Highly Efficient Monocationic Palladacycles of Chelating Diphosphines in C_2H_4/CO Copolymerization

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Received January 10, 2000

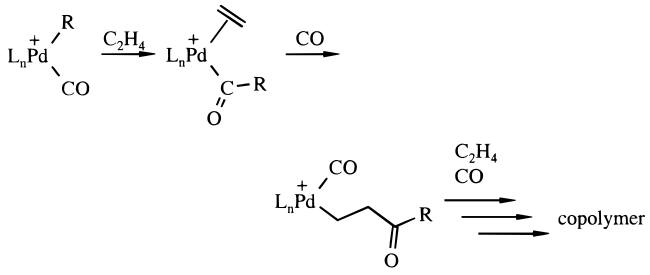
Cationic palladacycles of the general formula [{*o*-$C_6H_4(CH_2)N(R)_2Pd(P^\frown P)$}][X] ($P^\frown P$ = $Ph_2P(CH_2)_3PPh_2$, $(PhCH_2)_2C(CH_2PPh_2)_2$; X = Cl, PF_6, $B(C_6H_5)_4$; R = H, CH_3, $CH_2C_6H_5$) and [{*o*-$(CH_2)C_6H_4P$(*o*-Tol)$_2Pd(P^\frown P)$}][X] ($P^\frown P$ = $Ph_2P(CH_2)_3PPh_2$; X = Cl, PF_6) have been prepared and structurally characterized in the former case (X-ray structure analysis for X = PF_6, R = CH_3). They are resistant to air and moisture, both in solution and the solid state, and represent one of the most active single-component catalyst systems for the perfectly alternating C_2H_4/CO copolymerization in aprotic solvents. Stoichiometric model reactions provide insight into the mechanism, suggesting that insertion of carbon monoxide into the carbon−palladium(II) bond initiates the catalytic cycle.

Introduction

Nearly 50 years of research have been dedicated to metal-catalyzed alternating C_2H_4/CO copolymerization since the first discovery by Reppe et al.[1] Active palladium catalysts were reported by Drent et al. only in 1991.[2] The importance of polyketone polymers made via this elegant method is highlighted by the introduction of Shell's terpolymer Carilon in 1995.[3]

The catalytic systems are generally based on palladium(II) salts with chelating diphosphine ligands, either as in situ systems with a Brønsted acid as cocatalyst[4] or as preformed catalysts,[5] plus an oxidant such as benzoquinone. The stepwise migratory insertion of CO and alkenes into palladium−alkyl and palladium−acyl bonds are the key steps in catalytic polyketone formation (Scheme 1).[6] Propagation errors (double CO or ethylene insertions) are not observed.[7] Recent advances in this field include (i) water-soluble catalyst systems,[8] (ii) single-component nickel catalysts,[9] (iii) chiral palladium(II) complexes for the enantioselective copolymerization of propene and CO,[10] and (iv) alternative ligand systems.[11]

Scheme 1. Key Steps in Catalytic Polyketone Formation



However, with all of the above-mentioned catalysts, a protic solvent or cosolvent is necessary to initiate copolymerization. The active species is monocationic; the dicationic precursors transform into monocationic Pd−R species (R = H, alkoxy, C(O)OR, alkyl) prior to initiation of the copolymerization. Brookhart and co-workers prepared monocationic palladium−methyl complexes which initiate the living copolymerization of *tert*-butylstyrene and CO in aprotic solvents at room temperature

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10.1021/om0000212 CCC: $19.00
Publication on Web 07/11/2000

under 1 atm of CO.[12] More recently, Nozaki and coworkers reported the enantioselective, living copolymerization of propene and CO catalyzed by monocationic palladium−alkyl complexes bearing chiral phosphine−phosphite ligands.[13] The exceptionally high molecular weights of the resulting copolymers are due to the absence of acid cocatalysts and the use of aprotic solvents, in which the termination steps involving the formation of alkyl and ester end groups from protolysis of the metal−alkyl bonds or alcoholysis of the metal−acyl bonds are not present.

We now report on monocationic palladacycles of chelating diphosphines in alkene/CO copolymerization. High activity, extraordinary stability, and the ease of preparation promise success for this new class of single-component catalysts in producing high-molecular-weight poly(3-oxotrimethylene) in aprotic solvents.

Results and Discussion

Preparation and Characterization of the Catalysts. The reaction of the neutral dimeric palladacycles $[\{o\text{-}(CH_2)C_6H_4P(o\text{-}Tol)_2Pd(\mu\text{-}Cl)\}_2]$, $[\{o\text{-}C_6H_4(CH_2)N(CH_3)_2\text{-}Pd(\mu\text{-}Cl)\}_2]$, and $[\{o\text{-}C_6H_4(CH_2)N(H)(CH_2C_6H_5)Pd(\mu\text{-}Cl)\}_2]$, respectively, with 2 equiv of the corresponding chelating diphosphine ligand gives colorless solutions of the chloride salts of the monocationic complexes **1a**−**8a**, which were isolated and spectroscopically characterized in the case of **1a** and **2a**. Upon addition of $[NH_4][PF_6]$, compounds **1b**−**8b** (Chart 1) precipitate as analytically pure white solids in >85% yield. Similarly, anion exchange with $[Na][BPh_4]$ yielded **1c**.

Crystals of complex **1b** suitable for X-ray structure determination were grown by vapor diffusion of diethyl ether into a saturated acetonitrile solution. The crystal structure determination showed the compound to be monomeric, with the diphosphine ligands chelating the palladium(II) center (Figure 1).

The remaining two coordination sites of the square-planar palladium(II) center are occupied by the nitrogen donor and the adjacent *ortho* carbon of the anionic bidentate benzylamine-derived ligand. Summaries of important bond distances and angles for complex **1b** and crystal data, data collection, and refinement details appear in Tables 1 and 2, respectively. The Pd−P distances (2.2460(6) and 2.3706(7) Å) in **1b** are consistent with the *trans* influence of the aryl group being greater than that of the amine. This difference is accompanied by a lengthening of the Pd−C bond to 2.050(2) Å (cf. a typical value of ca. 1.98 Å[14]). Angular distortions from the ideal square-planar geometry for the palladium center in **1b** are minimal, with the exception of those introduced by the five-membered chelate ring for the anionic CN-chelate ligand. Other

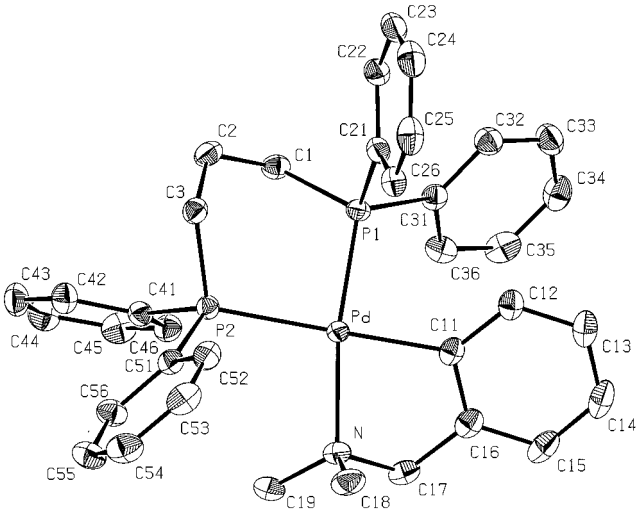
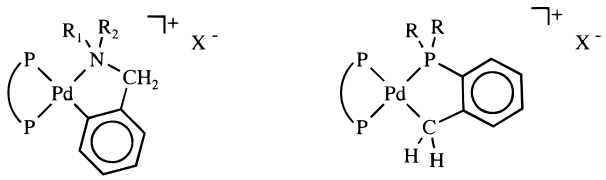


Figure 1. ORTEP drawing of the molecular structure of the monocationic part of **1b**. Thermal ellipsoids are at the 50% probability level. Hydrogens omitted for clarity.

Chart 1. Monocationic Catalysts for the C_2H_4/CO Copolymerization



1 P^P = $Ph_2P(CH_2)_3PPh_2$, $R_1 = R_2 = CH_3$, X = Cl (**1a**), PF_6 (**1b**), BPh_4 (**1c**).

2 P^P = $(PhCH_2)_2C(CH_2PPh_2)_2$, $R_1 = R_2 = CH_3$, X = Cl (**2a**), PF_6 (**2b**).

3 P^P = $Ph_2P(CH_2)_3PPh_2$, $R_1 = H$, $R_2 = CH_2Ph$, X = Cl (**3a**), PF_6 (**3b**).

4 P^P = $(PhCH_2)_2C(CH_2PPh_2)_2$, $R_1 = H$, $R_2 = CH_2Ph$, X = Cl (**4a**), PF_6 (**4b**).

5 P^P = $Ph_2P(CH_2)_2PPh_2$, $R_1 = R_2 = CH_3$, X = Cl (**5a**), PF_6 (**5b**).

6 P^P = $Ph_2P(o\text{-}C_6H_4)PPh_2$, $R_1 = R_2 = CH_3$, X = Cl (**6a**), PF_6 (**6b**).

7 P^P = $Ph_2P(CH_2)PPh_2$, $R_1 = R_2 = CH_3$, X = Cl (**7a**), PF_6 (**7b**).

8 P^P = $Ph_2P(CH_2)_3PPh_2$, R = $o\text{-}C_6H_4CH_3$, X = Cl (**8a**), PF_6 (**8b**).

Table 1. Selected Interatomic Distances (Å) and Angles(deg) for 1b

Pd−P1	2.2460(6)	Pd−N	2.1663(17)
Pd−P2	2.3706(7)	Pd−C11	2.050(2)
P1−Pd−P2	89.99(3)	C1−P1−C21	104.04(11)
P1−Pd−N	166.47(7)	C1−P1−C31	104.55(10)
P1−Pd−C11	90.54(6)	C21−P1−C31	107.11(10)
P2−Pd−N	100.11(6)	Pd−P2−C3	109.32(8)
P2−Pd−C11	173.01(6)	Pd−P2−C41	122.43(8)
N−Pd−C11	80.53(9)	Pd−P2−C51	110.36(8)
Pd−P1−C1	111.36(7)	C3−P2−C41	102.05(10)
Pd−P1−C21	117.48(7)	C3−P2−C51	103.12(11)
Pd −P1−C31	111.30(7)	C41−P2−C51	107.65(10)

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Table 2. Crystal Data and Details of the Data Collection and of the Final Structure Refinement Calculation for 1b

chem formula	$C_{36}H_{38}F_6NP_3Pd$
fw	798.00
color/shape	colorless/fragment
cryst size (mm)	0.41 × 0.36 × 0.25
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	10.997(1)
b (Å)	11.636(1)
c (Å)	15.940(2)
α (deg)	80.65(2)
β (deg)	71.25(1)
γ (deg)	65.34(1)
V (Å^3)	1754.4(4)
Z	2
T (K)	153
ρ_{calcd} (g cm^{-3})	1.511
μ (mm^{-1})	0.725
F_{000}	812
λ (Å)	0.710 73
scan method	φ-scan
θ range (deg)	1.93−25.72
data collcd (h,k,l)	±13, ±14, ±19
no. of rflns collcd	24 266
no. of indep rflns	6196 (all data)
no. of obsd rflns ($I > 2\sigma(I)$)	5515 (obsd)
no. of params refined	631
R_{int}	0.0311
R1[a] (obsd/all)	0.0239/0.0282
wR2[b] (all)	0.0625
GOF[c] (all)	1.008
weights a/b[d]	0.0417/0.6023
max, min $\Delta\rho$ (e Å^{-3})	+0.49, −0.41

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $GOF = [\sum w(F_o^2 - F_c^2)^2/(NO - NV)]^{1/2}$. [d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = [\max(0 \text{ or } F_o^2) + 2F_c^2]/3$.

Table 3. Selected Spectroscopic Data for Compounds 1b−8b

complex	selected ^{31}P NMR data: δ (ppm)	$^2J_{PP}$ (Hz)	FAB-MS [M]$^+$ (100% intensity)
1b	−2.73, 26.83	53.54	653
2b	2.79, 28.90	52.09	833
3b	1.51, 26.96	54.50	715
4b	3.62, 22.29	54.10	895
5b	33.04, 42.02	24.87	639
6b	40.76, 42.09	24.86	687
7b	−1.71, −26.46	52.11	625
8b	−3.44, 12.74	59.46	822

bond distances and angles within the molecule are unexceptional and do not require comment.

^{1}H, ^{13}C, and ^{31}P NMR spectra[15] of complexes **1b**−**8b** are in agreement with their assigned structures. Most characteristic are the ^{31}P NMR data, with the chelating diphosphine ligands appearing as doublets in the range δ −3.5 to 42.5 (Table 3). The mass spectra (FAB ionization) of **1b**−**8b** show the presence of ion fragments corresponding to the monocationic diphosphine-chelated palladacycles (Table 3). The IR spectra of **3b** and **4b** show NH stretching absorptions at 3276.0 and 3272.7 cm^{-1}, respectively.

Complexes **1b**−**8b** are soluble in polar aprotic solvents such as dichloromethane, chloroform, acetonitrile, and pyridine. They are insensitive toward air and water in the solid state.

Catalytic Copolymerization of Ethene and Carbon Monoxide. The bis-chelated palladium complexes **1**−**8** were examined in the C_2H_4/CO copolymerization reaction, with and without 1,4-benzoquinone as a cocatalyst in both protic and aprotic solvents. Perfectly alternating polyketones with characterization data (elemental analyses, melting point, IR and ^{1}H and ^{13}C NMR spectra) in agreement with the literature were obtained (Table 4).[2,5] Our typical values of temperature (70 °C), catalyst concentration (5 × 10^{-5} M), and total pressure (60−80 bar) are in the usual range of highly efficient catalytic systems based on Pd(dppp)X_2 precursors (X = unidentate ligand) employed in methanolic solutions.

Table 4. Summary of Reaction Conditions for CO/C_2H_4 Copolymerization Reactions

entry	catalyst[a]	solvent (amt (mL))	reacn time (h)	yield (kg of copolymer/g of Pd)
1	[Pd(dppp)(bipy)][PF_6]$_2$/43 mg of BQ	MeOH (80)	8	29.5
2	**1b**	CH_2Cl_2 (80)	12	13.2
3	**1b**/15 mg of BQ	CH_2Cl_2 (100)	7	16.3
4	**1b**	THF (90)	35	8.6
5	**1b**	toluene (100)	12	0.5
6	**1c**	CH_2Cl_2 (80)	12	0.2
7	**1a**	CH_2Cl_2 (80)	12	0.0
8	**2b**	CH_2Cl_2 (80)	12	10.0
9	**2b**/15 mg of BQ	CH_2Cl_2 (80)	12	24.4
10	**3b**	CH_2Cl_2 (80)	12	15.1
11	**3b**/15 mg of BQ	CH_2Cl_2 (80)	14	33.0
12	**4b**	CH_2Cl_2 (80)	12	16.0
13	**4b**/15 mg of BQ	CH_2Cl_2 (80)	14	30.0
14	**5b**	CH_2Cl_2 (80)	12	0.00
15	**6b**	CH_2Cl_2 (80)	12	0.2
16	**7b**	CH_2Cl_2 (80)	12	0.0
17	**8b**	CH_2Cl_2 (80)	12	3.9

[a] Catalyst concentrations of 5 × 10^{-5} M were used. Abbreviations: BQ = 1,4-benzoquinone; bipy = 2,2′-bipyridine; dppp = 1,3-bis(diphenylphosphino)propane.

A remarkable decrease in the yield of the copolymer is evidenced with the increasing coordinating ability of the bidentate anionic C−D (D = NR_2, P(*o*-Tol)$_2$) ligand, −NHBz < −NMe_2 ≪ −P(*o*-Tol)$_2$ (entries 2, 10, and 17, Table 4), which is presumably due to the blocking of coordination sites by the two-electron-donating D-groups preventing alkene/CO coordination and insertion in copolymer formation, as expected. The yields of up to ca. 33 kg of copolymer/g of palladium (entry 11, Table 4) compare to those obtained by [Pd(dppp)(2,2′-bipyridine)][PF_6]$_2$, which is one of the most active catalyst systems reported to date.[5] As expected, catalyst **1a** (entry 7, Table 4) containing the strongly coordinating chloride counteranion showed *no* catalytic activity. Also, complex **1c** (entry 6, Table 4), with the [BPh_4]$^-$ anion was almost completely inactive, with the active species decomposing quickly to give palladium black. A similar behavior was reported when the compound [Pd(2,2′-bipyridine)$_2$(BPh_4)$_2$] was used as a catalyst precursor for the reductive carbonylation of nitroaromatic compounds into urethanes and was explained by assuming a phenyl group transfer from the anion to palladium(II).[16] Besides dichloromethane as the solvent of choice, some other commonly used solvents were employed in the catalytic investigations, highlighting perhaps both

(15) ^{13}C NMR spectra were not recorded for **2b**, **3b**, and **8b** because of their poor solubility.

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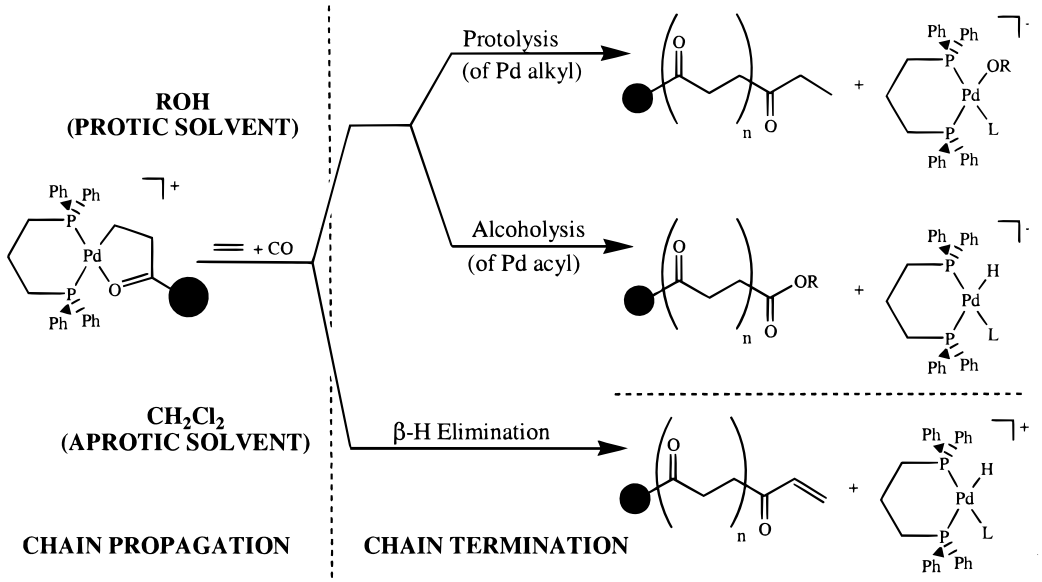
Scheme 2. Chain Termination Steps Occurring in Protic and Aprotic Solvents



solvent polarity and Lewis base donor strength effects. Prolonged reaction times were necessary when the copolymerizations were performed in coordinating solvents such as tetrahydrofuran (entry 4, Table 4). Toluene (entry 5, Table 4) is not suitable for this catalyst system, probably due to the insolubility of complexes **1**−**8** in nonpolar solvents.

Enhanced activities were observed with substituents on the C2 position of the diphosphine ligand backbone (entries 3 and 9, Table 4). This beneficial effect of a modified backbone was very recently described by Bianchini et al.[8c] The electronic and steric properties of the P_2Pd cavity can be influenced by substitution of the dppp backbone, and an increased electron density at the palladium center was found to have a positive influence on the catalytic activity for the *N*,*N*-dimethyl-substituted catalysts **1b** and **2b**, but unfortunately not for the *N*,*N*-HBz analogues **3b** and **4b**. Using anything other than C3-bridged diphosphine ligands led to drastically lowered copolymer yields (entries 14−16, Table 2), as observed in the early reports of Drent et al.[2]

Mechanistic Considerations. When C_2H_4/CO copolymerization is performed in protic solvents such as methanol, both protolysis of palladium−alkyl bonds and esterification of palladium−acyl bonds take place (Scheme 2).[17] In aprotic solvents such as dichloromethane the only chain termination mechanism that is operative is β-H-elimination resulting in vinyl end groups (Scheme 2), and high-molecular-weight copolymers are thus obtained.[18] Whereas in the former case a large excess of an oxidant cocatalyst such as 1,4-benzoquinone is necessary to reactivate the palladium−hydride species formed by methanolysis of palladium−acyl bonds, the effect of oxidants is often negligible in the latter case. In our studies using aprotic solvents, when the catalytic experiments were conducted in the presence of 1,4-benzoquinone, enhanced activities were found (entries 3, 9, 11, and 13, Table 4).

Analysis of the solvent by GC/MS after the removal of all solid products from the reaction mixture confirmed the absence of co-oligomeric products. No end groups could be seen in the ^{13}C NMR spectra of the copolymers obtained from using **1b**−**8b**, which indicates the exclusive formation of very high molecular weight copolymers. The monocationic palladium complexes **1b**−**8b**, bearing one palladium−carbon bond, directly enter the catalytic cycle; no induction period associated with the transformation of the palladacyclic complexes to other species that are the active monocationic species has been observed.

In addition, the palladium(II) end group of the white copolymers did not decompose, even after workup in humid air. Suspended in dichloromethane and pressurized with the monomers, these active polymers reinitiated the copolymerization. A similar behavior has recently been reported for the living CO/alkene alternating copolymerization promoted by [iodo(*endo*-6-phenyl-2-norbornene-*endo*-5σ,2π)(PPh_3)Pd^{II}].[19]

To enhance the chain termination by either protolysis of palladium−alkyl/aryl bonds or alcoholysis of palladium−acyl bonds and gain further insight into the activation steps of the catalytic cycle, we carried out the copolymerization reaction catalyzed by **1b** in protic alcohol solvents (Scheme 3). Again, no co-oligomeric products could be observed by GC/MS; instead, the corresponding *o*-carbalkoxy-substituted benzylamine derivatives **9** and **10** are formed as the only organic decomposition products in high yields (Scheme 3). Compounds **9** and **10** are probably formed by CO insertion into the palladium−sp^2 carbon bond of complex **1b**, followed by alcoholysis of the resulting palladium−acyl compounds.

No reaction occurred between the monocationic complex **1b** and ethene (T = 80 °C, p = 60 bar, CH_2Cl_2). Colorless solutions of complex **1b** in dichloromethane immediately turn deep red when treated with 1 bar of CO at room temperature in dichloromethane. Although it is not possible to isolate and structurally characterize

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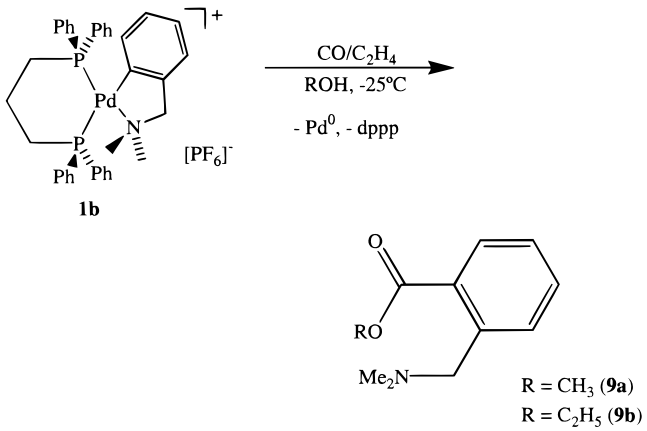
Scheme 3. Reaction of 1b with CO in Alcohols



the product of this reaction, the spectroscopic properties of this solution suggest that CO insertion into the palladium−aryl bond takes place. The very strong IR absorption (KBr) at 1713.7 cm^{-1} is characteristic for a [Pd]−C(O)R group.[20] ^{13}C NMR experiments of **1b** with ^{13}CO (1 bar) in CD_2Cl_2 showed the presence of both σ-coordinated ^{13}CO (δ 168.9: [Pd]−CO) and inserted acetyl groups (δ 241.6: [Pd]−$^{13}C(O)R$).[21] Presumably these observed species are [(dppp)Pd(CO)(*o*-$C_6H_4NCH_2Me_2$)]$^+$, prior to CO insertion, and the CO-inserted product, [(dppp)Pd(C(O)-*o*-$C_6H_4NCH_2Me_2$)]$^+$. These results suggest that the first step of this perfectly alternating copolymerization is CO insertion into the palladium−carbon bond of the monocationic catalyst **1b**, followed by the stepwise migratory insertion of ethene and CO into palladium−acyl and palladium−alkyl bonds. Such a mechanism would lead to a keto end group, −C(O)-*o*-$C_6H_4CH_2NMe_2$. As was the case for the identification of the end group arsing from termination of the copolymers produced in our system, we could not identify the keto end groups by either GC/MS or ^{13}C NMR spectroscopic techniques due to the very high molecular weight of the copolymers produced.

Conclusion

Monocationic palladium(II) complexes of chelating diphosphines are efficient ethene/CO copolymerization catalysts. High activity, easy accessibility, and exceptional stability are excellent prerequisites for industrial applications. Detailed investigations focusing on terpolymerization reactions and stereoselective copolymerization of higher alkenes are ongoing in our laboratories.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or nitrogen. Methanol and ethanol were dried over Mg, and dichloromethane was dried over CaH_2; all were distilled prior to use using conventional procedures. Other solvents were used as received. All the described synthetic procedures herein do not require the use of dried solvents, and yields quoted are for reactions in technical grade solvents, which were used as received. $Pd(OAc)_2$ was obtained from Degussa AG. Other chemicals were obtained from Aldrich and used as received. [{*o*-$(CH_2)C_6H_4P$(o-Tol)$_2Pd(\mu$-Cl)}$_2$], [{*o*-C_6H_4-$(CH_2)N(CH_3)_2Pd(\mu$-Cl)}$_2$], [{*o*-$C_6H_4(CH_2)N(H)(CH_2C_6H_5)Pd(\mu$-Cl)}$_2$], and $(PhCH_2)_2C(CH_2PPh_2)_2$ were prepared according to the literature.[8,22,23] ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX 400 spectrometer in $CDCl_3$ or CD_2Cl_2 and referenced to the residual ^1H resonances of the solvents. ^{31}P NMR spectra were referenced to H_3PO_4 as an internal standard. Elemental analyses were performed by the microanalytical laboratory at our institute. Melting points were determined in glass capillaries under air. IR spectra were recorded on a FT-IR Perkin-Elmer 1680 spectrometer. Mass spectra were recorded on a Varian MAT 311a spectrometer using FAB ionization (xenon/*p*-nitrobenzyl alcohol matrix). GC/MS spectra were obtained on a Hewlett-Packard 5890 instrument.

General Procedure for the Preparation of Complexes 1a−8a. A suspension of the dimeric precursors (1.00 mmol) [{*o*-$(CH_2)C_6H_4P$(*o*-Tol)$_2Pd(\mu$-Cl)}$_2$], [{*o*-$C_6H_4(CH_2)N(CH_3)_2Pd(\mu$-Cl)}$_2$], and [{*o*-$C_6H_4(CH_2)N(H)(CH_2C_6H_5)Pd(\mu$-Cl)}$_2$], respectively, and 2 equiv of the corresponding chelating diphosphine ligand (2.00 mmol) in MeOH (15 mL) was stirred at room temperature for 3 h, yielding a colorless clear solution. The solvent was removed in vacuo, and the remaining white solid was washed with diethyl ether (15 mL) to give the analytically pure chloride salts of the monocationic palladacyclic complexes. Yields: 1.29 g (1.88 mmol, 94%), **1a**; 1.58 g (1.82 mmol, 91%), **2a**.

Compound 1a. Mp: 235 °C dec. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ 7.83−6.21 (m, 24H, CH), 4.14 (s, 2H, NCH_2), 2.88 (br, 4H, PCH_2), 2.34 (s, 6H, NCH_3), 1.88 (m, 2H, CH_2). ^{13}C NMR (100.53 MHz, $CDCl_3$, 25 °C, ppm): δ 140.51−122.98 (m, $C_{aromatic}$), 66.75 (NCH_2), 50.38 (NCH_3), 26.99 (br, PCH_2), 25.08 (br, PCH_2), 19.12 (CH_2). $^{31}P\{^1H\}$ NMR (161.83 MHz, $CDCl_3$, 25 °C, ppm): δ 24.67, −5.48 (AB, $^2J_{PP}$ = 53.58 Hz). MS (FAB, *m*/*z* (%)): 653 (100) [M − Cl]$^+$, 518 (18) [Pd(dppp)]$^+$, 227 (29) [M − dppp − Cl]$^+$. Anal. Found: C, 62.84; H, 5.95; N, 2.43. Calcd for $C_{36}H_{38}NClP_2Pd$: C, 62.80; H, 5.56; N, 2.03.

Compound 2a. Mp: 209 °C dec. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm): δ 7.86−6.52 (m, 34H, CH), 3.88 (s, 2H, NCH_2), 2.56 (br, 4H, PCH_2), 2.23 (s, 6H, NCH_3), 2.11 (s, 4H, CH_2). ^{13}C NMR (100.53 MHz, CD_2Cl_2, 25 °C, ppm): δ 144.07−123.20 (m, $C_{aromatic}$), 65.78 (NCH_2Ph), 47.71 (NCH_3), 41.40 (CH_2), 39.86 (CH_2), 33.56 (br, PCH_2), 31.78 (br, PCH_2). $^{31}P\{^1H\}$ NMR (161.83 MHz, CD_2Cl_2, 25 °C, ppm): d 28.48, 2.98 (AB, $^2J_{PP}$ = 52.42 Hz). MS (FAB, *m*/*z* (%)): 833 (100) [M − Cl]$^+$. Anal. Found: C, 70.01; H, 5.99; N, 1.82. Calcd for $C_{50}H_{50}NClP_2Pd$: C, 69.13; H, 5.80; N, 1.61.

General Procedure for the Preparation of Complexes 1b−8b and 1c. A MeOH/H_2O (2:1; 7 mL) solution of complexes **1a**−**8a** (1.00 mmol), respectively, was treated with a MeOH/H_2O (2:1; 3 mL) solution of $[NH_4][PF_6]$ (3.00 mmol, 489 mg) to give **1b**−**8b**, respectively, as white precipitates which were washed two times with MeOH/H_2O (2:1; 5 mL) and diethyl ether (10 mL) and dried in vacuo. Yields: 758 mg (0.95 mmol, 95%), **1b**; 910 mg (0.93 mmol, 93%), **2b**; 765 mg (0.89 mmol, 89%), **3b**; 936 mg (0.90 mmol, 90%), **4b**; 713 mg (0.91 mmol, 91%), **5b**; 722 mg (0.87 mmol, 87%), **6b**; 678 mg (0.88 mmol, 88%), **7b**; 822 mg (0.85 mmol, 85%), **8b**.

Compound 1b. Mp: 211 °C dec. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm): δ 8.02−6.37 (m, 24H, CH), 4.06 (s, 2H, NCH_2), 2.24 (br, 10H, PCH_2 and NCH_3), 1.83 (m, 2H, CH_2). ^{13}C NMR (100.53 MHz, CD_2Cl_2, 25 °C, ppm): δ 138.11−122.54 (m, $C_{aromatic}$), 65.70 (NCH_2), 51.00 (NCH_3), 27.84 (br, PCH_2), 24.67 (br, PCH_2), 18.66 (CH_2). $^{31}P\{^1H\}$ NMR (161.83 MHz, CD_2Cl_2, 25 °C, ppm): δ 26.83, −2.73 (AB, $^2J_{PP}$ = 53.54 Hz), −143.43 (sept, $^1J_{PF}$ = 713.25 Hz, PF_6^-). MS (FAB, *m*/*z* (%)):

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(23) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.

653 (100) [M − PF_6]$^+$, 518 (12) [Pd(dppp)]$^+$, 227 (27) [M − dppp − PF_6]$^+$. Anal. Found: C, 66.34; H, 5.98; N, 2.21. Calcd for $C_{36}H_{38}NF_6P_3Pd$: C, 66.21; H, 5.86; N, 2.14.

Compound 2b. Mp: 193 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm): δ 7.94−6.52 (m, 34H, CH), 4.11 (s, 2H, NCH_2), 2.46−2.27 (m, 14H, PCH_2, NCH_3 and CH_2Ph). $^{31}P\{^1H\}$ NMR (161.83 MHz, CD_2Cl_2, 25 °C, ppm): δ 28.90, 2.79 (AB, $^2J_{PP}$ = 52.09 Hz), −143.65 (sept, $^1J_{PF}$ = 711.59 Hz, PF_6^-). MS (FAB, *m*/*z* (%)): 833 (100) [M − PF_6]$^+$. Anal. Found: C, 61.06; H, 5.03; N, 1.28. Calcd for $C_{50}H_{50}NF_6P_3Pd$: C, 61.39; H, 5.15; N, 1.43.

Compound 3b. Mp: 205 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm): δ 7.72−6.43 (m, 29H, CH), 3.71 (br, 2H, NCH_2), 3.33 (br, 2H, NCH_2), 2.63 (br, 4H, PCH_2), 1.93 (m, 2H, CH_2). $^{31}P\{^1H\}$ NMR (161.83 MHz, CD_2Cl_2, 25 °C, ppm): δ 26.96, 1.51 (AB, $^2J_{PP}$ = 54.50 Hz), −143.05 (sept, $^1J_{PF}$ = 709.19 Hz, PF_6^-). MS (FAB, *m*/*z* (%)): 715 (100) [M − PF_6]$^+$. Anal. Found: C, 57.94; H, 4.93; N, 1.54. Calcd for $C_{41}H_{40}NF_6P_3Pd$: C, 57.25; H, 4.69; N, 1.63.

Compound 4b. Mp: 190 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm): δ 7.81−6.38 (m, 39H, CH), 4.71 (br, 2H, NCH_2), 3.75 (br, 2H, NCH_2), 2.69 (m, 4H, PCH_2), 1.64 (br, 4H, CH_2Ph). ^{13}C NMR (100.53 MHz, CD_2Cl_2, 25 °C, ppm): δ 138.11−122.54 (m, $C_{aromatic}$), 66.07 (NCH_2), 59.08 (NCH_2), 43.46 (CH_2), 43.01 (CH_2), 28.13 (br, PCH_2), 27.84 (br, PCH_2), 15.31 ($C(CH_2Ph)_2$). $^{31}P\{^1H\}$ NMR (161.83 MHz, CD_2Cl_2, 25 °C, ppm): δ 22.29, 3.62 (AB, $^2J_{PP}$ = 54.10 Hz), −144.08 (sept, $^1J_{PF}$ = 711.57 Hz, PF_6^-). MS (FAB, *m*/*z* (%)): 895 (100) [M − PF_6]$^+$. Anal. Found: C, 63.63; H, 5.35; N, 1.26. Calcd for $C_{55}H_{52}NF_6P_3Pd$: C, 63.50; H, 5.04; N, 1.35.

Compound 5b. Mp: 202 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm): δ 8.24−6.59 (m, 24H, CH), 4.19 (s, 2H, NCH_2), 2.54 (s, 6H, NCH_3), 2.58−2.23 (m, 4H, PCH_2). ^{13}C NMR (100.53 MHz, CD_2Cl_2, 25 °C, ppm): δ 140.87−123.55 (m, $C_{aromatic}$), 74.80 (NCH_2), 52.22 (NCH_3), 31.88 (m, PCH_2), 28.28 (m, PCH_2). $^{31}P\{^1H\}$ NMR (161.83 MHz, CD_2Cl_2, 25 °C, ppm): δ 42.02, 33.04 (AB, $^2J_{PP}$ = 24.87 Hz), −143.98 (sept, $^1J_{PF}$ = 712.93 Hz, PF_6^-). MS (FAB, *m*/*z* (%)): 639 (100) [M − PF_6]$^+$. Anal. Found: C, 54.36; H, 4.3; N, 1.99. Calcd for $C_{35}H_{36}NF_6P_3Pd$: C, 53.62; H, 4.63; N, 1.79.

Compound 6b. Mp: 208 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm): δ 7.73−6.64 (m, 28H, CH), 4.15 (s, 2H, NCH_2), 2.57 (s, 6H, NCH_3). ^{13}C NMR (100.53 MHz, CD_2Cl_2, 25 °C, ppm): δ 143.46−122.48 (m, $C_{aromatic}$), 74.42 (NCH_2), 52.36 (NCH_3). $^{31}P\{^1H\}$ NMR (161.83 MHz, CD_2Cl_2, 25 °C, ppm): δ 42.09, 40.76 (AB, $^2J_{PP}$ = 24.86 Hz), −143.69 (sept, $^1J_{PF}$ = 712.07 Hz, PF_6^-). MS (FAB, *m*/*z* (%)): 687 (100) [M − PF_6]$^+$. Anal. Found: C, 56.48; H, 4.45; N, 1.78. Calcd for $C_{39}H_{34}NF_6P_3Pd$: C, 56.43; H, 4.13; N, 1.69.

Compound 7b. Mp: 183 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm): δ 7.81−6.65 (m, 24H, CH), 4.15 (s, 2H, NCH_2), 4.10 (br, 2H, PCH_2P), 2.85 (s, 6H, NCH_3). ^{13}C NMR (100.53 MHz, CD_2Cl_2, 25 °C, ppm): δ 150.15−123.65 (m, $C_{aromatic}$), 72.65 (NCH_2), 52.69 (NCH_3), 40.59 (br, PCH_2P). $^{31}P\{^1H\}$ NMR (161.83 MHz, CD_2Cl_2, 25 °C, ppm): δ −1.71, −26.46 (AB, $^2J_{PP}$ = 52.11 Hz), −143.10 (sept, $^1J_{PF}$ = 709.61 Hz, PF_6^-). MS (FAB, *m*/*z* (%)): 625 (100) [M − PF_6]$^+$. Anal. Found: C, 53.93; H, 4.34; N, 1.76. Calcd for $C_{34}H_{34}NF_6P_3Pd$: C, 53.04; H, 4.45; N, 1.82.

Compound 8b. Mp: 169 °C dec. $^{31}P\{^1H\}$ NMR (161.83 MHz, CD_2Cl_2, 25 °C, ppm): δ 41.42 (dd, $^2J_{PP}$(trans) = 332.93 Hz, $^2J_{PP}$(cis) = 35.67 Hz), 12.74 (dd, $^2J_{PP}$(trans) = 332.93 Hz, $^2J'_{PP}$(cis) = 59.46 Hz), −3.44 (dd, $^2J_{PP}$(cis) = 35.67 Hz, $^2J'_{PP}$(cis) = 59.46 Hz), −142.98 (sept, $^1J_{PF}$ = 710.39 Hz, PF_6^-). MS (FAB, *m*/*z* (%)): 822 (100) [M − PF_6]$^+$, 518 (15) [Pd(dppp)]$^+$. Anal. Found: C, 60.01; H, 4.98. Calcd for $C_{48}H_{46}F_6P_4Pd$: C, 59.61; H, 4.79.

Compound 1c. A MeOH/H_2O (2:1; 7 mL) solution of **1a** (1.00 mmol) was treated with a MeOH/H_2O (2:1; 3 mL) solution of [Na][BPh_4] (3.00 mmol) to give **1c** as a white precipitate which was washed two times with MeOH/H_2O (2:1; 5 mL) and diethyl ether (10 mL) and dried in vacuo. Yield: 0.92 g (89 mmol, 89%). Mp: 198 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, ppm): δ 8.74−6.20 (m, 44H, CH), 4.06 (s, 2H, NCH_2), 2.24 (br, 10H, PCH_2P and NCH_3). ^{13}C NMR (100.53 MHz, CD_2Cl_2, 25 °C, ppm): δ 164.17 (q, BC, $^1J_{BC}$ = 49.25 Hz), 140.11−121.54 (m, $C_{aromatic}$), 64.54 (NCH_2Ph), 51.96 (NCH_3), 26.35 (br, PCH_2), 24.32 (br, PCH_2), 19.24 (CH_2). $^{31}P\{^1H\}$ NMR (161.83 MHz, CD_2Cl_2, 25 °C, ppm): δ 24.65, −1.98 (AB, $^2J_{PP}$ = 50.98 Hz). MS (FAB, *m*/*z* (%)): 653 (100) [M − PF_6]$^+$, 518 (12) [Pd(dppp)]$^+$. Anal. Found: C, 73.93; H, 5.34; N, 1.32. Calcd for $C_{60}H_{56}NBP_2Pd$: C, 74.27; H, 5.82; N, 1.44.

Methyl 2-((Dimethylamino)methyl)benzoate (9) and Ethyl 2-((Dimethylamino)methyl)benzoate (10). Carbonylation of the monocationic complexes **1b** and **3b** (1.00 mmol, 979 mg) in alcohol was carried out at 60 °C with CO at atmospheric pressure for 10 h. The precipitated palladium black was separated by filtration and the solvent evaporated to dryness. The residues were purified on a silica gel column with dichloromethane to give **9** and **10**. Yields: 103 mg (0.63 mmol, 63%), **9**; 143 mg (0.69 mmol, 69%), **10**.

Compound 9. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ 7.81−7.23 (m, 4H, CH), 4.09 (s, 2H, CH_2), 3.88 (s, 3H, OCH_3), 2.47 (s, 6H, NCH_3). MS (FAB, *m*/*z* (%)): 193 (21) [M]$^+$, 178 (100) [M − CH_3]$^+$, 162 (17) [M − OCH_3]$^+$, 149 (10) [M − $N(CH_3)_2$]$^+$, 133 (61) [M − $C(O)OCH_3$]$^+$.

Compound 10. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ 7.84−7.16 (m, 4H, CH), 4.36 (q, 2H, CH_2, $^3J_{HH}$ = 7.52 Hz), 4.16 (s, 2H, CH_2), 2.58 (s, 6H, NCH_3), 1.39 (t, 3H, CH_3, $^3J_{HH}$ = 7.52 Hz). MS (FAB, *m*/*z* (%)): 207 (22) [M]$^+$, 192 (53) [M − CH_3]$^+$, 178 (55) [M − C_2H_5]$^+$,162 (38) [M − OC_2H_5]$^+$, 133 (100) [M − $C(O)OC_2H_5$]$^+$.

Copolymerization Reactions. The copolymerization reactions were carried out in a mechanically stirred 300 mL Parr autoclave by introducing the catalyst (5×10^{-6} mmol) and the solvent. The autoclave was pressurized sequentially with a 1:1 mixture of ethene and then carbon monoxide to a total pressure of 60 bar. The vessel was closed and heated to 70 °C and the copolymerization carried out isothermally by allowing the pressure to decrease during the course of reaction. After the reaction time, the autoclave was cooled to room temperature and the residual pressure discharged. The polymer formed was filtered off, washed with methanol, and vacuum-dried.

X-ray Crystallography for 1b. Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in Table 2. Crystals of complex **1b s**uitable for X-ray structure determination were grown by vapor diffusion of diethyl ether into a saturated acetonitrile solution. Preliminary examination and data collection were carried out on an imaging plate diffraction system (IPDS; Stoe&Cie) equipped with a rotating anode (Nonius FR591: 50 kV, 80 mA, 4.0 kW) and graphite-monochromated Mo Kα radiation. Data collection was performed at 153 K within the θ range of 1.93°< θ < 25.72° with an exposure time of 120 s per image (rotation scan modus from φ = 0° to 360° with $\Delta\varphi$ = 2.0°). A total number of 24 266 reflections were collected. After merging (R_{int} = 0.0311) a sum of 6196 independent reflections remained and were used for all calculations. Data were corrected for Lorentz and polarization effects. Corrections for absorption and decay effects were applied with the program Decay.[24a] The unit cell parameters were obtained by full-matrix least-squares refinements of 4974 reflections with the program

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Cell.[24a] The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms of the asymmetric unit were refined anisotropically. All hydrogen atoms were found in the difference Fourier map and refined freely with individual isotropic thermal displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at R1 = 0.0282, wR2 = 0.0625, GOF = 1.008, and maximum shift/error <0.001. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 24c. All calculations were performed on a PC workstation (Intel Pentium II) with a Linux system, including the programs PLATON, SIR92, and SHELXL-97.[24]

Acknowledgment. We are grateful to Dr. Karl Öfele for suggestions and fruitful discussions. This work was supported by the Alexander von Humboldt-Stiftung (fellowship for M.G.G.) and the Fonds der Chemischen Industrie (studentship for J.S.). We also thank Degussa AG for generous gifts of palladium starting compounds.

Supporting Information Available: Detailed tables of the data collection details, atomic coordinates, thermal displacement parameters, and bond distances and angles for **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0000212