Macromolecules **1996,** *29,* 2755−2763

(η^3-Allyl)palladium(II) and Palladium(II) Nitrile Catalysts for the Addition Polymerization of Norbornene Derivatives with Functional Groups

Joice P. Mathew, Annette Reinmuth, Jennifer Melia,
Noeleen Swords, and Wilhelm Risse*

Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

Received October 13, 1995; Revised Manuscript Received January 22, 1996[⊗]

ABSTRACT: Cycloaliphatic polyolefins with functional groups were obtained by Pd(II)-catalyzed homo- and copolymerizations of norbornene derivatives. Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid, the corresponding methyl ester, 2-(hydroxymethyl)bicyclo[2.2.1]hept-5-ene, and the corresponding octanoate and decanoate were used as the monomers in these addition polymerizations. Pd(II)−nitrile catalysts $[Pd(RCN)_4][BF_4]_2$ (with R = CH_3 and C_2H_5) quite selectively polymerized the exo isomers of the esters of 2-(hydroxymethyl)bicyclo[2.2.1]hept-5-ene. Monomer mixtures containing an 80/20 ratio of endo/exo isomers were converted into polymers containing more than 50% of exo units. ^{1}H NMR studies showed that the predominant fraction of the endo isomer remained unreacted. The nitrile based Pd catalysts were not sufficiently active to polymerize the monomers with electron-withdrawing substituents linked to the bicyclic unit at ambient temperature. In-situ prepared (η^3-allyl)palladium complexes with associated tetrafluoroborate and hexafluoroantimonate ions were found to be substantially more active. They were able to catalyze the addition polymerization of norbornene derivatives containing a large proportion of endo isomers. Quantitative monomer conversions were achieved for aliphatic esters of 2-(hydroxymethyl)bicyclo[2.2.1]hept-5-ene. Random copolymers of norbornene and the latter esters with molecular weights M_n(GPC) above 100 000 were prepared. The (η^3-allyl)palladium compounds were suitable for the polymerization of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid methyl ester; high molecular weight materials were obtained via copolymerization with norbornene. Furthermore, addition polymers containing 0.2 carboxylic acid group per repeating unit were prepared by the copolymerization of norbornene and bicyclo[2.2.1]hept-5-ene-2-carboxylic acid. The hexafluoroantimonate-based (η^3-allyl)Pd(II) catalyst had a higher polymerization activity than the Pd compound with the smaller BF_4^- counterion which was rationalized by a slightly stronger association of BF_4^- with the (η^3-allyl)Pd(II) unit.

Introduction

The incorporation of functional or reactive groups into polymer chains can provide enhanced intra- and intermolecular interactions (e.g., polar, hydrogen-bonding, or ionic interactions). These interactions modify specific properties of materials, such as glass transition, rubbery modulus above the glass transition, dynamic mechanical behavior, melt rheology, relaxation behavior, dielectric properties, and solution behavior.[1] For example, the presence of ionic groups leads to improved mechanical strength and increased glass transition temperatures in ionomers.[2] Functional groups can promote miscibility or compatibility of polymer blends;[3] in adhesion and coatings applications, they can be responsible for adhesive bonding to surfaces of various substrates such as inorganic solids, organic polymers, pigments, and dyes.[4]

Polyolefins pepared by transition metal catalyzed processes are important materials, as they make up a substantial proportion of the commercially available thermoplastics.[5] However, most transition metal catalysts rapidly react with functional groups and become inactive for polymerization, which restricts their uses for monomers with functional groups.[6]

Compounds based on late transition metals such as Mo, Os, and Ru have been found useful for ring-opening olefin metathesis polymerizations (ROMP) of cycloolefins with functional groups.[7] A precursor method has been reported for transition metal catalyzed addition polymerizations (Ziegler−Natta polymerizations), which involves the synthesis of polymers with 9-borabicyclononane substituents and their subsequent conversions into polyolefins with hydroxyl groups.[8] Advances toward the direct polymerization of polar monomers via Ziegler−Natta catalysis have been described with cationic catalysts of the type $Cp^*_2ZrCH_3^+\cdots X^-$ with $X^- = B(C_6F_5)_4^-$ or $H_3CB(C_6F_5)_3^-$. These zirconocene complexes have been found to tolerate trialkylsiloxy and dialkylamino substituents.[9]

$PdCl_2$ and several nonionic Pd(II)−halide complexes catalyze the addition polymerization of norbornene derivatives with functional groups at reaction temperatures above 100 °C. Moderate yields of products with molecular weights generally below 10 000 have been reported.[10] High molecular weight addition polymers of norbornene derivatives with carboxylic ester groups were recently obtained with $[Pd(CH_3CN)_4][BF_4]_2$ at ambient temperature[11] and with palladium(II)−alkyl complexes.[12] However, good polymer yields (above 70%) were produced with $[Pd(CH_3CN)_4][BF_4]_2$ only when pure exo isomers were used as the monomers. The present contribution describes subsequent investigations on the different reactivities of exo- and endo-substituted norbornene derivatives in these addition polymerizations. (η^3-Allyl)palladium(II) catalysts with weakly coordinating counterions are presented which have a substantially increased activity for the polymerization of endo-substituted norbornene derivatives.

Results and Discussion

Pd(II)-Catalyzed Homopolymerizations of Norbornene Derivatives. We previously reported initial investigations about the olefin addition polymerization of carboxylic esters of bicyclo[2.2.1]hept-5-enyl-2-methanol **1a−h** (eq 1).[11] These reactions were carried out with $[Pd(CH_3CN)_4][BF_4]_2$ as the catalyst in nitromethane at 20 °C. Ester-substituted cycloaliphatic polyolefins, poly-

---

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

0024-9297/96/2229-2755$12.00/0

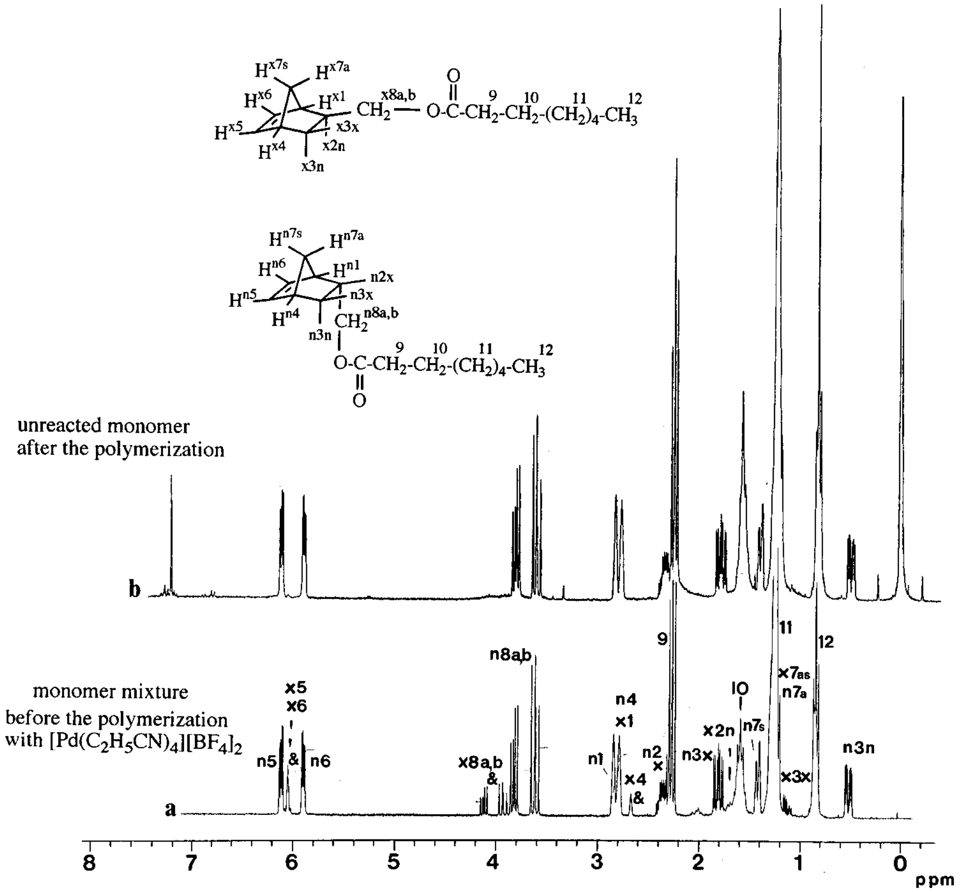
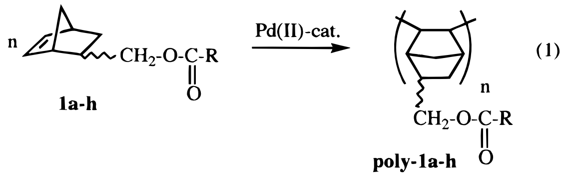


Figure 1. (a) ^{1}H NMR spectrum of the octanoic acid ester of 2-(hydroxymethyl)bicyclo[2.2.1]hept-5-ene (**1c**) (exo/endo = 20/80) in $CDCl_3$, the monomer used for the polymerization with $[Pd(C_2H_5CN)_4][BF_4]_2$. Characteristic signals corresponding to the exo isomer are marked by "&". (b) ^{1}H NMR spectrum of the low molecular weight fraction isolated after the addition polymerization of the monomer mixture of (a) with $[Pd(C_2H_5CN)_4[BF_4]_2$; exclusively the endo isomer is recovered from the filtrate after precipitation of the addition polymer poly-**1c** (no. 2 of Table 1).

Table 1. Pd(II)-Catalyzed Homopolymerizations of Bicyclo[2.2.1]hept-5-enyl-2-methyl Carboxylates 1c and 1d

no.	M[a]	[M]/[Pd(II)][b]	Pd(II)catal[c]	t/h[d]	M_n(GPC)[e]	M_w/M_n[e]	yield/%
1	**1c**	100/1	$[Pd(CH_3CN)_4][BF_4]_2$	16	7200[f]	1.67	25
2	**1c**	100/1	$[Pd(C_2H_5CN)_4][BF_4]_2$	120	6800[f]	1.28	40
3	**1d**	50/1	$[Pd(CH_3CN)_4][BF_4]_2$	16	3900	1.56	22
4	**1d**	50/1	$\{(\eta^3-allyl)Pd(BF_4)\}$	6	17800	1.68	39
5	**1d**	50/1	$\{(\eta^3\text{-allyl})Pd(BF_4)\}$	18	9700	2.18	74
6	**1d**	50/1	$\{(\eta^3\text{-allyl})Pd(BF_4)\}$	48	9600	2.40	97
7	**1d**	150/1	$\{(\eta^3\text{-allyl})Pd(BF_4)\}$	48	8800	2.46	100
8	**1d**	50/1	$\{(\eta^3\text{-allyl})Pd(SbF_6)\}$	18	25000	2.19	99

[a] Norbornene derivative used for the addition polymerization. [b] Mole ratio of monomer to monomeric Pd(II) species (a 50/1 ratio of monomer to (η^3-allyl)Pd catalyst corresponds to a 100/1 mole ratio of norbornene derivative to $[(\eta^3\text{-allyl})PdCl]_2$ used for the in-situ catalyst preparation). [c] Palladium catalyst. [d] Reaction time at 20 °C; solvent was nitromethane for polymerizations 1 and 3, nitrobenzene/dichloromethane, volume ratio of 4/1 for 2, and chlorobenzene for 4–8. [e] M_n(GPC) and M_w/M_n are the relative number-average molecular weight and the polydispersity index, respectively, determined by GPC, calibration with polystyrene standards. [f] Concentrations of **1c** in chlorobenzene as high as 0.7–0.8 g/dL were used for the GPC analysis because of the small difference in refractive index between polymer and solvent.



1, poly-1	a	b	c	d	e	f	g	h
R	CH_3	n-C_4H_9	n-C_7H_{15}	n-C_9H_{19}	n-$C_{11}H_{23}$	C_6H_5	4-Cl-C_6H_4	3-NO_2-C_6H_4

1a,b,f, with molecular weights M_n as high as 163 000 had been prepared from the pure exo isomers of norbornene derivatives **1a,b,f**. The polymer yields were generally above 70%.[11] Considerably lower yields were obtained from monomers **1a**–**h** which contain the endo isomer as the major component. The product yields ranged only from 20 to 32% for norbornene derivatives with an endo/exo isomer ratio of 80/20.

The yield of poly(5,6-bicyclo[2.2.1]hept-5-ene) derivative poly-**1c** increased only slightly from 25% to 40% (2, Table 1) with the use of $[Pd(C_2H_5)_4][BF_4]_2$ in a solvent mixture of nitrobenzene/dichloromethane, volume ratio 4/1 (instead of nitromethane) after a reaction time of 120 h (instead of 16 h). The soluble low molecular weight fraction recovered from the filtrate after precipitation of the polymer with methanol contained exclusively unreacted endo isomer. The ^{1}H NMR spectrum of Figure 1b does not show any signals corresponding to the exo isomer. (Characteristic signals of

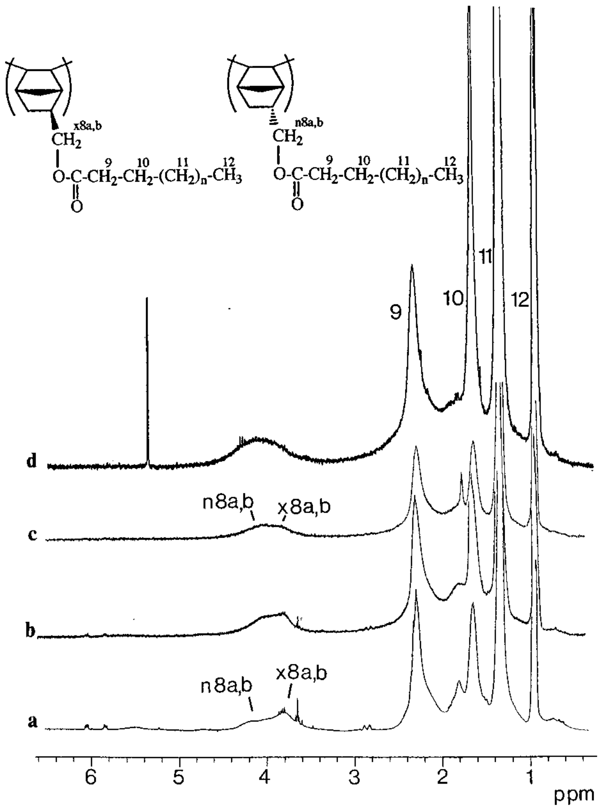


Figure 2. ^{1}H NMR spectra ($CDCl_3$) of (a) the addition polymer poly-**1c** prepared from the octanoic acid ester of 2-(hydroxymethyl)bicyclo[2.2.1]hept-5-ene) (**1c**) (exo/endo = 20/80) with $[Pd(CH_3CN)_4][BF_4]_2$ in nitromethane (no. 1 of Table 1); (b) the addition polymer poly-**1c** obtained from the reaction with $[Pd(C_2H_5CN)_4[BF_4]_2$ in a solvent mixture of dichloromethane/nitrobenzene, volume ratio 1/4 (no. 2 of Table 1); (c) the addition polymer poly-**1d** prepared from the decanoic ester of 2-(hydroxymethyl)bicyclo[2.2.1]hept-5-ene) (**1d**) (exo/endo = 20/80) with $\{(\eta^3\text{-allyl})Pd(BF_4)\}$ after 18 h at 20 °C (no. 5 of Table 1); (d) the addition polymer poly-**1d** prepared with $\{(\eta^3\text{-allyl})Pd(SbF_6)\}$ after 18 h at 20 °C (no. 8 of Table 1). Characteristic is the region of $\delta = 4.3-3.7$ ppm.

the exo-derivative are marked in the ^{1}H NMR spectrum of the original monomer mixture (Figure 1a).)

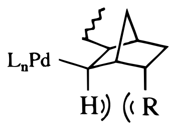
The ^{1}H NMR spectrum of poly-**1c** prepared in nitromethane (no. 1, Table 1) confirms that predominantly the exo-derivative has been incorporated into the polymer chain. Figure 2a shows a broad signal between $\delta = 3.7$ and 3.9 ppm which corresponds to the CH_2OCO protons of incorporated exo units.[13] A second, partially overlapping broad signal of weaker intensity at $\delta = 3.9-4.3$ ppm is assigned to the CH_2OCO group of incorporated endo units. Cycloaliphatic polyolefin poly-**1c** prepared with $[Pd(C_2H_5CN)_4][BF_4]_2$ in nitrobenzene/dichloromethane (2, Table 1) contains only a slightly higher amount of endo-substituted repeating units (Figure 2b). The intensity of the signal corresponding to the endo-linked substituents is slightly increased.

Three possible causes for the lower reactivity of the endo derivatives can be discussed:

(a) The endo isomer might act as a chelating ligand with the olefin and the ester group coordinating to palladium. This means that the bicyclic olefin unit binds to Pd(II) with its endo face, which is an inconvenient configuration for chain propagation.

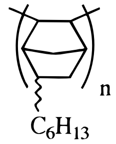
(b) A growing chain with two neighboring endo-substituted norbornene units linked to the transition metal might be sufficiently sterically demanding to restrict access and π-coordination of a new incoming norbornene ligand.

Chart 1. Weak Repulsive 2,6-Interaction



(c) The cis–exo addition of Pd and the previously σ-bonded polymer chain converts the olefin hydrogens into axial aliphatic hydrogens which encounter a weak unfavorable 2,6-steric interaction with the endo-linked substituent (Chart 1).

Also 5-hexyl-2-norbornene with an endo/exo ratio of 80/20 was only partially converted into poly(5-hexyl-2,3-bicyclo[2.2.1]hept-2-ene) (poly-**1k**) upon reaction with

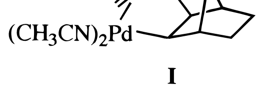


poly-1k

$[Pd(CH_3CN)_4][BF_4]_2$. The yields of poly-**1k** were typically in the range of 25–50%. No coordinating effect would be expected from the pure hydrocarbon substituent C_6H_{13}. This indicates that effects other than chelation mentioned in (a) have a significant influence on the reduced polymerizability of endo-substituted norbornene derivatives.

Usually, the endo-substituted isomer is predominant in a large number of norbornene derivatives which are accessible by Diels–Alder reactions. The synthesis of the pure exo isomers often requires additional experimental operations.[7n,11,14] Therefore, it was desired to develop catalysts with a higher activity for *endo*-norbornene derivatives.

The activity of the tetrakisnitrile palladium(II) catalysts is affected by the presence of the electron-donating nitrile ligands. The addition of 4 equiv of acetonitrile to a mixture obtained from the reaction of $[(\eta^3\text{-allyl})PdCl]_2$ and $AgBF_4$ (mole ratio 1/2) produces a catalyst composition with a drastically reduced polymerization activity. No poly(2,3-bicyclo[2.2.1]hept-2-ene) was obtained after the reaction with 100 equiv of norbornene for 4 h at 20 °C. Palladium complex **I** was formed, which contains just a single unit of norbornene inserted into the Pd allyl unit.



I

Two highly effective in-situ prepared (η^3-allyl)Pd(II) catalysts **IIa** and **IIb** were obtained by the reaction of the (η^3-allyl)palladium chloride dimer with silver hexafluoroantimonate or silver tetrafluoroborate in the absence of any additional potentially coordinating compound other than the solvents dichloromethane or chlorobenzene (eqs 2a and 2b, Scheme 1).[15] Gravimetric determination of the AgCl liberated in these reactions showed that all of the chlorine of the allylpalladium chloride dimer is removed upon reaction with the silver salts.

The Pd(η^3-allyl) compounds **IIa** and **IIb** showed a considerably higher activity for the polymerization of endo-substituted norbornene derivatives than the previously discussed Pd–nitrile complexes. A 74% monomer conversion of **1d** with an endo/exo ratio of 80/20 was

Scheme 1. Preparation of (η^3-Allyl)Pd(II) Catalysts for the Addition Polymerization of Norbornene Derivatives

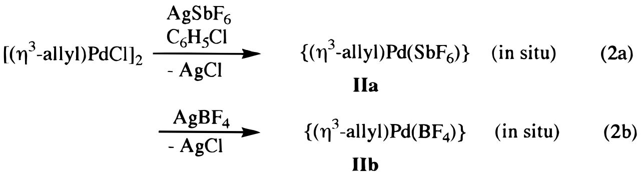
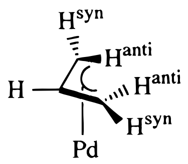


Table 2. ^{1}H NMR Shifts of (η^3-Allyl)palladium Complexes in CD_2Cl_2 (at 20 °C)



Pd complex	δ/ppm CH$_2$(anti)	CH$_2$(syn)	CH
[(allyl)PdCl]$_2$	2.98	4.05	5.40
{(allyl)Pd(BF$_4$)} (**IIb**)	3.52	4.64	5.93
{(allyl)Pd(SbF$_6$)} (**IIa**)	3.74	4.87	6.08

obtained with **IIb** after 18 h at 20 °C (5, Table 1). The Pd(η^3-allyl) catalyst with the bigger hexafluoroantimonate counterion, **IIa**, was even more active and led to a quantitative polymerization of the same monomer after 18 h at 20 °C (8,Table 1). For comparison, a reaction time of 48 h at 20 °C was required to produce a quantitative polymer yield with catalyst **IIb** (6, Table 1).

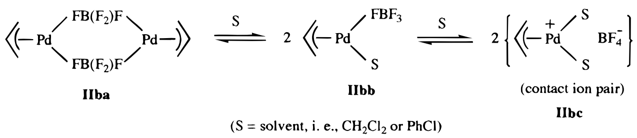
The molecular weights M_n(GPC) of poly-**1d** prepared with **IIb** decreased from 17 800 to 9600 and the molecular weight distributions M_w/M_n became broader, as reaction time and thus monomer conversions was increased (4−6, Table 1). These results indicate that propagation is faster than initiation, and chain transfer and termination occur quite readily. The latter side reactions become more prominent with decreasing monomer concentrations and with an increasing ratio of endo to exo-substituted monomer. (The endo/exo ratio increased from 80/20 to 86/14 after 39% total monomer conversion of **1d**.)

Traces c and d of Figure 2 show that the broad signal at $\delta = 3.9-4.3$ ppm is becoming more intense than the signal at $\delta = 3.7-3.9$ ppm with increasing amounts of monomer conversion, reflecting higher proportions of endo-substituted norbornene repeating units in samples of poly-**1c** obtained with **IIb** and **IIa**, respectively.

The charge density and the electrophilicity of the (η^3-allyl)Pd unit increases upon removal of the chlorine ligands from [(η^3-allyl)PdCl]$_2$. This is reflected in a downfield shift of the ^{1}H NMR signals of the allyl protons (Table 2). The signals assigned to the terminal anti and syn CH$_2$ protons and the internal >CH proton of the η^3-allyl ligand move from $\delta = 2.98$, 4.05, and 5.40 ppm to $\delta = 3.52$, 4.64, and 5.93 ppm, respectively, when [(η^3-allyl)PdCl]$_2$ is converted into the (η^3-allyl)palladium tetrafluoroborate complex **IIb**. A further downfield shift of these proton signals to $\delta = 3.74$, 4.87, and 6.08 ppm is recorded for palladium complex **IIa** with the larger counterion SbF_6^-. The different NMR shifts of **IIa** and **IIb** indicate a weak Pd−F interaction for the smaller anion BF_4^- in **IIb**.[16,17]

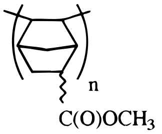
Further indications for an associative interaction between Pd and BF_4^- come from ^{19}F NMR spectroscopic studies. Two relatively broad singlets in a 1/4 intensity ratio were recorded at $\delta = -150.25$ and -150.31 ppm (471 MHz at $T = -80$ °C) corresponding to the fluorine atoms of the ^{10}B and ^{11}B isotopomers of BF_4^- associated with the (η^3-allyl)Pd^{II} unit. A sharp set of two small singlets due to coexisting free BF_4^- was detected at slightly lower field, $\delta = -147.1$ ppm (~2% of the intensity of the upfield signals). The absence of any additional fine structure in the main upfield signals indicates either rapid exchange between the bridging and the terminal fluorine atoms of coordinated BF_4^- (anion "spinning") or the presence of a tightly associated contact ion pair.

Scheme 2



The presence of the solvent is important for the stability of complexes **IIa** and **IIb**. Both complexes were stable in solution for ~1 h at 20 °C, and then small amounts of black Pd particles began to form, indicating the onset of decomposition. The decomposition was only slightly accelerated in the presence of air. Both Pd catalysts rapidly decomposed during attempts to isolate them as solids upon removal of the solvent in vacuum. We would like to suggest an equilibrium of the rapidly exchanging Pd species **IIba, IIbb,** and **IIbc** (Scheme 2) present in solution. (The solvents we used in these studies were dichloromethane and chlorobenzene.) The X-ray crystal structure of an Ag/Pd-based transition metal complex containing dichloromethane as a weakly coordinating ligand was recently reported by Strauss et al.[18] It has been proposed that CH_2Cl_2 can also act as a ligand in other transition metal complexes.[17c,19]

The difference in the coordinative strength (or association) of BF_4^- and SbF_6^- is also reflected in the higher activity of complex **IIa**, which leads to quantitative polymer formation of poly-**1d** within a shorter reaction time than with **IIb**. Both Pd catalysts **IIa** and **IIb** were used for the polymerization of 5-norbornene-2-carboxylic acid methyl ester (exo/endo = 20/80, [M]/[I] = 50/1). After 90 h at 20 °C, the addition polymer poly-**3** with a molecular weight M_n(GPC) = 7100 ($M_w/M_n = 1.7$) was obtained in a 68% yield with the hexafluoroantimonate-based catalyst **IIa**. A 59% yield of poly-**3** with M_n(GPC) = 4600 ($M_w/M_n = 2.2$) was isolated from a polymerization with the tetrafluoroborate-based catalyst **IIb** under otherwise identical reaction conditions. The catalysts based on [Pd(RCN)$_4$][BF$_4$]$_2$ were not sufficiently reactive to produce any poly-**3** at ambient temperatures.



poly-3

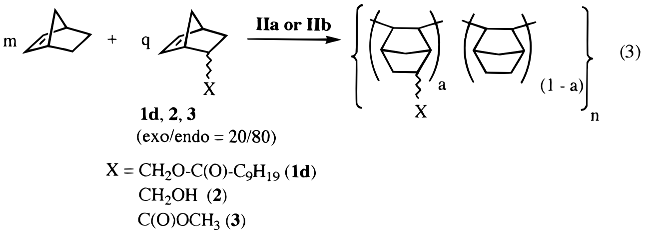
Copolymerizations of Norbornene and Norbornene Derivatives with (η^3-allyl)Pd(II) Catalysts Containing Weakly Coordinating Counterions. The number of functional groups per repeating unit was varied by copolymerizing norbornene derivatives containing ester, hydroxyl, and carboxylic acid groups with norbornene (eqs 3 and 4). In-situ prepared (η^3-allyl)palladium hexafluoroantimonate (**IIa**) and (η^3-allyl)-

Table 3. Pd(II)-Catalyzed Copolymerizations of Norbornene and Norbornene Derivatives with Functional Groups ($X = CH_2OC(O)C_9H_{19}$, CH_2OH, C(O)OMe, C(O)OH in eqs 3 and 4)

no.	Pd(II) catal[a]	[M]/[Pd(II)][b]	t/h[c]	M_n(GPC)[d]	M_w(GPC)[d]	a/%[e]	yield/%
	(a) Comonomer: Decanoic Ester of 2-(Hydroxymethyl)bicyclo[2.2.1]hept-5-ene[i]						
10	**IIb** (BF_4^-)	125/1	3	48 000	112 000	0.17	94
11	**IIa** (SbF_6^-)	125/1	0.2	164 000	960 000	0.18	65
12	**IIa** (SbF_6^-) (+ 10 equiv of H_2O)	125/1	18	185 000	524 000	0.15	78
13	**IIa** (SbF_6^-) (+ 15 equiv of H_2O)	125/1	18	152 000	368 000	0.16	84
14	**IIa** (SbF_6^-) (+ 10 equiv of H_2O)	250/1	1	213 000	563 000	0.14	73
	(b) Comonomer: 2-(Hydroxymethyl)bicyclo[2.2.1]hept-5-ene[i]						
15	**IIa** (SbF_6^-)	50/1	71	18 500[f]	27 000[f]	0.15	79
16	**IIa** (SbF_6^-) (+ 5 equiv of H_2O)	50/1	71	13 200[f]	20 500[f]	0.14	64
	(c) Comonomer: Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid Methyl Ester[i]						
17	**IIa** (SbF_6^-) (+ 10 equiv of H_2O)	100/1	24	64 000	184 000	0.08	79
18	**IIa** (SbF_6^-) (+ 10 equiv of H_2O)	50/1	15	60 000	233 000	0.10	83
19	**IIb** (BF_4^-)	50/1	25	10 500	51 000	0.18	97
	(d) Comonomer: Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid Methyl Ester[i]						
20	**IIa** (SbF_6^-)	50/1	69	25 000	102 000	0.38	76

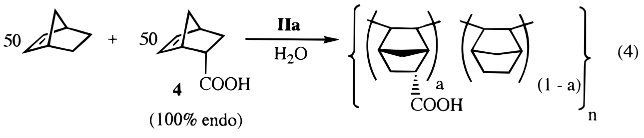
no.	Pd(II) catal[a]	[M]/[Pd(II)][b]	t/h[c]	η_{inh}/dL/g[g]	a/%[h]	yield/%
	(e) Comonomer: Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid[i]					
21	**IIa** (SbF_6^-) (+ 20 equiv of H_2O)	100/1	1	0.52	0.20	49

[a] Pd(II) catalysts used for the copolymerizations were (η^3-allyl)palladium hexafluoroantimonate (**IIa**) or (η^3-allyl)palladium tetrafluoroborate complex (**IIb**), prepared in situ. [b] Molar ratio of monomers to monomeric Pd(II) species ([M]/[Pd(II)]) of 250/1 corresponds to a 500/1 mole ratio of comonomers (norbornene plus norbornene derivative) to $[(\eta^3\text{-allyl})PdCl]_2$ (used for the in-situ catalyst synthesis). [c] Reaction time at 20 °C, solvent chlorobenzene. [d] M_n(GPC), M_w(GPC), number- and weight-average molecular weights determined by GPC calibrated with polystyrene standards. [e] a, number of functional groups per repeating unit in copolymers prepared from monomers **2** and **3** according to eq 3 (determined by ^{1}H NMR spectroscopy). [f] Number- and weight-average molecular weights determined by GPC in chlorobenzene at 20 °C after conversion of the hydroxyl groups into decanoate substitutents. [g] Inherent viscosity determined for a 3 g/L solution in THF at 25 °C. [h] a, number of functional groups per repeating unit according to eq 4 determined by IR spectroscopy (1702 and 804 cm^{-1}). [i] For (a): ($X = CH_2OC(O)C_9H_{19}$, **1d**; molar ratio of **1d** to norbornene, 20/80, exo/endo ratio of **1d**, 20/80). For (b): ($X = CH_2OH$, **2**; molar ratio of **2** to norbornene, 20/80. exo/endo ratio of **2**, 20/80). For (c): $X = C(O)OCH_3$, **3**; exo/endo ratio of **3**, 20/80; molar ratio of **3** to norbornene, 20/80. For (d): $X = C(O)OCH_3$, **3**; exo/endo ratio of **3**, 20/80; molar ratio of **3** to norbornene, 50/50. For (e): X = C(O)OH, **4**; 100% endo, molar ratio of **4** to norbornene, 50/50.



1d, **2**, **3**
(exo/endo = 20/80)

$X = CH_2O\text{-}C(O)\text{-}C_9H_{19}$ (**1d**)
CH_2OH (**2**)
$C(O)OCH_3$ (**3**)



4
(100% endo)

palladium tetrafluoroborate (**IIb**) were used as the catalysts. The functional monomers were the decanoic acid ester of 2-(hydroxymethyl)bicyclo[2.2.1]hept-5-ene (**1d**), 2-(hydroxymethyl)bicyclo[2.2.1]hept-5-ene, **2**, bicyclo-[2.2.1]hept-5-ene-2-carboxylic acid methyl ester (**3**), and bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (**4**). The endo/exo-ratio of monomers **1d**, **2**, and **3** was 80/20 (eq 3). The pure endo-acid **4** was used for the preparation of a copolymer with free carboxylic acid groups (eq 4).

A comonomer feed ratio of 20/80 was selected for the copolymerizations of decanoic ester **1d** with norbornene. The resulting copolymers (10–14, Table 3) contained between 14 and 18% of ester units incorporated, which corresponds to $0.14 \leq a \leq 0.18$ in eq 3. The number of ester side chains per repeating unit was determined from the intensity of the ^{1}H NMR triplet at $\delta = 0.88$ ppm corresponding to the terminal CH_3 group of the decanoate chain and from the intensity of the broad signal at $\delta = 3.7$–4.2 ppm corresponding to $CH_2OC(O)$ protons. The small difference to the theoretical value of $a = 0.20$ reflects a slightly higher reactivity of the unsubstituted norbornene in the addition polymerization.

The copolymerization reactions led to higher molecular weight products than the homopolymerizations of the norbornene derivatives. The molecular weights M_n(GPC) of copolymers 11–14 (Table 3) prepared with the hexafluoroantimonate-based catalyst **IIa** were in the range of 152 000–213 000. These values are noticeably higher than $M_n(\text{GPC}) = 40\,000$ of polymer 10 (Table 3) synthesized with the tetrafluoroborate based-catalyst **IIb**. The copolymerization with catalyst **IIa** (11, Table 3) was stopped after 12 min in order to prevent uncontrolled gelation of the polymerization mixture.[20] The very high acitivity of **IIa** was sufficiently reduced by the addition of 10–15 equiv of water to the polymerization mixture to allow the preparation of high molecular weight products which remained soluble after longer reaction times (12–14, Table 3). Monomer conversions above 70% were reached for polymerizations with **IIa** in the presence of 10 eq of H_2O after 1 h (14, Table 3). These copolymers remained soluble after a reaction time of 18 h (12 and 13, Table 3).[21]

Polymers 10–14 (Table 3) were soluble in chlorobenzene, chloroform, and toluene (polymer 10 was also soluble in THF), which contrasts with a more limited solubility of unsubstituted poly(2,3-bicyclo[2.2.1]hept-2-ene). The solubility of the latter polymer prepared via Pd catalysis is restricted to chlorobenzene, other aryl halides, and polyhalogenated olefins.

The copolymerization of a 80/20 mole ratio of norbornene and 2-(hydroxymethyl)norbornene (**2**) proceeded more slowly than the previous copolymerizations. A 79% yield of a copolymer with 0.15 hydroxyl group per repeating unit (determined via ^{1}H NMR spectroscopy) was obtained after 71 h at 20 °C (15, Table 3). The resulting copolymer was soluble in chlorobenzene and chloroform at a slightly elevated temperature of 50 °C. A molecular weight M_n of 18 500 was determined by GPC in chlorobenzene at 20 °C after converting the hydroxyl groups into decanoic ester substituents. The addition of 5 eq of H_2O to the polymerization mixture led to a slightly reduced yield of a copolymer (16, Table 3) with M_n(GPC) = 13 200 (of the decanoate derivative).

Cycloaliphatic polyolefins with methyl carboxylate side chains were obtained from the copolymerization of norbornene and 5-norbornene-2-carboxylic acid methyl ester (**3**; 17–20, Table 3). The molecular weights of these copolymers with M_n(GPC) values between 10 500 and 64 000 were considerably higher than the molecular weights of poly-**3** obtained by the homopolymerization of **3**. As for the previous samples, 10–16 of Table 3, the molecular weight distributions are quite broad, which indicates a nonliving polymerization system.

The ester derivative **3** is slightly less reactive than norbornene in the addition polymerization which leads to copolymers with a lower number of ester-substituted repeating units than expected from the comonomer ratio of the feed ($a < q/(q + m)$ in eq 3). The level of comonomer incorporation of **3**, a in eq 3, was determined from the intensity of the ^{1}H NMR signal at $\delta = 3.5-3.7$ ppm corresponding to the $CH_3OC(O)$ protons.

Copolymers 17–19 (Table 3) with less than 20% of ester-substituted monomeric units incorporated were soluble in chlorobenzene and chloroform. A higher level of methyl ester substitution such as $a = 0.38$ in 20 of Table 3 led to additional solubility in toluene and THF.

A norbornene-based copolymer with 0.20 carboxylic acid group per repeating unit was obtained from the Pd(II)-catalyzed polymerization of norbornene and *endo*-5-norbornene-2-carboxylic acid (**4**), using a 50/50 mole ratio of norbornene to **4**. The resulting copolymer 21 (Table 3) was soluble in THF but insoluble in chlorobenzene due to the protic polar substituents. The inherent viscosity in THF was 0.52 dL/g.[22] No polyelectrolyte effect was observed. The solution viscosity increased only marginally upon further dilution.

Conclusions

In-situ (η^3-allyl)palladium complexes with weaky coordinating tetrafluoroborate and hexafluoroantimonate ions were found to be highly active catalysts for the addition polymerization of norbornene derivatives with functional groups. The activity of the palladium catalyst increased with increasing size of the counterion and decreasing association with Pd(II). In contrast to two ionic palladium–nitrile complexes, the (η^3-allyl)palladium complexes were also effective catalysts for the polymerization of the endo isomers of norbornene derivatives. Homo- and copolymers of polycycloolefins with ester and hydroxyl groups were prepared. A product with 0.2 acid group per repeating unit was obtained from the copolymerization of norbornene and bicyclo[2.2.1]hept-5-ene-2-carboxylic acid.

Experimental Section

General Procedures and Materials. All work involving air- and/or moisture-sensitive compounds was carried out by using standard high-vacuum, Schlenk or drybox (M. Braun) techniques. NMR spectra were recorded on Jeol GX270 (270.05 MHz) and Varian Unity 500 (499.8 MHz) instruments. Inherent viscosities were determined for polymer solutions (0.3 g/dL) in THF at 25 °C. Gel permeation chromatographic (GPC) analyses utilized a Polymer Standards Service column (10 μm gel, SDV linear, 60 cm), a Knauer HPLC Pump 64, and a Waters differential refractometer (R 401). All GPC analyses were performed on solutions in chlorobenzene (0.4–0.8 g/dL). Calibration was based on five polystyrene standards ranging from M_n 5200 to 580 000 ($M_w/M_n < 1.1$). Dichloromethane and chlorobenzene were dried over CaH_2 and distilled. Pyridine was distilled from KOH. Nitrobenzene and nitromethane were dried by stirring over P_4O_{10} and then vacuum-distilled. Diethyl ether was vacuum transferred from sodium benzophenone ketyl and stored under nitrogen. Toluene (Aldrich), THF (Merck), methanol (BDH), and nitrosonium tetrafluoroborate (Aldrich) were used as obtained from the suppliers. Acetonitrile, propionitrile, and dichloromethane-d_2 were dried over CaH_2 and then vacuum-transferred. Nitromethane-d_3 (Aldrich) was dried over 4 Å molecular sieves and then vacuum-transferred. Octanoyl chloride and decanoyl chloride (Aldrich) were used without further purification. 2-(Hydroxymethyl)bicyclo[2.2.1]hept-5-ene (exo/endo = 20/80) (Aldrich) was vacuum-distilled. The corresponding octanoic and decanoic acid esters were prepared as previously described.[11] Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid methyl ester (**3**) (exo/endo = 20/80) was prepared by a Diels–Alder reaction of cyclopentadiene and methyl acrylate.[14a] *endo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (**4**) was prepared and separated from the exo isomer according to procedures by Roberts et al.[14a] and Ver Nooy and Rondestvedt.[14b] All monomers were dried over CaH_2 and vacuum-distilled. $[Pd(CH_3CN)_4][BF_4]_2$ was prepared according to a procedure published by Schramm and Wayland.[23] (η^3-Allyl)palladium chloride dimer[24] was synthesized from sodium tetrachloropalladate, allyl chloride, and carbon monoxide, all from Aldrich.

Preparation of Tetrakis(propionitrile)palladium(II) Bis(tetrafluoroborate). A 100-mL Schlenk flask was charged with 563 mg (5.29 mmol) of palladium sponge, 1.50 g (12.84 mmol) of nitrosonium tetrafluoroborate, and 4.5 mL (81.7 mmol) of propionitrile. A green solution formed upon stirring at ambient temperature. The NO formed was removed by applying a slight vacuum. After 10 min, 7.5 mL of nitromethane was added (under nitrogen). The mixture was kept stirring at 20 °C, and NO was removed by applying a vacuum at 30–45-min intervals for 4 h. The color of the solution gradually changed from green to yellow. After a total reaction time of 16 h at 20 °C, the solution was filtered from unreacted $NOBF_4$ and then added to 18 mL of diethyl ether to precipitate the cationic palladium nitrile complex. The product was filtered and dried at 0.01 Torr and 20 °C for 7 h. Yield: 2.0 g (76%). ^{1}H NMR (CD_3NO_2): δ 3.01 (q, $J = 7.5$ Hz, 2H, CH_2), 1.39 (t, $J = 7.5$ Hz, 3H, CH_3). ^{13}C NMR (CD_3NO_2): δ 129.30 (CN), 13.47 (CH_2), 9.51 (CH_3). IR (Nujol): 2341 (m), 1152 (s), 1089 (s), 1005 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{20}B_2F_8N_4Pd$: C, 28.81; H, 4.03; N, 11.20. Found: C, 28.75; H, 3.94; N, 11.39.

In-Situ Preparation of Pd Complex IIb for NMR Analysis. $[(\eta^3\text{-allyl})PdCl]_2$ (22 mg, 0.060 mmol) and 37 mg (0.190 mmol, 58% excess) of $AgBF_4$ were stirred in 1.3 mL of CD_2Cl_2. After 30 min at 20 °C, the yellow mixture was passed through a Whatman PTFE syringe filter with 0.45-μm pore size to remove the AgCl formed. ^{1}H NMR (CD_2Cl_2): δ 5.93 (tt, $J_1 = 12.1$ Hz, $J_2 = 6.8$ Hz, 1H, CH), 4.64 (d, $J = 6.8$ Hz, 2H, CH_2(syn)), 3.52 (d, $J = 12.1$ Hz, 2H, CH_2(anti)). ^{13}C NMR (CD_2Cl_2): δ 116.2 (*C*H), 67.0 (*C*H_2).

A solution for ^{19}F NMR spectroscopy was prepared similarly: 52.8 mg (144 μmol) of $[(\eta^3\text{-allyl})PdCl]_2$ and 56.2 mg (289 μmol) of $AgBF_4$ in 1.5 mL of CD_2Cl_2, 30 min at 20 °C. ^{19}F NMR: (CD_2Cl_2, 20 °C), δ −148.0 (br s, free BF_4^- and unknown side product, 5%), −153.9 (br s, BF_4^- of Pd(allyl) complex, 95%); (0 °C), −147.0 (br s, unknown side product, 3%), −147.9 (free BF_4^-, 2%), −153.2 (br s, BF_4^- of Pd(allyl) complex, 95%); (−40 °C), −146.6 (br s, side product, 3%), −147.35 (s, free $^{10}BF_4^-$), −147.41 (s, free $^{11}BF_4^-$), −151.73 (br s, $^{10}BF_4^-$ of Pd(allyl) complex), −151.79 (br s, $^{11}BF_4^-$ of Pd(allyl) complex); (−80 °C), −146.1 (br s, side product, 3%),−147.08 (s, free $^{10}BF_4^-$), −147.14 (s, free $^{11}BF_4^-$), −150.25 (br s, $^{10}BF_4^-$ of Pd(allyl) complex), −150.31 (br s, $^{11}BF_4^-$ of Pd(allyl) complex).

In-Situ Preparation of Pd Complex IIa for ^{1}H NMR Analysis. $[(\eta^3\text{-allyl})PdCl]_2$ (22 mg, 0.060 mmol), 50 mg (0.145 mmol, 21% excess) of $AgSbF_6$, and 1.3 mL of CD_2Cl_2 were stirred for 30 min at 20 °C and filtered. ^{1}H NMR (CD_2Cl_2): δ 6.08 (tt, $J_1 = 12.3$ Hz, $J_2 = 6.8$ Hz, 1H, CH), 4.87 (d, $J = 6.8$ Hz, 1H, CH_2(syn)), 3.74 (d, $J = 12.3$ Hz, 1H, CH_2(anti)).

In-situ preparation of **5a** for ^{13}C NMR analysis: 42.4 mg (0.116 mmol) of $[(\eta^3\text{-allyl})PdCl]_2$, 86.0 mg (0.259 mmol, 8% excess) of $AgSbF_6$, and 1.3 mL of CD_2Cl_2, 30 min at 20 °C. ^{13}C NMR (CD_2Cl_2): 118.5 (*C*H), 70.4 (*C*H2).

Gravimetric Determination of AgCl Liberated in the Preparation of IIb. $[(\eta^3\text{-allyl})PdCl]_2$ (24.7 mg, 0.068 mmol), 32.2 mg (0.165 mmol, 22% excess) of $AgBF_4$, and 2 mL of CH_2Cl_2 were stirred for 30 min at 20 °C. The mixture was filtered through a Whatman PTFE syringe filter with 0.45-μm pore size to capture the AgCl formed. The syringe filter was thoroughly washed with dichloromethane, methanol (to remove unreacted $AgBF_4$), and again with dichloromethane. The filter was dried (in the dark) at 40 °C and 0.01 Torr until the weight remained constant. Weight increase of the filter due to AgCl formed: 18.7 mg corresponding to 96.6% of the theoretical value (assuming that all of the chloride has been abstracted).

Preparation of Polymers. Homopolymerization of Bicyclo[2.2.1]hept-5-enyl-2-methyl Octanoate (1c) (Endo/Exo = 80/20) with $[Pd(CH_3CN)_4][BF_4]_2$ in Nitromethane. Preparation of Poly-1c (1, Table 1). A 25-mL Schlenk flask was charged with 17 mg (0.038 mmol) of $[Pd(CH_3CN)_4][BF_4]_2$ and 5 mL of nitromethane. The norbornene derivative **1c** (957 mg, 3.83 mmol) was added with a syringe. After 16 h at 20 °C, the viscous solution was poured into a mixture of 30 mL of methanol to precipitate the polymer. The cloudy mixture was left standing for 24 h, and the polymer settled in the form of an oil on the bottom of the flask. The supernatant was decanted off, and the oily polymer was carefully washed with methanol (twice) and dried at 80 °C and 0.01 Torr. Yield: 239 mg (25%); M_n(GPC) = 7200, M_w(GPC) = 12 000. ^{1}H NMR ($CDCl_3$): δ 4.3−3.9 (br m, $CH_2OC(O)$ endo), 3.9−3.7 (br m, CH_2-OC(O exo), 2.3−2.2 (br m, 2H, $OC(O)CH_2$), 2.20−1.95 (br m, H^1, H^4, partial overlap with 2.3−2.2), 1.9−1.5 (br m, H^5, H^6, H^{2x}, H^{3x}, partially resolved), 1.60 (br m, 2H, $OC(O)CH_2CH_2$), 1.4−1.0 (br m, $H^{7s,a}$, H^{2n}, H^{3n}, partially overlapped by 1.27), 1.27 (br m, 8H, $C(O)CH_2CH_2(CH_2)_4$), 0.88 (br t, 3H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 173.8−173.5 (C═O), 67.9−66.3 (CH_2OC-(O)), 34.4 ($OC(O)CH_2$), 31.7 ($CH_2CH_2CH_3$), 29.2 ($CH_2(CH_2)_2$-CH_3), 29.0 ($C(O)(CH_2)_2CH_2$), 25.0 ($C(O)CH_2CH_2$), 22.6 (CH_2-CH_3), 14.1 (CH_3), in addition an unresolved set of signals due to several triad structures between $\delta = 53$ and 30 (C^7−C^1).

Polymerization of 1c (Endo/Exo = 80/20) with $[Pd(C_2H_5CN)_4][BF_4]_2$ in Nitrobenzene/Dichloromethane (Volume Ratio 4/1) (2, Table 1). The catalyst solution was prepared from 21 mg (42 μmol) of $[Pd(C_2H_5CN)_4][BF_4]_2$ in 1 mL of dichloromethane. A monomer solution of 1.01 g (4.0 mmol) of monomer **1c** in 4 mL of nitrobenzene was added. After 120 h at 20 °C, the polymer was isolated as described above. Yield: 400 mg (40%), M_n(GPC) = 6800, M_w(GPC) = 8700. ^{1}H NMR ($CDCl_3$) is presented in Figure 2b. ^{13}C NMR ($CDCl_3$) as above.

The clear supernatant liquid decanted off the precipitated polymer was subjected to a vacuum of 0.4 Torr at 20 °C to remove the methanol and the nitrobenzene. A residue of 580 mg remained which consisted exclusively of unreacted endo monomer **1c** as shown by the ^{1}H NMR spectrum in Figure 1b.

Homopolymerization of Bicyclo[2.2.1]hept-5-enyl-2-methyl Decanoate (1d) (Endo/Exo = 80/20) with In-Situ (η^3-Allyl)palladium Tetrafluoroborate (IIb). Preparation of Poly-1d (6, Table 1). A sample vial was charged with 13.2 mg (3.6×10^{-5} mol) of (η^3-allyl)palladium chloride dimer, 20 mg (10.3×10^{-5} mol) of silver tetrafluoroborate, and 2 mL of chlorobenzene. The catalyst mixture was stirred for 20 min at 20 °C. The silver chloride formed was filtered off with a syringe filter (0.45 μm). The clear yellow solution was added to 1 g (3.6×10^{-3} mol) of the decanoic acid ester of 2-(hydroxymethyl)-5-bicyclo[2.2.1]heptene. The reaction mixture was stirred for 48 h at 20 °C, and the polymer was isolated by precipitation with methanol. The product was dried at 79 °C for 12 h. Yield: 0.97 g (97%); M_n(GPC) = 9600, M_w(GPC) = 23 000. ^{1}H NMR ($CDCl_3$): shifts identical with those of poly-**1c**, the intensity of $\delta = 1.27$ corresponds to 12H. ^{13}C NMR ($CDCl_3$): shifts identical with those of poly-**1c**, in addition: δ 29.5 ($C(O)(CH_2)_3CH_2$), 29.3 ($C(O)(CH_2)_4CH_2$).

Homopolymerization of Bicyclo[2.2.1]hept-5-enyl-2-methyl Decanoate (1d) (Endo/Exo = 80/20) with In-Situ (η^3-Allyl)palladium Tetrafluoroborate (IIa). Preparation of Poly-1d (8, Table 1). The same procedure as above was used with 13.2 mg (3.6×10^{-5} mol) of $[(\eta^3\text{-allyl})PdCl]_2$, 33.0 mg ($9.6 \times 10^{-5}$ mol) of $AgSbF_6$, and 1.00 g (3.60×10^{-3} mol) of monomer **1d**, 18 h at 20 °C. Yield: 99%; M_n(GPC) = 25 000, M_w(GPC) = 55 000.

The other polymerizations of Table 1 were carried out in a similar fashion.

Copolymerization of Norbornene and Bicyclo[2.2.1]-hept-5-enyl-2-methyl Decanoate (1d) (Endo/Exo = 80/20) with IIa (12, Table 3). A mixture of 29.4 mg (8.04×10^{-5} mol) of $[(\eta^3\text{-allyl})PdCl]_2$, 85 mg ($2.47 \times 10^{-4}$ mol) of $AgSbF_6$, and 5 mL of chlorobenzene was stirred for 20 min at 20 °C. The yellow catalyst mixture was filtered and added to a monomer solution which contained 1.5 g (16.0 mmol) of norbornene, 1.1 g (4.0 mmol) of **1d**, 29 μL (1.6 mmol) of H_2O, and 20 mL of chlorobenzene. The polymerization was carried out at 20 °C for 18 h. The copolymer was precipitated by addition to 150 mL of methanol, filtered, washed with MeOH, and dried at 70 °C for 12 h. Yield: 2.0 g (80%); M_n(GPC) = 184 000, M_w(GPC) = 524 000. ^{1}H NMR ($CDCl_3$): δ 4.3−3.7 (br m, $CH_2OC(O)$), 2.27 (br m, $OC(O)CH_2$), 1.57 (br m, OC(O)-CH_2CH_2), 1.26 (br m, $(CH_2)_6CH_3$), 0.88 (t, CH_3). All of these signals are superimposed over a set of very broad unresolved signals between 2.3 and 1.0 ppm (H^1 to $H^{7s,a}$). From the intensity of the signals at $\delta = 0.88$ and 4.3−3.7 the mole fraction of **1d** incorporated in the copolymer was determined as 15% ($a = 0.15$ in Table 3). ^{13}C NMR ($CDCl_3$): δ 173.9−173.5 (C═O), 67.8−66.5 ($CH_2OC(O)$), 34.4 ($OC(O)CH_2$), 31.7 ($CH_2CH_2CH_3$), 29.5 ($C(O)(CH_2)_3CH_2$), 29.3 ($C(O)(CH_2)_2CH_2$), 29.2 ($CH_2(CH_2)_2CH_3$), 29.0 ($C(O)(CH_2)_2CH_2$), 25.0 ($C(O)CH_2CH_2$), 22.6 (CH_2CH_3), 14.1 (CH_3), in addition an unresolved set of signals due to several triad structures was observed between $\delta = 53$ and 30 (C^7−C^1).

Palladium-containing end groups were removed by a reduction reaction with $NaBH_4$. Polymer (0.5 g) was dissolved in 25 mL of chlorobenzene. Methanol was added dropwise until the solution became slightly turbid (~1 mL of MeOH). Then 0.1 g of $NaBH_4$ was added, and the mixture was stirred for 3 h at 20 °C. The mixture was kept standing for 16 h for the black Pd(0) particles to coagulate and then filtered. The volume of the solution was reduced in vacuum to approximately one third of its volume, and then the polymer was precipitated with methanol, filtered, and dried. This sample was used for elemental analysis. Anal. Calcd for $(C_7H_{10})_{0.85}/(C_{18}H_{30}O_2)_{0.15}$: C, 85.36; H, 10.69. Found: C, 85.76; H, 10.72.

Polymerizations 10, 11, 13, and 14 (Table 3) were carried out in a similar fashion.

Copolymerization of Norbornene (nbe) and 2-(Hydroxymethyl)bicyclo[2.2.1hept-5-ene (2) (Endo/Exo = 80/20) with IIa (15, Table 3). A catalyst solution was prepared from 20 mg (5.5×10^{-5} mol) of $[(\eta^3\text{-allyl})PdCl]_2$, 45 mg ($1.3 \times 10^{-4}$ mol) of $AgSbF_6$, and 2 mL of chlorobenzene. The polymerization was carried out with 0.411 g ($4.4 \text{ x } 10^{-3}$ mol) of nbe and 0.136 g (1.1×10^{-3} mol) of **2** (endo/exo = 80/20) in 2 mL of chlorobenzene. The copolymer was isolated after 1 h at 20 °C. Yield: 0.43 g (79%). The polymer was soluble in chloroform and chlorobenzene at elevated temperatures. It remained mainly insoluble in these solvents at room temperature. ^{1}H NMR (bromobenzene-d_5, 60 °C): δ 3.8−3.2 (br m, CH_2O and CH_2OH), 2.4−2.1 (br m, H^1([**2**]), H^4([**2**]), H^{2x}([**2**]), H^1([nbe]), H^4-([nbe])), 1.9−1.6 (very broad multiplet, partially overlapping with neighboring signals, H^5([**2**]), H^6([**2**]), H^2([nbe]), H^3([nbe])), 1.5−1.3 (br m, unresolved, H^{2n}([**2**]), $H^{7s,a}$([**2**]), H^{3x}([**2**]), H^{5x}-([nbe]), H^{6x}([nbe]), H^{7s}([nbe])), 1.2−1.0 (br m, overlapping with previous signal, H^{3n}([**2**]), H^{5n}([nbe]), H^{6n}([nbe]), H^{7a}([nbe])). From the intensity of the signal at $\delta = 3.8$−3.2 the mol fraction of incorporated hydroxymethyl derivative was calculated as 15% ($a = 0.15$ in eq 3).

For molecular weight analysis, the hydroxyl groups of the copolymer were converted into the corresponding decanoic ester groups. A mixture of 204 mg of copolymer 15 (Table 3), 10 mL of pyridine, and 2 mL of decanoyl chloride was heated to 80 °C for 3h. The product was precipitated with methanol, filtered, washed with methanol, and dried. Yield: 271 mg of decanoic ester derivative (which contained traces of pyridine hydrochloride and decanoic acid); M_n(GPC) = 18 500, M_w(GPC) = 27 000. The ^{1}H NMR and ^{13}C NMR chemical shifts were identical with those of copolymer 12 (Table 3).

Copolymer 16 (Table 3) was prepared and analyzed in a similar fashion.

Copolymerization of nbe and Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid Methyl Ester (3) (Endo/Exo = 80/20) with IIa (18, Table 3). The catalyst solution consisted of 60.2 mg (16.5×10^{-5} mol) of [(η^3-allyl)PdCl]$_2$, 113 mg (32.9×10^{-5} mol) of $AgSbF_6$, and 5 mL of chlorobenzene, filtered and added to a monomer mixture of 1.24 g (13.2 mmol) of nbe, 0.5 g (3.3 mmol) of **3**, 59 μL (3.3 mmol) of water, and 10 mL of chlorobenzene. The reaction mixture was stirred for 15 h at 20 °C. The polymer was isolated and dried as described above. Yield: 1.44 g (83%); M_n(GPC) = 60 000, M_w(GPC) = 233 000. ^{1}H NMR ($CDCl_3$): δ 3.6 (br s, C(O)OCH$_3$), 2.8−2.6 (br m, H^{2x}([**3**])), 2.4−2.0 (very broad unresolved m, overlapping with neighboring signals, H^{2n}([**3**]), H^1([**3**]), H^4([**3**]), H^1([nbe]), H^4([nbe])), 1.9−1.6 (very broad m, overlapping with neighboring signals, H^{3x}([**3**]), H^5([**3**]), H^6([**3**]), H^2([nbe]), H^3([nbe])), 1.55−1.25 (br m, overlapping with neighboring signals, H^{7s,a}([**3**]), H^{3n}([**3**]), H^{5x}([nbe]), H^{6x}([nbe]), H^{7s}([nbe])), 1.2−1.0 (very broad m, overlapping with previous signal, H^{5n}([nbe]), H^{6n}([nbe]), H^{7a}([nbe])).

From the intensity of the signal at $\delta = 3.6$, the mol fraction of incorporated ester derivative was determined as 10% ($a = 0.10$ in eq 3).

Copolymers 17, 19, and 20 (Table 3) were prepared in a similar fashion.

Copolymerization of Norbornene and Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid (100% Endo) (4) with IIa (21, Table 3). A catalyst solution containing the following was used: 17.5 mg (4.8×10^{-5} mol) of [(η^3-allyl)PdCl]$_2$, and 32.9 mg (9.8×10^{-5} mol) of $AgSbF_6$ in 3 mL of chlorobenzene. A monomer solution containing the following was used: 450 mg (4.78 mmol) of nbe, 660 mg (4.78 mmol) of **4**, and 17.5 μL (9.7 mmol) of H_2O. The reaction was carried out for 1 h at 20 °C. The copolymer was isolated and dried as described above. Yield: 49%, $\eta_{inh} = 0.52$ dL/g in THF.

Palladium of the end groups was removed by bubbling a mixture of argon and hydrogen (volume ratio of 90/10) through a polymer solution in THF for 3 h. Palladium(0) precipitated and was removed by filtration over silica gel. ^{1}H NMR (THF-d_8): δ 11.0−10.2 (vbr, COOH), 2.7−2.5 (br m, H^{2x}([**4**])), 2.4−2.0 (very broad unresolved m, overlapping with neighboring signals, H^{2n}([**4**]), H^1([**4**]), H^4([**4**]), H^1([nbe]), H^4([nbe])), 1.9−1.6 (very broad m, overlapping with neighboring signals, H^{3x}([**4**]), H^5([**4**]), H^6([**4**]), H^2([nbe]), H^3([nbe])), 1.55−1.25 (br m, overlapping with neighboring signals, H^{7s,a}([**4**]), H^{3n}([**4**]), H^{5x}([**4**]), H^{6x}([nbe]), H^{7s}([nbe])), 1.2−1.0 (very broad m, overlapping with previous signal, H^{5n}([nbe]), H^{6n}([nbe]), H^{7a}([nbe])). IR (KBr): 3500−2500 (m), 2949 (s), 2865 (s), 1702 (s), 1452 (m), 1150 (w), 1337 (w), 1298 (m), 1260 (m), 1223 (m), 1110 (m), 937 (w), 804 (m), 705 cm^{-1} (w). The mol fraction of incorporated acid **4** was determined from the intensity of 1702 and 804 cm^{-1}: $a = 0.20$ (eq 4); calibration with mixtures of the hompolymers of poly(2,3-bicyclo[2.2.1]hept-2-ene) and poly(5,6-bicyclo[2.2.1]-hept-5-ene-2-carboxylic acid). (A low molecular weight hompolymer of the acid **4** (with $\eta_{inh} = 0.08$ dL/g in THF) was prepared from 3.8×10^{-5} mol of [(η^3-allyl)PdCl]$_2$, 7.7×10^{-5} mol of $AgSbF_6$, 7.7 mmol of **4**, and 3 mL of chlorobenzene, 68 h at 20 °C, precipitation with *n*-hexane, 45% yield).

Acknowledgment. We thank Dr. Brian L. Goodall and Dr. Ken Glass for many helpful discussions, and Dr. Lynda K. Johnson for very friendly general advice. We are very grateful to Mrs. Geraldine Fitzpatrick and Mr. Eric Connor for valuable technical assistance. Financial support by EOLAS (now Forbairt), EC-Human Capital and Mobility, BFGoodrich, and BASF is gratefully acknowledged. We thank Johnsson Matthey for a generous loan of transition metal compounds.

References and Notes

(1) (a) Fried, J. R. *Polymer Science and Technology*; Prentice Hall PTR: Englewood Cliffs, NJ, 1995. (b) Cowie, J. M. G. *Polymers: Chemistry and Physics of Modern Materials*, 2nd ed; Chapman & Hall: New York, 1991.

(2) Pineri, M.; Eisenberg, A. *Structure and Properties of Ionomers*; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1987.

(3) Paul, D. R.; Newman, S.; *Polymer Blends*; Academic Press, Inc.: New York, 1978; Vols. I and II.

(4) Wake, W. C. *Adhesion and the Formulation of Adhesives*, 2nd ed.; Applied Science Publishers, Ltd.: London, 1982.

(5) (a) Galli, P. *Macromol. Symp.* **1995**, *89*, 13. (b) Weissermel, K. H.; Arpe, J. *Industrial Organic Chemistry*; VCH Publishers: Weinheim, Germany, 1993.

(6) (a) Fink, G.; Mülhaupt, R.; Brintzinger, H. H. *Ziegler Catalysts*; Springer-Verlag: Berlin, 1995. (b) Kaminsky, W.; Sinn, H. *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Springer-Verlag: Berlin, 1988. (c) Boor, J. Jr., *Ziegler−Natta Catalysts and Polymerization*; Academic Press: New York, 1979.

(7) Leading references: (a) Grubbs, R. H. Lecture presented at ISOM 11, International Symposium on Olefin Metathesis and Related Chemistry. Durham, England, July 1995. (b) Kanaoka, S.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 4707. (c) Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H. *Macromolecules* **1992**, *25*, 3345. (d) Bazan, G. C.; Schrock, R. R.; Cho, H.-N.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495. (e) Mortell, K. H.; Gingras, M.; Kiessling, L L. *J. Am. Chem. Soc.* **1994**, *116*, 12053. (f) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (g) Novak, B. M., Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542. (h) Novak, B. M., Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960. (i) Amir-Ebrahimi, V.; Byrne, D.; Hamilton, J. G.; Rooney, J. J. *Macromol. Chem. Phys.* **1995**, *196*, 327. (j) Bell, B.; Hamilton, J. G.; Law, E. E.; Rooney, J. J. *Macromol. Rapid. Commun.* **1994**, *15*, 543. (k) Feast, W. J.; Harrison, D. B. *Polymer* **1991**, *32*, 558. (l) Zenkl, E.; Stelzer, F. *J. Mol. Catal.* **1992**, *76*, 1. (m) Thorn-Csanyi, E.; Harder, C.; Dahlke, B. *J. Mol. Catal.* **1992**, *76*, 93. (n) Castner, K. F.; Calderon, N. *J. Mol. Catal.* **1982**, *15*, 47. (o) Porri, L.; Diversi, P.; Lucherini, A.; Rossi, R. *Makromol. Chem.* **1975**, *176*, 3131. (p) Porri, L.; Rossi, R.; Diversi, P.; Lucherini, A. *Makromol. Chem.* **1974**, *175*, 3075. (q) Matsumoto, S.; Kumatsu, K.; Igarashi, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1977**, *18*, 110. (r) Charbonage de France, French Patent 1,556,215; *Chem. Abstr.* **1969**, *71*, 71703h. (s) Rinehart, R. H.; Smith, H. P. *J. Polym. Sci., Polym. Lett.* **1965**, *3*, 1049.

(8) (a) Chung, T. C.; Rhubright, D. *Macromolecules* **1991**, *24*, 970. (b) Chung, T. C. *Macromolecules* **1988**, *21*, 865.

(9) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679.

(10) (a) Schultz, R. G. *J. Polym. Sci., Polym. Lett.* **1966**, *4*, 541. (b) McKeon, J. E.; Stracher, P. S. US. Pat. 3330815, 1967; *Chem. Abstr.* 1967, *67*, 64884g.

(11) Breunig, S.; Risse, W. *Makromol. Chem.* **1992**, *193*, 2915.

(12) Addition homopolymers and block copolymers of diethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylates serving as precursor polymers to polyacetylenes have been prepared with π-stabilized Pd(II) alkyl complexes: (a) Safir, A. L.; Novak, B. M. *Macromolecules* **1995**, *28*, 5396. (b) Safir, A. L.; Novak, B. M. *Macromolecules* **1993**, *26*, 4072. Ni- and Pd-catalyzed polymerizations of predominantly alkyl-substituted norbornene derivatives have recently been described in the following: (c) Maezawa, H.; Matsumoto, J.; Aiura, H.; Asahi, S. (Idemitsu Kosan Co. Ltd., Jpn.). Eur. Pat. Appl. 445 755 A2, 1991. (d) Goodall, B. L.; Benedikt, L. H.; McIntosh, L. H., III; Barnes, D. A.; Rhodes, L. F. (BFGoodrich). Patent WO 95/14048, 1995. (e) Goodall, B. L.; Benedikt, G. M.; McIntosh, L. H., III; Barnes, D. A. (BFGoodrich). U.S. Patent 5 468 819, 1995.

(13) These assignments are based on a comparison with the ^{1}H NMR signals of the exo- and endo-linked CH$_2$OCO substituents of the bicyclo[2.2.1]heptyl-2-methyl octanoate. After hydrogenation of **1c**, the endo-substituted CH$_2$OCO group

does not experience the deshielding effect of the olefin any more, and the corresponding ^{1}H NMR signals are shifted from $\delta = 3.61$ and 3.81 to 3.92 and 4.07 ppm, respectively.

(14) (a) Roberts, J. D.; Trumbull, E. R., Jr.; Bennett, R.; Armstrong, R. *J. Am. Chem. Soc.* **1950**, *72*, 3116. (b) Ver Nooy, C. D.; Rondestvedt, C. S., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 3586. (c) Arjona, O.; de la Pradilla, R. F.; Plumet, J.; Viso, A. *J. Org. Chem.* **1991**, *56*, 6227. (d) Nelson, G. L.; Kuo, C.-L. *Synthesis* **1975**, 105. (e) Magoon, E. F.; Slaugh, L. H. *J. Organomet. Chem.* **1973**, *55*, 409.

(15) More stable (η^3-allyl)palladium complexes have been prepared via the addition of stronger electron-donating ligands to solutions obtained from reactions of (η^3-allyl)palladium chloride dimer with silver salts, e.g.: Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620.

(16) The presence of a weak Pd−F interaction is likely for complex **IIa** containing the SbF_6^- counterion.[17] However, currently we cannot provide any experimental proof for that interaction. In any case, the ^{1}H NMR data show that the Pd−F interaction is stronger in complex **IIb**.

(17) Stable transition metal complexes containing tetrafluoroborate or hexafluoroantimonate as weakly coordinating ligands have been isolated and characterized by X-ray crystallography and NMR and IR spectroscopy, e.g.: (a) Hersh, W. H. *Inorg. Chem.* **1990**, *29*, 713. (b) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2869. (c) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405. (d) Horn, E.; Snow, M. R.; Tiekink, E. *Aust. J. Chem.* **1987**, *40*, 761. (e) Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599. (f) Shelly, K.; Bartczak, T.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1985**, *24*, 4325. (g) Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Inorg. Chim. Acta* **1982**, *68*, 75. (h) Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186. (i) Roulet, R.; Vouillamoz, R. *Helv. Chim. Acta* **1974**, *57*, 2139.

(18) Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfsberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 2349.

(19) Fernández, J. M.; Gladysz, J. A. Inorg. Chem. **1986**, *25*, 2672.

(20) Very high molecular weights, a higher stereoregularity, or a small amount of potential side reactions with the ester groups can be responsible for the low solubility of copolymers when the activity of catalyst **IIa** is not moderated.

(21) The molecular weight distributions of most of the products listed in Table 3 are very broad, which is currently not fully understood. Fast chain propagation in comparison to initiation and small amounts of secondary reactions at the functional groups are potential causes for high polydispersities (M_w/M_n between 2 and 6) of polymers prepared with the highly active catalysts **IIa** and **IIb**. However, we have previously shown that the less active nitrile-based catalysts $[Pd(RCN)_4][BF_4]_2$ behave in a more controlled way, when the pure exo ester derivatives of **1a,b,f** were polymerized.[11] A nearly linear relationship between molecular weight and the mole ratio of monomer to Pd catalyst was found for polymerizations with the nitrile-based Pd catalysts. The polydispersities of poly-**1a,b,f** obtained with monomer to Pd catalyst ratios below 200/1 were in the range of 1.2−1.6.

(22) For comparison, a poly(bicyclo[2.2.1]hept-2-ene) sample with $\eta_{inh} = 0.42$ dL/g in chlorobenzene had a M_n(GPC) of 55 000 (GPC calibrated with polystyrene).

(23) Schramm, R. F.; Wayland, B. B. *J. Chem. Soc., Chem. Commun.* **1968**, 898.

(24) Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.

MA9515285