Novel, Efficient, Palladium-Based System for the Polymerization of Norbornene Derivatives: Scope and Mechanism

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[(1,5-Cyclooctadiene)(CH_3)Pd(Cl)], when reacted in situ with 1 equiv of a monodentate phosphine ligand and 1 equiv of the complex $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ was found to catalyze the vinyl addition polymerization of norbornene derivatives, including those with pendant oxygen functionalities. For norbornene, a polymerization rate of 1000 tons norbornene/mol Pd·h was observed at 25 °C. For several norbornene derivatives, the molecular weight of the polymer was found to decrease with increasing amounts of added 2-propanol. Mechanistic data confirm a vinyl insertion mechanism for these polymerizations. The polymerization rate was found to decrease dramatically for norbornene derivatives with pendant oxygen functionalities. The effect of coordinating solvents and the uptake of *endo* vs *exo* isomers for functionalized norbornenes was tested. Experiments show that (a) the *endo* isomer reacts more slowly than the *exo* isomer and (b) both isomers react much more slowly compared to norbornene derivatives lacking coordinating functionalities. Reaction of 5-norbornene carboxylic acid ethyl ester with the $[(Et_3P)_2Pt(H)]^+$ fragment yields the *endo*-inserted product exhibiting intramolecular coordination of the ester functionality to the platinum center. The formation of chelates, both upon the coordination of the *endo*-fuctionalized nobornene and in the *endo*-inserted product, appears to be responsible, in part, for the observed decrease in polymerization rate for functional norbornene derivates. A further reason for the diminution of activity of *both* the *endo*- and the *exo*-functionalized isomers is simply the coordination of the functionality. Of the two factors, the latter is the dominant one.

Introduction

Poly(norbornene)s are of considerable interest because of their unique physical properties, such as high glass transition temperature, optical transparency, and low birefringence. Norbornene is known to polymerize by several mechanisms (Figure 1). Ring-opening metathesis polymerization (ROMP) yields poly(1,3-cyclopentylenevinylene), which retains one double bond in each polymeric repeat unit.[1] Cationic polymerization involves rearrangement of the norbornene framework and generally produces moderate yields of poly(2,7-bicyclo[2.2.1]-hept-2-ene) oligomer.[2] Vinyl addition polymerization of the monomer produces poly(2,3-bicyclo[2.2.1]hept-2-ene), a saturated polymer.[1g,2a,3]

One current focus of research is the vinyl addition polymerization of norbornene derivatives with pendant functionalities. The resultant polymers are important because of the novel combination of properties they permit. Furthermore, certain functionalities allow for postpolymerization modification, thus providing an entry into other kinds of polymeric materials. Transition metal-catalyzed addition polymerization of functional norbornenes, particularly those containing oxygen functionalities, has proved to be difficult. This is especially true for the *endo*-functionalized norbornenes, which

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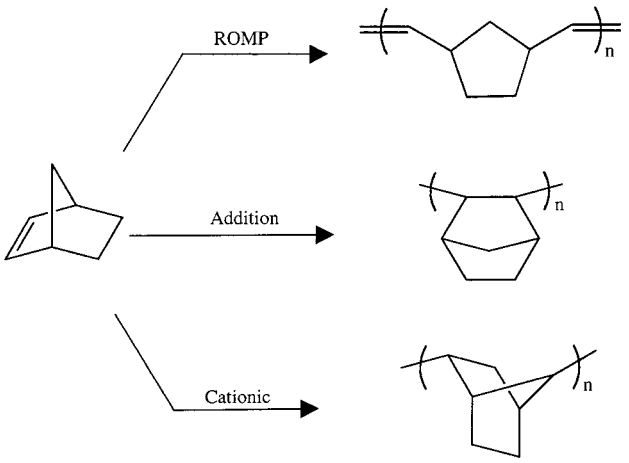

Figure 1. Polymerization mechanisms for norbornene.

constitute the vast majority of available functional norbornenes.[3f,h,l,q] It has been presumed that this is due to catalyst inhibition by coordination of the functionality to the metal center. A related issue is the stereochemistry of the alkene insertion step in the metal-catalyzed norbornene polymerizations. While published studies on the insertion of norbornene into metal−carbon bonds indicate an *exo*, *exo* insertion stereochemistry,[4] the possibility exists for an *endo*, *endo* insertion stereochemistry if the metal is coordinated to the functional group in an *endo*-functionalized norbornene.

Following our initial work on the addition polymerization of norbornene by $[Pd(CH_3CN)_4](BF_4)_2$,[3b,c] there have been several reports on palladium(II)- and related nickel(II)-catalyzed polymerizations of norbornene.[1g,3d−r] Herein, we report a ligand-deficient, cationic, palladium(II)-based system for the addition polymerization of a wide variety of norbornene derivatives under mild conditions. To our knowledge, this system displays the highest rate of polymerization for norbornene reported thus far (1000 tons norbornene/mol Pd·h at 25 °C). Additionally, we delineate for the first time the relative preference for the incorporation of the *exo* versus *endo* isomer in a norbornene polymerization process. Finally, using a model platinum-based system, we demonstrate the *endo*, *endo* insertion of an *endo*-functionalized norbornene ester derivative into a metal−hydride bond in tandem with intramolecular coordination of the ester moiety to the metal center. The isolation of this species has bearing on the polymerization rate depression observed for ester-functional norbornenes.

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Experimental Section

General Procedures and Materials. All work involving air and moisture sensitive compounds was carried out using standard Schlenk or drybox techniques (dinitrogen atmosphere). NMR analyses of polymers were performed on a Brüker DPX 300 NMR spectrometer at ambient temperature, using $CDCl_3$ as solvent unless otherwise noted. Other NMR data [^1H, $^{31}P\{^1H\}$, and ^{13}C] were obtained on a Brüker AMX 500 NMR spectrometer operating at 500.14, 202.47, and 125.77 MHz, respectively. ^{31}P NMR was referenced to external 85% H_3PO_4. Size exclusion chromatography data were obtained on a Waters SEC System using a three-column bank (Styragel 7.8 × 300 mm columns, 100−5000 D, 500−30 000 D, 2000−4 000 000 D), a Waters 410 differential refractometer, and a Waters 600 HPLC pump/controller. Size exclusion chromatography was performed in chloroform at ambient temperature and calibrated to poly(styrene) standards. Thermal gravimetric analysis data were obtained on a Universal V1.13A TA instrument in dinitrogen with a 10 °C/min ramp rate to 800 °C.

The *exo* and *endo* isomers of norbornenes were separated and quantified by gas chromatography. GC data were obtained on a Varian Model 3700 instrument fitted with a Waters DB-5 capillary column and an FID detector. GC was carried out with a ramp rate of 10°/min, from a beginning temperature of 35 °C to a final temperature of 300 °C. Baseline separation of *endo* and *exo* isomers of functionalized norbornenes was evident by GC. Note that control experiments confirmed that no isomerization occurred in the GC. The percentage of each unreacted isomer during the course of a polymerization reaction was determined mathematically. From these data, the relative uptake of the two isomers in the polymerization reaction was assessed. These reactions were relatively large scale (25 g of monomer and 50 mL of solvent) with approximately 1% chlorobenzene used as an internal standard.

Mass spectra were recorded on a Finnegan MAT 95Q mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 1800 spectrometer using polystyrene film as a standard. Samples were prepared on diamond cells in the drybox.

Dichloromethane was obtained from Aldrich and dried over CaH_2, distilled and degassed, and stored over molecular sieves in the glovebox prior to use. 2-Propanol was dried similarly and stored under a dinitrogen atmosphere. PPh_3 was obtained from Aldrich and used without further purification. Norbornene was obtained from ICN Pharmaceuticals. Bicyclo-[2,2,1]hepta-2,5-diene (98%, inhibited), dicyclopentadiene, 5-ethylidene-2-norbornene (99%), 5-vinyl-2-norbornene (95%, mixture of *endo* and *exo*), and *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride were obtained from Aldrich. 5-Triethoxysilyl-2-norbornene was obtained from Gelest. 5-Norbornenecarboxylic acid ethyl ester (73% *endo*, 27% *exo*), 5-norbornenecarboxylic acid *tert*-butyl ester (64% *endo*, 36% *exo*), and butylnorbornene (81% *endo*, 19% *exo*) were provided by BF Goodrich. All monomers were degassed with prepurified nitrogen prior to use.

Table 1. Crystallographic Data for $[Pt(C_7H_{10}C(O)OEt)(PEt_3)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (1)

formula: $C_{54}H_{57}BF_{24}O_2P_2Pt$	Z (molecules/cell) = 2
color of crystal: colorless	volume = 3145.26 Å^3
crystal dimens: 0.05 × 0.26 × 0.40 mm	calcd density = 1.544 g/cm^3
space group: $P\bar{1}$	wavelength = 0.71069
a = 13.274(2)	molecular weight = 1461.85
b = 19.020(2)	temperature = −71 °C
c = 13.074(2)	$R(F)$ = 0.0623
β = 104.72(1)	$R_w(F_o)$ = 0.0449

[(1,5-Cyclooctadiene)Pd(CH_3)(Cl)] (1,5-cyclooctadiene = 1,5-COD) was prepared as previously reported[5] and stored under vacuum prior to use. $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ was prepared according to the literature method published by Brookhart et al.[6] or purchased from Boulder Scientific. Wilkinson's catalyst, $RhCl[P(C_6H_5)_3]_3$, was obtained from Johnson Matthey.

Homopolymerization of Norbornene. In an inert (N_2) atmosphere, 0.001 g (3.02 × 10^{-7} mol) of [(1,5-COD)Pd(CH_3)(Cl)], 1 equiv of PPh_3, and 1 equiv of $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ were placed into a small vial. To this was added approximately 5 mL of dichloromethane, and the mixture gently shaken to dissolve the solids. A 100 μL portion of this stock solution was then added to 10 g (0.106 mol) of norbornene dissolved in approximately 5 mL of dichloromethane in a 100 mL GC vial containing a stir bar. The solution was placed on a magnetic stir plate and stirred rapidly for about 3 min, after which time polymerization was complete (i.e., a solid mass of polymer formed in the reaction vessel). The product was washed in methanol and dried in vacuo. The resultant polymer was found to be insoluble in all common laboratory solvents. TGA: 5% mass loss at 403 °C, 10% at 422 °C.

Homopolymerization of Dicyclopentadiene. In an inert (N_2) atmosphere, 0.003 g (1.13 × 10^{-5} mol) of [(1,5-COD)Pd(CH_3)(Cl)], 1 equiv of PPh_3, and 1 equiv of $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ were placed into a 100 mL GC vial. To this was added approximately 5 mL of dichloromethane, and the mixture gently shaken to dissolve the catalyst. Dry, degassed dicyclopentadiene (0.106 mol) was added to the solution, and the mixture was stirred rapidly. The polymerization was complete within approximately 5 min. The product was washed with methanol and dried in vacuo. The resultant polymer was found to be insoluble in all common laboratory solvents.

Homopolymerizations of 5-Ethylidene-2-norbornene, 5-Vinyl-2-norbornene, and 5-Methylene-2-norbornene. In an inert (N_2) atmosphere, [(1,5-COD)Pd(CH_3)(Cl)], 1 equiv of PPh_3, and 1 equiv of $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ were placed into a 100 mL GC vial containing a magnetic stir bar. To this was added approximately 5 mL of dichloromethane. Monomer was then added to the flask in the appropriate amount (see Table 3). The flask was sealed with a rubber septum and stirred. Polymer product was obtained by dissolving the resulting yellow solid in chloroform, then precipitating the polymer in acidified (3 M HCl) methanol to obtain a white solid.

Poly(5-ethylidene-2-norbornene): M_n(SEC) 21 600; M_w(SEC) 48 600; MWD 2.3. ^{1}H NMR ($CDCl_3$) (ppm): 5.33 (b, 1H, =C*H*CH$_3$), 1.53 (b, =CHC*H*$_3$), 0.72−3.09 (b).

Poly(5-vinyl-2-norbornene): M_n(SEC) 28 100; M_w(SEC) 40 100; MWD 1.4. ^{1}H NMR ($CDCl_3$) (ppm): 5.78 (b, 1H), 4.91 (b, 2H), 0.27−2.58 (b, 9H). TGA: 5% mass loss at 381 °C, 10% loss at 406 °C.

Poly(5-methylene-2-norbornene): M_n(SEC) 6400; M_w(SEC) 20 500; MWD 3.2. ^{1}H NMR ($CDCl_3$) (ppm): 4.76 (b, 2H), 0.61−3.09 (b, 8H).

Homopolymerization of 5-Triethoxysilyl-2-norbornene and 5-Norbornenecarboxylic Acid *tert*-Butyl and Ethyl Esters. In an inert (N_2) atmosphere, the appropriate amount of [(1,5-COD)Pd(CH_3)(Cl)] (see Table 3), 1 equiv of PPh_3, and 1 equiv of $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ were placed into a 100 mL GC vial. To this was added approximately 5 mL of dichloromethane and the mixture swirled to dissolve the catalyst. The appropriate monomer was then added to the solution. The flask was sealed with a rubber septum, taken out of the glovebox, and placed into a 46 °C (or 60° for the ester monomers) oil bath. After 22 h (or 24 h for the ester monomers), the product was obtained by precipitation in methanol.

Poly(bicycloheptenyltriethoxysilane): M_n(SEC) 8500; M_w(SEC) 12 700; MWD 1.5. ^{1}H NMR ($CDCl_3$) (ppm): 3.72 (b, 6H, Si(OC*H*$_2$CH$_3$)$_3$), 1.12 (b, Si(OCH$_2$C*H*$_3$)$_3$), 0.4−2.56 (b).

Poly(5-norbornenecarboxylic acid *tert*-butyl ester): M_n(SEC) 3500; M_w(SEC) 6400; MWD 1.8. ^{1}H NMR ($CDCl_3$) (ppm): 1.5 (s, b, −C(C*H*$_3$)$_3$), 0.8−3.5 (b).

Poly(5-norbornenecarboxylic acid ethyl ester): M_n(SEC) 4300; M_w(SEC) 6500; MWD 1.5. ^{1}H NMR ($CDCl_3$) (ppm): 4.3 (b, COOC*H*$_2$CH$_3$), 1.3 (b, COOCH$_2$C*H*$_3$), 1.0−3.1 (b).

Hydrogenation of Poly(5-vinyl-2-norbornene). In an inert (N_2) atmosphere, 0.337 g (2.81 × 10^{-3} mol monomer units) of poly(5-vinyl-2-norbornene), 0.052 g (5.6 × 10^{-5} mol) of $RhCl(PPh_3)_3$, and approximately 10 mL of dichloromethane were combined in an autoclave. The autoclave was charged to approximately 50 psi with hydrogen and stirred in a 50 °C oil bath for 70 h. Product was obtained in quantitative yield by precipitation in methanol. ^{1}H NMR ($CDCl_3$) (ppm): 0.93 (b, CH$_2$C*H*$_3$), 1.63 (b, C*H*$_2$CH$_3$), 0.09−2.68 (m, b).

Copolymerization of 5-Ethylidene-2-norbornene and 5-Triethoxysilyl-2-norbornene. In an inert (N_2) atmosphere, 0.020 g (7.6 × 10^{-5} mol) of [(1,5-COD)Pd(CH_3)(Cl)], 0.020 g (7.6 × 10^{-5} mol) of PPh_3, and 0.068 g (7.7 × 10^{-5} mol) of $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ were placed in a round-bottom flask. To this was added approximately 5 mL of dichloromethane and the mixture gently shaken to dissolve the solids. To this was added 8.39 × 10^{-3} mol of 5-ethylidene-2-norbornene and 1.81 × 10^{-3} mol of 5-triethoxysilyl-2-norbornene. The contents of the flask were stirred in the glovebox for approximately 5 min and then sealed with a rubber septum. The flask was removed from the glovebox and stirred in a 46 °C oil bath for 24 h. Product was obtained by precipitation in methanol and dried in vacuo to obtain 68% yield. Resultant polymer composition: 1 silyl norbornene:3.7 ethylidene norbornene. M_n(SEC) 8600; M_w(SEC) 12 300; MWD 1.4. ^{1}H NMR ($CDCl_3$) (ppm): 5.18 (b, C*H*CH$_3$), 3.75 (b, Si(OC*H*$_2$CH$_3$)$_3$), 1.12 (b, Si(OCH$_2$C*H*$_3$)$_3$), 1.42 (b, CHC*H*$_3$), 0.39−2.91 (b).

Table 2. Selected Bond Distances and Angles for 1

Bond Distances (Å)	
Pt(1)−P(2)	2.355(3)
Pt(1)−P(9)	2.211(3)
Pt(1)−O(16)	2.173(24)
Pt(1)−C(24)	2.083(12)
O(16)−C(17)	1.26(4)
C(17)−C(18)	1.46(3)
C(18)−C(19)	1.61(4)
C(18)−C(22)	1.89(3)
C(19)−C(20)	1.44(4)
C(2)−C(21)	1.58(4)
C(20)−C(23)	1.63(4)
C(21)−C(22)	1.61(3)
C(22)−C(24)	1.521(18)
C(23)−C(24)	1.543(27)
C(26)−C(27)	1.461(15)
O(25)−C(17)	1.394(25)
O(25)−C(26)	1.420(13)
Bond Angles (deg)	
P(2)−Pt(1)−P(9)	101.36(11)
P(2)−Pt(1)−O(16)	86.8(6)
P(9)−Pt(1)−C(24)	85.6(3)
O(16)−Pt(1)−C(24)	87.4(7)

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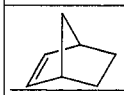
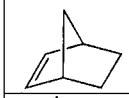
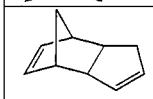
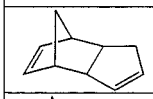
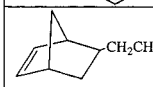
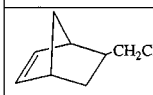
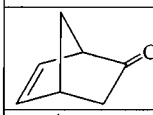
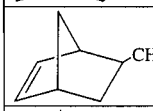
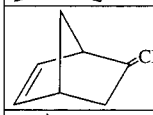
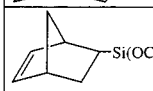
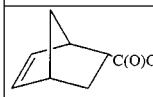
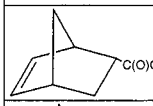
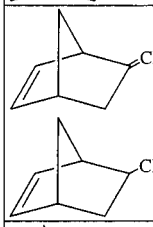
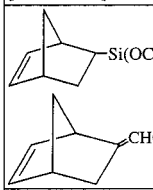
Table 3. Typical Polymerization Results[a]

Monomer	Catalyst (mol Pd), L	Monomer (mol)	Reaction Time	Temp. (°C)	Yield (%)	M_w[b]	Polydispersity (M_w/M_n)
	3.0×10^{-7}, PPh_3	0.106	<2 min	Ambient	~100	----	----
	7.6×10^{-5}, PPh_3, 1000 eq. $(CH_3)_2CHOH$	0.015	24h	46	23	4,000	1.2
	1.1×10^{-5}, PPh_3	0.106	<5 min	Ambient	~100	----	----
	7.6×10^{-5}, PPh_3, 1000 eq. $(CH_3)_2CHOH$	0.015	24h	46	25	4,200	1.1
	7.6×10^{-5}, PPh_3	0.053	~2 min	Ambient	~100	212,900	3.5
	3.8×10^{-5}, PCy_3	0.019	15 min	Ambient	~100	249,500	2.2
	7.6×10^{-5}, PPh_3	0.015	13h	Ambient	~100	48,600	2.3
	7.6×10^{-5}, PPh_3	0.015	13h	Ambient	95	40,100	1.4
	7.6×10^{-5}, PPh_3	0.020	45h	46	75	20,500	3.2
	7.6×10^{-5}, PPh_3	0.004	22h	46	88	12,700	1.5
	2.9×10^{-5}, PPh_3	0.012	24h	60	40	6500	1.5
	2.9×10^{-5}, PPh_3	0.010	24h	60	38	6400	1.8
	7.6×10^{-5}, PPh_3	8.33×10^{-3} mol vinyl NB, 8.32×10^{-3} mol ethylidene NB	24h	46	65	19,800	3.4
	7.6×10^{-5}, PPh_3	8.39×10^{-3} mol ethylidene NB, 1.81×10^{-3} mol silyl NB	24h	46	68	12,300	1.4

[a] Reactions were performed under N_2 atmosphere in ca. 5 mL of CH_2Cl_2, L = ancillary ligand (1 equiv), $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ (1 equiv). [b] Obtained relative to poly(styrene) standards in $CHCl_3$.

Copolymerization of 5-Ethylidene-2-norbornene and 5-Vinyl-2-norbornene. In an inert (N_2) atmosphere, 0.020 g (7.6×10^{-5} mol) of [(1,5-COD)Pd(CH_3)(Cl)], 0.020 g (7.6×10^{-5} mol) of PPh_3, and 0.068 g (7.7×10^{-5} mol) of $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ were placed in a round-bottom flask. To this was added approximately 5 mL of dichloromethane and the mixture gently shaken to dissolve the solids. To this was added 8.33×10^{-3} mol of 5-vinyl-2-norbornene and 8.32×10^{-3} mol of 5-ethylidene-2-norbornene. The contents of the flask were stirred in the glovebox for approximately 5 min and sealed with a rubber septum. The flask was removed from the glovebox and stirred in a 46 °C oil bath for approximately 24

h. Product was obtained by precipitation in methanol and dried in vacuo to obtain 65% yield. Resultant polymer composition: 1 (5-ethylidene-2-norbornene):0.9 (5-vinyl-2-norbornene). M_n-(SEC) 5800; M_w(SEC) 19 800; MWD 3.4. ^{1}H NMR ($CDCl_3$) (ppm): 5.69 (b, C*H*=CH_2), 5.27 (b, C*H*CH_3), 4.89 (b, CH=CH_2), 0.60−3.32 (b, 17H).

Polymerizations in the Presence of 2-Propanol. In the glovebox, appropriate quantities of [(1,5-COD)Pd(CH_3)(Cl)], PPh_3, and $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ were placed in a 25 mL round-bottom flask. The flask was then sealed with a rubber septum, taken out of the glovebox, and connected to a nitrogen bubbler. The monomer dissolved in approximately 5 mL of dry, degassed methylene chloride was injected into the flask. The flask was gently shaken, and then appropriate equivalents of dry, degassed 2-propanol were injected. The dinitrogen purge was removed and the reaction allowed to proceed.

Isomerization of *cis*-5-Norbornene-*endo*-2,3-dicarboxylic Anhydride. The isomerization is a modification of a published procedure.[7] *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (35.0 g, 0.213 mol) was weighed into a round-bottom flask and heated to 190 °C, melting the white solid material into a yellowish liquid. After 3 h at this temperature, the liquid was cooled to room temperature, solidifying the material into a yellowish solid. To this solid was then added 100 mL of toluene, and the mixture was slurried for 1 h. A yellowish solution with white insoluble material was formed. The slurry was then filtered through a porous glass frit. The resulting filtered solid was washed twice with toluene, filtered, and dried in vacuo (35 °C/0.01 Torr). A yield of 7.5 g (21%) of 91% pure *cis*-norbornene-*exo*-2,3-dicarboxylic anhydride was obtained, the remainder was due to the unreacted *endo* isomer. ^{1}H NMR ($CDCl_3$) (ppm): 6.34 (s, 2H), 3.45 (s, 2H), 3.01 (s, 2H), 1.67 (d, 1H), 1.45 (d, 1H).

Synthesis of *cis*-Norbornene-*exo*-2,3-dimethylester. *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (7.5 g, 0.046 mol) was dissolved in 30 mL of methanol in a round-bottom flask equipped with a reflux condenser. To this was added a solution of four drops of fuming sulfuric acid in 10 mL of methanol. The mixture was heated to reflux for 4 h. A yellowish solution resulted after cooling to room temperature. The methanol was then removed in vacuo on a rotary evaporator, giving a yellowish viscous liquid. This liquid was then dissolved in toluene and treated with 50 mL of 0.1 M NaOH solution in water. The aqueous layer was decanted, and the organic layer was washed three times with 100 mL of distilled water. The resulting light yellow solution was then treated with activated carbon, filtered, and stripped of toluene in vacuo; 1.0 g (10% yield) of *cis*-norbornene-*exo*-2,3-dimethylester was recovered, which was determined to be 91% pure, the remainder being the *endo* isomer. ^{1}H NMR ($CDCl_3$) (ppm): 6.21 (s, 2H), 3.65 (s, 6H), 3.10 (s, 2H), 2.62 (s, 2H), 2.11 (b d, 1H), 1.50 (b d, 1H).

Synthesis of *cis*-Norbornene-*endo*-2,3-dimethylester. *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (20.0 g, 0.122 mol) was dissolved in 100 mL of methanol in a round-bottom flask equipped with a reflux condenser. To this was added a solution of two drops of fuming sulfuric acid in 10 mL of methanol, and the mixture heated to reflux for 4 h. A yellowish-green solution resulted after cooling to room temperature. The methanol was then removed in vacuo on a rotary evaporator, giving an orange viscous liquid. This liquid was then dissolved in toluene and treated with 50 mL of 0.1 M NaOH. The aqueous layer was decanted, and the organic layer extracted two times with 100 mL of distilled water. The resulting light pink solution was then treated with activated carbon, filtered, and stripped of toluene in vacuo; 13 g (51% yield) of *cis*-norbornene-*endo*-2,3-dimethylester was recovered (>98% purity). ^{1}H NMR ($CDCl_3$) (ppm): 6.26 (s, 2H), 3.61 (s, 6H), 3.29 (s, 2H), 3.16 (s, 2H), 1.48 (d, 1H), 1.33 (d, 1H).

Polymerization of *cis*-Norbornene-*exo*-2,3-dimethylester. To a GC vial was added [(1,5-COD)Pd(CH_3)(Cl)] (0.020 g, 7.6×10^{-5} mol) and 0.020 g (1 equiv) of triphenylphosphine. The two were dissolved in approximately 5 mL of CH_2Cl_2, and then monomer (0.150 g, 7.2×10^{-4} mol) was added to the solution. The flask was briefly shaken, and then $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ (0.068 g, 7.7×10^{-5} mol) was added. The flask was sealed, taken out of the glovebox, and placed into a 60 °C oil bath for 24 h. The polymer was then precipitated with methanol, filtered, and dried under vacuum to afford 0.027 g of polymer product (18%).

Polymerization of *cis*-Norbornene-*endo*-2,3-dimethylester. To a GC vial was added [(1,5-COD)Pd(CH_3)(Cl)] (0.020 g, 7.6×10^{-5} mol) and 0.020 g (1 equiv) of triphenylphosphine. The two were dissolved in approximately 5 mL of CH_2Cl_2, and then monomer (0.150 g, 7.2×10^{-4} mol) was added to the solution. The flask was briefly shaken, and then $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ (0.068 g, 7.7×10^{-5} mol) was added. The flask was sealed, taken out of the glovebox, and placed into a 60 °C oil bath for 24 h. Addition of the dark yellow mixture to methanol resulted in no precipitation of polymer.

Synthesis of PtHCl(PEt_3)$_2$. This procedure is a modification of a published method.[8] To a mixture of $PtCl_2(PEt_3)_2$ (0.500 g, 1.00×10^{-3} mol) and $HNEt_3$ (5 mL) in MeOH (12 mL) was added $NaBH_4$ (0.040 g, 1.5×10^{-3} mol). The mixture was stirred for 1 h and the solvent removed in vacuo. The resulting solid was sublimed (75 °C at 10 mmHg). The sublimed solid was extracted with pentane. The extract was filtered through Celite filter aid and dried in vacuo to give a white solid. Yield: 0.43 g (93%). ^{1}H NMR (toluene-d_8, ppm): 1.63 (m, 12H), 1.00 (overlapping d of t, 18 H), −16.90 (t, J_{PH} = 15 Hz, J_{PtH} = 1265 Hz). ^{31}P NMR (toluene-d_8, ppm): 23.9 (s, J_{PtP} = 2734 Hz).

Purification of $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$. Commercially available $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ was dissolved in methylene chloride and filtered. The methylene chloride of the filtrate was allowed to evaporate over the course of several days. Large white crystals of the hydrate of $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ formed, which were covered with beige impurities. The crystals were washed with dry methylene chloride under inert atmosphere to remove the impurities. The crystals were dried in vacuo overnight at 90 °C and then ground with a mortar and pestle in the drybox. The nearly white powder was then dried further under vacuum at 90 °C for 70 h.

Synthesis of [PtH(η^2-$C_7H_9C(O)OEt$)(PEt_3)$_2$][B(3,5-$(CF_3)_2C_6H_3$)$_4$]. To a fluorobenzene (0.6 mL) solution of $PtHCl(PEt_3)_2$ (0.010 g, 2.1×10^{-5} mol) and $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ (0.020 g, 2.3×10^{-5} mol) was added ethyl ester of 5-norbornene carboxylic acid (20 μL). The solution became yellow-brown. The volatiles were removed in vacuo to give a yellow oil. ^{1}H NMR (CD_2Cl_2, ppm): −7.62 (t, J_{PH} = 11 Hz, J_{PtH} = 855 Hz, approximately 75% of the total, *endo* isomer), −7.63 (t, J_{PtH} = 835 Hz, approximately 25% of the total, *exo* isomer). ^{31}P NMR (CD_2Cl_2, ppm): 11.26 (s, J_{PtP} = 2368 Hz, approximately 75% of the total, *endo* isomer), 11.34 (s, J_{PtP} = 2364 Hz, approximately 25% of the total, *exo* isomer).

Synthesis of [PtH(η^2-C_7H_{10})(PEt_3)$_2$][B(3,5-$(CF_3)_2C_6H_3$)$_4$]. A reaction vessel was charged with $PtHCl(PEt_3)_2$ (0.010 g, 2×10^{-3} mol), $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ (0.020 g, 2.3×10^{-5} mol), norbornene (0.010 g, 1.1×10^{-4} mol), and fluorobenzene (0.6 mL) followed by vigorous shaking. A white precipitate and a yellow-brown solution resulted. After about 2 h, the volatiles were removed in vacuo. Spectroscopic characterization of the resulting white residue is consistent with the formation of [PtH(η^2-C_7H_{10})(PEt_3)$_2$][B(3,5-$(CF_3)_2C_6H_3$)$_4$]. ^{1}H NMR (CD_2Cl_2, ppm): 7.72 (s, 8H), 7.56 (s, 4H), 4.05 (t, 2H, J_{PH} = 5 Hz J_{PtH} = 45 Hz), 2.99 (s, 2H), 2.13 (b s, 6H), 1.67 (s, 2H), 1.60 (s, 1H), 1.30 (s, 1H), 1.18 (d, 2H), 1.07 (t, 9H), −7.90 (t, J_{PH} = 11.5 Hz, J_{PtH} = 853 Hz, 1H). ^{31}P NMR (CD_2Cl_2, ppm): 11.0 (s, J_{PtP} = 2390 Hz).

(7) Craig, D. *J. Am. Chem. Soc.* **1951**, *73*, 4889.

(8) Phillips, J. R.; Trogler, W. C. *Inorg. Synth.* **1992**, *29*, 189.

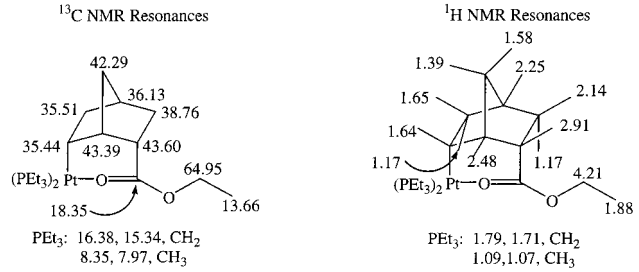


Figure 2. ^{1}H and ^{13}C NMR assignments for inserted ethyl ester of the 5-norbornene-2-carboxylic acid portion of the platinum complex **1**.

Synthesis of [Pt(C$_7$H$_{10}$C(O)OEt)(PEt$_3$)$_2$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (1). A Schlenk flask was charged with solid PtHCl-(PEt$_3$)$_2$ (0.235 g, 5.02×10^{-4} mol) and Na$^+$[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$B$^-$ (0.489 g, 5.51×10^{-4} mol). To this mixture was added norbornene carboxylic acid ethyl ester (0.835 g, 5.02×10^{-3} mol) and fluorobenzene (10 mL). The mixture was stirred at 45 °C for 48 h. A yellow solution resulted along with the precipitation of sodium chloride. The reaction mixture was filtered through Celite filtering aid. The remaining precipitate was washed with additional fluorobenzene (3 × 10 mL). The filtrate was concentrated to about 5 mL and subsequently layered with pentane (40 mL) to eventually give a white precipitate and a yellow oil after 2 days. The oil was decanted along with the solvent, and the solid was dried in vacuo. The solid was extracted with methylene chloride and filtered through Celite filtering aid. Volatiles were removed from the filtrate to give a yellowish oil. The oil was extracted a second time with methylene chloride, filtered through Celite filtering aid, and concentrated to about 1 mL volume. The solution was layered with pentane (25 mL) and allowed to stand at room temperature overnight to give a white solid. Yield: 0.30 g (40%). ^{31}P NMR ($CDCl_3$, ppm): 25.45 (d, $J_{PP} = 13$ Hz, $J_{PtP} = 1648$ Hz), 12.21 (d, $J_{PP} = 13$ Hz, $J_{PtP} = 5008$ Hz). IR (diamond cell): ν(CO) 1629 cm^{-1}. FD-MS: m/z 598 [M$^+$] exhibited expected isotope pattern for platinum.

Based on extensive 2-D NMR spectral characterization (see Supporting Information), the ^{1}H and ^{13}C NMR assignments can be made for the inserted ethyl ester of 5-norbornene-2-carboxylic acid portion of the platinum complex (Figure 2).

X-ray Structure Determination of [Pt(C$_7$H$_{10}$C(O)OEt)-(PEt$_3$)$_2$][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] (1). A sample of the compound was dissolved in methylene chloride, filtered through Celite, concentrated to about 1 mL, and layered with about 20 mL of toluene and stored at 0 °C. After 3−4 days, some thin, well-shaped crystals formed. Several of the platelike crystals were examined at −170 °C and found to have very broad and weak diffraction. It was finally discovered that the crystals underwent a phase transition. It was possible, however, to transfer a crystal to the goniostat at −71 °C without going through a phase transition.

After transferring the crystal to the goniostat at −71 °C, a systematic search of a limited hemisphere of reciprocal space was used to determine that the crystal possessed no symmetry or systematic absences corresponding to one of the triclinic space groups. Subsequent solution and refinement confirmed the centrosymmetric $P\bar{1}$. The data were collected using a standard moving crystal, moving detector technique 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 (MULTAN78) and Fourier techniques. During the initial refinement, the norbornyl group was badly distorted and exhibited excessive anisotropic thermal ellipsoids. After numerous attempts it was possible to resolve the disorder by modeling with two alternative conformations for the norbornyl group. These two conformations are shown in the Supporting Information. Hydrogen atoms were placed in fixed idealized positions, and they were included as isotropic contributors in the final cycles of refinement. A partial occupancy/disordered solvent is present in the cell at a center of inversion. The solvent could not be identified and was modeled as partial occupancy carbon atoms.

A final difference Fourier was featureless; the largest peaks, 1.12 e/A^3, were located at the metal site. Crystallographic data are presented in Table 1. Fractional coordinates, isotropic and anisotropic parameters, and a complete set of bond distances and angles are found in the Supporting Information. Selected bond distances and angles are given in Table 2. A complete set of distances and angles, atomic coordinates, and thermal parameters are given in the Supporting Information.

Results and Discussion

1. Catalyst. The catalyst was generated *in situ* by the addition of 1 equiv each of a monodentate phosphine (L) and Na$^+$[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$B$^-$ to a solution of [(1,5-cyclooctadiene)(CH$_3$)Pd(Cl)]. The addition of 1 equiv of the monodentate phosphine generates the known chloro-bridged dimer, [Pd(L)(CH$_3$)(Cl)]$_2$. This transformation can be followed by ^{1}H and ^{31}P NMR spectroscopy. For example, in the ^{1}H NMR spectrum, the methyl group on the palladium moves from a singlet at 1.12 ppm in [(1,5-cyclooctadiene)(CH$_3$)Pd(Cl)] to a broad singlet at 0.11 ppm upon the addition of 1 equiv of tricyclohexylphosphine, indicating the formation of [Pd(PCy$_3$)(CH$_3$)-(Cl)]$_2$. This is accompanied by the appearance of uncoordinated 1,5-COD peaks at 5.55 and 2.34 ppm. In the same vein, for [Pd(PPh$_3$)(CH$_3$)(Cl)]$_2$, the methyl on the palladium appears as a broad singlet at 0.63 ppm in the ^{1}H NMR spectrum and the phosphorus atoms exhibit a singlet at 40.0 ppm in the ^{31}P{^{1}H} NMR spectrum. Polymerizations are accomplished by the addition of 1 equiv of Na$^+$[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$B$^-$ to [Pd-(L)(CH$_3$)(Cl)]$_2$. This presumably generates the highly reactive (solvent/monomer-coordinated) cationic species [Pd(L)(CH$_3$)]$^+$[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$B$^-$, which is unstable in the absence of the monomer, forming metallic palladium with time.

2. Polymer Synthesis and Characterization. Table 3 shows typical polymerization results obtained. It is noteworthy that for norbornene, using a monomer-to-catalyst ratio of 351,000 to 1, quantitative conversion to polymer was observed within the time of mixing. To our knowledge, this makes the catalyst the fastest of those reported in the literature.[3] The molecular weight and polydispersity values were not obtained because of its insolubility in traditional SEC solvents. However, as shown in Table 3, the presence of a butyl substituent results in the formation of a soluble polymer.

Table 4 shows the effect of solvent on the polymerization of 5-ethylidene-2-norbornene. The common laboratory solvents methylene chloride, toluene, and chlorobenzene provide near quantitative yield of polymer, and there was no practical difference between them with regard to level of effectiveness. The small deviation from a quantitative yield was due to loss of product during workup. In the case where no solvent was employed and the catalyst components were added to the liquid monomer, the yield was significantly reduced. This, and the higher polydispersity value, can be explained by the

Table 4. Solvent Effect on the Addition Polymerization of 5-Ethylidene-2-norbornene[a]

	solvent			
	CH_2Cl_2	$C_6H_5CH_3$	C_6H_5Cl	none
yield (%)	95	91	91	42
molecular weight (M_w)	21 500	18 900	17 700	24 100
polydispersity (M_w/M_n)	1.45	1.37	2.42	6.26

[a] 8.42×10^{-3} mol of (1,5-COD)Pd(CH_3)(Cl), 1 equiv of $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$, 1 equiv of PPh_3, ~2 g of monomer, 48 °C, 19 h.

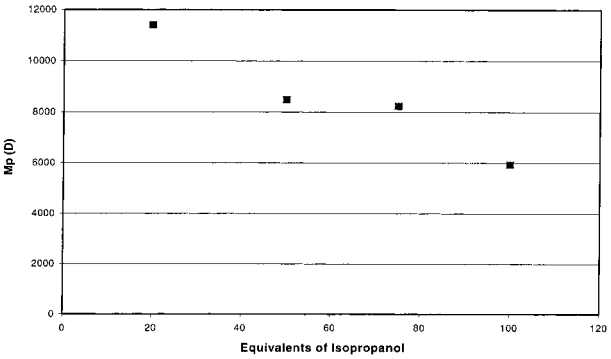


Figure 3. Molecular weight vs added 2-propanol for poly(2-*n*-butyl-5-norbornene).

greatly increased viscosity and concomitant reduced monomer diffusion rate even during the initial polymerization period.

An interesting procedure for the control of the molecular weight of poly(norbornene) derivatives involves the addition of an alcohol. For example, a soluble, lower molecular weight poly(norbornene) was formed when 1000 equiv of 2-propanol was added to the reaction mixture (Table 3). Presumably, chain termination through protic cleavage of the palladium−carbon bond occurs in the presence of alcohols. Figure 3 summarizes the results of a more systematic study on the monotonic decrease in the molecular weight of poly(5-butylnorbornene) with increasing amounts of added 2-propanol. Increasing the concentration of 2-propanol also gives lower conversion to polymer.

Thermogravimetric analysis was performed for poly(norbornene) and poly(vinylnorbornene). Thermograms obtained showed a single decomposition temperature with a steep mass−loss curve. The observed decomposition temperatures for both poly(norbornene) and poly(vinylnorbornene) exceeded 400 °C.

Copolymerizations were also successfully performed for 5-ethylidene-2-norbornene and 5-vinyl-2-norbornene, as well as 5-ethylidene-2-norbornene and 5-triethoxysilyl-2-norbornene. The copolymers were characterized by ^{1}H NMR spectroscopy and size exclusion chromatography. The ^{1}H NMR spectrum of the ethylidene/vinyl copolymer showed a broad olefinic signal at 4.4−6.2 ppm. The size exclusion chromatograph was unimodal, indicating the formation of a copolymer, as opposed to a mixture of two homopolymers. Likewise, the ^{1}H NMR spectrum of the 5-ethylidene-2-norbornene/5-triethoxysilyl-2-norbornene copolymer showed a broad vinylic signal at 5.0−5.4 ppm and a resonance at 3.6−3.8 ppm due to the methylene hydrogens of the silyl ether functionality. The size exclusion chromatograph of the copolymer was also unimodal.

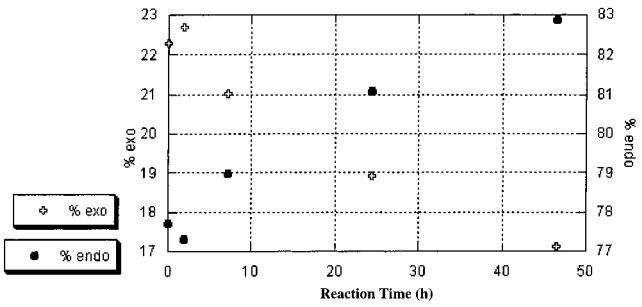


Figure 4. Plot of unreacted monomer vs time for the polymerization of 5-norbornene-2-carboxylic acid ethyl ester.

3. Polymer Modification. We have used [RhCl(PPh_3)$_3$] to hydrogenate poly(5-vinyl-2-norbornene). The ^{1}H NMR spectrum shows the clean disappearance of the vinyl signals at 4.7−5.1 and 5.5−6.0 ppm and the appearance of methyl and methylene signals at 0.93 and 1.63 ppm, respectively.

4. Polymerization Mechanism. The possibility that the polymerization proceeds through a mechanism other than coordination polymerization by vinyl addition was examined. Ring-opening metatheses polymerization can be excluded due to the absence of expected olefinic resonances in the ^{1}H NMR spectra of the polymers. Radical polymerization of norbornene is not known to yield high polymers. In any case, radical inhibitors were not removed from the monomers prior to polymerization. An ionic, especially cationic, polymerization mechanism has also been excluded. The addition of 1000 equiv of water, an ion trap, to the reaction mixture did not retard the polymerization of norbornene. The polymerization was also not retarded by the addition 5 equiv (per Pd) of the cationic inhibitor 2,6-di-*tert*-butylpyridine.

5. Reactivity of *exo* versus *endo* Isomer in Polymerization. The activity as well as the molecular weight of the polymer is drastically attenuated on moving from norbornene to its derivatives with pendant oxygen functionalities (Table 3). Based on the ^{13}C NMR shifts, one can surmise that the electronic effect of the substituent on the C=C bond is minimal. Thus, the vinyl carbons of the norbornene resonate at 135.5 ppm, while those of 5-norbornene-2-carboxylic acid ethyl ester appear at 137.7 and 132.5 ppm (*endo*) and 138.1 and 135.9 ppm (*exo*).

To ascertain whether the observed decrease in polymerization efficiency was due to the slower polymerization of the *endo* isomer of the functionalized norbornenes, a series of experiments was performed using known *exo*, *endo* mixtures of norbornene carboxylic acid esters. Figure 4 shows the uptake profile versus time for the polymerization of 5-norbornene-2-carboxylic acid ethyl ester starting with a monomer isomer ratio of 22% *exo* to 78% *endo*.

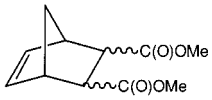
It is very clear that there is a preferential uptake of the *exo* isomer in the polymerization reaction. A similar observation was made when the polymerization of 5-norbornene-2-carboxylic acid *tert*-butyl ester was carried out (Table 5).

To further probe the higher reactivity of the *exo* isomer, the pure *exo* and *endo* isomers of 5-norbornene-2,3-dicarboxylic acid dimethyl ester were synthesized. The starting material, *endo*-5,6-norbornene dicarboxylic

Table 5. Reaction Time vs *exo*/*endo* Ratio in the Unreacted Monomer, NB−C(O)O^{t}Bu[a]

elapsed time (h)	% *exo*	% *endo*
0	36.3	63.7
1.75	32.2	67.8
5.83	29.5	70.5
18.58	27.2	72.8

[a] 3.78×10^{-4} mol of (1,5-COD)Pd(CH_3)(Cl), 1 equiv of PPh_3, 1 equiv of $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$, 25 mL of CH_2Cl_2, 50 °C, 10 g of monomer, 1/5 solution removed at each interval.



Exo isomer: 18% conversion Endo isomer: 0% conversion

Reaction conditions: 0.15 g (exo) or 1.00 g (endo) monomer; 7.56×10^{-5} mol (1,5-cyclooctadiene)Pd(CH_3)(Cl); 1 equiv. PPh_3; 1 equiv. $Na[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]$; 5 mL CH_2Cl_2; 60°C, 48 h.

Figure 5. Polymerization of the pure *exo* and *endo* isomers of 5-norbornene-2,3-dicarboxylic acid dimethyl ester.

acid anhydride (*endo*-nadic anhydride), is readily isomerized to the more thermodynamically stable *exo* isomer by thermolysis and crystallization. In a subsequent step both the *endo*- and *exo*-nadic anhydrides were ring-opened in methanol in the presence of a catalytic amount of sulfuric acid. In the case of the *endo* isomer greater than 98% pure material was obtained. The *exo* compound was 91% isomerically pure, the rest being the *endo* compound. Figure 5 shows the results for polymerizations of the pure isomers using the aforementioned catalyst. The catalyst shows a complete preference for the *exo* isomer over the *endo* for this monomer when only the pure isomer is present.

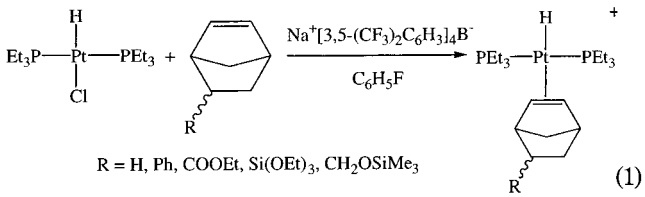
An interesting question involves the extent of conversion of the pure *exo* isomer of 5-norbornene-2,3-dicarboxylic acid dimethyl ester. If chelation of the double bond and oxygen functionality to the metal center is the most important reason for the attenuation of the polymerization activity, the *exo* isomer should be just as reactive as the parent, nonfunctionalized, norbornene. Clearly, the incomplete conversion of the *exo* isomer must be due to a second factor, presumably the coordination of the functionality to the metal center. To verify the possibility of the ester group of the monomer slowing down the polymerization through coordination, the polymerization of the parent norbornene was carried out in the presence of ethyl acetate (reaction conditions: 4 g norbornene, 7.56×10^{-5} mol of (1,5-cyclooctadiene)-Pd(CH_3)(Cl), 1 equiv of PPh_3, 1 equiv of $Na[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]$, 5 mL of ethyl acetate, 2 mL of chlorobenzene, 60 °C, 24 h). In very sharp contrast to the high polymerization rate in noncoordinating solvents (cf., Table 3), the presence of ethyl acetate led to only a 9% yield. Additionally, the polymer obtained had a significantly lower molecular weight and was soluble in chloroform (M_w = 157 000).

6. Synthesis of the Model System, *trans*-[$(Et_3P)_2$-Pt(H)(R−NB)]$^+$ (R−NB = 5-norbornene-2-R). One reason that the ester-functionalized norbornenes are so reluctant to polymerize may be due to the *endo* isomer, which typically represents 70−80% of the total isomer content. The *endo* isomer can easily chelate a metal center since both the norbornene double bond and the pendant ester functionality are readily accessible on the *endo* face of the norbornene. For the *exo* isomer the disposition of the pendant functionality is such that the norbornene double bond and ester cannot simultaneously bind to the metal, on either the *endo* or *exo* face of the norbornene.

Given the published studies that indicate that the insertion of nonfunctionalized norbornenes into metal−carbon bonds occurs with *exo, exo* stereochemistry,[4] we sought to determine whether the presence of an *endo* functionality would change the insertion stereochemistry.

Because of the relative instability of the catalytically active palladium species, detailed studies encompassing the coordination and insertion of norbornene derivatives were carried using the $[(Et_3P)_2Pt(H)]^+$ fragment. This species was produced in situ via chloride ion abstraction from *trans*-$[(Et_3P)_2Pt(H)(Cl)]$ with $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ in fluorobenzene. The formation of the cation is an equilibrium process; the fragment is present only in a small steady-state concentration and immediately reacts with added norbornene, which drives the reaction to completion.

When reacted with *trans*-$[(Et_3P)_2Pt(H)(Cl)$ and 1.05 equiv of $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$, substituted norbornenes formed *trans*-$[(Et_3P)_2Pt(H)(\eta^2\text{-norbornene-R})]^+$ instantaneously and quantitatively (eq 1).



R = H, Ph, COOEt, $Si(OEt)_3$, CH_2OSiMe_3 (1)

The products were characterized by in situ NMR spectroscopy. The ^1H NMR spectra of the reaction mixtures with R = H and COOEt in CD_2Cl_2 showed hydride signals as binomial triplets, flanked by ^{195}Pt-satellites, and shifted ca. 9 ppm downfield from that in *trans*-$[(Et_3P)_2Pt(H)(Cl)]$. For R = H, the olefinic protons of the coordinated norbornene appeared as a broad triplet, also flanked by Pt-satellites, while the $^{31}P\{^1H\}$ NMR spectrum showed a singlet with Pt-satellites. By virtue of coupling with ^{195}Pt, the above data unambiguously establish the structure of the adduct as that shown in eq 1. For the general case with R ≠ H the two phosphines are inequivalent; however, a single peak was observed by $^{31}P\{^1H\}$ NMR for each isomer of norbornene−R mixture (*exo* and *endo*; ratios of the $^{31}P\{^1H\}$ NMR signal intensities corresponded to the norbornene−R isomer ratios). The close similarity of the $^{31}P\{^1H\}$ NMR chemical shifts of the norbornene adduct and those of norbornene−R, as well as hydride chemical shifts for R = H and COOEt, clearly suggests analogous structures for norbornene−R adducts. Evidently, the center of asymmetry (substituted methine carbon attached to the R group) is too remote from the metal center to significantly influence the environment of the phosphines. The $^{31}P\{^1H\}$ NMR data are collected in Table 6, showing marginal variations of δ_P and J_{P-Pt} with R.

7. Reactivity of *trans*-[$(Et_3P)_2Pt(H)(R−NB)]^+$ (R−NB = 5-norbornene-2-R). Heating the norbornene−R adducts in fluorobenzene in the presence of 5−10-fold

Table 6. $^{31}P\{^1H\}$ NMR Data of *trans*-PtH(η^2-RNB)$(PEt_3)_2^+$ in PhF at RT

R	δ_{endo}[a] (J_{Pt-P})[b]	δ_{exo}[a] (J_{Pt-P})[b]
H	11.02 (2386)	11.02 (2386)
Ph	10.85 (2377)	11.17 (2375)
$COOCH_2CH_3$	10.87 (2366)	11.01 (2363)
$Si(OCCH_2CH_3)_3$	11.14 (2391)	11.42 (2389)
$CH_2OSi(CH_3)_3$	11.04 (2385)	11.21 (2382)

[a] In ppm. [b] In Hz.

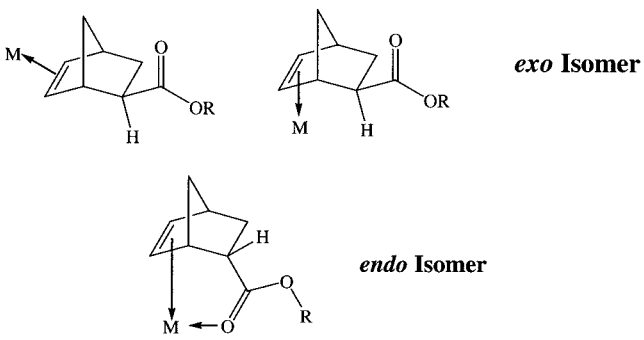


Figure 6. Modes of bonding for ester-functionalized norbornene.

excess of norbornene−R for 18 h led to polymerization for R = H, Ph, $Si(OEt)_3$, and CH_2OSiMe_3. In situ NMR experiments gave precipitated polymers upon addition of the NMR tube contents to acetone. $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures, recorded prior to precipitation, showed only the unreacted *trans*-$[(Et_3P)_2Pt(H)(\eta^2$-norbornene-R)$]^+$. Scale-up of the polymerization reactions with norbornene to platinum molar ratios of 1000 to 1 in fluorobenzene for 65 h confirmed polymerization activity. The highest yield of polynorbornene was obtained with R = H (85%). However, the presence of the functionality was found to considerably decrease the catalyst's activity.

Heating the NB−COOEt adduct of $(Et_3P)_2PtH^+$ in fluorobenzene in the presence of 5 equiv of NB−COOEt led to the appearance of multiple peaks in the $^{31}P\{^1H\}$ NMR spectrum, in addition to those of unreacted *trans*-$[(Et_3P)_2Pt(H)(\eta^2$-NB−COOEt)$]^+$. The major product (**1**) formed in up to 80% nonisolated yield (depending on the reaction conditions) and showed two mutually coupled doublets, each flanked by Pt-satellites with unequal J_{P-Pt}. The magnitude of the P−P coupling, 13 Hz, is characteristic of *cis*-disposition of the phosphines. The remarkably different $^{31}P\{^1H\}$ NMR chemical shifts and platinum−phosphorus coupling constants (P_A, 24.76 ppm, 1630 Hz; P_B, 11.53 ppm, 4993 Hz) indicate that ligands of considerably different *trans*-influence are coordinated *trans* to the inequivalent phosphines. Comparison of the above $^{31}P\{^1H\}$ NMR parameters of **1** with those of $[(Et_3P)_2Pt(\eta^3$-C,O-$CH_2-CH_2COOMe)]^+$ [9] (where the acrylate moiety is bonded to both carbon and carbonyl oxygen to form a five-membered metallocycle) (P_A, 22.5 ppm, 1860 Hz; P_B, 7.0 ppm, 4414 Hz; J_{P-P} = 13.5 Hz) showed notable similarity, indicating a very similar ligand environment around the metal. This suggests that the structure of **1** is that shown in Figure 7. Further spectroscopic evidence for this structural assignment is given below.

(9) Sorato, C.; Venanzi, L. M. *Inorg. Synth.* **1989**, *26*, 134.

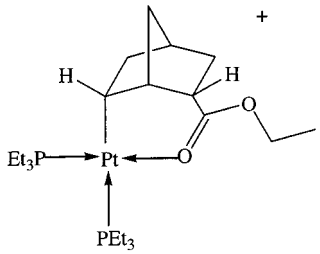


Figure 7. Structure of **1**.

Successive recrystallization of the solids from the reaction mixture gives analytically pure **1** in 40% yield as a colorless, air-stable solid. The ^1H NMR spectrum of **1** showed signals corresponding to a total of 10 protons in addition to the resonances of six phosphine ethyl groups, the ethyl group of the ester functionality, and the aromatic signals of the counterion. No hydride signal was observed. Extensive one- and two-dimensional proton and carbon NMR spectra further clarified the structure of **1**. With the aid of 2D-COSY and 2D-NOESY NMR spectra, all ^1H and ^{13}C signals were assigned as shown in Figure 2.

Mass spectroscopy of **1** confirmed the elemental composition derived from ^1H NMR spectra. Both FD and MALDI-TOF MS spectra of **1** showed a peak with the nominal mass of 598 amu and an isotopic distribution consistent with the proposed structure.

The IR spectrum of **1** showed a carbonyl stretch at 1629 cm^{-1}, shifted by 105 cm^{-1} to a lower frequency from that of pure NB−COOEt. Such a red shift of ν-(C=O) strongly suggests coordination of the carbonyl group to the metal.

In summary, the spectroscopic data indicate that the formation of **1** results from the insertion of a single *endo*-NB−COOEt moiety into the Pt−H bond of $(Et_3P)_2PtH^+$. The carbonyl oxygen of the ester substituent is coordinated to the metal, forming a bidentate ligand that occupies two *cis* sites around platinum. Similar $^{31}P\{^1H\}$ NMR patterns were also obtained with pure *endo*-dimethyl ester of norbornene. Pure *exo*-dimethyl ester of norbornene gave a notably different and more complicated mixture. Under no conditions did ester-substituted norbornenes polymerize with *trans*-$[(Et_3P)_2Pt(H)(\eta^2$-NB−R)$]^+$.

To clarify the stereochemistry around the α-carbon of the inserted NB−COOEt, the solid-state structure of **1** was determined by X-ray crystallography. Crystals of **1** suitable for X-ray diffraction were grown from CH_2Cl_2/toluene. The solid-state structure of **1** suffers a disorder involving in particular the norbornane fragment. It was possible to model the disorder with two alternative conformations for the norbornyl group. An equal occupancy of each conformer was used in the model to facilitate resolving the disorder present in the crystal structure. Figure 8 shows an ORTEP view of one of the conformations (see Supporting Information for additional details). Selected bond distances and angles for this conformation are found in Table 2.

Results from the X-ray study clearly show that the platinum-hydride moiety has inserted into the double bond on the *endo* face of the norbornene substrate. This is highly unusual and unexpected. Typically norbornene coordinates to metals on the *exo* face and then undergoes

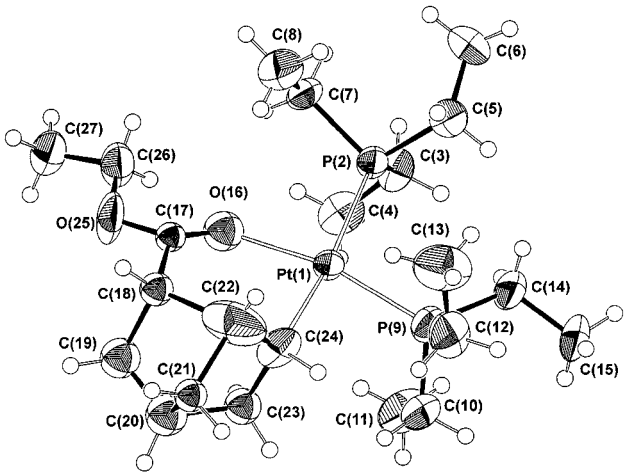


Figure 8. ORTEP representation of *cis*-Pt(η^2-C,O-(*endo*,-*endo*)-NB−$COOCH_2CH_3$)$(P(CH_2CH_3)_3)_2^+$.

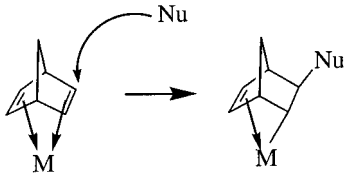


Figure 9. Formation of the *endo*-σ,π-bonded complex.

insertion chemistry on the same face. There are numerous examples of insertion on the *exo* face of norbornene substrates found in the literature.[4] Formation of *endo*-palladium or platinum−carbon α,π-bonded complexes are reported in the literature. However, their formation is typically the result of nucleophilic attack by an anionic species[10] on the *exo*-face of the norbornene derivative, such as norbornadiene, in which the metal is coordinated to the *endo* face of the norbornene derivative (Figure 9).

The platinum metal center in complex **1** exhibits square-planar geometry. The summation of bond angles of the platinum inner coordination sphere is approximately 360°. The bond angle (101.36(11)°) between the two phosphines is splayed out from the ideal. The other inner coordination angles are as a result less than 90°. The two Pt−P bond distances in **1** are substantially different from one another. The Pt−P2 distance is 2.355(3) Å. The Pt−P9 bond distance is significantly shorter at 2.211(3) Å.

Similar coordination environments are established for platinum and palladium by X-ray methods[11] (Figure 10). As was found for **1**, the complexes in Figure 10 exhibit square-planar environments and longer metal−phosphorus distances for those phosphines that are *trans* to carbon and shorter distances for those *trans* to oxygen. This is expected due to the stronger *trans* influence of a carbon σ-bonded to a metal compared to a neutral, two-electron oxygen donor. All of the complexes in

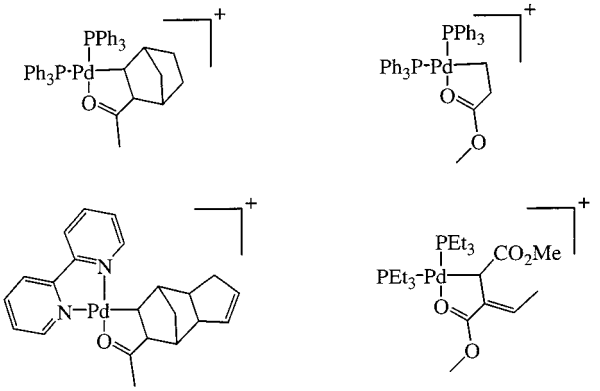


Figure 10. Complexes with coordination environments similar to **1**.

Figure 10 contain five-membered metallocyclic rings, while **1** contains a six-membered metallocycle.

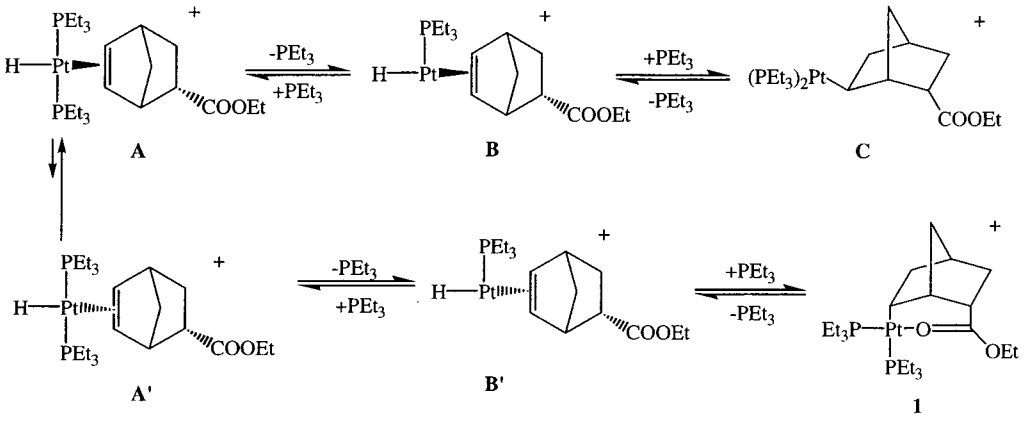
The accumulated experimental data allow some conclusions to be drawn regarding the formation of **1** (Scheme 1). A general outline of the reaction sequence leading from [*trans*-$(Et_3P)_2$Pt(H)(Cl)], Na^+[3,5-$(CF_3)_2C_6H_3]_4B^-$, and 5-norbornenecarboxylic acid ethyl ester to the alkene-inserted **1** consists of the following basic steps. Chloride removal with Na^+[3,5-$(CF_3)_2C_6H_3]_4B^-$ allows for coordination of the ester-functionalized norbornene through the C=C bond leading to a platinum−norbornene adduct with *trans* phosphine ligands. The insertion of the coordinated C=C bond into the Pt−H bond requires *cis*-disposition of the hydride and the coordinated alkene; hence a *trans* to *cis* rearrangement of the primary product must occur prior to the insertion step. The latter is presumably mediated by phosphine dissociation: the 14-electron T-shaped transient species B or B′ in Scheme 1. After the *trans* to *cis* rearrangement, insertion occurs either prior to or following phosphine coordination. The ester functionality is also coordinated to platinum in **1**. While no kinetic experiments have been carried out to establish the postulated inverse [PEt_3] rate dependence, it was found that increasing the steric bulk of the phosphines accelerates the insertion process. The reactions of the analogous *trans*-$(Ph_3P)_2$Pt(H)(Cl) and *trans*-$(Cy_3P)_2$Pt(H)(Cl) do not require elevated temperatures; the latter species actually polymerizes NB−COOEt, albeit with low activity. The discovery that conversion of *trans*-$(Et_3P)_2$Pt(H)(η^2-NB−$COOEt)^+$ to **1** reaches an upper limit is also consistent with the rate-inhibiting effect of free phosphine; the inserted product **1** has *cis*-configuration of the two Et_3P ligands, one of which is *trans* to the alkyl group which has a high *trans*-influence (cf. $J_{Pt-P} = 1630$ Hz). This feature likely facilitates phosphine dissociation from **1**, which, in turn, inhibits the conversion of *trans*-$(Et_3P)_2$Pt(H)(η^2-NB−$COOEt)^+$ to **1**.

By virtue of the *endo*:*exo* composition of the NB−COOEt, the actual sequence of transformations is more complex. The coordination of *endo* NB−COOEt to the $(Et_3P)_2Pt(H)^+$ fragment needs to occur on the *endo* face (A′) in order to form **1**. Although the stereochemistry of NB−COOEt coordination in *trans*-$(Et_3P)_2$Pt(H)(η^2-NB−$COOEt)^+$ has not been determined, it is likely to be on the *exo* face. The *exo* face of norbornene is less sterically congested than the *endo* face. Indeed, the previous reports on the insertion of (unsubstituted) norbornene

(10) (a) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. 1, p 161. (b) Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1973**, 60, 427, and references therein.

(11) (a) Brock, C. P.; Attig, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 1319. (b) Brumbaugh, J. S.; Whittle, R. R.; Parvez, M.; Sen, A. *Organometallics* **1990**, *9*, 1735. (c) Hinkle, R. J.; Stang, P. J.; Arif, A. M. *Organometallics* **1993**, *12*, 2510. (d) Markies, B. A.; Kruis, D.; Rietveld, M. H. P.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, 117, 5263.

Scheme 1. Reaction Equilibria Leading to the Formation of 1



into metal−carbon bonds indicate an *exo, exo* stereochemistry.[4] Thus, the formation of **1** requires the prior migration of the $(Et_3P)_2Pt(H)^+$ fragment from the *exo* to the *endo* face of NB−COOEt. This isomerization likely occurs via NB−COOEt dissociation and is kinetically slow: ^1H and $^{31}P\{^1H\}$ NMR spectra of both *trans*-$(Et_3P)_2Pt(H)(\eta^2$-NB−COOEt$)^+$ and *trans*-$(Et_3P)_2Pt(H)(\eta^2$-norbornene$)^+$, recorded at 65 °C in chlorobenzene-d_5, show virtually no change with respect to those recorded at ambient temperature. More importantly, the likely *exo*-coordination of NB−COOEt to the $(Et_3P)_2Pt(H)^+$ fragment indicates the nonparticipation of the carbonyl group in determining the regiochemistry of the first interaction with the alkene: if the carbonyl group were to coordinate first to the $(Et_3P)_2Pt(H)^+$ fragment, the subsequent coordination of the C=C bond would occur through the *endo* face, at least for *endo*-NB−COOEt.

An interesting question is why the insertion occurs at the *endo* face even though the alkene is initially coordinated through the *exo* face. It is likely that insertion does occur at the *exo* face, but the resultant product (C) cannot be stabilized by coordination of the carbonyl oxygen and β-hydrogen abstraction from C regenerates the starting alkene adduct. On the other hand, the product derived through insertion at the *endo* face (**1**) is more stable because of the coordination of the carbonyl group. Thus, while the *exo* insertion may be kinetically fast, the *endo* insertion product is thermodynamically favored.

The reverse reaction, **1** to *trans*-$(Et_3P)_2Pt(H)(\eta^2$-*endo*-norbornene−COOEt$)^+$, takes place, although it is very slow. Heating a chlorobenzene-d_5 solution of **1** in the presence of 5 equiv of 1-hexene at 65 °C for 18 h led to nearly complete isomerization of the terminal olefin into a mixture of internal unsaturated isomers. The $^{31}P\{^1H\}$ NMR spectra of the reaction mixture showed that ca. 90% of **1** remained intact, while the remaining 10% rearranged to *trans*-$(Et_3P)_2Pt(H)(\eta^2$-*endo*-NB−COOEt$)^+$, the latter being responsible for isomerization of 1-hexene. A similar $^{31}P\{^1H\}$ NMR spectrum was obtained when 5 equiv of NB−COOEt was used instead of 1-hexene. It therefore appears that **1** can β-hydrogen eliminate the inserted alkene, producing the catalytically active hydride adduct.

Conclusion

A palladium(II)-based catalyst system has been described for the efficient polymerization of norbornene derivatives, including those with pendant oxygen functionalities. The very high polymerization rates and the ability to control polymer molecular weight through the addition of an alcohol make the system attractive from a practical standpoint. For functional norbornenes, the rates of polymerization are substantially slower than for the nonfunctional monomers. It has been demonstrated that for such functional norbornenes, the *exo* isomer is preferentially incorporated into the growing polymer chain. Finally, by using a model platinum-based system, we have for the first time demonstrated the *endo, endo* insertion of the *endo* isomer of an ester-functionalized norbornene forming a chelated platinum complex. The formation of chelates, both upon the coordination of the *endo*-functionalized norbornene and in the *endo*-inserted product, appears to be responsible, in part, for the observed decrease in polymerization rate for functional norbornene derivates. A further reason for the diminution of activity of *both* the *endo*- and the *exo*-functionalized isomers is simply the coordination of the functionality to the metal center.

Acknowledgment. This research was supported by a grant from the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-84ER13295), and the Advanced Technology Program of NIST (ATP Project 95-05-0038). The authors would like to thank Seth B. Harkins for synthesizing $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ used in portions of this work, Dr. Ian Harrison for usage of the DSC, Dr. Shahid Murtuza for assistance in its use, and Dr. Richard Vicari for suggesting an alternative synthesis of the 5,6-norbornenedicarboxylic acid methyl esters. We would also like to thank Elf Atochem, North America, for their analysis of poly(norbornene) and poly(vinyl norbornene) samples.

Supporting Information Available: Details regarding the ^1H and ^{13}C 2D-NMR spectra and assignments for complex **1**, ORTEP representations of two alternate solutions to the disorder found in the X-ray structural study of **1**, and a complete set of distances and angles, atomic coordinates, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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