Title
Switchable Polymerization of Norbornene Derivatives by a Ferrocene-Palladium(II) Heteroscorpionate Complex

Permalink
https://escholarship.org/uc/item/81k3p7d7

Journal
EUROPEAN JOURNAL OF INORGANIC CHEMISTRY

ISSN
1434-1948

Authors
Abubekrov, M
Shepard, SM
Diaconescu, PL

Publication Date
2016-06-01

DOI
10.1002/ejic.201501295

Peer reviewed
Switchable Polymerization of Norbornene Derivatives by a Palladium(II) Ferrocene Heteroscorpionate Complex

Mark Abubekerov, Scott M. Shepard, and Paula L. Diaconescu*

Abstract: The ferrocene-chelating heteroscorpionate complex \([\text{fc}(\text{PPH}_3)\text{BH}(3,5-\text{Me}_2\text{pz})_2)\text{PdMe} (\text{fc} = 1,1'-\text{ferrocenediyl}, \text{pz} = \text{pyrazole})\) catalyzes the addition polymerization of norbornene and norbornene derivatives upon oxidation with \([\text{Fc}[\text{BAr}^f]]\) (acetyl ferrocenium tetrakis(3,5-norbornene and norbornene derivatives upon oxidation with \([\text{Fc}[\text{BAr}^f]]\) (acetyl ferrocenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate). In situ reduction of \([(\text{fc}^{P,B})\text{PdMe}]\text{BAr}^f\) in the presence of a substituted norbornene results in significant decrease of catalytic activity. Addition of one equivalent of oxidant restores the activity.

Introduction

Vinyl polynorbornenes are important materials for optical applications due to their excellent thermal stability, high glass transition temperatures, small birefringence, and dielectric loss.\(^1\)\(^-\)\(^5\) However, polynorbornenes are brittle, even at high molecular weights, display poor adhesion to common substrates, poor solubility in common organic solvents, and cannot be melt processed due to decomposition.\(^6\)\(^-\)\(^9\) Modifying the norbornene monomers with functional groups increases the solubility of the resulting polymers and improves their processability.\(^10\) The substitution of norbornenes, typically at the 5-position, can be achieved via a Diels-Alder reaction, in some cases, directly from dicyclopentadiene and a dienophile.\(^11\) Polymers obtained from the substituted monomers show improved adhesive and mechanical properties while retaining similar optical properties as the unsubstituted polynorbornenes.\(^1\)\(^,\)\(^4\)\(^,\)\(^12\)

Amongst transition metal catalysts, palladium-based systems are highly active toward norbornene polymerization and produce high molecular weight vinyl polynorbornenes.\(^1\)\(^,\)\(^13\)\(^-\)\(^20\) Most palladium catalysts feature bidentate or monodentate supporting ligands since an open coordination sphere is necessary for monomer coordination.\(^9\)\(^,\)\(^10\)\(^,\)\(^13\)\(^-\)\(^15\)\(^,\)\(^21\)\(^-\)\(^25\) Commonly employed systems also require the use of strong Lewis acids/alkylating reagents (i.e. methylalumoxane, fluorinated arylboranes/alkyl aluminum complexes) as co-catalysts to generate a metal-alkyl fragment and an empty coordination site.\(^1\)\(^,\)\(^7\) The resulting catalytic species are typically not stable in the absence of monomer, and in certain cases, have further complications arising from the possible monomer/co-catalyst interactions.\(^15\)\(^,\)\(^26\) Alternatively, in cases when an open coordination sphere cannot be readily obtained, such as allyl palladium complexes, the use of hemilabile supporting ligands has been reported.\(^27\) Weakly coordinating components of these ligands can be readily displaced by more nucleophilic olefins. On the other hand, the use of a tridentate supporting ligand would severely limit the availability of an empty coordination site. A possible solution is the incorporation of a labile component into the ligand framework, similar to those in hemilabile ligands, resulting in an effective polymerization system without the need for a co-catalyst. Additionally, controlling the lability of a supporting ligand can be accomplished by a method similar to the one utilized in redox-switchable hemilabile ligands.\(^28\) An appropriate placement of a redox-active group into a ligand framework provides a method of influencing both the electronic and steric properties of the transition metal complex through oxidation of the ligand. Because of our interest in redox active ferrocene-based chelating ligands,\(^29\)\(^-\)\(^33\) we set out to investigate the effects of the redox switch on the lability of the ferrocene-chelating heteroscorpionate ligand in the palladium methyl complex, \([(\text{fc}(\text{PPH}_3)\text{BH}(3,5-\text{Me}_2\text{pz})_2)\text{PdMe} (\text{fc} = 1,1'-\text{ferrocenediyl}, \text{pz} = \text{pyrazole})\) in the presence of norbornene derivatives. Herein, we report the first palladium system supported by a tridentate ligand modified by an on/off redox switch for the addition polymerization of norbornene and norbornene derivatives.

Results and Discussion

Synthesis and characterization of palladium complexes. The palladium complex \((\text{COD})\text{PdMeCl}\) was prepared via transmetallation of \((\text{COD})\text{PdCl}\) with trimethylaluminum, instead of using alkyl tin reagents,\(^34\) in a mixture of THF and diethyl ether, similarly to the synthesis of \([\text{Pd}_2(\mu-\text{Cl})_3\text{Me}_2(\text{PEt}_3)_3]\).\(^34\) The characterization of the desired product was accomplished by \(^1\)H NMR spectroscopy (Figure S1), which was consistent with previously published results.\(^35\) Addition of \((\text{fc}^{P,B})\text{Li}(\text{THF})_2\) to \((\text{COD})\text{PdMeCl}\) in THF led to the isolation of \((\text{fc}^{P,B})\text{PdMe}(\text{C}_7\text{H}_8)\) as red crystals in 77.1% yield.

Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Drive East, Los Angeles, CA 90095, U.S.A.
Fax: 1 (310) 206-4038
E-mail: pld@chem.ucla.edu
Homepage: http://copper.chem.ucla.edu/pldgroup/index.htm
Supporting information for this article is available on the WWW under http://www.eurjic.org/ or from the author.
(Eq 1). The solid-state molecular structure of \((\text{fc}^{P,B})\text{PdMe}\) was determined using single-crystal X-ray diffraction (Figure 1). The coordination environment around the palladium center is in a distorted square planar geometry \((\tau = 0.16)^{36}\) similar to the nickel analogue, \((\text{fc}^{P,B})\text{NiMe}\).\(^{37}\) The metal-donor atom distances \(\text{P}(1)-\text{Pd}(1), 2.2107(4) \text{ Å}; \text{C}(1)-\text{Pd}(1), 2.0454(18) \text{ Å}; \text{N}(3)-\text{Pd}(1), 2.0938(14) \text{ Å}; \text{N}(1)-\text{Pd}(1), 2.1097(14) \text{ Å}\) are comparable with values reported for similar complexes: 1-(mesityl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolyl methyl triphenylphosphine palladium(II) \((\text{Pd}-\text{P}, 2.2858(9) \text{ Å}; \text{Pd-C}, 2.041(3) \text{ Å})^{38}\) \((\text{TPMeMe})\text{Pd(methallyl)}\) \((\text{TPMeMe} = \text{hydrotris}(3,5\text{-dimethylpyrazolyl})\text{borate})\), \(\text{Pd-N}, 2.090(2) \text{ and } 2.086(2) \text{ Å})^{39}\).

However, unlike for the nickel analogue, the resonance signals in the corresponding \(^1\text{H}\) NMR spectrum (Figure S2) are sharp, easily discernable, and are consistent with a diamagnetic complex.

Electrochemical studies performed on \((\text{fc}^{P,B})\text{PdMe}\) show a quasi-reversible curve with a redox potential of \(-0.27 \text{ V vs. Fc/Fc}^+\) (Figure 2), suggesting that ferrocenium salts may be used as chemical oxidants. On an NMR scale, the oxidation of the palladium complex with one equivalent of acetyl ferrocenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate \([\text{AcFc}][\text{BArF}])\) results in the appearance of paramagnetically shifted and broadened signals in the \(^1\text{H}\) NMR spectrum (Figure S8). The \(^{11}\text{B}\) NMR spectrum (Figure S10) shows a significant upfield shift of the signal corresponding to the \((\text{fc}^{P,B})\text{PdMe}\) complex, from \(-7.6\) to \(-65.2\) ppm, upon oxidation. However, the oxidized complex is \(^{31}\text{P}\) NMR silent. Reduction with one equivalent of cobaltocene \((\text{Cp}_2\text{Co})\) restores the original complex, \((\text{fc}^{P,B})\text{PdMe}\), with no appearance of decomposition or side products (Figures S6 and S7). On a larger scale, the addition of \((\text{fc}^{P,B})\text{PdMe}\) to a suspension of \([\text{AcFc}][\text{BArF}]\) in toluene resulted in the isolation of \([\text{fc}^{P,B})\text{PdMe}][\text{BArF}]\) as dark brown solids in 84\% yield (Eq 2). The presence of the \([\text{BArF}]^-\) counter ion was confirmed by the presence of a singlet at \(\delta = -6.1\) and \(-62.2\) ppm in the \(^{11}\text{B}\) and \(^{19}\text{F}\) NMR spectra (Figures S10 and S9), respectively. Attempts to grow X-ray quality crystals from various neat solvents and solvent combinations were unsuccessful and only dark brown oils were obtained. However, besides spectroscopic characterization, elemental analysis also agrees with the formulation of \([\text{fc}^{P,B})\text{PdMe}][\text{BArF}]\).

\[
\text{[(fc}^{P,B})\text{PdMe}][\text{BArF}] \quad \text{THF} \quad \text{[(fc}^{P,B})\text{PdMe}][\text{BArF}] \quad (2)
\]

![Figure 1](image1.png)

**Figure 1.** Molecular structure drawing of \((\text{fc}^{P,B})\text{PdMe}\) with thermal ellipsoids at 50\% probability; hydrogen atoms are omitted for clarity. Selected distances (\(\text{Å}\)) and angles (\(\circ\)): \(\text{P}(1)-\text{Pd}(1), 2.2107(4); \text{C}(1)-\text{Pd}(1), 2.0454(18); \text{N}(1)-\text{Pd}(1), 2.1097(14); \text{N}(3)-\text{Pd}(1), 2.0938(14); \text{P}(1)-\text{Pd}(1)-\text{C}(1), 91.71(7); \text{P}(1)-\text{Pd}(1)-\text{N}(3), 95.98(4); \text{P}(1)-\text{Pd}(1)-\text{N}(1), 84.99(5); \text{C}(1)-\text{Pd}(1)-\text{N}(3), 174.78(6); \text{C}(1)-\text{Pd}(1)-\text{P}(1), 161.95(4).\)

Electrochemical studies performed on \((\text{fc}^{P,B})\text{PdMe}\) show a quasi-reversible curve with a redox potential of \(-0.27 \text{ V vs. Fc/Fc}^+\) (Figure 2), suggesting that ferrocenium salts may be used as chemical oxidants. On an NMR scale, the oxidation of the palladium complex with one equivalent of acetyl ferrocenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate \([\text{AcFc}][\text{BArF}])\) results in the appearance of paramagnetically shifted and broadened signals in the \(^1\text{H}\) NMR spectrum (Figure S8). The \(^{11}\text{B}\) NMR spectrum (Figure S10) shows a significant upfield shift of the signal corresponding to the \((\text{fc}^{P,B})\text{PdMe}\) complex, from \(-7.6\) to \(-65.2\) ppm, upon oxidation. However, the oxidized complex is \(^{31}\text{P}\) NMR silent. Reduction with one equivalent of cobaltocene \((\text{Cp}_2\text{Co})\) restores the original complex, \((\text{fc}^{P,B})\text{PdMe}\), with no appearance of decomposition or side products (Figures S6 and S7). On a larger scale, the addition of \((\text{fc}^{P,B})\text{PdMe}\) to a suspension of \([\text{AcFc}][\text{BArF}]\) in toluene resulted in the isolation of \([\text{fc}^{P,B})\text{PdMe}][\text{BArF}]\) as dark brown solids in 84\% yield (Eq 2). The presence of the \([\text{BArF}]^-\) counter ion was confirmed by the presence of a singlet at \(\delta = -6.1\) and \(-62.2\) ppm in the \(^{11}\text{B}\) and \(^{19}\text{F}\) NMR spectra (Figures S10 and S9), respectively. Attempts to grow X-ray quality crystals from various neat solvents and solvent combinations were unsuccessful and only dark brown oils were obtained. However, besides spectroscopic characterization, elemental analysis also agrees with the formulation of \([\text{fc}^{P,B})\text{PdMe}][\text{BArF}]\).

\[
\text{[(fc}^{P,B})\text{PdMe}][\text{BArF}] \quad \text{THF} \quad \text{[(fc}^{P,B})\text{PdMe}][\text{BArF}] \quad (2)
\]

![Figure 2](image2.png)

**Figure 2.** Cyclic voltammogram recorded with a glassy carbon electrode at 100 mV/s in THF, 0.10 M \([\text{Bu}_4\text{N}][\text{PF}_6]\) containing 5.0 mM \((\text{fc}^{P,B})\text{PdMe}).\)
Knowing the strength of the palladium-phosphorus and palladium-nitrogen bonds in (fcP,B)PdMe is necessary for understanding its catalytic activity. Addition of four equivalents of tert-butyl isocyanide (BuNC) to (fcP,B)PdMe resulted in the isolation of (fcP,B)Pd(C(Me)NtBu)(CNtBu)·(C7H8) as an orange crystalline material (Eq 3). The new compound is the product of a migratory insertion of one equivalent of BuNC into the palladium-carbon bond and the coordination of a second equivalent of BuNC to the palladium metal center. The two pyrazoles are not chemically equivalent in the 1H NMR spectrum (Figure 3), suggesting that only one of them is coordinated to palladium. The phosphine is in a solution state equilibrium between a free and palladium bound phosphine as observed by two peaks at -14.9 ppm and 9.4 ppm, respectively, in the 31P NMR spectrum (Figure S15). However, no reaction occurs upon the addition of benzonitrile or ferrocenyldiphenylphosphine to (fcP,B)PdMe, suggesting that weaker nucleophiles cannot displace the supporting ligand. Similarly, addition of acetonitrile to [(fcP,B)PdMe][BARF] results in no reaction. However, oxidation (fcP,B)PdMe with [AcFc][BARF] in the presence of ferrocenyldiphenylphosphine results in the disappearance of the two 31P NMR singlets at 30.5 ppm and -16.1 ppm (Figure S11) that correspond to the two ferrocene compounds, and the appearance of a singlet at 24.0 ppm (Figure S12) corresponding to a palladium-bound FePPh2.

Polymerization of norbornene and norbornene derivatives. The reduced ferrocene complex, (fcP,B)PdMe, in the presence of norbornene showed no polymerization activity even when heating up to 100 °C in benzene. This absence of activity suggests that norbornene is too weak of a nucleophile to compete for a coordination site with the supporting ligand. On the other hand, in the presence of a stronger nucleophile, such as tert-butyl isocyanide, the phosphine of the supporting ligand is almost entirely displaced. Reducing the nucleophilic character of the supporting ligand through the oxidation of the ferrocene moiety, as was observed in the case of ferrocenyldiphenylphosphine coordination, promotes monomer coordination.

The oxidation of the ferrocene backbone with [10-Fc][BARF] turns “on” the activity of the (fcP,B)PdMe complex toward the polymerization of norbornene. The polymerization of 100 equivalents of norbornene (NB) reaches completion within an hour at 70 °C. However, the poor solubility of norbornene homopolymers in common organic solvents prevents their characterization by gel permeation chromatography (GPC) on regular instruments and complicates the in situ investigation of the “on/off” redox switch. To overcome these complications, norbornene derivatives (Figure 4) 5-butyl-bicyclo[2.2.1]hept-2-ene (NBa), 5-(triethoxysilyl)-bicyclo[2.2.1]hept-2-ene (NBb), 5-(trimethylsilyl)-bicyclo[2.2.1]hept-2-ene (NBc), and 5-cyclohexyl-bicyclo[2.2.1]hept-2-ene (NDb) were prepared and their polymerization results are summarized in Table 1. The polymerization of ca. 100 equivalents of the substituted norbornenes was monitored by 1H NMR spectroscopy, until no further monomer conversion was observed. The obtained polymers were characterized by gel permeation chromatography (GPC). A large discrepancy was found between the experimental and theoretical values of the molecular weights, suggesting a poorly controlled polymerization process, with the PDI (PDI = Mw/Mn) values ranging from 1.5 to 3.6. A similar wide distribution of PDI values is observed in the literature for the polymerization of norbornenes by group 10 metals. The polymerization activity for palladium complexes toward norbornene is largely dependent on the coordination environment around the metal center and the substituents on the monomer and can vary greatly from just a few numbers to several millions. By comparison, the oxidized ferrocene heteroscorpionate complex shows a relatively low activity with turnover frequencies ranging from 12.5 to 81 molnb molPd-1 h-1.

The in situ redox switch was performed with 5-triethoxysilyl norbornene. Starting with the oxidized complex [(fcP,B)PdMe][BARF] in the presence of 100 equivalents of monomer results in the polymerization of 35 equivalents in 20 min at 70 °C (Table 1, entry 6). The addition of one equivalent of Cp2Co relative to the palladium complex severely reduces the catalytic activity. The polymerization of 5 equivalents of NBb observed during this time can be attributed to a small number of catalytically active complex present in solution, due to the slow rate of reduction of the palladium compound by Cp2Co, which takes up to 30 min at ambient temperature to reach completion. No further conversion upon heating of the reaction solution at 70 °C for 20 min is observed once the reduction process is complete. The oxidation with [10-Fc][BARF] restores the catalytic activity (Figure 5). The slow rate of reduction of the catalyst would account for the shoulder peak observed in the GPC graph of the isolated polymer (Figure S37).

To gain a better understanding of how the redox switches affect the polymerization reaction, the influence of ligand oxidation upon electron donating abilities of individual ferrocene substituents was considered. The oxidation of ferrocenyldiphenylphosphine reduces the electron donating ability of the phosphine donor, resulting in the increase of the CO stretching frequency by several wave numbers in rhenium carbonyl complexes. Alternatively, oxidation of a ferrocene containing tris(pyrazolyl)borate molybdenum carbonyl complex resulted in virtually no change in the stretching frequency of the carbonyl ligands. Based on these literature reports and our observations, we propose a mechanism for the redox switch (Figure S34).
The influence of the redox switch supporting ligands; such species yield high molecular weight investigated. Compound [(fc P,B)PdMe][BArF] shows a reversible ligand in palladium catalyzed norbornene polymerization was. The application of a ferrocene-chelating heteroscorpionate increases the lability of norbornene does not occur, the polymerization process is halted with this catalyst.

Conclusions

The involvement of alternative mechanisms in the polymerization of norbornene was also considered. In principle, “naked” Pd might be generated in situ through loss of the supporting ligands; such species yield high molecular weight polynorbornenes. However, the influence of the redox switch on the polymerization of norbornene suggests that the supporting ligand remains attached to palladium throughout the polymerization process. Alternatively, polymerization of norbornene by a cationic mechanism yields oligomeric materials with low molecular weights. The reaction of norbornenes with [(Fc][BArF]) (Figure S25-S28) under similar polymerization conditions as those used for [(P,B)PdMe][BArF]) yielded no isolable polymeric material, suggesting that cationic polymerization by the oxidant is not a viable mechanism in this system.

Experimental Section

General considerations. All reactions were performed using standard Schlenk techniques or in an MBraun drybox (<1 ppm O2/H2O) unless noted otherwise. All glassware, cannulae, and Celite were stored in an oven at > 425 K before being brought into the drybox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs and transferred to the glovebox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. NMR spectra were recorded at ambient temperature on Bruker AV-300, AV-400, AV-500, and DRX-500 spectrometers unless otherwise noted. Proton and carbon chemical shifts are given relative to residual solvent peaks. Phosphorus, boron, and fluorine chemical shifts are given relative to external standards, H3PO4, Et2O·BF3, and trifluoroacetic acid, respectively. [(P,B)Li(THF)] was prepared using a literature procedure, and, unless otherwise noted, all reagents were acquired from commercial sources and used as received. Elemental analyses were performed on an Exeter Analytical, Inc. CE-440 Elemental Analyzer. Molecular weights of the polymers were determined by GPC-LLS (Gel Permeation Chromatography, Laser Light Scattering). GPC-LLS uses an Agilent liquid chromatograph equipped with an Agilent 1200 series pump and autosampler, three Phenogel 5 µm Narrow Bore columns, a Wyatt Optilab differential refractometer, Wyatt Tristar miniDAWN and a Wyatt Viscosstar viscometer. A flow rate of 1.0 mL/min was used and samples were dissolved in chloroform with 0.25% triethylamine. Results were calibrated to narrow molecular weight polystyrene standards.

(COD)PdMeCl. A suspension of (COD)PdCl2 (247.7 mg, 0.868 mmol) in 6 mL of Et2O/THF (1:2 vol %) was cooled to -78 °C. Trimethylaluminum (125.1 mg, 1.735 mmol) in 1 mL of hexanes was added slowly, the reaction mixture was removed from the cold well, and stirred at ambient temperature until the solution became colorless. Methanol was added to solvolyse the aluminum by-products and volatile substances were removed under reduced pressure. The desired product was extracted with THF and filtered through Celite. THF was removed under reduced pressure and the resulting off-white solids were washed with Et2O (2 × 2 mL) to afford the final product (185.3 mg, 80.5 %). This procedure was carried out multiple times in similar scales with yields ranging from 50-80%. 1H NMR (CDCl3, 500 MHz, 298 K); δ (ppm) 1.18 (s, 3H, PdCH3), 2.47 (m, 4H, CH2), 2.58 (m, 2H, CH2), 2.65 (m, 2H, CH2), 5.15 (t, 2H, CH2), 5.91 (t, 2H, CH2).

(fcpP,B)PdMe. To (COD)PdMeCl (155.1 mg, 0.585 mmol) in 10 mL of THF, (fcpP,B)Li(THF)2 (384.3 mg, 0.532 mmol) in 5 mL of THF was added dropwise. The reaction solution was stirred for 16 h at ambient temperature. Volatile substances were removed under reduced pressure and the desired product was extracted into 10 mL of toluene and filtered through Celite. Reduction in volume of the toluene solution to 4 mL and layering with 4 mL of hexanes afforded red crystalline material after 24 h at -35 °C.

**Figure 5.** Comparison of 5-(triethoxysilyl)-bicyclo[2.2.1]hept-2-ene polymerization using a redox switch and not using a redox switch using [(fcpP,B)PdMe][BArF] as a catalyst.
Table 1: Polymerization of norbornene derivatives by in situ generated [(fc^8)PdMe][BARF].

<table>
<thead>
<tr>
<th>entry</th>
<th>monomer</th>
<th>time (h)</th>
<th>conversion (%)</th>
<th>M_n theo</th>
<th>M_n exp</th>
<th>PDI</th>
<th>TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NB</td>
<td>1</td>
<td>78</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>64</td>
</tr>
<tr>
<td>2</td>
<td>NBa</td>
<td>1</td>
<td>79</td>
<td>12.2</td>
<td>30.6</td>
<td>3.63</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>NBb</td>
<td>1</td>
<td>58</td>
<td>14.9</td>
<td>37.0</td>
<td>2.52</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>NBc</td>
<td>0.5</td>
<td>33</td>
<td>5.8</td>
<td>8.8</td>
<td>2.10</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>NBd</td>
<td>2</td>
<td>27</td>
<td>4.4</td>
<td>1.4</td>
<td>1.48</td>
<td>12.5</td>
</tr>
<tr>
<td>6</td>
<td>NBb</td>
<td>1.33</td>
<td>27</td>
<td>13.0</td>
<td>30.6</td>
<td>3.04</td>
<td>38.3</td>
</tr>
</tbody>
</table>

Conditions: monomer (0.50 mmol), catalyst (0.005 mmol), oxidant (0.005 mmol), d_6-benzene as a solvent (0.5 mL) and 1,3,5-trimethoxybenzene (0.10 mmol) as an internal standard. All experiments were performed at 70 °C, except for entry 5, performed at 100 °C. M_n are reported in 10^3 g/mol; PDI = M_n/M_w, TOF = (mol_n in polymer) mol^-1 Pd h^-1. In the case of entry 1, the isolated yield is reported instead of conversion.

Decanting of the solution and washing of the remaining solids with hexanes (3 × 2 mL) and cold toluene (3 × 1 mL) yields the product as a red crystalline material (321.9 mg, 77.1 %) in two crops. Crystals of [(fc^8)PdMe] always contain one molecule of toluene per molecule of compound as supported by NMR spectroscopic data. X-ray quality crystals were obtained from dicyclopentadiene (20.0 mmol) and the corresponding olefin being allowed to cool to ambient temperature. The reactor was then heated to 220-240 °C for two hours before being allowed to cool to ambient temperature. The reactor was opened and the resulting tan oil was distilled at 2.5 torr to afford a colorless liquid.

5-butyl-bicyclo[2.2.1]hept-2-ene (NBa). Distilled at 35 °C and 2.5 torr to afford a colorless liquid (44.0 mmol). The reactor was purged with nitrogen and sealed. The reactor was then heated to 220-240 °C for two hours before being allowed to cool to ambient temperature. The reactor was opened and the resulting tan oil was distilled at 2.5 torr to afford a colorless liquid.
5-(triethoxysilyl)-bicyclo[2.2.1]hept-2-ene (NBb). Distilled at 65 °C and 2.5 torr to afford a colorless liquid (46.8%) as a mixture of exo and endo isomers. 1H NMR (CDCl 3, 500 MHz, 298 K): δ (ppm) 0.46 (m, 1H), 1.07 (m, 1H), 1.23 (m, 9H), 1.35 (m, 1H), 1.76 (m, 1H), 1.86 (m, 1H), 2.92 (m, 2H), 3.76-3.86 (m, 6H), 5.92-6.13 (m, 2H, olefinic). 13C NMR (CDCl 3, 500 MHz, 298 K): δ (ppm) 137.9, 135.4, 134.8, 133.8, 58.6, 58.4, 47.1, 44.3, 42.9, 42.6, 42.3, 27.1, 26.4, 20.9, 20.4, 18.5, 18.4.

5-(trimethylsilyl)-bicyclo[2.2.1]hept-2-ene (NBc). Distilled at 30 °C and 2.5 torr to afford a colorless liquid (37.7%) as a mixture of exo and endo isomers. 1H NMR (CDCl 3, 500 MHz, 298 K): δ (ppm) -0.09-0.00 (s, 9H), 0.31 (m, 1H), 0.90-1.14 (m, 2H), 1.29-1.51 (m, 2H), 1.85 (m, 1H), 2.72-2.93 (m, 1H), 3.21 (m, 1H), 5.48-6.16 (m, 2H, olefinic). 13C NMR (CDCl 3, 500 MHz, 298 K): δ (ppm) 137.1, 136.5, 134.1, 51.7, 47.0, 44.9, 43.0, 42.62, 42.57, 27.3, 27.1, 25.4, 25.3, -1.3, -1.8.

NMR Scale Polymerizations. In a small vial, (fc P,B)PdMe (5 μmol) was added to one equivalent of [AcFc][BArF] in 0.2 mL of C6D6 and stirred until the oxidant was consumed. The oxidized complex was added an external standard, 1,3,5-trimethoxybenzene (0.1 mmol), and monomer (0.5 mmol); the total solution volume was increased to 0.5 mL of C 6D 6. The polymerization was monitored by 1H NMR spectroscopy until the conversion has stopped or reached completion. The contents of the NMR tube was diluted with 1 mL of dichloromethane and poured into 10 mL of methanol to yield white solids. The product was collected on a glass frit, washed with additional 5 mL of methanol and kept under reduced pressure until it reached a consistent weight. For the control experiments, [AcFc][BArF] or Cp2Co (5 μmol) was used instead of (fc P,B)PdMe while the rest of the conditions above were kept the same.

Electrochemical studies. Cyclic voltammetry studies were carried out in a 20 mL scintillation vial with electrodes fixed in position by a rubber stopper, in a 0.10 M tetrabutylammonium hexafluorophosphate solution in THF. A glassy carbon working electrode (planar circular area = 0.071 cm²), a platinum reference electrode (planar circular area = 0.031 cm²), and a silver-wire pseudo-reference electrode were purchased from CH Instruments. Before each cyclic voltammogram was recorded, the working and auxiliary electrodes were polished with an aqueous suspension of 0.05 μm alumina on a microcloth polishing pad. Cyclic voltammograms were acquired with a CH Instruments CHI630D potentiostat and recorded with CH Instruments software (version 13.04) with processing on Origin 9.2. All potentials are given with respect to the ferrocene-ferrocceniun couple.

Acknowledgements

This work was supported by NSF, Grant 1362999 to PLD and CHE-1048804 for NMR spectroscopy. We thank Mr. Jonathan Brosmer for assistance with elemental analysis experiments.

Keywords: switchable • catalysis • redox • polymerization • palladium

References


X-ray crystallography. X-ray quality crystals were obtained from various concentrated solutions placed in a -35 °C freezer in the glove box unless otherwise specified. Inside the glove box, the crystals were coated with oil (STP Oil Treatment) on a microscope slide, which was brought outside the glove box. The X-ray data collections were carried out on a Bruker SMART 1000 single crystal X-ray diffractometer using MoKα radiation and a SMART APEX CCD detector. The data was reduced by SAI NPLUS and an empirical absorption correction was applied using the package SADABS. The structure was solved and refined using SHELXTL (Bruker 1998, SMART, SAINT, XPREP AND SHELXTL, Bruker AXS Inc., Madison, Wisconsin, USA). Tables with atomic coordinates and equivalent isotropic displacement parameters, with all the bond lengths and angles, and with anisotropic displacement parameters are listed in the cif.
35. Salo, E. V.; Guan, Z., Organometallics 2003, 22, 5033.

A cationic ferrocene-chelating heteroscorpionate palladium methyl complex catalyses the addition polymerization of norbornene and norbornene derivatives. Redox switchable polymerization of these monomers was also accomplished.