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Alternating Copolymers of Functional Alkenes with Carbon Monoxide

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ABSTRACT: The alternating copolymerization of functional alkenes, $CH_2{=}CH(CH_2)_xOH$ (x = 2, 3, 4, 9), $CH_2{=}CH(CH_2)_xCOOH$ (x = 1, 2, 4, 8), and 4-allylanisole, with carbon monoxide was achieved by using $[Pd(Me\text{-}DUPHOS)(MeCN)_2](BF_4)_2$ [Me-DUPHOS = 1,2-bis(2,5-dimethylphospholano)benzene] as the catalyst. The resultant polymers were optically active with isotactic sequences in the backbone. With most alkenes, the polymers had poly(1,4-ketone) and/or "regular" poly(spiroketal) (i.e., 1,6-dioxaspiro[4.4]nonane) enchainments. However, with 4-penten-1-ol and 3-buten-1-ol, the participation of the pendant hydroxyl group in intrachain reactions led to the formation of unusual polycyclic repeating units in the backbone. A comparison of $[Pd(Me\text{-}DUPHOS)(MeCN)_2](BF_4)_2$ with $[Pd(DPPP)(MeCN)_2](BF_4)_2$ [DPPP = 1,3-bis(diphenylphosphino)propane] indicated that the former was a significantly better catalyst for the alternating copolymerization of alkenols and alkenoic acids with carbon monoxide.

The palladium(II)-catalyzed alternating copolymerization of alkenes with carbon monoxide is of great current interest[1] due to the low monomer costs, the potential photodegradability of the copolymers,[2] and the presence of carbonyl groups in the polymer backbone that lend themselves to further functionalizations.[3] A major goal in the area is the synthesis of copolymers using *functional* alkenes. The resultant highly functionalized materials are likely to be of practical importance given the varied applications of the presently known functional polymers.[4] Although the alternating copolymerization of functional alkenes with CO has rarely been reported, there is no good reason why such alkenes cannot be used as substrates. Indeed, one of the advantages of using a late transition metal, such as Pd(II), as catalyst is that it is unlikely to be poisoned or deactivated by the presence of oxygen, nitrogen, or halogen functionalities, either in the solvent or in the substrate (the alkene−CO copolymerization proceeds smoothly in the presence of acids and in water, alcohols, nitroalkanes, and halogenated hydrocarbons[1,5]). In this respect it differs from those alkene homopolymerization or alkene metathesis catalysts that are derived from the early transition metal ions.[6]

There are a few reports of the alternating copolymerization of functional alkenes with CO. Using $Pd[(1,10\text{-phenanthroline})(CH_3CN)_2]^{2+}$ as catalyst, we had earlier reported the terpolymerization of CO, styrene, and either ω-undecylenyl alcohol or ω-undecylenic acid with a 6:1 ratio of styrene to the the latter alkene in the polymer.[7] Interestingly, the styrene−CO segments in these polymers were syndiotactic. Additionally, Drent has reported the copolymerization of ω-undecylenic acid with CO using $R_2P(CH_2)_3PR_2$ (R = aryl, alkyl) ligated Pd(II) complexes.[8] Although ω-undecylenyl alcohol and ω-undecylenic acid are technically functionalized alkenes, the functionality is far removed from the C═C bond. Indeed, the copolymerization stopped or became very slow when alkenes with the functionality closer to the C═C bond were employed. A possible reason for the failure, thus far, to successfully copolymerize most functional alkenes with CO may be that the functional group blocks a coordination site on the metal through coordination. Therefore, we have examined the catalytic activity of a Pd(II) complex bearing a bulky chelating phosphine. As described below, we have now succeeded in the copolymerization of alkenes bearing alcohol and acid functionalities that are much closer to the C═C bond. Moreover, since the phosphine employed was chiral, the synthesis of chiral polymers with isotactic sequences in the backbone has resulted.[9] Finally, with certain alkenols, we have synthesized copolymers that incorporate very unusual polycyclic repeating units in the backbone.

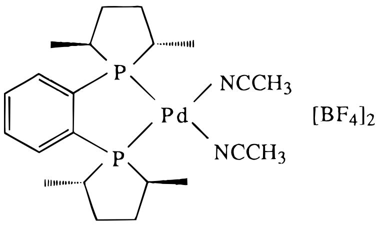

Figure 1. Catalyst used for the copolymerization of functionalized alkenes with carbon monoxide.

Alkenols $CH_2{=}CH{-}(CH_2)_x{-}OH$ x = 2,3,4,9

Alkenoic acids $CH_2{=}CH{-}(CH_2)_x{-}COOH$ x = 1,2,4,8

Figure 2. Monomers that were copolymerized with carbon monoxide.

Results and Discussion

Catalyst and Monomers. The catalyst used for the alternating copolymerization of functional alkenes with carbon monoxide was $[Pd((R,R)\text{-}Me\text{-}DUPHOS)(MeCN)_2](BF_4)_2$ [(R,R)-Me-DUPHOS = (−)-1,2-bis((2R,5R)-2,5-dimethylphospholano)benzene] (Figure 1).[10] It was prepared in situ by dissolving $[Pd(MeCN)_2](BF_4)_2$[11] and (R,R)-Me-DUPHOS in a 1:1 molar ratio in a 2:1 (v/v) solvent mixture of nitromethane and methanol.

α-Alkenes bearing hydroxyl (alkenols) and carboxylic acid (alkenoic acids) groups shown in Figure 2 were copolymerized with carbon monoxide to yield perfectly alternating, optically active copolymers. Alkenols that were successfully copolymerized were ω-undecylenyl alcohol ($C_{11}OH$), 5-hexen-1-ol (C_6OH), 4-penten-1-ol (C_5OH), and 3-buten-1-ol (C_4OH). Allyl alcohol did not yield a copolymer. Alkenoic acids that were successfully copolymerized with CO were ω-undecylenic acid

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Scheme 1

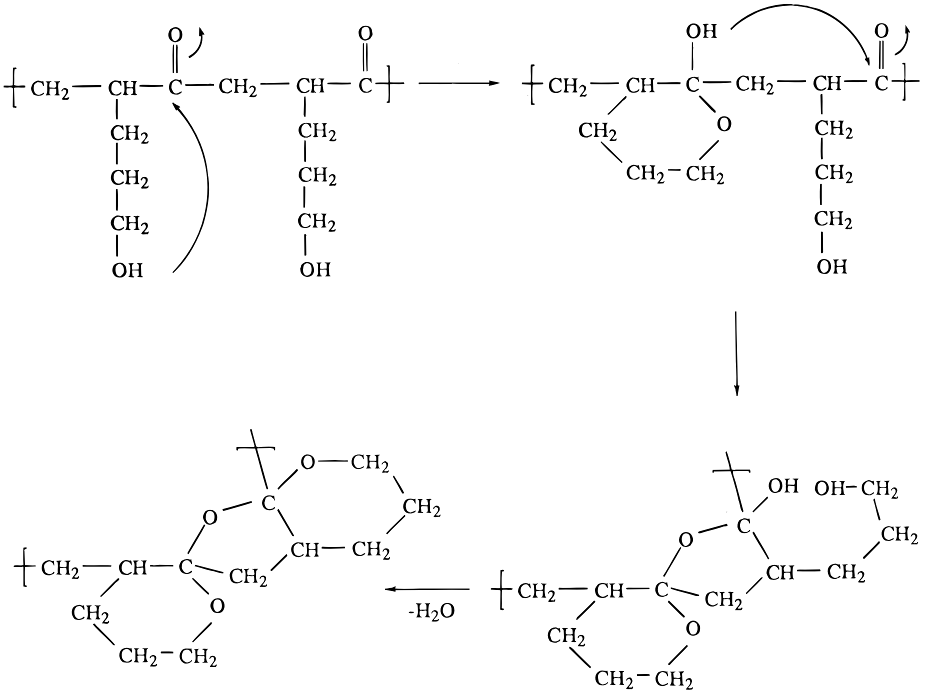


Table 1. Molar Optical Rotations and Molecular Weights of Alternating Alkenol−CO Copolymers

copolymer	$[\Phi]^{24}_D$ (c, mg/mL, solvent)	M_p (M_w/M_n)[a]
ω-undecylenyl alcohol−CO	+30° (5.3, THF)	1.3×10^4 (1.5)
5-hexen-1-ol−CO	+34° (6.3, CH_3OH)	4.5×10^4 (2.0)
4-penten-1-ol−CO	+43° (4.9, $CHCl_3$)	1.0×10^4 (1.9)
3-buten-1-ol−CO	−35° (5.7, $CHCl_3$)	1.4×10^4 (1.7)

[a] Molecular weights were measured by GPC relative to polystyrene standards using Waters Styragel columns.

($C_{10}COOH$), 6-heptenoic acid (C_6COOH), 4-pentenoic acid (C_4COOH), and 3-butenoic acid (C_3COOH).

Alternating Copolymers of Alkenols with Carbon Monoxide. The alkenol−CO copolymers formed exhibited a range of structures as well as solubilities. The molar optical rotation and the molecular weights of alkenol−CO copolymers formed are listed in Table 1. In addition to the alkenols, 4-allylanisole (AA) was also copolymerized with CO to give a highly isotactic, optically active copolymer.

ω-Undecylenyl alcohol−CO ($C_{11}OH$−CO) copolymer formed had a pure, "regular", poly(spiroketal) structure with 1,6-dioxaspiro[4.4]nonane units in the backbone.[9a] The ^{13}C NMR spectrum in THF-d_8 showed resonances around 114.6 ppm due to the ketal group and at 45.3 and 42.0 ppm due to the CH_2CH units in the polymer backbone. The $(CH_2)_9$ units in the branch appeared at 62.8 (CH_2OH), 34.3, 31.6, 31.1, 31.0, 30.9, 30.3, 29.7, and 27.2 ppm. The ^1H NMR spectrum in THF-d_8 showed broad resonances at 2.16 and 1.96 ppm due to the CH_2CH units in the polymer backbone and at 3.47 (CH_2OH), 1.48, and 1.33 ppm due to the $(CH_2)_9$ units in the branch. The poly(spiroketal) structure was maintained even in an acidic solvent like 1,1,1,3,3,3-hexafluoro-2-propanol. Thus, when the polymer was stirred in a 1:2 (v/v) mixture of 1,1,1,3,3,3-hexafluoro-2-propanol and THF-d_8, no conversion to poly(1,4-ketone) was observed in 6 weeks as monitored by ^{13}C NMR spectroscopy.

In contrast to the $C_{11}OH$−CO copolymer, the 5-hexen-1-ol−CO (C_6OH−CO) copolymer was a methanol-soluble poly(1,4-ketone). The IR spectrum (KBr) showed absorptions at 3358 cm^{-1} due to the hydroxyl groups and at 1703 cm^{-1} due to the carbonyl groups. The ^{13}C NMR spectrum in CD_3OD showed resonances around 214.6 ppm due to the carbonyl group and at 46.7 and 45.6 ppm due to the CH_2CH units in the polymer backbone. The $(CH_2)_4$ units in the branch appeared at 62.7 (CH_2OH), 33.6, 32.3, and 24.3 ppm.

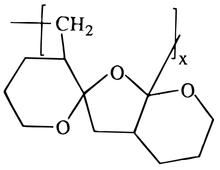


Figure 3. Structure of 4-penten-1-ol−CO copolymer.

The dominant repeating unit of the 4-penten-1-ol−CO (C_5OH−CO) copolymer is shown in Figure 3. Besides this unit, small amounts of poly(1,4-ketone) and "regular" poly(spiroketal) units (i. e., 1,6-dioxaspiro[4.4]nonane units) were also present (approximate carbon ratios obtained by integration of the ^{13}C NMR spectrum, 87.5: 8: 4.5, respectively). The formation of the structure shown in Figure 3 can be rationalized by invoking the participation of the hydroxyl group in an intramolecular reaction to form stable five- and six-membered spiroketal rings (Scheme 1). This polymer was also found to be stable in acidic solvents like 1,1,1,3,3,3-hexafluoro-2-propanol and could not be converted to pure poly(1,4-ketone). The ^{13}C NMR spectrum in $CDCl_3$ showed resonances at 108.8 and 106.9 ppm due to the ketal groups. The assignment of these absorptions was made on the basis of the absorptions of tertiary carbons in the ^{13}C NMR spectra of 1,6-dioxospiro[4.4]nonane, 1,6-dioxospiro[4.5]decane, and 1,7-dioxospiro[5.5]-undecane (Figure 4).[12] Resonances due to the carbons next to the oxygens occurred at 62.9 and 62.4 ppm. The other carbons showed a series of broad resonances between 46 and 19 ppm. In addition, there were small absorptions at 213.3 and 115.0 ppm due to the presence of 1,4-keto groups and the "regular" spiroketal groups, respectively. The IR spectrum (KBr) showed very weak

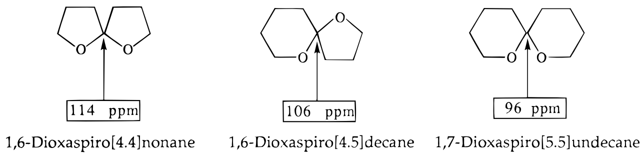


Figure 4. ^{13}C NMR resonances for the ketal carbons in model compounds.

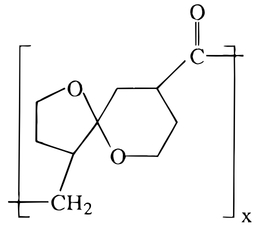
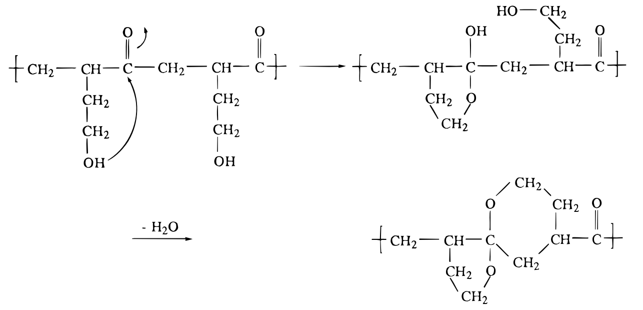


Figure 5. Structure of 3-buten-1-ol−CO copolymer.

Scheme 2



absorptions at 1710 and 3476 cm^{-1} due to the keto and the hydroxyl groups, respectively. There was a strong absorption at 750 cm^{-1} due to the C−O−C linkages.

The 3-buten-1-ol−CO (C_4OH−CO) copolymer has a structure shown in Figure 5 that can be explained by invoking an attack of the hydroxyl group on the carbonyl carbon, followed by the elimination of water (Scheme 2). The ^{13}C NMR spectrum of the copolymer in $CDCl_3$ (Figure 6) showed resonances at 211.6 and 104.5 ppm due to the 1,4-keto groups and the ketal units, respectively. The ketal unit was assigned on the basis of the resonance of the tertiary carbon in the ketal group in 1,6-dioxospiro[4.5]decane at 106 ppm (Figure 4). Resonances due to the other carbons in the spiroketal rings appeared at 65.8, 60.6, 44.9, 40.6, 33.5, 30.4, and 27.5 ppm. The CH_2CO units in the polymer backbone that were outside the rings appeared at 43.1 ppm. The IR spectrum (KBr) had absorptions at 754 and 1710 cm^{-1} due to the ketal units and the keto groups, respectively. Absorption expected around 3400 cm^{-1} due to the hydroxyl group was absent.

4-Allylanisole−CO copolymer (AA−CO) formed consisted of a mixture of poly(1,4-ketone) and “regular” poly(spiroketal) units (i.e., 1,6-dioxaspiro[4.4]nonane units). The ^{1}H NMR spectra of AA−CO copolymer in $CDCl_3$ showed the resonances due to the methoxy group at 3.72 ppm for the poly(1,4-ketone) units and at 3.63 ppm for the poly(spiroketal) units. Integration of these peaks gave the ratio of poly(1,4-ketone) units to poly(spiroketal) units as 1:2. The mixture was converted to pure poly(1,4-ketone) by stirring in a 2:1 (v/v) mixture of chloroform and 1,1,1,3,3,3-hexafluoro-2-propanol for 8 h followed by precipitation in ether. The molar optical rotation in $CHCl_3$ increased from +20° to +100° upon conversion to the pure poly(1,4-ketone). The ^{13}C NMR spectrum of the pure poly(1,4-ketone) in a 2:1 (v/v) mixture of $CDCl_3$ and 1,1,1,3,3,3-hexafluoro-2-propanol showed a single resonance due to keto groups at 214.9 ppm. The absorptions due to the $CHCH_2$ units in the polymer backbone and the CH_2 units in pendant appear at 48.2, 44.0, and 36.5 ppm, respectively. The assignments were confirmed by a ^{1}H-coupled ^{13}C NMR spectrum which showed a doublet at 48.2 ppm ($J = 133$ Hz) and triplets at 44.0 ($J = 126$ Hz) and 36.5 ppm ($J = 133$ Hz). The OCH_3 units in the pendant appeared as a quartet ($J = 144$ Hz) at 55.9 ppm. The phenyl carbons appeared at 158.1 (s), 131.4 (s), 130.6 (d, $J = 162$ Hz), and 114.73 (d, $J = 158$ Hz) ppm. The relatively narrow lines observed (Figure 7) are consistent with a highly stereoregular, head-to-tail polymer, and the observation of optical rotation indicates that the polymer was isotactic.[9a]

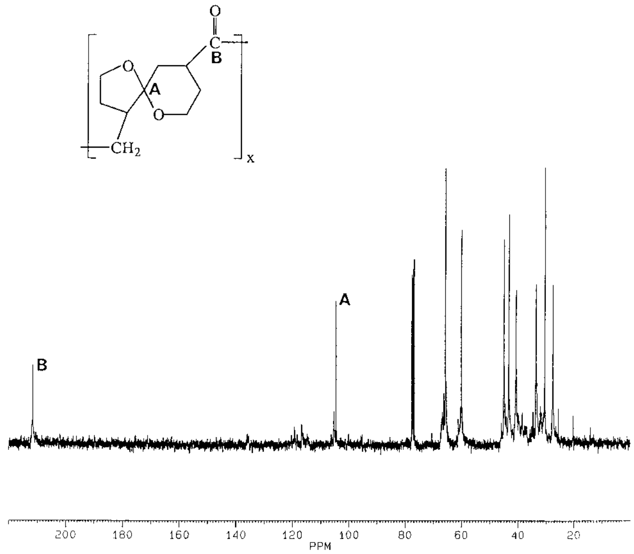


Figure 6. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) spectrum for the 3-buten-1-ol−CO copolymer.

Alternating Copolymers of Alkenoic Acids with Carbon Monoxide. The copolymerization of alkenoic acids with CO invariably led to polymers in which the acid functionality was converted to the corresponding methyl ester due to the use of methanol in the solvent mixture. The molar optical rotations and the molecular weights of the alkenoic acid−CO copolymers obtained are listed in Table 2.

ω-Undecylenic acid−CO copolymer ($C_{10}COOH$−CO) was essentially poly(1,4-ketone) and was soluble in acetone. The ^{13}C NMR spectrum in acetone-d_6 showed a single carbonyl resonance at 213.2 ppm. The $CHCH_2$ units in the polymer backbone appeared at 45.7 and 46.5 ppm, respectively, as dominant singlets. The relatively narrow lines observed (Figure 8) is again consistent with a highly stereoregular, head-to-tail polymer with the observation of optical rotation showing that the polymer was isotactic. The IR spectra (KBr) showed absorptions at 1740 and 1709 cm^{-1} due to the ester and the keto groups in the polymer.[9a]

The 6-heptenoic acid−CO copolymer (C_6COOH−CO) and the 4-pentenoic acid−CO copolymer (C_4COOH−CO) were similar in being methanol soluble with mixtures of 1,4-keto and “regular” spiroketal units in the backbone. The ^{13}C NMR spectrum (CD_3OD) of the C_6COOH−CO copolymer showed broad resonances at 214.1 and 115.2 ppm due to the keto groups and the spiroketal units, respectively (approximate carbon ratios obtained by integration of the ^{13}C NMR spectrum, 1:1). The absorptions due to the $CHCH_2$ units in the polymer backbone appeared at 47.2, 46.6, 45.7, and 45.3 ppm

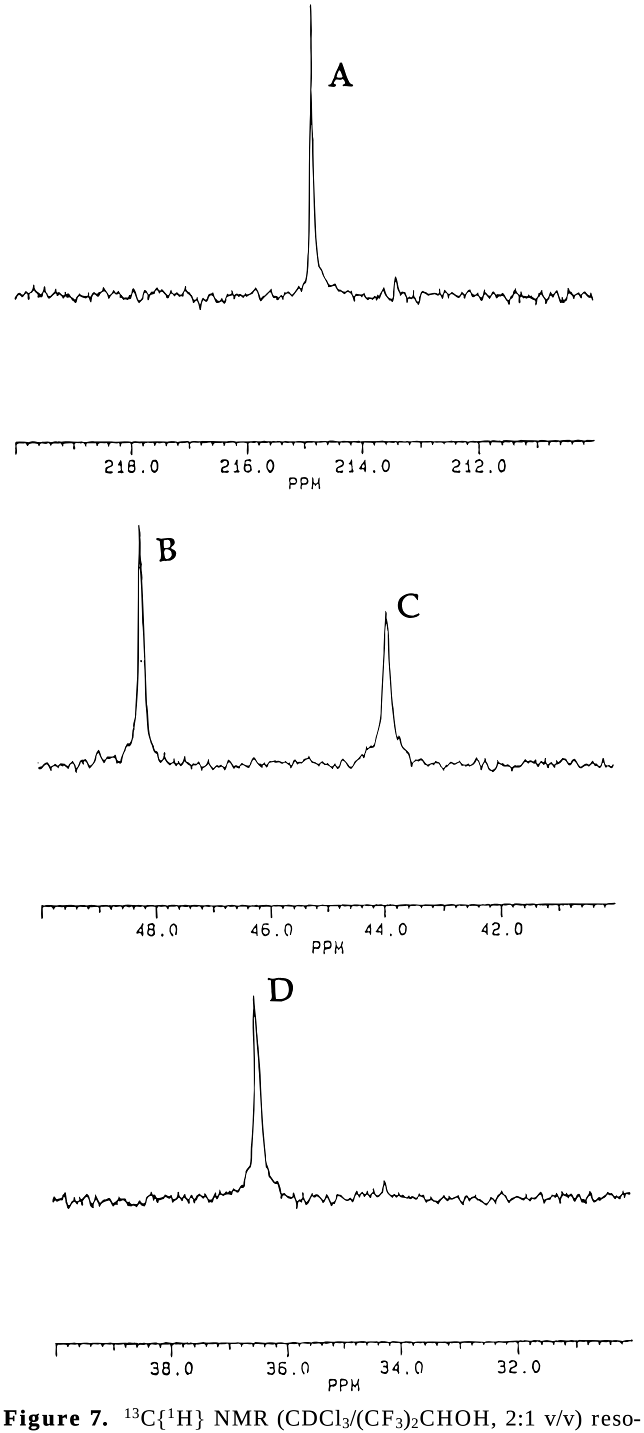


Figure 7. $^{13}C\{^1H\}$ NMR ($CDCl_3/(CF_3)_2CHOH$, 2:1 v/v) resonances for the backbone carbonyl (A), methine (B) and methylene (C) groups, and the methylene (D) group in the branch of the 4-allylanisole−CO copolymer.

while the CH_2 units in the pendant appeared at 35.0, 34.8, 32.2, 30.1, 29.3, 27.6, 26.7, and 26.2 ppm. The ^{13}C NMR spectrum (CD_3OD) of the C_4COOH−CO copolymer showed broad resonances due to the keto groups at 213.1 and 213.8 ppm and spiroketal units at 115.0 ppm (approximate carbon ratios obtained by integration of the ^{13}C NMR spectrum, 1:3, respectively). The absorptions due to the $CHCH_2$ units in the polymer backbone appeared at 46.0, 45.2, 44.5, and 41.8 ppm while the CH_2 units in the pendant appeared at 33.4, 32.1, 27.4, and 25.8 ppm. The IR spectrum (KBr) of the C_4COOH−CO copolymer showed absorptions at 1736 and 1708 cm^{-1} due to the ester groups and the keto groups, respectively.

Table 2. Molar Optical Rotations and Molecular Weights of Alternating Alkenoic Acid−CO Copolymers

copolymer	$[\Phi]^{24}_D$ (*c*, mg/mL, solvent)	M_p (M_w/M_n)[a]
ω-undecylenic acid−CO	+36° (4.3, acetone)	$>10^6$
6-heptenoic acid−CO	+25° (5.1, CH_3OH)	7.8×10^4 (2.9) + $>10^{6}$[b]
4-pentenoic acid−CO	+20° (5.2, CH_3OH)	1.2×10^5 (5.8)
3-butenoic acid−CO	−12° (4.9, $(CF_3)_2CHOH$)	

[a] Molecular weights were measured by GPC relative to polystyrene standards using Waters Styragel columns; the peaks were very broad indicating high polydispersities. [b] Bimodal distribution.

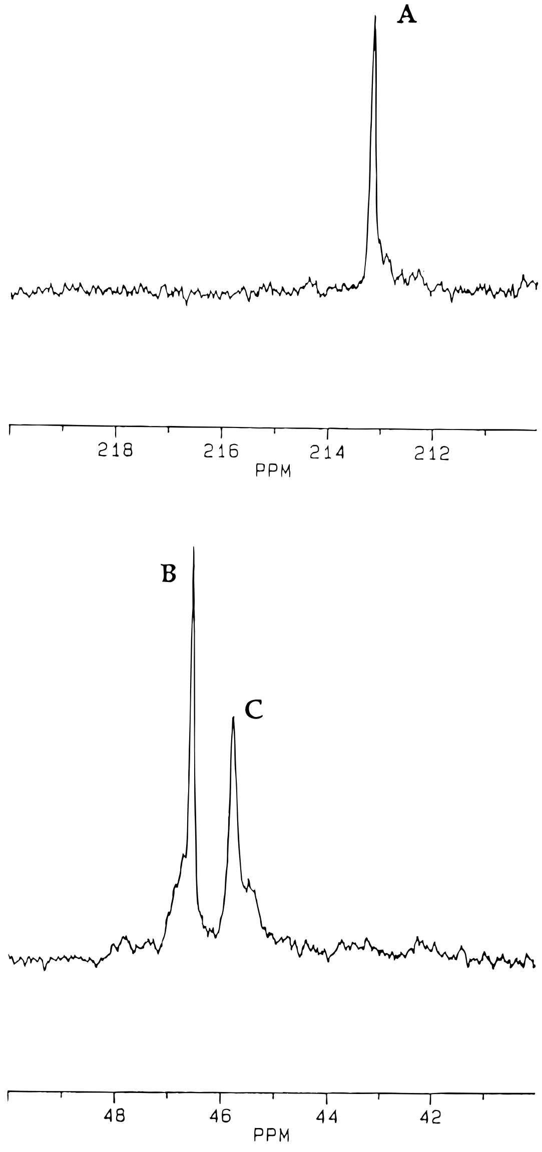


Figure 8. $^{13}C\{^1H\}$ NMR (acetone-d_6) resonances for the backbone carbonyl (A), methine (B), and methylene (C) groups of the ω-undecylenic acid−CO copolymer.

Finally, the 3-butenoic acid−CO (C_3COOH−CO) copolymer was also synthesized. However, it remains poorly characterized since it was only soluble in 1,1,1,3,3,3-hexafluoro-2-propanol. The presence of a resonance at 115.1 ppm and the absence of any resonance around 213 ppm in the ^{13}C NMR spectrum obtained in 1,1,1,3,3,3-hexafluoro-2-propanol appear to indicate a predominantly "regular" poly(spiroketal) structure for the polymer.

Ligand Effects. The effect of the chelating phosphine coordinated to the metal on the copolymerization

Table 3. Yields of Alternating α-Alkene−CO Monoxide Copolymers Obtained Using [Pd((*R*,*R*)-Me-DUPHOS)(MeCN)$_2$](BF$_4$)$_2$ and [Pd(DPPP)(MeCN)$_2$](BF$_4$)$_2$ as Catalysts

copolymer	ligand	yield[a] (g)
3-buten-1-ol−CO	(*R*,*R*)-Me-DUPHOS	1.9
3-buten-1-ol−CO	DPPP	trace
4-pentenoic acid−CO	(*R*,*R*)-Me-DUPHOS	1.8
4-pentenoic acid−CO	DPPP	0.2

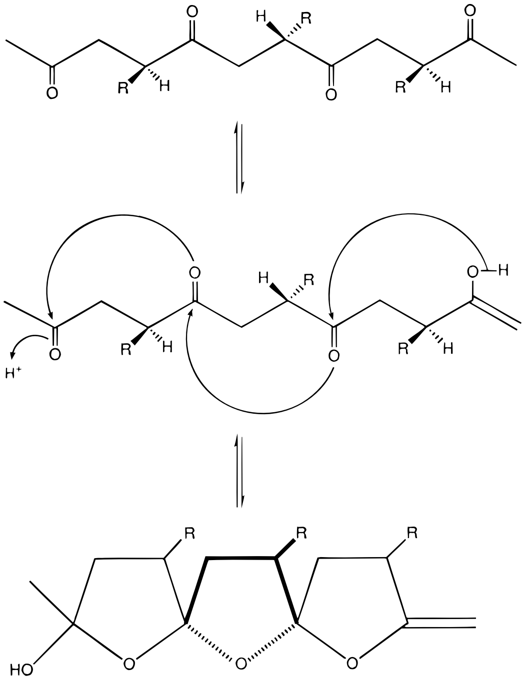
[a] The reactions were run under standard conditions at 40−50 °C for 1 day.

rate was examined briefly. For the copolymerization of ethene and propene with CO, DPPP (1,3-bis(diphenylphosphino)propane)[1d] was previously found to be superior to (*R*,*R*)-Me-DUPHOS.[9a] However, under identical conditions, the copolymerization of functional alkenes with CO gave greatly reduced yields when (*R*,*R*)-Me-DUPHOS was replaced by DPPP (Table 3).

One possible reason for the ineffectiveness of [Pd(DPPP)(MeCN)$_2$](BF$_4$)$_2$ for the copolymerization reaction when compared to [Pd((*R*,*R*)-Me-DUPHOS)(MeCN)$_2$](BF$_4$)$_2$ is that the former efficiently isomerized the substrate terminal alkene to the unreactive internal isomer. However, this possibility was ruled out through the following series of experiments. Neither of the two Pd(II) complexes was found to catalyze the isomerization of 3-buten-1-ol. In the case of 4-pentenoic acid, extensive isomerization was observed with both catalysts (<10% terminal alkene left after 1 day at 50 °C, the composition of the internal isomers was interestingly different for the two catalysts; see Experimental Section). However, the real question was whether isomerization ocurred *during* copolymerization, and accordingly, we examined the composition of the unreacted pentenoic acid left *after* the alternating copolymerization of 4-pentenoic acid with CO was performed using [Pd(DPPP)(MeCN)$_2$](BF$_4$)$_2$ as the catalyst. As estimated from the ^{1}H NMR spectrum, >80% of the unreacted pentenoic acid was in the form of the terminal isomer. It is clear, therefore, that alkene isomerization was *not* the reason for the lower copolymerization activity of [Pd(DPPP)(MeCN)$_2$](BF$_4$)$_2$ compared to [Pd((*R*,*R*)-Me-DUPHOS)(MeCN)$_2$](BF$_4$)$_2$.

Finally, an interesting issue that arises from our work on the alternating copolymerization of functional alkenes with carbon monoxide is whether the 1,4-keto and spiroketal units occur in blocks. In several instances (e.g., the 4-allylanisole−CO poly(spiroketal/1,4-ketone) copolymer), the relatively sharp resonances observed in the ^{13}C NMR spectrum for the two kinds of repeating units tend to support such a possibility. In other instances, either broad and/or multiple resonances were observed. While this may be ascribed to the presence of randomly interspaced 1,4-keto and spiroketal units in the backbone, it may also be a reflection of the lack of high tacticity in the polymer. In any case, it should be noted that a tandem cyclization mechanism for the formation of the spiroketal structure from 1,4-keto units is likely to lead to a "blocky" structure (see Scheme 3).

Scheme 3



Experimental Section

Materials. C.P. grade chemicals were used as received unless otherwise stated.

(−)-1,2-Bis((2*R*,5*R*)-2,5-dimethylphospholano)benzene ((*R*,*R*)-Me-DUPHOS) and 1,3-bis(diphenylphosphino)propane (DPPP) were purchased from Strem Chemicals. [Pd(MeCN)$_4$](BF$_4$)$_2$ was prepared according to the literature method.[11] Nitromethane was dried over CaH$_2$ and vacuum-transferred. Methanol was dried over sodium methoxide and vacuum-transferred. 3-Buten-1-ol, 4-penten-1-ol, 5-hexen-1-ol, ω-undecylenyl alcohol, ω-undecylenic acid, and 4-pentenoic acid were obtained from Aldrich. 3-Butenoic acid and 6-heptenoic acid were obtained from Fluka.

General Methods. All catalyst solutions were prepared in a dry nitrogen-filled glovebox. The copolymerization of alkenes with carbon monoxide was performed under nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM300 FT-NMR spectrometer. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to internal tetramethylsilane (TMS) or to the solvent resonance at the appropriate frequency. IR spectra (KBr) were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. Molecular weights of polymers were measured on a Water Associates liquid/gel permeation chromatograph using Microstyragel columns and a differential refractometer. Polystyrene standards were used to calibrate the instrument. Optical rotation measurements of chiral polymers were performed on a Perkin-Elmer 241 polarimeter using a sodium lamp. The melting points of the polymers were determined under a nitrogen atmosphere using a Perkin-Elmer differential scanning calorimeter equipped with a 7 series thermal analysis system. A heating rate of 20 °C/min was used.

Copolymerization of ω-Undecylenyl Alcohol with Carbon Monoxide. To a solution containing 4.5×10^{-2} mmol of [Pd(MeCN)$_4$](BF$_4$)$_2$ and 4.5×10^{-2} mmol of (*R*,*R*)-Me-DUPHOS in 9 mL of a 2:1 (v/v) mixture of CH$_3$NO$_2$ and CH$_3$OH was added 8.5 g of ω-undecylenyl alcohol. The resultant solution was placed in a 125 mL Parr bomb under nitrogen and charged with 1000 psi of CO. After stirring for 24 h at 40 °C, the excess carbon monoxide was released and the solution was filtered. Diethyl ether was added to the filtrate to precipitate out the polymer (5.1 g). The polymer was washed with acetone and dried under vacuum: ^{1}H NMR (THF-d_8) (ppm) 3.47 (2H, br), 2.16 (2H, br), 1.96 (1H, br), 1.48 (3H, br), 1.33 (13H, br); ^{13}C{^{1}H} NMR (THF-d_8) (ppm) 114.6, 62.8, 45.3, 42.0, 34.3, 31.6, 31.1, 31.0, 30.9, 30.3, 29.7, 27.2; IR (KBr) (cm^{-1}) 3404, 1708, 1057, 825. Anal. Calcd: C, 72.7, H, 11.1. Found: C, 71.6, H, 11.4. Molar optical rotation, $[\Phi]^{24}_{D} = +30°$ ($c = 5.3$ mg/mL, THF). $M_p = 1.3 \times 10^4$, $M_n = 1.1 \times 10^4$, $M_w = 1.6 \times 10^4$, $M_w/M_n = 1.5$. $T_m = 176$ °C.

Copolymerization of 5-Hexen-1-ol with Carbon Monoxide. The copolymerization was carried out following a procedure analogous to the one employed for ω-undecylenyl alcohol. A 4.7 g sample of 5-hexen-1-ol was used and the reaction was carried out at 50 °C. At the end of the reaction, the reaction mixture was added dropwise to ether resulting in the formation of a precipitate. The precipitate was dissolved in methanol and run through a short-stem silica gel column to remove the catalyst; 4.5 g of the polymer was obtained: ^{1}H NMR (CD_3OD) (ppm) 4.87 (1H, s), 3.55 (2H, br), 2.94 (2H, m), 2.76 (1H, d, $J = 16$ Hz), 1.58 (4H, br), 1.33 (2H, br); $^{13}C\{^{1}H\}$ NMR (CD_3OD) (ppm) 214.6, 62.7, 46.7, 45.6, 33.6, 32.3, 24.3; IR (KBr) (cm^{-1}) 3358, 1703, 1058. Anal. Calcd: C, 65.6, H, 9.4. Found: C, 65.4, H, 9.6. Molar optical rotation, $[\Phi]^{24}_{D} = +34°$ ($c = 6.3$ mg/mL, CH_3OH). $M_p = 4.5 \times 10^4$, $M_n = 3.2 \times 10^4$, $M_w = 6.4 \times 10^4$, $M_w/M_n = 2.0$.

Copolymerization of 4-Penten-1-ol with Carbon Monoxide. The copolymerization was carried out following a procedure analogous to the one employed for ω-undecylenyl alcohol. An 8.3 g sample of 4-penten-1-ol was used. At the end of the reaction, unreacted monomer and the solvent were removed under reduced pressure. The polymer was purified by running its solution in chloroform through a short-stem silica gel column to remove the catalyst residue, followed by precipitation in diethyl ether. The polymer (8.0 g) was filtered and dried under vacuum: ^{1}H NMR ($CDCl_3$) (ppm) 3.58−3.86 (4H, br), 1.33−2.28 (14H, br); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) (ppm) 108.8, 106.9, 62.9, 45.8, 43.1, 42.0, 37.3−39.4 (br), 30.3−31.5 (m), 19.6−25.8 (m, br), small peaks at 213.3, 114.9; IR (KBr) (cm^{-1}) 3476, 1710, 1058, 865, 750. Molar optical rotation, $[\Phi]^{24}_{D} = +43°$ ($c = 4.9$ mg/mL, $CHCl_3$). $M_p = 1.0 \times 10^4$, $M_n = 0.7 \times 10^4$, $M_w = 1.4 \times 10^4$, $M_w/M_n = 1.9$. $T_m = 128$ °C.

Copolymerization of 3-Buten-1-ol with Carbon Monoxide. The copolymerization was carried out following a procedure analogous to the one employed for ω-undecylenyl alcohol. An 8.4 g sample of 3-buten-1-ol was used, and the reaction was carried out for 20 h. At the end of this period, the solvent and the unreacted monomer were removed under vacuum to obtain 1.9 g of solid polymer. The polymer was purified by running its solution in chloroform through a short-stem silica gel column to remove the catalyst: ^{1}H NMR ($CDCl_3$) (ppm) 3.69−3.85 (4H, m), 2.97 (1H, m), 2.59 (2H, m), 2.32 (2H, m), 1.54−1.85 (5H, m); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) (ppm) 211.6, 104.5, 65.8, 60.1, 44.9, 43.1, 40.6, 33.5, 30.4, 27.5; IR (KBr) (cm^{-1}) 1710, 754. Molar optical rotation, $[\Phi]^{24}_{D} = -35°$ ($c = 5.7$ mg/mL, $CHCl_3$). $M_p = 1.4 \times 10^4$, $M_n = 1.1 \times 10^4$, $M_w = 1.8 \times 10^4$, $M_w/M_n = 1.7$. $T_m = 81$ °C.

Copolymerization of 4-**Allylanisole with Carbon Monoxide.** The copolymerization was carried out following a procedure analogous to the one employed for ω-undecylenyl alcohol. A 9.7 g sample of 4-allylanisole was used. The polymer precipitated out of the reaction solution as a white solid which was filtered, washed with methanol, and dried under vacuum. The polymer thus formed was found to have a mixture of 1,4-ketone and “regular” spiroketal units in the backbone. Pure poly(1,4-ketone) was obtained by stirring the polymer in a 2:1 (v/v) mixture of $CHCl_3$ and $(CF_3)_2CHOH$ for 8 h followed by precipitation in diethyl ether.

4-Allylanisole−CO Poly(spiroketal/1,4-ketone) (1:2) Copolymer: ^{1}H NMR ($CDCl_3$) (ppm) 6.93 (4H, d, $J = 8.6$ Hz), 6.90 (2H, d, $J = 8.3$ Hz), 6.74 (4H, d, $J = 8.6$ Hz), 6.56 (2H, d, $J = 8.3$ Hz), 3.72 (6H, s), 3.63 (3H, s), 3.01 (2H, br), 2.29−2.74 (11H, m), 1.94 (1H, br), 1.78 (1H, br); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) (ppm) 211.3, 158.1, 157.5, 133.0, 130.4, 129.3, 129.9, 113.8, 113.5, 55.1, 55.0, 47.5, 45.3, 44.0, 40.6, 36.2, 33.7; IR (KBr) (cm^{-1}) 1708, 1245, 1033, 821. Anal. Calcd: C, 75.0, H, 6.8. Found: C, 74.2, H, 6.9. Molar optical rotation, $[\Phi]^{24}_{D} = +20°$ ($c = 5.3$ mg/mL, $CHCl_3$). $M_p = 1.3 \times 10^4$, $M_n = 1.1 \times 10^4$, $M_w = 1.5 \times 10^4$, $M_w/M_n = 1.4$. $T_m = 160$ °C.

4-Allylanisole−CO Pure Poly(1,4-ketone) Copolymer: ^{1}H NMR (2:1 (v/v) $CDCl_3/(CF_3)_2CHOH$) (ppm) 6.97 (2H, d, $J = 8.6$ Hz), 6.80 (2H, d, $J = 8.6$ Hz), 3.74 (3H, s), 3.06 (1H, m), 2.76 (2H, m), 2.57 (1H, d, $J = 16$ Hz), 2.36 (1H, dd, $J = 7.9$, 14 Hz); $^{13}C\{^{1}H\}$ NMR (2:1 (v/v) $CDCl_3/(CF_3)_2CHOH$) (ppm) 214.9, 158.1, 131.4, 130.6, 114.7, 55.8, 48.2, 43.9, 36.5; ^{13}C NMR (2:1 (v/v) $CDCl_3/(CF_3)_2CHOH$) (ppm) 214.9 (s), 158.1 (s), 131.4 (s), 130.6 (d, $J = 162$ Hz), 114.7 (d, $J = 158$ Hz), 55.9 (q, $J = 144$ Hz), 48.2 (d, $J = 133$ Hz), 43.9 (t, $J = 126$ Hz), 36.5 (t, $J = 133$ Hz); IR (KBr) (cm^{-1}) 1706, 1248, 1034. Molar optical rotation, $[\Phi]^{24}_{D} = +100°$ ($c = 5.3$ mg/mL, $CHCl_3$).

Copolymerization of ω-Undecylenic Acid with Carbon Monoxide. The copolymerization was carried out following a procedure analogous to the one employed for ω-undecylenyl alcohol. A 5.8 g sample of ω-undecylenic acid was used, and the reaction was carried out for 36 h. At the end of this period, the unreacted monomer and the solvent were removed under vacuum and the polymer (4.1 g) was purified by running its solution in acetone through a short-stem silica gel column to remove the catalyst: ^{1}H NMR (acetone-d_6) (ppm) 3.62 (3H, s), 2.93−3.02 (2H, m), 2.72 (1H, d, $J = 15$ Hz), 2.30 (2H, t, $J = 6.8$ Hz), 1.60 (2H, m), 1.34 (12H, m); $^{13}C\{^{1}H\}$ NMR (acetone-d_6) (ppm) 213.2, 175.4, 52.0, 45.7, 46.5, 34.9, 34.7, 32.6, 30.9, 30.5, 30.4, 28.0, 26.2; IR (KBr) (cm^{-1}) 1740, 1709. Anal. Calcd: C, 69.0, H, 9.8. Found: C, 68.2, H, 9.7. Molar optical rotation, $[\Phi]^{24}_{D} = +36°$ ($c = 4.3$ mg/mL, acetone). $M_p > 10^6$.

Copolymerization of 6-Heptenoic Acid with Carbon Monoxide. The copolymerization was carried out following a procedure analogous to the one employed for ω-undecylenyl alcohol. A 2 g sample of 6-heptenoic acid was used, and the reaction was carried out at 50 °C. At the end of this period, the reaction solution was filtered and the solvent was removed under vacuum. The polymer (0.43 g) thus obtained was washed with ether and hexane and dried under vacuum: ^{1}H NMR (CD_3OD) (ppm) 3.66 (6H,s), 2.94 (4H, m), 2.76 (2H, m), 2.33 (4H, m), 1.61 (7H, m), 1.33 (5H, m); $^{13}C\{^{1}H\}$ NMR (CD_3OD) (ppm) 214.1, 175.9, 115.2, 52.2, 47.2, 46.6, 45.7, 45.3, 35.0, 34.8, 32.2, 30.1, 29.3, 27.6, 26.7, 26.2; IR (KBr) (cm^{-1}) 1740, 1713. Anal. Calcd: C, 63.5, H, 8.2. Found: C, 62.4, H, 8.6. Molar optical rotation, $[\Phi]^{24}_{D} = +25°$ ($c = 5.1$ mg/mL, CH_3OH). $M_p = 7.8 \times 10^4$, $M_n = 4.6 \times 10^4$, $M_w = 13.3 \times 10^4$, $M_w/M_n = 2.9$, (+ $M_p > 10^6$) (bimodal distribution).

Copolymerization of 4-Pentenoic Acid with Carbon Monoxide. The copolymerization was carried out following a procedure analogous to the one employed for ω-undecylenyl alcohol. A 5 g sample of 4-pentenoic acid was used, and the reaction was carried out at 52 °C. At the end of the reaction, the reaction solution was filtered and the solvent was removed under vacuum. The polymer thus isolated was washed with ether and dried under vacuum; 1.8 g of polymer was obtained: ^{1}H NMR (CD_3OD) (ppm) 3.62 (6H, s), 2.93 (2H, m), 2.77 (1H, m), 2.12−2.69 (5H, m), 2.01 (2H, m), 1.77 (2H, m), 1.54 (2H, m); $^{13}C\{^{1}H\}$ NMR (CD_3OD) (ppm): 213.8, 213.1, 177.5, 176.2, 175.9, 175.2, 115.0, 52.3, 46.0, 45.2, 44.5, 41.8, 33.4, 32.1, 27.4, 25.8; IR (KBr) (cm^{-1}) 1736, 1708. Anal. Calcd: C, 59.2, H, 7.0. Found: C, 58.8, H, 6.7. Molar optical rotation, $[\Phi]^{24}_{D} = +20°$ ($c = 5.2$ mg/mL, CH_3OH). $M_p = 1.2 \times 10^5$, $M_n = 0.5 \times 10^5$, $M_w = 2.9 \times 10^4$, $M_w/M_n = 5.8$.

Copolymerization of 3-Butenoic Acid with Carbon Monoxide. The copolymerization was carried out following a procedure analogous to the one employed for ω-undecylenyl alcohol. A 3 g sample of 3-butenoic acid was used, and the reaction was carried out for 36 h. At the end of this period, the reaction solution was filtered and the solvent were removed under vacuum. The polymer thus obtained (0.62 g) was washed with methanol: ^{1}H NMR ($(CF_3)_2CHOH$, DMSO-d_6 capillary) (ppm) 3.58 (3H, s), 1.52−3.09 (5H, br); $^{13}C\{^{1}H\}$ NMR (CD_3OD) (ppm) 180.3 (br), 176.9 (br), 115.1(br), 52.5 (s), 31.3−40.5 (br); IR (KBr) (cm^{-1}) 1787, 1735. Anal. Calcd: C, 56.2, H, 37.5. Found: C, 55.6, H, 38.7. Molar optical rotation, $[\Phi]^{24}_{D} = -12°$ ($c = 4.9$ mg/mL, $(CF_3)_2CHOH$).

Copolymerizations Using DPPP as the Ligand. A procedure analogous to those described above was used with 4.5×10^{-2} mmol of DPPP replacing (*R*,*R*)-Me-DUPHOS.

Alkene Isomerization Studies. A 2.25×10^{-2} mmol sample of $[Pd(MeCN)_4](BF_4)_2$ and 2.25×10^{-2} mmol of either (*R*,*R*)-Me-DUPHOS or DPPP were codissolved in 1.5 mL of CD_3NO_2. A 1 g sample of 4-pentenoic acid was added to this mixture, and the resultant solution was stirred at 50 °C for 1 day. At the end of this period, the extent of isomerization was assessed from the ^{1}H NMR spectrum of the reaction mixture. Using (*R*,*R*)-Me-DUPHOS as the ligand, the ratio of 4-pentenoic acid:3-pentenoic acid:2-pentenoic acid = 7.6:30.8:61.6. Using DPPP as the ligand, the ratio of 4-pentenoic acid:3-pentenoic acid:2-pentenoic acid = 9:72.7:18.3. The extent of isomerization during an actual polymerization reaction involving DPPP as the ligand was determined by analyzing the unreacted pentenoic acid left after the alternating copolymerization of 4-pentenoic acid with CO was performed under the standard conditions. The ratio of 4-pentenoic acid:3-pentenoic acid:2-pentenoic acid = 82.8:3.4:13.8.

When 3-buten-1-ol was used as the substrate, no significant isomerization was observed with either phoshine as the ligand.

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