Homo- and Copolymerization of Strained Cyclic Olefins with New Palladium(II) Complexes Bearing Ethylene-Bridged Heterodonor Ligands

Adnan S. Abu-Surrah,* Kristian Lappalainen,1 Mika Kettunen,1 Timo Repo,1 Markku Leskelä,1 Hamdallah A. Hodali,2 Bernhard Rieger3

1 Department of Chemistry, Laboratory of Inorganic Chemistry, Box 55, 00014 University of Helsinki, Finland
2 Department of Chemistry, Faculty of Science, University of Jordan, Amman, Jordan
3 Anorganische Chemie II, Universität Ulm, D-89069 Ulm, Germany

Introduction
Cyclic polyolefins incorporating rigid structural units have recently received significant interest due to their remarkable thermomechanical and optical properties.[1] These materials are amorphous, transparent with excellent heat resistance. Besides early transition metal-based catalysts,[1,4,5] Pd(II) compounds have been used for the polymerization of cyclic monomers, where the polymerization involves exclusively the π-bond and leaves the bicyclic monomer unit intact.[3] Neutral catalysts such as PdCl2,[4] and Pd(NCPh)2Cl2,[5] produce oligomers at reaction temperatures above 70 °C, while cationic palladium complexes[3,6,7] (e.g. [Pd(CH3CN)4](BF4)2, 1) in which four weakly coordinating nitrile ligands are attached to the metal center, are active catalysts for the polymerization of norbornene.[3,6] However, no control of the polymer microstructure is feasible by using these chelate-free solvated Pd(II) complexes. The isolated polynorbornenes have low solubility, molecular weight up to 1.0 × 105 g/mol, and show high glass transition temperatures (Tg > 300 °C).[3,4]

Recently, we introduced new palladium(II) complexes bearing ethylene-bridged bisindolinyl amine ligands together with weakly coordinated water moieties as highly active, single component catalysts for the insertion polymerization of norbornene.[8] Herein, we report the application of some cationic palladium(II) catalysts (4–6) bearing ethylene-bridged bidentate ligands containing donor atoms such as phosphorus, arsenic and sulfur for the homopolymerization of norbornene (bicyclo[2.2.1]hept-2-
ene) and phenylnorbornene (5-phenylbicyclo[2.2.1]hept-2-ene) and copolymerization of norbornene with carbon monoxide. A quantitative monomer conversion can be reached by the right choice of the ligand or reaction conditions. The new family of catalysts is an extension of our studies on both the polymerization of cyclic olefins and the chemistry of heteroatom-containing ligands.\[8±10\]

**Experimental Part**

**Materials**

All reactions were carried out under dry argon using standard Schlenk techniques. CH$_2$Cl$_2$ and 1,2-dichlorobenzene were purified by distillation over CaH$_2$. Nitrobenzene and CH$_3$CN were dried over P$_2$O$_5$ and distilled. The ligands (S$^4$-As) (1) and (S$^4$-P) (2) were prepared according to literature procedures.\[10\] [Pd(NCCH$_3$)$_4$](BF$_4$)$_2$ (5) was purchased from Aldrich and purified by distillation over CaH$_2$. Nitrobenzene and CH$_3$CN were purified by distillation over CaH$_2$. CH$_2$Cl$_2$ and 1,2-dichlorobenzene were purified by Schlenk techniques. CH$_2$Cl$_2$ and 1,2-dichlorobenzene were then dried in vacuum.

**Polymerization Experiments**

**Homopolymerization of Norbornene:** Norbornene was added (Table 1) to a solution of the Pd(II) complex (4–6) (50 mg) in CH$_2$Cl$_2$ (50 ml), 1,2-dichlorobenzene (5.0 ml) and nitrobenzene (2 ml). The reaction mixture was stirred at room temperature. At the end of the reaction period (Table 1) the reaction was quenched by adding methanol and the polymer was isolated by filtration, washed with excess methanol and dried in vacuum at 80°C. The product was dissolved in CH$_2$Cl$_2$, and the filtrate was evaporated to dryness.

- **[Pd(S$^4$-As)(NCCH$_3$)$_4$](BF$_4$)$_2$ (4), [Pd(S$^4$-P)(NCCH$_3$)$_4$](BF$_4$)$_2$ (5), and [(P$^4$-P)Pd(NCCH$_3$)$_4$](BF$_4$)$_2$] (6)** were prepared following a previously published procedure.\[11\] A filtered solution of the ligand (0.675 mmol) in CH$_2$Cl$_2$ (15 ml) was added to a filtered solution of [Pd(NCCH$_3$)$_4$](BF$_4$)$_2$ (0.30 g, 0.675 mmol) in CH$_3$CN (15 ml) was then stirred at room temperature for 6 h. At the end of this period, the remaining ethene was vented off and the reaction was quenched by addition of excess methanol. The product was filtered, washed with methanol (100 ml) and dried in vacuum.

**Copolymerization Attempt with Ethene:** A solution of the Pd(II) complex (4) (50 mg, 0.075 mmol) in CH$_2$Cl$_2$ (150 ml) and norbornene (5.0 g) was placed in a 300 ml mechanically stirred steel autoclave which was then charged with ethene (10 bar). The reaction mixture was stirred at room temperature for 6 h. At the end of this period, the remaining ethene was vented off and the reaction was quenched by addition of excess methanol. The product was filtered, washed with methanol (100 ml) and dried in vacuum.

**Copolymerization with Carbon Monoxide:** A solution containing the Pd(II) complex (5), (50 mg, 0.075 mmol) in CH$_2$Cl$_2$ (100 ml), MeOH (0.5 ml) and norbornene (5.0 g) were placed in a 300 ml mechanically stirred steel autoclave which was then charged with carbon monoxide (30 bar). The reaction mixture was stirred at room temperature for 12 h. At the end of this period, the remaining carbon monoxide was vented off and the reaction was quenched by addition of methanol. The product was purified by adding CH$_2$Cl$_2$ (50 ml) followed by filtration over a short pad of silica gel in order to remove catalyst residues. The product was purified by adding CH$_2$Cl$_2$ (50 ml) followed by filtration over a short pad of silica gel in order to remove catalyst residues.

**Methods**

Elemental analyses were performed by the Microanalytical Laboratories of the University. $^1$H NMR spectra were recorded on a Bruker AC 200 spectrometer. Solid state $^1$C NMR spectra were recorded on a Bruker DSX 400 instrument. Infrared spectra (CsI pellet) were measured on a Bruker IFS66V spectrometer. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) at 135°C in 1.24-trichlorobenzene relative to polystyrene standards. DSC data were collected by a Perkin-Elmer DSC-7 with 20 K/min heating rate. Thermal gravimetric analysis (TGA) was carried out on a Perkin-Elmer TGS 2 (heating rate 10 K/min).
Homo- and Copolymerization of Strained Cyclic Olefins with New Palladium(II) Complexes

Results and Discussion

Homopolymerization reactions of norbornene and phenylnorbornene (endo/exo ratio of 80/20) were carried out using the palladium(II) complexes 4–6 (Figure 1) at room temperature in a reaction medium consisting of a mixture of dichloromethane, 1,2-dichlorobenzene and nitrobenzene. The amorphous, transparent polymer products consist of 2,3-linked monomer units (Figure 2, A); no indications for ring opened species could be observed.

The complexes with phosphine ligands [Pd(P-xP)(NCCH3)2](BF4)2 (6) and [Pd(S-xP)(NCCH3)2](BF4)2 (5) showed a considerably higher activity for norbornene polymerization than the corresponding [Pd(S-xAs)(NCCH3)2](BF4)2 (4) complex under similar reaction conditions (Table 1, entries 4, 8, and 9). The higher rate of monomer conversion using the complex 6 might be due to the stronger trans influence of the ligand (P-xP, 3) compared to the mixed ligands (S-xP, 2) and (S-xAs, 1) which leads to the weakening of the in situ formed Pd-alkyl bond allowing therefore faster monomer insertion. Our previous investigations on the corresponding alkyl palladium(II) and platinum(II) complexes showed also that the weakening effect caused by the donor atom on the metal-alkyl bond trans to it increases in the order P > As > N > S.[9]

Almost a quantitative monomer conversion can be reached by the right choice of the ligand or reaction conditions. At initial mole ratio of 600/1 (Nor/Pd), an increase of both molecular weight and monomer conversion with increasing reaction period was observed when catalyst 5 was used (Table 1, entry 5–7).

Using [Pd(S-xAs)(X)2](BF4)2 (4) as a catalyst the homopolymerization reactions of norbornene were carried out starting with various initial molar ratios of monomer (norbornene) to catalyst (Table 1, entry 1–4). 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.[8] The molecular weight distribution of the products improves with increasing monomer conversion.

**Table 1.** Homopolymerization results of norbornene.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Cat.</th>
<th>Nor/Pd (mole ratio)</th>
<th>Time h</th>
<th>Mw × 10^3 g/mol</th>
<th>Mw/Mn</th>
<th>Yield g</th>
<th>Conversion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S-xAs</td>
<td>4</td>
<td>100</td>
<td>2</td>
<td>2.13</td>
<td>1.86</td>
<td>0.36</td>
<td>51.4</td>
</tr>
<tr>
<td>2</td>
<td>S-xAs</td>
<td>4</td>
<td>300</td>
<td>2</td>
<td>2.81</td>
<td>2.01</td>
<td>1.61</td>
<td>75.9</td>
</tr>
<tr>
<td>3</td>
<td>S-xAs</td>
<td>4</td>
<td>600</td>
<td>2</td>
<td>3.22</td>
<td>1.93</td>
<td>3.64</td>
<td>86.1</td>
</tr>
<tr>
<td>4</td>
<td>S-xAs</td>
<td>4</td>
<td>808</td>
<td>0.5</td>
<td>3.89</td>
<td>1.59</td>
<td>3.67</td>
<td>63.8</td>
</tr>
<tr>
<td>5</td>
<td>S-xP</td>
<td>5</td>
<td>600</td>
<td>2</td>
<td>1.33</td>
<td>1.81</td>
<td>2.54</td>
<td>56.1</td>
</tr>
<tr>
<td>6</td>
<td>S-xP</td>
<td>5</td>
<td>600</td>
<td>6</td>
<td>2.37</td>
<td>2.17</td>
<td>4.21</td>
<td>92.9</td>
</tr>
<tr>
<td>7</td>
<td>S-xP</td>
<td>5</td>
<td>600</td>
<td>6</td>
<td>2.52</td>
<td>1.89</td>
<td>4.52</td>
<td>99.8</td>
</tr>
<tr>
<td>8</td>
<td>S-xP</td>
<td>5</td>
<td>808</td>
<td>2</td>
<td>2.57</td>
<td>1.87</td>
<td>5.48</td>
<td>89.5</td>
</tr>
<tr>
<td>9</td>
<td>P-xP</td>
<td>6</td>
<td>808</td>
<td>2</td>
<td>4.73</td>
<td>1.91</td>
<td>5.0</td>
<td>100</td>
</tr>
</tbody>
</table>

**a)** Polymerization conditions: solvent, CH2Cl2 (50 ml), 1,2-dichlorobenzene (5.0 ml), nitrobenzene (1.0 ml); room temperature.

**b)** Measured by GPC (relative to polystyrene).

Figure 1. Structure of the dicationic palladium(II) complexes 4, 5, and 6.

Figure 2. Polymerization of norbornene and phenylnorbornene with complexes 4, 5, and 6.
obtained is in the range expected for single-site catalyst species.4

The IR spectra of the polymers are similar to those of the previously described vinyl-type poly(norbornene)s, prepared by Pd(II)-catalysis.5,6,14 No absorption bands due to double bonds resulting from ring opening were observed. The solid state 13C NMR spectrum of the polymer prepared by the complex [Pd(NCCH3)4](BF4)2 (1) shows only two broad peaks over the ranges 53.9–58.8 and 37.7–40.9 ppm with peak maxima at 53.9 and 39.0 ppm, respectively. In contrast, the products obtained by the compounds that carry bidentate chelates (4–5) give six broad signals at 58.0, 52.5, 50.0, 40.0, 35.0, 30.0 ppm, which indicate a relatively stronger stereoregularity in the polymer.

According to thermogravimetric analysis (TGA) under nitrogen, all poly(norbornene)s are stable up to 330 °C, but the polymers prepared utilizing the complexes that carry phosphorus as a donor atom (5, 6), show higher stability. A weight loss of about 4% was recorded between 330 °C and 425 °C then a fast degradation starts at around 440 °C. This is about 100 °C higher compared to the polymer produced by catalyst 4, where the fast decomposition commences at 330 °C.

When the bulky monomer phenylnorbornene with endo/exo ratio of 80/20 was used, low polymer yields were obtained (Table 2). Predominantly the exo-isomer underwent the polymerization reaction.15 The exo-substituted units can be easily distinguished from the endo-isomer by IR- spectroscopy (ν(π(⋯H))).15,16 The IR spectra (region between 600–800 cm−1) of the isolated poly (phenylnorbornene) showed a strong absorption at 697 cm−1 which can be ascribed to the ester carbonyls (end group), respectively.15,16 Elemental analysis of the isolated polymer indicates a norbornene to carbon monoxide ratio of 1:1.

The copolymer was also analyzed by DSC and was found to be crystalline material compared to the amorphous norbornene homopolymer. The melting temperature of norbornene/CO copolymer (Tm ≈ 241 °C) is relatively high and comparable to that of ethene-carbon monoxide alternating copolymer (257 °C).20 In addition, a glass transition temperature (Tg) was observed for the copolymer at 161 °C which is lower than that of the homopolymer (Tg ≈ 330 °C), but very high for a polyketone material.21

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Φa × 104(b)</th>
<th>Mw/Mn</th>
<th>Yield</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(SrAs)(NCCH3)2][BF4]2 (4)</td>
<td>3.63</td>
<td>3.65</td>
<td>0.51</td>
<td>9.3</td>
</tr>
<tr>
<td>2</td>
<td>Pd(SrAs)(NCCH3)2][BF4]2 (4)</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.40</td>
<td>12.8</td>
</tr>
<tr>
<td>3</td>
<td>Pd(SrP)(NCCH3)2][BF4]2 (5)</td>
<td>5.43</td>
<td>2.63</td>
<td>0.35</td>
<td>6.9</td>
</tr>
<tr>
<td>4</td>
<td>Pd(PrP)(NCCH3)2][BF4]2 (6)</td>
<td>1.04</td>
<td>1.17</td>
<td>0.20</td>
<td>4.5</td>
</tr>
</tbody>
</table>

a Polymerization conditions: solvent, CH2Cl2 (50 ml), 1,2-dichlorobenzene (5.0 ml), nitrobenzene (1.0 ml); room temperature; time, 2 h; Pd/phenylnorbornene (mole ratio), 1:400 (entry 2, 1:800).

b Measured by GPC (relative to polystyrene standards) in THF.

c n.d.: not determined.
In conclusion, we have shown that cationic Pd(II) compounds which contain heteroatom-donor ligands are effective single site catalysts for homopolymerization of cyclic olefins. Variation of the donor atom has a significant influence on the rate of the reaction. The homopolymerization of norbornene(s) (poly(2,3-bicyclo[2.2.1]hept-2-ene) are amorphous, highly stable and have high molar weight and Tg around 330°C, while poly(phenynorbornene) showed lower stability, but a remarkable solubility in most organic solvents. Both molecular weight and thermal behavior of polynorbornene can be tailored using ethene as a chain transfer agent. Utilizing the catalysts (4) norbornene-carbon monoxide alternating copolymer was also prepared. The isolated material is crystalline and it has a melting temperature (Tm) of 241°C.

Acknowledgement: We thank Mr. Erkki Aitola for GPC measurements. Support by the International Center for Mobility (CIMO) and the University of Helsinki-Finland, is gratefully acknowledged.

Received: January 3, 2000
Revised: May 8, 2000


