Tailored Cationic Palladium(II) Compounds as Catalysts for Highly Selective Dimerization and Polymerization of Vinylic Monomers: Synthetic and Mechanistic Aspects[1]

Zhaozhong Jiang and Ayusman Sen*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

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The electrophilic palladium(II) compounds Pd(2,6-di-*tert*-butylpyridine)$_2$(CH_3NO_2)$_2$(BF_4)$_2$ (1), Pd(PPh_3)$_2$(BF_4)$_2$ (2), and Pd($Ph_2PCH_2CH_2PPh_2$)(BF_4)$_2$ (3) were found to be highly selective catalysts for the acyclic dimerization of vinyl monomers (styrene, ethylene, and propylene) and the linear polymerization of *p*-divinylbenzene, the reactions proceeding through a carbocationic mechanism. One manifestation of the high selectivity was the ability to catalyze the dimerization of ethylene in the presence of propylene and styrene in the presence of α-methylstyrene even though the second member of each pair was normally significantly more reactive in reactions involving carbocationic intermediates. The linear polymerization of *p*-divinylbenzene involved in step-growth mechanism. The synthesis of a telechelic polymer through cross-coupling between the terminal vinyl groups of linear poly(*p*-divinylbenzene) and the vinyl group of a functionalized styrene derivative was also achieved. The reaction rates for the linear dimerization of styrene and the linear polymerization of *p*-divinylbenzene were found to be first order in the monomer concentration and fractional order in the catalyst concentration. Mathematical modeling indicated that the fractional order in the catalyst concentration was due to preequilibria involving anion dissociation from the metal center, and actually, the catalytic species in the case of 2 was found to be the dication, Pd(PPh_3)$_2^{2+}$.

The cationic polymerization of vinylic monomers[2] is a procedure of great practical importance. The initiators are generally strong Bronsted acids or main-group Lewis acids that react with the monomer to form propagating carbocations. The generally fast reaction rates and the low concentrations of the active sites have been major impediments for detailed mechanistic studies on such systems. It is, therefore, not surprising that quantitative information about the initiating and propagating cationic species and their interactions with counteranions is scarce.[2]

Recently, a number of cationic, electrophilic transition metal compounds have been demonstrated to be efficient initiators for the cationic oligomerization and polymerization of olefins.[3] However, the mechanistic steps involved in initiation and propagation have not been hitherto explored. An important advantage that the transition metal compounds have over the traditional cationic initiators is the possibility of tailoring their activity and selectivity by a rational choice of ligands. The palladium(II) cation is a test case because of its high electrophilicity[3] and well-established coordination chemistry.[4] Indeed, by changing the ligands around the Pd(II) cation, we have succeeded in systematically varying the reactivity and selectivity of the metal center vis-à-vis the vinylic monomers. This has led to the discovery of highly selective catalysts for the acyclic dimerization of styrene and linear polymerization of *p*-divinylbenzene. Additionally, the cationic oligomerization and polymerization reactions catalyzed by the ligand-attenuated palladium(II) species proceeded at measurable rates at ambient temperature or above. This also allowed us to examine the kinetics and mechanisms of the initiation and propagation steps in some detail. In particular, the reaction rates were found to be first order in monomer concentration and fractional order in the catalyst concentration. The latter was due to the association of the counteranion with the cationic Pd(II) center, and a quantitative relationship between equilibrium constants for successive anion dissociation and the reaction order for the catalyst was established.

Experimental Section

Analytical Instrumentation. ^{1}H NMR and ^{13}C NMR spectra, either coupled or decoupled, were recorded on a Bruker WP 200 or AM 300 FT-NMR spectrometer. The chemical shifts reported were referenced to internal tetramethylsilane (TMS) or to the solvent resonance at the appropriate frequency. ^{31}P NMR spectra, proton homodecoupled spectra, and ^{13}C DEPT spectra were recorded on a Bruker AM 300 FT-NMR spectrometer. The chemical shifts of the ^{31}P NMR resonances were referenced to external phosphoric acid. ^{19}F NMR spectra were recorded on a Bruker WP 200 FT-NMR spectrometer. The ^{19}F NMR resonances were referenced to external Et_4NBF_4 in CD_3NO_2. IR spectra were recorded on a Perkin-Elmer Model 281B spectrometer as KBr pellets. Routine gas chromatographs were conducted with a Varian 3700 gas chromatograph equipped with a flame ionization detector using a 4-m × $^1/_8$-in. stainless steel column packed with 20% ethylene glycol/silver nitrate on 45/60 mesh Chromosorb PNAW or a SUPELCO 15-m × 0.53-mm fused-silica capillary column. The cutting and weighing technique was employed for quantitative analysis. GC-MS was performed with a Kratos MS-25 GC-MS equipped with a 25-m J&W DB5 capillary column. The high-resolution mass spectrum of 1,3-diphenyl-1-butene was recorded on a Kratos MS-9/50 magnetic sector electron impact mass spectrometer. Molecular weight measurements of the polymers were performed on a Waters Associates liquid/gel permeation chromatograph using Microstyragel columns and a UV detector. Polystyrene standards

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were used to calibrate the instrument. Elemental analyses were performed by Galbraith Laboratories, Inc.

General Procedure. Preparation and manipulation of all the transition metal complexes or reactions involving the complexes were carried out under anaerobic conditions using Schlenk techniques or in a Vacuum Atmospheres drybox, except as noted. Reagent-grade chemicals were used. Dichloromethane, chloroform, chloroform-*d*, acetonitrile, acetonitrile-d_3, nitromethane, nitromethane-d_3, pentane, and benzene were dried over calcium hydride and vacuum-transferred to and stored in a dry nitrogen-filled box before use. Diethyl ether was refluxed over sodium/benzophenone and distilled. 2,6-Di-*tert*-butylpyridine, styrene, α-methylstyrene, β-methylstyrene, 3-nitrostyrene, and *p*-methoxystyrene were dried over calcium hydride and distilled. Styrene and *p*-methoxystyrene were stored in a refrigerator under dry nitrogen. Other chemicals were stored in a dry nitrogen-filled glovebox. 1,2-Bis(diphenylphosphino)ethane was dried under vacuum at 60 °C and stored under nitrogen. $Pd(PPh_3)_2Cl_2$ and $AgBF_4$ were used as received. 1,3,3-Trimethyl-1-phenylindan,[5] 4-methyl-2,4-diphenyl-2-pentene,[5] 4-methyl-2,4-diphenyl-1-pentene,[5] $[Pd(CH_3CN)_4](BF_4)_2$,[6] and $Pd(pyridine)_2Cl_2$[7] were prepared according to literature methods. Vinylbenzyl chloride (para and meta isomeric mixture) was dried over calcium hydride, purified by distillation, and then degassed and stored in a refrigerator under nitrogen.

Preparation of Pd(2,6-di-*tert*-butylpyridine)$_2$(CH$_3$NO$_2$)$_2$(BF$_4$)$_2$, 1. Into a stirred solution of 400 mg (0.900 mmol) of $[Pd(CH_3CN)_4](BF_4)_2$ in 10 mL of CH_3NO_2 was added dropwise 404.4 μL (1.80 mmol) of 2,6-di-*tert*-butylpyridine. After 1 day at room temperature, 75 μL of styrene was added, and the resultant mixture was stirred for another day. At the end of this period, a brown solution was obtained by filtration. Addition of Et_2O/pentane generated two liquid layers. The bottom brown layer was isolated, dissolved in small amount of CH_3NO_2, and precipitated by adding benzene/Et_2O/pentane. The needle-shaped crystals precipitated slowly in about 20 min. The brown crystals (310 mg, 44%) were washed with pentane and dried under vacuum. ^1H NMR (CD_3NO_2) (ppm): 8.58 (2H, t, J = 8.2 Hz), 8.02 (4H, d, J = 8.2 Hz), 1.58 (36H, s). ^1H NMR (CD_3CN) (ppm): 8.45 (2H, t, J = 8.2 Hz), 7.90 (4H, d, J = 8.2 Hz), 1.51 (36H, s). $^{13}C\{^1H\}$ NMR (CD_3NO_2) (ppm): 164.6, 149.2, 124.1, 38.0, 28.9. Anal. Calcd for $PdC_{28}H_{48}N_4O_4B_2F_8$: C, 42.8; H, 6.1; N, 7.1. Found: C, 43.1; H, 6.1; N, 6.6. GC of the aqueous solution of complex 1 showed two peaks which were identified to be CH_3NO_2 and 2,6-di-*tert*-butylpyridine by comparison with authentic samples.

Preparation of Pd(PPh$_3$)$_2$(BF$_4$)$_2$, 2. A mixture of 0.500 g (0.71 mmol) of $Pd(PPh_3)_2Cl_2$, 0.277 g (1.42 mmol) of $AgBF_4$, and 20 mL of nitromethane was allowed to stir at room temperature for 2 days. Following the filtration of the generated white precipitate (AgCl), a brown solution was obtained. Vacuum was applied to remove the solvent. The remaining viscous liquid was dissolved in 10 mL of dichloromethane. Complete evaporation of the solution yielded an orange solid. The product was reprecipitated in CH_2Cl_2/Et_2O/pentane, washed with pentane, and vacuum-dried. The overall yield was 0.52 g, 91%. ^1H NMR (CD_3NO_2) (ppm): 7.6 (m). ^1H NMR (CD_3CN) (ppm): 7.8–7.3 (m). ^{31}P NMR (ppm): (CD_3NO_2) 42.51 (s); (CD_3CN) 38.44 (s); ($CDCl_3$) 38.61 (s). ^{19}F NMR (relative to Et_4NBF_4 in CD_3NO_2 = 0 ppm) (ppm): (CD_3CN) 1.08 (s); (CD_3NO_2) 9.11 (d, J_{P-F} = 7.5 Hz), 2.41 (d, J_{P-F} = 14.5 Hz), 0.0 (br). IR (KBr): 1200–1000 cm^{-1} (BF_4^-). Anal. Calcd for $PdC_{36}H_{30}P_2B_2F_8$: C, 53.70; H, 3.73; P, 7.71. Found: C, 53.05; H, 3.87; P, 7.29.

Preparation of Pd(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(BF$_4$)$_2$, 3. A solution of 0.179 g (0.45 mmol) of 1,2-bis(diphenylphosphino)ethane in 6 mL of benzene was added dropwise to a stirred solution of 0.200 g (0.45 mmol) of $[Pd(CH_3CN)_4](BF_4)_2$ in 5 mL of nitromethane. The resultant mixture was stirred at room temperature for 12 h. At the end of the reaction, a white precipitate was formed. After filtration and washing with benzene, 0.24 g of white compound was obtained (yield: 79%). ^1H NMR (CD_3NO_2) (ppm): 7.63 (4H, t, J = 7.5 Hz), 7.48 (8H, t, J = 7.5 H), 7.35 (8H, m), 2.82 (4H, t, J_{P-H} = 12.7 Hz). ^{31}P NMR (CD_3NO_2) (ppm): 60.9 (s). No coordinated CH_3NO_2 was detected by GC.

Preparation of Pd(pyridine)$_2$(CH$_3$NO$_2$)$_n$(BF$_4$)$_2$ (n = 2 or 3), 4. A solution of 0.500 g (1.49 mmol) of $Pd(pyridine)_2Cl_2$ in 10 mL of $CHCl_3$ was added dropwise to a stirred solution of 0.580 g (2.98 mmol) of $AgBF_4$ in 20 mL of nitromethane. The resultant mixture was allowed to stir at room temperature for 30 h. After the generated white precipitate (AgCl) was removed by filtration, a brown compound was obtained by removal of the solvent under vacuum. The compound (0.58 g) was washed with diethyl ether and dried under vacuum. ^1H NMR (CD_3CN) (ppm): 8.83 (4H, m), 7.96 (2H, m), 7.52 (4H, m). $^{13}C\{^1H\}$ NMR (CD_3CN) (ppm): 153.5, 152.6, 152.4, 152.1, 142.5, 142.3, 142.0, 141.5, 128.7, 128.4, 128.3, 127.4. GC spectrum of the aqueous solution of 4 showed two peaks which were identified to be nitromethane and pyridine using authentic samples. The CH_3NO_2 present in the compound could be removed by repeated reprecipitation in diethyl ether.

Preparation of 2,6-Di-*tert*-butylpyridinium Tetrafluoroborate, 5. The compound was prepared by mixing a 1:1 equivalent of HBF_4 (48 wt % solution in water) and 2,6-di-*tert*-butylpyridine, which immediately resulted in precipitation of white crystals. The crystals were washed with diethyl ether and vacuum-dried. ^1H NMR (CD_3NO_2) (ppm): 8.58 (1H, t, J = 8.2 Hz), 8.03 (2H, d, J = 8.2 Hz), 1.58 (18H, s). $^{13}C\{^1H\}$ NMR (CD_3NO_2) (ppm): 164.6, 149.2, 124.1, 37.9, 28.9.

Dimerization of Ethylene. A solution of 1 (2 mg) in CD_3NO_2 (0.7 mL) was placed in a 125-mL Parr bomb, which was then charged with 500 psi of ethylene. The pressure dropped to 400 psi after stirring at room temperature for 12 h. Yield of butenes: 1.7 g. Both the ^1H NMR and ^{13}C NMR spectra indicated that 2-butene isomers were the predominant products formed during the reaction. $CH_3CH{=}CHCH_3$: ^1H NMR (CD_3NO_2) (ppm) 5.45 (2H, m), 1.60 (6H, m); $^{13}C\{^1H\}$ NMR (CD_3NO_2) (ppm) 125.9 (trans), 124.1 (cis), 18.2 (trans), 12.6 (cis). The ratio of trans to cis isomer of 2-butene was determined from both GC and the ^{13}C NMR spectrum to be 7:3. With the same procedure described above, using 3 instead of 1, the same products were observed.

Dimerization of Propylene. The reaction was carried out according to a procedure analogous to that employed for ethylene. Either 1 or 3 (2 mg) was used as the catalyst. Propylene (140 psi) was used instead of ethylene. The reaction products were analyzed by GC–MS using authentic samples and identified as 4-methyl-2-pentene, 2-methyl-2-pentene, and 2-methyl-1-pentene (relative ratios of 1.7:1.2:1.0).

Dimerization of a Mixture of Ethylene and Propylene. A solution of either 1 or 3 (2 mg) in nitromethane (0.7 mL) was placed in a Parr bomb which was then charged with 140 psi of propylene and 140 psi of ethylene, bringing the total pressure to 280 psi. The reaction mixture was allowed to stir at room temperature for 12 h. The products were analyzed by GC–MS using authentic samples and identified as *trans*-2-butene, *cis*-2-butene, 1-pentene, *trans*-2-pentene, and *cis*-2-pentene (relative ratios: 7.5:4.0:1.0:3.5:3.5). The above reaction was also run in a 5:100 (v/v) mixture of acetonitrile and nitromethane. However, no pentenes were observed. 2-Butene was the exclusive dimer formed in the reaction.

Dimerization of Styrene. At room temperature, all of the four Pd(II) complexes, 1–4, were found to selectively catalyze the dimerization of styrene in nitromethane to exclusively form 1,3-diphenyl-1-butene. The reactions were monitored by ^1H NMR spectroscopy, and no detectable side product was formed. The catalytic syntheses of 1,3-diphenyl-1-butene, using 1 and 3, are illustrated respectively as follows.

Using 1 as Catalyst. A mixture consisting of 20 mg of 1, 2 mL of nitromethane, and 5 mL of styrene was stirred at 45 °C for 12 h. The solution was diluted by addition of diethyl ether and then run through a short-stem, silica gel chromatography column to remove the catalyst. Distillation of the eluate (127

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°C/1.3 × 10^{-2} Torr) yielded 1.0 g of 1,3-diphenyl-1-butene (turnover = 190). MS: 208.1266 (M^+). ^1H NMR ($CDCl_3$) (ppm): 7.29 (10H, m), 6.39 (2H, d, J = 4.5 Hz), 3.46 (1H, m), 1.46 (3H, d, J = 7.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 145.6, 137.5, 135.2, 128.5, 127.3, 127.0, 126.2, 126.1, 42.5, 21.2. The ^{13}C NMR DEPT experiment showed that the styrene dimer had no CH_2 group.

Using 3 as Catalyst. Styrene (1 mL) was stirred over 3 (30 mg) at room temperature for 12 h. At the end of the reaction, the catalyst was removed by filtration. Simple vacuum distillation of the filtrate (127 °C/1.3 × 10^{-2} Torr) resulted in pure 1,3-diphenyl-1-butene.

Oligomerization of α-Methylstyrene. Ambient Temperature. A solution of 1, 2, or 3, in CD_3NO_2, was found to be inactive toward α-methylstyrene at room temperature. A nitromethane solution of 4 gradually reacted with α-methylstyrene to form 1,3,3-trimethyl-1-phenylindan as the major product as identified by GC using an authentic sample.

45 °C. Into a solution of 1 (2 mg) in CH_3NO_2 (1 mL) was added 20 μL of α-methylstyrene. The resultant mixture was allowed to stir at 45 °C for 2 h. The reaction products were directly analyzed by GC–MS using corresponding authentic samples and were found to consist of 1,3,3-trimethyl-1-phenylindan, 4-methyl-2,4-diphenyl-2-pentene, and 4-methyl-2,4-diphenyl-1-pentene, as well as unidentified higher oligomers (relative ratios 1:2.1:3.0:20.9).

Reaction with β-Methylstyrene. The reactions were run at room temperature in a NMR tube using CD_3NO_2 as the solvent. A 1:2 molar ratio of the catalyst (2 mg) to the monomer was used. ^1H NMR spectra were taken after 12 h. No reaction was observed with 1, 2, or 3.

Dimerization of Styrene in the Presence of α-Methylstyrene and β-Methylstyrene. The reaction, using 1, 2, or 3 as the catalyst, was carried out according to a procedure analogous to that employed for β-methylstyrene. A mixture of styrene, α-methylstyrene, and β-methylstyrene was used instead of β-methylstyrene alone. One molar equivalent of each of the three monomers to the catalyst (2 mg) was chosen. The reaction was run for 24 h. ^1H NMR spectra at the end of the period clearly showed that, in each case, styrene had totally reacted and 1,3-diphenyl-1-butene was formed while α-methylstyrene and β-methylstyrene remained unconverted.

Polymerization of p-Methoxystyrene. Bulk Polymerization Using 1 or 3. To 700 μL of *p*-methoxystyrene was added 20 mg of 1. The resultant mixture solidified at room temperature in approximately 2 min. The formed polymer was dissolved in 50 mL of chloroform. After it was filtered and concentrated (to 10 mL), the viscous solution was dropwise added to stirred methanol. The precipitated white polymer (0.5 g, 70%) was washed with methanol and vacuum-dried. Poly(*p*-methoxystyrene), M_p (GPC) = 1.4 × 10^6 versus polystyrene. ^1H NMR ($CDCl_3$) (ppm): 6.5 (4H, br), 3.73 (3H, br), 1.73 (1H, br), 1.34 (2H, br). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 157.4, 137.8, 128.5, 113.3, 67.7, 55.0, 39.6. The polymerization of *p*-methoxystyrene by 3 occurred in an analogous manner.

Solution Polymerization Using 2. To a solution of 10 mg of 2 in 0.5 mL of nitromethane was added 100 μL of *p*-methoxystyrene. In approximately 2 min, a white polymer began to precipitate from the solution. The reaction was stopped in 1 h. The polymer (in 81% yield) was washed with nitromethane and then dried under vacuum. The NMR spectra of the poly(*p*-methoxystyrene) thus prepared were identical to that reported above.

Reaction with 3-Nitrostyrene. Either 1 or 4 (2 mg) was dissolved in 0.7 mL of CD_3NO_2. To the solution was added ca. 1 equiv of 3-nitrostyrene. ^1H NMR spectra showed that, in either case, 3-nitrostyrene remained unreacted after heating at 50 °C for 2 h.

Dimerization of Styrene in the Presence of Inhibitors. In the Presence of the Strong Inhibitor 2,6-Di-*tert*-butylpyridine. To a mixture of 1 (5 mg, 6.4 × 10^{-3} mmol) and 2,6-di-*tert*-butylpyridine (1.4 μL, 6.4 × 10^{-3} mmol) in 700 μL of CD_3NO_2 was added 6 μL of styrene. The solution was allowed to stand at room temperature for 10 h. The ^1H NMR spectrum showed no species other than the starting materials.

In the Presence of the Weak Inhibitor Tetraethylammonium Tetrafluoroborate. Two solutions were prepared: solution A, 10 mg of 2 dissolved in 200 μL of CD_3NO_2; solution B, 27 mg of Et_4NBF_4 in 200 μL of CD_3NO_2. To one NMR tube were added 40 μL of solution A (containing 2.5 × 10^{-3} mmol of 2) and 600 μL of nitromethane-d_3, while into a second one were added 40 μL of solution A, 580 μL of nitromethane-d_3, and 20 μL of solution B (containing 12.4 × 10^{-3} mmol of Et_4NBF_4). Both NMR tubes were shaken, and 10 μL of styrene was added. The reactions were allowed to run at room temperature for 2 h. ^1H NMR spectra were taken at the end of this period, with the peaks integrated using the CHD_2NO_2 residue as the standard. It was found that, in the absence of Et_4NBF_4, 1,3-diphenyl-1-butene was formed 1.26 times as fast as in the presence of Et_4NBF_4.

Isomerization of 1,3-Diphenyl-1-butene to 1,3-Diphenyl-2-butene. A 2-mg sample of complex 1 and 6 μL of 1,3-diphenyl-1-butene were mixed in 0.7 mL of CD_3NO_2. After the solution stood at room temperature for 48 h, the ^1H NMR spectrum was taken and analyzed. It was observed that part of 1,3-diphenyl-1-butene had been transformed to 1,3-diphenyl-2-butene with an E to Z ratio of 4:1 (assuming that the major product was the thermodynamically favored E isomer, as was found in ethylene dimerization). The ratio was calculated from integrations of the corresponding resonances. ^1H NMR (CD_3NO_2) (ppm): (*E*)-1,3-Diphenyl-2-butene 7.3 (m), 5.65 (1H, tq, J = 7.5, 1.4 Hz), 3.32 (2H, d, J = 7.5 Hz), 2.08 (3H, s); (*Z*)-1,3-Diphenyl-2-butene 7.3 (m), 5.97 (1H, tq, J = 7.4, 1.4 Hz), 3.56 (2H, d, J = 7.4 Hz), 2.13 (3H, s). As monitored by ^1H NMR, it was also observed that when a mixture of 1,3-diphenyl-1-butene and styrene was used instead of 1,3-diphenyl-1-butene, the above isomerization reaction started only after complete conversion of styrene to 1,3-diphenyl-1-butene.

Reactivity of 5 toward Styrene. Compound 5 (6 mg) and styrene (6 μL) were codissolved in 0.7 mL of CD_3NO_2. The ^1H NMR spectrum of the solution, after standing at room temperature for 6 h, indicated no new species.

Preparation of p-Divinylbenzene (p-DVB). *p*-DVB was isolated from Aldrich divinylbenzene concentrate (which contained 55–60% divinylbenzene with a ratio of meta to para isomer of about 2.5) by a modified literature method.[8] According to the published procedure, the divinylbenzene mixture is first brominated and pure crystalline *p*-divinylbenzene tetrabromide is isolated, which is then reductively debrominated back to *p*-divinylbenzene. In the final step, *p*-DVB is distilled, which often causes polymerization and decreases the yield. We, therefore, modified the final step as follows. *p*-DVB solution, after extraction in chloroform or chloroform-*d*, was washed with distilled water 10 times, dried with anhydrous sodium sulfate and calcium hydride, and then filtered. The filtrate was determined to be a solution of pure *p*-DVB by both ^1H NMR and GC. The pure *p*-DVB in chloroform or chloroform-*d* was used directly for polymerization reactions and its concentration was measured by ^1H NMR using α-methylstyrene as the standard. ^1H NMR ($CDCl_3$) (ppm): *p*-divinylbenzene 7.36 (4H, s), 6.69 (2H, dd, J = 10.8, 17.6 Hz), 5.73 (2H, d, J = 17.6 Hz), 5.23 (2H, d, J = 10.8 Hz).

Linear Polymerization of p-Divinylbenzene. In a typical reaction, 5 mg of 2 was dissolved in a mixture of nitromethane (2.0 mL) and chloroform (5.0 mL), followed by addition of 2.0 mL of *p*-DVB solution (0.44 M) in $CHCl_3$. The reaction mixture was kept under nitrogen in a round-bottom flask tightly capped with a glass stopcock. The solution was allowed to stir at 68 °C for 30 h. At the end of the reaction, the resultant solution was run through a short-stem silica gel chromatography column to remove the catalyst, and the solvent was removed to isolate the polymer. The white solid polymer was washed with methanol and dried under vacuum. Yield: 0.115 g (92%). M_p (GPC) =

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3900. ^{1}H NMR ($CDCl_3$) (ppm): 7.30–7.15 (4H, m), 6.34 (2H, br), 3.59 (1H, br), 1.44 (3H, br), three small absorptions at 6.69, 5.73, and 5.23 ppm were also observed due to the terminal vinyl groups. $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): sp^2 carbons above 110 ppm, 42.26 (sp^3 methine), 21.12 (methyl).

Preparation of Terminally Functionalized Linear Poly(*p*-DVB). Typically, 5 mg of 2 was dissolved in a mixture of nitromethane (2.0 mL) and chloroform (5.0 mL), followed by addition of 2.0 mL of *p*-DVB solution in $CHCl_3$ (0.439 M). The resultant mixture was kept under nitrogen in a round-bottom flask, tightly capped with a glass stopcock. After stirring at 42 °C for 30 h, to the solution was added 134 μL of vinylbenzyl chloride (1 equiv relative to *p*-DVB). The new mixture was stirred at 55 °C for another 30 h. The final solution was eluted down a short-stem silica gel chromatograph column to remove the palladium catalyst, and the solvent was pulled off to yield a white polymer. The product was washed with methanol. The percentage of the terminal vinyl groups of the linear poly(*p*-DVB) capped by vinylbenzyl chloride was calculated to be 33% on the basis of the ^{1}H NMR spectrum of the isolated polymer product. ^{1}H NMR ($CDCl_3$) (ppm): 7.38–7.16 (m), 6.69 (m), 6.38 (br), 5.71 (d, J = 17.6 Hz), 5.20 (d, J = 10.8 Hz), 4.58 (s), 4.55 (s), 3.62 (br), 1.45 (br).

Kinetics of the Acyclic Dimerization of Styrene Catalyzed by 1. All reactions were carried out in NMR tubes. During the experiments, the catalyst was first dissolved in nitromethane-d_3 and then styrene was added. The resultant solution was kept under nitrogen in a tightly capped NMR tube and frozen with liquid nitrogen before reaction. In actual practice, for both convenience and accuracy, ca. 30 mg of 1 was weighed and dissolved in a certain amount of nitromethane-d_3 (approximately 1 mL). The calculated amount of the catalyst solution, the solvent, and the monomer (styrene) were added with a microsyringe (error < 0.2 μL) and mixed together in a NMR tube. The dimerization reaction was performed in a NMR instrument by heating a spinning NMR tube containing the reaction solution at a given temperature. The ^{1}H NMR spectra were automatically collected at set intervals of time. Through the course of the reaction, the concentration of 1 remained constant. Calculation of the reaction rate was based on the change in intensity of the proton resonances of the vinyl group of styrene. The CHD_2NO_2 residue of nitromethane-d_3 was used as the standard. The rate law for the styrene dimerization reaction was as follows:

$$-\mathrm{d}[\text{styrene}]/\mathrm{d}t = k[\mathbf{1}]^m[\text{styrene}]^n$$

The order n for styrene was determined to be 1 on the basis of our observation that a plot of log[styrene] versus time gives a straight line with a slope = k' ($k' = k[\mathbf{1}]^m$). By variation of the concentration of the catalyst, 1, different k' values were obtained. The order m was evaluated from the slope of the plot of log k' versus log[1]. The activation parameters, E_a and $\Delta H^{\ddagger}$, were obtained from conventional temperature-dependent kinetic experiments performed over a temperature range of 22–45 °C. The corresponding $\Delta S^{\ddagger}$ was calculated from the $\Delta H^{\ddagger}$ according to the equation $\Delta S^{\ddagger} = \Delta H^{\ddagger}/T + 4.58 \log(k/T) - 47.4$.

Kinetics of the Linear Polymerization of *p*-DVB and the Molecular Weight Dependence of Poly(*p*-DVB) on Reaction Time. The kinetics of the linear polymerization of *p*-DVB catalyzed by 2 were studied by ^{1}H NMR spectroscopy using a procedure analogous to that employed for the styrene dimerization reaction catalyzed by complex 1. *p*-DVB was used as the monomer while a 1:2 (v/v) mixture of nitromethane-d_3 and chloroform-d was used instead of pure nitromethane-d_3. During the experiments, 2 was dissolved in a mixture of nitromethane-d_3 and chloroform-d and a solution of *p*-DVB in $CDCl_3$ was added. The reaction mixture was kept under nitrogen in a closed NMR tube and frozen with liquid nitrogen before reaction. In actual practice, ca. 30 mg of 2 was weighed and dissolved in a certain amount of nitromethane-d_3 (600 μL). Calculated amounts of the catalyst solution, the solvents, and the monomer solution (in $CDCl_3$) were added with a microsyringe and mixed in a NMR tube. The polymerization reactions were performed in a NMR instrument at controlled temperatures. ^{1}H NMR spectra were automatically recorded at specified intervals. The intensity change in the proton resonances of the vinyl groups, contributed by both the monomer and the polymer, was used to measure the reaction rate. The CHD_2NO_2 residue was chosen as the standard. In addition, the molecular weight (M_n) of the polymer formed was also determined from the ratio of the polymer terminal vinyl groups to the internal olefin methine groups.

Results and Discussion

Synthesis of the Palladium(II) Complexes.[9] Complexes 1 and 3 were prepared through a ligand substitution reaction according to eq 1. Complexes 2 and 4 were

$$[\mathrm{Pd(CH_3CN)_4}](\mathrm{BF_4})_2 + 2\mathrm{L} \xrightarrow[\text{room temp}]{\mathrm{CH_3NO_2}} \mathrm{Pd(L)_2(CH_3NO_2)}_n(\mathrm{BF_4})_2 \quad (1)$$

1: L = 2,6-di-*tert*-butylpyridine, $n = 2$

3: L = $0.5Ph_2PCH_2CH_2PPh_2$, $n = 0$

$$\mathrm{Pd(L)_2Cl_2} + 2\mathrm{AgBF_4} \xrightarrow[\text{room temp}]{\mathrm{CH_3NO_2}} \mathrm{Pd(L)_2(CH_3NO_2)}_n(\mathrm{BF_4})_2 + 2\mathrm{AgCl} \quad (2)$$

2: L = Ph_3P, $n = 0$

4: L = pyridine, n = 2 or 3

prepared through halide-abstraction reaction using $AgBF_4$ according to eq 2. The reactions were generally clean and products could be purified by recrystallization and washing with appropriate solvents. An exception was complex 1. In the preparation of 1, a small amount of the starting reagent, $[Pd(CH_3CN)_4]_2(BF_4)_2$, remained unreacted at the end of the reaction. Because of the similar solubilities of 1 and $[Pd(CH_3CN)_4](BF_4)_2$, it was difficult to purify 1 by recrystallization. Therefore, styrene was added to solve the problem. 1 remained in solution while it catalyzed the dimerization of styrene. On the other hand, $[Pd(CH_3CN)_4](BF_4)_2$ rapidly polymerized styrene,[3] coprecipitated with the resultant polymer, and gradually decomposed to palladium metal. Thus, only 1 was left in solution after the mixture was treated with styrene.

The Pd(II) complexes were examined through NMR spectroscopy, elemental analysis, and GC. No coordinated nitromethane was found for compounds 2 and 3 containing tertiary phosphine ligands. Complexes 1 and 4 with pyridine ligands were determined by both elemental analysis and GC to have coordinated nitromethane. For example, nitromethane and ligand peaks were observed in the GC of aqueous solutions of both 1 and 4. However, the nitromethane was, at best, loosely bound in these compounds and was lost upon repeated reprecipitation in diethyl ether or on prolonged exposure to high vacuum. The ^{13}C NMR spectrum of 1 in CD_3NO_2 exhibited only one set of resonances due to coordinated 2,6-di-*tert*-butylpyridine, thereby indicating that 1 existed only in one isomeric form. Considering the coordination of two

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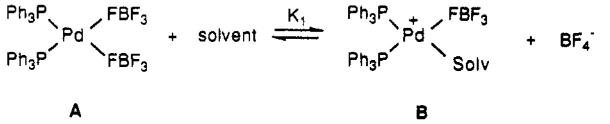
[9] Analogous solvated cationic complexes of Pd(II) and Pt(II) have been previously reported: (a) Reference 3b. (b) Hartley, F. R.; Murray, S. G.; Wilkinson, A. *Inorg. Chem.* 1989, *28*, 549.

exceedingly bulky ligands to a single metal ion, we believe that 1 was most likely present in the more sterically stable trans form. Compound 2 was found to have a cis configuration. The ^{19}F NMR spectrum of 2 exhibited doublets involving trans ^{19}F–^{31}P coupling. No triplet was observed. The ^{13}C NMR spectrum of 4 in either nitromethane or acetonitrile exhibited resonances arising from four different coordinated pyridines, indicating that 4 in solution was a mixture of isomers. Structures having either four coordinating ligands or five, or both, were possible for 4.[4]

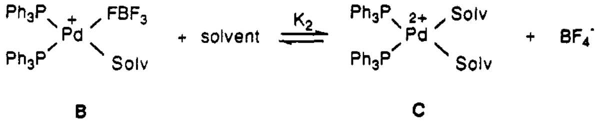
In nitromethane solution, 2 and 3 were stable while complexes 1 and 4 started to decompose within days. Interestingly, in the presence of styrene, the stability of both 1 and 4 in nitromethane was markedly increased, with no significant decomposition observed in 1–2 weeks.

Complexes 1–4 were readily soluble in polar solvents such as nitromethane. The solubility in nonpolar solvents such as benzene was much lower. However, 2 was soluble in chloroform.

Anion Ligand Dissociation Constants for 2 in Solution. In CD_3NO_2. The ^{19}F NMR spectrum of 2 in CD_3NO_2 (6.6×10^{-3} M) consisted of three absorptions, two of which exhibited ^{19}F–^{31}P coupling: δ (relative to Et_4NBF_4 = 0 ppm), 0 (br), 2.41 (d, J_{F-P} = 14.5 Hz), 9.11 (d, J_{F-P} = 7.5 Hz), intensity ratio 147:23:9. This observation is consistent with the following anion dissociation equilibria (eqs 3 and 4). Assuming that A and B corresponded to species with chemical shifts 9.11 and 2.41 ppm, respectively, the relative concentrations were: [A] = 4.5, [B] = 23, [C] = 62. The concentration of free BF_4^- can be calculated to be 1.08×10^{-2} M. Therefore,



(3)



(4)

$$K_1 = [B][BF_4^-]/[A] = 5.52 \times 10^{-2}\ M$$

$$K_2 = [C][BF_4^-]/[B] = 2.91 \times 10^{-2}\ M$$

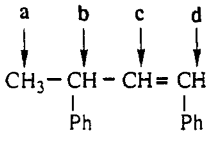
If, on the other hand, supposing that A corresponded to the species at δ_F = 2.41 ppm and B corresponded to the species at δ_F = 9.11 ppm, K_1/K_2 = 0.05 was obtained. Since the first dissociation constant for a salt is almost always larger than the second one, we conclude that the chemical shift of A was 9.11 ppm and the chemical shift of B was 2.41 ppm.

In 1:2 (v/v) CD_3NO_2 and $CDCl_3$ Mixture. The ^{19}F NMR spectrum of a 5.18×10^{-2} M solution of 2 in 1:2 (v/v) $CD_3NO_2/CDCl_3$ exhibited three absorptions at 0.23, 2.49, and 9.18 ppm (external reference: Et_4NBF_4 in CD_3NO_2), in the intensity ratio 50:14:11. As outlined above, by assuming that species A and B corresponded to the resonances at 9.18 and 2.49 ppm, respectively, we obtained 1.76×10^{-2} M for K_1 and 8.88×10^{-3} M for K_2.

Solvent Effects on the Olefin Dimerization Reactions. When catalyzed by complex 1, 2, or 3, ethylene, propylene, and styrene underwent dimerization at ambient temperature in nitromethane to form *linear* dimers. In the case of propylene, 4-methyl-2-pentene, 2-methyl-2-pentene, and 2-methyl-1-pentene were formed in the relative ratios of 1.7:1.2:1.0. It was found that the solvent had a dramatic effect on the reactivity of the olefin substrate. For example, no reaction was observed for styrene in acetonitrile in the presence of 1 or 2. In the codimerization reaction of ethylene and propylene, the butene and pentene isomers, *trans*-2-butene, *cis*-2-butene, 1-pentene, *trans*-2-pentene, and *cis*-2-pentene (relative ratios 7.5:4.0:1.0:3.5:3.5), were formed in nitromethane. However, when 5% by volume of acetonitrile was added, the reactivity of propylene was totally shut down and butenes were formed as the exclusive products.

Acetonitrile has been shown to be a significantly better ligand than nitromethane for cationic, electrophilic metal centers,[3] and the reactivity of a given metal species with a given olefin is significantly attenuated in acetonitrile when compared to nitromethane.[3] Therefore, our observations on the effect of acetonitrile on the catalytic dimerization reactions can be rationalized by proposing that while ethylene could effectively compete with acetonitrile for a coordination site on the metal, the bulkier propylene and styrene were unable to do so and, hence, failed to react.

Dimerization of Styrene. Compounds 1–3, *both in solution and in solid state*, were effective catalysts for the acyclic dimerization of styrene to 1,3-diphenyl-1-butene.[10] Solution-phase dimerization was usually carried out in CH_3NO_2 or $CH_3NO_2/CHCl_3$ mixture. However, it was more convenient to omit the solvent and use the Pd(II) compound in the solid form. This allowed the catalyst to be removed simply by filtration at the end of the reaction. With either procedure, several hundred turnovers were observed over a 12-h period. Neither indans nor higher oligomers were observed as side products in the dimerization reaction. The product, 1,3-diphenyl-1-butene, was determined to be a mixture of cis and trans isomers by following a ^{1}H NMR homodecoupling experiment.



$$\overset{a}{CH_3}-\underset{Ph}{\overset{b}{CH}}-\overset{c}{CH}=\underset{Ph}{\overset{d}{CH}}$$

When protons c and d (c and d have essentially identical chemical shifts) were irradiated, the resonance corresponding to proton b converted to two sets of quartets (Figure 1). Presumably, the one with higher intensity belonged to the more stable trans isomer and the other belonged to the cis isomer.

While complexes 1–3 catalyzed the dimerization of styrene to 1,3-diphenyl-1-butene, no reaction was observed with α-methylstyrene and β-methylstyrene at ambient temperature. Furthermore, when any one of the above Pd(II) compounds was added to a 1:1 mixture of styrene

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[10] Some other reports on styrene dimerization: (a) Higashimura, T.; Sawamoto, M. *Adv. Polym. Sci.* **1984**, *62*, 49. (b) Sen, A.; Lai, T.-W. *Organometallics* **1983**, *2*, 1059.

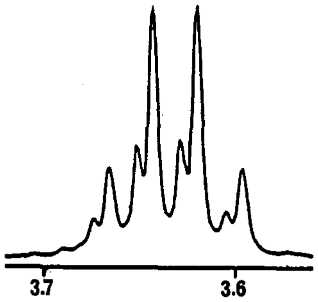


Figure 1. ^1H NMR resonance of proton b when coupled to proton a only in 1,3-diphenyl-1-butene.

and either α-methylstyrene or β-methylstyrene at ambient temperature, *only* styrene was dimerized. This selectivity is remarkable especially for α-methylstyrene, since α-methylstyrene is normally much more reactive than styrene in reactions involving carbocations.[11]

The reactivity difference between styrene on one hand and α-methylstyrene and β-methylstyrene on the other may be ascribed to steric factors. The bulkier α-methylstyrene and β-methylstyrene are expected to coordinate less strongly than styrene and thus are likely to be less reactive. In support of this proposal, we observed that selectivity for styrene was lost when $Pd(pyridine)_2(CH_3NO)_n(BF_4)_2$, **4**, which lacked the bulky *tert*-butyl substituents at the ortho positions of the pyridine ligand (cf. **1**), was used as the catalyst. Unlike **1**, **4** was found to catalyze the dimerization of *both* styrene and α-methylstyrene (the latter to mainly 1,3,3-trimethyl-1-phenylindan[12]) at ambient temperature.

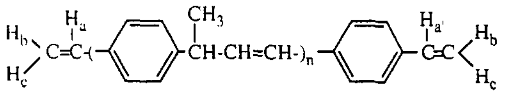
The linear dimerization of styrene was inhibited by the addition of either a coordinating ligand (or solvent) or a BF_4^--containing salt, such as Et_4NBF_4. Between the two, the inhibition by a coordinating ligand appeared to be stronger. For example, the addition of 1 equiv of 2,6-di-*tert*-butylpyridine to **1** totally shut down the reactions catalyzed by **1**, while the addition of 5 equiv of Et_4BF_4 to **2** only slowed the rate of the reactions catalyzed by **2**. The weaker inhibition by BF_4^- was consistent with the common-ion effect and further supported our assumption that anion ligand dissociation equilibria existed for the catalysts in solution and that the solvated Pd(II) species was more catalytically active than the species containing coordinated BF_4^- ions.

Several pieces of evidence supported a carbocationic mechanism for the linear dimerization of styrene. First, despite the fact that α-methylstyrene was *unreactive* at room temperature, it was converted by the same catalyst to cyclic and linear dimers, 1,3,3-trimethyl-1-phenylindan, 4-methyl-2,4-diphenyl-2-pentene, and 4-methyl-2,4-diphenyl-1-pentene, as well as higher oligomers, (relative ratios 1:2.1:3.0:20.9) at 45 °C. The product distribution was similar to that obtained with $BF_3{\cdot}Et_2O$, a typical cationic initiator.[5] Second, no reaction was observed when *m-nitrostyrene was employed since the nitro group was* expected to have a destabilizing influence on the carbocation formed. On the other hand, *p*-methoxystyrene, which had an electron-releasing methoxy group, was converted to a polymer with a MW as high as 1.4×10^6.

A proton (H^+), derived from Bronsted acids, is known to be an initiator for the cationic oligomerization and polymerization of olefins.[13] However, 2,6-di-*tert*-butylpyridinium tetrafluoroborate was found to be inactive under our reaction conditions.

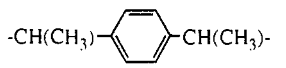
Linear Polymerization of *p*-Divinylbenzene.[14] In the polymerization of *p*-DVB, a mixture of nitromethane and chloroform was chosen as the solvent. The choice is based on our observation that the catalyst, **2**, was only active in the presence of a noncoordinating, polar solvent such as nitromethane while poly(*p*-DVB) was only soluble in less polar solvents such as chloroform. A mixture of nitromethane and chloroform, which was capable of both activating the catalyst and dissolving the formed polymer, therefore made the polymerization proceed homogeneously and efficiently through the course of the reaction. The solvent activation of the catalyst was believed to involve dissociation of the coordinated anion BF_4^- and will be discussed later.

The structure of the linear poly(*p*-divinylbenzene), as determined from its ^1H NMR spectra, involved the following unsaturated backbone:

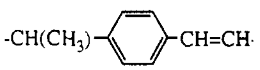


The similarity of the ^1H NMR spectra of 1,3-diphenyl-1-butene (linear styrene dimer) and poly(*p*-divinylbenzene) further confirms the above proposed structure.

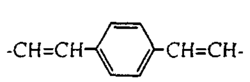
The ratio of terminal vinyls next to the $-C_6H_4-CH(CH_3)-$ group versus those next to the $-C_6H_4-CH{=}CH-$ group was determined to be approximately 1 by proton homodecoupling NMR experiments on the low molecular weight poly(*p*-DVB). In the ^1H NMR spectrum of a low molecular weight poly(*p*-DVB), protons a and a′ were observed at 6.69 ppm as multiplets, and upon irradiating proton b, turned into two sets of doublets (protons a and a′ coupled with proton c with $J_{ac} = J_{a'c} = 6.7$ Hz) with almost the same intensities. We attribute this observation to the existence of three kinds of repeating units, "head-to-head", "head-to-tail", and "tail-to-tail", in the polymer backbone.



head-to-head



head-to-tail



tail-to-tail

The molecular weight of poly(*p*-DVB) formed versus reaction time is shown in Figure 2. It is obvious that during the polymerization reaction, molecular weight increased exponentially. This observation was consistent with a step-growth mechanism rather than addition polymerization. The proposed route to linear poly(*p*-DVB) is shown in Figure 3.

The effect of reaction conditions, such as reaction temperature, concentration of the catalyst, and concen-

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[11] For a comparison of reactivity ratios, see ref 2b, p 328.

[12] Conversion of styrene derivatives to indans: see refs 2b and 3.

[13] Reference 2b, p 81.

[14] Linear polymerization of *p*-divinylbenzene using oxyacids as initiators: (a) Reference 10a. (b) Hasegawa, H.; Higashimura, T. *Macromolecules* **1980**, *13*, 1350.

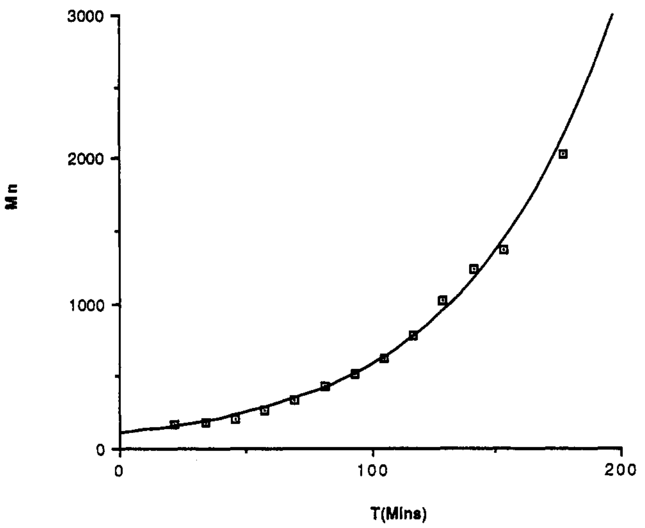


Figure 2. Molecular weight dependence of linear poly(*p*-divinylbenzene) on reaction time.

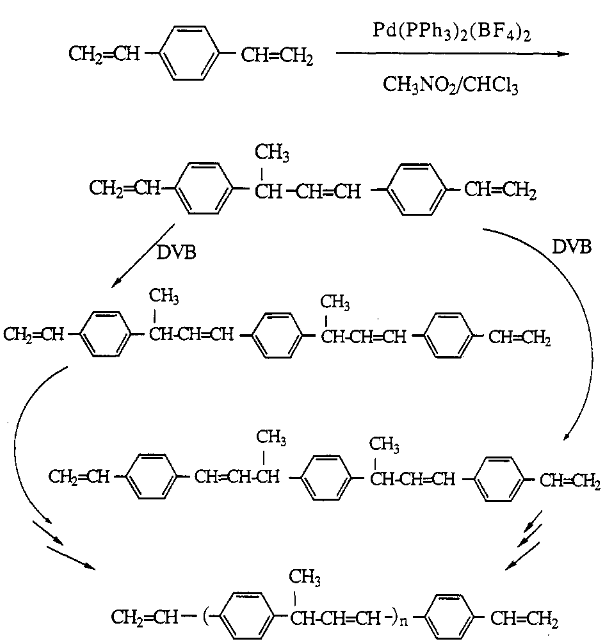


Figure 3. Step-growth polymerization of *p*-divinylbenzene.

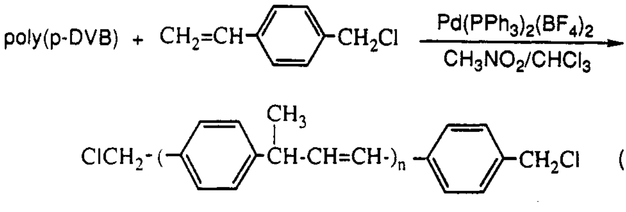
Table I. Variation in Molecular Weight of Poly(*p*-divinylbenzene) with Reaction Conditions[a]

monomer (mol/L)	catalyst, **2** (mg/mL)	reacn temp (°C)	M_n
0.10	0.56	42	390
0.10	0.56	68	2830
0.20	0.56	58	610
0.20	1.12	58	3830

[a] All reactions were run for 30 h. A solvent mixture consisting of 2:7 (v/v) CH_3NO_2 and $CHCl_3$ was used.

tration of the monomer, on the molecular weight of the polymer formed was examined and is summarized in Table I. Clearly, an increase in reaction temperature or the catalyst concentration greatly favored the formation of higher molecular weight poly(*p*-DVB).

Synthesis of Poly(*p*-DVB) with Functional Terminal Groups. Polymers with functional terminal groups are useful for the construction of block, as well as chain-extended, polymers.[15] Cross coupling between the terminal vinyl groups of linear poly(*p*-DVB) and the vinyl group of functionalized styrene derivatives, catalyzed by **2**, should result in the formation of terminally functionalized poly(*p*-DVB). In a preliminary experiment, we have chosen to couple (chloromethyl)styrene with poly(*p*-DVB) (eq 5) and the experimental results are summarized in Table II.



(5)

Kinetics and Mechanism of the Acyclic Dimerization of Styrene. The following rate law was observed for the acyclic dimerization of styrene catalyzed by **1** (eq 6).

$$-\mathrm{d}[\text{styrene}]/\mathrm{d}t = k[\mathbf{1}]^{0.70}[\text{styrene}] \qquad (6)$$

The activation parameters observed were E_a = 8.5 kcal/mol, $\Delta H^{\ddagger}$ = 7.9 kcal/mol, and $\Delta S^{\ddagger}$ = −32 cal/(mol·K). The negative entropy of activation and the reaction order in styrene were consistent with a rate-determining step involving the association of one styrene, presumably the first one, to the catalyst. In support of this hypothesis, no coordination of styrene to the catalyst was observed by ^1H NMR spectroscopy in a 1:1 mixture of the catalyst and styrene at low temperatures (<−10 °C).

Figure 4 outlines a possible mechanism for the acyclic dimerization of styrene. In the key intermediate, D, the propagated carbocation was stabilized by donation of electron density from a Pd(II) d-orbital. The carbocation, thus stabilized, no longer participated in electrophilic attack on the γ-phenyl group or on an olefin to form a cyclic indan or a higher oligomer (polymer), respectively. Instead, a H^+ ion was lost to eventually form the linear dimer. β-Hydrogen abstraction apparently did not occur since 2,4-diphenyl-1-butene or its more stable isomer, 1,3-diphenyl-2-butene, was not observed (1,3-diphenyl-1-butene was observed to isomerize slowly to 1,3-diphenyl-2-butene[16] but only after all the styrene was consumed). The ability of the Pd(II) center to donate electron density to the carbocation would, of course, depend on the ancillary ligands present, with strongly donating ligands aiding the process.[3] Hence, it was understandable that the presence of relatively strong donors like pyridine or tertiary phosphine led to olefin dimerization whereas $[Pd(CH_3CN)_4](BF_4)_2$, which only posessed the weakly ligating CH_3CN ligand, was an effective catalyst for the polymerization of styrene (typical MW 70 000) and oligomerization of ethylene and propylene. With the latter complex, no stabilization of the carbocation occurred and, therefore, its reactivity was not attenuated. Even when the carbocation was stabilized, it was possible to participate in electrophilic attack if a highly electron-rich olefin was present, and this explained the formation of polymer when *p*-methoxystyrene was used as the substrate. Thus, whether dimer or higher oligomers (polymer) were formed depended critically on both the ancillary ligands present on the metal and the nature of the olefin that was used as the substrate.

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(15) Review: *Telechelic Polymers: Synthesis and Applications*; Goethals, E. J., Ed.; CRC: Boca Raton, FL, 1989.

(16) Mechanism of C=C bond isomerization in olefins by cationic electrophilic Pd(II) complexes: Sen, A.; Lai, T.-W. *Inorg. Chem.* **1984**, *23*, 3257.

Table II. Reaction of Linear Poly(*p*-DVB) with (Chloromethyl)styrene[a]

M_n of poly(*p*-DVB)	poly(*p*-DVB) (mg/mL)	**2** (mg/mL)	reacn temp (°C)	(chloromethyl)styrene (mg/mL)	percentage of terminal vinyl groups capped
510	12.7	0.56	55	14.9	33
510	12.7	1.12	68	44.7	70

[a] Both reactions were run for 30 h. A solvent mixture consisting of 2:7 (v/v) CH_3NO_2 and $CHCl_3$ was used. The percentage of the terminal vinyl groups reacted was calculated from the ^1H NMR spectrum of the isolated product polymer.

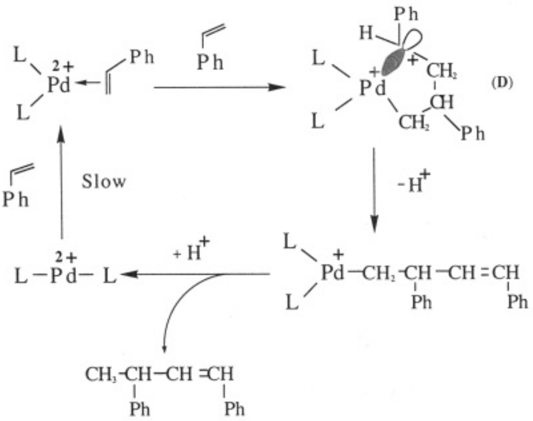

Figure 4. Mechanism for the linear dimerization of styrene.

Kinetics and Mechanism of the Linear Polymerization of *p*-Divinylbenzene. The following rate law was observed for the linear polymerization of *p*-divinylbenzene catalyzed by **2** in a 1:2 (v/v) $CH_3NO_2/CHCl_3$ mixture (eq 7), where vinyl is the sum of the terminal

$$-d[\text{vinyl}]/dt = k[\mathbf{2}]^{0.64}[\text{vinyl}] \qquad (7)$$

vinyl groups of the polymer and the monomer. The activation parameters were $E_a = 20$ kcal/mol, $\Delta H^{\ddagger} = 19$ kcal/mol, and $\Delta S^{\ddagger} = +1.2$ cal/(mol·K).

It should be noted that the rate expression shown in eq 7 was obeyed even at the very late stage of the polymerization reaction when M_n was up to 2000, indicating that the reactivity of the terminal vinyl groups of poly(*p*-DVB) was independent of the length of the polymer chain.[17]

The almost identical rate expressions for the acyclic dimerization of styrene by **1** and the linear polymerization of *p*-divinylbenzene by **2** (cf. eqs 6 and 7) strongly suggested mechanistically similar pathways for the two reactions. While the reaction order for the vinyl species was understandable, the fractional order observed for the catalyst was curious. A clue to this behavior came from the observation that the catalyst (compound **2**) for the linear polymerization of *p*-DVB was active in a $CH_3NO_2/CHCl_3$ mixture but not in $CHCl_3$ alone; i.e., a polar solvent was required to activate the catalyst. Since the reaction order in the vinyl species implied its coordination to the metal center in the rate-determining step (rds), the solvent effect could be rationalized on the basis of the requirement for the dissociation of one or more BF_4^- anions to allow the vinyl species to coordinate.

As described previously, in CH_3NO_2, K_1 and K_2, the equilibrium constants for the successive dissociation of BF_4^- anions from **2** (see eqs 3 and 4), were found to be 5.52×10^{-2} and 2.91×10^{-2} M, respectively. Not unexpectedly, changing the solvent from pure CH_3NO_2 to 1:2 $CH_3NO_2/CHCl_3$ (v/v) resulted in a decrease in K_1 and K_2 to 1.76×10^{-2} and 8.88×10^{-3} M, respectively. As shown below, the fractional reaction order in catalyst followed directly from the assumption that the actual catalytically active species was formed by the dissociation of one or more BF_4^- from the Pd(II) center.

Table III. Dependence of $x - y$ and y on c in the Case of Stepwise Dissociation of Two BF_4^- Ions

10^3c (M)	$10^4(x-y)$ (M)	10^3y (M)
1.5	3.28	1.127
2.0	5.15	1.389
2.5	7.22	1.619
3.0	9.38	1.820
3.5	11.63	2.000

Formation of Active Catalytic Species by the Stepwise Dissociation of Two BF_4^- Anion Ligands. In the catalytic system for the linear polymerization of *p*-DVB, the two equilibria that are involved are

$$L_2PdX_2 \overset{K_1}{\rightleftharpoons} L_2PdX^+ + X^-$$

$$L_2PdX^+ \overset{K_2}{\rightleftharpoons} L_2Pd^{2+} + X^-$$

$$L = PPh_3,\ X = BF_4$$

Quantitatively,

$$\begin{array}{llll} & L_2PdX_2 & \overset{K_1}{\rightleftharpoons} L_2PdX^+ & + X^- \\ \text{initial conc} & c & 0 & 0 \\ \text{equil conc} & c - x & x - y & x + y \end{array}$$

$$\begin{array}{llll} & L_2PdX^+ & \overset{K_2}{\rightleftharpoons} L_2Pd^{2+} & + X^- \\ \text{initial conc} & x & 0 & 0 \\ \text{equil conc} & x - y & y & x + y \end{array}$$

Hence,

$$K_1 = (x + y)(x - y)/(c - x)$$

$$K_2 = y(x + y)/(x - y)$$

Therefore,

$$x = (y^2 + K_2y)/(K_2 - y)$$

$$(K_1 - 4K_2)y^3 + K_1cy^2 - (K_1K_2^2 + 2K_1K_2c)y + K_1K_2^2c = 0$$

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[17] For discussions on the variation of reactivity of the terminal group as a function of the chain length in other polymerization systems, see: (a) Ito, K.; Tsuchida, H.; Kitano, T. *Polym. Bull.* **1986**, *15*, 425. (b) Cameron, G. G.; Chisholm, M. S. *Polymer* **1985**, *26*, 437. (c) Kennedy, J. P.; Lo, C. Y. *Polym. Bull.* **1985**, *13*, 343. (d) Kennedy, J. P.; Miza, H. *J. Polym. Sci., Chem. Educ.* **1983**, *21*, 1033.

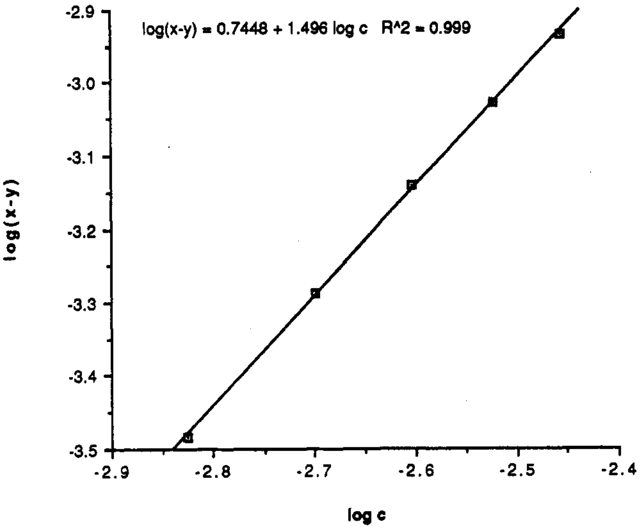


Figure 5. Correlation between $x - y$ and c in the case of stepwise dissociation of two BF_4^- ions.

For complex **2** dissolved in a 1:2 (v/v) ratio of CH_3NO_2/$CHCl_3$, $K_1 = 1.76 \times 10^{-2}$ M and $K_2 = 8.88 \times 10^{-3}$ M. Therefore,

$$x = (y^2 + 8.88 \times 10^{-3}y)/(8.88 \times 10^{-3} - y)$$

$$y^3 - 0.982cy^2 + (0.775 \times 10^{-4} + 1.744 \times 10^{-2}c)y - 0.775 \times 10^{-4}c = 0$$

From the above equations, $x - y$ and y were evaluated for different values of c and these are summarized in Table III. Plots of $\log(x - y)$ versus $\log c$ and $\log y$ versus $\log c$ were also obtained and are shown in Figures 5 and 6. The reaction order in $[Pd(II)]_{total}$ (c) could be evaluated from the slopes of the above plots. Thus, $y = Ac^{0.68}$ and $x - y = Bc^{1.5}$, where A and B are constants.

If L_2PdX^+ was the only active species,

$$\text{rate} = k[Pd(II)]_{total}^{1.5}[\text{vinyl}]$$

If L_2Pd^{2+} was the only active species,

$$\text{rate} = k[Pd(II)]_{total}^{0.68}[\text{vinyl}]$$

The latter was almost identical to the rate expression derived independently from the kinetic studies. Clearly, $Pd(PPh_3)_2^{2+}$ must be the predominant catalytically active species in the polymerization of *p*-DVB. Furthermore, the fractional order observed for **1** in the styrene dimerization reaction must also be due to similar anion dissociation steps. In support of this hypothesis, we have observed that the above reaction was inhibited by the addition of $Et_4N^+BF_4^-$ to the reaction mixture.

Finally, it should be noted that while polar solvents were required to cause the dissociation of coordinated BF_4^- ion(s) and allow catalysis to occur, many such solvents were also capable of coordinating to the metal center. In those solvents, the vinylic substrate would still be prevented from approaching the metal ion and, as a result, the reaction would not proceed.[3] As an example of this phenomenon, no catalysis was observed in CH_3CN although the ^{19}F NMR spectrum of **2** in this solvent indicated the complete dissociation of the BF_4^- ions.

Conclusion

We have discovered a series of cationic, electrophilic, Pd(II) compounds that are highly selective catalysts for the acyclic dimerization of vinyl monomers (styrene, ethylene, and propylene) and the linear polymerization of *p*-divinylbenzene. One manifestation of high selectivity is the ability to catalyze the dimerization of ethylene in the presence of propylene and styrene in the presence of α-methylstyrene even though the second member of each pair was normally significantly more reactive in reactions involving carbocationic intermediates.

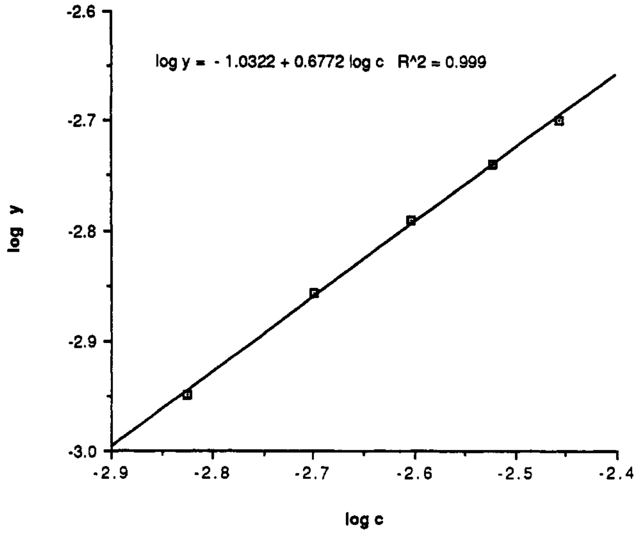


Figure 6. Correlation between y and c in the case of stepwise dissociation of two BF_4^- ions.

Table IV. Comparison between Pd(II) and Oxyacid Based Catalyst Systems for the Linear Polymerization of *p*-Divinylbenzene

	catalyst	solvent	[monomer] (M)	reacn temp (°C)
Pd(II) system	$Pd(PPh_3)_2(BF_4)_2$	polar (CH_3NO_2)	higher	40–70
oxy acid system	$AcClO_4$	nonpolar (benzene)	<0.1 only	>70 only

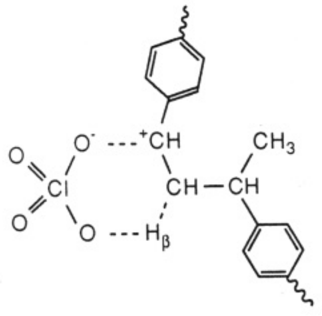
The reaction rates for the acyclic dimerization of styrene and the linear polymerization of *p*-divinylbenzene were found to be first order in the monomer concentration and fractional order in the catalyst concentration. Mathematical modeling indicated that the fractional order in the catalyst concentration was due to preequilibria involving anion dissociation from the metal center and it was possible to identify the actual catalytic species.

The linear polymerization of *p*-divinylbenzene involved a step-growth mechanism. The synthesis of a telechelic polymer through cross-coupling between the terminal vinyl groups of linear poly(*p*-DVB) and the vinyl group of a functionalized styrene derivative was also achieved.

The oxyacid catalyzed synthesis of linear poly(divinylbenzene) has been reported by Higashimura et al.[14] According to them, intermediate E was involved in each step.

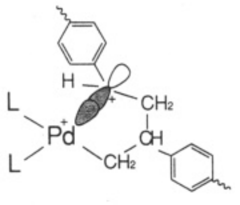
Nonpolar solvents, such as benzene, were required to induce the tight ion-pair formation and suppress the nucleophilic attack by monomer (i.e., propagation). The multidentate structure of the counteranion allows a second oxygen atom to interact specifically with the β-hydrogen of the propagating cation and promotes β-hydrogen elimination to form the linear polymer. The reason the polymerization reaction had to be carried out at high temperatures (>70 °C) was not given.

In contrast, for our Pd(II) catalyst system, a polar solvent was essential for the activation of the catalyst by anion



E

dissociation. Interaction of the filled metal d-orbital with the empty π-orbital of the propagated carbocation (see intermediate D) was presumably involved in the polymerization of *p*-DVB.



D

Table IV compares the two catalytic systems. The advantage of our system lay in the ability to use lower reaction temperatures (<70 °C) and higher monomer concentrations (>0.1 M).

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