

Palladium(II)-Catalyzed Alternating Copolymerization of Allene with Carbon Monoxide and the Synthesis of Terpolymer with *Alt*-Allene-Carbon Monoxide and *Alt*-Ethene-Carbon Monoxide Blocks. Synthetic and Mechanistic Aspects

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Abstract: The alternating copolymerization of 3,3-dimethylallene with carbon monoxide was achieved using [Pd(PPh₃)₂(MeCN)₂](BF₄)₂ as the catalyst. The use of bidentate phosphines resulted in drastically reduced yields. In order to gain insight into the copolymerization mechanism, the stepwise successive insertions of 3,3-dimethylallene and carbon monoxide into palladium–carbon bonds in the complexes, Pd(PPh₃)₂(Me)(Cl), [Pd(PPh₃)₂(C(O)-C₆H₄-Me-p)(MeCN)](BF₄), and [Pd[(Dppp)(Me)(MeCN)](BF₄) (Dppp: 1,3-bis(diphenylphosphino)propane), were studied. These studies, in turn, led to a novel living catalytic system which was used to synthesize a terpolymer with *alt*-allene-carbon monoxide and *alt*-ethene-carbon monoxide blocks.

The alternating copolymers of alkenes with carbon monoxide are of great current interest from scientific as well as technological standpoints.¹ In contrast, the copolymerization of other unsaturated substrates with carbon monoxide has received far less attention. The alternating allene-carbon monoxide copolymers would be of particular interest due to the expected high degree of unsaturation in the backbone which would make the polymers amenable to further functionalizations. Even simple hydrogenation would lead to polymers that are otherwise inaccessible from alkenes and carbon monoxide due to the steric bulk of the alkene (see below for a specific example). To our knowledge, the only report of the alternating copolymerization of an allene with carbon monoxide resides in a patent; however, the structure of the resultant polymer has not been described.² Recently, Vrieze and co-workers have published elegant studies on the stepwise insertions of allene and carbon monoxide into the palladium–carbon bonds of complexes with a rigid bidentate nitrogen ligand.³ Not reported, however, was the ability of these complexes to catalyze the alternating allene-carbon monoxide copolymerization. Herein, we report the palladium(II)-catalyzed syntheses of alternating copolymer of allene and carbon monoxide. In order to gain insight into the copolymerization mechanism, the stepwise successive insertions of 3,3-dimethylallene and carbon monoxide into palladium–carbon bonds in neutral and cationic palladium(II) complexes with mono- and bidentate phosphines were studied. These studies, in turn, led to a novel living catalytic system which was used to synthesize a terpolymer with *alt*-allene-carbon monoxide and *alt*-ethene-carbon monoxide blocks. **This is the first synthesis of a terpolymer consisting of alternating copolymer blocks incor-**

porating three different classes of monomers (alkene, allene, and carbon monoxide).

Results and Discussion

The Alternating Copolymerization of 3,3-Dimethylallene with Carbon Monoxide. The catalyst used for the alternating copolymerization of 3,3-dimethylallene (DMA) with carbon monoxide was [Pd(PPh₃)₂(MeCN)₂](BF₄)₂. It was prepared in situ by dissolving [Pd(MeCN)₄](BF₄)₂⁴ and triphenylphosphine in a 1:2 molar ratio in a 2:1 (v/v) solvent mixture of nitromethane and methanol. As in previous work on analogous alkene-carbon monoxide copolymerizations, nitromethane was needed to dissolve the catalyst precursor while the function of the methanol was to generate the initial metal hydride.¹ The polymer synthesized was found to have a high degree of unsaturation with pendant vinylic functionalities present in conjugation with backbone keto groups. It was characterized by ¹H- and ¹³C-NMR and IR spectroscopy.

The alternating 3,3-dimethylallene-carbon monoxide (DMA-CO) copolymer comprised mainly of the repeating units represented by structure **I** in Figure 1. The ¹H-NMR spectrum in CDCl₃ showed resonances from 1.12 to 1.94 ppm due to the methyl protons. The CH₂ units in the backbone appeared as multiple peaks from 3.03 to 3.77 ppm. The ¹³C-NMR spectrum in CDCl₃ showed multiple resonances from 20.0 to 31.1 ppm due to the methyl carbons. The CH₂ carbons in the backbone appeared from 42.8 to 44.8 ppm as broad peaks. The vinyl carbons showed resonances from 109.3 to 152.3 ppm, and the carbonyl group appeared at 203.0 ppm. The IR (CDCl₃) spectrum showed an absorption at 1686 cm⁻¹, characteristic of conjugated ketones.

Structure **I** is expected to result from the 1,2-insertions of DMA into palladium–acyl bonds. However, the presence of repeat units with structure **II** (Figure 1) resulting from the 3,2-insertions of DMA cannot be ruled out. This is mainly because of the fact that the methyl protons in structure **I** are allylic and would not be expected as low as 1.12 ppm in ¹H-NMR spectrum. In order to obtain a copolymer comprising only of

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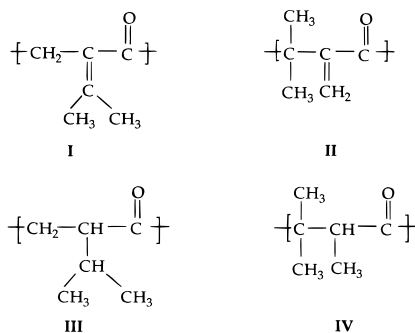


Figure 1. Possible structures for the alternating copolymer of 3,3-dimethylallene with carbon monoxide and the corresponding hydrogenated derivative.

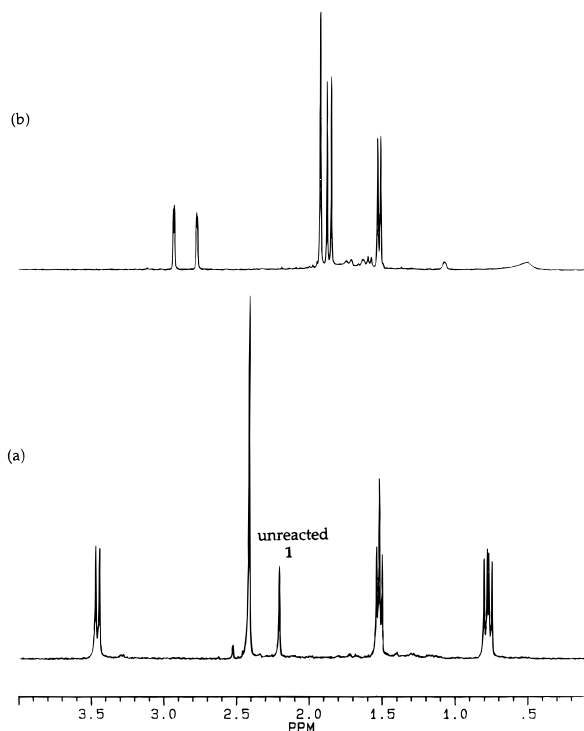


Figure 2. $^1\text{H-NMR}$ (CDCl_3) spectra of (a) $[\text{Pd}(\text{PPh}_3)_2(\eta^3\text{-C}_5\text{H}_8\text{-C}(\text{O})\text{-C}_6\text{H}_4\text{-Me-p})](\text{BF}_4)$, **4**, and (b) $\text{Pd}(\text{PPh}_3)_2(\eta^3\text{-C}_5\text{H}_8\text{-Me})(\text{Cl})$, **7**.

repeat units represented by structure **II**, copolymerization of 1,1,3,3-tetramethyl allene (TMA) with carbon monoxide was attempted using the same catalytic system. The yield of the TMA-CO copolymer obtained was very low, thereby implying that the insertion of the substituted end of the allene is not as facile. The $^1\text{H-NMR}$ spectrum of the TMA-CO copolymer in CDCl_3 showed the resonances due to the allylic methyls as broad peaks centered at 1.81 and 1.62 ppm. The other two methyls in the backbone appeared as multiple peaks from 0.94 to 1.03 ppm. It can thus be concluded that trace amounts of structure **II** are present in the DMA-CO copolymer. The predominant structure, however, is that represented by **I**.

The hydrogenation of the highly unsaturated DMA-CO copolymer was attempted using palladium on carbon and platinum catalysts. The polymer was dissolved in chloroform and was exposed to dihydrogen in the presence of the catalyst for 2 days. The structure of the hydrogenated copolymer would be expected to be mainly **III** with trace amounts of **IV** (Figure 1). The $^1\text{H-NMR}$ spectrum of the hydrogenated copolymers showed new broad resonances around 1.95 and 2.58 ppm due to the CH units formed. The resonances due to the methyl peaks shifted upfield from 1.12–1.94 to 0.83–1.76 ppm. The IR (CDCl_3) spectrum now showed an absorption at 1708 cm^{-1} due

Table 1. Yields of the Alternating Copolymer of 3,3-Dimethylallene and Carbon Monoxide as a Function of the Phosphine Added to $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2^a$

| ligand | yield (g) |
|--------------------------|-----------|
| PPh_3 (2 equiv) | 1.00 |
| PPh_3 (3 equiv) | 1.09 |
| Dppp | 0.10 |
| (<i>R,R</i>)-Me-Duphos | 0.15 |

^a Reaction conditions: 3.8×10^{-2} mmol of $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$ + ligand in 3 mL of a 2:1 (v/v) mixture of CH_3NO_2 and CH_3OH , 1 g of 3,3-dimethylallene + 500 psi of CO, 2 days at 40°C .

to the keto groups, indicating the loss of conjugation with double bonds. However, resonances due to unsaturation present in original DMA-CO copolymer still remained to a small extent. Further hydrogenation using the same catalysts did not show any change in the NMR spectra of the copolymer.

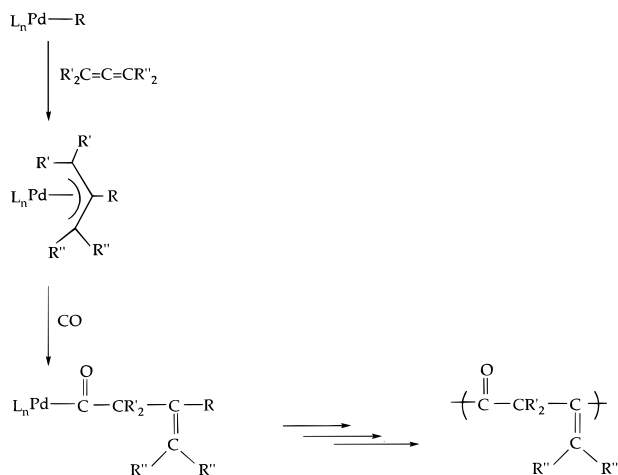
The structure of the hydrogenated copolymers (**III** and **IV**) may be alternatively obtained by the copolymerization of 3-methyl-1-butene and 2-methyl-2-butene with carbon monoxide. However, attempts to copolymerize these monomers with carbon monoxide using $[\text{Pd}(\text{PPh}_3)_2(\text{MeCN})_2](\text{BF}_4)_2$ or $[\text{Pd}(\text{Dppp})(\text{MeCN})_2](\text{BF}_4)_2$ (Dppp: 1,3-bis(diphenylphosphino)propane) as the catalyst did not yield appreciable amounts of copolymers. It is clear that the copolymers of allenes and carbon monoxide can be useful precursors to polymers that are otherwise inaccessible from alkenes and carbon monoxide due to the steric bulk of the alkene.

The effect of a chelating ligand on the palladium(II)-catalyzed copolymerization of DMA with carbon monoxide was studied using Dppp and (*R,R*)-Me-Duphos (= 1,2-bis(2,5-dimethylphospholano)benzene). It was previously observed that chelating bidentate phosphines were far superior to monodentate phosphines in the copolymerization of alkenes with carbon monoxide.¹ The results summarized in Table 1, however, show an opposite trend for the copolymerization of DMA with carbon monoxide. Triphenylphosphine was found to be significantly better than either of the bidentate ligands, and, interestingly, increasing the amount of triphenylphosphine in the reaction mixture did not affect the yield. The structure of the copolymer obtained in all cases was the same. The mechanistic origin of the difference between the reactivities of complexes with monodentate and bidentate phosphines became apparent during the study of the successive insertions of DMA and carbon monoxide into palladium-carbon bonds in the corresponding neutral and cationic palladium(II) complexes.

Mechanistic Aspects of the Copolymerization of 3,3-Dimethylallene with Carbon Monoxide. Analogous to the chain growth mechanism established for the copolymerization of alkenes with carbon monoxide,¹ the copolymerization of allenes with carbon monoxide would be expected to proceed by the alternate insertions of allene and carbon monoxide into a palladium-carbon bond (Scheme 1). However, the insertion of an allene into a palladium-acyl bond would result in the formation of a η^3 -allyl complex, as opposed to a σ -alkyl complex in the case of the insertion of an alkene into a palladium-acyl bond: it has been established that the insertion of allene in a Pd-R complex takes place via migration of the R group to the central electrophilic carbon atom of the allene.³ In order to gain further insight into the individual steps in the polymer chain-growth sequence, the insertions of allene and carbon monoxide into palladium-carbon bonds in three different kinds of palladium(II) complexes were studied.

trans- $[\text{Pd}(\text{PPh}_3)_2(\text{C}(\text{O})\text{C}_6\text{H}_4\text{-Me-p})(\text{MeCN})](\text{BF}_4)$, **1**, reacted with DMA in CDCl_3 in 6 h at ambient temperature to form the η^3 -allyl complex, **4** (Scheme 2). The $^{31}\text{P-NMR}$ spectrum of **4**

Scheme 1



in CDCl_3 showed two doublets at 24.0 ppm ($J = 43$ Hz) and 26.5 ppm ($J = 43$ Hz) indicating that the two phosphine ligands are now inequivalent and therefore *cis* to each other. The $^1\text{H-NMR}$ spectrum in CDCl_3 (Figure 2) showed the two methyl groups of the allene at 0.78 ppm (dd, $J = 6.3, 9.9$ Hz) and 1.53 ppm (t, $J = 5.6$ Hz), while the CH_2 appeared as a doublet at 3.48 ppm ($J = 8.0$ Hz). The methyl of the *p*-tolyl group appeared at 2.41 ppm as a singlet. Complex **4**, when exposed to carbon monoxide (50 psi) for 18 h at ambient temperature in the presence of a few equivalents of DMA, underwent multiple successive insertions of DMA and carbon monoxide to yield oligomers of DMA and carbon monoxide *still bonded to the metal*. Two different kinds of species, **5** and **6** (Scheme 2), were present as determined by ^{31}P - and $^1\text{H-NMR}$ spectroscopy. The $^{31}\text{P-NMR}$ spectrum in CDCl_3 showed a singlet at 19.36 ppm due to the *trans*-Pd-acyl species, **5**,⁶ and a pair of doublets at 23.93 and 26.85 ppm ($J = 41$ Hz) due to the *cis*- η^3 -allyl species, **6**. The absence of any vinylic protons in the $^1\text{H-NMR}$ spectrum supports a 1,2-insertion of DMA resulting in methylene units next to carbonyl groups with pendant $=\text{C}(\text{CH}_3)_2$ groups. The CH_2 units appeared as multiple singlets between 3.60 and 3.73 ppm. The CH_2 unit of the η^3 -allyl fragment of **6** appeared as a doublet at 3.28 ppm ($J = 8.0$ Hz) (similar to *cis*- η^3 -allyl complex **4**). The methyl protons derived from DMA in both species appeared as multiple resonances from 0.72 to 1.98 ppm; the methyl of the *p*-tolyl fragments appeared as singlets from 2.36 to 2.41 ppm. This made it difficult to determine the exact number of DMA molecules (x and y for **5** and **6**, respectively) that have inserted; however, integration of the resonances at 3.60–3.73 versus those at 2.36–2.41 ppm indicated an average of two DMA units per tolyl group present.

In contrast to complex **1**, *trans*-Pd(PPh_3)₂(Me)(Cl), **2**, reacted with DMA in CDCl_3 only on being heated to 45 °C for 1 day. The product, **7** (Scheme 3), showed a broad singlet at 27.48 ppm in the $^{31}\text{P-NMR}$ spectrum in CDCl_3 at ambient temperature. However, on lowering the temperature to 233 K, the spectrum consisted of a pair of doublets at 25.84 and 26.96 ($J = 41$ Hz) ppm. The $^{31}\text{P-NMR}$ parameters are very close to those of complex **4**, thereby indicating that a cationic *cis*- η^3 -allyl complex **7** was being formed by displacement of the chloride ion. The $^1\text{H-NMR}$ spectrum in CDCl_3 (Figure 2) showed a pair of doublets for the two protons of the methylene unit at 2.76 and 2.92 ppm ($J = 2.1$ Hz) and a pair of doublets for the two methyl groups derived from DMA at 1.51 ($J = 5.9$ Hz) and 1.86 ($J =$

8.7 Hz) ppm. The methyl on the central carbon of the allyl ligand appeared as a singlet at 1.91 ppm. It is clear that the difference in the reactivities of complexes **1** and **2** arose mainly due to the anion: complex **1** with a noncoordinating anion was significantly more reactive than **2**.

Complex **2** when heated with a few equivalents of DMA and 200 psi of carbon monoxide for 2 days at 40 °C showed multiple successive insertions of DMA and carbon monoxide giving a mixture of two kinds of species, **8** and **9** (Scheme 3). Complexes **8** and **9** were similar to complexes **5** and **6** obtained from **1**, except the anion was chloride. The $^{31}\text{P-NMR}$ spectrum in CDCl_3 showed a broad resonance at 27.50 ppm for **9** indicative of a *cis*- η^3 -allyl complex (cf., compound **7**) and a sharp singlet at 19.27 ppm for **8** ascribable to a *trans*-Pd-acyl complex. When ^{13}C was employed, a singlet at 236.8 ppm was observed in the $^{13}\text{C-NMR}$ spectrum (CDCl_3) due to the carbonyl group next to the metal in compound **8**. The absence of any ^{31}P -coupling was consistent with a *trans* structure with the phosphines *cis* to the metal-bound organic fragment. The carbonyl groups in the backbone of compounds **8** and **9** that are adjacent to the DMA units appeared as multiple resonances from 201.4 to 206.0 ppm. The η^3 -allyl ligand of complex **9** showed broad peaks at 2.68 and 2.89 ppm in the $^1\text{H-NMR}$ spectrum in CDCl_3 (cf., compound **7**). The CH_2 units derived from DMA that were adjacent to carbonyl groups appeared as multiple singlets from 3.60 to 3.78 ppm. The methyl protons derived from DMA appeared from 1.73 to 1.97 ppm. Finally, a broad singlet at 2.24 ppm indicated the presence of a terminal acetyl group formed by the initial insertion of carbon monoxide into the starting Pd-methyl bond. Integration of the resonances at 3.60–3.78 ppm versus that for the terminal acetyl group indicated an average of five DMA units per acetyl group present.

The effect of a chelating phosphine was examined using complex **3**, $[\text{Pd}(\text{Dppp})(\text{Me})(\text{MeCN})](\text{BF}_4)$. Complex **3** reacted with DMA in 6 h at ambient temperature to give a η^3 -allyl complex, **10a** (Scheme 4). The $^{31}\text{P-NMR}$ spectrum in CDCl_3 showed a pair of doublets at 8.29 and 10.59 ppm ($J = 63$ Hz) for the two inequivalent *cis* phosphorus atoms. The resonances for the two inequivalent protons of the methylene units appeared at 3.07 (d, $J = 10.0$ Hz) and 3.57 (dd, $J = 2.2, 6.0$ Hz) ppm in the $^1\text{H-NMR}$ spectrum. The two methyls showed resonances at 1.12 (dd, $J = 8.0, 10.0$ Hz) and 1.22 (t, $J = 6.2$ Hz) ppm, while the methyl on the central carbon of the allyl appeared at 2.01 ppm as a singlet. Complex **10a** did not undergo insertion of a carbon monoxide molecule even on exposure to 200 psi of carbon monoxide for 1 day. The difficulty associated with the insertion of carbon monoxide into the palladium-carbon bond of complex **10a** was consistent with poor catalytic activity exhibited by complexes with bidentate ligands in the alternating copolymerization of DMA with carbon monoxide.

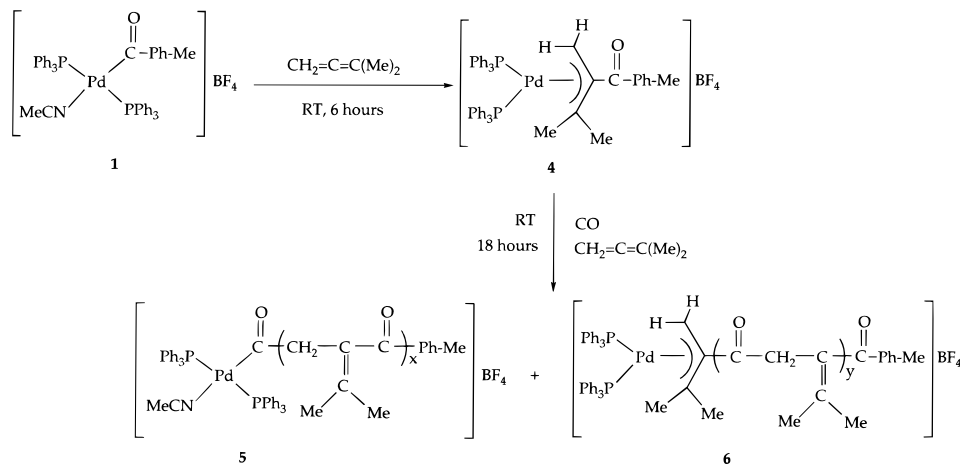
Analogous insertion reactions carried out with 1,1,3,3-tetramethylallene (TMA) instead of DMA did not give well-defined products in good yield with complexes **1** and **2**. Complex **3**, however, reacted with TMA at ambient temperature in 1 day to give a symmetrical η^3 -allyl complex, **10b** (Scheme 4). The $^{31}\text{P-NMR}$ spectrum in CDCl_3 showed a singlet at 9.10 ppm for the two equivalent phosphorus atoms. The four methyls showed resonances as multiplets from 1.24 to 1.35 ppm, while the methyl on the central carbon of the allyl group appeared at 2.16 ppm as a singlet. The general reluctance of TMA to undergo insertion into palladium-carbon bonds was consistent with our inability to form the alternating TMA-carbon monoxide copolymer in good yields.

Formation of Terpolymer with *Alt*-Ethene-Carbon Monoxide and *Alt*-Allene-Carbon Monoxide Blocks. We had

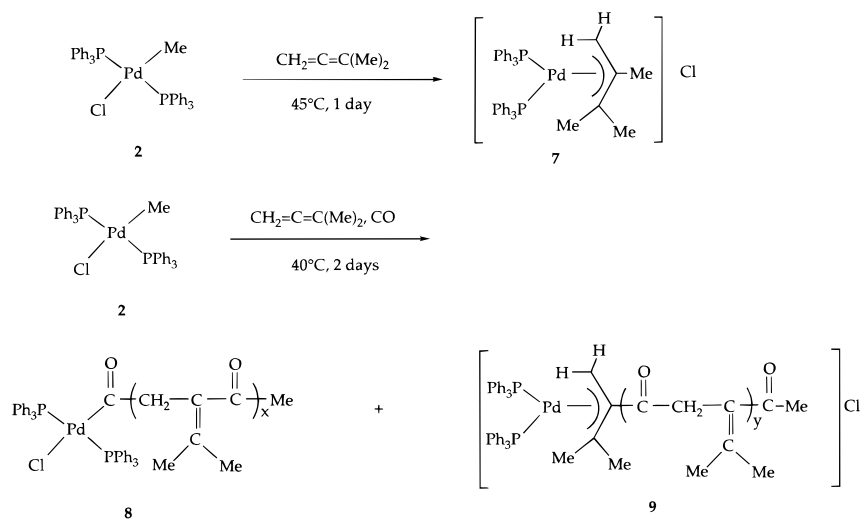
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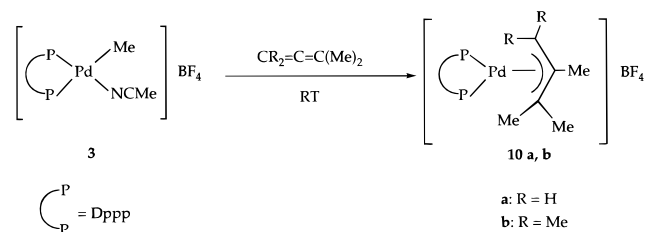
Scheme 2



Scheme 3

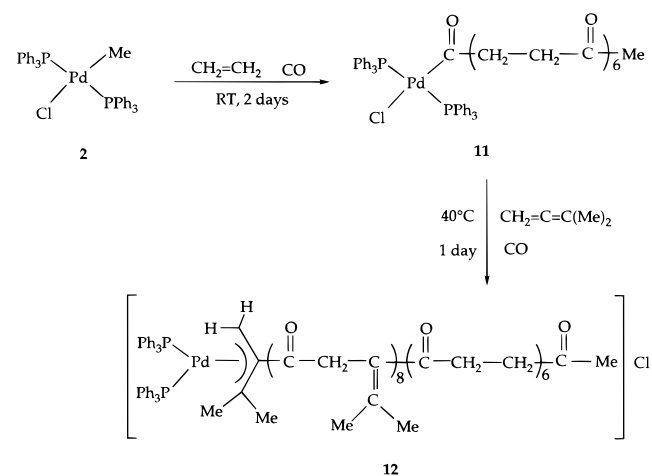


Scheme 4



earlier demonstrated that neutral palladium(II)-acyl complexes can be used as initiators for the copolymerization of ethene and carbon monoxide and that *the resultant copolymer chain remains bonded to the metal*.⁷ Also, as described in the preceding section, neutral palladium(II) complexes undergo successive insertions of allene and carbon monoxide *and the resultant copolymer chain also remains attached to the metal*. The similarity between the two catalyst systems gave rise to the possibility of combining these two copolymerizations. Hence, starting with a neutral palladium complex, an oligomeric alternating ethene-carbon monoxide (E-CO) block was first synthesized. The resulting palladium-acyl complex was then reacted with DMA and carbon monoxide to yield an oligomeric block of DMA-CO (Scheme 5). The formation of the two blocks were restricted to oligomeric lengths in order to follow the reactions by ³¹P-NMR and ¹H-NMR spectroscopy.

Scheme 5



Complex **2**, Pd(PPh₃)₂(Me)(Cl), when exposed to 100 psi each of ethene and carbon monoxide at ambient temperature for 2 days gave rise to **11**, (PPh₃)₂Pd[C(O){CH₂CH₂C(O)}_xMe](Cl) (*x* ≈ 6). The ³¹P-NMR spectrum in CDCl₃ showed a single peak at 19.55 ppm indicating the presence of only one kind of palladium-acyl species and the complete conversion of the starting complex. When ¹³CO was employed, the carbonyl group next to the metal appeared at 235.8 ppm, while the rest of the carbonyl groups in the metal-bound oligomeric chain exhibited resonances between 206.9 and 208.0 ppm in the ¹³C-

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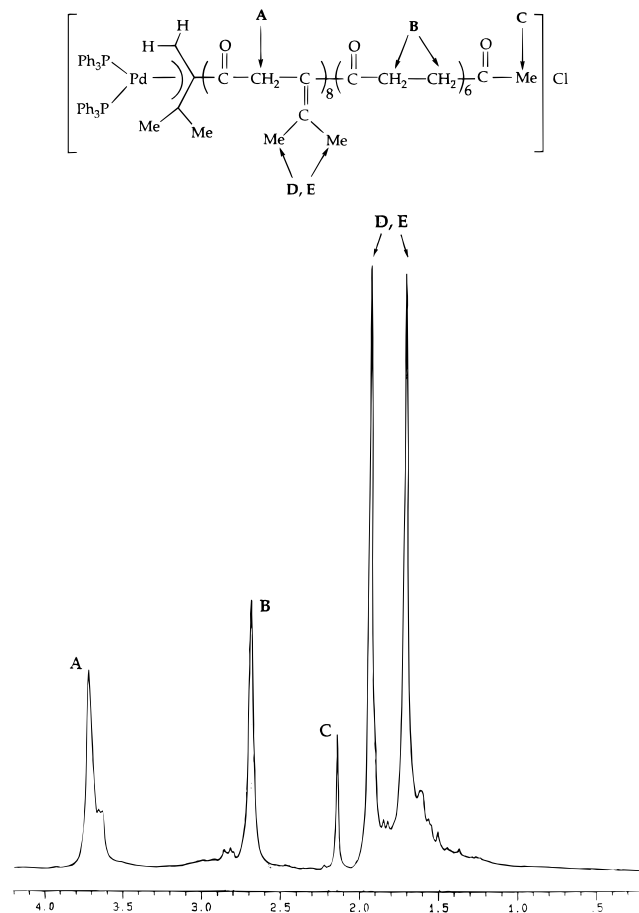


Figure 3. $^1\text{H-NMR}$ (CDCl_3) spectra of (a) $\text{Pd}(\text{PPh}_3)_2[\eta^3\text{-C}_5\text{H}_8\text{-C(O)CH}_2\text{CM}_2)_8(\text{C(O)CH}_2\text{CH}_2)_6\text{C(O)Me}]\text{Cl}$, **12**.

$^1\text{H-NMR}$ spectrum (CDCl_3). The $^1\text{H-NMR}$ spectrum in CDCl_3 showed the ethene unit nearest to palladium as a set of two multiplets at 2.33 and 2.27 ppm. The next ethene unit appeared as multiplets at 2.14 and 2.46 ppm. The rest of the ethene protons gave a single peak at 2.69 ppm. Additional evidence that the ethene-CO copolymer chain remains bonded to the metal in similar complexes are given in a previous publication.⁷ Complex **11** when placed in the presence of a few equivalents of DMA and 200 psi of carbon monoxide at 40 °C for 1 day gave **12**, which showed a broad peak at 27.52 ppm in the $^{31}\text{P-NMR}$ spectrum indicating that it was a *cis*- η^3 -allyl complex. When complex **11**, generated using ^{13}CO was used, the $^{13}\text{C-NMR}$ spectrum (CDCl_3) of **12** generated therefrom revealed that the signal due to the carbonyl group next to the metal had disappeared and was replaced by resonances at 202.5–208.3 ascribable to the presence of a DMA-CO block (cf. compounds **8** and **9**). Clearly, the formation of the DMA-CO block was initiated by the insertion of DMA into the Pd-acyl bond in compound **11**. The $^1\text{H-NMR}$ spectrum of **12** in CDCl_3 showed the E-CO block as a broad singlet at 2.69 ppm and the CH_2 units in the DMA-CO block at 3.73 ppm (Figure 3). Integration of these two peaks gave a ratio of repeat units in the two blocks to be 3:4. The methyls of the DMA-CO block appeared at 1.72 and 1.94 ppm. The methyl group of the starting complex **2** was observed as a singlet at 2.15 ppm indicating an acetyl end-group.

Conclusion

Using $[\text{Pd}(\text{PPh}_3)_2(\text{MeCN})_2](\text{BF}_4)_2$ as the catalyst, 3,3-dimethylallene was successfully copolymerized with carbon monoxide to form a highly unsaturated polyketone. Studies

indicated that cationic palladium(II) complexes with monodentate phosphines show fast successive insertions of allene and carbon monoxide into an initial palladium-carbon bond. The poor catalytic activity for the allene-carbon monoxide copolymerization exhibited by palladium(II) complexes with bidentate phosphines appears to be due to the difficulty associated with the insertion of carbon monoxide into the palladium-carbon bond of the corresponding η^3 -allyl complexes. Since the η^3 -allyl ligand occupies two coordination positions on the metal, the coordination of carbon monoxide prior to its insertion (assuming that insertion occurs from a four-coordinate intermediate⁸) would require either an η^3 to η^1 isomerization of the allyl ligand or the dissociation of one of the coordinated phosphorus atoms. Because of the "chelate effect", the latter would be significantly more difficult in the case of the bidentate phosphines. On the other hand, because Pd-N bonds tend to be weaker than Pd-P bonds, the corresponding insertion should proceed more readily in complexes with bidentate nitrogen ligands as has been reported.^{3b}

Finally, it was possible to design a system that allowed *simultaneously* the living alternating copolymerizations of ethene and carbon monoxide as well as allene and carbon monoxide. The use of this system led to the synthesis of a terpolymer with *alt*-ethene-carbon monoxide and *alt*-allene-carbon monoxide blocks. **This is the first synthesis of a terpolymer consisting of alternating copolymer blocks incorporating three different classes of monomers (alkene, allene, and carbon monoxide).**

Experimental Section

Materials. C.P. grade chemicals were used as received unless otherwise stated. Triphenylphosphine, 1,3-bis(diphenylphosphino)propane (Dppp), and (–)-1,2-bis((2*R*,5*R*)-2,5-dimethylphosphalano)benzene ((*R,R*)-Me-DUPHOS), were purchased from Strem Chemicals. $\text{Pd}[(\text{MeCN})_4](\text{BF}_4)_2$,⁴ *trans*- $[\text{Pd}(\text{PPh}_3)_2(\text{COC}_6\text{H}_4\text{-Me-}p)(\text{MeCN})](\text{BF}_4)$,⁶ $[\text{Pd}(\text{Dppp})(\text{Me})(\text{MeCN})](\text{BF}_4)$,⁵ and $\text{Pd}(\text{PPh}_3)_2(\text{Me})(\text{Cl})$ ⁵ were prepared according to the literature methods. Nitromethane and chloroform were dried over CaH_2 and vacuum-transferred. Methanol was dried over sodium methoxide and vacuum-transferred. 3,3-Dimethylallene (DMA) and 1,1,3,3-tetramethylallene (TMA) were obtained from Aldrich.

General Methods. All catalyst solutions were prepared in a dry nitrogen-filled glovebox. The copolymerization of allene and alkene with carbon monoxide was performed under nitrogen atmosphere. ^1H - and ^{13}C -NMR spectra were recorded on a Bruker AM300 FT-NMR spectrometer. The chemical shifts of ^1H - and ^{13}C -NMR were referenced to internal tetramethylsilane (TMS) or to the solvent resonance at the appropriate frequency. IR spectra (CDCl_3) 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.

Copolymerization of 3,3-Dimethylallene with Carbon Monoxide.

To a solution containing 3.8×10^{-2} mmol (17 mg) of $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$ and 7.6×10^{-2} mmol (20 mg) of triphenylphosphine in 3 mL of a 2:1 (v/v) mixture of CH_3NO_2 and CH_3OH was added 1 g of 3,3-dimethylallene (DMA). The resultant solution was placed in a 125 mL Parr bomb under nitrogen and charged with 500 psi of CO. After stirring for 2 days at 40 °C, the excess carbon monoxide was released, and the solution was filtered. The remaining monomer and solvents were removed under vacuum to obtain 1.0 g of polymer. The polymer was dissolved in chloroform and run through a short-stem silica gel column for further purification. It was then dried under vacuum for 1 day.

$^1\text{H-NMR}$ (CDCl_3) (ppm): 1.12–1.94 (br), 3.03–3.77 (m), 5.86 (m). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) (ppm): 20.0–31.1 (m), 42.8–44.8 (b), 109.3–152.3 (m), 203.0 (m). IR (CDCl_3) (cm^{-1}): 1686. M_p : 4.3×10^3 (MWD = 3.8), 6.7×10^4 (very broad).

Copolymerization Using Other Ligands. A procedure analogous to the one described above was used with 3.8×10^{-2} mmol (19 mg) of Dppp, 11.4×10^{-2} mmol (30 mg) of triphenylphosphine, and 3.8×10^{-2} mmol (14 mg) of (*R,R*)-Me-DUPHOS, respectively.

Copolymerization of 1,1,3,3-Tetramethylallene with Carbon Monoxide. A procedure analogous to the one described for 3,3-dimethylallene was employed using 0.5 g of 1,1,3,3-tetramethylallene. At the end of the reaction, the excess gas was released, and the monomer and solvents were removed under vacuum. Only a trace of copolymer was obtained.

Hydrogenation of the Copolymer of 3,3-Dimethylallene and Carbon Monoxide. 5% Pd/C (100 mg) was added to 10 mL of a solution containing 300 mg of DMA-CO copolymer in CDCl_3 . The resultant solution was placed in a 125 mL Parr bomb and charged with 100 psi of dihydrogen. After stirring for 2 days at room temperature, the excess dihydrogen was released. The solution was filtered and run through a short-stem silica gel column to remove the catalyst.

$^1\text{H-NMR}$ (CDCl_3) (ppm): 0.83–1.76 (br), 1.95 (br), 2.58 (br), 3.57 (m), 4.96 (br), 5.83(m). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) (ppm): 16.0–30.9 (br,m), 42.0–45.0 (m), 107.3–152.3 (m), 203.0 (m). IR (CDCl_3) (cm^{-1}): 1708.

Hydrogenation was also attempted using Pt instead of Pd/C in the procedure described above. The results were identical to those obtained using Pd/C as the catalyst.

Insertion of 3,3-Dimethylallene and Carbon Monoxide into Palladium–Carbon Bonds. All the reactions were done in NMR tubes, and the complexes were characterized in situ.

[Pd(PPh₃)₂(C(O)C₆H₄-Me-p)(MeCN)](BF₄), 1: $^1\text{H-NMR}$ (CDCl_3) (ppm): 1.52 (3H, s), 2.2 (3H, s), 6.82 (2H, d, $J = 7$ Hz), 7.68 (12H, m), 7.45 (2H, d, $J = 7$ Hz), 7.26 (18H, m). $^{31}\text{P-NMR}$ (CDCl_3) (ppm): 20.50.

[Pd(PPh₃)₂(η^3 -C₅H₈-C(O)C₆H₄-Me-p)](BF₄), 4. To a solution containing 25 mg (2.9×10^{-2} mmol) of **1** in 0.8 mL of CDCl_3 was added 3×10^{-3} mL (3.1×10^{-2} mmol) of DMA. The solution was allowed to stand at room temperature for 6 h. $^1\text{H-NMR}$ (CDCl_3) (ppm): 0.78 (3H, dd, $J = 6.3, 9.9$ Hz), 1.53 (3H, t, $J = 5.6$ Hz), 2.41 (3H, s), 3.48 (2H, d, $J = 8.0$ Hz), 7.37 (24H, m), 7.67 (8H, m), 7.90 (2H, d, $J = 8.0$ Hz). $^{31}\text{P-NMR}$ (CDCl_3) (ppm): 24.0 (d, $J = 42.7$ Hz), 26.5 (d, $J = 43.2$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) (ppm): 22.0 (s), 22.1 (d, $J = 5.0$ Hz), 22.4 (d, $J = 3.3$ Hz), 65.7 (d, $J = 31.1$ Hz), 94.2 (s), 112.1 (dd, $J = 4.0, 26.3$ Hz), 128.1–146.5 (phenyl carbons), 194.4 (s). IR (CDCl_3) (cm^{-1}): 1664.

Pd(PPh₃)₂(Me)(Cl), 2: $^1\text{H-NMR}$ (CDCl_3) (ppm): -0.13 (3H, t, $J = 5.9$ Hz), 7.42 (30H, m). $^{31}\text{P-NMR}$ (CDCl_3) (ppm): 30.93 (s).

Pd(PPh₃)₂(η^3 -C₅H₈-Me)(Cl), 7. To a solution containing 25 mg (3.7×10^{-2} mmol) of **2** in 0.8 mL of CDCl_3 was added 4×10^{-3} mL (4.1×10^{-2} mmol) of DMA. The solution was allowed to stand at 45 °C for 1 day. $^1\text{H-NMR}$ (CDCl_3) (233 K) (ppm): 0.84 (3H, b), 1.31 (3H, b), 1.99 (3H, b), 3.12 (1H, b), 3.61 (1H, b), 7.02–7.65 (30H, m). $^{31}\text{P-NMR}$ (CDCl_3) (233 K) (ppm): 25.84 (d, $J = 41$ Hz), 26.96 (d, $J = 41$ Hz). $^1\text{H-NMR}$ (CDCl_3) (298 K) (ppm): 1.51 (3H, d, $J = 5.9$ Hz), 1.86 (3H, d, $J = 8.7$ Hz), 1.91 (3H, s), 2.76 (1H, d, $J = 2.1$ Hz), 2.92 (1H, d, $J = 2.1$ Hz), 7.02–7.65 (30H, m). $^{31}\text{P-NMR}$ (CDCl_3) (298 K) (ppm): 27.48 (b).

[Pd(Dppp)(Me)(MeCN)](BF₄), 3: $^1\text{H-NMR}$ (CDCl_3) (ppm): 0.32 (3H, dd, $J = 2.6, 7.3$ Hz), 1.79 (3H, s), 1.78 (2H, m), 2.50 (4H, m),

7.36 (20H, m). $^{31}\text{P-NMR}$ (CDCl_3) (ppm): -3.44 (d, $J = 54.8$ Hz), 27.20 (d, $J = 54.7$ Hz).

[Pd(Dppp)(η^3 -C₅H₈-Me)](BF₄), 10a. To a solution containing 20 mg (3.0×10^{-2} mmol) of **3** in 0.8 mL of CDCl_3 was added 3×10^{-3} mL (3.1×10^{-2} mmol) of DMA. The solution was allowed to stand at room temperature for 6 h. $^1\text{H-NMR}$ (CDCl_3) (ppm): 1.12 (3H, dd, $J = 8.0$ Hz), 1.22 (3H, t, $J = 6.2$ Hz), 1.68 (2H, m), 1.89 (3H, s), 2.75 (2H, m), 2.95 (2H, m), 3.07 (1H, d, $J = 10.0$ Hz), 3.57 (1H, dd, $J = 2.2, 6.0$ Hz), 7.43 (20H, m). $^{31}\text{P-NMR}$ (CDCl_3) (ppm): 8.29 (d, $J = 63$ Hz), 10.59 (d, $J = 63$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) (ppm): 18.8 (s), 22.0 (s), 23.0 (d, $J = 5.3$ Hz), 25.8 (d, $J = 2.8$ Hz), 26.1 (d, $J = 2.1$ Hz), 26.5 (dd, $J = 4.3, 25.9$ Hz), 68.3 (dd, $J = 3.2, 28.3$ Hz), 94.2 (s), 101.9 (dd, $J = 6.2, 29.7$ Hz), 126.1–133.9 (phenyl carbons).

Complexes **1** and **2** did not give any well defined products in appreciable yield with TMA.

[Pd(Dppp)(η^3 -C₇H₁₂-Me)](BF₄), 10b. To a solution containing 20 mg (3.0×10^{-2} mmol) of **3** in 0.8 mL of CDCl_3 was added 4.0 mg (4.2×10^{-2} mmol) of TMA. The solution was allowed to stand at room temperature for 1 day. $^1\text{H-NMR}$ (CDCl_3) (ppm): 1.24–1.35 (12H, m), 2.16 (3H, s), 2.69 (4H, m), 3.04 (2H, m), 7.40 (20H, m). $^{31}\text{P-NMR}$ (CDCl_3) (ppm): 9.10 (s). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) (ppm): 18.5 (s), 20.0 (s), 21.1 (s), 27.5 (s), 27.5 (d, $J = 27$ Hz), 96.8 (t, $J = 18$ Hz), 118.1 (t, $J = 7$ Hz), 127.7–134.71 (phenyl carbons).

Formation of Terpolymer with *Alt*-Ethene-Carbon Monoxide and *Alt*-Allene-Carbon Monoxide Blocks. Pd(PPh₃)₂(Me)(Cl) (25 mg, 3.7×10^{-2} mmol) was dissolved in 1.0 mL of CDCl_3 and placed in a 125 mL Parr bomb which was then charged with 100 psi each of ethene and carbon monoxide. After 1 day, the excess gases were released, and the product **11** was characterized in situ by ^1H and ^{31}P -NMR spectroscopy.

11: $^1\text{H-NMR}$ (CDCl_3) (ppm): 1.27 (2H, Pd-CO-CH₂-CH₂-CO-CH₂-CH₂-(CO-CH₂-CH₂)_n-CO-Me), 2.14 (5H, Pd-CO-CH₂-CH₂-CO-CH₂-CH₂-(CO-CH₂-CH₂)_n-CO-Me), 2.33 (2H, Pd-CO-CH₂-CH₂-CO-CH₂-CH₂-(CO-CH₂-CH₂)_n-CO-Me), 2.46 (2H, Pd-CO-CH₂-CH₂-CO-CH₂-CH₂-(CO-CH₂-CH₂)_n-CO-Me), 2.69 (16H, Pd-CO-CH₂-CH₂-CO-CH₂-CH₂-(CO-CH₂-CH₂)_n-CO-Me), 7.40 (18H, m), 7.77 (12H, m). $^{31}\text{P-NMR}$ (CDCl_3) (ppm): 19.55. See ref 7 for further details.

DMA (12 mg, 0.2 mmol) was added to the above solution of complex **11** in CDCl_3 , formed in situ from 25 mg (3.7×10^{-2} mmol) of Pd(PPh₃)₂(Me)(Cl). This was placed in a 125 mL Parr bomb and charged with 200 psi of carbon monoxide. The reaction was allowed to proceed for 1 day at 40 °C. At the end of this time period excess carbon monoxide was released, and the product **12** was characterized by ^1H - and ^{31}P -NMR spectroscopy.

12: $^1\text{H-NMR}$ (CDCl_3) (ppm): 1.72 (24H, bs), 1.94 (24H, bs), 2.15 (3H, s), 2.69 (24H, bs), 3.73 (16H, bs), 7.42 (18H, m), 7.67 (12H, m). $^{31}\text{P-NMR}$ (CDCl_3) (ppm): 27.52 (b). IR (CDCl_3) (cm^{-1}): 1679 (br).

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