

Polymerization of norbornene by palladium(II) complexes bearing ethylene-bridged bisindolinyl- or bis(1,2,3,4-tetrahydroquinolinyl) ligands

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Abstract

Novel moisture and air stable, cationic palladium(II) amine complexes (**1–4**) of the general type $[\text{Pd}(\text{N} \cap \text{N})(\text{X})_2](\text{BF}_4)_2$, [$\text{N} \cap \text{N}$ = 1,2-bis(*N*-indolinyl)ethane (BIE) **1**, **3**; 1,2-bis(*N*-1,2,3,4-tetrahydroquinolinyl)ethane (BTQE) **2**, **4**; X = NCCH_3 , H_2O] were found to catalyze the polymerization reaction of bicyclo[2.2.1]hept-2-ene at room temperature. The amorphous polymer products consist of 2,3-linked norbornene units; no indications for ring opened species could be observed. The polymerization activity of the diaqua-complexes **3**, **4** is superior compared to their acetonitrile analogues due to a facile activation by a Wacker-type reaction. The cationic Pd(II)-compounds are inactive towards homo- and copolymerization reactions of polar monomers, like acrylates or carbon monoxide. However, addition of methylacrylate resulted in polynorbornene products with increased molecular weight and narrow molecular weight distributions. © 1998 Elsevier Science B.V.

1. Introduction

The insertion polymerization of norbornene ¹ [1–9] was first mentioned in the early 1960's [10]. Beside Ti(IV) and Zr(IV)-based catalysts [10–12], Pd(II) compounds have been also applied successfully for the insertion polymerization of norbornene. Risse et al. [5] and Sen et al. [6,7] reported that cationic palladium(II) complexes bearing four weakly coordinated nitrile ligands are highly active catalysts for this type

of polymerization. The isolated poly(norbornene)s have relatively low solubility and show high glass transition temperatures ($T_g > 300^\circ\text{C}$) [5]. The Pd(II) catalyzed polymerization reactions are living in character as being indicated by narrow molecular weight distributions. Palladium(II) complexes bearing bidentate nitrogen containing ligands have been also applied for copolymerization reactions of alkenes with carbon monoxide [13–16] or with acrylate derivatives ([17–19] and references therein).

Recently, we reported on the synthesis and structural characterization of new palladium(II) complexes bearing rigid ethylene-bridged bisindolinyl- and bis(1,2,3,4-tetrahydroquinolinyl) amine ligands together with weakly coordinated acetonitrile or water moieties [20]. Herein we describe the ability of this new catalyst family

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¹ Different methods for polymerization of norbornene (bicyclo[2.2.1]hept-2-ene) are known: ring-opening metathesis polymerization (ROMP), cationic polymerization, radical polymerization and the vinyl-type olefin addition (1,2-insertion), where the polymerization involves exclusively the π -bond and leaves the bicyclic monomer unit intact.

Table 1
Results of norbornene polymerization^a

Run	Cat.	Norbornene/Pd (mol ratio)	Yield (g)	Conversion (%)	$10^{-4} \times \overline{M}_w$ (g/mol) ^b	$\overline{M}_w/\overline{M}_n$ ^b
1	1	600	3.50	70	7.5	1.31
2	2	600	2.90	58	21.0 ^c	1.42
3	3	600	4.83	97	7.1	1.46
4	4	600	4.60	92	8.9	2.17
5	4	50	0.22	55	6.5	1.84
6	4	100	0.55	70	7.2	1.91
7	4	300	2.07	89	8.7	2.02
8	4	1000	6.31	81	8.2	1.62

^aPolymerization conditions: Catalyst, 50 mg; reaction time, 1 h, T_p , 25°C; solvent, 50 ml CH_2Cl_2 , 5 ml 1,2-dichlorobenzene, 2 ml nitrobenzene.

^bMeasured by GPC relative to polystyrene.

^cRelative to linear polyethene standards.

to act as high activity, single component catalysts for the insertion polymerization of norbornene.

2. Experimental

Palladium (II) complexes $[\text{Pd}(\text{BIE})(\text{NCCCH}_3)_2](\text{BF}_4)_2$ (**1**), $[\text{Pd}(\text{BTQE})(\text{NCCCH}_3)_2](\text{BF}_4)_2$ (**2**), $[\text{Pd}(\text{BIE})(\text{OH}_2)_2](\text{BF}_4)_2$ (**3**), $[\text{Pd}(\text{BTQE})(\text{OH}_2)_2](\text{BF}_4)_2$ (**4**), were prepared according to literature procedures [5]. Reagent grade chemicals were used as received unless otherwise stated. CH_2Cl_2 was distilled from CaH_2 . Elemental analyses were performed by the Microanalytical Laboratories of the University. Molecular weights and molecular weight

distributions were determined by gel permeation chromatography (GPC) relative to polystyrene or narrow polyethene standards. IR spectra were recorded on a Bruker IFS113V spectrometer, TGA and DSC data were collected by a Perkin-Elmer DSC-7 with 10°C/min heating rate.

2.1. Polymerization experiments

Homopolymerization of norbornene: To a solution of the Pd(II) complex **1**, **2**, **3** or **4** (0.5 mg) in CH_2Cl_2 (50 ml), 1,2-dichlorobenzene (5.0 ml) and nitrobenzene (2 ml), norbornene was added (Table 1). The reaction mixture was stirred at room temperature for 1 h. At the end of this period the reaction was quenched by addition of methanol and the polymer was iso-

Table 2
Polymerization of norbornene in the presence of methylacrylate^a

Run	Norbornene/acrylate (mol ratio)	Yield (g)	$10^{-4} \times \overline{M}_w$ (g/mol) ^b	$\overline{M}_w/\overline{M}_n$ ^b
1	10.0	2.26	6.88	1.31
2	4.0	3.0	7.23	1.42
3	2.0	3.28	7.69	1.46
4	1.0	4.39	7.79	2.17
5	Acrylate, neat	— ^c	—	—

^aPolymerization conditions: Catalyst **4**, 50 mg; norbornene, 5.0 g; reaction time, 1 h; T_p , 25°C; solvent, 50 ml CH_2Cl_2 , 5 ml 1,2-dichlorobenzene, 2 ml nitrobenzene.

^bMeasured by GPC relative to polystyrene standards.

^cNo polymerization.

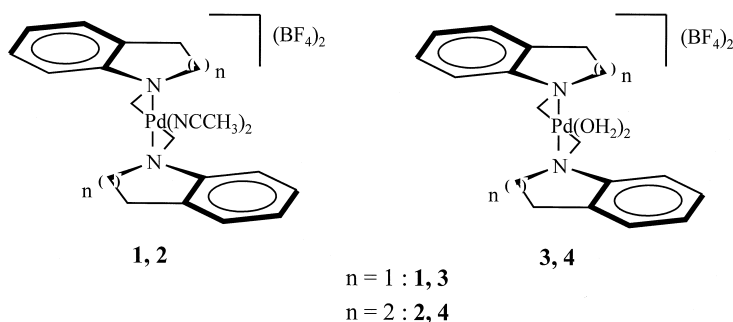


Fig. 1. Structure of the diacetonitrile- (1, 2) and diaquo (3, 4) complexes.

lated by filtration, washed with excess methanol and dried in vacuum at 80°C.

(C₇H₁₀)_n (94.16 g per monomer unit): Calc. C 89.29, H 10.7; found C 89.00, H 10.58.

Polymerization in the presence of methylacrylate: To a solution of the Pd(II) complex **4**, (0.5 mg, 0.082 mmol) in CH₂Cl₂ (50 ml), 1,2-dichlorobenzene (5.0 ml) and nitrobenzene (2 ml) norbornene (5.0 g) and methylacrylate (Table 2) were added. The reaction mixture was stirred at room temperature for 4 h and then poured into methanol, washed with excess methanol (200 ml) and dried in vacuum.

3. Results and discussion

The air- and moisture-stable palladium(II) complexes **1–4**, bearing ethylene-bridged bisindolyl- or bis(1,2,3,4-tetrahydroquinoliny) moieties (Fig. 1) and weakly coordinating acetonitrile or water ligands catalyze the polymerization of norbornene to amorphous², transparent poly(2,3-bicyclo [2.2.1]hept-2-ene) at room temperature in a reaction medium consisting of a mixture of dichloromethane, 1,2-dichlorobenzene and nitrobenzene.

² (a) Despite the chiral arrangement of BIE and BTQE at Pd(II) no influence on the product's stereoregularity was observed; (b) Interestingly, the diacetonitrile palladium(II) complex which bears the pure σ -donor ligand *N,N*-tetramethylethylene diamine (TMEDA) showed very poor activity, leading only to traces of the polymer product.

The diaquo compounds **3, 4** show a considerably higher activity for norbornene polymerization than the corresponding acetonitrile complexes **1, 2** (Table 1), leading to nearly quantitative norbornene conversion after 10 min.

The broader molecular weight distributions of the products obtained with **3** or **4** can be attributed to the formation of a heterogeneous reaction system by partial precipitation of the polymer before all the monomer had been consumed³ [21]. The higher rate of conversion of **3** and **4** compared to the acetonitrile complexes **1** and **2** might be due to fast, Wacker-like activation reaction [22–24] (Fig. 2). According to the same mechanism water might also activate Pd(II)-phosphine complexes in CO/alkene copolymerization reactions [25,26]. In analogy to this well investigated process, a liberated H₂O-molecule adds as nucleophile to the initially formed dicationic alkene complex **A**, leading to a metal alkyl bond (**B**) in which coordinated monomer can insert after displacement of the second H₂O-ligand (**C**)⁴.

³ Relatively high polydispersities of poly(2,3-bicyclo[2.2.1]hept-2-ene) samples have been already observed for high molecular weight polymers prepared with [Pd(NCCH₃)₄]²⁺.

⁴ Another possible mechanism involves a *cis*-(intramolecular) insertion reaction (migration of coordinated OH⁻, formed in situ in the presence of water) to give the σ -bonded β -hydroxyalkyl-palladium complex intermediate; cf. Ref. [22]. In order to learn more about the activation mechanism in those rigid and well defined complexes, further studies on the nature of the end groups in low molecular weight products and on the activation kinetics are underway.

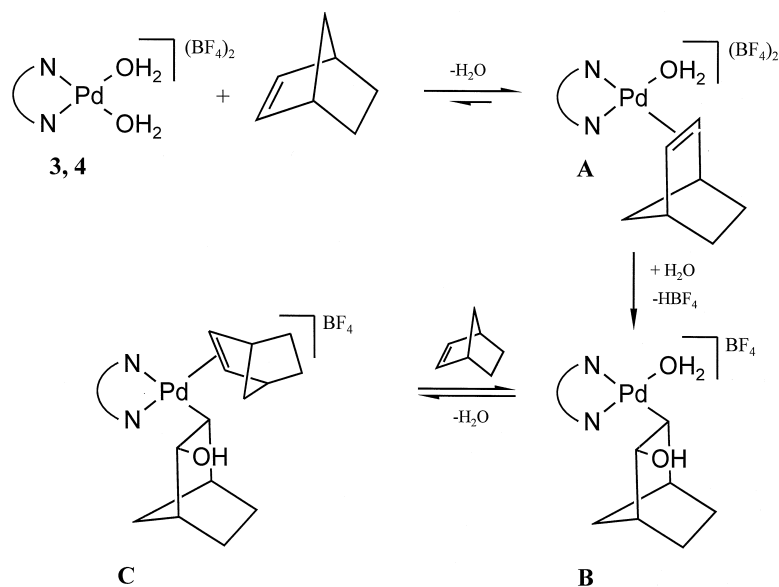


Fig. 2. Possible, Wacker-type activation mechanism for the aquo complexes.

Using $[\text{Pd}(\text{BTQE})(\text{OH}_2)_2](\text{BF}_4)_2$ (**4**) the polymerization reactions were carried out starting with various initial molar ratios of monomer (norbornene) to catalyst (Table 1). The relation between molecular weight and monomer conversion is approximately linear up to norbornene/Pd(II) ≈ 600 ⁵ Refs. [13,27]. At higher molar ratios, both the polymer yield and the molecular weight are increased. We would like to ascribe this effect to the ability of excess norbornene to serve as a solubilizing agent. The IR-spectra of the polymers are similar to those of the previously described vinyl-type poly(norbornene)s, prepared by Pd(II)-catalysis [4,11]. No absorption bands due to double bonds resulting from ring opening were observed.

According to thermogravimetric analysis (TGA) under nitrogen, the poly(norbornene)s prepared in this study behave similar to the polymers described previously by Risse et al. [5], where decomposition commences at 335°C.

The catalyst system used above showed no activity towards homopolymerization of polar α -olefins such as acrylate derivatives. Also addition of such monomers (or of CO) together with norbornene to a catalyst solution leads to the formation of pure poly(2,3-bicyclo [2.2.1]hept-2-ene). Right now, we have no genuine explanation for the fact that polar monomers, like CO or acrylates are not incorporated into the polymer chain. However, higher amounts of acrylate lead to slightly increased molecular weights and to improved monomer conversions (Table 2).

The Pd(II)-diaquo complexes **3**, **4** are highly active for norbornene polymerization as single-component catalysts. Due to the ease of structural variations of their rigid ligand systems they might open the way to a new family of late transition metal cycloolefin polymerization catalysts.

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⁵ This might suggest a living character of the Pd(II)-catalyzed polymerization reaction also in the case of σ -donor ligands, like BIE and BTQE. A similar dependence was already reported before.

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