89397-83-1; $\mathrm{Ag[(CH_3)_3CC{\equiv}CC(CH_3)_3]}$, 89397-84-2; $\mathrm{Ag[C_6H_5C{\equiv}CC_6H_5]}$, 89397-85-3; $\mathrm{Au[CH_3C{\equiv}CH]}$, 89397-86-4; $\mathrm{Au[CH_3C{\equiv}CCH_3]}$, 89397-87-5; $\mathrm{Cu[C_2H_2]_2}$, 65881-79-0; $\mathrm{Cu[CH_3C{\equiv}CH]_2}$, 89397-88-6; $\mathrm{Cu[(CH_3)_3CC{\equiv}CH]_2}$, 89397-89-7; $\mathrm{Cu[CF_3C{\equiv}CH]_2}$, 89397-90-0; $\mathrm{Cu[CH_3C{\equiv}CCH_3]_2}$, 89397-91-1; $\mathrm{Cu[(CH_3)_3CC{\equiv}CC(CH_3)_3]_2}$, 89397-92-2; $\mathrm{Cu[C_6H_5C{\equiv}CC_6H_5]_2}$, 89397-93-3; $\mathrm{CuCH{=}\dot{C}H}$, 89397-62-6; $\mathrm{CuCH{=}\dot{C}CH_3}$, 89397-63-7; $\mathrm{CuCH{=}\dot{C}CF_3}$, 89397-64-8; $\mathrm{CuCH{=}\dot{C}C_6H_5}$, 84074-16-8; $\mathrm{AgCH{=}\dot{C}H}$, 73373-74-7; $\mathrm{AgCH{=}\dot{C}CH_3}$, 89397-65-9; *cis*-$\mathrm{AgCH{=}\dot{C}C(CH_3)_3}$, 89397-66-0; *trans*-$\mathrm{AgCH{=}\dot{C}C(CH_3)_3}$, 89397-67-1; $\mathrm{AgCH{=}\dot{C}CF_3}$, 89397-68-2; $\mathrm{AgCH{=}\dot{C}C_6H_5}$, 84074-17-9; $\mathrm{AuCH{=}\dot{C}H}$, 84074-14-6; $\mathrm{AuCH{=}\dot{C}CH_3}$, 89397-69-3; *cis*-$\mathrm{AuCH{=}\dot{C}C(CH_3)_3}$, 89397-70-6; *trans*-$\mathrm{AuCH{=}\dot{C}C(CH_3)_3}$, 89397-71-7; *cis*-$\mathrm{AuCH{=}\dot{C}C_6H_5}$, 84074-19-1; *trans*-$\mathrm{AuCH{=}\dot{C}C_6H_5}$, 84074-18-0; $\mathrm{CuC[C(CH_3)_3]{=}\dot{C}C(CH_3)_3}$, 89397-72-8; *cis*-$\mathrm{CuC(C_6H_5){=}\dot{C}C_6H_5}$, 89397-73-9; *trans*-$\mathrm{CuC(C_6H_5){=}\dot{C}C_6H_5}$, 89397-74-0; *cis*-$\mathrm{AgC[C(CH_3)_3]{=}\dot{C}C(CH_3)_3}$, 89397-75-1; *trans*-$\mathrm{AgC[C(CH_3)_3]{=}\dot{C}C(CH_3)_3}$, 89397-76-2; $\mathrm{AgC(C_6H_5){=}\dot{C}C_6H_5}$, 89397-77-3; $\mathrm{AuC(C_6H_5){=}\dot{C}C_6H_5}$, 89397-78-4; Cu, 7440-50-8; Au, 7440-57-5; Ag, 7440-22-4; $\mathrm{CH_3C{\equiv}CH}$, 74-99-7; $\mathrm{(CH_3)_3CC{\equiv}CH}$, 917-92-0; $\mathrm{CF_3C{\equiv}CH}$, 661-54-1; $\mathrm{CH_3C{\equiv}CCH_3}$, 503-17-3; $\mathrm{(CH_3)_3CC{\equiv}CC(CH_3)_3}$, 17530-24-4; $\mathrm{CF_3C{\equiv}CCF_3}$, 692-50-2; $\mathrm{C_6H_5C{\equiv}CC_6H_5}$, 501-65-5; $\mathrm{C_2H_2}$, 74-86-2.

Palladium(II)-Catalyzed Copolymerization of Carbon Monoxide with Ethylene. Direct Evidence for a Single Mode of Chain Growth[1]

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The series of cationic Pd(II) compounds $\mathrm{[Pd(PPh_3)_n(CH_3CN)_{4-n}](BF_4)_2}$ (n = 1–3), which may be synthesized in situ or separately, were found to catalyze the copolymerization of CO and $\mathrm{C_2H_4}$ at 25 °C and at a combined pressure of as low as 300 psi, in noncoordinating solvents such as $\mathrm{CHCl_3}$ and $\mathrm{CH_2Cl_2}$. Higher reaction temperatures were required in coordinating solvents, in the presence of excess $\mathrm{PPh_3}$, or when more basic tertiary phosphines were used instead of $\mathrm{PPh_3}$. The ethylene–carbon monoxide copolymer (E–CO copolymer) was a high melting solid having a regular structure with alternating carbon monoxide and ethylene units. The mechanism of the copolymerization is thought to involve a single mode of stepwise chain growth with alternate insertions of carbon monoxide and ethylene into a preformed Pd–alkyl bond. The intermediacy of Pd(II)–alkyl and –acyl species was supported by the observed catalytic activity of $\mathrm{Pd(PPh_3)_2(Me)(solv)^+}$ and $\mathrm{Pd(PPh_3)_2(COMe)(solv)^+}$. The use of alcohols as solvents for the copolymerization reaction resulted in the synthesis of polyketo esters of the type $\mathrm{RO({-}COCH_2CH_2{-})_nH}$. Schultz–Flory plots of the oligomeric polyketo esters formed resulted in straight lines, supporting a stepwise chain growth mechanism. The rate of termination was found to decrease with increasing steric size and decreasing nucleophilicity of the alcohol used. The $\nu_{\mathrm{C=O}}$ for the E–CO copolymer was abnormally low, and there was a monotonic decrease in $\nu_{\mathrm{C=O}}$ with increasing n for the solid oligomeric polyketo esters. This was tentatively ascribed to the presence of intra- and intermolecular dipolar bonding between carbonyl groups.

The formation of polyketones through the copolymerization of CO with olefins is a reaction of significant practical importance. Because of the relative reactivity of the carbonyl group, these polyketones are expected to constitute a new class of photodegradable[2] and, perhaps, biodegradable polymers. In addition, because of the ease with which the carbonyl group can be chemically modified, such polyketones should be excellent starting materials for other, new types of functional polymers.[3]

Table I

	free radical initiated[4]	γ-radiation induced[5]	palladium catalyzed[6]
reaction conditions			
total pressure, psi	200–15 000	2100–2800	800–1900
temp, °C	120–165	25–90	95–135
product properties			
$\mathrm{CO/C_2H_4}$	0.8–0.1	~1[b]	1
structure	random	variable	alternate
mp, °C	<25–117[a]	~180[b]	125–350
mol wt	280–7800	[c]	[c]

[a] Corresponds to copolymer of mol wt 1800.[4b]
[b] Corresponds to a particular sample.[5b] [c] Not reported.

Prior to our initial communication,[1] three basic methods for the copolymerization of CO with $\mathrm{C_2H_4}$ were described in the literature[4-6] and their reaction conditions and the properties of the resultant ethylene–carbon monoxide copolymers (E–CO copolymers) are summarized in Table I. Only the palladium-catalyzed process yielded a regular alternating E–CO copolymer with $\mathrm{CO/C_2H_4}$ ratio of 1. However, the reported procedures involved significantly elevated temperatures and pressures and, furthermore, no mechanistic information was available concerning this

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(1) Transition Metal Catalyzed Copolymerization of Carbon Monoxide with Olefins. 2. For part 1, see: Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1982**, *104*, 3520.

(2) (a) Heskins, M.; Guillet, J. E. *Macromolecules* **1970**, *3*, 224. (b) Hartley, G. H.; Guillet, J. E. *Ibid.* **1968**, *1*, 413. (c) Hartley, G. H.; Guillet, J. E. *Ibid.* **1968**, *1*, 165.

(3) For chemical modifications of the E–CO copolymer, see ref 4b and 5a.

(4) (a) Coffman, D. D.; Pinkney, P. S.; Wall, F. T.; Wood, W. H.; Young, H. S. *J. Am. Chem. Soc.* **1952**, *74*, 3391. (b) Brubaker, M. M.; Coffman, D. D.; Hoehn, H. H. *Ibid.* **1952**, *74*, 1509. (c) Brubaker, M. M. U.S. Patent 2 495 286, 1950.

(5) (a) Morishima, Y.; Takizawa, T.; Murahashi, S. *Eur. Polym. J.* **1973**, *9*, 669. (b) Chatani, Y.; Takizawa, T.; Murahashi, S.; Sakata, Y.; Nishimura, Y. *J. Polym. Sci.* **1961**, *55*, 811.

(6) (a) Nozaki, K. U.S. Patent 3 835 123, 1974. (b) Nozaki, K. U.S. Patent 3 694 412, 1972. (c) Nazaki, K. U.S. Patent 3 689 460, 1972. (d) Fenton, D. M. U.S. Patent 3 530 109, 1970.

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Table II

wt (mg) of $[Pd(CH_3CN)_4](BF_4)_2$[a]	additive	additive/Pd(II) molar ratio	total pressure,[b] psi	temp, °C	wt (mg) of E-CO copolymer[c]
50	none	0	1000	25	0
50	PPh_3	1	1000	25	750
50	PPh_3	2	1000	25	900
50	PPh_3	3	1000	25	600
50	PPh_3	4	1000	25	0
50	PPh_3	4	400	60	840[d]
50	PPh_3	6	1000	25	0
50	$PMePh_2$	2	1000	25	0
50	$PMePh_2$	2	1000	60	900
50	P-*n*-Bu_3	2	1000	25	0
50	PCy_3	2	1000	25	0
50	$P(OPh)_3$	2	1000	25	670
50	$AsPh_3$	2	1000	25	540
50	NPh_3	2	1000	25	0

[a] 10 ml of $CHCl_3$ was used as solvent. [b] $P_{CO}/P_{C_2H_4} = 1$. [c] Reactions were run for 24 h except where noted. [d] Reaction run for 18 h.

novel and potentially useful reaction. In this paper, we report that a series of cationic Pd(II) complexes catalyzed the copolymerization of CO and C_2H_4 under unusually mild conditions (25 °C and total pressure of as low as 300 psi). In addition, we present direct evidence that this reaction proceeded by a single mode of stepwise chain growth and we indicate a novel method for the control of molecular weight distribution in the E–CO copolymer. Our studies have also led to the first catalytic synthesis of polyketo esters of the type $RO(-COCH_2CH_2-)_nH$ (R = alkyl; $n > 2$[7]).

Results and Discussion

A. Catalyst Systems. The cationic Pd(II) compound $[Pd(CH_3CN)_4](BF_4)_2$,[8] **1**, was rapidly reduced to Pd metal by CO. However, the series of compounds $[Pd(PPh_3)_n(CH_3CN)_{4-n}](BF_4)_2$ (n = 1–3), containing the stabilizing ligand PPh_3, were found to catalyze the copolymerization of CO and C_2H_4 at 25 °C and at a combined pressure of as low as 300 psi ($P_{CO}/P_{C_2H_4} = 1$), in noncoordinating solvents such as $CHCl_3$ and CH_2Cl_2. At 60 °C, the minimum required combined pressure was 200 psi. This series of cationic Pd(II) compounds were formed in situ by the addition of appropriate equivalents of PPh_3 to **1**. Alternatively, the compounds $[Pd(PPh_3)_2(CH_3CN)_2](BF_4)_2$, **2**, and $[Pd(PPh_3)_3(CH_3CN)](BF_4)_2$, **3**, were synthesized separately and used as catalysts. The effect of the added stabilizing ligand on the catalytic activity of **1** is shown in Table II. Two trends are clearly evident. While the addition of a stabilizing ligand was necessary for catalytic activity, the addition of highly basic tertiary phosphines suppressed this activity. It is possible that in the presence of basic ligands, CO was bound too strongly to the Pd(II) center, thus effectively poisoning the catalyst. Furthermore, the addition of an excess of the stabilizing ligand also suppressed catalytic activity presumably due to the blockage of all available coordination sites (see section C).

B. Characterization of the E–CO Copolymer. The E–CO copolymer samples obtained were high melting (mp >200 °C) white solids. The elemental analysis of a copolymer sample indicated a CO/C_2H_4 ratio of 1. The structure of the copolymers could be discerned from their solid-state ^{13}C NMR spectra (Figure 1). There were two resonances, at 38.3 and 211.8 ppm, respectively, with an approximate intensity ratio of 2:1. The resonance at 211.8 ppm was ascribed to the carbonyl carbons and was within the range expected for a $-CH_2COCH_2-$ unit.[9] The 38.3 ppm absorbance was due to the α-methylene carbons. The absence of any resonance at ~24 ppm (observed in case of random E–CO copolymers[10]) indicated the absence of β-methylene carbons, leading to the conclusion that our E–CO copolymer had a regular structure with alternating carbon monoxide and ethylene units.

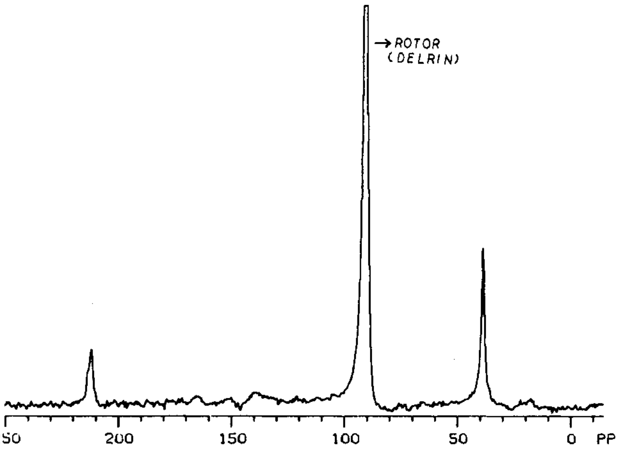

Figure 1. ^{13}C NMR spectrum (37.7 MHz) of solid E–CO copolymer. The rotor (Delrin) consisted of $-CH_2O-$ units.

C. Mechanism of the Copolymerization Reaction. A rational mechanism for the formation of the E–CO copolymer would involve the alternate insertions of CO and C_2H_4 into a preformed Pd–alkyl bond (Scheme I). Two possible factors may favor the insertion of CO into a Pd–alkyl bond over the corresponding insertion of C_2H_4. Because of the greater binding ability of CO, the local concentration of CO would be expected to be significantly higher than C_2H_4. In addition, there appears to be a greater inherent tendency for CO to insert into transition metal–alkyl bonds when compared to the corresponding insertion of olefins.[11] By contrast, while the insertion of olefins into metal–acyl bonds is known,[12] the corresponding insertion of CO has never been directly observed.[13] Thus,

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(7) For a previous catalytic synthesis of $n = 2$ compound, see: Tsuji, J.; Morikawa, M.; Kiji, J. *Tetrahedron Lett.* **1963**, 1437.

(8) Schramm, R. F.; Wayland, B. B. *Chem. Commun.* **1968**, 898.

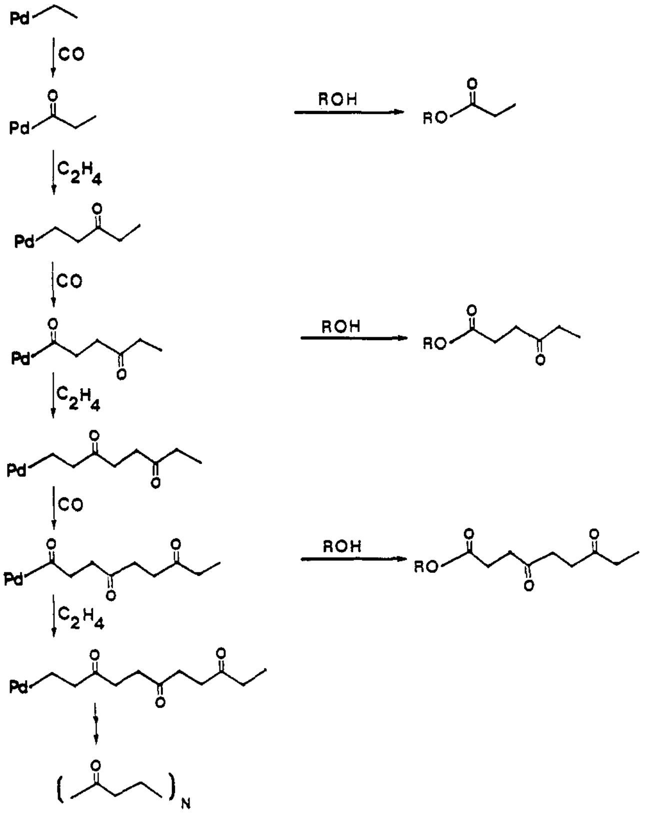
(9) Jackman, L. M.; Kelly, D. P. *J. Chem. Soc. B* **1970**, 102.

(10) Wu, T.-K.; Ovenall, D. W.; Hoehn, H. H. In "Applications of Polymer Spectroscopy"; Brauer, E. G., Ed.; Academic Press: New York, 1978, p 19.

(11) (a) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books, Mill Valley, CA 1980; p 259. (b) For a specific comparison, see: Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604.

(12) For specific examples, see: Tsuji, J. "Organic Synthesis by Means of Transition Metal Complexes"; Springer-Verlag: New York, 1975.

Scheme I



the proposed mechanism forces the alternate addition of carbon monoxide and ethylene units to the growing polymer chain. The slow step in the chain propogation is almost certainly the insertion of C_2H_4 into the Pd–acyl bond. This is because if the corresponding insertion of CO into the Pd–alkyl bond was slow, one should have observed products arising from a competing β-hydrogen abstraction step. In the absence of CO, the compounds $[Pd(PPh_3)_n(CH_3CN)_{4-n}](BF_4)_2$ (n = 1–3) were found to catalyze the rapid dimerization of C_2H_4 (eq 1). The formation of C_4H_8 clearly indicated that β-hydrogen abstraction from Pd–alkyl species is fast compared to further insertions of C_2H_4.

$$C_2H_4 \xrightarrow[25\ °C,\ CHCl_3]{Pd(PPh_3)_n(CH_3CN)_{4-n}{}^{2+}/(n = 1\text{–}3)} C_4H_8 \qquad (1)$$

The intermediacy of cationic Pd(II)–alkyl and –acyl species in the copolymerization reaction was supported by the observation that the species generated by the reaction of $AgBF_4$ with $Pd(PPh_3)_2(Me)(I)$, **4**, and $Pd(PPh_3)_2(COMe)(Cl)$, **5** (presumably $Pd(PPh_3)_2(Me)(solv)^+$ and $Pd(PPh_3)_2(COMe)(solv)^+$, respectively[14]) were also active catalysts for the copolymerization reaction under conditions identical with those used for $[Pd(PPh_3)_n(CH_3CN)_{4-n}](BF_4)_2$ (n = 1–3). Most significantly, the corresponding neutral compounds **4** and **5** as well as $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$ were competely inactive under these conditions, perhaps indicating of the crucial need for easily accessible coordination sites. This was also supported by the observation that although catalyst preparations with PPh_3/Pd^{2+} ratios of 1–3 were active, those with ratios 4 and 6 were found to be inactive except at elevated temperatures (Table II). Similarly, no copolymerization was observed at 25 °C in coordinating solvents such as CH_3CN and THF. Copolymerization occurred in THF, however, at 60 °C. A further reason for the markedly enhanced catalytic activity of the cationic Pd(II) complexes when compared to their corresponding neutral analogues may be their reduced ability to strongly bind CO and C_2H_4, thus facilitating their transfer in the insertion reactions.

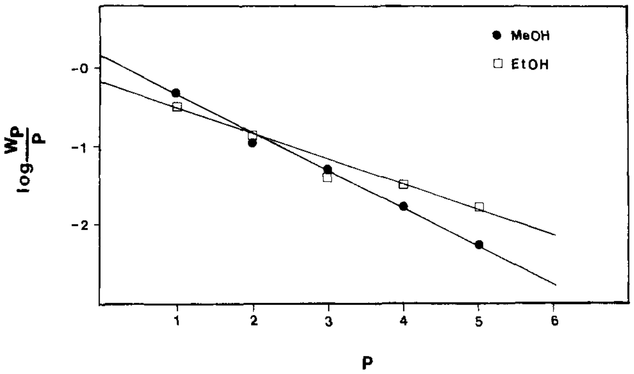


Figure 2. Plots of log (W_p/P) vs. P for oligomeric polyketo esters ($[Pd(PPh_3)_2(CH_3CN)_2{}^{2+}]$ = 0.023 M; initial pressure, $P_{CO} = P_{C_2H_4}$ = 500 psi; reaction temperature, 70 °C). solvent: MeOH (●); EtOH (□).

Table III[a]

	α	
solv	from slope	from intercept
MeOH	0.33	0.31
MeOD	0.38	0.35
EtOH	0.46	0.44

[a] $[Pd(PPh_3)_2(CH_3CN)_2{}^{2+}]$ = 0.023 M; initial pressure, $P_{CO} = P_{C_2H_4}$ = 500 psi; reaction temp, 70 °C.

The origin of the initial Pd–alkyl species in aprotic solvents is uncertain but is almost certainly related to the observed catalytic dimerization of C_2H_4 in the absence of CO. The high molecular weight and the very poor solubility of the E–CO copolymer did not allow us to identify the end groups.

D. Copolymerization in Alcoholic Solvents. Direct evidence for a mechanism involving a single mode of chain growth as depicted in Scheme I came from our studies on the copolymerization reaction in alcoholic solvents. The mechanism, as outlined in Scheme I, involves the formation of Pd–acyl species as intermediates at *every alternate step* in the propagation sequence. Since the formation of esters through the reactions of transition-metal acyls with alcohols is well precedented,[15] it should be possible to intercept the propagation sequence if the copolymerization was carried out in the presence of alcohols (i.e., eq 2).[16]

$$Pd(\text{-}COCH_2CH_2\text{-})_nH \xrightarrow{ROH} RO(\text{-}COCH_2CH_2\text{-})_nH \qquad (2)$$

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(13) There are some reports in the literature on transition metal catalyzed "double carbonylation" reactions, where the products may possibly arise from the insertion of CO into metal–acyl bonds, see: (a) Ozawa, F.; Soyama, H.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* **1982**, *23*, 3383. (b) Kobayashi, T.; Tanaka, M. *J. Organomet. Chem.* **1982**, *233*, C64. (c) Francalanci, F.; Foa, M. *J. Electroanal. Chem.* **1982**, *232*, 59. (d) Alper, H.; des Abbayes, H. *J. Organomet. Chem.* **1977**, 134, C11. However, in a recent study, we have demonstrated that these reactions do not, in fact, proceed through such a mechanistic step and, furthermore, the model compound $PdCOCOPh(Cl)(PPh_3)_2$ spontaneously decarbonylated at 25 °C to $PdCOPh(Cl)(PPh_3)_2$ and that the rate of decarbonylation was independent of CO pressure of up to 700 psi. For details, see: Chen, J.-T.; Sen, A. *J. Am. Chem. Soc.* **1984**, *106*, 1506.

(14) Similar cationic Pt(II) species are known, see: (a) Clark, H. C.; Ruddick, J. D. *Inorg. Chem.* **1970**, *9*, 1226. (b) Kubota, M.; Rothrock, R. K.; Geibel, J. *J. Chem. Soc., Dalton Trans.* **1973**, 1267.

(15) For specific examples, see ref 12.

(16) Reppe had observed the formation of polyketo acids by the $K_2[Ni(CN)_4]$ catalyzed cooligomerization of CO and C_2H_4 in water, see: Reppe, W. *U.S. Patent* 2577208, 1951. However, no mechanistic details are available for this system, and the limited data presented in the patent did not allow us to construct Schultz–Flory plots for the reaction products.

Table IV

compd	$\bar{\nu}_{C=O}$ (KBr), cm^{-1}
$MeO(-COCH_2CH_2-)_1H$	1735
$MeO(-COCH_2CH_2-)_2H$	1735, 1715
$MeO(-COCH_2CH_2-)_3H$	1735, 1710
$MeO(-COCH_2CH_2-)_4H$	1735, 1705
$MeO(-COCH_2CH_2-)_5H$	1735, 1700
$(-COCH_2CH_2-)_n$	1695 (br)

Indeed, the formation of esters of the type $RO(-COCH_2CH_2-)_nH$ was observed when the solvent for the copolymerization reaction was ROH (R = Me, Et). The polyketo esters corresponding to n = 1–5 were separated and quantified,[17] and the results are presented in the form of Schultz–Flory plots[18] in Figure 2. W_p was the weight fraction (minus RO and H; R = Me, Et) of that oligomer whose degree of polymerization was P. A straight line for such a plot indicated a single mode of stepwise chain growth. A quantity, α, equal to (rate of propagation)/(rate of propagation + rate of termination) may be derived from both the slope and the point of intercept, and its values in three different solvents are given in Table III.[19] The change in α from 0.32 to 0.45 on going from MeOH to EtOH indicated that the rate of termination was 1.74 times slower in EtOH than in MeOH (1.21, assuming that the rates of termination were first order in alcohol and correcting for the concentration of alcohol). The above calculation was based on the assumption of identical propogation rates in MeOH and EtOH. This was checked in the following way. $Pd(PPh_3)_2(COMe)(Cl)$ was refluxed with a mixture containing equal volumes of MeOH and EtOH. At the end of the reaction, the ratio of $MeOCOCH_3$ and $EtOCOCH_3$ was measured and found to be 1.56 (1.08, assuming that the rates of formation of the esters were first order in alcohol and correcting for the concentration of alcohol). The proximity of this value to that derived previously indicates that the rate of propogation was virtually independent of the alcohol used. We ascribe the slower rate of termination in EtOH compared to MeOH, to the greater steric size of EtOH. In support of this argument, only high molecular weight ($n > 5$) polyketo esters were obtained with t-BuOH as solvent. Furthermore, only methyl esters were formed in 1:1 mixture (v/v) of MeOH and t-BuOH, indicating a substantially higher rate of termination with MeOH compared to that with t-BuOH. The termination rate was also dependent on the relative nucleophilicity of the alcohol employed, since only the higher polyketo esters ($n > 5$) were obtained when CF_3CH_2OH was used as solvent. The ratio of the rates of termination in MeOH and MeOD was 1.22, indicating a small but significant deuterium isotope effect.

In principal, it should be possible to lower α (i.e., lower the rate of propogation compared to the rate of termination) by lowering the P_{CO} and $P_{C_2H_4}$. Indeed, $EtOCOCH_2CH_3$ was the only product observed, when the reaction was conducted in EtOH with an initial combined pressure of 100 psi instead of 1000 psi ($P_{CO}/P_{C_2H_4}$ = 1).

It is clear that the rate of termination relative to the rate of propagation in the copolymerization of CO and C_2H_4 is critically dependent on the nature of the alcohol and its concentration. This observation provides us with the unique opportunity to control the molecular weight distribution in the E–CO copolymer by a judicioius choice of solvent systems with an alcohol as one of the components. We are testing this possibility.

E. IR Spectra of the E–CO Copolymer. Two remarkable features of the high molecular weight E–CO copolymer that was formed in chlorinated solvents were its insolubility in common organic solvents and the abnormally low $\bar{\nu}_{C=O}$ (~1695 cm^{-1} (KBr)) of its carbonyl groups. We *tentatively* ascribe these phenomena to the presence of the type of intra- and intermolecular dipolar bonding between carbonyl groups shown in I. In support of this argument, we have observed a monotonic decrease in $\bar{\nu}_{C=O}$ with increasing n for the solid oligomeric polyketo esters $MeO(-COCH_2CH_2-)_nH$ (Table IV). Such a dipolar interaction is less likely in solution, and, indeed, while the carbonyl groups in $MeO(-COCH_2CH_2-)_5H$ exhibited a $\bar{\nu}_{C=O}$ = 1700 cm^{-1} in the solid state, the corresponding value in $CHCl_3$ solution was 1710 cm^{-1} (broad).

I

Experimental Section

Analytical Instrumentation. IR spectra were recorded on a Perkin-Elmer Model 580 spectrophotometer. ^1H NMR spectra were recorded on either a Varian EM360 spectrometer or Bruker WM360 and WP200 FT-NMR spectrometers. ^{31}P NMR spectra were recorded on a JEOL PS-100 FT-NMR spectrometer. Solid-state ^{13}C NMR spectra were recorded by Professor J. P. Fackler and Professor W. Ritchey at the Materials Research Laboratory of Case Western Reserve University. Gas chromatography was performed on a Varian 3700 gas chromatograph equipment with a flame ionization detector.

General Procedure. Reagent grade solvents were used. $CHCl_3$, CH_2Cl_2, and CH_3CN were dried by stirring over P_2O_5. THF was dried by stirring over Na/benzophenone. All solvents were deoxygenated either by vacuum distillation or by purging with N_2 prior to their use. CO and C_2H_4 (C.P. grade) were used as received. $Pd(PPh_3)_2Cl_2$,[20] $Pd(PPh_3)_4$,[21] $Pd(PPh_3)_2(Me)(I)$,[22] 4, and $Pd(PPh_3)_2(COMe)(Cl)$,[22] 5, were prepared by literature procedures.

Preparation of $[Pd(CH_3CN)_4](BF_4)_2$,[8] 1. A 1.0-g sample of Pd sponge and 2.2 g of $NOBF_4$ were stirred in 50 mL of CH_3CN under vacuum. NO generated in the course of the reaction was removed periodically. After being stirred for 12 h, the mixture was filtered to yield a yellow filtrate from which a pale yellow compound was obtained by the additional of anhydrous ether. The compound was washed with anhydrous ether and dried under vacuum: 4.1 g, 98%; ^1H NMR (CD_3NO_2) δ 2.65 (s); IR (Nujol) $\bar{\nu}_{C\equiv N}$ 2335 cm^{-1}, $\bar{\nu}_{BF_4^-}$ 1100–1000, 760 cm^{-1}. Anal. Calcd for $PdC_8H_{12}N_4B_2F_8$: C, 21.7; H, 2.7; N, 12.6. Found: C, 21.8; H, 2.9; N, 12.3.

Preparation of $[Pd(PPh_3)_2(CH_3CN)_2](BF_4)_2$, 2. A 0.25-g sample of 1 and 0.295 g of Ph_3P were stirred in 30 mL of CH_2Cl_2 for 1 h. Following concentration of the yellow solution under vacuum, a yellow solid was obtained by adding anhydrous ether. The compound was washed with anhydrous ether and dried under vacuum (0.40 g, 80%): ^1H NMR (CD_3NO_2) δ 7.4–7.2 (30 H, m), 1.85 (6 H, s); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) 32.1 ppm (s); IR (Nujol) $\bar{\nu}_{C\equiv N}$ 2335 cm^{-1}, $\bar{\nu}_{BF_4^-}$ 1100–1000 cm^{-1}.

Preparation of $[Pd(PPh_3)_3(CH_3CN)](BF_4)_2$, 3. A 0.20-g sample of 1 and 1.2 g of PPh_3 were stirred in 30 mL of CH_2Cl_2

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(17) We were unable to separate the higher homologs quantitatively. However, these were characterized by their ^1H NMR and IR spectra.

(18) Henrici-Olive, G.; Olive, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136.

(19) α is a function of P_{CO} and $P_{C_2H_4}$. Therefore, its values in different solvents are for comparisons only.

(20) Chatt, J.; Mann, F. G. *J. Chem. Soc.* **1939**, 1622.

(21) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(22) Fitton, P.; Johnson, M. P.; McKeon, J. E. *Chem. Commun.* **1968**, 6.

for 30 min. A greenish yellow solution was obtained, and following precipitation by the addition of anhydrous ether, an air-stable greenish yellow solid was isolated. The solid was washed with anhydrous ether and dried under vacuum (0.48 g, 97%): $^{31}P\{^1H\}$ NMR ($CDCl_3$, −40 °C) 34.5 (1 P, t, J_{pp} = 11.7 Hz), 27.6 ppm (2 P, d, J_{pp} = 11.7 Hz); IR (Nujol) $\bar{\nu}_{C\equiv N}$ 2335 cm^{-1}, $\bar{\nu}_{BF_4^-}$ 1100–1000 cm^{-1}.

Copolymerization of CO and C_2H_4. In a typical reaction, 50 mg of 1 and 59 mg of PPh_3 (2 equiv relative to Pd) were codissolved in 10 mL of $CHCl_3$ and the solution placed in a 125-mL Parr bomb under N_2 atmosphere. The bomb was then pressurized with 500 psi of CO and further pressurized with 500 psi of C_2H_4, bringing the total pressure to 1000 psi. The contents of the bomb were stirred magnetically at 25 °C for 24 h. At the end of this period, the total pressure had dropped to 640 psi. After depressurization, 0.91 g of the solid E–CO copolymer was obtained as a precipitate. The catalyst impurities present in the E–CO copolymer were removed by Soxhlet extraction with CH_2Cl_2, yielding a white polymer, mp 260 °C. Anal. Calcd for $(COCH_2CH_2)_n$: C, 64.3; H, 7.1. Found: C, 64.0; H, 7.1.

The above procedure was used in other reactions where the temperature, time, pressure, solvent, and the added ligand and/or the Pd compound were varied.

Preparation of $RO(-COCH_2CH_2-)_nH$. The experimental procedure was similar to that used for the synthesis of the high molecular weight E–CO copolymer. In a typical reaction, 0.25 g of 1 and 0.295 g of PPh_3 (2 equiv relative to Pd) were codissolved in 25 mL of MeOH and the solution placed in a 125-mL Parr bomb under N_2 atmosphere. The bomb was then pressurized up with CO (500 psi) and C_2H_4 (500 psi), and the contents were stirred at 70 °C for 14 h. At the end of this period, the combined pressure had dropped to 525 psi (at 25 °C). The contents were filtered to remove the higher molecular weight ($n > 6$), methanol-insoluble, polyketo esters (0.20 g, these were characterized separately). The filtrate yielded 2.10 g of the methanol-soluble polyketo esters $MeO(-COCH_2CH-)_nH$ (n = 1–6). These were separated either on a silica gel column or by gas chromatography using a 10% SP-2100 column. For samples separated by column chromatography, quantitative analysis was performed by using ^1H NMR spectroscopy. For samples separated by gas chromatography, quantitative analysis was done by comparison with standard samples. $MeO(-COCH_2CH_2-)_nH$: selected ^1H NMR and IR spectral data. $n = 1$: ^1H NMR ($CDCl_3$) δ 3.60 (3 H, s, CH_3O), 2.27 (2 H, q, J = 7.2 Hz, $CH_3\mathit{CH_2}COO$), 1.10 (3 H, t, J = 7.2 Hz, $\mathit{CH_3}CH_2COO$); IR (KBr) $\bar{\nu}_{COOCH_3}$, 1735 cm^{-1}. $n = 2$: ^1H NMR ($CDCl_3$) δ 3.67 (3 H, s, CH_3O), 2.74 (2 H, t, J = 6.6 Hz, $CH_3OCO\mathit{CH_2}CH_2$), 2.59 (2 H, t, J = 6.6 Hz, $CH_3OCOCH_2\mathit{CH_2}$), 2.49 (2 H, q, J = 7.2 Hz, $CO\mathit{CH_2}CH_3$), 1.08 (3 H, t, J = 7.2 Hz, $COCH_2\mathit{CH_3}$); IR (KBr) $\bar{\nu}_{COOCH_3}$ 1735 cm^{-1}, $\bar{\nu}_{CH_2COCH_2}$ 1715 cm^{-1}. $n = 3$: ^1H NMR ($CDCl_3$) δ 3.67 (3 H, s, CH_3O), 2.79 (2 H, t, J = 6.5 Hz, $CH_3OCO\mathit{CH_2}CH_2$), 2.57 (2 H, t, J = 6.5 Hz, $CH_3OCOCH_2\mathit{CH_2}$), 2.73 (4 H, m, $CO\mathit{CH_2CH_2}CO$), 2.48 (2 H, q, J = 7.3 Hz, $CO\mathit{CH_2}CH_3$), 1.05 (3 H, t, J = 7.3 Hz, $COCH_2\mathit{CH_3}$); IR (KBr) $\bar{\nu}_{COOCH_3}$, 1735 cm^{-1}, $\bar{\nu}_{CH_2COCH_2}$, 1710 cm^{-1}. $n \geq 6$: ^1H NMR ($CDCl_3$) δ 3.67 (3 H, s, CH_3O), 2.73 (<20 H, br, $CO\mathit{CH_2CH_2}CO$), 2.43 (2 H, q, J = 7 Hz, $CO\mathit{CH_2}CH_3$), 1.08 (3 H, t, J = 7 Hz, $COCH_2\mathit{CH_3}$); IR (KBr) $\bar{\nu}_{COOCH_3}$, 1730 cm^{-1}, $\bar{\nu}_{CH_2COCH_2}$, 1695 cm^{-1}.

Catalytic Dimerization of C_2H_4. In a typical reaction, 50 mg of 1 and 59 mg of PPh_3 (2 equiv relative to Pd) were codissolved in 10 mL of $CHCl_3$ and placed in a 125-mL Parr bomb under N_2 atmosphere. The bomb was then pressurized with C_2H_4 to 900 psi. After the mixture was stirred at 25° for 24 h, the pressure had dropped to 650 psi. At the end of this period, C_2H_4 was vented and the organic products were separated from the catalyst by vacuum distillation. Gas chromatographic analysis (using 20% $AgNO_3$ in ethylene glycol on Chromosorb, 4M) of the products indicated the presence of 1-butene, *trans*-2-butene, and *cis*-2-butene in the ratio of 35.5:45.6:18.9.

Reaction of $Pd(PPh_3)_2(COMe)(Cl)$ with ROH. A 0.20-g sample of $Pd(PPh_3)_2(COMe)(Cl)$ was suspended in 10 mL of a 1:1 (v/v) mixture of MeOH and EtOH and the solution heated to reflux for 3 h under N_2 atmosphere. At the end of this period, the organic products were separated from the precipitated Pd metal by vacuum distillation. Gas chromatographic analysis using a 10% SP-2100 column indicated the formation of CH_3COOMe and CH_3COOEt in the ratio of 61:39.

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Registry No. 1, 21797-13-7; 2, 89397-47-7; 3, 78736-29-5; $Pd(PPh_3)_2(COMe)(Cl)$, 41910-22-9; E-CO copolymer, 25052-62-4; CO, 630-08-0; C_2H_4, 74-85-1; $MeO(COCH_2CH_2)H$, 554-12-1; $MeO(COCH_2CH_2)_2H$, 2955-62-6; $MeO(COCH_2CH_2)_3H$, 66085-98-1; $MeO(COCH_2CH_2)_4H$, 79977-25-6; $MeO(COCH_2CH_2)_5H$, 89378-34-7; MeOH, 67-56-1; EtOH, 64-17-5; 1-butene, 106-98-9; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1.