental Section for details). The other minor peaks were not fully characterized, but, most probably, they are either 2,1-complexes or diastereomers of **3e**(1,2)OP-*trans*-CO or **3e**(1,2)-OP-*cis*-CO due to the opposite configuration at the α-position of the CH_2Rf group. Using MeDuPHOS (**2f**), the corresponding acetylpalladium complex was not quantitatively converted to the corresponding alkyl complex.[28]

Because the NMR experiments were carried out in the absence of CO pressure, the subsequent CO-insertion did not occur. Instead, appearance of α,β-unsaturated ketones was detected as a result of the β-hydride elimination from **3**. After 144 h, $CH_2{=}C(COCH_3)CH_2C_8F_{17}$ (**4**) and its reduced compound **4′** were produced with **2a**.[29] On the other hand, with **2e**, a mixture of $CH_3COCH{=}CHCH_2C_8F_{17}$ (**5**) and **4′** (**5**/**4′** = 82/18, estimated by ^1H NMR spectra) was given accompanied by a trace amount of **4** in 14 days at room temperature. The total yield of **5** and **4′** was 85% when the acetylpalladium $[CH_3C({=}O)Pd(NCMe)(\mathbf{2e})]^+[BAr^F]^-$ was treated with an equimolar amount of **1a**. Thus, it is further confirmed that the **1a**

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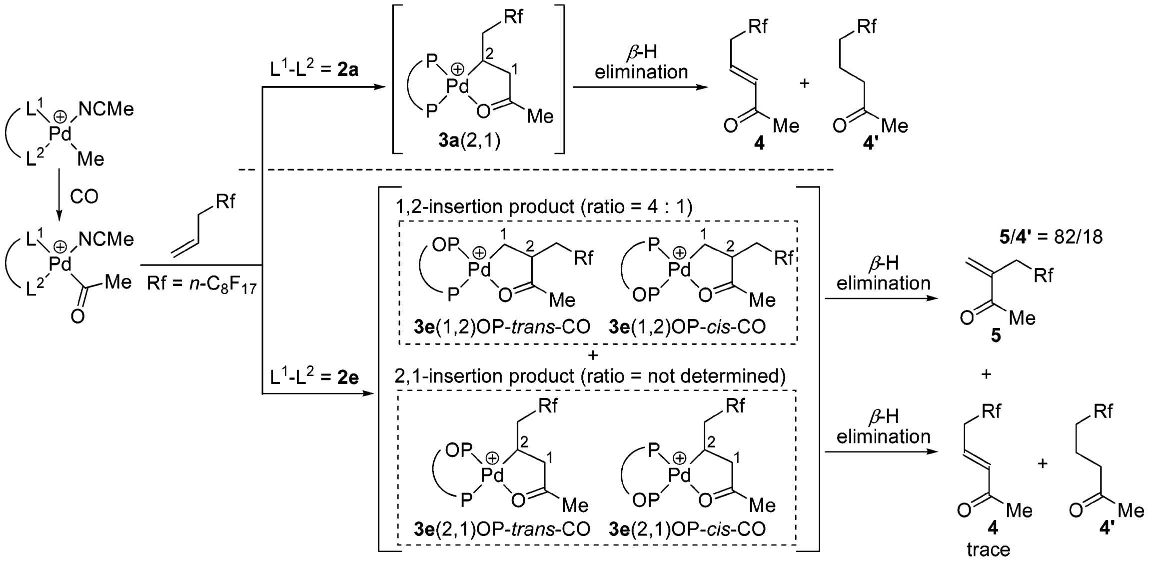
(27) For the platinum complex, the reaction from metal hydroxide to hydride via CO insertion and β-hydrogen elimination was suggested. Torresan, I.; Michelin, R. A.; Marsella, A.; Zanardo, A.; Pinna, F.; Strukul, G. *Organometallics* **1991**, *10*, 623–631. For the palladium complex, an insertion reaction of CO to hydroxide complex to form the corresponding hydroxycarbonylpalladium complex by using a PCP pincer-type ligand was reported. Campora, J.; Palma, P.; del Rio, D.; Alvarez, E. *Organometallics* **2004**, *23*, 1652–1655.

(28) Before consumption of the added 1equivalent of fluoroalkene **1a**, the acetylpalladium complex completely disappeared accompanied by a new unidentified peak (δ_P 108.4)

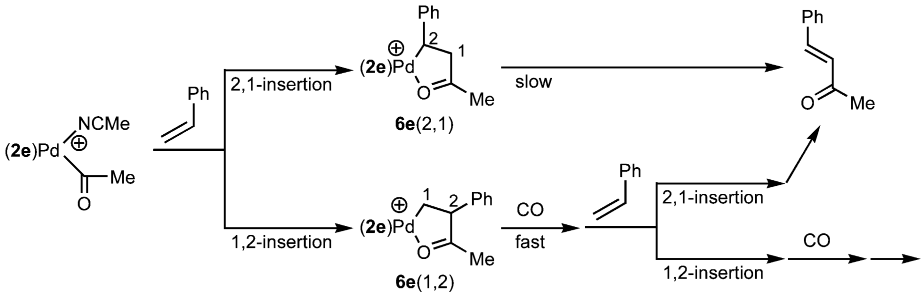
(29) Disproportionation reaction of alkylpalladium complexes to form both β-hydride eliminated product and reduced product was reported. Albeniz, A. C.; Espinet, P.; Lopez-Fernandez, R. *Organometallics* **2003**, *22*, 4206–4212.

Scheme 4. The Reactions of Acetylpalladium Complexes **2** with 1 equiv of $CH_2{=}CHCH_2C_8F_{17}$ (**1a**)[a]



[a] Counteranions (BAr^F) are omitted for clarity.

Scheme 5. Characteristic 1,2-Insertion of Styrene into Acetylpalladium Complex Bearing a BINAPHOS Ligand



insertion exclusively takes place via 2,1-insertion with **2a**. In sharp contrast, it is indicated that the **1a** insertion proceeds via both 1,2- and 2,1-fashion with **2e**, the 1,2-insertion being the major pathway. Using **2f** as a ligand, a mixture of **5** and **4** was given in a ratio of 85:15, suggesting the preferential 1,2-insertion similarly to the results with **2e**.

The Factors That Enabled the 1a/CO Copolymerization. As mentioned above, the **1a**/CO copolymerization proceeded smoothly with **2e** and the unique 1,2-insertion of **1a** to acylpalladium species was detected with **2e**. Here, we will discuss the results in relation to our previous studies. We reported the selective 1,2-insertion of styrene to acyl complex $[CH_3C({=}O)Pd(NCMe)(\mathbf{2e})]^+[BAr^F]^-$ (Scheme 5).[22] The palladium-catalyzed styrene/CO copolymerization usually requires the use of bidentate sp^2-nitrogen ligands, and ligand **2e** is the only exception of bidentate phosphorus ligands in terms of its effectiveness for the styrene/CO co-oligomerization.[22,30] We proposed that the bulky ligand **2e** preferred the 1,2-insertion to the 2,1-, so that the steric repulsion between the ligand and the phenyl group of styrene would be avoided. The unique styrene/CO co-oligomerization with **2e** was thus attributed to the facile CO insertion in the 1,2-adduct **6e**(1,2). In fact, the high-pressure NMR studies under 2.0 MPa of CO revealed that, under the polymerization process, the **6e**(2,1) was visible but not **6e**(1,2). The result suggests that (1) no further polymerization took place once the 2,1-insertion occurred to give **6e**(2,1) while (2) further polymerization underwent from **6e**(1,2) until finally the catalyst ends up with 2,1-insertion.[30] From the 2,1-adduct, the β-hydride elimination eventually underwent to give the α,β-unsaturated ketones. Here in the present study with fluoroalkene **1a**, again the 2,1-product such as **3a**(2,1) seems to be the "dead end" that is not involved in the further polymerization. Thus, the higher yield of **1a**/CO copolymerization with **2e** than that with **2a** should be attributed to the selective formation of the 1,2-adduct **3e**(1,2).

The different reactivity between the 1,2-adduct and the 2,1-adduct should come from either the step **C** to **D** (carbonyl coordination) or the step **D** to **A** (carbonyl insertion) in Scheme 1. Alkylpalladium **C** bearing $CH_2{-}n\text{-}C_8F_{17}$ on the α-carbon to palladium (=2,1-adduct) is likely to form a stronger five-membered chelation by lowering the electron density of the palladium center.[5] The CO-coordination **C**→**D** should become less favorable with the stronger chelation. In addition, the electron-deficient α-carbon in **D** should retard the subsequent CO insertion to the metal−carbon bond (**D**→**A**) by lowering the nucleophilicity of the migrating α-carbon atom.[5,12] As is shown in Scheme 6, such electronic disadvantage of the $CH_2{-}n\text{-}C_8F_{17}$ group is successfully avoided in the 1,2-adduct. That means that the electron-withdrawing substituent is on the β-position of the palladium and the α-carbon is less electron deficient.

Thus, using **2e**, the alternating copolymerization of **1a** with CO was managed to take place. However, the polymerization was much slower than that of 1-hexene (Table 1, compare runs

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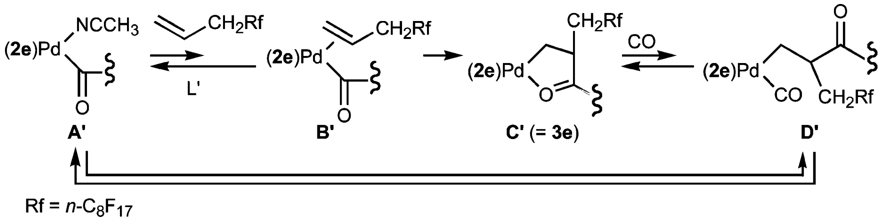
(30) Iggo, J. A.; Kawashima, Y.; Liu, J.; Hiyama, T.; Nozaki, K. *Organometallics* **2003**, *22*, 5418−5422.

Scheme 6. Proposed Catalytic Cycle Containing the Advantageous 1,2-Insertion of Fluoroalkene into the Acylpalladium Complex



7 and 14). This should be attributed to the disfavorable olefin coordination **A′→B′**. Noteworthy is that the equilibrium between **C′** and **D′** also affected the rate as was demonstrated in the higher yield under the higher CO pressure (Table 1, runs 6−8). Summarizing the above observations, it seems that there exist three pre-equilibriums **C′**−**D′**, **D′**−**A′**, and **A′**−**B′** before the rate-determining step **B′** to **C′**.

Conclusion

The palladium-catalyzed alternating copolymerization of fluoroalkenes represented as $CH_2{=}CH{-}CH_2{-}C_nF_{2n+1}$ with CO was successfully achieved using (*R*,*S*)-BINAPHOS (**2e**) as a ligand. The copolymer obtained from $CH_2{=}CH{-}CH_2{-}C_8F_{17}$ (**1a**) existed as a mixture of polyspiroketal and polyketone, while that from $CH_2{=}CH{-}CH_2{-}C_4F_9$ (**1b**) was a pure polyspiroketal. Detailed NMR spectroscopic studies demonstrated that the higher reactivity with (*R*,*S*)-BINAPHOS (**2e**) than that with the conventional ligand DPPP (**2a**) can be attributed to the unique 1,2-insertion of the fluoroalkene to acylpalladium species with **2e**. Taft's σ^* value of 0.90 for $-CH_2CF_3$ is the highest value ever reported for the olefin substituents involved in the copolymerization.

It is well-known that the chain-running of a late transition metal, such as palladium or nickel, becomes a problematic issue in the homopolymerization of olefins bearing functional groups. That is, the metal often migrates on an alkyl complex to form complexes that are either stabilized by coordination of the functional group to the metal center[7,9] or ready to get decomposed, for example, via β-heteroatom elimination.[8] Thus, even if the original olefinic bond is separated from the functional group by methylene spacers, the isomerization takes place to deactivate the metal center without waiting for the next monomer to insert. In this viewpoint, it is of interest to note that the alkyl complex is protected from the rapid chain-running in the copolymerization with CO because of the stable five-membered chelate **C′** in Scheme 6. As a result, the CH_2Rf group in **C′** was kept at the β-position without migrating to the α-position of the metal center.

Experimental Section

General. All manipulations involving the air- and moisture-sensitive compounds were carried out using standard Schlenk techniques or in a glove box under argon. All NMR spectra except CP-MAS were recorded using JEOL JNM-ECP500 spectrometer. CP/MAS NMR spectra were recorded using JEOL JNM-ECA920 spectrometer. $CHCl_3$ (^1H) and H_3PO_4 (^{31}P) were employed as internal and external standards, respectively. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on an Applied Biosystems BioSpectrometry Workstation model Voyager-DE STR spectrometer using dithranol as a matrix. Melting points were measured on a Yanagimoto micro melting point apparatus MP-500D and are uncorrected. Thermal characterizations were conducted with a Mettler DSC 30 system at a scanning rate of 10 °C min^{-1} and a Rigaku ThermoPlus TG 8120 at a scanning rate of 10 °C min^{-1}. β-Eliminated olefinic products were separated by using a recycling preparative HPLC (LC-928, Japan Analytical Industries, 60 cm × 20ϕ Jaigel-1H and 2H, $CHCl_3$ eluent). Chemicals were purchased from Wako Pure Chemical Industries Ltd., Strem Chemicals Inc., and were used without further purification unless otherwise specified. Solvents were purified by distillation under argon after drying over standard drying agents. Carbon monoxide (99.9%) was obtained from Senda-gas Co. $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$,[31] Pd(Me)(Cl){(*R*,*S*)-BINAPHOS},[32] and Pd(Me)(Cl)(dppp)·$0.5Et_2O$[33] were prepared according to the literature.

Synthesis of Fluorinated Olefin 1b. To a 200 mL three-necked round-bottom flask filled with nonafluorobutyl iodide (30.0 mL, 174 mmol) and $(PhCOO)_2$ (1.22 g, 5.00 mmol) was added allyl acetate (21.5 g, 0.200 mmol) dropwise at 70 °C. The resulting reaction mixture was stirred several hours at 70 °C until nonafluorobutyl iodide was consumed. The reaction mixture was added dropwise to refluxing methanol suspended with zinc dust (15.3 g, 210 mmol), and the whole mixture was stirred under reflux for an hour. After filtration through Celite, the upper layer of the resulting filtrate was separated and washed with water. The resulting liquid was kept under molecular sieves 13X, and was distilled through a Vigreaux column over CaH_2. A colorless liquid (14 g, 54% yield) was obtained. The product was almost pure but contains about 1% of impurity, which could not be separated; bp 82 °C. The spectroscopic data were in agreement with the reported data.[34]

General Procedure for Copolymerization of Olefins 1 with CO. To a 1 mL toluene solution of (cod)PdMeCl (5.3 mg, 0.020 mmol) was added 1 mL of a toluene solution of ligand **2** (0.020 mmol), and the mixture was stirred for several hours (1−20 h) at ambient temperature. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2. To this solution was added an acetonitrile solution of $Na\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$ (18.0 mg, 0.020 mmol), and the mixture was stirred for an hour at room temperature. After removal of the solvents, the residue was dissolved in CH_2Cl_2 (2.0 mL) and olefin **1** (5.2 mmol) was added. The solution was degassed by three freeze−pump−thaw cycles and transferred into an autoclave. The autoclave was pressurized with CO, and the solution was stirred with a stirring bar at 60 °C. After CO gas was released, methanol was added to the mixture. After evaporation of the volatiles, the mixture was dried under vacuum, and then the resulting products were collected in runs 1−5 and 10−16. For the experiments in runs 6−9, addition of methanol to the reaction mixture provided the polymeric product as solid precipitates. The solid products were collected by filtration and dried under vacuum. Product in run 2, IR (KBr) 1716 cm^{-1}, mp 89−94 °C; run 11, IR (KBr) 1718 cm^{-1}; run 12, mp 182−183 °C.

Under the conditions of run 9, the use of 2.37 g of **1a** resulted in 2.04 g (80.6%) of white solids. The thermal property of the product was analyzed via DSC and TGA. The obtained DSC curve showed the melting point was 182−183 °C, and the TGA curve showed that the

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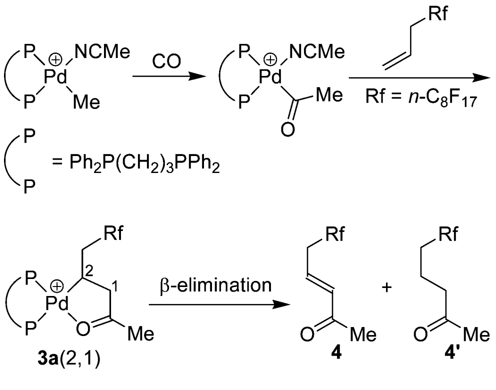
(32) Nozaki, K.; Sato, N.; Tonomura, Y.; Yasutomi, M.; Takaya, H.; Hiyama, T.; Matsubara, T.; Koga, N. *J. Am. Chem. Soc.* **1997**, *119*, 12779−12795.

(33) Dekker, G.; Elsevier, C. J.; Vrieze, K.; Vanleeuwen, P. *Organometallics* **1992**, *11*, 1598−1603.

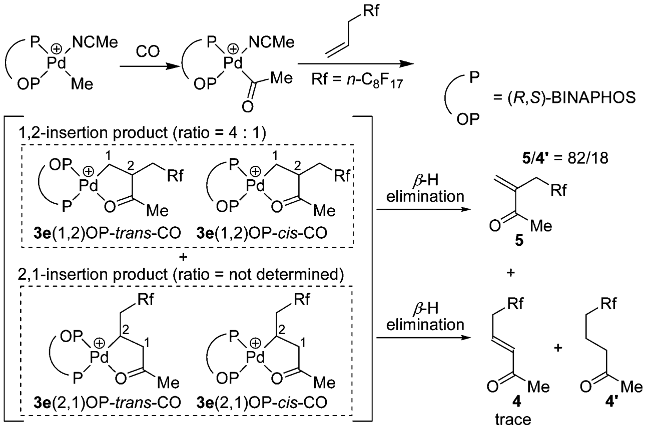
(34) Hu, C. M.; Qing, F. L.; Huang, W. Y. *J. Org. Chem.* **1991**, *56*, 2801−2804.

product decomposed at the same or a little higher temperature than the melting point. IR (KBr): 1718 cm^{-1}, mp 182−183 °C. Under the conditions of run 13, 200 mg of gray solid was obtained. The MALDI-TOF-MS spectrum of the product was shown in Figure 1. IR (KBr): 1718 cm^{-1}.

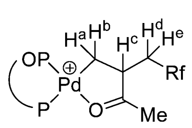
Insertion of 1a into [Pd(COMe)(CH_3CN)(2a)]{B[3,5-(CF_3)$_2$$C_6H_3$]$_4$} To Afford Alkyl Complex 3a(2,1). A solution of Na[B{3,5-(CF_3)$_2$$C_6H_3$}$_4$] (93.0 mg, 0.105 mmol) in CH_3CN (2.0 mL) was added to a solution of Pd(Me)(Cl)(**2a**)·0.5Et_2O (61.0 mg, 0.100 mmol) in CH_2Cl_2 (2.0 mL). After the solution was stirred for an hour at ambient temperature, solvent was removed in vacuo. Dichloromethane was added and removed in vacuo three times to reduce the remaining MeCN. The resulting solid was dissolved in CH_2Cl_2 (2 mL), and **1a** (0.60 mL, 2.1 mmmol) was added to this solution. After the solution was bubbled with CO, the mixture was stirred for 7 h at 0 °C. Solvents were removed in vacuo, and the residue was washed with hexane (10 mL) twice at 0 °C, and then dissolved in CH_2Cl_2. The solids were removed by filtration through a Celite pad at 0 °C, and the solvent was evaporated. The crude product was washed with hexane (10 mL) twice and dried in vacuo at 0 °C. Formation of the 2,1-product **3a(2,1)** as a single product was judged by NMR spectroscopy: ^{31}P NMR ($CDCl_3$, 202 MHz, 0 °C) δ 26.8 (d, $J = 61$ Hz), −4.9 (d, $J = 61$ Hz); ^1H NMR ($CDCl_3$, 500 MHz, 0 °C) δ 7.75−7.28 (m, 32H, Ar), 3.30−3.14 (m, 2H), 2.61 (m, 3H), 2.33 (s, 3H), 2.26 (m, 2H), 1.83 (brs, 1H), 1.69 (m, 1H), 1.49 (m, 2H); a part of ^{13}C NMR ($CDCl_3$, 125 MHz, 0 °C, Rf moiety could not be characterized) δ 234.6 (d, $J = 10$ Hz, $COCH_3$), 161.6 (q, $J = 100$ Hz, ipso to B atom in $^-BAr_4$), 134.7−126 (m, Ar), 55.8 (s, CH_2), 40.6 (dd, $J = 93$ Hz, 5 Hz, CH), 32.8 (t, $J = 21$ Hz, CF_2CH_2), 28.6 (s, CH_3CO), 27.4 (dd, $J = 35$ Hz, 9 Hz, PCH_2), 26.1 (d, $J = 24$ Hz), 18.4 (s, CH_2CH_2P); ^{19}F NMR ($CDCl_3$, 470 MHz, 0 °C) δ −62.2 (s, 24F, $ArCF_3$), −80.7 (s, 3F, CF_3), −108.8(d, $J = 274$ Hz, 1F, CH_2CFF), −115.3 (d, $J = 274$ Hz, 1F, CH_2CFF), −121.8 (s, 2F, CF_2), −122 (s, 4F, CF_2), −122.9(s, 2F, CF_2), −123.3 (s, 2F, CF_2), −126.2(s, 2F, CF_2). After the solution was kept for 144 h at room temperature, β-hydride elimination from **3a(2,1)** afforded α,β-unsaturated ketone **4** and saturated ketone **4′**. Because **4** could not be isolated, **4** was partly assigned by the ^1H NMR spectrum of the mixture of **4** and **4′**. **4′** was completely characterized by isolation from the following experiment with **3e**. **4**: ^1H NMR ($CDCl_3$, 500 MHz) δ 6.69 (dt, $J = 16$, 7 Hz, 1H, CH═CHCO), 6.29 (d, $J = 16$ Hz, 1H, CH═CHCO), 3.03 (td, $J = 18$, 7 Hz, 2H, CF_2CH_2), 2.30 (s, 3H, $COCH_3$).



Insertion of 1a into [Pd(COMe)(CH_3CN)(2e)]{B[3,5-(CF_3)$_2$$C_6H_3$]$_4$} To Afford Alkyl Complexes 3e. Cationic methylpalladium species was prepared from Pd(Me)(Cl)(**2e**) (92.6 mg, 0.10 mmol) in the same procedure as that from Pd(Me)(Cl)(**2a**). To its CH_2Cl_2 (2 mL) solution, **1a** (1.5 mL, 5.1 mmol) was added and CO was bubbled through the solution. After the solution was stirred for 8 h at ambient temperature, the volatiles were removed in vacuo. The crude product was dissolved in CH_2Cl_2, and the solid materials were removed by filtration through a Celite pad. The filtrate was dried in vacuo, and the residue was washed with hexane (10 mL) five times. The residue was dissolved in $CDCl_3$ to make an NMR sample. The ^{31}P NMR spectrum of this sample showed six pairs of doublets (six doublets for phosphine and six doublets for phosphite); three pairs were detected as separated peaks, and the other three pairs were overlapping each other. The ratio of the six pairs was 54%, 11%, 8% for the separated three pairs and 27% for the sum of the overlapped three pairs.[26] Comparison of the obtained ^{31}P NMR spectra with those of previously reported [Pd($CH_2CH(CH_3)$-$COCH_3$)(**2e**)][B{3,5-(CF_3)$_2$$C_6H_3$}$_4$][32] and [Pd($CH_2CH(Ph)COCH_3$)(**2e**)]-[B{3,5-($CF_3$)$_2$$C_6H_3$}$_4$][22] enabled us to assign the major isomer as **3e(1,2)OP-*trans*-CO**, which resulted via the 1,2-insertion of **1a** to the acetylpalladium complex. Similarly, the second largest pair of peaks was assigned as the isomeric 1,2-insertion complex (**3e(1,2)OP-*cis*-CO**). Characterization of the other minor peaks was not completed, but some of the peaks are possibly due to the 2,1-products judging from the following results.



3e(1,2)OP-*trans*-CO. ^{31}P NMR ($CDCl_3$, 202 MHz) δ 139.2 (d, $J = 65$ Hz), 14.1 (d, $J = 65$ Hz); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.40 (br, 1H, H^c), 2.98 (br, 1H, H^b), 2.72 (br, 2H, H^d and H^e), 2.52 (br, 1H, H^a), 2.19 (s, 3H, CH_3), H−H COSY experiment revealed the spin−spin coupling between H^a,H^b and H^c, and H^c and H^d,H^e (spectra are in the Supporting Information); ^{13}C NMR ($CDCl_3$, 125 MHz, Rf and BINAPHOS moiety could not be characterized) δ 237.8 (d, $J = 9.2$ Hz, $COCH_3$), 53.3 (CH), 35 (br, CF_2CH_2, $PdCH_2$), 28.1 (CH_3). **3e-(1,2)OP-*cis*-CO.** ^{31}P NMR ($CDCl_3$, 202 MHz) δ 148.9 (d, $J = 61$ Hz), 29.7 (d, $J = 61$ Hz). The other four small pairs of doublets could not be completely assigned. ^{31}P NMR ($CDCl_3$, 202 MHz) δ 137.98 (d, $J = 61.0$ Hz), 137.87 (d, $J = 61.0$ Hz), 137.80 (d, $J = 65.4$ Hz), 136.18 (d, $J = 65.4$ Hz), 16.85 (d, $J = 65.4$ Hz), 15.18 (d, $J = 61.0$ Hz), 14.65 (d, $J = 65.4$ Hz), 14.01 (d, $J = 65.4$ Hz).



3e(1,2)OP-*trans*-CO

Leaving the NMR samples for 14 days at ambient temperature resulted in the decomposition of the complex and formation of β-hydride eliminated product (**5** and a trace amount of **4**) and protonated product (**4′**) as was observed by ^1H NMR spectroscopy (**5**/**4′** = 82/18). The major olefinic product **5** was purified by silica gel column chromatography (Et_2O/hexane = 1/1, Rf = 0.6) and recycling preparative HPLC and characterized by NMR and IR spectroscopies and mass spectrometry, although a trial for the isolation of pure **5** was not successful due to its high volatility. **5**: ^1H NMR ($CDCl_3$, 500 MHz) δ 6.39 (s, 1H, C═CHH), 6.17 (s, 1H, C═CHH), 3.17 (t, $J = 19$ Hz, 2H, CF_2CH_2), 2.41 (s, 3H, $COCH_3$); ^{13}C NMR ($CDCl_3$, 125 MHz, italicized peaks of Rf moiety were assigned by independently measured ^{13}C-{^{19}F} NMR spectrum) δ 197.3 (CO), 138.0 (C═CH_2), 131.4 (C═CH_2), *117.1*, *117.0*, *111.1*, *111.0*, *110.8*, *110.7*, *110.2*, *108.4*, 30.3 (t, $J = 22$ Hz, CF_2CH_2), 25.2 ($COCH_3$); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −80.6 (s, 3F, CF_3CF_2), −113.1 (s, 2F, CF_2), −121.5 (s, 2F, CF_2), −121.8 (s, 4F, CF_2), −122.6 (s, 2F, CF_2), −123.0 (s, 2F, CF_2), −126.0 (s, 2F, CF_2); GC−MS *m*/*z* 501.3 (M), 486.1 (M − Me), 482.3 (M − F). **4′**: ^1H NMR ($CDCl_3$, 500 MHz) δ 2.57 (t, $J = 7$ Hz, 2H, $COCH_2$), 2.17 (s, 3H, $COCH_3$), 2.09 (m, 2H, CF_2CH_2), 1.90 (m, 2H, $CH_2CH_2CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, italicized peaks of Rf moiety were assigned by independently measured $^{13}C\{^{19}F\}$ NMR spectrum) δ 207.1 (CO), *118.4*, *117.1*, *111.1*, *111.0*, *110.8*, *110.7*, *110.2*, *108.4*, 42.1, 29.9, 29.9 (t, $J = 21$ Hz, CF_2CH_2), 14.5; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −80.6 (s, 3F, CF_3CF_2), −114.3 (s, 2F, CF_2), −121.6 (s, 2F, CF_2), −121.8 (s, 4F, CF_2), −122.6 (s, 2F, CF_2), −123.4 (s, 2F, CF_2), −126.0 (s, 2F, CF_2); GC−MS *m*/*z* 503.3 (M), 488.3 (M − Me), 484.3 (M − F).

Estimation of the Yield of 5 and 4′ from [Pd(COMe)(CH_3CN)(2e)][B{3,5-(CF_3)$_2$$C_6H_3$}$_4$] and 1a. A CH_2Cl_2 (2 mL) solution of [Pd(COMe)(CH_3CN)(**2e**)][B{3,5-(CF_3)$_2$$C_6H_3$}$_4$] (0.020 mmol) was prepared according to the procedure described above. To this was added **1a** (0.029 mL, 0.020 mmol), and the mixture was warmed to 50 °C. After 22 h, the existence of **5** and **4′** with a ratio of 82:18 was detected via the ^1H NMR spectrum. The sum of these two olefinic products corresponded to more than 85% of the initial acetylpalladium complex, as was determined by using CH_2Cl_2 as an internal standard.

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Supporting Information Available: DSC and TGA charts of poly(**1a**-*alt*-CO), ^{31}P and ^{13}C NMR spectra of **3a**(2,1), and ^{31}P NMR and H−H COSY spectra of the isomeric mixture of **3e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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