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Addition Polymerization of Norbornene-Type Monomers. High Activity Cationic Allyl Palladium Catalysts

John Lipian, Richard A. Mimna, John C. Fondran, Dmitry Yandulov,[1] Robert A. Shick, Brian L. Goodall,[2] and Larry F. Rhodes*

Promerus LLC, 9921 Brecksville Road, Brecksville, Ohio 44141

John C. Huffman

Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

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ABSTRACT: A family of high activity catalysts for the vinyl addition polymerization of norbornene-type monomers based on cationic η^3-allylpalladium complexes coordinated by phosphine ligands has been discovered. The palladium complex $[(\eta^3\text{-allyl})Pd(tricyclohexylphosphine)(ether)][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (**2**) was found to copolymerize 5-butylnorbornene and 5-triethoxysilylnorbornene (95:5 molar ratio) with truly high activity and is capable of producing more than a metric ton of copolymer per mole Pd per hour. Multicomponent catalyst systems based on the addition of salts of weakly coordinating anions (e.g., $Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ or $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$) to $(\eta^3\text{-allyl})Pd(X)(PR_3)$ (X = chloride, acetate, nitrate, trifluoroacetate, and triflate) in the presence of norbornene-type monomers were developed. NMR tube experiments confirm that $Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ abstracts the Cl ligand from the palladium complex forming the cationic complex in situ. Control experiments confirmed that a high activity polymerization system requires a palladium cation containing an allyl ligand, a neutral, two-electron-donor phosphine ligand, and a weakly coordinating counterion. Those complexes where X contained electron-withdrawing groups such as trifluoroacetate or triflate were found to be the most active catalyst precursors. η^3-Allylpalladium catalyst precursors with larger cone angle phosphine ligands yield lower molecular weight polymers. The poly(norbornene) molecular weights can be further tuned by addition of α-olefin chain transfer agents to the reaction mixture. The catalyst systems were also found to polymerize norbornene-type monomers in aqueous media to high conversion at very low catalyst loadings. The effect of molecular weight on thermomechanical properties was explored.

Introduction

Interest in cyclic olefin polymers has increased dramatically over the past decade. The attractive properties of this type of polymer such as high glass transition temperature, high optical transparency, low birefringence, and low moisture absorption have been the reasons for the increased interest. Cyclic olefin polymers include ring-opened metathesis polymers (both hydrogenated and unhydrogenated versions), vinyl addition copolymers with acyclic comonomers such as ethylene, and vinyl addition homopolymers of cyclic olefins.

We have concentrated on the vinyl addition homopolymerization of cyclic olefins of the norbornene type due to the very high glass transition temperature of the parent norbornene homopolymer. Moreover, norbornene derivatives are readily synthesized by the Diels−Alder addition of cyclopentadiene to a dieneophile that can contain a wide variety of functional groups. In this manner, the properties of the polymer can be tailored to exhibit a range of properties. Several groups have studied the vinyl addition polymerization of norbornene. The literature up to the year 2000 has been reviewed.[3]

Recently, we published the discovery of a family of late transition metal cationic catalysts that polymerize norbornene monomers.[4] Of the single component catalysts in this family, $[(\eta^3\text{-allyl})Ni(1,5\text{-cyclooctadiene})]^+$, was the most extensively examined. The palladium analogue was of interest due to its greater tolerance of norbornene-type monomers containing functional pendant groups.[5] Therefore, it was disappointing to find that the Pd analogue appeared to polymerize norbornene at a more sluggish rate when compared to Ni.

Since then we have sought palladium systems that exhibited higher activity. We have published results on the polymerization efficacy of an in situ system produced by the reaction of Pd(Me)(Cl)(1,5-COD) (COD = cyclooctadiene) and PPh_3 in the presence of $NaB(3,5\text{-}(CF_3)_2C_6H_3)_4$.[6] In this system, the reaction of Pd(Me)(Cl)(1,5-cyclooctadiene) and PPh_3 forms the known dimeric species $[Pd(Me)(Cl)(PPh_3)]_2$. Presumably, in the presence of the sodium salt of the weakly coordinating borate anion, $B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$, the highly reactive (solvent/monomer-coordinated) cationic species "$[Pd(Me)(PPh_3)][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$" formed (eq 1). This species is an extremely active catalyst for norbornene polymerization.

$$\begin{tikzcd} 2\,\text{Pd(Me)(Cl)(1,5-COD)} + 2\,PPh_3 \arrow[r] & {[\text{Pd(Me)(Cl)}(PPh_3)]_2} \arrow[d, "2\,NaB(3,5\text{-}(CF_3)_2C_6H_3)_4"] \\ & 2\,\text{"[Pd(Me)(PPh3)]}[B(3,5\text{-}(CF_3)_2C_6H_3)_4]\text{"} \end{tikzcd} \qquad (1)$$

A class of palladium complexes that we found particularly attractive were cationic η^3-allylpalladium complexes coordinated by phosphine ligands. Such complexes are known to participate in the catalytic dimerization and oligomerization of olefins,[7] telomerization of butadiene,[8] and dimerization and co-dimerization of functionalized olefins,[9] to name a few reactions. We have

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* To whom correspondence should be addressed: E-mail: larry.rhodes@promerus.com. FAX: 216-447-5464.

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investigated these types of palladium derivatives for their norbornene polymerization efficacy[10] and report here our findings.

Experimental Section

General Considerations. All manipulations of organometallic complexes were carried out under an atmosphere of prepurified argon or nitrogen using standard Schlenk or drybox techniques. Solvents (Aldrich, anhydrous grade) were purchased from Aldrich and used after sparging with nitrogen. THF and ether were dried over sodium benzophenone ketyl under nitrogen, vacuum transferred, and stored over 4 Å molecular sieves.

[(η^3-allyl)Pd(Cl)]$_2$, tricyclohexylphosphine, tri-*o*-tolylphosphine, triphenylphosphine, tris(pentafluorophenyl)phosphine, tri-*n*-butylphosphine, tri-*tert*-butylphosphine, tri-*i*-propylphosphine, silver trifluoroacetate, silver triflate, silver acetate, and silver nitrate were purchased from Strem Chemical and used as received. Methylmagnesium bromide, sodium lauryl sulfate, hexene-1, and tribenzylphosphine were obtained from Aldrich. Lithium tetrakis(pentafluorophenylborate)·2.5Et$_2$O and sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate were purchased from Boulder Scientific. The sodium salt was purified according to Hennis et al.[6] 5-Butylnorbornene was obtained from BFGoodrich. 5-Triethoxysilylnorbornene was obtained from Gelest. 2,6-Bis[4-azidophenyl]methylene-4-ethylcyclohexanone was purchased from Toyo Gosei, and Irganox 1076 was obtained from Ciba Specialty Chemicals, H(Et$_2$O)$_2$[tetrakis-(bis(3,5-trifluoromethyl)phenyl)borate] was prepared as reported.[11]

Instrumental Analysis. The ^{1}H, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker AMX-500 NMR spectrometer operating at 500.14, 470.53, and 202.47 MHz, respectively. Chemical shifts for ^{1}H NMR spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. The ^{19}F NMR spectra were referenced to external CFCl$_3$, while the ^{31}P NMR spectra were referenced to external H$_3$PO$_4$.

Molecular weight measurements were made on a Waters 150C GPC instrument equipped with a refractive index detector. Polymer samples were dissolved in monochlorobenzene (50 mg/15 mL) and filtered through a 0.45 Teflon filter. All molecular weights are relative to polystyrene standards.

Elemental analyses were performed by Robertson Microlit Laboratories, Inc., Madison, NJ.

Tensile modulus and elongation at break of polymer films (approximately 3−4 mil thick) were determined on an Instron 5500R instrument according to ASTM standard D1708 after the samples were conditioned according to ASTM D618−90. An average of five runs is reported.

The X-ray diffractometer utilized for data collection was designed and constructed locally at the Molecular Structure Center (Indiana University). A Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) was modified by addition of stepping 20-position filter/attenuator wheel. All motors were driven by a locally designed ISA board in an IBM-PC compatible computer. The computer also contained a timer/scaler board which was used to accumulate the counts from the scintillation counter used with the goniostat. The control software, PCPS.EXE, is the Picker software written by W. E. Streib of the Molecular Structure Center.

(η^3-Allyl)palladium(tricyclohexylphosphine) Chloride (1). The following procedure is a modification of that reported by Brookhart.[9a] To [(η^3-allyl)Pd(Cl)]$_2$ (1.00 g, 2.73 mmol) was added about 75 mL of toluene to give a yellow solution with a small amount of insolubles. To this mixture was added tricyclohexylphosphine (1.55 g, 5.53 mmol) dissolved in about 20 mL of toluene. A clear yellow solution resulted that was allowed to stir at room temperature for 2 h. The solvent was removed in vacuo to yield a pale yellow powder which was dissolved in THF and stirred overnight. The THF was then removed in vacuo to give an off-white powder that was washed with 50 mL of ether three times. The resulting free-flowing, off-white powder was dried in vacuo. Yield: 1.6 g (63%). ^{31}P NMR (CD$_2$Cl$_2$): δ 41.1 (s). ^{1}H NMR (CD$_2$Cl$_2$): δ 5.40 (m, 1H), 4.49 (br t, 1H), 3.49 (d of d, 1H), 3.42 (s, 1H), 2.59 (d, 1H), 2.14 (m, 3H), 1.90 (br s, 6H), 1.80 (s, 6H), 1.72 (s, 3H), 1.47 (br s, 6H), 1.27 (s, 9H).

[(η^3-allyl)Pd(PCy$_3$)(ether)][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] (2). The following procedure is a modification of that reported by Brookhart.[9a] (η^3-allyl)palladium(tricyclohexylphosphine) chloride (1.00 g, 2.16 mmol) was dissolved in ether and cooled to −78 °C. Methylmagnesium bromide (720 μL of 3 M solution in ether, 2.16 mmol) was added dropwise. The mixture was stirred at −78 °C for 1 h after which the solvent was removed in vacuo. The solid was extracted twice with pentane and filtered. The solution was stored at −20 °C overnight. A precipitate formed, and the flask was further cooled to −78 °C. The resulting solid was collected and dried. Yield: 0.50 g (52%). NMR spectra are in agreement with the formation of (η^3-allyl)Pd(methyl)(tricyclohexylphosphine). ^{31}P NMR (CD$_2$Cl$_2$): δ 42.3 (s). ^{1}H NMR (CD$_2$Cl$_2$): δ 4.99 (m, 1H), 3.45 (d, 1H), 3.31 (br t, 1H), 2.39 (d of d, 1H), 2.33 (d, 1H), 2.00 (m, 3H), 1.86 (br s, 6H), 1.78 (br s, 6H), 1.71 (s, 3H), 1.39 (br s, 6H), 1.24 (br s, 9H).

To a flask containing (η^3-allyl)Pd(methyl)(tricyclohexylphosphine) (0.26 g, 0.58 mmol) was added H(Et$_2$O)$_2$[tetrakis-(bis(3,5-trifluoromethyl)phenyl)borate] (0.59 g, 0.58 mmol). The contents of the flask were cooled to −78 °C, and 15 mL of ether was added. The mixture warmed slightly to facilitate dissolution and then recooled to −78 °C. After the mixture was stirred for 3 h, the solvent was removed in vacuo to give a brown-yellow solid. After this was washed with pentane twice and dried in vacuo, a beige crystalline solid was isolated. Yield: 0.69 g (87%). ^{31}P NMR (CD$_2$Cl$_2$): δ 43.1 (s). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.72 (s, 8H), 7.56 (s, 4H), 5.83 (br m, 1H), 5.15 (br s, 1H), 4.05 (br s, 1H), 3.95 (br s, 1H), 3.44 (q, 4H), 3.20 (br s, 1H), 1.16 (t, 6H), and peaks from 2.05 to 1.10 due to tricyclohexylphosphine.

(η^3-Allyl)palladium(tri-*o*-tolylphosphine) Chloride (3). The following procedure is a modification of that reported by Widenhofer.[12] To a [(η^3-allyl)PdCl]$_2$ (1.50 g, 4.10 mmol) solution in about 25 mL of methylene chloride was added tri-*o*-tolylphosphine (2.50 g, 8.22 mmol) as a methylene chloride solution. The solution was allowed to stir overnight. The solvent was removed in vacuo to yield a pale yellow powder. Yield: 3.50 g (88%). ^{31}P NMR (CD$_2$Cl$_2$): δ 21.4 (s). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.58 (br t, 3H), 7.40 (t, 3H), 7.24 (m, 6H), 5.60 (m, 1H), 4.57 (t, 1H), 3.55 (d of d, 1H), 3.16 (br s, 1H), 2.30 (br s, 1H), 2.19 (s, 9H).

(η^3-Allyl)palladium(tri-*o*-tolylphosphine) Nitrate (4). To a suspension of silver nitrate (0.935 g, 5.50 mmol) in methylene chloride was added a methylene chloride solution of [(η^3-allyl)Pd(Cl)]$_2$ (1.00 g, 2.73 mmol) and tri-*o*-tolylphosphine (1.66 g, 5.45 mmol). After the mixture was stirred overnight, it was filtered to give an orange filtrate. This solution was concentrated and layered with pentane. The resulting white solid was isolated. Anal. Calcd for C$_{24}$H$_{26}$O$_3$NPPd: C, 56.10; H, 5.10; N, 2.73. Found: C, 55.39; H, 5.09; N, 2.50. ^{31}P NMR (CD$_2$Cl$_2$): δ 20.3 (s). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.50−7.20 (m, 12H), 5.70 (m, 1H), 4.85 (t, 1H), 3.95 (d of d, 1H), 2.60 (br s, 2H), 2.20 (s, 9H).

(η^3-Allyl)palladium(tri-*o*-tolylphosphine) Acetate (5). To a suspension of silver acetate (0.919 g, 5.51 mmol) in methylene chloride was added a methylene chloride solution of [(η^3-allyl)Pd(Cl)]$_2$ (1.00 g, 2.73 mmol) and tri-*o*-tolylphosphine (1.66 g, 5.45 mmol). After the mixture was stirred overnight, it was filtered to give an orange filtrate. This solution was concentrated and layered with pentane. The resulting white solid was isolated. Yield: 1.8 g (65%). Anal. Calcd for C$_{26}$H$_{29}$O$_2$PPd: C, 61.12; H, 5.72. Found: C, 60.31; H, 5.90. ^{31}P NMR (CD$_2$Cl$_2$): δ 20.8 (s). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.50−7.20 (m, 12H), 5.60 (m, 1H), 4.67 (t, 1H), 3.80 (d of d, 1H), 2.50 (br s, 2H), 2.20 (s, 9H).

(η^3-Allyl)palladium(tri-*o*-tolylphosphine) Triflate (6). To a methylene chloride solution (10 mL) of [(η^3-allyl)Pd(Cl)]$_2$ (1.50 g, 4.10 mmol) was added a methylene chloride solution (10 mL) of tri-*o*-tolylphosphine (2.50 g, 8.21 mmol). This solution was added to a methylene chloride solution of silver triflate (2.11 g, 8.19 mmol). A precipitate formed immediately. The reaction mixture was shielded from room light and allowed to stir overnight. The resulting slurry was filtered through Celite to yield an orange filtrate. The methylene chloride was removed in vacuo to give a yellow powder, which was washed with pentane twice and an 80:20 mixture of pentane:ether and then dried in vacuo. Yield: 4.05 g (82%). Anal. Calcd for $C_{25}H_{26}O_3F_3SPPd$: C, 49.96; H, 4.37. Found: C, 49.86; H, 4.33. ^{31}P NMR (CD_2Cl_2): δ 21.4 (s). ^1H NMR (CD_2Cl_2): δ 7.44 (m, 6H), 7.26 (m, 6H), 5.70 (br s, 1H), 5.10 (br s, 1H), 3.95 (br s, 1H), 3.20 (br s, 1H), 2.37 (br s, 1H), 2.19 (s, 9H).

(η^3-Allyl)palladium(tri-*o*-tolylphosphine) Trifluoroacetate (7). [(η^3-allyl)Pd(Cl)]$_2$ (4.21 g, 11.5 mmol) was dissolved in 40 mL of methylene chloride. This solution was added to a cooled (−15 °C) methylene chloride (40 mL) solution of tri-*o*-tolylphosphine (7.00 g, 23.0 mmol). The mixture was allowed to stir for 30 min and was then added to a methylene chloride (20 mL) slurry of silver trifluoroacetate (5.08 g, 23.0 mmol) that was protected from light and was cooled to −15 °C. The mixture was allowed to stir at room temperature for 12 h. The mixture was then filtered through a 0.2 μm Teflon filter to remove AgCl. The resulting yellow filtrate was concentrated and layered with pentane (about a 4-fold volumetric excess). The flask was stored at −20 °C for 3 days. Large crystals of the product formed that were filtered, washed with pentane, and dried in vacuo. Yield: 8.10 g (62%). Anal. Calcd for $C_{26}H_{26}O_2F_3PPd$: C, 55.28; H, 4.64. Found: C, 55.38; H, 4.47. ^{31}P NMR (CD_2Cl_2): δ 20.5 (s). ^1H NMR (CD_2Cl_2): δ 7.50−7.20 (m, 12H), 5.65 (m, 1H), 4.85 (t, 1H), 3.91 (d of d, 1H), 3.03 (br s, 1H), 2.25 (br s, 1H), 2.21 (s, 9H).

(η^3-Allyl)palladium(tricyclohexylphosphine) Triflate (8). A methylene chloride solution of ([(η^3-allyl)palladium-(tricyclohexylphosphine) chloride (1.00 g, 2.16 mmol) was added to a methylene chloride solution of silver triflate (0.565 g, 2.20 mmol). The reaction mixture was shielded from room light and allowed to stir for 18 h. The resulting slurry was filtered to yield a light yellow filtrate. The methylene chloride was removed in vacuo to give a free-flowing white powder. Yield: 1.05 g (84%). Anal. Calcd for $C_{22}H_{38}O_3F_3SPPd$: C, 45.80; H, 6.65. Found: C, 45.74; H, 6.70. ^{31}P NMR (C_6D_6): δ 42.2 (s). ^1H NMR (C_6D_6): δ 5.10 (t, 1H), 4.66 (m, 1H), 3.64 (d of d, 1H), 2.62 (s, 1H), 1.95 (d, 1H), and peaks from 1.9 to 1.0 due to tricyclohexylphosphine.

Polymerizations. 25 mL Scale. In the drybox, 5-butylnorbornene (4.58 g, 30.5 mmol), 5-triethoxysilylnorbornene (0.42 g, 1.6 mmol), and lithium tetrakis(pentafluorophenyl)-borate·$2.5Et_2O$ (0.0028 g, 0.0033 mmol) were combined in a vial equipped with a magnetic stirbar and diluted with 16 mL of toluene. In a separate vial [(η^3-allyl)Pd(Cl)]$_2$ (0.00033 mmol, 100 μL of a 0.0033 M solution in toluene) and the phosphine of choice (0.00069 mmol, 53 μL of a 0.013 M solution in toluene) were combined. This was added to the monomer solution. The vial was sealed and heated to 65 °C for 4 h with stirring. If the solutions became too viscous, they were diluted with toluene and then poured into acetone to precipitate the polymer. The polymer was filtered and dried under vacuum. Yields were determined gravimetrically. ^1H NMR ($CDCl_3$): δ 3.7 (br s, 6H, $Si(OCH_2CH_3)_3$), 3.0−0.7 (several broad peaks, aliphatic, cycloaliphatic and $Si(OCH_2CH_3)_3$).

Polymerizations. 0.5 L Scale. In a typical polymerization, 45.8 g of 5-butylnorbornene (305 mmol), 4.2 g of 5-triethoxysilylnorbornene (16.4 mmol), and 6.7 g of hexene-1 (80 mmol) diluted with toluene to a total volume of 320 mL were added to a clean, dry 500 mL stainless steel reactor. The mixture was heated to 65 °C with agitation. To this mixture was added lithium tetrakis(pentafluorophenyl)borate·$2.5Et_2O$ (35.5 mg, 0.0408 mmol) in 4 mL of toluene. Approximately 5.0 mg of (η^3-allyl)palladium(tri-*o*-tolylphosphine) triflate (0.0082 mmol) in 3 mL of toluene was added to the reactor. After 4 h, the reactor was cooled, and the reactor contents were poured into acetone to precipitate the polymer which was filtered and dried in vacuo overnight. Yield: 44.7 g (90%).

Polymerization of Norbornene in Hexene-1 solvent Using 8. Norbornene (5.0 g, 0.053 mol), $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$ (0.231 g, 0.265 mmol), and **8** (0.032 g, 0.053 mmol) were weighed into a vial. To this solid mixture was added hexene-1 (8.35 g). Immediately, a white precipitate began to from which increased over time. After about 5−10 min, the mixture became a solid. The polymer was washed with acetone, filtered, and dried under vacuum. Yield: 4.97 g (99%). ^1H NMR (*o*-dichlorobenzene-*d*$_4$): δ 5.35 (br m, hexenyl end group), 2.5−0.85 (several broad peaks, aliphatic and cycloaliphatic).

Polymerizations. Aqueous. In a typical polymerization, 5 g of 5-butylnorbornene (0.033 mmol) added to 100 mL of deoxygenated, deionized water containing 1.0 wt % sodium lauryl sulfate. To this mixture was added a mixture of [(η^3-allyl)Pd(Cl)]$_2$ (0.12 mg, 0.00033 mmol) and tricyclohexylphosphine (0.19 mg, 0.00066 mmol) in 0.5 mL of toluene followed by lithium tetrakis(pentafluorophenyl) borate·$2.5Et_2O$ (2.9 mg, 0.0033 mmol). The mixture was agitated with a mechanical stirrer and heated to 65 °C for 4 h. The mixture became opaque and polymer began to precipitate. The mixture was dissolved in toluene and then precipitated into an excess of acetone. The polymer was filtered and dried in a vacuum oven at 65 °C. Yield: 3.3 g (66%).

Formulation and Preparation of Films for Thermomechanical Testing. Polymer solutions of between 20 and 30% in mesitylene were formulated with 3 wt % 2,6-bis[4-azidophenyl]methylene-4-ethylcyclohexanone (bis(aryl azide) cross-linker) and 0.5 wt % Irganox 1076 (antioxidant). These solutions were cast on glass plates using a doctor blade. The films were dried and cured in an oven at 250 °C for 1 h under vacuum. Typically films of 3−4 mil thickness were produced.

X-ray Crystallography of (η^3-Allyl)palladium(tri-*o*-tolylphosphine) Triflate (6). Pale yellow crystals suitable for X-ray analysis grew from a concentrated methylene chloride/pentane solution after storage at −20 °C for 2 weeks. A sample, still damp from the solvent medium, was cleaved to form a nearly equidimensional transparent fragment which was then affixed to a glass fiber using silicone grease. After the crystal was transferred to the goniostat and cooled to −171 °C, a systematic search of a limited hemisphere of reciprocal space was used to determine that the crystal possessed symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/c$. Subsequent solution and refinement confirmed this choice.

The data were collected using standard moving crystal-moving detector techniques with fixed backgrounds at each extreme of the scan. Data were corrected for absorption, and Lorentz and polarization effects, and equivalent reflections were then averaged. The structure was solved using direct methods (SHELXTL) and Fourier techniques. A difference Fourier located most of the hydrogen atoms except those located on the allyl group. The two largest peaks were located adjacent to the carbon atoms in the allyl group such that a disorder was apparent. After several cycles, it was possible to resolve the disorder, with two conformations (in a ratio of 38:62) present. At this point it was possible to locate the hydrogen atoms of the major allyl component. All hydrogen atoms, including the latter were included as isotropic contributors to the final cycles of refinement. A final difference Fourier was featureless, the largest peaks, 0.48 e/A^3, were located at the metal site.

Crystal data for **6** are presented in Table 1 while selected bond distances and angles are given in Table 2. Complete crystallographic details can be found in a CIF file in the Supporting Information.

Results and Discussion

Single Component Catalysts. According to our previous report, a truly active polymerization complex for norbornene-type monomers seemed to require a cationic palladium complex containing a methyl initiating ligand, a neutral, two-electron-donor phosphine ligand, and a weakly coordinating counterion. These attributes are found in the putative "$[Pd(Me)(PPh_3)]$-$[B(3,5-(CF_3)_2C_6H_3)_4]$". Unfortunately, this proposed spe-

Table 1. Crystal Data for (η^3-Allyl)palladium(tri-*o*-tolylphosphine) Triflate (6)

chemical formula	$C_{25}H_{26}F_3O_3PPdS$
color	pale yellow
fw	600.93
temp, °C	-171
wavelength, Å	0.71069
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	11.134(1)
b, Å	11.629(1)
c, Å	19.361(1)
β, °	93.57(1)
V, Å^3	2502.08
Z	4
D_{calcd}, g/cm^{-3}	1.595
abs coeff, mm^{-1}	9.371
F(000)	1216
cryst size, mm	$0.14 \times 0.14 \times 0.17$
2θ range for collcn, deg	5.0−50.0
limiting indices	$-13 < h < +4$
	$0 < k < 13$
	$-22 < l < +22$
no. of reflcns collcd	5120
no. of indep reflcns	4392
abs cor	none
refinement method	full-matrix
data/restraints/params	3882/0/439
goodness-of-fit on F^2	1.444
final *R* indices [$I > 2\sigma(I)$]	0.014
R indices (all data)	0.0300
extinction coeff	none
largest diff peak and hole, e/A^3	0.48; -0.42

Table 2. Selected Bond Distances and Angles in (η^3-Allyl)palladium(tri-*o*-tolylphosphine) Triflate (6)

type	length, Å)	type	angle, deg)
Pd1−C10	2.085(3)	P13−Pd1−O3	96.39(6)
Pd1−C11	2.148(5)	P13−Pd1−C10	94.81(10)
Pd1−C12	2.265(13)	P13−Pd1−C11	130.40(15)
Pd1−P13	2.3242(8)	P13−Pd1−C12	159.5(3)
Pd1−O3	2.1497(20)	O3−Pd1−C10	168.63(11)
C10−C11	1.401(6)	O3−Pd1−C11	131.29(16)
C11−C12	1.392(15)	O3−Pd1−C12	101.7(4)
		C10−Pd1−C12	67.0(4)
		C10−C11−C12	118.8(7)

cies was unstable in the absence of monomer and eventually formed metallic palladium.[6] Thus, we sought a stable complex that would nevertheless act as a high activity catalyst.

A search of the literature uncovered a route to an η^3-allylpalladium compound supported by tricyclohexylphosphine (PCy_3), containing a labile ether ligand and a weakly coordinating anion: [(η^3-allyl)Pd(PCy_3)(ether)]-[B(3,5-$(CF_3)_2C_6H_3)_4$] (**2**).[9a] Given that allyl complexes such as [(η^3-allyl)Ni(1,5-cyclooctadiene)]$^+$ and [(η^3-allyl)-Pd(1,5-cyclooctadiene)]$^+$ polymerize norbornene-type monomers, we believed that **2** would make a good candidate catalyst complex.

Following a modification of a literature preparation, **2** was formed by reaction of [$H(Et_2O)_2$][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] with (η^3-allyl)Pd(Me)(PCy_3) which was synthesized by addition of MeMgBr to (η^3-allyl)Pd(Cl)(PCy_3) (**1**). This complex was then added to a toluene solution containing a mixture of 5-butylnorbornene and 5-triethoxysilylnorbornene (95:5 molar ratio) at monomer to catalyst molar ratios of 1000:1 and 10 000:1. In both cases, a quantitative yield of copolymer was obtained. Even at 50 000:1 and ultimately at 100 000:1 molar ratio of monomer to Pd, significant conversions to polymer were obtained (64 and 29% respectively). As the catalyst loading was decreased from 1000:1 to 50 000:1, the activity increased from 39 to 1184 kg of polymer produced/(mol of Pd/h). Complex **2** is truly a high activity catalyst, capable of creating more than a metric ton of copolymer per mole of Pd per hour. Details of the copolymerizations are presented in Table 3.

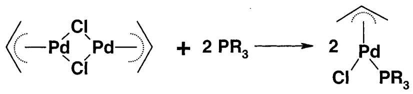
Table 3. Copolymerization of 5-Butylnorbornene and 5-Triethoxysilylnorbornene (95:5 Molar Ratio) Using 2[a]

run	monomer:Pd (molar ratio)	convn, %	activity, kg of polymer/mol of Pd·h
1	1000:1	100	39
2	10000:1	100	388
3	50000:1	64	1184
4	100000:1	29	1125

[a] Polymerizations carried out at a 2.0 M concentration of monomers in toluene for 4 h at 65 °C.

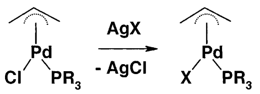
Multicomponent Catalyst Systems. Once the high activity nature of **2** had been established, we sought methods of producing the active initiator in situ. Our efforts concentrated on producing η^3-allylpalladium phosphine procatalysts containing anionic ligands that could act as leaving groups in the presence of salts of weakly coordinating anions. In this manner, the salt of the weakly coordinating anion would act as an activator by opening a coordination site on Pd once occupied by the anionic leaving group. The open coordination site would in turn be filled by incoming norbornene monomer. Ideally, this approach would use commercially available or readily synthesized η^3-allylpalladium procatalysts and activators such as Na[B(3,5-$(CF_3)_2C_6H_3)_4$] or Li[B$(C_6F_5)_4$]·2.5Et_2O.

We chose to use [(η^3-allyl)Pd(Cl)]$_2$ as the starting material to synthesize a variety of phosphine adducts: (η^3-allyl)Pd(Cl)(PR_3). These complexes were readily accessed simply by addition of PR_3 to [(η^3-allyl)Pd(Cl)]$_2$. The neutral, two-electron-donor phosphine cleaves the dimer complex into monomeric units (eq 2).[13]



(2)

The monomeric chloride complexes can be further reacted with silver salts to replace the chloride with more weakly coordinating anions such as acetate, nitrate, trifluoroacetate and triflate (eq 3). The monomeric chloride complex can be isolated prior to reaction with the silver salts. Or, for convenience, the addition of phosphine followed by addition of the silver salt can be carried out in one pot without isolation of the chloride intermediate. Complexes **3**−**8** were synthesized using these approaches and satisfactorily characterized by a combination of ^1H and ^{31}P NMR spectrometry and, for new complexes, elemental analysis.



R = *o*-tolyl, X = chloride (**3**)
o-tolyl, X = nitrate (**4**)
o-tolyl, X = acetate (**5**)
o-tolyl, X = triflate (**6**)
o-tolyl, X = trifluoroacetate (**7**)
R = cyclohexyl, X = triflate (**8**)

(3)

X-ray Structure of (η^3-Allyl)palladium(tri-*o*-tolylphosphine) Triflate. Crystals of complex (η^3-

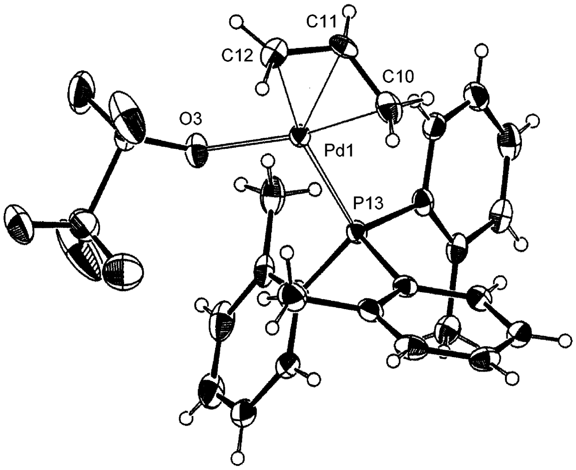


Figure 1. ORTEP representation of (η^3-allyl)palladium(tri-*o*-tolylphosphine) triflate (**6**).

allyl)palladium(tri-*o*-tolylphosphine) triflate (**6**) that were suitable for X-ray structure determination were grown by cooling a methylene chloride/pentane solution of **6**. During the course of solving the structure, it was found that the η^3-allyl group of the complex suffered from disorder, but the disorder could be readily modeled and resolved. An ORTEP view of the complex is shown in Figure 1; the major conformer of **6** is used in Figure 1. Selected bond distances and angles found in **6** are given in Table 2.

The structure of **6** is typical for allyl complexes of palladium. The coordination geometry is best described as distorted square planar if one regards C10 and C12 (of the allyl ligand), P13 (of the phosphine ligand), and O3 (of triflate) as the corners of the square. The sum of the angles containing these atoms around Pd is close to 360°.

The allyl carbon−carbon distances C10−C11 (1.401(6) Å) and C11−C12 (1.392(15) Å) are identical; no localization of the allyl ligand from η^3 toward η^1-coordination is evident. The Pd−C12 bond distance (2.265(3) Å) is substantially longer than the Pd−C10 (2.085(3) Å) distance. This is due to the influence of the ligands trans to C12 and C10. The phosphine phosphorus has a greater trans influence than the oxygen of triflate, resulting in a longer Pd−C12 bond distance. A similar trend is found in the X-ray structure of (η^3-2-methallyl)Pd(triphenylphosphine)(chloride).[14] The Pd−C bond distance in this complex trans to the phosphorus containing ligand is longer (2.211(6) Å) than the Pd−C bond trans to chloride (2.120(5) Å). For [(η^3-2-methallyl)Pd(trifluoroacetate)]$_2$, in which the terminal carbons of the allyl ligands are trans to the oxygens of two trifluoroacetate bridging ligands, the Pd−C distance is comparable to that found in **6** (2.096(5) and 2.073(5) Å).[15]

Polymerization Using Multicomponent Catalyst Systems. Our initial studies involved the copolymerization of 5-butylnorbornene and 5-triethoxysilylnorbornene (95:5 molar ratio) and focused on establishing the essential components for high activity. In the first experiment, [(η^3-allyl)Pd(Cl)]$_2$ was reacted with PCy$_3$ in the presence of monomer (150 000:1:1 mol of monomer to Pd to PCy$_3$). Addition of phosphine to the palladium dimer forms the monomeric complex, (η^3-allyl)Pd(Cl)(PCy$_3$). No polymer was obtained even after heating this mixture for 4 h at 65 °C. In the second experiment, [(η^3-allyl)Pd(Cl)]$_2$ was reacted with Li[B(C$_6$F$_5$)$_4$]·2.5Et$_2$O again in the presence of monomer under identical conditions. The lithium salt should abstract the chloride from the palladium complex to form a cationic palladium complex. Nevertheless, no polymer was obtained. However, once all three components were added, the allylpalladium complex, the phosphine, and the salt of the weakly coordinating anion, good conversion to polymer was obtained (85%). Thus, we obtained further evidence that a palladium cation containing an initiating hydrocarbyl ligand such as allyl, a neutral, two-electron-donor phosphine ligand, and a weakly coordinating counterion are necessary attributes for high activity.

Table 4. Effect of Anionic Leaving Groups on the Polymerization of 5-Butylnorbornene:5-Triethoxynorbornene (95:5) Using (η^3-allyl)Pd(X)(P(*o*-tolyl)$_3$) and Li[B(C$_6$F$_5$)$_4$]·2.5Et$_2$O[a]

expt	X	convn, %	M_w ($\times 10^{-3}$)	composition[b]
1	nitrate	70	193	92:8
2	acetate	80	238	
3	chloride	84	187	
4	triflate	100	193	95:5
5	triflate	100	227	
6	triflate	100	205	
7	trifluoroacetate	100	212	
8	trifluoroacetate	100	206	
9	trifluoroacetate	100	198	

[a] Polymerizations were run in toluene for 4 h at 65 °C: [monomers] = 1.0 M, [Pd] = 0.026 mM, and [Li] = 0.13 mM. [b] Butylnorbornene to triethoxysilylnorbornene, molar ratio by ^{1}H NMR.

It remained then to prove that the multicomponent system forms the expected cationic palladium complex in situ. To this end, the reaction of 2 equiv of Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] with (η^3-allyl)Pd(Cl)(PCy$_3$) (formed from the reaction of [(η^3-allyl)Pd(Cl)]$_2$ and PCy$_3$) in the presence of 2 equiv of ether was followed by ^{1}H NMR spectrometry in deuterated methylene chloride. Within the time of mixing and measuring the spectrum, resonances were observed in the allyl region of the spectrum that were identical to those exhibited by **2**. Almost 54% of the starting chloride complex was transformed into the cationic product despite the fact that sodium is not known to be a particularly good halide abstractor. It is rather interesting to note that in contrast to the spectrum of the starting chloride, the allyl resonances of complex **2** in the presence of Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] are rather broad. This could be an indication of some dynamic process involving the allyl ligand.

Effect of Leaving Group on Norbornene-Type Monomer Polymerization. According to our working hypothesis for catalyst generation, the leaving group of the procatalyst is replaced by a more weakly coordinating anion and, perhaps, a solvent or monomer molecule, as the active catalyst is produced in situ. To assess the effect of the leaving group, X, on the polymerization efficacy of the system, a number of [(η^3-allyl)Pd(X)(P(*o*-tolyl)$_3$] procatalysts, where X = chloride, acetate, nitrate, trifluoroacetate, and triflate, were synthesized and investigated. The catalysts were generated in situ by reaction with Li[B(C$_6$F$_5$)$_4$]·2.5Et$_2$O in the presence of a 95:5 molar ratio of 5-butylnorbornene and 5-triethoxysilylnorbornene. The results of these copolymerizations are presented in Table 4.

The trifluoroacetate and triflate systems were run in triplicate and yielded 100% conversion in each case. The chloride, nitrate, and acetate systems gave between 70 and 84% conversion. It is clear from the data that trifluoroacetate and triflate form more active catalysts

Table 5. Effect of Phosphines on the Polymerization of 5-Butylnorbornene:5-Triethoxynorbornene (95:5) Using $[(\eta^3\text{-allyl})Pd(Cl)]_2$ and $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$[a]

run	PR_3	ν_{CO}, cm^{-1}	cone angle, deg	convn, %	M_w ($\times 10^{-3}$)	M_w/M_n
1	$P(t\text{-}Bu)_3$	2056	182	93	623	3.39
2	$P(i\text{-}Pr)_3$	2059	160	92	1526	2.38
3	PBu_3	2060	132	84	1507	2.98
4	$P(o\text{-tolyl})_3$	2066	194	69	249	3.91
5	PBz_3	2066	165	95	731	2.59
6	PPh_3	2069	145	94	682	2.98
7	$P(C_6F_5)_3$	2091	184	100	337	2.42

[a] Polymerizations were run in toluene for 4 h at 65 °C, [monomers] = 2.0 M, [Pd] = 0.042 mM, [Li] = 0.20 mM.

than chloride, nitrate, and acetate. This trend may be understood in light of the relative solvolysis rates of the leaving groups. Triflate anion undergoes solvolysis at a much faster rate than chloride, nitrate, and acetate.[16] Undoubtedly this is due to the electron-withdrawing power of the trifluoromethyl substituent, which makes the triflate anion inert and of low nucleophilicity. Similar arguments can be made for trifluoroacetate. Within the context of the proposed mechanism of catalyst generation, it is expected that more labile leaving groups would facilitate the formation of the active catalyst.

While the nature of the leaving group does influence the conversion of monomer to polymer, it does not seem to dramatically affect the molecular weight of the copolymer. The average value obtained for the M_w of polymer created by the triflate and trifluoroacetate leaving group-containing catalyst systems are essentially the same: 208 000 and 205 000, respectively. Both the chloride and the nitrate yield copolymers with slighty lower molecular weights, while the acetate is somewhat higher. Compared to phosphines, the effect of the leaving group on molecular weight is insignificant (see below).

Effect of Phosphine on the Polymerization of Norbornene-Type Monomers. One of the most, if not the most, important classes of ligands used in homogeneous catalysis is phosphines. According to Crabtree, "...tertiary phosphines (PR_3) are important because they constitute one of the few series of ligands in which electronic and steric properties can be altered in a systematic and predictable way over a wide range by varying R."[17] The steric and electronic properties of phosphines have been collated by Tolman[18] and serve as a basis for understanding the effect of phosphines on chemical reactions. Since phosphine seemed to be a necessary constituent for the present high activity catalysts, we aimed to understand the effect of the steric and electronic properties of the phosphine on norbornene-type monomer polymerization.

To facilitate the study of a variety of phosphines, the simplest in situ approach to accessing the catalyst was chosen: addition of the phosphine to $[(\eta^3\text{-allyl})Pd(Cl)]_2$ followed by addition of this mixture to monomer in the presence of $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$. The results of this study are given in Table 5.

All the experiments in Table 5 were carried out on a 5 g scale. Good to high conversion ranging from about 70% to 100% was obtained. There was a spread of weight-average molecular weights, depending on the phosphine ligand used, ranging from very high (>1.5 million) to significantly lower (around 250 000). The molecular weight distributions are monomodal although they tend to be broad in some cases. The molecular weight results are presented in Figure 2 as a function of phosphine donor ability (as measured by the electronic parameter, ν_{CO}) and steric properties (as measured by cone angle, θ) as defined by Tolman.

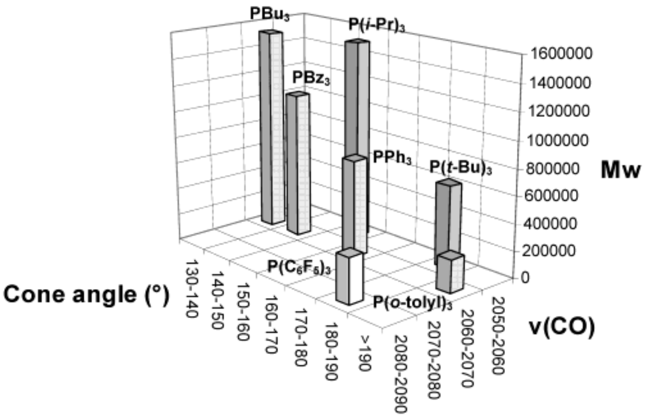


Figure 2. Effect of phosphine electronic and steric factors on copolymer M_w.

Although not all the possible combinations of cone angle and donor strength have been studied, a general trend emerges from the data collected thus far: *phosphines that are bulkier, i.e., have larger cone angles, yield lower molecular weights.* One of the more promising phosphine studied was $P(o\text{-tolyl})_3$ in that lower molecular weight polymers were accessible with good conversion. This catalyst was used in our study of the olefinic chain transfer agent, hexene-1 (see below).

NMR Characterization of Polymers. The polymers synthesized using the palladium catalysts described herein are of the vinyl addition poly(norbornene) variety. All polymers investigated contained no evidence of vinylidene resonances consistent with the absence of ROMP-type poly(norbornene).

Copolymer compositions for the 5-butylnorbornene: 5-triethoxysilylnorbornene 95:5 feed ratio copolymerizations could readily be determined by ^1H NMR analysis. The methylene protons of the 5-triethoxysilylnorbornene monomer (i.e., $-Si(OCH_2CH_3)_3$) resonate sufficiently upfield (~ 3.7 ppm) from the aliphatic region of the spectrum (~3.0 to 0.7 ppm) such that the incorporated 5-triethoxysilylnorbornene can be determined using the normalized integration intensity of these resonances relative to the aliphatic region. The comonomer composition was determined for two copolymers synthesized at 70% and 100% conversion (see experiments 1 and 4 in Table 4). The composition for the 100% conversion copolymer of course mimics that of the monomer feed ratio (95:5). However, the copolymer prepared at 70% conversion gave a 92:8 ratio of 5-butylnorbornene:5-triethoxysilylnorbornene. This suggests that the silyl functional monomer is incorporated into the copolymer preferentially over the butylnorbornene. Further reactivity ratio studies are needed in order to confirm and quantitate this hypothesis.

Effect of α-Olefin Chain Transfer Agents on Molecular Weight. We have learned from our previous work that $[(\eta^3\text{-allyl})Ni(1,5\text{-cyclooctadiene})]^+$ responds very well to olefinic chain transfer agents such as ethylene or hexene-1.[4] Molecular weights of poly(norbornene) are cut dramatically. However, by the same token, it has been recognized that the corresponding palladium complex, while giving lower molecular weight copolymer upon addition of α-olefins, is much less

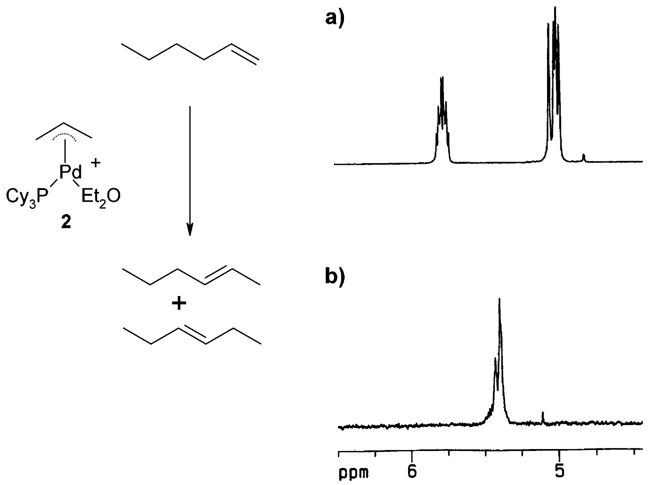


Figure 3. ^{1}H NMR spectrum of the olefinic region of hexene-1 before (a) and after addition of **2** (b).

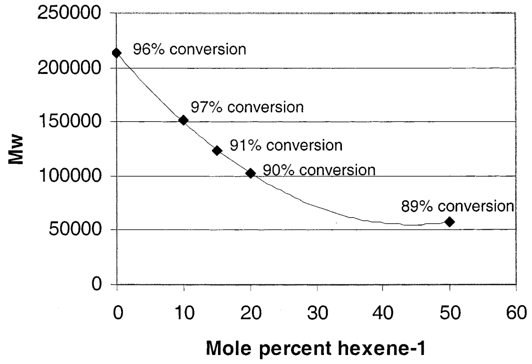


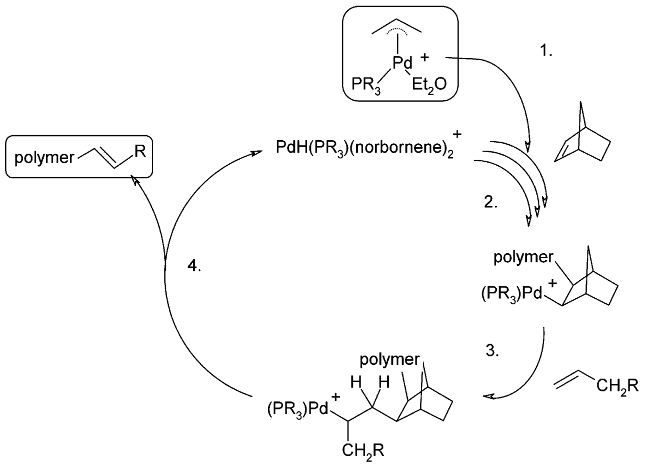
Figure 4. Effect of hexene-1 on 5-butylnorbornene:5-triethoxysilylnorbornene copolymer molecular weight using (η^3-allyl)Pd(trifluoroacetate)(P(*o*-tolyl)$_3$) and Li[B(C_6F_5)$_4$]·2.5Et$_2$O.

responsive to these chain transfer agents. The availability of a stable, isolable single component catalyst, namely **2**, allowed us to test for the salient feature of chain transfer: β-hydrogen elimination.

Complex **2** was reacted with an excess of hexene-1. Within 30 min, a ^{1}H NMR spectrum of the mixture was recorded. The results of this experiment are presented in Figure 3. It is apparent from these spectra that hexene-1 was isomerized to internal olefins as a consequence of rapid insertion and β-hydrogen elimination. This result is consistent with the intermediacy of a cationic palladium hydride species in this catalytic transformation. This result also suggested that hexene-1 would be an effective chain transfer agent for norbornene polymerization.

To test this hypothesis, copolymerizations of 5-butylnorbornene:5-triethoxysilylnorbornene (95:5) were carried out on a 0.5 L scale with increasing amounts of hexene-1 using the (allyl)palladium(tri-*o*-tolylphosphine)(trifluoroacetate)/Li[B(C_6F_5)$_4$]·2.5Et$_2$O system. The conversion and M_w results for the copolymerizations are presented in Figure 4 as a function of hexene-1 mole % concentration. The M_w of the copolymer drops from ca. 210 000 to about 55 000 as the hexene-1 concentration is increased. In all cases, conversions of 89% or greater are observed. These results are in contrast to the 2-propanol molecular weight modifier used for the multicomponent system, Pd(Me)(Cl)(1,5-COD), PPh$_3$, and NaB(3,5-(CF_3)$_2$$C_6H_3$)$_4$. In this system, while the molecular weight is reduced with increasing amounts of 2-propanol, the yield is also decreased.[6]

Scheme 1



Polymerization Mechanism. With the new, high activity catalysts, hexene-1 acts as a chain transfer agent as was found in the case of [(η^3-allyl)Ni(1,5-cyclooctadiene)]$^+$. By direct analogy, one can propose a mechanism for polymerization and chain transfer (see Scheme 1). The polymerization is initiated by insertion of the norbornene-type monomer into the palladium-allyl bond (step 1). Propagation occurs by repeating this insertion step with the resulting palladium-norbornyl complex (step 2). Insertion of the α-olefin followed by subsequent β-hydrogen elimination yields the olefin-terminated polynorbornene chain and the palladium hydride cation, [PdH(PR$_3$)(norbornene)$_2$]$^+$ as the proposed active species (steps 3 and 4). Given the amounts of hexene-1 required to decrease the molecular weights compared to, for example, [(η^3-allyl)Ni(1,5-cyclooctadiene)]$^+$, it is apparent that the present palladium system is less susceptible to chain transfer than these prior catalysts.[19]

Confirmation of the chain transfer mechanism comes from end group analysis of a low molecular weight homopolymer of norbornene made in hexene-1 using (η^3-allyl)palladium(tricyclohexylphosphine)(triflate) (**8**) and Li[B(C_6F_5)$_4$]·2.5Et$_2$O. ^{1}H NMR analysis of the polymer provided evidence for olefinic end groups; a broad multiplet was observed centered at about 5.3 ppm essentially identical to what is observed in Figure 3 for hexene-1 isomerization. This signal is consistent with internal olefinic protons of a hexene end group appended to the polymer chain that comes from the insertion of hexene-1 into and termination of the growing polymer chain.

Thermomechanical Properties of Palladium-Based Copolymer. The ability to control copolymer molecular weight with a combination of phosphine and chain transfer agent allowed us to explore the effect of molecular weight on copolymer thermomechanical properties. Information of this type is critical for determining the entanglement molecular weight for this new class of materials.

Copolymers 5-butylnorbornene and 5-triethoxysilylnorbornene (95:5 molar ratio) of varying molecular weights were subjected to tensile and dynamic mechanical analysis (DMA) measurements after films of the copolymer were cast from solution and cured using a bis(aryl azide) cross-linking additive: 2,6-bis[4-azidophenyl]methylene-4-ethylcyclohexanone.[20] During thermal treatment, the azide moieties decompose to form extremely reactive nitrenes which can insert into C−H

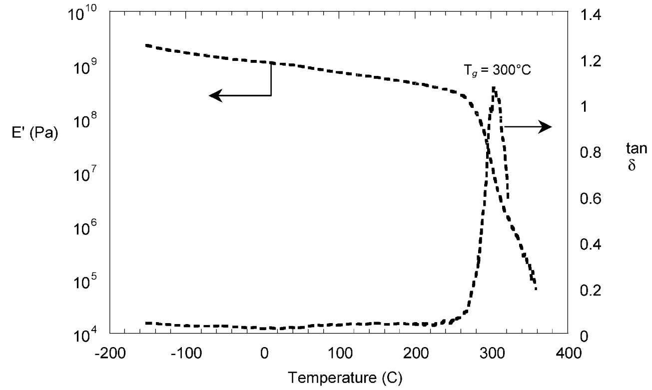


Figure 5. Comparison of DMA curves for Pd-based 95:5 5-butylnorbornene:5-triethoxysilylnorbornene copolymer films after cross-linking with bis(aryl azide).

Table 6. Effect of Molecular Weight on Elongation at Break, Tensile Modulus, and T_g for a 95:5 5-Butylnorbornene:5-Triethoxysilylnorbornene Copolymer Cross-Linked with Bis(aryl azide)

expt	M_w ($\times 10^{-3}$)	M_w/M_n	elongation at break,%	tensile modulus, psi	T_g(DMA), °C
1	160	2.66	18 ± 2.7	124 000	290
2	139	2.92	16.4 ± 2.5	121 000	300
3	128	3.12	10.3 ± 1.0	135 000	304
4	117	3.00	12.9 ± 1.1	126 000	300
5	102	2.98	6.1 ± 2.4	123 000	308

bonds forming cross-link sites in the polymer matrix. The results are given in Table 6.

From Table 6, it is evident that as the molecular weight falls, the elongation at break decreases while the modulus remains about the same. On the basis of these data, the lowest M_w acceptable, i.e., that does not sacrifice elongation, is about 139 000.

The T_g (based on DMA) of this polymer composition made with palladium catalysts described herein hovers around 300 °C. The DMA curve for the palladium-based copolymer is given in Figure 5. Interestingly, others have noted that the T_g for palladium-based homopolynorbornene is rather low (220 °C).[21] The reason for this difference is unclear, especially since the glass transition temperature for the native norbornene polymer would be expected to be higher than the 5-alkyl-substituted norbornene polymers.

Norbornene-Type Monomer Polymerization in Aqueous Media. According to Odian,[22] there are several advantages to running polymerizations in aqueous suspension or emulsion. Water is an environmentally acceptable diluent. The molecular weight of the polymer can often be regulated by the size of the monomer droplets/polymer particle. Heat transfer can be efficiently managed. Particle morphology/size can be controlled by the agitation and by the amount and type of surfactant employed. Very high solids of the resulting polymer can be made in aqueous suspension or emulsion without a concomitant increase in viscosity of the medium.

The discovery of very highly active palladium catalysts stabilized by phosphine ligands described herein has allowed us to explore the possibility of polymerization of norbornene-type monomers in alternative solvents/diluents given the tolerance of Pd toward functionality.

The first indication that the present high activity palladium catalyst system would work in the presence of water was evident when about 1000 ppm of water was added to a 5-butylnorbornene:5-triethoxysilylnorbornene copolymerization (95:5) with no deleterious effect on the yield when compared to an experiment run in dry toluene. Given the success of this experiment, several more experiments were conducted in water diluent in the absence and presence of ionic surfactants. These experiments are listed in Table 7 (where the catalyst system used was $[(\eta^3\text{-allyl})Pd(Cl)]_2$, PCy_3, $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$, and sodium lauryl sulfate or SLS).

Without added surfactant, good yields of a suspension or "bead" type homopolymer of 5-butylnorbornene can be obtained even at a monomer-to-Pd ratio of 50 000 to 1 (see experiment 1, Table 7). Addition of SLS does produce emulsion-type polymer, along with the "bead" type which is an indication that the emulsion polymer is not stable under these conditions. When more SLS is added in an attempt to rectify this, the conversions go down (runs 2−4). Photomicrographs of the polymer produced in aqueous suspension are presented in Figure 6. Two types of beads are observed: those with 30−50 μm diameters (more typical of suspension-type polymers) and those less than about 5 μm in size (more typical of emulsion-type polymers).

We have also examined the effect of a water-soluble phosphine ligand (the sodium salt of *m*-sulfonated triphenylphosphine) on the polymerization of 5-butylnorbornene in water. At a 50 000:1:5 ratio of monomer to palladium to $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$, an 89% yield of 5-butylnorbornene homopolymer was obtained as suspension "beads" in the presence of 0.5 wt % SLS. The M_w of this polymer was 1.03 million and the M_n was 384 000.

A patent[23] describes the suspension polymerization of norbornene using a cyclooctadienylpalladium chloride complex. In this disclosure, rather low yields (22%) of polymer are obtained at high (ca. 265:1 monomer to Pd molar ratio) catalyst loadings. Rinehart,[24] while describing the polymerization of norbornene using an allylpalladium chloride dimer as making a vinyl-type polymer, does not give any experimental details. The oligomerization of norbornene using $PdCl_2$ in aqueous media also has been studied.[25]

Concluding Remarks. In this contribution, we have described the development of high activity cationic (η^3-allyl)palladium catalysts for norbornene-type monomer

Table 7. Polymerization of 5-Butylnorbornene in Aqueous Media Using $[(\eta^3\text{-allyl})Pd(Cl)]_2$, PR_3, $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$, and Sodium Lauryl Sulfate (SLS)[a]

run	time, h	temp, °C	convn, %	PR_3	comments
1	4	65	90	PCy_3	toluene, 0.5 mL; water, 50 mL
2	4	25	42	PCy_3	0.5 wt % SLS; toluene, 0.5 mL; water, 100 mL
3	4	25	20	PCy_3	1.0 wt % SLS; toluene, 0.5 mL; water, 50 mL
4	4	65	66	PCy_3	1.0 wt % SLS; toluene, 0.5 mL; water, 100 mL
5	4	65	89	$P(m\text{-}C_6H_4SO_3Na)_3$	0.5 wt % SLS; water, 50 mL

[a] Molar ratio of 5-butylnorbornene:Pd:PCy_3:$Li[B(C_6F_5)_4]\cdot 2.5Et_2O$ = 50 000:1:1:5. Yields were obtained by precipitation into methanol, filtering, and drying.

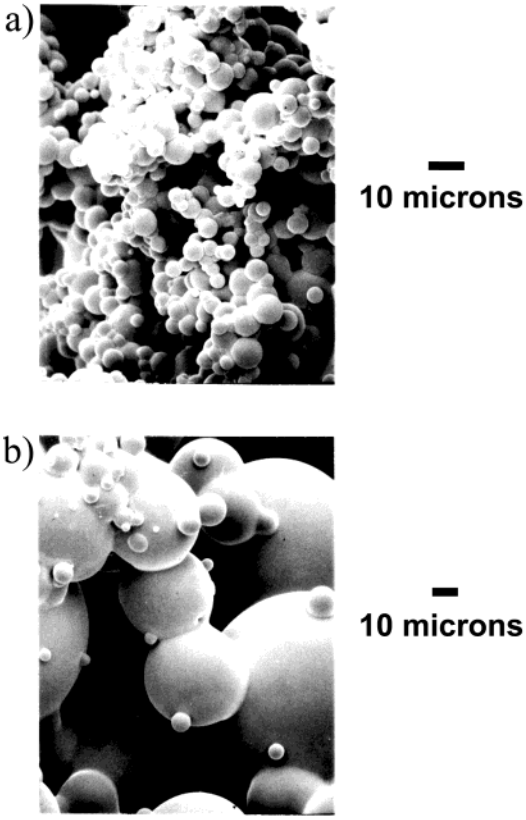


Figure 6. SEM photomicrographs of polymer beads produced in an aqueous polymerization of 5-butylnorbornene, both (a) small and (b) large "beads".

polymerization. Necessary attributes for high activity include coordination of a phosphine to a cationic palladium center and the presence of a weakly coordinating anion. These catalysts can be generated in situ by abstraction of leaving groups such as chloride, acetate, nitrate, triflate, and trifluoroacetate from palladium using a salt of a weakly coordinating anion. The steric properties of the phosphine employed in the catalyst system directly impacts the molecular weight of the polymer formed; the bulkier the phosphine, the lower the molecular weight. The molecular weight can be further tuned by addition of α-olefins such as hexene-1. These types of catalysts exhibit high polymerization activity even in water forming suspension or emulsion-type norbornene polymers.

Applicability of the catalysts of the type described herein is not limited to polymerization of norbornene-type monomers. Widenhoefer has reported that they catalyze the cycloisomerization of diethyl diallylmalonate in the presence of triethylsilane to form 4,4-dicarboethoxy-1,2-dimethylcyclopentene in high yield and high isomeric purity. The catalyst systems were operative in the presence of a variety of functionalities.[26]

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(2) Present address: Rohm and Haas Company, 727 Norristown Road, P.O. Box 904, Spring House, PA.
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