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# PALLADIUM CATALYZED COPOLYMERIZATIONS OF POLAR AND NON-POLAR MONOMERS 

A Dissertation in Chemistry by

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#### Abstract

Herein, a well-defined, neutral, phosphine-sulfonate ligated, palladium catalyst for the production of polyethene, poly(ethene-co-carbon monoxide, and polyethene-block-poly-(ethene-alt-carbon monoxide) co-oligomers is reported. The system is living under mild conditions and produces poly(ethene-cocarbon monoxide) with carbon monoxide content ranging from $0-50 \mathrm{~mol} \%$. Mechanistic studies suggest that an unusually small difference in the ethene and carbon monoxide binding affinities as well as enhanced decarbonylation play important roles in determining the copolymer composition. Furthermore, this system was found to be exceptionally tolerant of polar functional-groups, protic solvents, and aqueous emulsion. This allows for the production of copolymers of ethene with polar monomers, including functionalized norbornenes and styrenes. Finally,the effects of anions and $N$-substituted imines on the palladium-catalyzed copolymerization of imines with carbon monoxide was investigated.


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## List of Abbreviations

| Ac | acetyl (actinium does not appear in this document) |
| :---: | :---: |
| atm | atmosphere |
| CCD | charge-coupled device |
| COD (cod) | 1,5-cyclooctadiene (ligand) |
| COSY | correlation spectroscopy |
| Da | dalton |
| DBA (dba) | dibenzylideneacetone (ligand) |
| DPPP (dppp) | 1,3-bis(diphenylphosphino)propane (ligand) |
| DSC | differential scanning calorimetry |
| Et | ethyl |
| eu | entropy unit (calmol ${ }^{-1} \mathrm{~K}^{-1}$ ) |
| FT-IR | Fourier transform infrared spectroscopy |
| GPC | gel-permeation chromatography |
| Hex | hexyl |
| HMQC | heteronuclear multiple quantum coherence |
| IR | infrared spectroscopy |
| $M_{\mathrm{n}}$ | number average molecular weight |
| $\mathrm{M}^{t} \mathrm{BE}$ | methyl tert-butyl ether |
| $M_{\text {w }}$ | weight average molecular weight |
| NMR | nuclear magnetic resonance spectroscopy |
| PDI | polydispersity index ( $M_{\mathrm{w}} / M_{\mathrm{n}}$ ) |
| PE | polyethene |
| phen | 1,10-phenanthroline (ligand) |
| PK | polyketone |
| ppm | parts per million |
| psig | pounds per square inch gauge (above ambient pressure) |
| $\mathrm{P} \sim \mathrm{SO}_{3} \mathrm{H}$ | 2-[bis(2-methoxyphenyl)phosphino]benzenesulfonic acid |
| Py (py) | pyridine (ligand) |
| SADABS | Siemens area detector absorption correction program |
| SEC | size-exclusion chromatography |
| THF | tetrahydrofuran |
| $T_{\text {m }}$ | melt-transition temperature |
| TMEDA (tmeda) | $N, N, N^{\prime}, N^{\prime}$-tetramethylethylenediamine (ligand) |
| UV-vis | ultraviolet-visible spectroscopy |

## Preface

The work described in this dissertation was carried out between August 2003 and August 2009 under the direction of Dr. Ayusman Sen at the Pennsylvania State University. The body of this work is divided across four related projects, which are presented as chapters herein. With the exception of Chapter 5, these results have been published in the journal Organometallics and have been adapted for use in this dissertation with the permission of the American Chemical Society. ${ }^{1-4}$ It should be noted that because of the collaborative nature of projects within Dr. Sen's group, researchers other than myself contributed to the projects presented in the following chapters. The results of these collaborative efforts are included in order to maintain the context and completeness of each project. However, their inclusion should not be construed as a claim of sole-authorship. The division of labor for each project is clarified below.

The research presented in Chapter 1 was initiated by myself and performed in collaboration with the following people. The $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}(\mathrm{py})$ complex was synthesized by Dr. Sachin Borkar in consultation with Dr. David M. Conner and Dr. Brian L. Goodall of the Rohm and Haas company. The single-crystal used to obtain the X-ray diffraction data for the palladium-acyl complex shown in Figure 1.3 was grown by Dr. Borkar and analyzed by Dr. Hemant Yennawar.

The research presented in Chapter 2 was initiated by Dr. Rong Luo as a continuation of the research presented in Chapter 1, and her initial results can be found in her thesis. ${ }^{5}$ The bulk polymerization experiments and measurements that appear in Table 2.1 were performed by Dr. Luo. The kinetic and thermodynamic studies of monomer insertion and exchange were initiated by Dr. Luo and were completed and expanded by myself. This work was funded by the United States Department of Energy, Office of Basic Energy Sciences.

The research presented in Chapter 3 was initiated by Dr. Shengsheng Liu with assistance from Dr. Yennawar and was completed and expanded by Dr. Borkar and myself. Synthesis, characterization, and polymerization experiments for the crotylpalladium(phosphine-sulfonate) complex as well as some of the copolymerizations of ethene with functional norbornenes were performed by myself. The comparison of the rates of uptake for endo and exo isomers of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate was performed by Dr. Borkar and myself. This work was funded by the National Science Foundation and the Rohm and Haas Company.

The research presented in Chapter 4 was initiated by Dr. Borkar and was completed and expanded by myself. The study of the mechanism of styrene insertion was performed by myself. This work was funded by the United States Department of Energy.

The research presented in Chapter 5 was performed by myself with technical assistance from Paul Chiarulli.

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## Epigraph

"Slowly I came back from a weird, unfamiliar world to reassuring everyday reality. The horror softened and gave way to a feeling of good fortune and gratitude, the more normal perceptions and thoughts returned, and I became more confident that the danger of insanity was conclusively past."

## Chapter One

## Copolymerization of Ethene with Carbon Monoxide: Mechanism

### 1.1 Introduction

The palladium-catalyzed alternating copolymerization of ethene with carbon monoxide has been widely studied. ${ }^{1}$ The processing of the resultant polyketone (alt-Рк) is problematic due to its insolubility in common solvents and its very high melting point ( $\sim 265^{\circ} \mathrm{C}$ ), both of which result from high crystallinity brought about by dipolar interactions between carbonyl groups present at $50 \mathrm{~mol} \%$ in the copolymer. The problem of processability can be circumvented by lowering the carbon monoxide content of the copolymer by producing nonalternating copolymers. It has been suggested that as low as $5 \mathrm{~mol} \%$ to $10 \mathrm{~mol} \%$ carbon monoxide incorporation into polyethene would be sufficient to impart such desirable properties as adhesion, paintability, hardness, etc., without sacrificing the processibility associated with polyethene. ${ }^{1}$ However, traditional catalysts for the production of alkene/carbon monoxide copolymers do not yield materials with less than $50 \mathrm{~mol} \%$ carbon monoxide even at high alkene:carbon monoxide feed ratios. ${ }^{1}$ There are several reasons for the strict alternation observed with conventional catalysts: carbon monoxide binds more strongly to the active palladium species and inserts more readily into the Pd-alkyl bond than ethene does; however, successive insertions of carbon monoxide (i.e., insertion of carbon monoxide into a Pd-acyl bond) are thermodynamically disfavored.

Recently, a system that generates nonalternating ethene/carbon monoxide copolymers (nonalt-Рк) with as little as $35 \mathrm{~mol} \%$ carbon monoxide has been reported and it employs the anionic phosphine ligand bis(2-methoxyphenyl)phosphinobenzenesulfonic acid ( $\mathrm{P}^{\sim} \mathrm{SO}_{3} \mathrm{H}$ ), $\mathbf{1} .^{2,3}$ Additionally, the same system polymerizes ethene to linear polyethene ( PE ) unlike conventional phosphine or imine ligated palladium systems. A key unanswered mechanistic question is why copolymers with the full range of carbon monoxide incorporation from $0 \mathrm{~mol} \%$ to $50 \mathrm{~mol} \%$ cannot be synthesized using this system by simply raising the alkene:carbon monoxide feed ratio. Herein, we address this question and demonstrate that it is possible to produce nonalt- PK with as low as $10 \mathrm{~mol} \%$ carbon monoxide, albeit in low yields. Further, using a well-defined palladium complex with this ligand, we demonstrate the first catalytic system for the living polymerization of both PE and alt-РК, thereby allowing the synthesis of the block copolymer: polyethene-block-poly(ethene-alt-carbon monoxide).


Phosphine-sulfonate ligand $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3} \mathrm{H}\right), \mathbf{1}$.

### 1.2 Results and Discussion

### 1.2.1 Bulk Polymerization

The addition of small amounts of carbon monoxide to the monomer feed during ethene homopolymerization using the original $\mathrm{P}^{\sim} \mathrm{SO}_{3}^{-}$-based system caused a dramatic reduction in activity despite the system's ability to produce Ре, nonalt-Рк and alt-Рк. However, it was possible to produce nonalt-Рк incorporating as little as $10 \mathrm{~mol} \%$ carbon monoxide by adding only 5 psig carbon monoxide into an autoclave with 300 psig ethene (see Figure 1.1). This lowered the melting point of the copolymer to $118^{\circ} \mathrm{C}$ as determined by dsc analysis (see Figure A.24). The activity of the system could be improved by increasing the carbon monoxide pressure but not without restoring the near-alternating character of the resulting copolymer. The relationship between carbon monoxide pressure, yield, and composition is consistent with the mechanism originally proposed for the classical alternating copolymerization system (see Scheme 1.2). ${ }^{1,4}$ As shown, a chelate resting-state (A) exists in the catalytic cycle and, unlike carbon monoxide, the more weakly coordinating ethene is less able to disrupt the chelate ( $\mathbf{A} \rightarrow \mathbf{D}$ ), a requirement for sequential ethene insertions; note that this issue does not arise in ethene homopolymerization. However, carbon monoxide binding is strong enough to disrupt the chelate leading to further insertions ( $\mathbf{A} \rightarrow \mathbf{B} \rightarrow \mathbf{C} \rightarrow \mathbf{A}$ ). Thus, with conventional alternating copolymerization catalysts, carbon monoxide is required for the alkene insertion step to proceed.

### 1.2.2 Mechanistic Study

We sought to look for a stable chelate similar to A in Scheme 1.2 for the present system in order to confirm that it proceeds via the same general mechanism as bis-phosphine ligated systems. The active species in the original catalytic system reported by Drent and Pugh (prepared in situ from $\mathrm{Pd}(\mathrm{OAc})_{2}$ and $\mathrm{P} \sim \mathrm{SO}_{3} \mathrm{H}$ ) was not well-defined. ${ }^{2}$ Therefore, we used a model compound with a methyl group and pyridine occupying two coordination sites, cis- $\left(\mathrm{P}^{\wedge} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}(\mathrm{py}), 2$. This species was synthesized and characterized by ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}$ NMR spectroscopy, ir spectroscopy and single-crystal X-ray diffraction. The ortep structure of $\mathbf{2}$ is shown in Figure 1.3. All reactions were carried out in dichloromethane to maintain solubility of the products. When 2 in dichloromethane- $d_{2}$ was exposed to ethene at 100 psig and $25^{\circ} \mathrm{C}, \mathrm{PE}$ was produced. The ethene polymerization has living characteristics under these conditions and the chain-growth was monitored by ${ }^{1} \mathrm{H}$ nMR spectroscopy. The growth of the pe peak at 1.3 ppm was not accompanied by any signals in the vinyl region that would indicate chain termination by $\beta$-hydrogen abstraction. Also, methylene groups $\alpha$ and $\beta$ to the Pd center were seen, respectively, as multiplets at 0.8 ppm and 0.6 ppm , along with the methyl end-group at 0.9 ppm .


Figure 1.1: Effect of carbon monoxide pressure on polymer yield ( $\square$ ) and composition $(\diamond)$. Curves are presented only to guide the eye. Reaction conditions: $\mathrm{Pd}_{2}(\mathrm{DBA})_{3}, 10 \mu \mathrm{~mol} ; \mathrm{P}^{\sim} \mathrm{SO}_{3} \mathrm{H}, 10 \mu \mathrm{~mol} ; \mathrm{C}_{2} \mathrm{H}_{4}, 300 \mathrm{psig}$; dichloromethane- $d_{2}, 20 \mathrm{~mL} ; 75^{\circ} \mathrm{C} ; 3 \mathrm{~h}$.


Scheme 1.2: General catalytic cycle for alternating ethene/carbon monoxide copolymerization. ${ }^{1,4}$


Figure 1.3: Crystal structure of $\left(\mathrm{P}^{\wedge} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}(\mathrm{py})$, 2, and $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}(\mathrm{py})$, 3. Hydrogen atoms are omitted for clarity.

When 2 was exposed to a mixture of 50 psig carbon monoxide and 50 psig ethene in dichlorometh-ane- $d_{2}$ at $25^{\circ} \mathrm{C}$, alt-PK was formed. As with ethene homopolymerization, it was possible to observe stepwise insertion of carbon monoxide (or ${ }^{13} \mathrm{CO}$ for ${ }^{13} \mathrm{C}$ NMR experiments) and ethene into the growing, methylterminated co-oligomer. To accomplish this, 2 was first exposed to 15 psig carbon monoxide causing the immediate formation of cis- $\left(\mathrm{P}^{\wedge} \mathrm{SO}_{3}\right) \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}(\mathrm{py}), 3$. The ${ }^{1} \mathrm{H}$ NMR signal for $\mathrm{Pd}-\mathrm{CH}_{3}$ at 0.2 ppm was replaced by the $\mathrm{Pd}-\mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$ signal at 1.8 ppm . Also, the ${ }^{31} \mathrm{P}$ signal at 23 ppm was replaced by a signal at 11 ppm and a ${ }^{13} \mathrm{C}$ carbonyl signal appeared at 227 ppm . The infrared spectrum showed a carbonyl absorption at $1695 \mathrm{~cm}^{-1}$. Single-crystal X-ray diffraction data was also collected. The ortep structure is shown in Figure 1.3. The palladium-carbon bond in both $\mathbf{2}$ and $\mathbf{3}$ is found cis to the coordinated phosphine moiety, presumably because of the stronger trans-effect of phosphorus compared to oxygen. The insertion of carbon monoxide into the palladium-carbon bond of $\mathbf{2}$ was found to be reversible as shown by the following experiment. First, $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{Pd}^{13} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}(\mathrm{py})$ was formed by the insertion of ${ }^{13} \mathrm{CO}$ as confirmed by a strong carbonyl ${ }^{13} \mathrm{C}$ nmp signal at 227 ppm . The solvent and excess ${ }^{13} \mathrm{CO}$ were removed under vacuum and the product was re-dissolved in dichloromethane- $d_{2}$ before being exposed to 50 psig of regular ${ }^{12} \mathrm{CO}$. After $18 \mathrm{~h},{ }^{13} \mathrm{C}$ NMR analysis showed a lack of ${ }^{13} \mathrm{C}$ enrichment in the palladium complex, indicating slow decarbonylation of ${ }^{13} \mathrm{CO}$ followed by rapid insertion of ${ }^{12} \mathrm{CO}$ as predicted by Ziegler. ${ }^{5}$

When a solution of $\mathbf{3}$ in dichloromethane $-d_{2}$ was exposed to 100 psig ethene at $0^{\circ} \mathrm{C}$, slow insertion of ethene into the palladium-acyl bond occurred to give a mixture of $\left(\mathrm{P}^{\sim}-\mathrm{SO}_{3}\right) \mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}, 4$, and unreacted 3 but not pe. Nmr analysis showed a new terminal methyl ${ }^{1} \mathrm{H}$ nmr signal at 1.9 ppm and the methylene groups $\alpha$ and $\beta$ to the metal appeared as a doublet of triplets at 1.3 ppm and as a broad multiplet at 2.1 ppm , respectively. Also, a new ${ }^{31} \mathrm{P}$ signal appeared at 25 ppm and a broad ${ }^{13} \mathrm{C}$ carbonyl signal appeared at 216 ppm . A new carbonyl absorption was seen at at $1643 \mathrm{~cm}^{-1}$ in the infrared spectrum, which is consistent with the formation of a five-membered chelate like structure A in Scheme 1.2. ${ }^{6,7}$

Low-temperature ${ }^{1} \mathrm{H}$ NMR analysis suggests that the five-membered chelate 4 is likely in equilibrium with the open-chain, pyridine-coordinated analogue, $4 \cdot p y$, and that the former is favored at low temperatures. At $80^{\circ} \mathrm{C}$, a doublet due to the ortho-hydrogens of the free pyridine is observed at 8.7 ppm . Addi-
tionally, the doublet of triplets at 1.3 ppm and the multiplet at 2.1 ppm from the methylene groups $\alpha$ and $\beta$ to the metal, respectively, split into unique proton signals at $0.80 \mathrm{ppm}, 1.01 \mathrm{ppm}$ and 1.55 ppm with the fourth obscured by the methyl signal suggesting the presence of a rigid chelate ring structure.

In contrast to 2 and $\mathbf{3}$, the chelated species 4 was unreactive towards ethene alone at 100 psig and $25^{\circ} \mathrm{C}$ consistent with the notion that the alkene is too weakly binding to easily disrupt the chelate (or displace the coordinated pyridine) and give consecutive ethene insertions under these conditions. Under the more forcing conditions used to generate the data for Figure 1.1, ethene insertion does occur slowly resulting in nonalt-Рк. However, unlike alt-Рк formation, the yield of nonalt-РК is low because of the slowness of this step. We hypothesize that the step $\mathbf{A} \rightarrow \mathbf{D}$ of Scheme 1.2 does proceed in the present neutral system, albeit slowly, because the carbonyl group in species $\mathbf{A}$ binds less strongly to the metal unlike in the traditional cationic palladium systems used for alternating ethene/carbon monoxide copolymerizations.

Compound 4, when re-dissolved in dichloromethane and exposed to carbon monoxide at 50 psig and $25^{\circ} \mathrm{C}$, formed $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}, \mathbf{5}$, which corresponds to either structure $\mathbf{C}$ in Scheme 1.2 or its open-chain pyridine-coordinated analogue. The ${ }^{1} \mathrm{H}$ NMR signals for the $\mathrm{CH}_{2}$ groups $\alpha$ and $\beta$ to the metal in 5 were shifted to 1.9 ppm and 2.5 ppm , respectively. The ${ }^{31} \mathrm{P}$ signal at 25 ppm was replaced by a peak at 12 ppm and the ${ }^{13} \mathrm{C}$ carbonyl signal at 216 ppm was replaced by two carbonyl signals at 207 ppm and 228 ppm . Complex 5, in turn, was exposed to ethene at 100 psig and $0^{\circ} \mathrm{C}$ for 18 h . The ${ }^{31} \mathrm{P}$ NMR signal for the palladium-acyl species was shifted to 22 ppm indicating that it underwent ethene insertion to form a palladium-alkyl complex, 6, (similar to complex 4).

### 1.2.3 Block Copolymerization

Finally, the living nature of the ethene homopolymerization and ethene/carbon monoxide copolymerization allows the formation of PE and alt-PK blocks in a single chain. Block co-oligomers were synthesized to demonstrate this, while maintaining the solubility of the products in dichloromethane- $d_{2}$. First, $\mathbf{2}$ in dichloromethane- $d_{2}$ was exposed to ethene at 100 psig and $25^{\circ} \mathrm{C}$ for 2 h to grow a pe block with an average of 4 ethene units. The solvent and excess ethene was removed under vacuum and the re-dissolved system was then exposed to a $1: 1$ (p:p) mixture of ethene and carbon monoxide at 100 psig for 9 h to grow a second alt-Рк block. The PE and alt-Рк blocks were identified by their characteristic ${ }^{1} \mathrm{H}$ NMR chemical shifts at 1.3 ppm and 2.7 ppm , respectively. The connectivity between the two blocks was observed as two $\mathrm{CH}_{2}$ signals at 1.5 ppm and 2.4 ppm . The assignment of the connecting $\mathrm{CH}_{2}$ groups was established by comparing with the ${ }^{1} \mathrm{H}$ NMR shifts of 3-hexanone. The protons labeled $a$ and $b$ in $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O})-\mathrm{CH}_{2}^{a}-\mathrm{CH}_{2}^{b}-\mathrm{CH}_{3}$ are observed at 2.4 ppm and 1.6 ppm , respectively.

### 1.3 Conclusions

We have observed the first well-defined palladium-based system that catalyzes both the living homopolymerization of ethene, as well as the living copolymerization of ethene with carbon monoxide, which we demonstrated through the synthesis of polyethene-block-poly-(ethene-alt-carbon monoxide). Furthermore, it was possible to monitor chain growth by sequential insertions of carbon monoxide and ethene into palladium-carbon bonds allowing us to pinpoint the hitherto not well-understood reason for the general failure to obtain alkene/carbon monoxide copolymers with low carbon monoxide content.

### 1.4 Experimental Procedures

The following information applies to all experimental procedures unless otherwise noted. Chemical manipulations were performed under a dry nitrogen atmosphere using a glovebox or Schlenk techniques. All solvents, with the exception of NMR solvents, were distilled over calcium hydride and degassed using the freeze-pump-thaw technique. Ultra-high-purity ethene and ultra-high-purity carbon monoxide were obtained from MG Industries and used without further purification. Isotopically enriched chemicals were obtained in ampoules or lecture bottles from Cambridge Isotope Laboratories and used without further purification. NMR analysis was performed at ambient temperature using a Bruker DPX-300 spectrometer equipped with a multi-nuclear probe at 300.13 MHz for ${ }^{1} \mathrm{H}, 121.49 \mathrm{MHz}$ for ${ }^{31} \mathrm{P}$ or 75.4 MHz for ${ }^{13} \mathrm{C}$ NMR spectra. ${ }^{31} \mathrm{P}$ and ${ }^{13} \mathrm{C}$ NMR experiments were conducted with proton decoupling.

### 1.4.1 Synthesis of (tmeda) $\mathrm{PdCl}_{2}$

(tmeda) $\mathrm{PdCl}_{2}$ was synthesized under air by modifying the literature procedure. ${ }^{1}$ Potassium tetrachloropallidate (SI2g, 6.12 mmol ) was dissolved in distilled water $(20 \mathrm{~mL})$ and filtered through a fine-porosity frit. TMEDA ( $3.55 \mathrm{~g}, 30.6 \mathrm{mmol}$ ) was added to the filtrate and the mixture was stirred for 15 min and then cooled to $0^{\circ} \mathrm{C}$. The resulting yellow precipitate was collected by filtration and washed with cold water followed by diethyl ether. Yield $=1.5 \mathrm{~g}(83 \%)$.

### 1.4.2 Synthesis of (tmeda) $\mathrm{Pd}\left(\mathrm{CH}_{3}\right)_{2}$

(tmeda) $\mathrm{Pd}\left(\mathrm{CH}_{3}\right)_{2}$ was synthesized by following literature procedure. ${ }^{8}$

### 1.4.3 Synthesis of Phosphine-Sulfonate Ligand $P>\mathrm{SO}_{3} \mathrm{H}, 1$

The $\mathrm{P} \subset \mathrm{SO}_{3} \mathrm{H}$ ligand, $\mathbf{1}$ was synthesized by following literature procedure. ${ }^{2}$

### 1.4.4 Synthesis of Methylpalladium Complex $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}(\mathrm{py}), 2$

To a single-neck round-bottom flask $0.3 \mathrm{~g}(0.75 \mathrm{mmol})$ of 1 was suspended in 10 mL of dry tetrahydrofuran. To this $0.22 \mathrm{~g}(0.75 \mathrm{mmol})$ of (tmeda) $\mathrm{Pd}\left(\mathrm{CH}_{3}\right)_{2}$ was added and the reaction mixture was stirred for 30 min . To this five equivalents of pyridine $(0.29 \mathrm{~g}, 3.73 \mathrm{mmol})$ was added and stirred for another 30 min . Hexane was added to precipitate the product as a white powder, which was washed thoroughly with hexane and dried under vacuum. Yield $=0.42 \mathrm{~g}(95 \%) .{ }^{1} \mathrm{H}$ NmR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): 0.26 \mathrm{ppm}(\mathrm{d}, 3 \mathrm{H}), 3.69 \mathrm{ppm}(\mathrm{s}, 6 \mathrm{H}), 6.98 \mathrm{ppm}$ to $7.09 \mathrm{ppm}(\mathrm{m}, 4 \mathrm{H}), 7.32 \mathrm{ppm}(\mathrm{m}, 2 \mathrm{H}), 7.49 \mathrm{ppm}$ to $7.60 \mathrm{ppm}(\mathrm{m}, 7 \mathrm{H}), 7.92 \mathrm{ppm}(\mathrm{t}, 1 \mathrm{H}), 8.01 \mathrm{ppm}(\mathrm{t}, 1 \mathrm{H})$, $8.8 \mathrm{ppm}(\mathrm{d}, 2 \mathrm{H}) .{ }^{31} \mathrm{P}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): 22.76 \mathrm{ppm}$.

### 1.4.5 Bulk Polymerization

All bulk polymerization reactions were carried out in an open 100 mL serum bottle within a 300 mL autoclave with magnetic stirring. The bottle was charged with $0.010 \mathrm{~g} \mathrm{Pd}_{2}(\mathrm{dba})_{3}$ (Strem Chemicals), 0.010 g 1 and 20 mL dry, degassed dichloromethane. The autoclave was sealed and removed from the glovebox. The autoclave was then flushed with ethene, charged to the desired carbon monoxide pressure and charged with an additional 300 psig ethene. The autoclave was placed in a temperature-controlled oil bath at $100^{\circ} \mathrm{C}\left(75^{\circ} \mathrm{C}\right.$ internal autoclave temperature) with magnetic stirring for 3 h . The autoclave was
then cooled in an ice bath, vented to atmospheric pressure and opened. The resulting polymer was precipitated with methanol, collected by vacuum filtration and dried under high-vacuum overnight before analysis.

Polymer samples were dissolved in 1,1,1,3,3,3-hexafluoropropan-2-ol (Sigma-Aldrich) and benzene- $d_{6}$ for ${ }^{1} \mathrm{H}$ NMR analysis using 5 mm sample tubes (Norell). Carbon monoxide incorporation was determined from the following equation

$$
\begin{equation*}
[\mathrm{CO}]=\frac{A}{2 A+B} \tag{1.1}
\end{equation*}
$$

where $A$ is the integration of the methylene protons adjacent to a carbonyl group ( 2.6 ppm to 2.3 ppm ) and $B$ is the integration of methylene protons not adjacent to a carbonyl group ( 1.4 ppm to 1.2 ppm ). Note that Equation 1.1 is a simplified form of Equation 2.2 appearing on page 22 . The NmR spectrum for the 10 psig data point is presented in Figure A. 1 as a representative example.

Differential scanning calorimetry was performed by heating 1.3 mg of poly(ethene-co-carbon monoxide) at a rate of $5^{\circ} \mathrm{Cmin}^{-1}$ from $40^{\circ} \mathrm{C}$ to $280^{\circ} \mathrm{C}$ using a TA Instruments model DSC Q 100. The resulting data is presented in Section A.4.

### 1.4.6 Stepwise Insertion of Carbon Monoxide and Ethene

To observe the stepwise insertion of ethene and carbon monoxide, $5 \mathrm{mg}\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}(\mathrm{py})$ was dissolved in 0.5 mL of dichloromethane- $d_{2}$ in a high-pressure nmR tube (Wilmad, Quick Pressure Valve, 5 mm outer diameter, 8 in length, 0.77 mm wall thickness). The tube was charged to 50 psig with carbon monoxide and allowed to stand 20 min at $25^{\circ} \mathrm{C}$. $\left({ }^{13} \mathrm{C}\right.$-enriched carbon monoxide was used for ${ }^{13} \mathrm{C}$ NMR experiments and normal carbon monoxide was used for ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}$ nmr experiments.) The solvent and excess carbon monoxide were removed under vacuum and the product was re-dissolved in another 0.5 mL of dichloromethane- $d_{2}$. The tube was charged to 100 psig with ethene and allowed to stand overnight at $0^{\circ} \mathrm{C}$. Again, the solvent and excess ethene were removed under vacuum and the product was re-dissolved in 0.5 mL of dichloromethane- $d_{2}$. Finally, the tube was charged to 50 psig with carbon monoxide and allowed to stand 20 min at $25^{\circ} \mathrm{C}$. Spectra are presented in Section A.1.

### 1.4.7 Infrared Spectra Collection

Infrared spectra were collected using a Varian FTS 7000 series DigiLab Ft-IR spectrometer equipped with a ceramic IR source, KBr beamsplitter, deuterated triglycine sulfate detector and 632.8 nm HeNe laser with a 5 kHz laser modulation frequency. Samples were dissolved in dichloromethane and loaded into a demountable liquid-cell with 3 mm calcium fluoride windows and a 0.3 mm path-length. The sample chamber was flushed with dry nitrogen and data was collected from $4000 \mathrm{~cm}^{-1}$ to $900 \mathrm{~cm}^{-1}$ with a resolution of $1 \mathrm{~cm}^{-1}$. Dichloromethane was used as the background sample. Spectra are presented in Section A.3.

### 1.4.8 Crystal Structure Analysis for Methylpalladium Complex 2

A colorless, plate-shaped crystal of complex $2\left(\mathrm{C}_{26} \mathrm{H}_{26} \mathrm{NO}_{5} \mathrm{PPdS}\right)$ with approximate dimensions of $0.02 \times$ $0.07 \times 0.10 \mathrm{~mm}$ was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 103(2)K cooled by Rigaku-msc X-Stream 2000, on a Bruker Smart apex CCD area detector system equipped with a graphite monochromator and a Mo K $\alpha$ fine-focus sealed-tube ( $l=0.71073 \AA$ ) operated at 1600 W power ( $50 \mathrm{kV}, 32 \mathrm{~mA}$ ). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of $0.3^{\circ}$ in $\omega$ and an exposure time of 20 s per frame. The total data collection time was about 10 h . The frames were integrated with the Bruker saint
software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 16469 reflections to a maximum $q$ angle of $28.38^{\circ}$ ( $0.90 \AA$ resolution), of which 6269 were independent, completeness $=98.0 \%, R_{\text {intv }}=0.0535, R_{\text {sig }}=0.0803$ and 4561 were greater than $2 \sigma(\mathrm{I})$. The final cell constants: $a=11.484(5) \AA, b=13.828(6) \AA, c=16.239(6) \AA, \alpha=90^{\circ}$, $\beta=97.515(8)^{\circ}, \gamma=90^{\circ}$, volume $=2556.5(18) \AA^{3}$, are based upon the refinement of the XYZ-centroids of 3550 reflections above $20 \sigma$ (I) with $2.317^{\circ}<q<28.354^{\circ}$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (sadabs). The ratio of minimum to maximum apparent transmission was 0.1215 .

The structure was solved and refined using the Bruker shelxtl (version 6.1) software package, using the space group $\mathrm{P} 2(1) / \mathrm{c}$, with $Z=4$ for the formula unit, $\mathrm{C}_{26} \mathrm{H}_{26} \mathrm{NO}_{5} \mathrm{PPdS}$. The final anisotropic fullmatrix least-squares refinement on $F^{2}$ with 319 variables converged at $R_{1}=5.71 \%$ for the observed data and $\omega R_{2}=13.42 \%$ for all data. The goodness-of-fit was 1.033 . The largest peak on the final difference map was $1.052 \mathrm{e} \AA^{-3}$ and the largest hole was $-1.398 \mathrm{e} \AA^{-3}$. Based on the final model, the calculated density of the crystal is $1.564 \mathrm{gcm}^{-3}$ and $F(000)$ amounts to 1224 electrons. The data is presented in Section A.5.1.

### 1.4.9 Crystal Structure Analysis for Acylpalladium Complex 3

A yellow, plate-shaped crystal of complex $3\left(\mathrm{C}_{27} \mathrm{H}_{26} \mathrm{NO}_{6} \mathrm{PPdS}\right)$ with approximate dimensions of $0.05 \times$ $0.13 \times 0.17 \mathrm{~mm}$ was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 293(2)K cooled by Rigaku-msc X-Stream 2000, on a Bruker Smart apex ccd area detector system equipped with a graphite monochromator and a Mo K $\alpha$ fine-focus sealed tube ( $l=0.71073 \AA$ ) operated at 1600 W power ( $50 \mathrm{kV}, 32 \mathrm{~mA}$ ). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of $0.3^{\circ}$ in $\omega$ and an exposure time of 10 s per frame. The total data collection time was about 8 h . The frames were integrated with the Bruker saint software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 17068 reflections to a maximum $q$ angle of $28.36^{\circ}$ ( $0.90 \AA$ resolution), of which 6396 were independent, completeness $=97.3 \%, R_{\text {int }}=0.0693, R_{\text {sig }}=0.0924$ and 4577 were greater than $2 \sigma(\mathrm{I})$. The final cell constants: $a=11.567(2) \AA, b=14.097(3) \AA, c=16.198(3) \AA, \alpha=90^{\circ}, \beta=96.68(3)^{\circ}$, $\gamma=90^{\circ}$, volume $=2623.5(9) \AA^{3}$, are based upon the refinement of the XYZ-centroids of 3462 reflections above $20 \sigma$ (I) with $2.286^{\circ}<q<27.834^{\circ}$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (sadabs). The ratio of minimum to maximum apparent transmission was 0.0812 .

The structure was solved and refined using the Bruker shelxtl (version 6.1) software package, using the space group P2(1)/c, with $Z=4$ for the formula unit, $\mathrm{C}_{27} \mathrm{H}_{26} \mathrm{NO}_{6} \mathrm{PPdS}$. The final anisotropic fullmatrix least-squares refinement on $F^{2}$ with 337 variables converged at $R_{1}=5.29 \%$, for the observed data and $\omega R_{2}=12.89 \%$ for all data. The goodness-of-fit was 0.959 . The largest peak on the final difference map was $2.062 \mathrm{e} \AA^{-3}$ and the largest hole was $-0.818 \mathrm{e} \AA^{-3}$. Based on the final model, the calculated density of the crystal is $1.595 \mathrm{gcm}^{-3}$ and $F(000)$ amounts to 1280 electrons. The data is presented in Section A.5.2.

### 1.4.10 Low-Temperature Nuclear Magnetic Resonance Spectroscopy

A sample of 4 was prepared as described in Section 1.4.6 and loaded into the spectrometer using a 5 mm high-pressure tube. The sample was cooled under computer control by a stream of gas from boiling liquid nitrogen to a temperature of $-80^{\circ} \mathrm{C}$. The sample was allowed to equilibrate for 5 min before ${ }^{1} \mathrm{H}$ - and ${ }^{31} \mathrm{P}$ NMR spectra were taken. The sample was then warmed by $10^{\circ} \mathrm{C}$ and allowed to equilibrate before the magnetic field was re-shimmed, the probe was re-tuned and the next pair of spectra were taken. The
procedure was repeated for each $10^{\circ} \mathrm{C}$ increment from $-80^{\circ} \mathrm{C}$ to $20^{\circ} \mathrm{C}$. Stacked nMR spectra are presented in Section A.2.

### 1.4.11 Block Copolymerization

Block co-oligomers of polyethene and poly(ethene-alt-carbon monoxide) were prepared by dissolving $0.005 \mathrm{~g}\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}$ (py) in 0.5 mL of dichloromethane- $d_{2}$ in a high-pressure nmR tube (Wilmad, Quick Pressure Valve, 5 mm outer diameter, 8 in length, 0.77 mm wall thickness). The tube was charged with ethene at 100 psig and allowed to stand at $25^{\circ} \mathrm{C}$ for 2 h . The solvent and excess ethene were removed under vacuum. The system was re-dissolved in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ and charged with 50 psig ethene and 50 psig carbon monoxide and allowed to stand for an additional 9 h . Spectra are presented in Section A. 1

### 1.4.12 Decarbonylation

The $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{Pd}^{13} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$ (py) complex was prepared by exposing $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}$ (py) to 50 psig ${ }^{13} \mathrm{CO}$ as described in Section 1.4.6. The solvent and excess ${ }^{13} \mathrm{CO}$ were removed under vacuum before the product was re-dissolved in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ and exposed to un-enriched carbon monoxide at 50 psig overnight at ambient temperature. The ${ }^{13} \mathrm{C}$ nmR spectra of the $\left.\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{Pd}^{13} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}\right)(\mathrm{py})$ before and after exposure to unenriched carbon monoxide are shown in Section A.1. Note the carbonyl signal at 227 ppm and the free carbon monoxide signal at 185 ppm .

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## Chapter Two

## Copolymerization of Ethene with Carbon Monoxide: Kinetics and Thermodynamics

### 2.1 Introduction

The palladium-catalyzed alternating copolymerization of ethene and carbon monoxide ( CO ) has been studied extensively over the last three decades. ${ }^{1-5}$ The resultant polyketone is difficult to process because of its insolubility in common solvents and its high melting point $\left(\sim 260^{\circ} \mathrm{C}\right)$ brought about by the interchain dipolar interaction between carbonyl groups present at $50 \mathrm{~mol} \%$ in the copolymer. The problem of processability can be circumvented by lowering the carbon monoxide content in the copolymer. It has been suggested that incorporating as little as $\sim 5-10 \mathrm{~mol} \%$ carbon monoxide into polyethene would be sufficient to impart such desirable properties as adhesion, paintability, and hardness without sacrificing its processability. ${ }^{1}$ However, such materials are not attainable using conventional cationic palladium catalysts, which bear either a bidentate diphosphine ligand such as 1,3-bis(diphenylphosphino)propane (dppp) or a bidentate diimine ligand such as 1,10-phenanthroline (phen), and produce strictly alternating ethene/carbon monoxide copolymers even at high ethene:carbon monoxide ratios. ${ }^{1}$ While these catalysts are capable of oligomerizing ${ }^{6}$ or polymerizing ${ }^{7}$ ethene, consecutive ethene insertions are not observed in the presence of carbon monoxide due to the formation of a stable five-membered chelate following sequential carbon monoxide and ethene insertions, which can be opened by the strongly coordinating carbon monoxide, but not by ethene, as shown in Scheme 2.1. ${ }^{8-12}$ Consecutive carbon monoxide insertions are not observed for thermodynamic reasons. ${ }^{13,14}$

Recently, first Drent ${ }^{15}$ and then we ${ }^{8}$ and others ${ }^{16}$ have reported on neutral palladium complexes with anionic phosphine-sulfonate ligands $\left(\mathrm{P}^{\wedge} \mathrm{SO}_{3}^{-}\right)$that are able to form nonalternating ethene/carbon monoxide copolymers. The cause of consecutive ethene insertions has been ascribed to stereo-electronic destabilization of the five-membered chelate, which can then be disrupted by ethene ${ }^{15}$ and to decarbonylation of the six-membered chelate (Scheme 2.1). ${ }^{17,18}$

Herein, we report on the copolymerization of ethene with carbon monoxide to obtain copolymers with the full range of carbon monoxide incorporation: $1-50 \mathrm{~mol} \%$. Furthermore, we have examined, in detail, the mechanism of the nonalternating copolymerization through a combination of monomerbinding thermodynamics and monomer-insertion kinetics. These results show several key differences and similarities with traditional cationic alternating copolymerization catalysts ${ }^{10,19}$ and provide a more detailed explanation for the observed nonalternation in the phosphine-sulfonate-coordinated palladium system.


Scheme 2.1: Catalytic cycle for alternating copolymerization of ethene with carbon monoxide. R represents the growing polymer chain and $\mathrm{L} \sim \mathrm{L}$ represents a bidentate ligand.

$\mathrm{P} \sim \mathrm{SO}_{3}^{-}$ligand.

### 2.2 Results and Discussion

### 2.2.1 Bulk Polymerization

The combination of $\mathrm{P}^{-} \mathrm{SO}_{3} \mathrm{H}$ and palladium acetate $\left(\mathrm{Pd}(\mathrm{OAc})_{2}\right)$ in situ yields an active catalyst for the copolymerization of ethene with carbon monoxide as summarized in Table 2.1. The copolymer composition can be controlled by varying the ethene:carbon monoxide feed ratio and temperature. Entries 2, 3, and 6 were conducted under the same reaction conditions with different carbon monoxide pressures. Increasing the pressure from 15 psig to 25 psig increased the carbon monoxide content in the final product from $6 \mathrm{~mol} \%$ to $32 \mathrm{~mol} \%$. However, as noted previously, ${ }^{8}$ the copolymer yield decreased with decreasing carbon monoxide content. Entries 3,4 , and 5 were conducted under the same reaction conditions, but at different temperatures. Increasing the reaction temperature from $80^{\circ} \mathrm{C}$ to $110^{\circ} \mathrm{C}$ decreased the carbon monoxide content of the copolymer from $28 \mathrm{~mol} \%$ to $8 \mathrm{~mol} \%$. This temperature dependence was anticipated by Ziegler and co-workers on the basis of theoretical calculations for the ethene and carbon monoxide binding constants and the rate of decarbonylation. ${ }^{17,18}$

Table 2.1: Copolymerization of ethene with carbon monoxide using the catalyst formed in situ. ${ }^{a}$

| Entry | Temperature <br> $\left({ }^{( } \mathrm{C}\right)$ | CO <br> $(\mathrm{psig})$ | Yield <br> $(\mathrm{g})$ | Activity <br> $\left(\mathrm{gmmol}_{\mathrm{Pd}}^{-1} \mathrm{~h}^{-1}\right)$ | CO incorporation <br> $(\mathrm{mol} \%)^{b}$ | $T_{\mathrm{m}}$ <br> $\left({ }^{\circ} \mathrm{C}\right)$ | $M_{\mathrm{n}}$ | PDI $^{c}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 90 | 0 | 0.657 | 4.38 | 0 | 125.4 |  |  |
| 2 | 90 | 15 | 0.423 | 2.82 | 6 | 120.8 |  |  |
| 3 | 90 | 20 | 0.327 | 2.18 | 10 | 117.9 | 4460 | 3.5 |
| 4 | 80 | 20 | 0.172 | 1.15 | 28 | 115.9 |  |  |
| 5 | 110 | 20 | 0.696 | 4.64 | 8 | 120.2 |  |  |
| 6 | 90 | 25 | 0.206 | 1.37 | 32 | 97.2 | 37555 | 2.1 |
| 7 | 110 | 25 | 0.740 | 4.94 | 9 | 118.8 |  |  |

${ }^{a}$ Reaction conditions: ethene, $300 \mathrm{psig} ; \mathrm{Pd}(\mathrm{OAc})_{2}, 0.1 \mathrm{mmol} ; \mathrm{P} \subset \mathrm{SO}_{3} \mathrm{H}, 0.1 \mathrm{mmol} ; \mathrm{CH}_{2} \mathrm{Cl}_{2}, 10 \mathrm{~mL} ; 1.5 \mathrm{~h}$.
${ }^{b}$ Determined by ${ }^{1} \mathrm{H}$ nmR spectroscopy
${ }^{c}$ Determined by high-temperature GPC using polystyrene standards.

### 2.2.2 Polymer Characterization

The non-alternating structure of the copolymers was confirmed by ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}$ NMR spectroscopy as shown in Figure 2.2 and Figure 2.3. In the ${ }^{1} \mathrm{H}$ nmr spectra, the peak at 2.7 ppm was assigned to $\mathrm{CH}_{2}$ in alternating copolymer segments. The peaks at 2.4 ppm and 1.6 ppm were assigned to the $\mathrm{CH}_{2}$ groups $\alpha$ and $\beta$ to the carbonyl, respectively, for double ethene insertions. The peak at 1.3 ppm was assigned to ethene units not adjacent to a carbonyl group. In the ${ }^{13} \mathrm{C}$ NMR spectra, multiple peaks near 210 ppm indicated multiple chemical environments for the carbonyl groups in the final product. Double, triple, and quadruple ethene insertions were also indicated by signals between 20 ppm and 45 ppm . The chemical shift assignments are in good agreement with those previously reported for nonalternating copolymers of ethene with carbon monoxide. ${ }^{15}$

Differential scanning calorimetry showed a single melting point for all of the copolymers of ethene with carbon monoxide (Figure 2.4), confirming the formation of true copolymers. In copolymers with low carbon monoxide contents, the melting point decreased with increasing carbon monoxide incorporation,


Figure 2.2: ${ }^{1} \mathrm{H}$ NMR spectrum of non-alternating polyketone with $10 \mathrm{~mol} \%$ carbon monoxide incorporation in tetrachloroethane- $d_{2}$.



Figure 2.3: ${ }^{13} \mathrm{C}$ NMR spectrum of non-alternating polyketone with $10 \mathrm{~mol} \%$ carbon monoxide incorporation (above) and an expansion of the methylene region (below) in tetrachloroethane- $d_{2}$.
presumably due to the disruption of polyethene crystallinity. For example, increasing carbon monoxide content from $1 \mathrm{~mol} \%$ to $28 \mathrm{~mol} \%$ decreased the melting point from $125.3^{\circ} \mathrm{C}$ to $115.9^{\circ} \mathrm{C}$.


Figure 2.4: Melting transitions of copolymers of ethene and carbon monoxide.

It has been noted previously that the infrared spectra for solid samples of the alternating copolymer of ethene with carbon monoxide show an abnormally low carbonyl stretching frequency ( $v_{\mathrm{C}=\mathrm{o}} \approx$ $\left.1695 \mathrm{~cm}^{-1}\right) .{ }^{20}$ This phenomenon was attributed to the presence of intra- and interchain dipolar interactions between the carbonyl groups. Infrared spectra were collected for a series of copolymer samples with carbon monoxide incorporation ranging from $1 \mathrm{~mol} \%$ to $49 \mathrm{~mol} \%$. The corresponding carbonyl stretching frequency was observed to decrease from $1717 \mathrm{~cm}^{-1}$ to $1689 \mathrm{~cm}^{-1}$ with increasing carbon monoxide incorporation, consistent with dipolar interactions increasing with carbonyl concentration in the copolymer chain (see Appendix B).

### 2.2.3 Mechanistic Study

In order to better understand the reactivity of the phosphine-sulfonate-based catalyst, we constructed a complete catalytic cycle for the nonalternating copolymerization of ethene with carbon monoxide, using the well-defined, square-planar model complex $\left(\mathrm{P}^{\wedge} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}$ (py), 2.

Complex 2 was exposed to carbon monoxide at 50 psig in dichloromethane- $d_{2}$ and immediately formed palladium-acyl complex 3. Exposure of a solution of $\mathbf{3}$ in dichloromethane- $d_{2}$ to ethene at 80 psig and $50^{\circ} \mathrm{C}$ for 5 min resulted in slow insertion of ethene into the palladium-acyl bond to give a mixture of the five-membered chelate $\left(\mathrm{P}^{\wedge} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}, 4$, and unreacted 3.

Exposure of 4 to ethene generated an equilibrium mixture of 4 and its open-chain, ethene-coordinated analogue, 7. The presence of 7 was confirmed by ${ }^{1} \mathrm{H}$ NMR spectroscopy, which showed that the signal of the terminal methyl group shifted from 1.9 ppm to 1.4 ppm , and those of the $\mathrm{CH}_{2}$ groups $\alpha$ and $\beta$ to the metal center shifted from 1.3 ppm and 2.1 ppm to broad peaks at $0.8-1.1 \mathrm{ppm}$ and $1.5-1.7 \mathrm{ppm}$, respectively. As expected, ${ }^{9}$ coordinated ethene was not observed in the presence of excess monomer. The ${ }^{31} \mathrm{P}$ NMR signal at 23.6 ppm was shifted to 27.0 ppm , and the ${ }^{13} \mathrm{C}$ NMR carbonyl signal at 216 ppm was shifted to 201 ppm . The temperature-dependent equilibrium between 4 and 7 in dichloromethane- $d_{2}$ was monitored by ${ }^{13} \mathrm{C}$ nmr spectroscopy from $-90^{\circ} \mathrm{C}$ to $-70^{\circ} \mathrm{C}$. The van 't Hoff plot (see Appendix B) gives $\Delta H^{\circ}=0.68(7) \mathrm{kcalmol}^{-1}$ and $\Delta S^{\circ}=-1.1(3) \mathrm{eu}$. The calculated equilibrium constant $K_{1}$ at $25^{\circ} \mathrm{C}$ is
$0.548 \mathrm{Lmol}^{-1}$. Because impure 4 was used as a starting material, it is possible that residual $\mathbf{3}$ could influence the observed equilibrium by reaction with ethene to give 4 , which would result in slight underestimation of $K_{1}$ if the rate of insertion were fast relative to ring-opening of the chelate. However, the rate of insertion is negligible in this temperature range.


Exposure of 4 to carbon monoxide generated an equilibrium mixture of 4 and its open-chain, carbon monoxide-coordinated analogue, 8. The presence of $\mathbf{8}$ was confirmed by ${ }^{1} \mathrm{H}$ NMR spectroscopy, which showed that the signal of the terminal methyl group shifted from 1.9 ppm to 1.4 ppm and those of the $\mathrm{CH}_{2}$ groups $\alpha$ and $\beta$ to the metal center shifted from 1.3 ppm and 2.1 ppm to broad peaks at $0.8-1.1 \mathrm{ppm}$ and $1.5-1.7 \mathrm{ppm}$, respectively. The ${ }^{31} \mathrm{P}$ NMR signal at 23.6 ppm was shifted to 26.6 ppm and the ${ }^{13} \mathrm{C}$ NMR carbonyl signal at 216 ppm was shifted to 201 ppm . The temperature dependent equilibrium between 4 and 8 in dichloromethane- $d_{2}$ was monitored by ${ }^{13} \mathrm{C}$ nMR spectroscopy from $-90^{\circ} \mathrm{C}$ to $-70^{\circ} \mathrm{C}$. The van 't Hoff plot (see Appendix B) gives $\Delta H^{\circ}=3.2(2) \mathrm{kcalmol}^{-1}$ and $\Delta S^{\circ}=17.2(12) \mathrm{eu}$. The calculated equilibrium constant $K_{2}$ at $25^{\circ} \mathrm{C}$ is $27.4 \mathrm{Lmol}^{-1}$. In this case, although impure 4 was used as a starting material, the presence of palladium-acyl complex $\mathbf{3}$ had no influence on the equilibrium because carbon monoxide is unreactive toward 3.


The rate of migratory insertion of ethene into palladium-methyl complex $\mathbf{2}, k_{\mathrm{E}}$, to give palladiumpropyl complex 9 was determined by ${ }^{1} \mathrm{H}$ NMR spectroscopy. The presence of 9 was confirmed by ${ }^{1} \mathrm{H}$ NMR spectroscopy, which showed that the $\mathrm{PdCH}_{3}$ signal shifted from 0.2 ppm to 1.0 ppm and was accompanied by the appearance of $\mathrm{CH}_{2}$ groups $\alpha$ and $\beta$ to the metal center at 0.8 ppm and 1.3 ppm , respectively. The ${ }^{31} \mathrm{P}$ NMR signal at 22.7 ppm was broadened and shifted to 27.1 ppm . First-order kinetics were observed under excess ethene, and the rate is zero-order in ethene. This indicates that migratory insertion is the ratelimiting step rather than coordination or pyridine displacement. The Eyring plot (see Appendix B) gives activation parameters of $\Delta H^{\ddagger}=17.7(1) \mathrm{kcalmol}^{-1}$ and $\Delta S^{\ddagger}=-13.6(4) \mathrm{eu}$, which are somewhat higher than those reported by Brookhart and co-workers for the analogous cationic dppp-ligated system ( $\Delta H^{\ddagger}=$ $\left.15.2(7) \mathrm{kcalmol}^{-1}, \Delta S^{\ddagger}=-6.2(29) \mathrm{eu}\right) .{ }^{19}$ Our observation is consistent with the suggestion by Rieger that a higher energy barrier for ethene insertion may account for the low activity of the neutral phosphinesulfonate system compared to the traditional cationic systems. ${ }^{16}$ Unlike the dppp system, $\beta$-H elimination of propene was not observed.


The rate of migratory insertion of carbon monoxide into palladium-methyl complex $\mathbf{2}, k_{\mathrm{CO}}$, to give palladium-acyl complex $\mathbf{1 0}$ was also determined by ${ }^{1} \mathrm{H}$ NMR spectroscopy. The presence of $\mathbf{1 0}$ was confirmed by ${ }^{1} \mathrm{H}$ nmr spectroscopy, which showed that the $\mathrm{PdCH}_{3}$ signal at 0.2 ppm was replaced by $\mathrm{PdC}(\mathrm{O})$ $\mathrm{CH}_{3}$ at 1.8 ppm . The ${ }^{31} \mathrm{P}$ nmp signal at 22.7 ppm was broadened and shifted to 11.4 ppm . Second-order kinetics were observed under excess carbon monoxide, and the rate is first-order in carbon monoxide. The Eyring plot (see Appendix B) gives activation parameters of $\Delta H^{\ddagger}=16.6(8) \mathrm{kcalmol}^{-1}$ and $\Delta S^{\ddagger}=$ 20.0(434)eu, which are again somewhat higher the parameters for the analogous cationic dppp-ligated system reported by Brookhart and co-workers ( $\Delta H^{\ddagger}=14.8(7) \mathrm{kcalmol}^{-1}$ and $\left.\Delta S^{\ddagger}=0.1(4) \mathrm{eu}\right) .{ }^{19}$ The rate law also differs from the cationic dppp system, which was observed by Brookhart and co-workers to be first-order overall and zero-order in carbon monoxide. ${ }^{19}$ This suggests that, unlike the conversion of 2 to 9 , the rate-limiting step is not the migratory insertion of the monomer, but rather the associative displacement of pyridine from 2.


These results suggest that the principal difference between the neutral phosphine-sulfonate system and the traditional cationic systems is the unusually small difference in the binding affinity of carbon monoxide and ethene in the former. ${ }^{10,19}$ The ratio of the carbon monoxide and ethene binding constants $\left(K_{2}: K_{1}\right)$ is $\sim 50: 1$ at $25^{\circ} \mathrm{C}$, compared to $\sim 10^{4}: 1$ for cationic palladium complexes bearing a bidentate nitrogen ligand ${ }^{10}$ or a bidentate phosphine ligand. ${ }^{19}$ As discussed by others, ${ }^{18,19}$ the extent of double ethene insertion is controlled, in part, by the equilibrium ratio of the palladium-alkyl carbonyl (11) to palladiumalkyl olefin (12) complexes, $K_{\text {eq }}$, and the relative rates of migratory insertion for these two species, $K_{\mathrm{CO}}$ and $K_{\mathrm{E}}$, respectively. The factors controlling the ratio of alternating to nonalternating propagation are illustrated by Scheme 2.5 and Equation 2.1.

The equilibrium constant, $K_{\text {eq }}$, was estimated from the ratio of [11] to [12] multiplied by the ratio of $[\mathrm{CO}]$ to $\left[\mathrm{C}_{2} \mathrm{H}_{4}\right]$ in dichloromethane at $25^{\circ} \mathrm{C}$ with a partial pressure of 0.5 atm for each monomer. The propagation rates were extrapolated from the Eyring plots obtained from the kinetics of migratory insertion of carbon monoxide and ethene. From Equation 2.1, it is apparent that the favorable $K_{\text {eq }}$ is offset by the slow rate of ethene insertion since one would expect a double ethene insertion to occur only once for every $6.4 \times 10^{4}$ alternating insertions under these conditions. Although this is more frequent than either the $\sim 10^{5}$ reported for the bidentate diphosphine system ${ }^{19}$ or the $\sim 10^{6}$ reported for the bidentate diimine system, ${ }^{10}$ it is still effectively alternating.

Although this model system has previously shown functional group tolerance and polymerization ac-



Scheme 2.5: Kinetics of non-alternating copolymerization of ethene with carbon monoxide. R represents the growing polymer chain and $\mathrm{P}^{\wedge}-\mathrm{O}$ represents the phosphine-sulfonate ligand.

$$
\begin{aligned}
\frac{\text { Alternation }}{\text { Non-alternation }} & =K_{\mathrm{eq}}\left(\frac{k_{\mathrm{CO}}}{k_{\mathrm{E}}}\right) \\
& \approx\left(\frac{[\mathbf{1 1}]}{[\mathbf{1 2 ]}}\right)\left(\frac{k_{\mathrm{CO}}}{k_{\mathrm{E}}}\right) \\
& =\left(\frac{K_{2} \times[\mathrm{CO}]}{K_{1} \times\left[\mathrm{C}_{2} \mathrm{H}_{4}\right]}\right)\left(\frac{\left(1730 \mathrm{Lmol}^{-1} \mathrm{~s}^{-1}\right) \times[\mathrm{CO}]^{1}}{\left(6.11 \times 10^{-4} \mathrm{~s}^{-1}\right) \times\left[\mathrm{C}_{2} \mathrm{H}_{4}\right]^{0}}\right) \\
& =\left(\frac{\left(27.4 \mathrm{Lmol}^{-1}\right) \times\left(7.3 \times 10^{-3} \mathrm{molL}^{-1}\right)}{\left(0.584 \mathrm{Lmol}^{-1}\right) \times\left(0.11 \mathrm{molL}^{-1}\right)}\right)\left(\frac{\left(1730 \mathrm{Lmol}^{-1} \mathrm{~s}^{-1}\right) \times\left(7.3 \times 10^{-3} \mathrm{molL}^{-1}\right)}{\left(6.11 \times 10^{-4} \mathrm{~s}^{-1}\right)}\right) \\
& =6.4 \times 10^{4}
\end{aligned}
$$

Equation 2.1: Estimation of the ratio of alternating- to non-alternting-propagation during copolymerization of ethene with carbon monoxide. Conditions: 0.5 atm ethene, 0.5 atm carbon monoxide, $25^{\circ} \mathrm{C}$. Monomer concentrations are those reported by Rix and coworkers. ${ }^{10}$
tivity similar to the system prepared in situ, ${ }^{8,21}$ these results indicate that significant differences exist between the two. We propose three likely reasons for this discrepancy. First, the presence of the pyridine ligand may affect the apparent $K_{\text {eq }}$ by establishing an equilibrium between the pyridine- and monomercoordinated palladium species. Second, the rates of monomer insertion observed for palladium-methyl complex 2 may differ significantly from those of complexes 11 and 12. In particular, the kinetics of ethene insertion into the $\mathrm{Pd}-\mathrm{CH}_{3}$ bond of 2 is unlikely to be representative of ethene insertion into the palladium-carbon bond of a growing polymer chain. These first two concerns could be circumvented by working with pure samples of complex 4 . However, while 4 has been reported, ${ }^{22}$ we were unable to isolate a sample pure enough for NMR studies. Finally, Equation 2.1 assumes that decarbonylation occurs to a negligible extent. The reversibility of carbon monoxide insertion has been addressed by Ziegler and co-workers, ${ }^{17,18}$ who calculated that the de-insertion of carbon monoxide from the copolymer chain $(\operatorname{PdC}(\mathrm{O}) \mathrm{R})$ followed by ethene coordination and insertion leads to decreased incorporation of carbon monoxide.

Previously, we observed decarbonylation in compound $3 .{ }^{8}$ However, we did not determine conclusively whether the $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$ species exists in its open- or chelate-form because the presence of monomer is sufficient to disrupt the chelate. A direct comparison of the rates of decarbonylation of the palladium-acyl species in the neutral, phosphine-sulfonate complex, ( $\mathrm{P}^{\sim} \mathrm{SO}_{3}$ ) $\mathrm{Pd}{ }^{13} \mathrm{C}(\mathrm{O})$ $\mathrm{CH}_{3}($ py $)$, and its cationic analogue, (dppp) $\mathrm{Pd}^{13} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}(\mathrm{py})+\mathrm{BF}_{4}^{-}$, was performed. The rate of decarbonylation, $k_{\text {obs(CO) }}^{-1}$, was measure by using ${ }^{13} \mathrm{C}$ NMR spectroscopy to observe the loss of ${ }^{13} \mathrm{C}$ enrichment in the palladium-acyl species, 10, and its dppp-bearing analogue in the presence of natural carbon monoxide.

The neutral phosphine-sulfonate system was found to have an approximate $k_{\text {obs(CO) }}^{-1}$ of $5.6 \times 10^{-6} \mathrm{~s}^{-1}$ while the cationic diphosphine system was found to have an approximate $k_{\mathrm{obs}(\mathrm{CO})}^{-1}$ of $2.8 \times 10^{-5} \mathrm{~s}^{-1}$. Thus, the classic cationic system actually undergoes decarbonylation with exchange more readily than the phos-phine-sulfonate system. However, again, our model system differs from the system acting in situ because the rate of decarbonylation in the cationic diphosphine system may be reduced by the formation of sixmembered chelates (see Scheme 2.6). Ziegler and co-workers showed that, unlike the cationic diphosphine system, the neutral, sterically demanding metal center of the phosphine-sulfonate system does not readily form a six-membered chelate with the growing polyketone chain. In this scenario, decarbonylation of a neutral phosphine-sulfonate complex would not require the disruption of a chelate and, consequently, would have a lower $\Delta H^{\ddagger}$. Furthermore, because a decarbonylation event can affect the copolymer composition only if it is followed by exchange between carbon monoxide and ethene ( $\mathbf{1 1} \rightarrow \mathbf{1 2}$ ) and the subsequent insertion of the latter, the higher relative binding affinity of ethene in the phosphinesulfonate system (i.e., low $K_{\text {eq }}$ ) may enhance the effective rate of decarbonylation. Ultimately, further study will be required to fully quantify the effect of decarbonylation on the catalytic cycle.

The very different coordinating abilities of the two ends of the phosphine-sulfonate ligand pose an interesting mechanistic problem. It has been shown that the removal or the substitution of the sulfonate group by a carboxylate functionality strongly attenuates ${ }^{23}$ catalysis. According to Ziegler, ${ }^{17}$ because of the stronger trans effect of the phosphine, the complex is most stable when the palladium-carbon bond in the growing polymer chain is located cis to the phosphine. As discussed previously, the crystal structures of 2 and $\mathbf{3}$ bear this out. ${ }^{8}$ However, the insertion barrier is much lower when the palladium-carbon bond in the growing polymer chain is located trans to the phosphine. Thus, the overall polymerization may proceed through the following series of steps: (a) coordination of a monomer to the complex with the palladiumcarbon bond cis to the phosphine, (b) isomerization to the complex with the palladium-carbon bond trans to the phosphine, and (c) migratory insertion of the monomer to re-form the complex with the palladium-carbon bond cis to the phosphine. As shown in Scheme 2.7, the cis-trans isomerization may be viewed as a pseudorotation, and the ability of the sulfonate group to coordinate through multiple oxygens


Scheme 2.6: Decarbonylation of a copolymer chain. If a six-membered chelate is formed between the metal center and the growing polymer chain, it acts as a trapping ligand and must be disrupted before decarbonylation can proceed. $R$ represents the growing polymer chain and $L \sim L$ represents a bidentate ligand.
may to aid this process.


Scheme 2.7: Possible mechanism for the isomerization of the catalytic species from the complex with the Pd-C bond cis to the phosphine to the complex with the $\mathrm{Pd}-\mathrm{C}$ bond trans to the phosphine that begins with a pseudorotation of the phosphine-sulfonate ligand. R represents the growing polymer chain and L represents a coordinated monomer.

### 2.3 Conclusions

We have demonstrated the synthesis of a series of nonalternating copolymers of ethene with carbon monoxide using a neutral palladium catalyst bearing a phosphine-sulfonate ligand. It is possible to control the degree of carbon monoxide incorporation from $0-50 \mathrm{~mol} \%$ by varying the monomer feed ratio and reaction temperature.

By examining the kinetic and thermodynamic parameters, we found that the catalyst displays an unusually small difference in its binding affinities for ethene and carbon monoxide. However, the difference in monomer binding affinity alone is not sufficient to explain the degree of nonalternation actually observed in this system. It appears that decarbonylation also plays a significant role in the nonalternation. Unlike the traditional cationic palladium complexes that catalyze the alternating copolymerization, the neutral complex formed from the anionic ligand disfavors the formation of $\mathrm{Pd}-\mathrm{O}$ chelates by coordination of the carbonyl group on the growing polymer chain. This, in turn, facilitates ethene coordination to the metal and subsequent insertion. We also found that the rate of decarbonylation in the traditional cationic diphosphine system is higher than in the neutral phosphine-sulfonate system when chelation is absent.

### 2.4 Experimental Procedures

Chemical manipulations, with the exception of polymer workup and analysis, were performed under a dry nitrogen atmosphere using a glovebox or Schlenk techniques. All solvents, with the exception of NMR solvents, were distilled over $\mathrm{CaH}_{2}$ and degassed using the freeze-pump-thaw technique. Ultra-high-purity ethene and ultra-high-purity carbon monoxide were obtained from MG Industries and used without further purification. Deuterated nmR solvents and ${ }^{13} \mathrm{CO}$ were obtained from Cambridge Isotope Laboratories and used without further purification. Palladium acetate (99\%) was purchased from Johnson Matthey and used as received. The phosphine-sulfonate ligand was synthesized by following the literature procedure. ${ }^{15}$ Palladium-methyl complex 2 was synthesized by following the literature procedure. ${ }^{8}$

Nuclear magnetic resonance spectroscopy was performed using a Bruker DPX-300 spectrometer with a variable-temperature, multinuclear probe at 300.13 MHz for ${ }^{1} \mathrm{H}, 121.49 \mathrm{MHz}$ for ${ }^{31} \mathrm{P}$, or 75.4 MHz for ${ }^{13} \mathrm{C}$ NMR spectra. ${ }^{31} \mathrm{P}$ and ${ }^{13} \mathrm{C}$ spectra were obtained with proton decoupling. Quantitative ${ }^{13} \mathrm{C}$ experiments were performed using a zgig pulse sequence and a delay of 120 s before each scan. High-pressure nMr tubes were obtained from Wilmad with a Quick Pressure Valve, 5 mm diameter, 0.77 mm wall thickness, and an 8 in length.

Nmp data: $2{ }^{1} \mathrm{H}$ nmr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta(\mathrm{ppm}) 0.22\left(\mathrm{~d}, 3 \mathrm{H}, \mathrm{PdCH}_{3}\right) ; 3.68\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{OCH}_{3}\right) ; 6.99$ (dd, 2H, Ar); 7.06 (b, 2H, Ar); 7.36 (m, 2H, Ar); 7.50 (m, 3H, Ar); 7.58 (t, 2H, Ar); 7.92 (t, 1H, Ar); 8.06 (dd, 1H, Ar); 8.75 (dd, $2 \mathrm{H}, \mathrm{Py}) .{ }^{31} \mathrm{P}$ nmr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta 23.4 \mathrm{ppm} .3{ }^{1} \mathrm{H}$ nmr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta(\mathrm{ppm}) 1.84\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}\right) ; 3.78$ (s, $6 \mathrm{H}, \mathrm{OCH}_{3}$ ); 7.03 (dd, 2H, Ar); 7.10 (m, 2H, Ar); 7.34 (m, 2H, Ar); 7.53 (m, 3H, Ar); 7.60 (m, 2H, Ar); 7.77 (m, 2H, Ar); $7.95(\mathrm{t}, 1 \mathrm{H}, \mathrm{Ar}) ; 8.09(\mathrm{dd}, 1 \mathrm{H}, \mathrm{Ar}) ; 8.81(\mathrm{~d}, 2 \mathrm{H}, \mathrm{Py}) .{ }^{31} \mathrm{P}$ nmR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta 11.0 \mathrm{ppm} .{ }^{13} \mathrm{C}$ nmr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta 227 \mathrm{ppm}\left(\mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}\right) .4{ }^{1} \mathrm{H}$ nmp $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta(\mathrm{ppm}) 1.30\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}\right) ; 1.89(\mathrm{~s}$, $3 \mathrm{H}, \mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$ ); 2.11 (b, 2H, $\mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$ ); 3.70 (s, $6 \mathrm{H}, \mathrm{OCH}_{3}$ ); 7.02 (dd, $2 \mathrm{H}, \mathrm{Ar}$ ); 7.09 (dd, $2 \mathrm{H}, \mathrm{Ar}) ; 7.34$ (m, 2H, Ar); 7.50 (dd, 3H, Ar); 7.59 (t, 2H, Ar); 7.67 (b, 2H, Ar); $7.90(\mathrm{t}, 1 \mathrm{H}, \mathrm{Ar}) ; 8.09$ (m, 1H, Ar); 8.79 (d, 2H, Py). ${ }^{31} \mathrm{P}$ nmr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta 23.6 \mathrm{ppm} .{ }^{13} \mathrm{C}$ nmp $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta 216 \mathrm{ppm}\left(\mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}\right) .7{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2},-70^{\circ} \mathrm{C}\right): \delta(\mathrm{ppm}) 0.8-1.1\left(\mathrm{~b}, 2 \mathrm{H},\left(\mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}\right) ; 1.4\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}\right) ; 1.5-\right.$ $1.7\left(\mathrm{~b}, 2 \mathrm{H}, \mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}\right) ; 3.6\left(\mathrm{~b}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right) ; 3.8\left(\mathrm{~b}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right) ; 5.4$ (s, free ethene); 6.7-8.0 (17H, Ar); 8.7 (b, 1H, Py); 8.8 (b, 1H, Py). ${ }^{31} \mathrm{P}$ nmp $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2},-70^{\circ} \mathrm{C}\right): \delta 27.0 \mathrm{ppm} .{ }^{13} \mathrm{C}$ nmr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2},-70^{\circ} \mathrm{C}\right): \delta 201 \mathrm{ppm}$ $\left(\mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}\right) \cdot 8{ }^{1} \mathrm{H}$ nmr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2},-70^{\circ} \mathrm{C}\right): \delta(\mathrm{ppm}) 0.8-1.1\left(\mathrm{~b}, 2 \mathrm{H},\left(\mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}\right) ; 1.4(\mathrm{~s}, 3 \mathrm{H}\right.$, $\mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$ ); 1.5-1.7 (b, 2H, $\mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$ ); 3.6 (b, $3 \mathrm{H}, \mathrm{OCH}_{3}$ ); 3.8 (b, 3H, OCH 3 ); 6.7-8.0 ( $17 \mathrm{H}, \mathrm{Ar}$ ); 8.7, 8.8 (b, 2H, Py). ${ }^{31} \mathrm{P}$ nMr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2},-70^{\circ} \mathrm{C}\right): \delta 26.6 \mathrm{ppm} .{ }^{13} \mathrm{C}$ nMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2},-70^{\circ} \mathrm{C}\right): \delta 201 \mathrm{ppm}$ $\left(\mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}\right) .9{ }^{1} \mathrm{H} \operatorname{nmR}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta(\mathrm{ppm}) 0.8\left(\mathrm{~b}, 2 \mathrm{H}, \mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}\right) 1.0\left(\mathrm{~b}, 3 \mathrm{H}, \mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$ 1.3 (b, 2H, $\mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}$ ) 3.7 ( $\mathrm{s}, 6 \mathrm{H}, \mathrm{OCH}_{3}$ ); 5.5 (s, free ethene); 6.9-8.2 ( $17 \mathrm{H}, \mathrm{Ar}$ ); 8.8, $8.9(\mathrm{~b}, 2 \mathrm{H}, \mathrm{Py}) .{ }^{31} \mathrm{P}$ nmR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta 27.1 \mathrm{ppm} .10{ }^{1} \mathrm{H}$ nmr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta(\mathrm{ppm}) 1.76\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}\right) ; 3.73\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{OCH}_{3}\right) ; 7.00$ (dd, 2H, Ar); 7.09 (b, 2H, Ar); 7.34 (dd, 2H, Ar); 7.50 (m, 3H, Ar); 7.60 (t, 2H, Ar); 7.93 (t, 1H, Ar); 8.03 (dd, $1 \mathrm{H}, \mathrm{Ar}) ; 8.73(\mathrm{~d}, 2 \mathrm{H}, \mathrm{Py}) .{ }^{31} \mathrm{P}$ nmr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta 11.4 \mathrm{ppm} .{ }^{13} \mathrm{C}$ nmr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta 227 \mathrm{ppm}\left(\mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}\right)$.

Differential scanning calorimetry was performed using a TA Instruments model DSC Q100 and heating 3 mg copolymer samples at a rate of $20^{\circ} \mathrm{Cmin}^{-1}$ from $40^{\circ} \mathrm{C}$ to $300^{\circ} \mathrm{C}$.

Infrared spectroscopy was performed using a Varian FTS 7000 series DigiLab FT-Ir spectrometer with a ceramic IR source, KBr beamsplitter, deuterated triglycine sulfate detector, and 632.8 nm HeNe laser with a 5 kHz laser modulation frequency. The sample chamber was flushed with dry nitrogen, and data was collected from $4000 \mathrm{~cm}^{-1}$ to $900 \mathrm{~cm}^{-1}$ with a resolution of $1 \mathrm{~cm}^{-1}$.

Bulk polymerization reactions were carried out in an open 50 mL serum bottle placed in a 125 mL autoclave with magnetic stirring. The bottle was charged with $22 \mathrm{mg}(0.10 \mathrm{mmol})$ of $\mathrm{Pd}(\mathrm{OAc})_{2}$ and 40 mg $(0.10 \mathrm{mmol})$ of $\mathrm{P}^{\wedge} \mathrm{SO}_{3} \mathrm{H}$ ligand and 10 mL of dichloromethane. The bottle was placed in the autoclave and removed from the glovebox. The autoclave was then charged with the desired amounts of ethene and
carbon monoxide. The autoclave was placed in an oil bath with magnetic stirring for 1.5 h . At the end of this period, the autoclave was cooled to room temperature, vented to the atmosphere, and opened. The resulting polymer was precipitated into acidified methanol, collected by vacuum filtration, and dried under high vacuum overnight before analysis. Polymers were dissolved in tetrachloroethane- $d_{2}$ at $100^{\circ} \mathrm{C}$ for NMR analysis. Carbon monoxide incorporation was determined by the integration of the $\mathrm{CH}_{2}$ protons using the formula

$$
\begin{equation*}
[\mathrm{CO}]=\frac{A+B}{2 A+2 B+C+D} \tag{2.2}
\end{equation*}
$$

where $A$ is the integral of the peak at 2.7 ppm corresponding to ethene units adjacent to two carbonyl units; $B$ and $C$ are the integrals of the peaks at 2.4 ppm and 1.6 ppm corresponding to $\mathrm{CH}_{2}$ protons $\alpha$ and $\beta$ to the carbonyl, respectively, in ethene units adjacent to one carbonyl unit (double insertion); and $D$ is the integral of the peak at 1.3 ppm corresponding to ethene units not adjacent to a carbonyl unit (multiple insertion).

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## Chapter Three

## Copolymerization of Ethene with Functional Norbornenes

### 3.1 Introduction

Metal-catalyzed addition polymerization that leads to materials incorporating relatively high amounts of functionalized vinyl monomers is an area of great current interest in synthetic polymer chemistry. ${ }^{1-3}$ The copolymers of ethene with norbornene show such superior properties as excellent transparency, high glass transition temperature, good solvent resistance, and high thermal stability. The range of desirable properties is expected to be further enhanced by the use of appropriately functionalized norbornene derivatives. The inherent difficulty of polymerizing functionalized vinyl monomers stems from the poisoning of the catalyst center by coordination of the functionality. Late transition metals are more tolerant of polar functionalities in the monomer and the formed polymer. A number of nickel and palladium compounds have been shown to catalyze the addition polymerization of functionalized norbornenes. ${ }^{4-17}$ However, most of them are ineffective for the copolymerization of ethene with norbornene because the former act as chain transfer agent through $\beta$-hydrogen abstraction. Therefore, in order to achieve the copolymerization of ethene with functionalized norbornenes, it is necessary for the catalyst to be both tolerant of functional groups and resistant to $\beta$-hydrogen abstraction. We, ${ }^{18}$ Grubbs, ${ }^{19,20}$ Bazan, ${ }^{21,22}$ Mecking, ${ }^{23}$ and others, ${ }^{16}$ have recently described nickel-based systems for the copolymerization of ethene with functionalized norbornenes. However, the extent of incorporation of the norbornene monomer is low ( $<25 \mathrm{~mol} \%$ ). Herein, we report on catalyst systems based on palladium complexes incorporating anionic $\mathrm{P} \subset \mathrm{SO}_{3} \mathrm{H}$ ligands. Two $\pi$-allyl complexes were synthesized and crystallographically characterized. Copolymerizations carried out using these, along with complexes formed in situ, shows unusual functionality tolerance from several standpoints. First, they catalyze the copolymerization of ethene with functionalized norbornene derivatives to form copolymers with very high norbornene content ( $>40 \mathrm{~mol} \%$ ). Second, the system is so highly tolerant of reactive functionalities that the copolymerization can even be carried out in the presence of water. The catalytic systems are based on that reported by Drent, ${ }^{24,25}$ who also reported the copolymerization of ethene with norbornene derivatives. ${ }^{25}$ Two related $\mathrm{P}^{\sim} \mathrm{SO}_{3} \mathrm{H}$ ligands, 2-[bis(2-methoxyphenyl)phosphino]benzenesulfonic acid (1) and 2-[bis(2,6-dimethoxyphenyl)phosphino]benzenesulfonic acid (13) were employed. The X-ray crystal structure of $\mathbf{1 3}$ was determined and is shown in Figure 3.1. In one series of experiments, the catalytic systems were formed in situ by combining bis(dibenzylideneacetone)palladium( 0 ) $\left[\mathrm{Pd}(\mathrm{dba})_{2}\right]$ and one of the ligands in 1:1.2 molar ratio.


Phosphine-sulfonate ligands.


Figure 3.1: Crystal structure of phosphine-sulfonate ligand 13. Hydrogen atoms are omitted for clarity.

### 3.2 Results and Discussion

The results of copolymerization of ethene with functionalized norbornenes are summarized in Table 3.1. The polyethene obtained in Entry 1 is predominantly linear as evidenced by a single dominant ${ }^{13} \mathrm{C}$ NMR resonance at 28 ppm and a $T_{\mathrm{m}}$ of $127.8^{\circ} \mathrm{C}$ (Dsc). As shown in Table 3.1, the activity for ethene copolymerization with norbornene or bicyclo[2.2.1]hept-5-enyl-2-methyl acetate is comparable or even higher than that of ethene homopolymerization (Entry 1 vs. Entries 2 and 3). In particular, the high copolymerization rate with bicyclo[2.2.1]hept-5-enyl-2-methyl acetate is remarkable. Lowering the ethene pressure from 500 psig to 150 psig lowers the copolymerization activity but leads to very high incorporation of functional norbornenes (e.g., Entries 4 and 5). Both the copolymerization activity and the level of functionalized norbornene incorporation into the resultant copolymer appear to be a sensitive function of the ligand. For example, under the same conditions, $\mathrm{Pd}(\mathrm{dba})_{2} /$ ligand 1 catalyst produced copolymers with $37.7 \mathrm{~mol} \%$ of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (Entry 4) and $22.6 \mathrm{~mol} \%$ of bicyclo[2.2.1]-hept-5-enyl-2-methyl acetate (Entry 6) while $\mathrm{Pd}(\mathrm{dba})_{2} /$ ligand 13 catalyst only generated copolymers with $31.2 \mathrm{~mol} \%$ of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (Entry 8 ) and $13.3 \mathrm{~mol} \%$ of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (Entry 10). On the other hand, there is little effect on copolymer molecular weight (e.g., Entry 6: $M_{\mathrm{n}}=47000, M_{\mathrm{w}} / M_{\mathrm{n}}=2.1$. Entry 10: $M_{\mathrm{n}}=49700, M_{\mathrm{w}} / M_{\mathrm{n}}=1.8$ ). The structures of the obtained copolymers were analyzed by ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectroscopy (Appendix C). The relative simplicity of the latter suggests structures with isolated norbornene units. Presumably the size of the norbornene monomer precludes its consecutive insertion. Thus only ethene-ethene-ethene, norbornene-ethene-ethene, and ethene-norbornene-ethene triads are present. The ${ }^{13} \mathrm{C}$ nmp assignments are based on our previous report; ${ }^{18}$ the resonance at 33.2 ppm can be assigned to the apical carbon of norbornene. The resonances from 41.6 ppm to 42.4 ppm and from 47.4 ppm to 48.2 ppm are due to the bridgehead CH and the CH carbons of the norbornene units in the polymer backbone. The $\mathrm{CH}_{2}$ carbons from ethene and norbornene units appear at 29.8 ppm and from 30.0 ppm to 31.8 ppm , respectively.

A very unusual feature of the present catalytic system is that while it tolerates coordinating functionalities present in norbornene derivatives and in acrylates ${ }^{24,25}$ allowing the copolymerization of these classes of monomers with ethene. Simple 1-alkenes such as propene, 1-hexene, and styrene cannot be polymerized. Analysis of products from attempted copolymerization with ethene reveals no detectable comonomer incorporation into polyethene chains. Furthermore, the rate of polyethene formation in the presence of these monomers is almost an order of magnitude slower. To our knowledge this is the only known alkene polymerization system that shows such a selectivity. We had earlier reported that the rate of insertion of vinyl monomers $\left(\mathrm{CH}_{2}=\mathrm{CHR}\right)$ into palladium-alkyl bonds in cationic complexes decreases with increasing donor ability of the substituent $\left(\mathrm{R}=\mathrm{CO}_{2} \mathrm{R}>\mathrm{H}>\right.$ alkyl). ${ }^{26}$ An alkene with an electronwithdrawing substituent coordinates less strongly to the electrophilic metal (i.e. $\sigma$-donation is more important than $\pi$-back-donation). ${ }^{27}$ Thus, a weaker metal-alkene bond has to be broken for the insertion to proceed (i.e., the destabilization of the alkene complex leads to a lower insertion barrier). ${ }^{27}$ Therefore, both the failure of 1 -alkenes to be incorporated in the present system and the attenuation of polymerization activity in their presence can be ascribed to stronger binding but slower insertion rate for 1-alkenes. As discussed above, the catalyst system is remarkably tolerant of coordinating functionalities present either in the monomer or in the reaction solvent. To further underscore this, we carried out the emulsion copolymerization of ethene with bicyclo[2.2.1]hept-5-enyl-2-methyl acetate in a 9:1 (v:v) mixture of water and toluene (the latter was required to dissolve the catalyst and the monomer) (Conditions: $\operatorname{Pd}(\mathrm{dba})_{2}$, $13.5 \mu \mathrm{~mol}$; ligand $\mathbf{1}, 16.2 \mu \mathrm{~mol}$; sodium dodecylsulfate, 0.9 g ; ethene, 500 psig ; bicyclo[2.2.1]hept-5-enyl-2methyl acetate, 3 g ; toluene, 10 mL ; water, $90 \mathrm{~mL} ; 95^{\circ} \mathrm{C}, 3 \mathrm{~h}$. Yield, 7.1 g ; activity, $175 \mathrm{~kg} \mathrm{~mol}_{\mathrm{Pd}}^{-1} \mathrm{~h}^{-1}$ ); norbornene, $13.4 \mathrm{~mol} \% M_{\mathrm{n}}=42000 ; M_{\mathrm{w}} / M_{\mathrm{n}}=1.9$ ). The lower activity is expected due to significantly reduced
Table 3.1: Copolymerization of ethene with functional norbornenes.

| Entry | Ligand or <br> Complex | Pd <br> $(\mu \mathrm{mol})$ | Ethene <br> $(\mathrm{psig})$ | Time <br> $(\mathrm{h})$ | Norbornene <br> functional group | Norbornene <br> $(\mathrm{mmol})$ | Incorporation <br> $(\mathrm{mol} \%)$ | Activity <br> $\left(\mathrm{kg} \mathrm{mol}_{\mathrm{Pd}}^{-1} \mathrm{~h}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :--- | :---: | :---: | :---: |
| $1^{a}$ | $\mathbf{1}$ | 4.5 | 500 | 1 |  |  |  | 520 |
| $2^{a}$ | $\mathbf{1}$ | 4.5 | 500 | 1 | -H | 11.7 | 22.6 | 618 |
| $3^{a}$ | $\mathbf{1}$ | 4.5 | 500 | 1 | $-\mathrm{CH}_{2} \mathrm{OC}(\mathrm{O}) \mathrm{CH}_{3}$ | 12.0 | 14.9 | 816 |
| $4^{a}$ | $\mathbf{1}$ | 4.5 | 150 | 3 | $-\mathrm{CH}_{2} \mathrm{OC}(\mathrm{O}) \mathrm{CH}_{3}$ | 18.1 | 37.7 | 221 |
| $5^{a}$ | $\mathbf{1}$ | 4.5 | 150 | 3 | $-\mathrm{C}(\mathrm{O}) \mathrm{OCH}_{2} \mathrm{CH}_{3}$ | 18.1 | 43.9 | 241 |
| $6^{a}$ | $\mathbf{1}$ | 4.5 | 250 | 3 | $-\mathrm{OC}(\mathrm{O}) \mathrm{CH}_{3}$ | 12.0 | 22.6 | 268 |
| $7^{a}$ | $\mathbf{1}$ | 4.5 | 250 | 3 | $-\mathrm{CH} \mathrm{OH}^{2}$ | 12.0 | 34.2 | 48 |
| $8^{a}$ | $\mathbf{1 3}$ | 4.5 | 150 | 3 | $-\mathrm{OC}(\mathrm{O}) \mathrm{CH}_{3}$ | 18.1 | 31.2 | 194 |
| $9^{a}$ | $\mathbf{1 3}$ | 4.5 | 250 | 3 | $-\mathrm{C}(\mathrm{O}) \mathrm{OCH}_{2} \mathrm{CH}_{3}$ | 12.0 | 16.7 | 73 |
| $10^{a}$ | $\mathbf{1 3}$ | 4.5 | 250 | 3 | $-\mathrm{OC}(\mathrm{O}) \mathrm{CH}_{3}$ | 12.0 | 13.3 | 233 |
| $11^{a}$ | $\mathbf{1 3}$ | 7.8 | 250 | 2 | $-\mathrm{CH} \mathrm{OH}_{2}$ | 12.0 | 24.2 | 67 |
| $12^{b}$ | $\mathbf{1 4}$ | 4.5 | 500 | 1 | -H | 11.7 | 31.0 | 167 |
| $13^{b}$ | $\mathbf{1 5}$ | 4.5 | 500 | 1 | $-\mathrm{H}^{2}$ | 11.7 | 18.5 | 528 |

$a$ Conditions: 1.2 equivalents of ligand, 10 mL toluene, $95^{\circ} \mathrm{C}$.
${ }^{b}$ Conditions: 2 equivalents of $\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{3}, 10 \mathrm{~mL}$ toluene, $95^{\circ} \mathrm{C}$.


Figure 3.2: Plot of endo/exo isomers present in unreacted bicyclo[2.2.1]hept-5-enyl-2-methyl acetate as a function of time in its copolymerization with ethene. Reaction conditions: ethene, 250 psig ; bicyclo[2.2.1]hept-5-enyl-2-methyl acetate, 2 g ; $\mathrm{Pd}(\mathrm{dba})_{2}, 4.5 \mu \mathrm{~mol}$; ligand $\mathbf{1}, 5.4 \mu \mathrm{~mol}$; toluene, $10 \mathrm{~mL} ; 1,1,2,2-$ tetrachloroethane, $50 \mu \mathrm{~L} ; 95^{\circ} \mathrm{C}$.
solubility of ethene in water. In an attempt to better define the catalysts, $\pi$-allyl (14) and $\pi$-1-methallyl (15) complexes incorporating the $\mathrm{P}^{-} \mathrm{SO}_{3} \mathrm{H}$ ligand 1 were synthesized by the reaction of the chloro-bridged $\pi$-allyl or $\pi$-1-methallyl dimer with the sodium salt of 1 in dichloromethane at $-20^{\circ} \mathrm{C} .{ }^{28}$ The crystal structures of complexes 14 and 15 are shown in Figure 3.3 and bond length and bond angles are given in Appendix C. In view of the expected significantly stronger trans effect of the phosphine ligand, it is not surprising that the palladium-carbon bond of the allyl group trans to it is significantly longer than the one trans to the sulfonate group (14, $2.22 \AA$ versus $2.09 \AA$; 15, $2.25 \AA$ versus $2.10 \AA$ ).

Neither complex 14 nor 15 showed significant activity towards the copolymerization of ethene and norbornene, presumably because the $\eta^{3}$-allyl group occupies two coordination positions thereby preventing the coordination of the incoming monomer. However, the polymerization activity was restored when 1 to 2 molar equivalents of $\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{3}$ were added (Table 3.1). Under these conditions, the polymerization activity of $\mathbf{1 5}$ was similar to that observed when the catalytic system was formed in situ. The activity of 14 was somewhat lower possibly because the smaller allyl group binds more tightly to the metal than the 1-methallyl group. The specific role played by $B\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{3}$ in activating 14 and $\mathbf{1 5}$ is currently under investigation. In conclusion, we have described catalyst systems based on palladium complexes incorporating anionic $\mathrm{P}^{\sim} \mathrm{SO}_{3} \mathrm{H}$ ligands. Two new $\pi$-allyl complexes were synthesized and crystallographically characterized. Copolymerizations carried out using these, along with complexes formed in situ, show functionality tolerance that was unusual from several standpoints. First, they catalyzes the copolymerization of ethene with functionalized norbornene derivatives to from copolymers with very high norbornene content ( $>40 \mathrm{~mol} \%$ ). Second, the system is so highly tolerant of reactive functionalities that the copolymerization can even be carried out in the presence of water.

Table 3.2: Solvent effect. ${ }^{a}$

| Run | Solvent | Yield | Activity | Norbornene <br> incorporation | $M_{\mathrm{n}}{ }^{b}$ | $M_{\mathrm{w}} / M_{\mathrm{n}}{ }^{b}$ |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: |
|  | $(\mathrm{~g})$ | $\left(\mathrm{kg} \mathrm{mol}_{\mathrm{Pd}}^{-1} \mathrm{~h}^{-1}\right)$ | (mol \%) |  |  |  |
| 1 | acetonitrile | 0 | 0 |  |  |  |
| 2 | dimethoxyethane | 1.59 | 118 | 5.62 | 66900 | 1.82 |
| 3 | ethanol | 0.43 | 32 | 38.2 |  |  |
| 4 | anisole | 1.80 | 133 | 34.6 | 61100 | 1.79 |
| 5 | toluene | 2.25 | 167 | 31.4 | 73000 | 1.91 |
| 6 | chlorobenzene | 1.40 | 104 | 29.0 | 60100 | 1.73 |

${ }^{a}$ Conditions: solvent, 10 mL ; bicyclo[2.2.1]hept-5-enyl-2-methyl acetate, 2 g ; ethene, 150 psig ; $\operatorname{Pd}(\mathrm{dba})_{2}, 4.5 \mu \mathrm{~mol}$; ligand $\mathbf{1}, 5.4 \mu \mathrm{~mol} ; 95^{\circ} \mathrm{C} ; 3 \mathrm{~h}$.
${ }^{b}$ Determined by size-exclusion chromatography relative to polystyrene standards.


Figure 3.3: Ortep diagrams of catalytic allylpalladium, 14, and crotylpalladium, 15, complexes. Hydrogen atoms are omitted for clarity. Chloroform molecule in 15 is omitted for clarity.

### 3.3 Experimental Procedures

### 3.3.1 General Procedures

Materials. All chemicals were purchased from Aldrich except where stated otherwise. The functionalized norbornene monomers used in this work were mixtures of endo and exo isomers. bicyclo[2.2.1]hept-5-ene-2-carboxylic acid ethyl ester (97\%), bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (97\%) and bicyclo-[2.2.1]hept-5-enyl-2-methyl acetate (97\%) were generously donated by the BF Goodrich Company. Palladium(II) acetate, and Bis(dibenzylideneacetone)palladium $(0)\left[\mathrm{Pd}(\mathrm{dba})_{2}\right]$, were obtained from the Johnson Matthey Company. Allylpalladium chloride dimer, 1-methallylpalladium chloride dimer and tris(pentafluorophenyl)borane were purchased from Strem chemicals and used without further purification. CP grade ethene was supplied by the Matheson Company and used without further purification.

All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. Solvents were degassed in 20L reservoirs and passed through two sequential purification columns. Oxygen was removed by a copper catalyst and water was removed by activated alumina.

### 3.3.2 Characterization

Nuclear magnetic resonance spectra were recorded at $125^{\circ} \mathrm{C}$ in 1,1,2,2-tetrachloroethane- $d_{2}$ on a Bruker DPX-300 spectrometer at 300.15 MHz for ${ }^{1} \mathrm{H}$ nMr and 75.4 MHz for ${ }^{13} \mathrm{C}$ nMr. The chemical shifts are referenced relative to the solvent. Molecular weights and molecular weight distributions were measured on a Shimadzu size exclusion chromatograph (SEC) using a flow rate of $1 \mathrm{mLmin}^{-1}$ and a three-column bed (Styragel HR $7.8 \times 300 \mathrm{~mm}$ columns with 5 mm bead size: 100 Da to 10000 Da ; 500 Da to 30000 Da ; and 5000 Da to 6000000 Da ), a Shimadzu RID 10A differential refractometer and SPD 10A UV-Vis detector. Samples for sEc were run in $\mathrm{CHCl}_{3}$ at ambient temperature and calibrated to polystyrene standards obtained from Aldrich. Gas chromatography data were obtained on a Hewlett-Packard 5890 Series II instrument fitted with an Alltech EC-5 column and flame ionization detector using 1,1,2,2-tetrachloroethane as an internal standard.

### 3.3.3 Synthesis of Ligand 1

This ligand was synthesized by two different procedures as illustrated in Scheme 3.4. The first procedure is the same as the literature procedure ${ }^{24,25}$ except that n-butyl lithium was used in the last step. In the second procedure, bis(2-methoxyphenyl)methoxyphosphine was converted to bis(2-methoxyphenyl)chlorophosphine as follows before reacting with lithium salt of benzenesulfonic acid. To a solution of bis(2methoxyphenyl)methoxyphosphine ( $1.89 \mathrm{~g}, 6.85 \mathrm{mmol}$ ) in THF ( 10 mL ) was added drop wise a solution of $\mathrm{PCl}_{3}(4.71 \mathrm{~g}, 34.3 \mathrm{mmol})$ in THF $(10 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$. The reaction was then allowed to stand for 5 h at room temperature. The unreacted $\mathrm{PCl}_{3}$ was removed under vacuum. The bis(2-methoxyphenyl)chlorophosphine solution in THF was added slowly to the lithium salt of benzenesulfonic acid at $-40^{\circ} \mathrm{C}$. The reaction was allowed to stand at room temperature for 16 h . Water $(40 \mathrm{~mL})$ was then added followed by the removal of THF in vacuum. The aqueous solution was acidified to a pH of 1 by adding concentrated $\mathrm{HCl}(37 \%)$. The precipitate was filtered off and the filtrate was washed with tert-butyl methyl ether ( 15 mL ). After extracting three times with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{~mL})$, the crude product was dried over anhydrous $\mathrm{MgSO}_{4}$. Solvent was removed under vacuum to afford a white powder $(1.05 \mathrm{~g}, 38.2 \%) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): 9.1 \mathrm{ppm}(1 \mathrm{H}, \mathrm{P}-\mathrm{H})$, 6.8 ppm to $8.4 \mathrm{ppm}\left(\mathrm{m}, 12 \mathrm{H}\right.$, phenyl), $3.8 \mathrm{ppm}\left(\mathrm{s}, 6 \mathrm{H}, \mathrm{OCH}_{3}\right) ;{ }^{31} \mathrm{P}$ NMR $\left(\mathrm{CDCl}_{3}\right):-9.6 \mathrm{ppm}$.


Scheme 3.4: Outline of ligand synthesis.

### 3.3.4 Synthesis Ligand 13

To a solution of benzenesulfonic acid ( $1.08 \mathrm{~g}, 6.84 \mathrm{mmol}$ ) in THF $(15 \mathrm{~mL})$ was added drop-wise n-butyl lithium ( $15 \mathrm{mmol}, 2.5 \mathrm{~mol} \mathrm{dm}^{-3}$ in hexane) at $0^{\circ} \mathrm{C}$. After stirring at room temperature for 18 h a solution of bis(2,6-dimethoxyphenyl)methoxyphosphine $(2.30 \mathrm{~g}, 6.86 \mathrm{mmol})$ in THF $(50 \mathrm{~mL})$ was added at $-40^{\circ} \mathrm{C}$ and the reaction was allowed to stand for further 12 h . Water $(40 \mathrm{~mL})$ was then added followed by the removal of THF in vacuum. The aqueous solution was acidified to a pH of 1 by adding concentrated $\mathrm{HCl}(37 \%)$. The precipitate was filtered off and the filtrate was washed with tert-butyl methyl ether ( 15 mL ). After extracting three times with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{~mL})$, the crude product was dried over anhydrous $\mathrm{MgSO}_{4}$. Solvent was removed under vacuum to afford a white powder $(1.25 \mathrm{~g}, 39.6 \%)$ The crystal for X-ray analysis was obtained at $-10^{\circ} \mathrm{C}$ from a mixture of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and hexane. ${ }^{1} \mathrm{H}$ nMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): 10.3 \mathrm{ppm}(1 \mathrm{H}, \mathrm{P}-\mathrm{H}), 6.6 \mathrm{ppm}$ to $8.4 \mathrm{ppm}\left(\mathrm{m}, 10 \mathrm{H}\right.$, phenyl), $3.6 \mathrm{ppm}\left(\mathrm{s}, 12 \mathrm{H}, \mathrm{OCH}_{3}\right) ;{ }^{31} \mathrm{P}$ NMR $\left(\mathrm{CDCl}_{3}\right):-29.3 \mathrm{ppm}$.

### 3.3.5 Synthesis of Allylpalladium Complex 14

Sodium carbonate $\left(\mathrm{Na}_{2} \mathrm{CO}_{3}\right)(0.315 \mathrm{~g}, 2.97 \mathrm{mmol})$ was added to a flask containing ligand $\mathbf{1}(1 \mathrm{~g}, 2.48 \mathrm{mmol})$ and 15 mL dichloromethane. The solution was stirred until it formed a white precipitate (approx. 4 h ). To this was added dichloromethane solution of allylpalladium chloride dimer $(0.45 \mathrm{~g}, 1.24 \mathrm{mmol})$ at $-20^{\circ} \mathrm{C}$, and stirring continued overnight. The reaction mixture was filtered and the filtrate was recrystallized using pentane as a non-solvent. Yield: $1.09 \mathrm{~g}(80 \%) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): 8.19 \mathrm{ppm}(1 \mathrm{H}, \mathrm{m}$, aromatic), 7.53 ppm $(2 \mathrm{H}, \mathrm{m}$, aromatic), $7.39 \mathrm{ppm}(1 \mathrm{H}, \mathrm{m}$, aromatic), 6.9 ppm to $7.2 \mathrm{ppm}(8 \mathrm{H}, \mathrm{m}$, aromatic), $5.66 \mathrm{ppm}(1 \mathrm{H}, \mathrm{m}$, $\mathrm{CH}), 4.74 \mathrm{ppm}(1 \mathrm{H}, \mathrm{m}, \mathrm{HCH}), 3.80 \mathrm{ppm}(1 \mathrm{H}, \mathrm{m}, \mathrm{HCH}), 3.14 \mathrm{ppm}(1 \mathrm{H}, \mathrm{m}, \mathrm{HCH}), 2.65 \mathrm{ppm}(1 \mathrm{H}, \mathrm{d}, \mathrm{HCH})$, $3.80 \mathrm{ppm}\left(6 \mathrm{H}, \mathrm{m}, \mathrm{OCH}_{3}\right) .{ }^{31} \mathrm{P}$ nmr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right):-2.9 \mathrm{ppm}(\mathrm{s})$. Because of general instability of this class of palladium compounds, elemental analysis was not attempted. However, $\mathbf{1 4}$ was judged pure by nmr spectroscopy (see Appendix C). Its structure was further established by X-ray crystallography.

### 3.3.6 Synthesis of Crotylpalladium Complex 15

Complex 15 was synthesized by using methallylpalladium chloride dimer by following the above procedure. Yield: $1.1 \mathrm{~g}(78 \%) .{ }^{1} \mathrm{H} \operatorname{nmR}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): 6.9 \mathrm{ppm}$ to $8.4 \mathrm{ppm}(12 \mathrm{H}, \mathrm{m}$, aromatic), $5.45 \mathrm{ppm}(1 \mathrm{H}, \mathrm{m}$, $\left.\mathrm{CH}=\mathrm{CHCH}_{3}\right), 4.62 \mathrm{ppm}\left(1 \mathrm{H}, \mathrm{m}, \mathrm{CH}=\mathrm{CHCH}_{3}\right), 3.74 \mathrm{ppm}\left(6 \mathrm{H}, \mathrm{s}, \mathrm{OCH}_{3}\right), 3.10 \mathrm{ppm}(1 \mathrm{H}, \mathrm{br}, \mathrm{HCH}-\mathrm{CH}=\mathrm{CH})$, $2.51 \mathrm{ppm}(1 \mathrm{H}, \mathrm{br}, \mathrm{HCH}-\mathrm{CH}=\mathrm{CH}), 1.76 \mathrm{ppm}\left(3 \mathrm{H}, \mathrm{m}, \mathrm{CH}=\mathrm{CHCH}_{3}\right) .{ }^{31} \mathrm{P}$ nmr $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right):-4.87 \mathrm{ppm}$ (s). Complex 15 was judged pure by NMr spectroscopy (see Appendix C). Its structure was further established by X-ray crystallography.

### 3.3.7 Copolymerization of Ethene with Functionalized Norbornenes

In a typical experiment (Table 3.1, Entry 4), a 300 mL , glass-lined, stainless-steel autoclave equipped with a magnetic stir-bar was placed into a $\mathrm{N}_{2}$-filled glovebox, charged with toluene ( 10 mL ), $\mathrm{Pd}(\mathrm{dba})_{2}(4.5 \mu \mathrm{~mol})$, ligand $\mathbf{1}(5.4 \mu \mathrm{~mol}$ pre-dissolved in 1 mL toluene), and bicyclo[2.2.1]hept-5-enyl-2-methyl acetate ( 3.0 g , 18.1 mmol ). The autoclave was removed from the glove box, charged to 150 psig with ethene, and heated in an oil bath at $95^{\circ} \mathrm{C}$ for 3 h . The reactor was then cooled to room temperature, vented to the atmosphere, and the contents were poured into 500 mL of HCl -acidified methanol. The precipitated polymer was washed then dried under vacuum. The composition of the copolymer was determined from the integration of the ${ }^{1} \mathrm{H}$ nmr peaks from $3.60-4.20 \mathrm{ppm}$ for the $\mathrm{CH}_{2} \mathrm{OCO}$ unit of bicyclo[2.2.1]hept-5-enyl-2methyl acetate and 1.2 ppm for the $\mathrm{CH}_{2}$ units of ethene. Yield: 2.98 g . Bicyclo[2.2.1]hept-5-enyl-2-methyl acetate incorporation: $37.7 \mathrm{~mol} \%$.

### 3.3.8 Determination of the Relative Uptake of endo and exo Isomers

In a $\mathrm{N}_{2}$-filled glovebox, a 300 mL , glass-lined, stainless-steel autoclave equipped with a magnetic stir bar was charged with 10 mL of toluene, $4.5 \mu \mathrm{~mol}$ of $\mathrm{Pd}(\mathrm{dba})_{2}, 5.4 \mu \mathrm{~mol}$ of ligand $\mathbf{1}$ (pre-dissolved in 1 mL of toluene), 12 mmol of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate, and $50 \mu \mathrm{~L}$ 1,1,2,2-tetrachloroethane as an internal standard. The autoclave was charged to 250 psig with ethene and then placed in an oil bath at $95^{\circ} \mathrm{C}$. The amount of unreacted exo and endo isomer present during the course of the reaction was determined by gas chromatography of samples taken at set intervals.

### 3.3.9 Emulsion Copolymerization of Ethene with Functionalized Norbornenes

In a $\mathrm{N}_{2}$-filled glovebox, a 600 mL glass-lined, stainless-steel autoclave equipped with a magnetic stir-bar was charged with toluene $(7 \mathrm{~mL}), \mathrm{Pd}(\mathrm{dba})_{2}(13.5 \mu \mathrm{~mol})$, ligand $\mathbf{1}(16.2 \mu \mathrm{~mol}$ pre-dissolved in 3 mL toluene $)$, and bicyclo[2.2.1]hept-5-enyl-2-methyl acetate ( $3.0 \mathrm{~g}, 18.1 \mathrm{mmol}$ ). The autoclave was then removed from the glovebox and sodium dodecylsulfate ( 0.9 g ) in degassed water ( 90 mL ) was added using a syringe. After charging to 500 psig with ethene, the reactor was placed in an oil bath at $95^{\circ} \mathrm{C}$ for 3 h . The reactor was then cooled to room temperature and the contents were poured into 500 mL of HCl -acidified methanol. Polymer was recovered by filtration. Yield: 7.1 g ; Bicyclo[2.2.1]hept-5-enyl-2-methyl acetate incorporation: $13.4 \mathrm{~mol} \% . M_{\mathrm{n}}=42000 ; M_{\mathrm{w}} / M_{\mathrm{n}}=1.9$.

### 3.3.10 Copolymerization with Functionalized Norbornenes Using 14 and 15

In a typical copolymerization experiment, a 300 mL glass-lined, stainless-steel autoclave equipped with a magnetic stir-bar was charged with toluene ( 10 mL ), $\mathbf{1 4}$ or $\mathbf{1 5}(4.5 \mu \mathrm{~mol})$, tris(pentafluorophenyl)borane ( $9 \mu \mathrm{~mol}$ ) and norbornene ( $1.1 \mathrm{~g}, 11.7 \mathrm{mmol}$ ) inside a $\mathrm{N}_{2}$-filled glovebox. The autoclave was charged to 500 psig with ethene and immersed in a preheated oil bath at $95^{\circ} \mathrm{C}$. After the desired time-period,
the autoclave was allowed to cool to room temperature and the polymer was precipitated in acidified methanol and dried under vacuum.

### 3.3.11 X-ray Structure Determination

The X-ray intensity data were measured at 98(2)K for 13, 108(2)K for 14, cooled by Rigaku-MSC X-Stream 2000 and $298(2) \mathrm{K}$ for $\mathbf{1 5}$, on a Bruker smart apex ccd area detector system equipped with a graphite monochromator and a Mo K $\alpha$ fine-focus sealed tube ( $\lambda=0.71073 \AA$ ) operated at 1600 W power ( 50 kV , 32 mA ). The detector was placed at a distance of 5.8 cm from the crystal.

Data collection: Bruker smart; cell refinement: Bruker saint; data reduction: Bruker saint; structure solving: shelxtl; structure refinement: SHELXTL; molecular graphics: ortep 3.2; publication preparation: shelxtl. ${ }^{29}$ Additional information is available in Appendix C.

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## Chapter Four

## Copolymerization of Ethene with Functional Styrenes

### 4.1 Introduction

The copolymers of ethene with styrene are of great current interest because of their anticipated high viscoelasticity, compatibility with other commodity polymers and excellent mechanical properties. ${ }^{1,2}$ Early transition metal-based systems are known to catalyze this copolymerization, but these cannot tolerate an oxygen functionality on the styrenic monomer and protic solvents cannot be employed for the reaction. ${ }^{3,4}$ Late-transition-metal polymerization systems are known for the polymerization of some monomers with oxygen functionalities. ${ }^{5,6}$ However, few ${ }^{7-9}$ have been shown to be effective for copolymerization of ethene with styrene; insertion of styrene typically leads to chain termination through $\beta$-H elimination. Recently, our group reported the first well-defined system for the copolymerization of ethene with a variety of styrene derivatives, including those with oxygen functionalities. ${ }^{10}$ Moreover, it was was possible to carry out the copolymerizations in protic solvents including water, allowing for the emulsion copolymerization of ethene and styrene. The same catalyst system can also be employed for the copolymerization of ethene with methyl vinyl ketone, vinylcyclohexane, and other 1-alkenes.

We and others ${ }^{11-14}$ have previously reported on the copolymerization of ethene with polar vinyl monomers, carbon monoxide, and norbornene derivatives using neutral palladium(II) systems bearing phos-phine-sulfonate ligands described by Drent and Pugh. ${ }^{6}$ In those studies, we found that the well-defined, square-planar model compound $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}(\mathrm{py}), 2,{ }^{12}$ with a methyl group and pyridine occupying positions cis and trans to the phosphine group, respectively, catalyzed ethene homopolymerization with slightly lower activity compared to the system generated in situ from 2-[bis(2-methoxyphenyl)phosphino]benzenesulfonic acid $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3} \mathrm{H}\right)$ and bis(dibenzylideneacetone)palladium(0), $\mathrm{Pd}(\mathrm{dba})_{2}$ or palladium(II) acetate $\left[\mathrm{Pd}(\mathrm{OAc})_{2}\right]$. However, unlike the system formed in situ, 2 was unreactive towards the copolymerizations of ethene with the polar vinyl monomers studied, presumably because they are too weakly coordinating to displace the coordinated pyridine. The addition of one or two equivalents of the Lewis acid, triphenylboron, was found to create a vacant coordination-site on the metal center and allows for easier coordination of the incoming monomer and subsequent insertion into the palladium-carbon bond.

However, the mechanism of insertion of styrene into the palladium-carbon bond remained unclear. In situ NMR spectra showed that the expected 2,1 -insertion of styrene into 2 to give an ( $\eta^{3}$-phenylpropyl)palladium complex, 16, followed by $\beta$-H elimination to yield 1-phenyl-1-propene was not the sole reaction pathway. The presence of NMR proton signals that could not be assigned to styrene, the palladium complex or 1-phenyl-1-propene led me to perform a detailed investigation and more fully elucidate the reaction mechanism.


Phosphine-sulfonate catalyst 2.

( $\eta^{3}$-phenylpropyl)palladium complex 16.

### 4.2 Results and Discussion

Initially, the synthesis of $\mathbf{1 6}$ was attempted by adapting the procedure used previously for the synthesis of ( $\eta^{3}$-crotyl) palladium complex 15 via an ( $\eta^{3}$-crotyl)palladium chloride dimer so that a pure sample could be compared with the in situ NMR spectra of this system. ${ }^{11}$ However, the ( $\eta^{3}$-phenylpropyl)palladium chloride dimer decomposed immediately and could not be isolated. Therefore, the reaction that had been observed in situ was scaled up and the reaction products were isolated for characterization. The reaction was found to produce exclusively 1-phenyl-1-propene and an ( $\eta^{3}$-phenylethyl) palladium complex, 17. The structure of the $\eta^{3}$-phenylethyl moiety was confirmed by a cosy nmr experiment and ${ }^{1} \mathrm{H}$ NMR splitting in an isolated sample of 17 which showed a doublet of doublets for the $\mathrm{CH}_{3}$ group, which is consistent with the complex splitting observed in the analogous ( $\eta^{3}$-crotyl)palladium complex 15 we reported previously ${ }^{11}$ (see Chapter 3). Also, the formation of $\eta^{3}$-phenylethyl complex 17 is supported by the absence of pyridine or other ligands to occupy the fourth coordination-site of palladium in isolated samples of $\mathbf{1 7}$ and the slow decomposition of $\mathbf{1 7}$ at ambient temperature to give styrene and palladium black.

The insertion of styrene into the palladium-carbon bond of $\mathbf{2}$ in dichloromethane- $d_{2}$ was observed in situ by NMR spectroscopy. At ambient temperature, 2 readily converts styrene to 1-phenyl-1-propene in the presence of $\mathrm{BPh}_{3}$ as confirmed by ${ }^{1} \mathrm{H}$ nmR signals at $6.5 \mathrm{ppm}(1 \mathrm{H}, \mathrm{d}), 6.3 \mathrm{ppm}(1 \mathrm{H}, \mathrm{m})$ and 1.9 ppm $(3 H, d)$. This is consistent with a 2,1 -insertion of styrene into the $\mathrm{Pd}-\mathrm{C}$ bond followed by rapid $\beta$ - H elimination to give a palladium hydride and 1-phenyl-1-propene. Additionally, the conversion of styrene to 17 was shown by ${ }^{1} \mathrm{H}$ NMR signals at $3.2 \mathrm{ppm}(1 \mathrm{H}, \mathrm{q})$ and $0.7 \mathrm{ppm}(3 \mathrm{H}, \mathrm{dd})$ along with the replacement of the ${ }^{31} \mathrm{P}$ NMR signal of 2 at 22.7 ppm with a new signal at 11.4 ppm . These observations are consistent with the 2,1 -insertion of styrene into the $\mathrm{Pd}-\mathrm{H}$ bond to give an 17, as shown in Scheme 4.1. This mechanism is supported by the reaction of 2 with styrene- $d_{8}$ to produce 1-phenyl-1-propene- $d_{7}$ with an unlabeled
methyl group and 17- $d_{9}$ with a fully deuterated phenylethyl moiety as determined by ${ }^{1} \mathrm{H}$ and ${ }^{2} \mathrm{H}$ NMR spectroscopy. Furthermore, addition of 100 psig of ethene to $17-d_{9}$ in dichloromethane at ambient temperature produced polyethene with a deuterated styrenic end-group. We examined the kinetics of styrene insertion into 2 under pseudo-first-order conditions by following the disappearance of the resonance at 22.7 ppm in the ${ }^{31} \mathrm{P}$ NMR spectrum. The reaction is first-order in styrene and the Eyring plot shows a $\Delta H^{\ddagger}$ of $64.3(6) \mathrm{kJ} \mathrm{mol}^{-1}$ and a $\Delta S^{\ddagger}$ of $-60(20) \mathrm{J} \mathrm{mol}^{-1} \mathrm{~K}^{-1}$.


Scheme 4.1: Conversion of methylpalladium complex 2 and styrene to ( $\eta^{3}$-phenylethyl) palladium complex 17 and 1-phenyl-1-propene.

Copolymerization using compound 2 with triphenylboron was also studied and the results are summarized in Table 4.1. Increasing the amount of comonomer in the feed results in its higher incorporation into the copolymer; however, the molecular weight is lowered. The ethene/styrene copolymerization also proceeds in the presence of one equivalent of the radical trap galvinoxyl, thereby eliminating the role of radicals in the copolymerization. The drop in activity in the presence of the trap can be attributed to the reaction of galvinoxyl with $\mathrm{Pd}-\mathrm{H}$ species that can attenuate metal-centered non-radical reactions. ${ }^{15,16}$ The solution copolymerizations of ethene with 4 -acetoxystyrene, 4 -vinylmethylbenzoate, and 4-fluorostyrene were also performed. The catalytic activities for the copolymerization reactions were $12800 \mathrm{~g} \mathrm{~mol}_{\mathrm{Pd}}^{-1} \mathrm{~h}^{-1}, 16500 \mathrm{~g} \mathrm{~mol}_{\mathrm{Pd}}^{-1} \mathrm{~h}^{-1}$, and $16100 \mathrm{~g} \mathrm{~mol}_{\mathrm{Pd}}^{-1} \mathrm{~h}^{-1}$, and the comonomer incorporations were $2.8 \mathrm{~mol} \%, 6.7 \mathrm{~mol} \%$, and $4.5 \mathrm{~mol} \%$, respectively. The hydrolysis of 4 -acetoxystyrene and 4 -vinylmethyl-benzoate-containing copolymers afforded materials bearing hydroxyl and carboxylic acid functionalities,
respectively.

Table 4.1: Copolymerization of ethene with polar vinyl monomers using complex $\mathbf{2}$ and triphenylboron. ${ }^{a}$

| entry | comonomer | amount <br> $(\mathrm{g})$ | ethene <br> $(\mathrm{psig})$ | time <br> $(\mathrm{h})$ | $M_{\mathrm{w}}$ | PDI $^{b}$ | activity $_{\left(\mathrm{gmol}_{\mathrm{Pd}} \mathrm{h}^{-1}\right)}$ | incorporation <br> $(\mathrm{mol} \%)$ |
| :---: | :--- | :---: | ---: | :---: | :---: | :---: | :---: | :---: |
| 1 | styrene | 1 | 100 | 7 | 7100 | 2.3 | 9900 | 4.1 |
| 2 | styrene | 5 | 100 | 7 | 4700 | 1.8 | 8260 | 7.5 |
| $3^{d}$ | styrene | 5 | 100 | 7 | 2000 | $1.3^{e}$ | 2750 | 7 |
| 4 | vinylcyclohexane | 1 | 100 | 7 | 8100 | 2.0 | 7570 | 5.2 |
| 5 | vinylcyclohexane | 3 | 100 | 5 | 3400 | 1.4 | 9640 | 11.8 |
| 6 | propene | 3 | 100 | 4 | 5000 | 1.7 | 33050 | $23.4^{f}$ |
| 7 | 1-hexene | 1 | 50 | 15 | 4000 | 3.1 | 4850 | 27 |
| 8 | 1-hexene | 2 | 50 | 15 | 2200 | $1.7^{e}$ | 4310 | 47 |
| 9 | 1-hexene | 3 | 50 | 15 | 1900 | $2.0^{e}$ | 5357 | $53 f$ |
| 10 | methyl vinyl ketone | 1 | 200 | 16 | 15500 | 2.4 | 1690 | 4.9 |
| 11 | methyl vinyl ketone | 1 | 100 | 16 | 9600 | 2.6 | 803 | 7.7 |

${ }^{a}$ Conditions: complex 2, $0.005 \mathrm{~g}\left(8.30 \times 10^{-6} \mathrm{~mol}\right) ; \mathrm{BPh}_{3}, 0.004 \mathrm{~g}\left(1.66 \times 10^{-5} \mathrm{~mol}\right) ; \mathrm{CH}_{2} \mathrm{Cl}_{2}, 5 \mathrm{~mL} ; 80^{\circ} \mathrm{C}$.
${ }^{b}$ By GPC analysis in 1,2-dichlorobenzene at $135^{\circ} \mathrm{C}$ using polystyrene standards.
${ }^{c}$ By ${ }^{1} \mathrm{H}$ nmr spectroscopy in 1,1,2,2-tetrachloroethane- $d_{2}$ at $110^{\circ} \mathrm{C}$.
${ }^{d}$ In the presence of one equivalent of galvinoxyl.
${ }^{e}$ By GPC analysis in THF at $35^{\circ} \mathrm{C}$ using polystyrene standards.
$f$ By ${ }^{1} \mathrm{H}$ NMR spectroscopy in chloroform- $d$.

The water contact angles for poly(ethene-co-functional styrene) copolymers were measured for thin films coated on glass slides. Poly(ethene-co-styrene) containing $4.1 \mathrm{~mol} \%$ of styrene exhibits an advancing contact angle of $101^{\circ}$ and a receding contact angle of $89^{\circ}$. The introduction of 4 -acetoxystyrene and 4vinylmethylbenzoate into the copolymer results in the contact angle dropping to $92^{\circ}$ (advancing) and $82^{\circ}$ (receding). However, the presence of 4-fluorostyrene results in a slight increase in contact angle with obtained values for poly(ethene-co-4-fluorostyrene) of $109^{\circ}$ (advancing) and $96^{\circ}$ (receding).

The copolymerization of ethene with other vinyl monomers such as vinylcyclohexane (vCH), propene, 1 -hexene, and methyl vinyl ketone (mvk) were also performed (Table 4.1). These monomers do not readily undergo radical copolymerization. Copolymerization of ethene with 1-hexene results in copolymers with an unusually high incorporation of 1-hexene. Copolymerization with a feed ratio of 3 g of 1-hexene to 50 psig of ethene resulted in material with $\sim 50 \mathrm{~mol} \%$ of 1 -hexene, as determined by ${ }^{1} \mathrm{H}$ NMR spectroscopy. The structures of all the copolymer materials were confirmed by ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ nMr spectroscopy. In the case of poly(ethene-co-styrene), the incorporation of the styrene was calculated by comparing the integration of the five aromatic protons of styrene with all the aliphatic protons appearing between 0.9 ppm and 1.9 ppm . The two resonances, a doublet at 6.3 ppm and a multiplet at 6.6 ppm , suggest the presence of $-\mathrm{CH}_{2} \mathrm{CH}=\mathrm{CHPh}$ chain-ends formed by styrene insertion and subsequent $\beta-\mathrm{H}$ elimination. The formation of poly(ethene-co-styrene) was further confirmed by ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NmR spectroscopy in 1,1,2,2-tetrachloroethane $-d_{2}$ at $110^{\circ} \mathrm{C}$. Both ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ nmp analysis revealed the formation of linear copolymers. The ${ }^{13} \mathrm{C}$ resonance at 28.6 ppm suggests the presence of ethene-ethene sequences, whereas resonances at $45 \mathrm{ppm}, 36 \mathrm{ppm}$, and 28 ppm represent [ $-(\mathrm{Ph}) \mathrm{CHCH}_{2} \mathrm{CH}_{2}-$ ] carbons (left to right), respectively, and confirm the ethene-styrene linkage. ${ }^{17}$ Further, the absence of resonances at 41 ppm and 34 ppm to 35 ppm demonstrates the absence of a styrene-styrene linkage and also indicates the absence of amorphous polystyrene generated by thermal radical polymerization. The end-group analysis performed on low-
molecular-weight poly(ethene-co-styrene) copolymer (Entry 3 in Table 4.1) shows three types of chainends: styrenic, vinyl, and alkyl (Figure 4.2). The percentage of the styrenic chain-ends is greater than for the other two end groups and is formed by $\beta$-H elimination following styrene insertion. The unsaturated carbons next to the aromatic ring show ${ }^{13} \mathrm{C}$ NMR resonances at 129 ppm and 131 ppm and are assigned by high-temperature HMQC analysis. The alkyl chain-ends are assigned on the basis of literature values. ${ }^{13}$ The vinyl chain-ends formed by $\beta$-H elimination following ethene insertion occur to a much lower extent than the styrenic end groups.

$\delta \delta: 45.21$
$\alpha \delta: 36.00$

$\alpha \gamma: 37.59$
$\beta \beta: 26.78$
$\beta \delta, \gamma \gamma, 28.55$

c: 26.71




g: 32.04
h : 21.2
i : 13.08

Figure 4.2: Assignment of ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of poly(ethene-co-styrene). (The Copolymer was dissolved in 1,1,2,2-tetrachloroethane- $d_{2}$ at $110^{\circ} \mathrm{C}$. Chemical shifts are assigned on the basis of literature values and are given in ppm. ${ }^{13,17}$ )

The ${ }^{1} \mathrm{H}$ nmp spectrum of poly(ethene-co-vinylcyclohexane) at $110^{\circ} \mathrm{C}$ in 1,1,2,2-tetrachloroethane- $d_{2}$ shows resonances at 5.1 ppm and 5.5 ppm , suggesting $-\mathrm{CH}_{2} \mathrm{CH}=\mathrm{CHC}_{6} \mathrm{H}_{11}$ chain-ends, which were further confirmed by ${ }^{13} \mathrm{C}$ NMR spectroscopy. The incorporation of vinylcyclohexane was determined by comparing cyclic CH protons from vinylcyclohexane with all other aliphatic protons. The vinylcyclohexane content values determined by ${ }^{13} \mathrm{C}$ NMR spectroscopy ( 2 s delay) are close to those calculated by ${ }^{1} \mathrm{H}$ NMR spectroscopy. ${ }^{18}$ Furthermore, the ${ }^{13} \mathrm{C}$ NMR resonances observed are in good agreement with literature values and suggest the presence of only isolated vinylcyclohexane units. Similar to the case for poly(ethene-co-styrene), poly(ethene-co-vinylcyclohexane) also shows unsaturated and alkyl chain-ends (Figure 4.3). The predominant unsaturated end group arises by $\beta$-H elimination following vinylcyclohexane insertion, and its percentage increases with an increase in the amount of vinylcyclohexane in the feed (Entries 4 and 5 in Table 4.1). The ${ }^{1} \mathrm{H}$ nmr spectra of both poly(ethene-co-propene) and poly(ethene-co-1-hexene) show vinyl chain-ends. The predominant ${ }^{1} \mathrm{H}$ nmp resonances for poly(ethene-co-1-hexene) ( $\sim 50 \mathrm{~mol} \%$ 1-hexene) correspond to those reported previously for the alternating copolymer. ${ }^{19,20}$

The copolymerization of ethene with methyl vinyl ketone was also performed (Table 4.1). The obtained molecular weights and level of methyl vinyl ketone incorporation were similar to those observed for poly(ethene-co-styrene).

DSC analysis of poly(ethene-co-styrene) $\left(4.3 \mathrm{~mol} \%\right.$ styrene) showed a $T_{\mathrm{m}}$ value of $106^{\circ} \mathrm{C}$, which is $23^{\circ} \mathrm{C}$





Figure 4.3: Assignment of ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of poly(ethene-co-vinylcyclohexane). (The Copolymer was dissolved in 1,1,2,2-tetrachloroethane- $d_{2}$ at $110^{\circ} \mathrm{C}$. Chemical shifts are assigned on the basis of literature values and are given in ppm. ${ }^{13,17}$ )
lower than for the corresponding linear polyethene. The low $T_{\mathrm{m}}$ value can be attributed to a drop in polyethene crystallinity due to incorporation of styrene units. The $T_{\mathrm{m}}$ values for poly(ethene-co-4-acetoxystyrene) and poly(ethene-co-4-fluorostyrene) were $114^{\circ} \mathrm{C}$ and $118^{\circ} \mathrm{C}$, respectively. Similarly, the DSC analysis of poly(ethene-co-vinylcyclohexane) containing $5.2 \mathrm{~mol} \%$ of vinylcyclohexane shows a $T_{\mathrm{m}}$ value of $109^{\circ} \mathrm{C}$, whereas the copolymer with $11.8 \mathrm{~mol} \%$ vinylcyclohexane does not show a $T_{\mathrm{m}}$ value but has a $T_{\mathrm{g}}$ value of $-9^{\circ} \mathrm{C}$.

In addition to the copolymerization of ethene with polar styrene derivatives, the unusual functionality tolerance of the catalyst system was demonstrated by performing the aqueous emulsion copolymerization of styrene with ethene. The emulsion copolymerization was performed using 5 g of styrene and 200 psig of ethene giving 0.3 g of copolymer with $5.8 \mathrm{~mol} \%$ of styrene incorporation. The high-temperature GPC analysis of the polymer shows a monomodal peak with a $M_{\mathrm{w}}$ value of 2500 and a PDI value of 1.5. Galvinoxyl and 2,6-di-tert-butylpyridine were added to suppress radical and cationic polymerizations, respectively, confirming that the obtained copolymer was formed by metal-catalyzed insertion polymerization.

### 4.3 Experimental Procedures

### 4.3.1 General Procedures

The following information applies to all experimental procedures unless otherwise noted. Chemical manipulations were performed under a dry nitrogen atmosphere using a glovebox box or Schlenk techniques. All solvents, with the exception of NMR solvents, were dried and degassed prior to use by either distillation over $\mathrm{CaH}_{2}$ followed by degassing using the freeze-pump-thaw technique or dried by passing through an activated alumina column followed by deoxygenating by passing over a copper catalyst. Ultra-highpurity ethene and ultra-high-purity carbon monoxide were obtained from MG Industries and used without further purification. Isotopically enriched chemicals were obtained from Cambridge Isotope Laboratories and used without further purification. Bis(dibenzylideneacetone)palladium(0) $\left[\mathrm{Pd}(\mathrm{dba})_{2}\right]$ was obtained from Strem Chemicals and used as received. The phosphine sulfonate ligand ${ }^{6,11} 2$-[bis(2-methoxyphenyl)phosphino]benzenesulfonic acid $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3} \mathrm{H}\right)$ and the corresponding neutral methylpalladium pyridine complex, $2,{ }^{12}$ were synthesized following literature procedures (see also Chapters 1 to 3 ). All other chemicals were obtained from Aldrich.

NMR analysis was performed using a Bruker DPX-300 spectrometer equipped with a variable-temperature, multi-nuclear probe at 300.13 MHz for ${ }^{1} \mathrm{H}-, 121.49 \mathrm{MHz}$ for ${ }^{31} \mathrm{P}$ - or 75.4 MHz for ${ }^{13} \mathrm{C}$ NMR spectra. ${ }^{31} \mathrm{P}$ - and ${ }^{13} \mathrm{C}$ NMR experiments were conducted with proton decoupling. Spectra were acquired using dichloromethane- $d_{2}$, chloroform- $d$ or 1,1,2,2-tetrachloroethane- $d_{2}$ as solvent. The chemical shifts are referenced relative to the residual solvent peak.

Polymers were analyzed at $110^{\circ} \mathrm{C}$ in tetrachloroethane- $d_{2}$ except for polyethene, which was analyzed at $80^{\circ} \mathrm{C}$ in 1,1,2,2-tetrachloroethane- $d_{2}$ and poly(ethene-co-1-hexene), which was analyzed at ambient temperature in chloroform- $d$.

The glass-transition temperature ( $T_{\mathrm{g}}$ ) and melt-transition temperature $\left(T_{\mathrm{m}}\right)$ of the polymers were obtained using a differential scanning calorimeter, TA Instruments DSC Q100, in the temperature range of $-70^{\circ} \mathrm{C}$ to $200^{\circ} \mathrm{C}$, with a heating rate of $10^{\circ} \mathrm{Cmin}^{-1}$. The values reported are calculated from the second heating cycle and are reported as the mid-point of the thermal transition.

Molecular weights and molecular weight distributions were measured on a Shimadzu size exclusion chromatograph (SEC) using a flow rate of $1 \mathrm{mLmin}^{-1}$ and a three-column bed (Styragel HR $7.8 \times 300 \mathrm{~mm}$ columns with 5 mm bead size: 100 Da to 10000 Da ; 500 Da to 30000 Da ; and 5000 Da to 6000000 Da ), a

Shimadzu RID 10A differential refractometer and SPD 10A UV-Vis detector. SEC samples were run in tetrahydrofuran at $35^{\circ} \mathrm{C}$ and calibrated to polystyrene standards. Similarly, the high temperature SEC analysis were performed with a Waters 150 CV instrument equipped with one Shodex AT 803 and two Shodex AT 806MS columns or Polymer Laboratories model 220 high-temperature chromatograph using polystyrene standards at $135^{\circ} \mathrm{C}$ or $140^{\circ} \mathrm{C}$ using 1,2 -dichlorobenzene or $1,2,4$-trichlorobenzene as the solvents.

Samples for water contact angle measurements were prepared by the evaporation of $3 \%(\mathrm{~m} / \mathrm{m})$ to $5 \%(\mathrm{~m} / \mathrm{m})$ solutions in 1,1,2,2-tetrachloroethane onto glass slides under ambient conditions. The water contact angles toward the air side of the polymer thin films were measured using a contact angle goniometer at $25^{\circ} \mathrm{C}$ with an accuracy of $2^{\circ}$. The reported values are the average of three measurements made at different positions of the film.

### 4.3.2 Copolymerization of Ethene with Styrene

In a typical experiment, a 300 mL glass-lined stainless steel autoclave equipped with a magnetic stir bar was charged with $8.3 \times 10^{-6} \mathrm{~mol}$ of $2,1.66 \times 10^{-5} \mathrm{~mol}$ of $\mathrm{BPh}_{3}, 10 \mathrm{~mL}$ of dichloromethane and 5 g of styrene. The autoclave was charged with ethene to 100 psig and then placed in a preheated oil bath at $80^{\circ} \mathrm{C}$ for 7 h . The autoclave was then cooled to room temperature and the polymer was precipitated in methanol. The polymer was thoroughly washed with methanol, purified by Soxhlet extraction in acetone and dried under vacuum.

### 4.3.3 Copolymerization of Ethene with Methyl Vinyl Ketone

In a typical experiment, a 300 mL glass-lined stainless steel autoclave equipped with a magnetic stir bar was charged with $8.30 \times 10^{-6} \mathrm{~mol}$ of $2,1.66 \times 10^{-5} \mathrm{~mol}^{2} \mathrm{BPh}_{3}, 10 \mathrm{~mL}$ of dichloromethane and 1 g of methyl vinyl ketone. The autoclave was charged with ethene to 100 psig and then placed in preheated oil bath at $80^{\circ} \mathrm{C}$ for 16 h . The autoclave was then cooled to room temperature and the polymer was precipitated in methanol. The polymer was thoroughly washed with methanol dried under vacuum.

### 4.3.4 Copolymerization of Ethene with Functional Styrenes

In a typical experiment, a 300 mL glass-lined stainless steel autoclave equipped with a magnetic stir bar was charged with $5 \mathrm{mg}\left(8.30 \times 10^{-6} \mathrm{~mol}\right)$ of $2,4 \mathrm{mg}\left(1.66 \times 10^{-5} \mathrm{~mol}\right)$ of $\mathrm{BPh}_{3}, 5 \mathrm{~mL}$ of dichloromethane and $6.16 \times 10^{-3} \mathrm{~mol}$ of functional styrene (4-acetoxystyrene, 4-vinylmethylbenzoate or 4-fluorostyrene). The autoclave was charged with ethene to 100 psig and then placed in preheated oil bath at $80^{\circ} \mathrm{C}$ for 7 h . The autoclave was then cooled to room temperature and the polymer was precipitated in methanol. The polymer was thoroughly washed with methanol and dried under vacuum.

### 4.3.5 Emulsion Copolymerization of Ethene and Styrene

A 300 mL glass-lined stainless steel autoclave equipped with magnetic stir bar and extra valve for liquid injection was charged with $7.8 \mathrm{mg}\left(1.35 \times 10^{-5} \mathrm{~mol}\right)$ of $\mathrm{Pd}(\mathrm{dba})_{2}, 6.5 \mathrm{mg}\left(1.61 \times 10^{-5} \mathrm{~mol}\right)$ of $\mathrm{P}^{-} \mathrm{SO}_{3} \mathrm{H}$ ligand, $10 \mathrm{mg}\left(2.37 \times 10^{-5} \mathrm{~mol}\right)$ of galvinoxyl, $7.2 \mathrm{mg}\left(2.96 \times 10^{-5} \mathrm{~mol}\right)$ of $\mathrm{BPh}_{3}, 5.6 \mathrm{mg}\left(2.96 \times 10^{-5} \mathrm{~mol}\right)$ of 2,6 -di-tert-butylpyridine, 10 mL of toluene and 5 g of styrene. The autoclave was then removed from the glovebox, and an aqueous solution of sodium dodecylbenzenesulfonate ( 0.9 g in 30 mL of degassed water) was injected and the autoclave was pressurized with ethene to 200 psig . The autoclave was then placed in a preheated oil bath at $90^{\circ} \mathrm{C}$ for 4 h . The autoclave was then cooled to room temperature and the polymer was precipitated in acidified methanol, washed thoroughly with methanol and distilled water then purified by Soxhlet extraction in acetone. The polymer was dried under high vacuum.

### 4.3.6 Hydrolysis of Poly(ethene-co-4-acetoxystyrene)

The hydrolysis of the copolymer was carried out in toluene solution at room temperature using hydrazine monohydrate. 0.1 g of the copolymer was suspended in 5 mL of toluene and 0.25 mL of hydrazine monohydrate was added with stirring. The reaction was allowed to proceed under nitrogen for 7 h . The resulting mixture was slowly added to a large excess of $5 \%$ aqueous hydrochloric acid. The obtained solid was filtered and washed thoroughly with large excess of methanol. The resulting hydrolysis product poly(ethene-co-4-hydroxystyrene) was dried under vacuum. The completion of the reaction was checked by ${ }^{1} \mathrm{H}$ NMR spectroscopy and showed the disappearance of the methyl resonance.

### 4.3.7 Synthesis of $\boldsymbol{\eta}^{3}$-Phenylethylpalladium Complex 17

First, the synthesis of ( $\eta^{3}$-phenylpropyl)palladium complex 16 was attempted by adapting the procedure we reported previously for $\eta^{3}$-allyl- and ( $\eta^{3}$-crotyl)palladium complexes (see Chapter 3 ). ${ }^{11} 1$-chloro-1phenylpropane was synthesized using a procedure adapted from a report by Lee and Kang. ${ }^{21}$ Chlorotrimethylsilane ( $10.864 \mathrm{~g}, 0.1 \mathrm{~mol}$ ); selenium oxide $(0.222 \mathrm{~g}, 0.002 \mathrm{~mol})$; and 1-phenyl-1-hydroxypropane $(6.810 \mathrm{~g}, 0.05 \mathrm{~mol})$ were combined in a round-bottom flask and refluxed under nitrogen. The mixture evolved acidic vapors and was converted to a clear, yellow solution. Total conversion of the alcohol was observed by ${ }^{1} \mathrm{H}$ NMR after 1 h . Silicon compounds were removed from the crude product under vacuum at room temperature until the yellow oil was free of silanes as determined by ${ }^{1} \mathrm{H}$ nmr. A biphasic mixture is temporarily formed during this process. Selenium compounds were removed by passing the crude product over a silica gel column using diethyl ether as the mobile phase. The final yield was $5.751 \mathrm{~g}(74.5 \%)$ of yellow oil with good purity and no apparent decomposition products.

The synthesis of ( $\eta^{3}$-phenylpropyl) palladium(II) chloride dimer was attempted by adapting the wellknown synthesis of ( $\eta^{3}$-allyl) palladium chloride dimer as reported by Nolan et al. ${ }^{22}$ and Bosnich et al. ${ }^{23}$ $\mathrm{Na}_{2} \mathrm{PdCl}_{4}\left(0.883 \mathrm{~g}, 294.21 \mathrm{gmol}^{-1}, 0.003 \mathrm{~mol}\right)$ was dissolved in hot, degassed water ( 1.5 mL ) and filtered. The Pd solution was then added to a solution of $\mathrm{PhCH}(\mathrm{Cl}) \mathrm{CH}_{2} \mathrm{CH}_{3}\left(1.389 \mathrm{~g}, 154.37 \mathrm{~g} \mathrm{~mol}^{-1}, 0.009 \mathrm{~mol}\right)$ in degassed methanol ( 30 mL ). Carbon monoxide was bubbled through the solution, which rapidly turned from red-brown to black in color. Repeating the procedure using trace or no carbon monoxide also failed to yield the dimer. However, substitution of chloropropene for 1-chloro-1-phenylpropene did give the ( $\eta^{3}$-allyl)palladium chloride dimer as expected. This indicated that the ( $\eta^{3}$-phenylpropyl)palladium chloride dimer is not sufficiently stable for isolation. The most likely route of decomposition is through $\beta$ elimination to give $\beta$-methylstyrene and a palladium hydride species that is then reduced to $\operatorname{Pd}(0)$ by carbon monoxide.

Finally, the in situ experiment was scaled up so that the products could be isolated and characterized individually. 0.120 g of $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}$ (py) $\left(0.2 \mathrm{mmol}, 601.95 \mathrm{~g} \mathrm{~mol}^{-1}\right)$ and 0.145 g of $\mathrm{BPh}_{3}(0.6 \mathrm{mmol}$, $242.12 \mathrm{~g} \mathrm{~mol}^{-1}$ ) with 0.020 g of styrene ( $0.2 \mathrm{mmol}, 104.15 \mathrm{~g} \mathrm{~mol}^{-1}$ ) were dissolved in a minimal amount of dichloromethane. The mixture was stirred for several hours at room temperature before being poured into rapidly stirring diethyl ether. The mixture was filtered and the solids were re-dissolved in dichloromethane and transferred to a diffusion chamber filled with hexane and allowed to crystallize overnight. The removal of dichloromethane gave two distinct, amorphous solids: white $\mathrm{BPh}_{3}$ and the yellow product. The product was re-precipitated with diethyl ether and dried. ${ }^{1} \mathrm{H}$ nmr analysis showed only signals at 8.1 ppm to $6.9 \mathrm{ppm}\left(\sim 17 \mathrm{H}\right.$, aromatic), $3.9 \mathrm{ppm}\left(\mathrm{OCH}_{3}, \mathrm{~s}\right), 3.6 \mathrm{ppm}\left(\mathrm{OCH}_{3}, \mathrm{~s}\right), 3.2 \mathrm{ppm}(\mathrm{CH}, \mathrm{q})$ and 0.64 ppm $\left(\mathrm{CH}_{3}, \mathrm{dd}\right) .{ }^{31} \mathrm{P}$ NmR showed a single peak at 11.4 ppm . A coupling of 10.7 Hz was observed in the CH signal at 3.2 ppm and in the $\mathrm{CH}_{3}$ signal at 0.64 ppm . The latter was also split with a $J$ of 6.8 Hz . A cosy experiment confirmed the correlation between these two protons, but did not correlate them to any others.

### 4.3.8 Analysis of Styrene Insertion Mechanism

In a typical experiment, 0.012 g of $2(20 \mu \mathrm{~mol}), 0.015 \mathrm{~g}$ of $\mathrm{BPh}_{3}(60 \mu \mathrm{~mol})$ and 0.004 g of styrene ( $40 \mu \mathrm{~mol}$ ) were dissolved in 1 g of dichloromethane- $d_{2}$ and allowed to react at ambient temperature in a sealed NMR tube. The reaction was monitored by ${ }^{1} \mathrm{H}-$ and ${ }^{31} \mathrm{P}$ NMR and, after $18 \mathrm{~h}, 17$ was precipitated by pouring the reaction mixture into rapidly stirring diethyl ether. The crude product was washed with diethyl ether then re-dissolved in a minimal amount of dichloromethane and placed in a diffusion chamber with hexanes. Slow evaporation of the solvent precipitated $\mathrm{BPh}_{3}$ followed by the 17 as a yellow powder. Styrene terminated polyethene was prepared using a high-pressure nMr tube (Wilmad, Quick Pressure Valve, 5 mm outer diameter, 8 in length, 0.77 mm wall thickness) containing a solution of $17-d_{9}$ as formed in situ from styrene- $d_{8}$. The tube was charged with ethene to 100 psig and, after 2 h at ambient temperature, the polymeric products were precipitated by pouring the reaction mixture into rapidly stirring acidified methanol and washing several times with methanol. The product was dissolved in hot 1,1,2,2-tetrachloroethane- $d_{2}$ and analyzed by ${ }^{1} \mathrm{H}$ - and ${ }^{31} \mathrm{P}$ nmr.

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## Chapter Five

## Copolymerization of Imines with Carbon Monoxide


#### Abstract

Please note that the following chapter will be expanded and submitted for publication in the journal Organometallics. If any differences exist between the text appearing in this dissertation and in the journal article, the latter should take precedence.


### 5.1 Introduction

The polyamides are a diverse class of polymers that include polypeptides, natural fibers, and synthetic polymers. Currently, these materials are synthesized by condensation of amino acids, condensation of diamines with dicarboxylic acids (or diacyl chlorides), or ring-opening polymerization of lactams. However, there is ongoing interest in developing a new route to polyamides via the copolymerization of imines with carbon monoxide, which would utilize relatively inexpensive and abundant monomers in an atomeconomical fashion.

The copolymerization of imines with carbon monoxide is analogous to the well known, palladiumcatalyzed insertion-copolymerization of ethene with carbon monoxide. However, in this case, copolymerization is prevented by the formation of stable, five-member palladicycles resulting from the sequential insertion of carbon monoxide and an imine into the palladium-carbon bond as shown in Scheme 5.1. Unlike the ketone formed by the sequential insertion of carbon monoxide and ethene, the resulting amide is not displaced by carbon monoxide, possibly due to resonance-stabilization. ${ }^{1-3}$ This was previously shown by our group for ( $\mathrm{L}^{-} \mathrm{L}$ ) $\mathrm{PdCH}_{3}^{+} \mathrm{BF}_{4}^{-}$systems, which undergo rapid insertion of carbon monoxide at 5 atm followed by slow insertion of $\mathrm{PhCH}=\mathrm{NPh}$ or $\mathrm{PhCH}=\mathrm{NCH}_{3}$ to form the inactive palladicycles, $(\mathrm{L} \sim \mathrm{L}) \mathrm{PdCH}(\mathrm{Ph}) \mathrm{N}(\mathrm{Ph}) \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$ and $(\mathrm{L} \frown \mathrm{L}) \mathrm{PdCH}(\mathrm{Ph}) \mathrm{N}\left(\mathrm{CH}_{3}\right) \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$, respectively. Similar results were observed with 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane (DPPP), 1,4-bis(diphenylphosphino)butane, 1,2-bis(dicyclohexylphosphino)ethane, $N, N, N^{\prime}, N^{\prime}$-tetramethylethylenediamine, and 2,2'-bipyridine ligands.

Despite efforts by Arndtsen ${ }^{4-7}$ and ourselves, ${ }^{1,8}$ there has been only a single report of a successful copolymerization of $\mathrm{PhCH}=\mathrm{NCH}_{3}$ with carbon monoxide by Sun and coworkers using an acylcobalt carbonyl catalyst. ${ }^{9}$ However, the active species was not well defined. Also, Beller and coworkers have demonstrated that palladium on carbon ${ }^{10}$ and tetrakis(triphenylphosphino)palladium(0) ${ }^{11}$ readily undergo oxidative addition of amido halides to form palladium-amides analogous to those formed by imineinsertion, which then undergo insertion of carbon monoxide to form palladium-acyl species. However, these were then hydrolyzed to give $N$-acyl- $\alpha$-amino acids.

Therefore, we sought to develop a well-defined palladium catalyst for the copolymerization of imines


Scheme 5.1: Proposed catalytic cycle for the copolymerization of imines with carbon monoxide where $L^{\wedge} \mathrm{L}$ is a bidentate ligand, R is the growing polymer chain, $\mathrm{R}^{\prime}$ is an aryl or alkyl group, and $\mathrm{R}^{\prime \prime}$ is an aryl group.
with carbon monoxide using two strategies. First, we attempted to weaken the palladium-amide interaction by altering the moiety on the imine nitrogen to reduce the electron-donating ability of the amide oxygen. To accomplish this, a series of $N$-substituted imines with electron-donating and electronwithdrawing groups were synthesized and their effect on the palladium-amide interaction was examined using variable-temperature NMR spectroscopy to determine the thermodynamics of insertion and IR spectroscopy to compare the relative stability of the resulting palladium-amide interactions. Second, we examined the effect of the anion on the system by synthesizing a series of (dppp) $\mathrm{PdCH}_{3}^{+} \mathrm{X}^{-}$complexes bearing anions of varying coordination strength and screening them for insertion of carbon monoxide and imine into the palladium-carbon bond.

### 5.2 Results and Discussion

### 5.2.1 Imine Effects

$N$-aryl imines were selected as a starting point for screening based on previous work in our group, ${ }^{2}$ which found that the rates of insetion for $N$-aryl imines into the Pd -acyl bond of the (dppp) $\mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}^{+} \mathrm{BF}_{4}^{-}$catalyst complex were superior to those of $N$-alkyl imines. A series of $N$-substituted benzylimine derivatives were synthesized and their insertion and chelating behavior with (dppp) $\mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}^{+} \mathrm{BF}_{4}^{-}$was observed as shown in Table 5.1. Insertion was monitored by ${ }^{1} \mathrm{H}$ NMR and thermodynamics of insertion were measured for select imines by variable-temperature ${ }^{1} \mathrm{H}$ nMr. Also, it was possible to compare the relative palladiumamide coordination strengths of the resulting palladicycles by using infrared spectroscopy to measure their carbonyl stretching frequencies, which we have previously shown to change by several wavenumbers upon coordination to the palladium center. ${ }^{12}$
$N$-(methoxy)benzylimine and $N$-methylbenzylimine were selected as the electron-donating and control imines, respectively. The use of $N$-(chloro)benzylimine as the electron-withdrawing imine was impractical because it readily decomposes at room temperature. Therefore, $N$-(trifluoromethyl)benzylimine was selected.

Table 5.1: Effect of $N$-substitution on imine insertion.

| Entry | Imine | $\Delta H^{\ddagger}$ <br> $\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$ | $\Delta S^{\ddagger}$ <br> $\left(\mathrm{kJ} \mathrm{K}^{-1} \mathrm{~mol}^{-1}\right)$ | $v_{\mathrm{C}=\mathrm{o}}$ <br> $\left(\mathrm{cm}^{-1}\right)$ |
| :---: | :--- | :---: | :---: | :---: |
| 1 | $\mathrm{PhCH}=\mathrm{N}-(p-\mathrm{Tol})$ | 100.9 | -0.1759 | 1672.9 |
| 2 | $\mathrm{PhCH}=\mathrm{N}-\mathrm{Ph}$ | 111.1 | 0.0548 | 1681.6 |
| 3 | $\mathrm{PhCH}=\mathrm{N}-\left(p-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{CF}_{3}\right)$ | 99.27 | -0.1769 | 1673.8 |
| 4 | $\mathrm{PhCH}=\mathrm{N}-\left(p-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{~F}\right)$ | 107.7 | -0.1737 | 1659.8 |
| 5 | $\mathrm{PhCH}=\mathrm{N}-\mathrm{C}_{6} \mathrm{~F}_{5}{ }^{a}$ | $\mathrm{~N} / \mathrm{A}$ | $\mathrm{N} / \mathrm{A}$ |  |
| 6 | $\mathrm{PhCH}=\mathrm{N}-\mathrm{OCH}_{3}{ }^{a}$ | $\mathrm{~N} / \mathrm{A}$ | $\mathrm{N} / \mathrm{A}$ |  |
| 7 | $\mathrm{PhCH}=\mathrm{N}-\mathrm{CH}_{3}$ |  |  |  |
| 8 | $\mathrm{PhCH}=\mathrm{N}-\mathrm{CF}_{3}$ |  |  |  |
| 9 | $\mathrm{PhCH}=\mathrm{N}-\mathrm{CN}^{a}$ | $\mathrm{~N} / \mathrm{A}$ | $\mathrm{N} / \mathrm{A}$ |  |
| 10 | $\mathrm{PhCH}=\mathrm{N}-\mathrm{S}^{a}(\mathrm{O})_{2} \mathrm{CH}_{3}{ }^{a}$ | N/A | N/A |  |
| 11 | $\mathrm{PhCH}=\mathrm{N}-\mathrm{Cl}^{b}$ | N/A | N/A |  |
| 12 | $\mathrm{PhCH}=\mathrm{N}-\mathrm{H}^{b}$ | N/A | N/A |  |

[^0]As expected, the entropy of the intramolecular reaction is small, but there was no clear correlation between activation energy, carbonyl stretching frequency, and the electron-withdrawing strength of the functional group. In no case was the insertion of a second carbon monoxide observed.

### 5.2.2 Anion Effects

One significant difference between the systems used by Beller ${ }^{10}$ and Kacker ${ }^{1}$ is the coordination strength of the anion, either a strongly-coordinating chloride or non-coordinating tetrafluoroborate anion, respectively. To test the effect of the anion, a series of (dppp) $\mathrm{PdCH}_{3}^{+} \mathrm{X}^{-}$complexes with anions of varying coordination strength were synthesized $\left(\mathrm{BF}_{4}^{-}<\mathrm{Tf}^{-}<\mathrm{Tos}^{-}<\mathrm{NO}_{3}^{-}<\mathrm{Br}^{-}<\mathrm{Cl}^{-}\right)$, dissolved in dichloromethane- $d_{2}$ $(1 \mathrm{~g})$ with $\mathrm{PhCH}=\mathrm{NPh}$, exposed to carbon monoxide at 5 atm , and heated to $80^{\circ} \mathrm{C}$. The reaction progress was monitored by ${ }^{1} \mathrm{H}$ nmr as shown in Table 5.2.

Table 5.2: Effect of anions on imine insertion.

| Entry | Anion | Solvent | Result |
| :---: | :--- | :--- | :--- |
| 1 | $\mathrm{BF}_{4}^{-}$ | tetrahydrofuran | CO, imine insertion |
| 2 | $\mathrm{BF}_{4}^{-}$ | dichloromethane | CO, imine insertion |
| 3 | $\mathrm{BF}_{4}^{-a}$ | dichloromethane | CO, imine insertion |
| 4 | $\mathrm{Tf}^{-}$ | tetrahydrofuran | CO insertion |
| 5 | $\mathrm{Tf}^{-}$ | dichloromethane | CO, imine insertion |
| 6 | $\mathrm{Tos}^{-}$ | tetrahydrofuran | CO insertion |
| 7 | $\mathrm{Tos}^{-}$ | dichloromethane | CO, imine insertion |
| 8 | $\mathrm{NO}_{3}^{-}$ | tetrahydrofuran | no insertion |
| 9 | $\mathrm{Br}^{-}$ | tetrahydrofuran | CO insertion |
| 10 | $\mathrm{Br}^{-}$ | dichloromethane | CO insertion |
| 11 | $\mathrm{Cl}^{-}$ | tetrahydrofuran | CO insertion |
| 12 | $\mathrm{Cl}^{-}$ | dichloromethane | CO insertion |

${ }^{a}$ Performed in the presence of tris(pentafluorophenyl)boron.
In no case was a second carbon monoxide insertion observed, even after extended heating at $80^{\circ} \mathrm{C}$. It was found that imine insertion was inhibited by the presence of strongly coordinating halide anions and tetrahydrofuran, which presumably block the fourth coordination site on the palladium center.

The reaction was also performed under conditions more similar to those used by Beller. ${ }^{11}$ First, trans$\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{PdCH}_{3} \mathrm{Br}$ was synthesized by addition of two equivalents of $\mathrm{PPh}_{3}$ to (cod) $\mathrm{PdCH}_{3} \mathrm{Br}$. This was then dissolved in $\mathrm{N}, \mathrm{N}$-dimethylformamide- $d_{7}$ with five equivalants of lithium bromide and 5 atm carbon monoxide. After heating to $80^{\circ} \mathrm{C}$ overnight, no imine insertion was observed.

Finally, the neutral, phosphine-sulfonate ligated palladium complex $\left(\mathrm{P}^{\circ} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}, \mathbf{1 8}$, which has been shown to be exceptionally resistant to poisoning by polar molecules (see Chapters 1 to 4 ), was tested as a copolymerization catalyst by suspending 18 in dichloromethane with three equivalents of either $\mathrm{PhCH}=\mathrm{NPh}$ or $\mathrm{PhCH}=\mathrm{NCH}_{3}$, charging to 30 psig with carbon monoxide and heating to $90^{\circ} \mathrm{C}$ for 1 h to give a clear, yellow solution. In both cases, carbon monoxide insertion was not followed by imine insertion.

### 5.2.3 Radical Polymerization

It was demonstrated by Kim and coworkers ${ }^{13}$ that $\mathrm{PhCH}=\mathrm{NCN}$, and to a lesser extent $\mathrm{PhCH}=\mathrm{NS}(\mathrm{O})_{2} \mathrm{CH}_{3}$, are able to undergo radical homopolymerization. This suggests the possibility of forming copolymers of
these imines with carbon monoxide in a manner similar to that employed for radical copolymerization with ethene and carbon monoxide. To test this concept, 1 mmol of either $\mathrm{PhCH}=\mathrm{NCN}$ or $\mathrm{PhCH}=\mathrm{NS}(\mathrm{O})_{2} \mathrm{CH}_{3}$ was dissolved in 4.1 mL ( 100 mmol ) of acetonitrile with $20 \mu \mathrm{~mol}$ of aibs. The mixture was then charged with carbon monoxide to 20 atm and heated in a $100^{\circ} \mathrm{C}$ bath for 3 days. The reaction mixtures were dissolved in dichloromethane- $d_{2}$ and analyzed by ${ }^{1} \mathrm{H}$ nmr, however no reaction was observed. The reactions were retried using 30 atm CO and 10.1 mL of chlorobenzene as solvent. After, 3 days in a $180^{\circ} \mathrm{C}$ oil bath, no reaction was observed.

### 5.3 Conclusions

After examining the ability of a series of benzylimine derivatives to undergo migratory insertion into a palladium-acyl bond and then act as a trapping ligand, we were unable to observe the sequential insertion of an imine followed by carbon monoxide, which we ascribe to the high stability of the palladium-amide chelate. This stability was not overcome by the use of a neutral, phosphine-sulfonate system. It was also found that strongly coordinating anions and solvents strongly inhibit imine insertion, presumably by blocking coordination to palladium.

### 5.4 Experimental Procedures

### 5.4.1 Synthesis of Imines

With the exception of $\mathrm{PhCH}=\mathrm{NCN}$ and $\mathrm{PhCH}=\mathrm{NS}(\mathrm{O})_{2} \mathrm{CH}_{3}$, imines were prepared by mixing benzaldehyde with one equivalent of aniline derivative in a minimal amount of methanol and refluxing in the absence of light for 3 h . Methanol and water were then removed under vacuum to give the products as oils. The products were soluble in all common organic solvents with the exception of $N$-(pentafluorophenyl)benzylimine, which was purified by precipitation with hexane to give a colorless plate-like crystals. $N$-(phenyl)benzylimine spontaneously crystallized. $N$-(4-fluorophenyl)benzylimine was purified by column chromatography using silica gel as the stationary phase and chloroform as the mobile phase. The remaining imines were purified by sublimation in a Petri dish placed between a hot plate and an ice bath.

### 5.4.2 Synthesis of $\boldsymbol{N}$-(Cyano)benzylimine

Unlike diaryl imines, those with strongly electron-withdrawing functional groups are readily hydrolyzed by ambient moisture and could not be synthesized by condensation of amines with aldehydes in the presence of molecular sieves. Therefore, $N$-(cyano)benzylimine was synthesized via an anhydrous route under a dry, nitrogen atmosphere by modifying procedures reported by Birkofer ${ }^{14}$ and Kim. ${ }^{13}$ Cyanamide was dissolved in dry tetrahydrofuran and added drop-wise to a tetrahydrofuran solution containing two equivalents of diethylamine and chlorotrimethylsilane. Triethylammonium chloride precipitated and was removed by filtration. Tetrahydrofuran, excess chlorotrimethylsilane, and triethylamine were removed by distillation $\left(65^{\circ} \mathrm{C}\right.$ at 1 atm$)$ to give $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{Si}\right)_{2} \mathrm{NCN}$ as a colorless liquid, which was pure by ${ }^{1} \mathrm{H}$ nmr. $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{Si}\right)_{2} \mathrm{NCN}$ and one equivalent of benzaldehyde were cooled to $0^{\circ} \mathrm{C}$ and two equivalents of titanium(IV) chloride were added drop-wise before the reaction mixture was refluxed overnight. The reaction mixture was cooled to give orange solids. These solids were dissolved in refluxing diethyl ether, hot-filtered, and cooled to yield yellow, feather-like crystals. These crystals were further purified by sublimation to yield white needle-like crystals of N -(cyano)benzylimine.

### 5.4.3 Imine Insertion

Except for the complexes containing $\mathrm{PhCH}=\mathrm{NCN}$ or $\mathrm{PhCH}=\mathrm{NS}(\mathrm{O})_{2} \mathrm{CH}_{3},(\mathrm{dppp}) \mathrm{PdCH}_{3}$ (imine) ${ }^{+} \mathrm{BF}_{4}^{-}$complexes were synthesized in the absence of light by dissolving (dppp) $\mathrm{PdCH}_{3} \mathrm{Cl}(0.114 \mathrm{~g}, 200 \mu \mathrm{~mol})$ with three equivalents of imine in dichloromethane ( 5 mL ). A solution of silver tetrafluoroborate ( $0.039 \mathrm{~g}, 200 \mu \mathrm{~mol}$ ) in acetonitrile ( 6 mL ) was added. Silver chloride immediately precipitated and was removed by filtration after 15 min . The crude product was reduced under vacuum, re-dissolved in a minimal amount of dichloromethane, and precipitated with hexanes to remove excess imine.
$\mathrm{PhCH}=\mathrm{NCN}$ and $\mathrm{PhCH}=\mathrm{NS}(\mathrm{O})_{2} \mathrm{CH}_{3}$ were insufficiently coordinating to form the corresponding palladium complexes in the presence of coordinating solvents like tetrahydrofuran or acetonitrile. However, silver tetrafluoroborate is insoluble in dichloromethane and other suitable non-polar solvents. Therefore, a solution of sodium tetrakis(3,5-trifluoromethylphenyl)borate (BArF) in dichloromethane was added to a solution of (dppp) $\mathrm{PdCH}_{3} \mathrm{Cl}$ in dichloromethane giving an orange solution. However, sodium chloride did not precipitate, even after evaporation and re-dissolution. Also, it was found that although silver hexafluoroantimonate is very soluble in dichloromethane, the dPPP ligand is reactive toward the hexafluoroantimonate anion.
(dppp) $\mathrm{PdCH}_{3}\left(\mathrm{OEt}_{2}\right)+\mathrm{BF}_{4}^{-}$was prepared using a method similar to that employed by Brookhart and coworkers for the synthesis of (phen) $\mathrm{PdCH}_{3}\left(\mathrm{OEt}_{2}\right)(\mathrm{BArF}) .{ }^{15}$ First, (dppp) $\mathrm{Pd}\left(\mathrm{CH}_{3}\right)_{2}$ was prepared in quantitative yield by dissolving (tmeda) $\mathrm{Pd}\left(\mathrm{CH}_{3}\right)_{2}$ (see Chapter 1) in a minimal amount of dichloromethane, adding one equivalent of DPPP, and precipitating with pentane. Next, $0.944 \mathrm{~g}(2 \mathrm{mmol})$ of $(\mathrm{dppp}) \mathrm{Pd}\left(\mathrm{CH}_{3}\right)_{2}$ was dissolved in a $3: 2(\mathrm{v}: \mathrm{v})$ mixture of dichloromethane and diethyl ether. In a separate container, 0.324 g ( 2 mmol ) of $\mathrm{HBF}_{4} \cdot \mathrm{OEt}_{2}$ was dissolved in a 3:2 (v:v) mixture of dichloromethane and diethyl ether. Both solutions were cooled using a cold-well and and combined drop-wise with rapid stirring. Methane evolution was observed and the solution turned from yellow to orange. After 15 min , the solution was poured into cold diethyl ether and the white precipitate was collected by filtration and dried under high vacuum. The product was stored at $-20^{\circ} \mathrm{C}$ until use. Yield $=1.044 \mathrm{~g}(84.5 \%)$.

In each trial, $20 \mu \mathrm{~mol}$ of (dppp) $\mathrm{PdCH}_{3}(\mathrm{imine})+\mathrm{BF}_{4}$ was dissolved in 1 g of dichloromethane $-d_{2}$ and pressurized to 2 atm with carbon monoxide. The clear solutions immediately turned bright yellow indicating the formation of the palladium-acyl species. ${ }^{1} \mathrm{H}$ NMR spectra were then recorded every 10 min at $25^{\circ} \mathrm{C}, 35^{\circ} \mathrm{C}$, and $45^{\circ} \mathrm{C}$ to generate first-order kinetics plots and Eyring plots.

In all cases except for $\mathrm{Br}^{-}$and $\mathrm{Cl}^{-}$, substitution of the anion was performed by dissolving (dppp) $\mathrm{PdCH}_{3}-$ Cl and AgX in a $6: 4$ (v:v) solution of acetonitrile and dichloromethane. Silver chloride immediately precipitated and was removed by filtration before the product was dried under high vacuum. (dppp) $\mathrm{PdCH}_{3} \mathrm{Br}$ was synthesized by dissolving palladium(II) bromide in concentrated hydrobromic acid followed by addition of excess 1,5-cyclooctadiene to precipitate (cod) $\mathrm{PdBr}_{2}$ as a bright orange solid. Dissolving the solid in dichloromethane and adding excess tetramethyltin gave (cod) $\mathrm{PdCH}_{3} \mathrm{Br}$, which was reduced under vacuum and washed with diethyl ether to remove tin compounds. Finally, adding one equivalent of DPPP gave the desired product.

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## Appendix A

## Copolymerization of Ethene with Carbon Monoxide: Mechanism

A. 1 Nuclear magnetic resonance spectroscopy data















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## A. 2 Low-temperature NMR spectroscopy data



Figure A.19: Low-temperature ${ }^{1} \mathrm{H}$ nmR spectra of $\left(\mathrm{P}^{\sim}-\mathrm{SO}_{3}\right) \mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}, 4$.


Figure A.20: Low-temperature ${ }^{1} \mathrm{H}$ nMR spectra of $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$, 4, (detail).


Figure A.21: Low-temperature ${ }^{31} \mathrm{P}$ nmR spectra of $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}, 4$.

## A. 3 Infrared spectroscopy data



Figure A.22: Infrared spectra of step-wise insertion of carbon monoxide and ethene.


Figure A.23: Infrared spectra of step-wise insertion of carbon monoxide and ethene (detail).

## A. 4 Differential scanning calorimetry data



Figure A.24: Differential scanning calorimetry analysis for poly(ethene-co-carbon monoxide) containing $10 \mathrm{~mol} \%$ carbon monoxide.

## A. 5 X-ray diffraction data

A.5.1 X-ray diffraction data for $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}(\mathrm{py}), 2$.


Figure A.25: Crystal structure for $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}($ py $), 2$.

Table A.1: Sample and crystal data for $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}(\mathrm{py}), 2$.

| Identification code | svb12s |  |
| :--- | :--- | :--- |
| Crystallization solvents | Dichloromethane and pentane |  |
| Crystallization method | Diffusion chamber |  |
| Empirical formula | $\mathrm{C}_{26} \mathrm{H}_{26} \mathrm{NO}_{5} \mathrm{PPdS}$ |  |
| Formula weight | 601.91 |  |
| Temperature | $103(2) \mathrm{K}$ |  |
| Wavelength | $0.71073 \AA$ |  |
| Crystal size | $0.10 \times 0.07 \times 0.02 \mathrm{~mm}$ |  |
| Crystal habit | Colorless plate |  |
| Crystal system | Monoclinic |  |
| Space group | $\mathrm{P} 2(1) / \mathrm{c}$ | $\gamma=90^{\circ}$ |
| Unit cell dimensions | $a=11.484(5) \AA .515(8)^{\circ}$ |  |
|  | $b=13.828(6) \AA$ |  |
|  | $c=16.239(6) \AA$ |  |
| Volume |  |  |
| $Z$ | $2556.5(18) \AA^{3}$ |  |
| Density (calculated) | 4 |  |
| Absorption coefficient | $1.564 \mathrm{gcm}{ }^{\circ}$ |  |
| $F(000)$ | 1224 |  |

Table A.2: Data collection and structure refinement for $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}($ py $), 2$.

| Diffractometer | CCD area detector |
| :--- | :--- |
| Radiation source | fine-focus sealed tube, Mo K $\alpha$ |
| Generator power | $1600 \mathrm{~W}(50 \mathrm{kV}, 32 \mathrm{~mA})$ |
| Detector distance | 5.8 cm |
| Data collection method | phi and omega scans |
| Theta range for data collection | $1.94^{\circ}$ to $28.38^{\circ}$ |
| Index ranges | $-15 \leq h \leq 13,-17 \leq k \leq 18,-21 \leq l \leq 19$ |

Table A.3: Atomic coordinates and equivalent isotropic atomic displacement parameters $\left(\AA^{2}\right)$ for $\left(\mathrm{P}^{\wedge} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}($ py $), 2$.

|  | X | Y | Z | $U_{\text {(eq) }}{ }^{a}$ |
| :---: | :---: | :---: | :---: | :---: |
| Pd1 | 0.24278(3) | $0.53711(2)$ | $0.172828(19)$ | 0.02048(11) |
| S1 | $0.46014(9)$ | 0.67826(8) | 0.22880(6) | 0.0189(2) |
| P3 | 0.19278 (10) | 0.62421(8) | 0.27846(7) | 0.0179(2) |
| O1 | 0.5588(3) | 0.7291(2) | $0.20185(18)$ | 0.0247(7) |
| O2 | 0.4881(3) | 0.6218(2) | $0.30312(17)$ | 0.0246(7) |
| N1 | 0.3037(3) | 0.4447(3) | 0.0845(2) | 0.0233(8) |
| O3 | 0.3978(3) | 0.6219(2) | $0.15974(17)$ | 0.0217(7) |
| O4 | 0.2161(3) | 0.7056(2) | $0.45084(18)$ | 0.0328(8) |
| C2 | 0.0392(4) | 0.6364(3) | 0.2912(3) | 0.0228(9) |
| C9 | 0.1786(4) | 0.8259(3) | 0.2925(3) | 0.0240(10) |
| C8 | 0.2485(4) | 0.7480(3) | 0.2752(2) | 0.0184(9) |
| C13 | 0.3590(4) | 0.7695(3) | 0.2514(2) | 0.0163(8) |
| C14 | 0.2595(4) | 0.5693(3) | 0.3752(3) | 0.0222(9) |
| C12 | 0.3949(4) | 0.8656(3) | 0.2457(3) | 0.0230(9) |
| O5 | 0.0041(3) | 0.7080(2) | 0.15926(19) | 0.0316(8) |
| C11 | 0.3233(4) | 0.9400(3) | 0.2618(3) | 0.0269(10) |
| C4 | -0.1217(4) | 0.6100(4) | 0.3714(3) | 0.0308(11) |
| C19 | 0.2659(4) | 0.6151(4) | 0.4517(3) | 0.0299(11) |
| C3 | -0.0034(4) | 0.6021(3) | 0.3616(3) | 0.0261(10) |
| C22 | 0.4098(5) | 0.3008(3) | 0.0622(3) | 0.0334(12) |
| C7 | -0.0425(4) | 0.6784(3) | 0.2278(3) | 0.0255(10) |
| C1 | 0.0974(4) | 0.4543(3) | 0.1745(4) | 0.0372(12) |
| C21 | 0.3460(4) | 0.3575(3) | 0.1098(3) | $0.0279(11)$ |
| C5 | -0.1984(4) | 0.6536(3) | 0.3101(3) | $0.0318(11)$ |
| C23 | 0.4298(5) | 0.3329(4) | -0.0134(3) | 0.0345(12) |
| C10 | 0.2149(4) | 0.9210(3) | 0.2856(3) | 0.0257(10) |
| C15 | 0.3038(4) | 0.4759(3) | 0.3720(3) | 0.0291(11) |
| C17 | 0.3640(5) | 0.4790(5) | 0.5181(3) | 0.0453(15) |
| C16 | 0.3551(4) | 0.4305(4) | 0.4430(3) | 0.0405(14) |
| C20 | 0.2189(6) | 0.7553(5) | 0.5278(3) | 0.0499(16) |
| C24 | 0.3864(5) | 0.4217(4) | -0.0409(3) | 0.0400(13) |
| C18 | 0.3198(4) | 0.5696(4) | 0.5233(3) | $0.0344(12)$ |
| C25 | 0.3253(5) | 0.4748(3) | 0.0101(3) | $0.0344(12)$ |
| C6 | $-0.1595(4)$ | $0.6875(3)$ | $0.2385(3)$ | 0.0320(11) |
| C26 | -0.0771(6) | 0.7506(6) | 0.0942(4) | 0.069(2) |

${ }^{a} U_{(\text {eq) }}$ is defined as one third of the trace of the orthogonalized $U_{i j}$ tensor.

Table A.4: Bond lengths $(\AA)$ for $\left(\mathrm{P} \sim \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}($ py $)$,
2.

| $\mathrm{Pd} 1-\mathrm{C} 1$ | $2.027(5)$ | $\mathrm{Pd} 1-\mathrm{N} 1$ | $2.108(3)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Pd} 1-\mathrm{O} 3$ | $2.165(3)$ | $\mathrm{Pd} 1-\mathrm{P} 3$ | $2.2317(12)$ |
| $\mathrm{S} 1-\mathrm{O} 2$ | $1.438(3)$ | $\mathrm{S} 1-\mathrm{O} 1$ | $1.449(3)$ |
| $\mathrm{S} 1-\mathrm{O} 3$ | $1.472(3)$ | $\mathrm{S} 1-\mathrm{C} 13$ | $1.786(4)$ |
| $\mathrm{P} 3-\mathrm{C} 2$ | $1.810(5)$ | $\mathrm{P} 3-\mathrm{C} 14$ | $1.821(4)$ |
| $\mathrm{P} 3-\mathrm{C} 8$ | $1.831(4)$ | $\mathrm{N} 1-\mathrm{C} 25$ | $1.331(6)$ |
| $\mathrm{N} 1-\mathrm{C} 21$ | $1.344(6)$ | $\mathrm{O} 4-\mathrm{C} 19$ | $1.375(6)$ |
| $\mathrm{O} 4-\mathrm{C} 20$ | $1.423(5)$ | $\mathrm{C} 2-\mathrm{C} 3$ | $1.385(6)$ |
| $\mathrm{C} 2-\mathrm{C} 7$ | $1.423(6)$ | $\mathrm{C} 9-\mathrm{C} 10$ | $1.389(6)$ |
| $\mathrm{C} 9-\mathrm{C} 8$ | $1.394(6)$ | $\mathrm{C} 9-\mathrm{H} 9$ | 0.9500 |
| $\mathrm{C} 8-\mathrm{C} 13$ | $1.405(6)$ | $\mathrm{C} 13-\mathrm{C} 12$ | $1.397(6)$ |
| $\mathrm{C} 14-\mathrm{C} 19$ | $1.388(6)$ | $\mathrm{C} 14-\mathrm{C} 15$ | $1.391(6)$ |
| $\mathrm{C} 12-\mathrm{C} 11$ | $1.364(6)$ | $\mathrm{C} 12-\mathrm{H} 12$ | 0.9500 |
| $\mathrm{O} 5-\mathrm{C} 7$ | $1.360(5)$ | $\mathrm{O} 5-\mathrm{C} 26$ | $1.440(6)$ |
| $\mathrm{C} 11-\mathrm{C} 10$ | $1.376(6)$ | $\mathrm{C} 11-\mathrm{H} 11$ | 0.9500 |
| $\mathrm{C} 4-\mathrm{C} 5$ | $1.379(7)$ | $\mathrm{C} 4-\mathrm{C} 3$ | $1.392(6)$ |
| $\mathrm{C} 4-\mathrm{H} 4$ | 0.9500 | $\mathrm{C} 19-\mathrm{C} 18$ | $1.394(6)$ |
| $\mathrm{C} 3-\mathrm{H} 3$ | 0.9500 | $\mathrm{C} 22-\mathrm{C} 23$ | $1.354(6)$ |
| $\mathrm{C} 22-\mathrm{C} 21$ | $1.376(6)$ | $\mathrm{C} 22-\mathrm{H} 22$ | 0.9500 |
| $\mathrm{C} 7-\mathrm{C} 6$ | $1.383(6)$ | $\mathrm{C} 1-\mathrm{H} 1 \mathrm{~A}$ | 0.9800 |
| $\mathrm{C} 1-\mathrm{H} 1 \mathrm{~B}$ | 0.9800 | $\mathrm{C} 1-\mathrm{H} 1 \mathrm{C}$ | 0.9800 |
| $\mathrm{C} 21-\mathrm{H} 21$ | 0.9500 | $\mathrm{C} 5-\mathrm{C} 6$ | $1.380(7)$ |
| $\mathrm{C} 5-\mathrm{H} 5$ | 0.9500 | $\mathrm{C} 23-\mathrm{C} 24$ | $1.377(7)$ |
| $\mathrm{C} 23-\mathrm{H} 23$ | 0.9500 | $\mathrm{C} 10-\mathrm{H} 10$ | 0.9500 |
| $\mathrm{C} 15-\mathrm{C} 16$ | $1.375(7)$ | $\mathrm{C} 15-\mathrm{H} 15$ | 0.9500 |
| $\mathrm{C} 17-\mathrm{C} 18$ | $1.358(8)$ | $\mathrm{C} 17-\mathrm{C} 16$ | $1.385(8)$ |
| $\mathrm{C} 17-\mathrm{H} 17$ | 0.9500 | $\mathrm{C} 16-\mathrm{H} 16$ | 0.9500 |
| $\mathrm{C} 20-\mathrm{H} 20 \mathrm{~A} 26 \mathrm{C}$ | 0.9800 | $\mathrm{C} 20-\mathrm{H} 20 \mathrm{~B}$ | 0.9800 |
| $\mathrm{C} 20-\mathrm{H} 20 \mathrm{C}$ | 0.9800 | $\mathrm{C} 24-\mathrm{C} 25$ | $1.368(7)$ |
| $\mathrm{C} 24-\mathrm{H} 24$ | 0.9500 | $\mathrm{C} 18-\mathrm{H} 18$ | 0.9500 |
| $\mathrm{C} 25-\mathrm{H} 25$ | 0.9500 | $\mathrm{C} 6-\mathrm{H} 6$ | 0.9500 |
| $\mathrm{C} 26-\mathrm{H} 26 \mathrm{~A}$ | 0.9800 | $\mathrm{C} 26-\mathrm{H} 26 \mathrm{~B}$ | 0.9800 |
|  |  |  |  |

Table A.5: Bond angles $\left({ }^{\circ}\right)$ for $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}($ py $), 2$.

| C1-Pd1-N1 | 90.80(17) | C1-Pd1-O3 | 174.99(17) | N1-Pd1-O3 | 84.91(13) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| C1-Pd1-P3 | 89.96(14) | N1-Pd1-P3 | 172.73(11) | O3-Pd1-P3 | 94.63(8) |
| O2-S1-O1 | 114.78(18) | O2-S1-O3 | 112.62(18) | O1-S1-O3 | 110.38(17) |
| O2-S1-C13 | 106.96(17) | O1-S1-C13 | 105.96(19) | O3-S1-C13 | 105.41(18) |
| C2-P3-C14 | 104.3(2) | C2-P3-C8 | 105.41(19) | C14-P3-C8 | 107.8(2) |
| C2-P3-Pd1 | 119.38(15) | C14-P3-Pd1 | 108.45(15) | C8-P3-Pd1 | 110.86(13) |
| C25-N1-C21 | 117.1(4) | C25-N1-Pd1 | 123.0(3) | C21-N1-Pd1 | 118.4(3) |
| S1-O3-Pd1 | 122.41(16) | C19-O4-C20 | 118.0(4) | C3-C2-C7 | 117.8(4) |
| C3-C2-P3 | 121.2(4) | C7-C2-P3 | 121.1(3) | C10-C9-C8 | 121.9(4) |
| C10-C9-H9 | 119.0 | C8-C9-H9 | 119.0 | C9-C8-C13 | 117.1(4) |
| C9-C8-P3 | 120.2(3) | C13-C8-P3 | 122.5(3) | C12-C13-C8 | 120.3(4) |
| C12-C13-S1 | 116.9(3) | C8-C13-S1 | 122.8(3) | C19-C14-C15 | 118.6(4) |
| C19-C14-P3 | 123.3(4) | C15-C14-P3 | 118.0(3) | C11-C12-C13 | 120.9(4) |
| C11-C12-H12 | 119.5 | C13-C12-H12 | 119.5 | C7-O5-C26 | 115.9(4) |
| C12-C11-C10 | 120.0(4) | C12-C11-H11 | 120.0 | C10-C11-H11 | 120.0 |
| C5-C4-C3 | 119.5(4) | C5-C4-H4 | 120.3 | C3-C4-H4 | 120.3 |
| O4-C19-C14 | 115.7(4) | O4-C19-C18 | 123.9(4) | C14-C19-C18 | 120.4(5) |
| C2-C3-C4 | 121.5(4) | C2-C3-H3 | 119.2 | C4-C3-H3 | 119.2 |
| C23-C22-C21 | 119.3(5) | C23-C22-H22 | 120.4 | C21-C22-H22 | 120.4 |
| O5-C7-C6 | 124.6(4) | O5-C7-C2 | 115.0(4) | C6-C7-C2 | 120.4(4) |
| Pd1-C1-H1A | 109.5 | Pd1-C1-H1B | 109.5 | H1A-C1-H1B | 109.5 |
| Pd1-C1-H1C | 109.5 | H1A-C1-H1C | 109.5 | H1B-C1-H1C | 109.5 |
| N1-C21-C22 | 122.5(4) | N1-C21-H21 | 118.8 | C22-C21-H21 | 118.8 |
| C4-C5-C6 | 120.6(5) | C4-C5-H5 | 119.7 | C6-C5-H5 | 119.7 |
| C22-C23-C24 | 119.2(5) | C22-C23-H23 | 120.4 | C24-C23-H23 | 120.4 |
| C11-C10-C9 | 119.7(4) | C11-C10-H10 | 120.2 | C9-C10-H10 | 120.2 |
| C16-C15-C14 | 120.8(5) | C16-C15-H15 | 119.6 | C14-C15-H15 | 119.6 |
| C18-C17-C16 | 121.0(5) | C18-C17-H17 | 119.5 | C16-C17-H17 | 119.5 |
| C15-C16-C17 | 119.5(5) | C15-C16-H16 | 120.3 | C17-C16-H16 | 120.3 |
| O4-C20-H20A | 109.5 | O4-C20-H20B | 109.5 | H20A-C20-H20B | 109.5 |
| O4-C20-H20C | 109.5 | H20A-C20-H20C | 109.5 | H20B-C20-H20C | 109.5 |
| C25-C24-C23 | 118.4(5) | C25-C24-H24 | 120.8 | C23-C24-H24 | 120.8 |
| C17-C18-C19 | 119.6(5) | C17-C18-H18 | 120.2 | C19-C18-H18 | 120.2 |
| N1-C25-C24 | 123.5(4) | N1-C25-H25 | 118.2 | C24-C25-H25 | 118.2 |
| C5-C6-C7 | 120.1(5) | C5-C6-H6 | 119.9 | C7-C6-H6 | 119.9 |
| O5-C26-H26A | 109.5 | O5-C26-H26B | 109.5 | H26A-C26-H26B | 109.5 |
| O5-C26-H26C | 109.5 | H26A-C26-H26C | 109.5 | H26B-C26-H26C | 109.5 |

Table A.6: Torsion angles $\left({ }^{\circ}\right)$ for $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}(\mathrm{py}), 2$.

| C1-Pd1-P3-C2 | -28.7(2) | N1-Pd1-P3-C2 | -124.6(8) |
| :---: | :---: | :---: | :---: |
| O3-Pd1-P3-C2 | 149.31(18) | C1-Pd1-P3-C14 | 90.4(2) |
| N1-Pd1-P3-C14 | -5.5(8) | O3-Pd1-P3-C14 | -91.58(17) |
| C1-Pd1-P3-C8 | -151.4(2) | N1-Pd1-P3-C8 | 112.6(8) |
| O3-Pd1-P3-C8 | 26.56(17) | C1-Pd1-N1-C25 | 121.1(4) |
| O3-Pd1-N1-C25 | -56.3(4) | P3-Pd1-N1-C25 | -142.9(7) |
| C1-Pd1-N1-C21 | -73.3(4) | O3-Pd1-N1-C21 | 109.2(4) |
| P3-Pd1-N1-C21 | 22.6(11) | O2-S1-O3-Pd1 | 51.4(2) |
| O1-S1-O3-Pd1 | -178.88(18) | C13-S1-O3-Pd1 | -64.9(2) |
| C1-Pd1-O3-S1 | -179.0(340) | N1-Pd1-O3-S1 | -148.3(2) |
| P3-Pd1-O3-S1 | 24.4(2) | C14-P3-C2-C3 | -3.3(4) |
| C8-P3-C2-C3 | -116.7(4) | Pd1-P3-C2-C3 | 118.0(3) |
| C14-P3-C2-C7 | 179.1(4) | C8-P3-C2-C7 | 65.7(4) |
| Pd1-P3-C2-C7 | -59.6(4) | C10-C9-C8-C13 | 0.8(6) |
| C10-C9-C8-P3 | -175.9(3) | C2-P3-C8-C9 | 8.1(4) |
| C14-P3-C8-C9 | -102.9(4) | Pd1-P3-C8-C9 | 138.6(3) |
| C2-P3-C8-C13 | -168.5(3) | C14-P3-C8-C13 | 80.5(4) |
| Pd1-P3-C8-C13 | -38.0(4) | C9-C8-C13-C12 | 0.0(6) |
| P3-C8-C13-C12 | 176.7(3) | C9-C8-C13-S1 | 178.9(3) |
| P3-C8-C13-S1 | -4.4(5) | O2-S1-C13-C12 | 118.3(3) |
| O1-S1-C13-C12 | -4.6(4) | O3-S1-C13-C12 | -121.7(3) |
| O2-S1-C13-C8 | -60.7(4) | O1-S1-C13-C8 | 176.4(3) |
| O3-S1-C13-C8 | 59.4(4) | C2-P3-C14-C19 | -65.0(4) |
| C8-P3-C14-C19 | 46.7(4) | Pd1-P3-C14-C19 | 166.7(3) |
| C2-P3-C14-C15 | 113.5(4) | C8-P3-C14-C15 | -134.8(4) |
| Pd1-P3-C14-C15 | -14.7(4) | C8-C13-C12-C11 | -1.0(6) |
| S1-C13-C12-C11 | 180.0(3) | C13-C12-C11-C10 | 1.3(7) |
| C20-O4-C19-C14 | 179.2(4) | C20-O4-C19-C18 | $-0.5(7)$ |
| C15-C14-C19-O4 | -177.3(4) | P3-C14-C19-O4 | 1.2(6) |
| C15-C14-C19-C18 | 2.4(7) | P3-C14-C19-C18 | -179.1(4) |
| C7-C2-C3-C4 | -1.5(7) | P3-C2-C3-C4 | -179.1(4) |
| C5-C4-C3-C2 | -0.5(7) | C26-O5-C7-C6 | -0.7(7) |
| C26-O5-C7-C2 | 179.9(5) | C3-C2-C7-O5 | -178.1(4) |
| P3-C2-C7-O5 | -0.4(5) | C3-C2-C7-C6 | 2.5(6) |
| P3-C2-C7-C6 | -179.8(3) | C25-N1-C21-C22 | 0.4(7) |
| Pd1-N1-C21-C22 | -166.0(4) | C23-C22-C21-N1 | $-0.9(8)$ |
| C3-C4-C5-C6 | 1.4(7) | C21-C22-C23-C24 | 0.3(8) |
| C12-C11-C10-C9 | -0.5(7) | C8-C9-C10-C11 | -0.6(7) |
| C19-C14-C15-C16 | $-1.3(7)$ | P3-C14-C15-C16 | -179.9(4) |
| C14-C15-C16-C17 | $-0.9(7)$ | C18-C17-C16-C15 | 2.0(8) |
| C22-C23-C24-C25 | 0.6(8) | C16-C17-C18-C19 | -0.8(8) |
| O4-C19-C18-C17 | 178.3(4) | C14-C19-C18-C17 | -1.4(7) |
| C21-N1-C25-C24 | 0.6(8) | Pd1-N1-C25-C24 | 166.3(4) |
| C23-C24-C25-N1 | -1.1(9) | C4-C5-C6-C7 | -0.3(7) |
| O5-C7-C6-C5 | 179.0(4) | C2-C7-C6-C5 | -1.7(7) |

Table A.7: Anisotropic atomic displacement parameters $\left(\AA^{2}\right)$ for $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}(\mathrm{py})$, 2. ${ }^{a}$

|  | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Pd1 | $0.02216(19)$ | 0.01702(18) | 0.02299(18) | -0.00182(14) | 0.00567(13) | -0.00023(14) |
| S1 | 0.0163(5) | 0.0206(5) | 0.0202(5) | -0.0008(4) | 0.0036(4) | 0.0011(4) |
| P3 | 0.0176(6) | 0.0159(5) | 0.0207(5) | 0.0013(4) | 0.0042(4) | 0.0016(4) |
| O1 | 0.0196(17) | 0.0277(17) | 0.0280(16) | -0.0018(13) | 0.0076(13) | -0.0034(13) |
| O2 | 0.0196(17) | 0.0304(17) | 0.0238(15) | 0.0049(13) | 0.0028(13) | 0.0086(13) |
| N1 | 0.028(2) | 0.0180(19) | 0.0250(19) | -0.0055(15) | 0.0077(16) | -0.0008(15) |
| O3 | 0.0231(17) | 0.0195(15) | 0.0235(15) | -0.0034(12) | $0.0065(13)$ | -0.0027(13) |
| O4 | 0.042(2) | 0.035(2) | 0.0212(16) | -0.0063(14) | $0.0034(14)$ | -0.0032(16) |
| C2 | 0.024(2) | 0.016(2) | 0.030(2) | -0.0022(18) | $0.0057(19)$ | 0.0012(18) |
| C9 | 0.016(2) | 0.026(2) | 0.030(2) | -0.0011(19) | 0.0044(19) | -0.0020(18) |
| C8 | 0.018(2) | 0.022(2) | 0.0151(19) | 0.0031(16) | 0.0020(16) | -0.0008(17) |
| C13 | 0.017(2) | 0.016(2) | 0.0151(18) | 0.0021(16) | 0.0003(16) | 0.0012(16) |
| C14 | 0.013(2) | 0.027(2) | 0.028(2) | 0.0090(18) | 0.0065(18) | -0.0006(18) |
| C12 | 0.021(2) | 0.025(2) | 0.022(2) | 0.0012(18) | -0.0020 (18) | -0.0052(18) |
| O5 | 0.0243(19) | 0.040(2) | 0.0294(17) | $0.0124(15)$ | $-0.0006(14)$ | 0.0073(15) |
| C11 | 0.032(3) | 0.016(2) | 0.032(2) | 0.0008(18) | 0.001(2) | -0.0034(19) |
| C4 | 0.024(3) | 0.037(3) | 0.033(3) | -0.006(2) | 0.008(2) | -0.009(2) |
| C19 | 0.021(3) | 0.043(3) | 0.025(2) | 0.004(2) | 0.0038(19) | -0.007(2) |
| C3 | 0.022(2) | 0.030(3) | 0.027(2) | -0.0016(19) | 0.0044(19) | -0.004(2) |
| C22 | 0.050(3) | 0.022(2) | 0.028(2) | -0.0032(19) | 0.001(2) | 0.006(2) |
| C7 | 0.024(3) | 0.019(2) | 0.034(2) | -0.0024(19) | 0.004(2) | 0.0012(19) |
| C1 | 0.027(3) | 0.027(3) | 0.060(3) | -0.015(2) | 0.013(2) | -0.011(2) |
| C21 | 0.041(3) | 0.021(2) | 0.022(2) | 0.0018(18) | 0.003(2) | 0.003(2) |
| C5 | 0.022(3) | 0.026(3) | 0.049(3) | -0.018(2) | 0.008(2) | -0.004(2) |
| C23 | 0.041(3) | 0.029(3) | 0.034(3) | -0.006(2) | 0.011(2) | 0.006(2) |
| C10 | 0.025(3) | 0.017(2) | 0.034(2) | -0.0047(19) | 0.004(2) | 0.0028(19) |
| C15 | 0.024(3) | 0.026(3) | 0.038(3) | 0.011(2) | 0.010(2) | 0.006(2) |
| C17 | 0.022(3) | 0.069(4) | 0.044(3) | 0.035(3) | 0.001(2) | -0.003(3) |
| C16 | 0.025(3) | 0.043(3) | 0.054(3) | 0.026(3) | 0.006(2) | 0.011(2) |
| C20 | 0.058(4) | 0.060(4) | 0.033(3) | -0.021(3) | 0.010(3) | -0.009(3) |
| C24 | 0.062(4) | 0.034(3) | 0.027(3) | 0.005(2) | 0.016(3) | 0.005(3) |
| C18 | 0.024(3) | 0.054(3) | 0.023(2) | 0.010(2) | -0.004(2) | -0.011(2) |
| C25 | 0.048(3) | 0.023(3) | 0.033(3) | 0.005(2) | 0.010(2) | 0.008(2) |
| C6 | 0.023(3) | 0.024(2) | 0.046(3) | -0.009(2) | -0.006(2) | 0.005(2) |
| C26 | 0.045(4) | 0.103(6) | 0.057(4) | 0.043(4) | -0.002(3) | 0.023(4) |

[^1]Table A.8: Hydrogen atom coordinates and isotropic atomic displacement parameters $\left(\AA^{2}\right)$ for $\left(\mathrm{P} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}$ (py), 2.

|  | $x / a$ | $y / b$ | $z / c$ | $U$ |
| :---: | :---: | :---: | :---: | :---: |
| H9 | 0.1039 | 0.8136 | 0.3095 | 0.029 |
| H12 | 0.4703 | 0.8792 | 0.2305 | 0.028 |
| H11 | 0.3482 | 1.0049 | 0.2567 | 0.032 |
| H4 | -0.1493 | 0.5856 | 0.4200 | 0.037 |
| H3 | 0.0492 | 0.5724 | 0.4041 | 0.031 |
| H22 | 0.4394 | 0.2399 | 0.0823 | 0.040 |
| H1A | 0.0319 | 0.4826 | 0.1376 | 0.056 |
| H1B | 0.0772 | 0.4514 | 0.2313 | 0.056 |
| $\mathrm{H} 1 \mathrm{C}$ | 0.1130 | 0.3888 | 0.1556 | 0.056 |
| H21 | $0.3313$ | 0.3341 | 0.1624 | 0.033 |
| H5 | -0.2788 | 0.6604 | 0.3171 | 0.038 |
| H23 | 0.4733 | 0.2946 | -0.0472 | 0.041 |
| $\mathrm{H} 10$ | 0.1651 | 0.9728 | 0.2972 | 0.031 |
| $\mathrm{H} 15$ | 0.2986 | 0.4432 | 0.3203 | 0.035 |
| H17 | $0.4016$ | 0.4484 | 0.5669 | 0.054 |
| H16 | $0.3841$ | 0.3664 | 0.4404 | $0.049$ |
| H20A | 0.1852 | 0.7140 | 0.5677 | 0.075 |
| H20B | 0.1730 | 0.8150 | 0.5193 | 0.075 |
| H20C | 0.3003 | 0.7710 | 0.5494 | 0.075 |
| H24 | 0.3987 | 0.4455 | -0.0939 | 0.048 |
| H18 | 0.3255 | 0.6017 | 0.5754 | 0.041 |
| H25 | 0.2967 | 0.5366 | -0.0085 | 0.041 |
| H6 | -0.2131 | 0.7172 | 0.1966 | 0.038 |
| H26A | -0.1350 | 0.7021 | 0.0720 | 0.104 |
| H26B | -0.0341 | 0.7735 | 0.0497 | 0.104 |
| H26C | -0.1173 | 0.8052 | 0.1167 | 0.104 |

## A.5.2 X-ray diffraction data for $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdC}(0) \mathrm{CH}_{3}(\mathrm{py}), 3$



Figure A.26: Crystal structure for $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}(\mathrm{py}), 3$.

Table A.9: Sample and crystal data for $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}(\mathrm{py}), 3$.

| Identification code | svb13 |  |
| :--- | :--- | :--- |
| Crystallization solvents | Dichloromethane and pentane |  |
| Crystallization method | Diffusion chamber |  |
| Empirical formula | $\mathrm{C}_{27} \mathrm{H}_{26} \mathrm{NO}_{6} \mathrm{PPdS}$ |  |
| Formula weight | 629.92 |  |
| Temperature | $293(2) \mathrm{K}$ |  |
| Wavelength | $0.71073 \AA$ |  |
| Crystal size | $0.17 \times 0.13 \times 0.05 \mathrm{~mm}$ |  |
| Crystal habit | yellow plate |  |
| Crystal system | Monoclinic |  |
| Space group | $\mathrm{P} 2(1) / \mathrm{c}$ |  |
| Unit cell dimensions | $a=11.567(2) \AA$ |  |
|  | $b=14.097(3) \AA$ |  |
|  | $c=16.198(3) \AA$ |  |
| Volume |  |  |
| $Z$ | $2623.5(9) \AA$ |  |
| Density (calculated) | 4 |  |
| Absorption coefficient | $1.595 \mathrm{gcm}^{\circ}$ |  |
| $F\left(0.891 \mathrm{~mm}^{-1}\right.$ |  |  |

Table A.10: Data collection and structure refinement for $\left(\mathrm{P} \subset \mathrm{SO}_{3}\right) \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}$ (py), 3.

| Diffractometer | CCD area detector |
| :--- | :--- |
| Radiation source | fine-focus sealed tube, Mo K $\alpha$ |
| Generator power | $1600 \mathrm{~W}(50 \mathrm{kV}, 32 \mathrm{~mA})$ |
| Detector distance | 5.8 cm |
| Data collection method | phi and omega scans |
| Theta range for data collection | 1.77 to $28.36^{\circ}$ |
| Index ranges | $-15 \leq h \leq 15,-18 \leq k \leq 17,-15 \leq l \leq 21$ |

Table A.11: Atomic coordinates and equivalent isotropic atomic displacement parameters $\left(\AA^{2}\right)$ for $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}($ py $), 3$.

|  | X | Y | Z | $U_{(\text {eq) }}$ |
| :---: | :---: | :---: | :---: | :---: |
| Pd1 | 0.75284 (3) | 0.46282(2) | $0.177177(19)$ | $0.01761(11)$ |
| S1 | 0.96633(8) | $0.32157(8)$ | $0.23298(6)$ | 0.0164(2) |
| P1 | $0.69709(9)$ | $0.37317(7)$ | $0.28125(6)$ | 0.0135(2) |
| O3 | 0.9904(2) | 0.3767(2) | 0.30802(17) | 0.0220(7) |
| O2 | $1.0654(2)$ | 0.2722(2) | 0.20661(17) | 0.0214(7) |
| C1 | 0.6094(4) | 0.5443(3) | 0.1780(3) | 0.0211(9) |
| N1 | 0.8131(3) | 0.5562(2) | 0.0887(2) | 0.0212(8) |
| O1 | 0.9066(2) | 0.3780(2) | $0.16310(16)$ | 0.0192(6) |
| C9 | 0.9007(3) | 0.1379(3) | 0.2473(3) | 0.0197(9) |
| C8 | 0.8650(3) | 0.2313(3) | 0.2534(2) | 0.0145(8) |
| C13 | 0.7520(3) | 0.2522(3) | 0.2744(2) | 0.0142(8) |
| O4 | 0.7176(3) | 0.2863(2) | $0.45171(18)$ | 0.0273(7) |
| C12 | 0.6796(4) | 0.1756(3) | 0.2854(3) | 0.0213(9) |
| C14 | 0.7611(3) | 0.4237(3) | 0.3796(3) | 0.0187(9) |
| C21 | 0.5426(3) | 0.3626(3) | 0.2931(3) | 0.0171(8) |
| C19 | 0.7673(4) | 0.3740(3) | 0.4545(3) | $0.0242(10)$ |
| C10 | 0.8274(4) | 0.0640(3) | 0.2593(3) | 0.0209(9) |
| C6 | 0.8878(5) | 0.5845(4) | -0.0398(3) | 0.0346(12) |
| C16 | 0.8536(4) | 0.5577(4) | 0.4524(3) | 0.0360(13) |
| C3 | 0.8420(4) | 0.6457(3) | 0.1108(3) | 0.0283(11) |
| C15 | 0.8050(4) | 0.5163(3) | 0.3795(3) | 0.0249(10) |
| C11 | 0.7166(4) | 0.0832(3) | 0.2778(3) | 0.0245(10) |
| C17 | 0.8631(4) | 0.5058(4) | 0.5263(3) | 0.0373(13) |
| C20 | 0.7252(5) | 0.2318(4) | 0.5258(3) | 0.0428(14) |
| C5 | 0.9187(4) | 0.6751(4) | -0.0160(3) | $0.0337(12)$ |
| C4 | 0.8975(5) | 0.7061(3) | 0.0607(3) | 0.0354(12) |
| C18 | 0.8196(4) | 0.4153(4) | 0.5275(3) | 0.0343(12) |
| C7 | 0.8350(4) | 0.5272(3) | 0.0132(3) | 0.0326(12) |
| O6 | 0.5097(3) | 0.2928(2) | $0.16075(18)$ | 0.0260(7) |
| O5 | 0.5999(3) | 0.5970(3) | 0.2324(2) | 0.0447(9) |
| C22 | 0.5005(4) | 0.3985(3) | 0.3642(3) | 0.0220(9) |
| C26 | 0.4632(3) | 0.3242(3) | 0.2299(3) | 0.0190(9) |
| C25 | 0.3462(4) | 0.3185(3) | 0.2400(3) | 0.0253(10) |
| C23 | 0.3824(4) | 0.3924(3) | 0.3736(3) | 0.0265(10) |
| C24 | 0.3067(4) | 0.3523(3) | 0.3119(3) | 0.0288(11) |
| C27 | 0.4325(5) | 0.2448(5) | 0.0993(3) | $0.0484(16)$ |
| C2 | 0.5315(5) | 0.5310(5) | 0.1024(3) | 0.0485(15) |

[^2]Table A.12: Bond lengths $(\AA)$ for $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \operatorname{PdC}(\mathrm{O}) \mathrm{CH}_{3}($ py $), 3$.

| Pd1-C1 | $2.019(5)$ | Pd1-N1 | $2.123(3)$ | Pd1-O1 | $2.177(3)$ | Pd1-P1 | $2.2601(11)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| S1-O3 | $1.442(3)$ | S1-O2 | $1.447(3)$ | S1-O1 | $1.486(3)$ | S1-C8 | $1.787(4)$ |
| P1-C14 | $1.821(4)$ | P1-C21 | $1.826(4)$ | P1-C13 | $1.827(4)$ | C1-O5 | $1.166(5)$ |
| C1-C2 | $1.446(7)$ | N1-C7 | $1.340(6)$ | N1-C3 | $1.343(6)$ | C9-C10 | $1.371(6)$ |
| C9-C8 | $1.387(6)$ | C9-H9 | 0.9300 | C8-C13 | $1.419(5)$ | C13-C12 | $1.391(6)$ |
| O4-C19 | $1.362(5)$ | O4-C20 | $1.419(5)$ | C12-C11 | $1.381(6)$ | C12-H12 | 0.9300 |
| C14-C19 | $1.395(6)$ | C14-C15 | $1.401(6)$ | C21-C22 | $1.397(6)$ | C21-C26 | $1.402(6)$ |
| C19-C18 | $1.392(6)$ | C10-C11 | $1.377(6)$ | C10-H10 | 0.9300 | C6-C7 | $1.373(6)$ |
| C6-C5 | $1.370(7)$ | C6-H6 | 0.9300 | C16-C15 | $1.377(6)$ | C16-C17 | $1.398(8)$ |
| C16-H16 | 0.9300 | C3-C4 | $1.383(6)$ | C3-H3 | 0.9300 | C15-H15 | 0.9300 |
| C11-H11 | 0.9300 | C17-C18 | $1.371(8)$ | C17-H17 | 0.9300 | C20-H20A | 0.9600 |
| C20-H20B | 0.9600 | C20-H20C | 0.9600 | C5-C4 | $1.366(7)$ | C5-H5 | 0.9300 |
| C4-H4 | 0.9300 | C18-H18 | 0.9300 | C7-H7 | 0.9300 | O6-C26 | $1.370(5)$ |
| O6-C27 | $1.428(6)$ | C22-C23 | $1.394(6)$ | C22-H22 | 0.9300 | C26-C25 | $1.385(6)$ |
| C25-C24 | $1.384(6)$ | C25-H25 | 0.9300 | C23-C24 | $1.371(7)$ | C23-H23 | 0.9300 |
| C24-H24 | 0.9300 | C27-H27A | 0.9600 | C27-H27B | 0.9600 | C27-H27C | 0.9600 |
| C2-H2A | 0.9600 | C2-H2B | 0.9600 | C2-H2C | 0.9600 |  |  |

Table A.13: Bond angles $\left({ }^{\circ}\right)$ for $\left(\mathrm{P}^{\wedge} \mathrm{SO}_{3}\right) \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}(\mathrm{py}), 3$.

| C1-Pd1-N1 | 89.22(15) | C1-Pd1-O1 | 174.30(14) | N1-Pd1-O1 | 86.17(12) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| C1-Pd1-P1 | 90.41(12) | N1-Pd1-P1 | 174.32(11) | O1-Pd1-P1 | 94.51(8) |
| O3-S1-O2 | 115.21(17) | O3-S1-O1 | 112.38(18) | O2-S1-O1 | 110.26(16) |
| O3-S1-C8 | 107.10(17) | O2-S1-C8 | 105.76(18) | O1-S1-C8 | 105.39(17) |
| C14-P1-C21 | 104.10(18) | C14-P1-C13 | 108.01(19) | C21-P1-C13 | 106.36(18) |
| C14-P1-Pd1 | 108.15(14) | C21-P1-Pd1 | 119.45(14) | C13-P1-Pd1 | 110.18(12) |
| O5-C1-C2 | 128.1(5) | O5-C1-Pd1 | 121.2(4) | C2-C1-Pd1 | 110.6(3) |
| C7-N1-C3 | 117.5(4) | C7-N1-Pd1 | 122.6(3) | C3-N1-Pd1 | 119.6(3) |
| S1-O1-Pd1 | 121.80(15) | C10-C9-C8 | 121.1(4) | C10-C9-H9 | 119.4 |
| C8-C9-H9 | 119.4 | C9-C8-C13 | 120.3(4) | C9-C8-S1 | 117.1(3) |
| C13-C8-S1 | 122.6(3) | C12-C13-C8 | 117.0(4) | C12-C13-P1 | 119.9(3) |
| C8-C13-P1 | 123.0(3) | C19-O4-C20 | 118.7(4) | C11-C12-C13 | 121.6(4) |
| C11-C12-H12 | 119.2 | C13-C12-H12 | 119.2 | C19-C14-C15 | 119.0(4) |
| C19-C14-P1 | 122.6(3) | C15-C14-P1 | 118.3(3) | C22-C21-C26 | 118.8(4) |
| C22-C21-P1 | 119.7(3) | C26-C21-P1 | 121.4(3) | O4-C19-C18 | 123.2(4) |
| O4-C19-C14 | 116.6(4) | C18-C19-C14 | 120.2(5) | C9-C10-C11 | 119.2(4) |
| C9-C10-H10 | 120.4 | C11-C10-H10 | 120.4 | C7-C6-C5 | 119.5(4) |
| C7-C6-H6 | 120.3 | C5-C6-H6 | 120.3 | C15-C16-C17 | 119.7(5) |
| C15-C16-H16 | 120.1 | C17-C16-H16 | 120.1 | N1-C3-C4 | 122.7(4) |
| N1-C3-H3 | 118.7 | C4-C3-H3 | 118.7 | C16-C15-C14 | 120.5(5) |
| C16-C15-H15 | 119.8 | C14-C15-H15 | 119.8 | C10-C11-C12 | 120.6(4) |
| C10-C11-H11 | 119.7 | C12-C11-H11 | 119.7 | C18-C17-C16 | 120.4(5) |
| C18-C17-H17 | 119.8 | C16-C17-H17 | 119.8 | O4-C20-H20A | 109.5 |
| O4-C20-H20B | 109.5 | H20A-C20-H20B | 109.5 | O4-C20-H20C | 109.5 |
| H20A-C20-H20C | 109.5 | H20B-C20-H20C | 109.5 | C4-C5-C6 | 119.1(4) |
| C4-C5-H5 | 120.5 | C6-C5-H5 | 120.5 | C5-C4-C3 | 118.7(5) |
| C5-C4-H4 | 120.6 | C3-C4-H4 | 120.6 | C17-C18-C19 | 120.1(5) |
| C17-C18-H18 | 120.0 | C19-C18-H18 | 120.0 | N1-C7-C6 | 122.4(4) |
| N1-C7-H7 | 118.8 | C6-C7-H7 | 118.8 | C26-O6-C27 | 116.7(3) |
| C21-C22-C23 | 120.5(4) | C21-C22-H22 | 119.8 | C23-C22-H22 | 119.8 |
| O6-C26-C25 | 124.1(4) | O6-C26-C21 | 115.8(3) | C25-C26-C21 | 120.1(4) |
| C24-C25-C26 | 120.2(4) | C24-C25-H25 | 119.9 | C26-C25-H25 | 119.9 |
| C24-C23-C22 | 119.8(4) | C24-C23-H23 | 120.1 | C22-C23-H23 | 120.1 |
| C23-C24-C25 | 120.6(4) | C23-C24-H24 | 119.7 | C25-C24-H24 | 119.7 |
| O6-C27-H27A | 109.5 | O6-C27-H27B | 109.5 | H27A-C27-H27B | 109.5 |
| O6-C27-H27C | 109.5 | H27A-C27-H27C | 109.5 | H27B-C27-H27C | 109.5 |
| C1-C2-H2A | 109.5 | C1-C2-H2B | 109.5 | H2A-C2-H2B | 109.5 |
| C1-C2-H2C | 109.5 | H2A-C2-H2C | 109.5 | H2B-C2-H2C | 109.5 |

Table A.14: Torsion angles ( ${ }^{\circ}$ ) for $\left(\mathrm{P}^{\wedge} \mathrm{SO}_{3}\right) \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}(\mathrm{py}), 3$.

| C1-Pd1-P1-C14 | -91.21(19) | N1-Pd1-P1-C14 | -5.0(10) |
| :---: | :---: | :---: | :---: |
| O1-Pd1-P1-C14 | 91.67(16) | C1-Pd1-P1-C21 | 27.4(2) |
| N1-Pd1-P1-C21 | 113.6(10) | O1-Pd1-P1-C21 | -149.68(17) |
| C1-Pd1-P1-C13 | 150.95(19) | N1-Pd1-P1-C13 | -122.8(10) |
| O1-Pd1-P1-C13 | -26.17(16) | N1-Pd1-C1-O5 | -102.8(4) |
| O1-Pd1-C1-O5 | -138.8(13) | P1-Pd1-C1-O5 | 71.6(4) |
| N1-Pd1-C1-C2 | 73.5(4) | O1-Pd1-C1-C2 | 37.5(16) |
| P1-Pd1-C1-C2 | -112.2(3) | C1-Pd1-N1-C7 | -120.6(4) |
| O1-Pd1-N1-C7 | 56.0(4) | P1-Pd1-N1-C7 | 153.1(8) |
| C1-Pd1-N1-C3 | 66.2(4) | O1-Pd1-N1-C3 | -117.1(3) |
| P1-Pd1-N1-C3 | -20.0(12) | O3-S1-O1-Pd1 | -50.1(2) |
| O2-S1-O1-Pd1 | 179.94(17) | C8-S1-O1-Pd1 | 66.2(2) |
| C1-Pd1-O1-S1 | -175.6(14) | N1-Pd1-O1-S1 | 148.3(2) |
| P1-Pd1-O1-S1 | -26.04(19) | C10-C9-C8-C13 | 1.6(6) |
| C10-C9-C8-S1 | -177.9(3) | O3-S1-C8-C9 | -118.6(3) |
| O2-S1-C8-C9 | 4.7(4) | O1-S1-C8-C9 | 121.5(3) |
| O3-S1-C8-C13 | 61.9(4) | O2-S1-C8-C13 | -174.7(3) |
| O1-S1-C8-C13 | -58.0(4) | C9-C8-C13-C12 | -2.1(6) |
| S1-C8-C13-C12 | 177.4(3) | C9-C8-C13-P1 | -178.5(3) |
| S1-C8-C13-P1 | 1.0(5) | C14-P1-C13-C12 | 106.0(3) |
| C21-P1-C13-C12 | -5.3(4) | Pd1-P1-C13-C12 | -136.1(3) |
| C14-P1-C13-C8 | -77.7(4) | C21-P1-C13-C8 | 171.1(3) |
| Pd1-P1-C13-C8 | 40.2(4) | C8-C13-C12-C11 | 1.2(6) |
| P1-C13-C12-C11 | 177.7(3) | C21-P1-C14-C19 | 67.6(4) |
| C13-P1-C14-C19 | -45.2(4) | Pd1-P1-C14-C19 | -164.4(3) |
| C21-P1-C14-C15 | -112.0(3) | C13-P1-C14-C15 | 135.2(3) |
| Pd1-P1-C14-C15 | 16.0(4) | C14-P1-C21-C22 | 5.2(4) |
| C13-P1-C21-C22 | 119.1(4) | Pd1-P1-C21-C22 | -115.6(3) |
| C14-P1-C21-C26 | -178.7(3) | C13-P1-C21-C26 | -64.8(4) |
| Pd1-P1-C21-C26 | 60.5(4) | C20-O4-C19-C18 | -3.8(6) |
| C20-O4-C19-C14 | 177.9(4) | C15-C14-C19-O4 | 176.5(4) |
| P1-C14-C19-O4 | -3.2(5) | C15-C14-C19-C18 | -1.9(6) |
| P1-C14-C19-C18 | 178.5(3) | C8-C9-C10-C11 | -0.2(7) |
| C7-N1-C3-C4 | -3.1(7) | Pd1-N1-C3-C4 | 170.4(4) |
| C17-C16-C15-C14 | 2.4(7) | C19-C14-C15-C16 | 0.0(6) |
| P1-C14-C15-C16 | 179.6(3) | C9-C10-C11-C12 | -0.8(7) |
| C13-C12-C11-C10 | 0.2(7) | C15-C16-C17-C18 | -2.9(7) |
| C7-C6-C5-C4 | 0.8(8) | C6-C5-C4-C3 | -2.0(8) |
| N1-C3-C4-C5 | 3.3(8) | C16-C17-C18-C19 | 1.0(7) |
| O4-C19-C18-C17 | -176.8(4) | C14-C19-C18-C17 | $1.4(7)$ |
| C3-N1-C7-C6 | 1.8(7) | Pd1-N1-C7-C6 | -171.5(4) |
| C5-C6-C7-N1 | -0.7(8) | C26-C21-C22-C23 | 2.7(6) |
| P1-C21-C22-C23 | 178.9(3) | C27-O6-C26-C25 | -5.1(6) |
| C27-O6-C26-C21 | 173.9(4) | C22-C21-C26-O6 | 178.1(4) |
| P1-C21-C26-O6 | 2.0(5) | C22-C21-C26-C25 | -2.8(6) |
| P1-C21-C26-C25 | -178.9(3) | O6-C26-C25-C24 | -179.7(4) |
| C21-C26-C25-C24 | 1.3(7) | C21-C22-C23-C24 | -1.1(7) |
| C22-C23-C24-C25 | -0.5(7) | C26-C25-C24-C23 | 0.4(7) |

Table A.15: Anisotropic atomic displacement parameters $\left(\AA^{2}\right)$ for $\left(\mathrm{P}^{-} \mathrm{SO}_{3}\right) \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}(\mathrm{py}), \mathbf{3}^{a}{ }^{a}$

|  | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Pd1 | 0.01805(17) | 0.01751(17) | 0.01780(18) | 0.00271(13) | 0.00430(13) | 0.00100(13) |
| S1 | 0.0108(5) | 0.0208(5) | 0.0172(5) | 0.0005(4) | 0.0008(4) | -0.0031(4) |
| P1 | 0.0131(5) | 0.0141(5) | 0.0131(5) | -0.0012(4) | 0.0012(4) | -0.0024(4) |
| O3 | 0.0191(15) | 0.0256(17) | 0.0210(16) | -0.0041(13) | 0.0004(12) | -0.0077(13) |
| O2 | 0.0129(14) | 0.0282(17) | 0.0238(16) | $0.0044(13)$ | 0.0051(12) | 0.0014(12) |
| C1 | 0.031(2) | 0.013(2) | 0.021(2) | 0.0036(18) | 0.0111(19) | -0.0048(18) |
| N1 | 0.0255(19) | 0.0177(19) | 0.0214(19) | 0.0053(15) | 0.0063(15) | $0.0035(15)$ |
| O1 | 0.0167(14) | 0.0219(16) | 0.0191(15) | 0.0055(12) | 0.0021(12) | 0.0005(12) |
| C9 | 0.013(2) | 0.023(2) | 0.022(2) | -0.0027(18) | -0.0024(17) | 0.0031(17) |
| C8 | 0.0133(19) | 0.019(2) | $0.0113(19)$ | -0.0007(16) | 0.0004(16) | -0.0018(16) |
| C13 | 0.017(2) | 0.018(2) | 0.0075(18) | 0.0001(15) | -0.0010(16) | 0.0003(16) |
| O4 | 0.0348(19) | 0.0339(19) | 0.0127(15) | 0.0046(14) | 0.0009(13) | -0.0011(15) |
| C12 | 0.016(2) | 0.022(2) | 0.027(2) | -0.0021(19) | 0.0051(18) | -0.0007(18) |
| C14 | 0.0119(19) | 0.023(2) | 0.021(2) | -0.0068(18) | 0.0046(17) | -0.0019(17) |
| C21 | 0.0140(19) | 0.016(2) | 0.021(2) | 0.0026(17) | 0.0020(17) | -0.0015(16) |
| C19 | 0.014(2) | 0.039(3) | 0.019(2) | -0.008(2) | -0.0006(17) | 0.0035(19) |
| C10 | 0.025(2) | 0.013(2) | 0.023(2) | -0.0031(17) | 0.0003(19) | 0.0009(17) |
| C6 | 0.053(3) | 0.031(3) | 0.023(3) | -0.001(2) | 0.017(2) | -0.002(2) |
| C16 | 0.024(2) | 0.034(3) | 0.050(3) | -0.028(3) | 0.004(2) | -0.007(2) |
| C3 | 0.037(3) | 0.027(3) | 0.021(2) | 0.002(2) | 0.003(2) | 0.002(2) |
| C15 | 0.020(2) | 0.021(2) | 0.034(3) | -0.011(2) | 0.006(2) | -0.0021(18) |
| C11 | 0.024(2) | 0.019(2) | 0.031(3) | 0.0011(19) | 0.005(2) | -0.0029(19) |
| C17 | 0.018(2) | 0.058(4) | 0.035(3) | -0.023(3) | -0.003(2) | 0.004(2) |
| C20 | 0.045(3) | 0.052(4) | 0.032(3) | 0.019(3) | 0.003(2) | 0.006(3) |
| C5 | 0.044(3) | 0.029(3) | 0.031(3) | 0.007(2) | 0.016(2) | -0.004(2) |
| C4 | 0.058(4) | 0.020(2) | 0.027(3) | 0.004(2) | 0.002(2) | -0.007(2) |
| C18 | 0.022(2) | 0.059(4) | 0.021(2) | -0.012(2) | 0.000(2) | 0.005(2) |
| C7 | 0.047(3) | 0.024(2) | 0.029(3) | -0.005(2) | 0.017(2) | -0.008(2) |
| O6 | 0.0204(16) | 0.0364(19) | 0.0199(16) | -0.0076(14) | -0.0037(13) | -0.0088(14) |
| O5 | 0.038(2) | 0.036(2) | 0.060(3) | 0.000(2) | 0.0069(18) | $0.0063(18)$ |
| C22 | 0.018(2) | 0.027(2) | 0.022(2) | -0.0005(19) | 0.0035(18) | 0.0023(18) |
| C26 | 0.015(2) | 0.018(2) | 0.022(2) | 0.0030(18) | -0.0021(17) | -0.0024(17) |
| C25 | 0.018(2) | 0.020(2) | 0.035(3) | 0.007(2) | -0.007(2) | -0.0038(18) |
| C23 | 0.017(2) | 0.034(3) | 0.030(3) | 0.007(2) | 0.0083(19) | 0.002(2) |
| C24 | 0.014(2) | 0.024(2) | 0.049(3) | 0.011(2) | 0.004(2) | 0.0020(18) |
| C27 | 0.040(3) | 0.067(4) | 0.037(3) | -0.022(3) | 0.000(3) | -0.020(3) |
| C2 | 0.037(3) | 0.062(4) | 0.046(3) | 0.008(3) | 0.000(3) | 0.020(3) |

[^3]Table A.16: Hydrogen atom coordinates and isotropic atomic displacement parameters $\left(\AA^{2}\right)$ for $\left(\mathrm{P}^{\circ} \mathrm{SO}_{3}\right) \mathrm{PdC}(\mathrm{O}) \mathrm{CH}_{3}(\mathrm{py}), 3$.

|  | $x / a$ | $y / b$ | $z / c$ | $U$ |
| :--- | :---: | :---: | ---: | :---: |
| H9 | 0.9756 | 0.1252 | 0.2349 | 0.024 |
| H12 | 0.6045 | 0.1868 | 0.2982 | 0.026 |
| H10 | 0.8523 | 0.0017 | 0.2549 | 0.025 |
| H6 | 0.9025 | 0.5619 | -0.0915 | 0.041 |
| H16 | 0.8801 | 0.6200 | 0.4524 | 0.043 |
| H3 | 0.8240 | 0.6680 | 0.1618 | 0.034 |
| H15 | 0.8013 | 0.5500 | 0.3300 | 0.030 |
| H11 | 0.6661 | 0.0334 | 0.2854 | 0.029 |
| H17 | 0.8990 | 0.5327 | 0.5751 | 0.045 |
| H20A | 0.8053 | 0.2179 | 0.5440 | 0.064 |
| H20B | 0.6830 | 0.1736 | 0.5153 | 0.064 |
| H20C | 0.6924 | 0.2670 | 0.5681 | 0.064 |
| H5 | 0.9536 | 0.7150 | -0.0515 | 0.040 |
| H4 | 0.9199 | 0.7666 | 0.0790 | 0.042 |
| H18 | 0.8252 | 0.3815 | 0.5771 | 0.041 |
| H7 | 0.8136 | 0.4660 | -0.0038 | 0.039 |
| H22 | 0.5516 | 0.4266 | 0.4057 | 0.026 |
| H25 | 0.2940 | 0.2918 | 0.1985 | 0.030 |
| H23 | 0.3551 | 0.4154 | 0.4215 | 0.032 |
| H24 | 0.2281 | 0.3479 | 0.3184 | 0.035 |
| H27A | 0.3974 | 0.1921 | 0.1244 | 0.073 |
| H27B | 0.4754 | 0.2222 | 0.0559 | 0.073 |
| H27C | 0.3730 | 0.2878 | 0.0763 | 0.073 |
| H2A | 0.5037 | 0.4668 | 0.0998 | 0.073 |
| H2B | 0.5724 | 0.5437 | 0.0553 | 0.073 |
| H2C | 0.4668 | 0.5737 | 0.1020 | 0.073 |
|  |  |  |  |  |

## Appendix B

## Copolymerization of Ethene with Carbon Monoxide: Kinetics and Thermodynamics



Figure B.1: Van 't Hoff plot for the equilibrium $4+\mathrm{C}_{2} \mathrm{H}_{4} \stackrel{K_{1}}{=} 7$.


Figure B.2: Van 't Hoff plot for the equilibrium $\mathbf{4}+\mathrm{CO} \stackrel{K_{2}}{\sim} \mathbf{8}$.


Figure B.3: Eyring plot for the migratory insertion reaction $\mathbf{2}+\mathrm{C}_{2} \mathrm{H}_{4} \xrightarrow{k_{\mathrm{E}}} \mathbf{9}$.


Figure B.4: Eyring plot for the migratory insertion reaction $\mathbf{2}+\mathrm{CO} \xrightarrow{k_{\mathrm{CO}}} \mathbf{1 0}$.


Figure B.5: Carbonyl region of infrared spectra of nonalternating polyketones with varying carbon monoxide content.






## Appendix C

## Copolymerization of Ethene with Functional Norbornenes

## C. 1 X-ray diffraction data for ligand $13 \cdot \mathbf{C H}_{2} \mathbf{C l}_{2}$

A total of 1850 frames were collected with a scan width of $0.3^{\circ}$ in $\omega$ and an exposure time of 10 s per frame. The total data collection time was about 8 h . The frames were integrated with the Bruker saint software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 15831 reflections to a maximum $\theta$ angle of $28.31^{\circ}(0.90 \AA$ resolution), of which 5915 were independent, completeness $=95.9 \%, R_{\text {int }}=0.0277, R_{\text {sig }}=0.0304$ and 5190 were greater than $2 \sigma(\mathrm{I})$. The final cell constants: $a=13.979(2) \AA, b=11.9196(17) \AA, c=15.071(2) \AA, \alpha=90^{\circ}, \beta=99.700(2)^{\circ}, \gamma=$ $90^{\circ}$, volume $=2475.2(6) \AA^{3}$, are based upon the refinement of the XYZ-centroids of 5313 reflections above $20 \sigma$ (I) with $2.189^{\circ}<\theta<28.271^{\circ}$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.911833.

The structure was solved and refined using the Bruker shelxtl (Version 6.1) software package, using the space group $\mathrm{P} 2(1) / \mathrm{c}$, with $Z=4$ for the formula unit, $\mathrm{C}_{23} \mathrm{H}_{25} \mathrm{Cl}_{2} \mathrm{O}_{7} \mathrm{PS}$. The final anisotropic full-matrix least-squares refinement on $F^{2}$ with 315 variables converged at $R_{1}=3.72 \%$, for the observed data and $w R_{2}=10.36 \%$ for all data. The goodness-of-fit was 1.070 . The largest peak on the final difference map was $0.559 \mathrm{e} \AA^{-3}$ and the largest hole was $-0.428 \mathrm{e} \AA^{-3}$. Based on the final model, the calculated density of the crystal is $1.469 \mathrm{gcm}^{-3}$ and $F(000)$ amounts to 1136 electrons.

Table C.1: Sample and crystal data for ligand $13 \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

| Empirical formula | $\mathrm{C}_{23} \mathrm{H}_{25} \mathrm{Cl}_{2} \mathrm{O}_{7} \mathrm{PS}$ |  |
| :--- | :--- | :--- |
| Formula weight | 547.36 |  |
| Temperature | $98(2) \mathrm{K}$ |  |
| Wavelength | $0.71073 \AA$ |  |
| Crystal size | $0.43 \times 0.39 \times 0.36 \mathrm{~mm}$ |  |
| Crystal habit | Clear brick |  |
| Crystal system | Monoclinic |  |
| Space group | $\mathrm{P} 2(1) / \mathrm{c}$ | $\beta=90^{\circ}$ |
| Unit cell dimensions | $a=13.979(2) \AA$ | $\gamma=90^{\circ}$ |
|  | $b=11.9196(17) \AA$ |  |
|  | $c=15.071(2) \AA$ |  |
| Volume | $2475.2(6) \AA^{3}$ |  |
| $Z$ | 4 |  |
| Density (calculated) | $1.469 \mathrm{gcm}^{-3}$ |  |
| Absorption coefficient | $0.453 \mathrm{~mm}^{-1}$ |  |
| $F(000)$ | 1136 |  |

Table C.2: Data collection and structure refinement of ligand $13 \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

| Diffractometer | CCD area detector |
| :--- | :--- |
| Radiation source | fine-focus sealed tube, Mo K $\alpha$ |
| Generator power | $1600 \mathrm{~W}(50 \mathrm{kV}), 32 \mathrm{~mA})$ |
| Detector distance | 5.8 cm |
| Data collection method | phi and omega scans |
| Theta range for data collection | $2.19^{\circ}$ to $28.31^{\circ}$ |
| Index ranges | $-18 \leq h \leq 18,-15 \leq k \leq 10,-20 \leq l \leq 19$ |

Table C.3: Atomic coordinates and equivalent isotropic atomic displacement parameters ( $\AA^{2}$ ) of ligand $\mathbf{1 3} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

|  | X | Y | Z | $U_{(\text {eq) }}{ }^{a}$ |
| :---: | :---: | :---: | :---: | :---: |
| S1 | 0.28783(2) | 0.41844 (3) | $0.20917(2)$ | 0.01480(9) |
| P1 | $0.19023(3)$ | 0.57880(3) | 0.34631(2) | $0.01214(9)$ |
| O6 | 0.03110 (8) | 0.45539(10) | 0.37571(7) | 0.0205(2) |
| O4 | 0.23379(8) | 0.72778 (10) | 0.49748 (7) | 0.0200(2) |
| O5 | 0.01396(8) | 0.66359(10) | $0.23357(7)$ | 0.0201(2) |
| O3 | $0.20821(8)$ | 0.45847 (10) | 0.14166 (7) | 0.0207(2) |
| O2 | 0.25387(8) | 0.36488(9) | $0.28523(7)$ | 0.0211(2) |
| O7 | 0.35477(8) | 0.52601(10) | 0.50028(7) | 0.0217(2) |
| O1 | $0.35974(8)$ | 0.35487(10) | $0.17213(8)$ | 0.0256(3) |
| C13 | 0.03845(10) | 0.73023(12) | $0.30718(10)$ | 0.0159(3) |
| C7 | 0.12449 (10) | 0.70251(12) | 0.36552(9) | 0.0143(3) |
| C2 | 0.43254(10) | 0.57549(13) | 0.22669(10) | 0.0169(3) |
| C19 | $0.10617(11)$ | 0.42663(13) | $0.44194(10)$ | 0.0179(3) |
| C12 | -0.01600(11) | 0.82257(13) | 0.32569(10) | 0.0183(3) |
| C6 | $0.30444(10)$ | 0.61396(12) | $0.31219(9)$ | 0.0136(3) |
| C3 | $0.47628(11)$ | 0.67707(13) | 0.25437(10) | 0.0187(3) |
| C10 | $0.10059(11)$ | 0.86103(13) | $0.46140(10)$ | 0.0192(3) |
| C14 | $0.19319(10)$ | 0.48462(12) | 0.43878(10) | 0.0156(3) |
| C1 | $0.34662(10)$ | 0.54364(12) | 0.25495(9) | 0.0139(3) |
| C15 | 0.27425(11) | 0.46491(13) | 0.50560(10) | 0.0182(3) |
| C5 | $0.34837(11)$ | 0.71695(13) | 0.33803(10) | 0.0180(3) |
| C8 | 0.15320 (10) | $0.76711(12)$ | 0.44357(10) | 0.0158(3) |
| C16 | 0.26847(12) | 0.38501(15) | $0.57213(11)$ | 0.0244(3) |
| C11 | $0.01637(11)$ | 0.88630(13) | 0.40198(11) | 0.0197(3) |
| C4 | $0.43377(11)$ | 0.74797(13) | 0.30921(10) | 0.0196(3) |
| C18 | 0.10044(12) | 0.34793(14) | 0.50841(11) | 0.0227(3) |
| C20 | -0.06148(12) | 0.40249(14) | 0.37525(12) | 0.0238(3) |
| C17 | $0.18282(13)$ | 0.32795(14) | 0.57202(12) | 0.0260(4) |
| C9 | 0.27297(13) | 0.79281(16) | 0.57494(12) | 0.0298(4) |
| Cl1 | $0.68111(4)$ | 0.52987(5) | $0.12308(4)$ | 0.04958(16) |
| C12 | $0.54263(4)$ | 0.68977 (6) | 0.02943(3) | 0.05127(17) |
| C21 | 0.66581(14) | 0.65504(18) | 0.05862(14) | 0.0359(4) |
| C22 | -0.08673(12) | 0.66091(15) | 0.19263 (11) | 0.0251(3) |
| C23 | $0.43148(12)$ | 0.52233(17) | 0.57699(11) | 0.0286(4) |

${ }^{a} U_{(\text {eq) })}$ is defined as one third of the trace of the orthogonalized $U_{i j}$ tensor.

Table C.4: Bond lengths ( $\AA$ ) of ligand $13 \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

| S1-O1 | $1.4441(12)$ | S1-O3 | $1.4559(11)$ | S1-O2 | $1.4596(11)$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| S1-C1 | $1.7852(15)$ | P1-C14 | $1.7846(15)$ | P1-C7 | $1.7867(15)$ |
| P1-C6 | $1.8070(14)$ | O6-C19 | $1.3646(18)$ | O6-C20 | $1.4387(18)$ |
| O4-C8 | $1.3567(18)$ | O4-C9 | $1.4312(19)$ | O5-C13 | $1.3605(18)$ |
| O5-C22 | $1.4387(18)$ | O7-C15 | $1.3543(19)$ | O7-C23 | $1.4389(18)$ |
| C13-C12 | $1.393(2)$ | C13-C7 | $1.404(2)$ | C7-C8 | $1.407(2)$ |
| C2-C3 | $1.388(2)$ | C2-C1 | $1.393(2)$ | C19-C18 | $1.384(2)$ |
| C19-C14 | $1.407(2)$ | C12-C11 | $1.389(2)$ | C6-C5 | $1.398(2)$ |
| C6-C1 | $1.402(2)$ | C3-C4 | $1.384(2)$ | C10-C11 | $1.387(2)$ |
| C10-C8 | $1.390(2)$ | C14-C15 | $1.403(2)$ | C15-C16 | $1.395(2)$ |
| C5-C4 | $1.387(2)$ | C16-C17 | $1.377(2)$ | C18-C17 | $1.389(2)$ |
| Cl1-C21 | $1.774(2)$ | Cl2-C21 | $1.754(2)$ |  |  |

Table C.5: Bond angles ( ${ }^{\circ}$ ) of ligand $13 \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

| O1-S1-O3 | $113.69(7)$ | O1-S1-O2 | $114.44(7)$ | O3-S1-O2 | $112.37(7)$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| O1-S1-C1 | $106.44(7)$ | O3-S1-C1 | $104.12(7)$ | O2-S1-C1 | $104.57(7)$ |
| C14-P1-C7 | $109.72(7)$ | C14-P1-C6 | $117.56(7)$ | C7-P1-C6 | $110.97(7)$ |
| C19-O6-C20 | $118.27(12)$ | C8-O4-C9 | $117.80(12)$ | C13-O5-C22 | $117.14(12)$ |
| C15-O7-C23 | $116.77(12)$ | O5-C13-C12 | $123.63(13)$ | O5-C13-C7 | $116.38(13)$ |
| C12-C13-C7 | $119.99(14)$ | C13-C7-C8 | $119.23(13)$ | C13-C7-P1 | $120.16(11)$ |
| C8-C7-P1 | $120.35(11)$ | C3-C2-C1 | $120.31(14)$ | O6-C19-C18 | $124.63(14)$ |
| O6-C19-C14 | $114.49(13)$ | C18-C19-C14 | $120.88(14)$ | C11-C12-C13 | $119.03(14)$ |
| C5-C6-C1 | $119.06(13)$ | C5-C6-P1 | $119.47(11)$ | C1-C6-P1 | $121.32(11)$ |
| C4-C3-C2 | $120.01(14)$ | C11-C10-C8 | $117.99(14)$ | C15-C14-C19 | $119.45(13)$ |
| C15-C14-P1 | $125.13(11)$ | C19-C14-P1 | $115.41(11)$ | C2-C1-C6 | $119.92(13)$ |
| C2-C1-S1 | $118.30(11)$ | C6-C1-S1 | $121.57(11)$ | O7-C15-C16 | $123.98(14)$ |
| O7-C15-C14 | $116.50(13)$ | C16-C15-C14 | $119.51(14)$ | C4-C5-C6 | $120.49(14)$ |
| O4-C8-C10 | $125.13(13)$ | O4-C8-C7 | $113.75(13)$ | C10-C8-C7 | $121.11(13)$ |
| C17-C16-C15 | $119.47(15)$ | C10-C11-C12 | $122.58(14)$ | C3-C4-C5 | $120.19(14)$ |
| C19-C18-C17 | $118.23(15)$ | C16-C17-C18 | $122.40(15)$ | C12-C21-Cl1 | $111.02(11)$ |

## C. 2 X-ray diffraction data for allylpalladium complex 14

A yellow, cuboidal shaped crystal of complex $14\left(\mathrm{C}_{23} \mathrm{H}_{22} \mathrm{O}_{5} \mathrm{PPdS}\right)$ with approximate dimensions of $0.11 \times$ $0.14 \times 0.20 \mathrm{~mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 108(2)K, cooled by Rigaku-MSC X-Stream 2000, on a Bruker Smart apex ccd area detector system equipped with a graphite monochromator and a Mo K $\alpha$ fine-focus sealed tube ( $\lambda=0.71073$ ) operated at 1600 W power $(50 \mathrm{kV}, 32 \mathrm{~mA})$. The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of $0.3^{\circ}$ in $\omega$ and an exposure time of 20 s per frame. The total data collection time was about 10 h . The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 14019 reflections to a maximum $\theta$ angle of $28.30^{\circ}(0.90 \AA$ resolution), of which 5208 were independent, completeness $=96.1 \%, R_{\text {int }}=0.0207, R_{\text {sig }}=0.0297$ and 4486 were greater than $2 \sigma(\mathrm{I})$. The final cell constants: $a=10.8667(11) \AA, b=17.0383(18) \AA, c=11.8080(13) \AA, \alpha=90^{\circ}$, $\beta=95.365(2)^{\circ}, \gamma=90^{\circ}$, volume $=2176.7(4) \AA^{3}$, are based upon the refinement of the XYZ-centroids of 5300 reflections above $20 \sigma$ (I) with $2.230^{\circ}<\theta<28.148^{\circ}$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (sadabs). The ratio of minimum to maximum apparent transmission was 0.393827 .

The structure was solved and refined using the Bruker shelxtl (Version 6.1) software package, using the space group P2(1)/n, with $Z=4$ for the formula unit, $\mathrm{C}_{23} \mathrm{H}_{22} \mathrm{O}_{5} \mathrm{PPdS}$. The final anisotropic full-matrix least-squares refinement on $F^{2}$ with 283 variables converged at $R_{1}=4.03^{\circ}$, for the observed data and $w R_{2}=11.34 \%$ for all data. The goodness-of-fit was 1.066 . The largest peak on the final difference map was $1.872 \mathrm{e} \AA^{-3}$ and the largest hole was $-1.480 \mathrm{e}^{-3}$. Based on the final model, the calculated density of the crystal is $1.672 \mathrm{gcm}^{-3}$ and $F(000)$ amounts to 1108 electrons.

Table C.6: Crystal data and structure refinements of complex 14.

| Empirical formula | $\mathrm{C}_{23} \mathrm{H}_{23} \mathrm{O}_{5} \mathrm{PPdS}$ |  |
| :--- | :--- | :--- |
| Formula weight | 547.84 |  |
| Temperature | $\mathrm{SI} 108(2) \mathrm{K}$ |  |
| Wavelength | $0.71073 \AA$ |  |
| Crystal size | $0.20 \times 0.14 \times 0.11 \mathrm{~mm}$ |  |
| Crystal habit | yellow cuboidal |  |
| Crystal system | Monoclinic |  |
| Space group | $\mathrm{P} 2(1) / \mathrm{n}$ | $\alpha=90^{\circ}$ |
| Unit cell dimensions | $a=10.8667(11) \AA$ | $\beta=95.365(2)^{\circ}$ |
|  | $b=17.0383(18) \AA$ |  |
|  | $c=11.8080(13) \AA$ |  |
| Volume | $2176.7(4) \AA^{3}$ |  |
| $Z$ | 4 |  |
| Density (calculated) | $1.672 \mathrm{gcm}^{-3}$ |  |
| Absorption coefficient | $1.055 \mathrm{~mm}^{-1}$ |  |
| $F(000)$ | 1108 |  |

Table C.7: Data collection and structure refinement for complex 14.

| Diffractometer | ccD area detector |
| :--- | :--- |
| Radiation source | fine-focus sealed tube, Mo K $\alpha$ |
| Generator power | $1600 \mathrm{~W}(50 \mathrm{kV}, 32 \mathrm{~mA})$ |
| Detector distance | 5.8 cm |
| Data collection method | phi and omega scans |
| Theta range for data collection | $2.10^{\circ}$ to $28.30^{\circ}$ |
| Index ranges | $-14 \leq h \leq 13,-22 \leq k \leq 21,-11 \leq l \leq 15$ |

Table C.8: Atomic coordinates and equivalent isotropic atomic displacement parameters $\left(\AA^{2}\right)$ for complex 14.

|  | X | Y | Z | $U_{(\mathrm{eq})}{ }^{a}$ |
| :---: | :---: | :---: | :---: | :---: |
| Pd1 | $0.49064(2)$ | $0.231227(14)$ | 0.65473(2) | $0.02094(10)$ |
| P1 | 0.49826(7) | $0.14067(4)$ | 0.79999(7) | $0.01721(16)$ |
| S1 | $0.45560(7)$ | 0.32795(4) | 0.88195(6) | 0.01966 (16) |
| $\mathrm{O} 2$ | 0.4966(2) | $0.32904(13)$ | $0.7657(2)$ | 0.0254(5) |
| O1 | $0.3238(2)$ | $0.05800(14)$ | $0.64534(19)$ | 0.0249(5) |
| C23 | 0.5022(5) | 0.1543(2) | 0.5192(3) | $0.0469(11)$ |
| O3 | $0.3323(2)$ | $0.29698(14)$ | 0.8836(2) | 0.0270(5) |
| C6 | 0.5532(3) | $0.26077(17)$ | 0.9648(3) | 0.0182(6) |
| C4 | 0.6780(3) | $0.23988(19)$ | 1.1428(3) | 0.0235(7) |
| C5 | 0.6099(3) | 0.28973 (18) | 1.0664(3) | 0.0201(6) |
| O4 | 0.4773(2) | 0.40363 (13) | 0.9345(2) | 0.0284(5) |
| C14 | 0.3521(3) | $0.09852(17)$ | 0.8344(3) | 0.0178(6) |
| O5 | $0.7505(2)$ | $0.14350(16)$ | $0.7482(2)$ | 0.0328(6) |
| C1 | 0.5667(3) | $0.18164(17)$ | 0.9354(3) | 0.0180(6) |
| C16 | 0.2027(3) | 0.0653(2) | 0.9662(3) | 0.0261(7) |
| C19 | 0.2774(3) | $0.05962(17)$ | 0.7479(3) | 0.0196(6) |
| C15 | 0.3121(3) | $0.10151(18)$ | 0.9427(3) | 0.0216(6) |
| C18 | 0.1674(3) | 0.02471(18) | 0.7702(3) | 0.0226(6) |
| C7 | 0.5935(3) | 0.05453(18) | 0.7788(3) | 0.0217(6) |
| C9 | 0.6226(4) | -0.0851(2) | 0.7579(3) | 0.0331(8) |
| C3 | $0.6901(3)$ | $0.16165(19)$ | 1.1153(3) | 0.0244(7) |
| $\mathrm{C} 20$ | 0.2664(3) | 0.0054(2) | 0.5610(3) | 0.0309(8) |
| C10 | $0.7411(4)$ | -0.0721(2) | 0.7299(3) | 0.0374(9) |
| $\mathrm{C} 12$ | 0.7150(3) | 0.0673(2) | 0.7499(3) | 0.0266(7) |
| $\mathrm{C} 17$ | 0.1310(3) | 0.02698(19) | 0.8795(3) | 0.0254(7) |
| C2 | $0.6359(3)$ | 0.13273 (18) | 1.0123(3) | 0.0227(6) |
| C11 | 0.7891(3) | 0.0037(3) | 0.7257(3) | 0.0344(8) |
| C13 | 0.8611(4) | 0.1620(3) | 0.6980(3) | 0.0418(10) |
| C8 | 0.5496(3) | -0.021 45(19) | 0.7831(3) | 0.0245(7) |
| C21 | 0.4755(4) | 0.2927(3) | 0.4879 (3) | 0.0429(10) |
| C22 | 0.5161(14) | 0.2246(4) | 0.4809(5) | 0.164(6) |

${ }^{a} U_{(\mathrm{eq})}$ is defined as one third of the trace of the orthogonalized $U_{i j}$ tensor.

Table C.9: Bond lengths ( $\AA$ ) for complex 14.

| Pd1-O2 | $2.117(2)$ | Pd1-P1 | $2.3028(8)$ | P1-C14 | $1.823(3)$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| P1-C7 | $1.827(3)$ | P1-C1 | $1.837(3)$ | S1-O4 | $1.441(2)$ |
| S1-O3 | $1.442(2)$ | S1-O2 | $1.483(2)$ | S1-C6 | $1.788(3)$ |
| O1-C19 | $1.355(4)$ | O1-C20 | $1.438(4)$ | C23-C22 | $1.294(8)$ |
| C23-H23A | 0.9800 | C23-H23B | 0.9800 | C23-H23C | 0.9800 |
| C6-C5 | $1.388(4)$ | C6-C1 | $1.403(4)$ | C4-C3 | $1.381(5)$ |
| C4-C5 | $1.399(4)$ | C4-H4 | 0.9500 | C5-H5 | 0.9500 |
| C14-C15 | $1.390(4)$ | C14-C19 | $1.409(4)$ | O5-C12 | $1.356(4)$ |
| O5-C13 | $1.424(4)$ | C1-C2 | $1.399(4)$ | C16-C15 | $1.390(4)$ |
| C16-C17 | $1.390(5)$ | C16-H16 | 0.9500 | C19-C18 | $1.382(4)$ |
| C15-H15 | 0.9500 | C18-C17 | $1.386(5)$ | C18-H18 | 0.9500 |
| C7-C8 | $1.382(5)$ | C7-C12 | $1.411(5)$ | C9-C10 | $1.378(6)$ |
| C9-C8 | $1.392(5)$ | C9-H9 | 0.9500 | C3-C2 | $1.391(4)$ |
| C3-H3 | 0.9500 | C20-H20A | 0.9800 | C20-H20B | 0.9800 |
| C20-H20C | 0.9800 | C10-C11 | $1.395(6)$ | C10-H10 | 0.9500 |
| C12-C11 | $1.394(5)$ | C17-H17 | 0.9500 | C2-H2 | 0.9500 |
| C11-H11 | 0.9500 | C13-H13A | 0.9800 | C13-H13B | 0.9800 |
| C13-H13C | 0.9800 | C8-H8 | 0.9500 | C21-C22 | $1.248(9)$ |
| C22-H22 | 0.9500 | Pd-C21 | $2.223(3)$ | Pd-C22 | $2.109(3)$ |
| Pd-C23 | $2.087(3)$ |  |  |  |  |

Table C.10: Bond angles ( ${ }^{\circ}$ ) for complex 14.

| O2-Pd1-P1 | $94.00(7)$ | C14-P1-C7 | $103.34(14)$ | C14-P1-C1 | $104.22(14)$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| C7-P1-C1 | $103.66(14)$ | C14-P1-Pd1 | $117.29(10)$ | C7-P1-Pd1 | $114.69(11)$ |
| C1-P1-Pd1 | $112.17(10)$ | O4-S1-O3 | $115.87(15)$ | O4-S1-O2 | $109.66(14)$ |
| O3-S1-O2 | $112.16(14)$ | O4-S1-C6 | $105.82(14)$ | O3-S1-C6 | $105.23(14)$ |
| O2-S1-C6 | $107.48(14)$ | S1-O2-Pd1 | $124.66(13)$ | C19-O1-C20 | $117.3(3)$ |
| C22-C23-H23A | 109.5 | C22-C23-H23B | 109.5 | H23A-C23-H23B | 109.5 |
| C22-C23-H23C | 109.5 | H23A-C23-H23C | 109.5 | H23B-C23-H23C | 109.5 |
| C5-C6-C1 | $120.5(3)$ | C5-C6-S1 | $116.0(2)$ | C1-C6-S1 | $123.4(2)$ |
| C3-C4-C5 | $119.4(3)$ | C3-C4-H4 | 120.3 | C5-C4-H4 | 120.3 |
| C6-C5-C4 | $120.5(3)$ | C6-C5-H5 | 119.8 | C4-C5-H5 | 119.8 |
| C15-C14-C19 | $118.4(3)$ | C15-C14-P1 | $123.0(2)$ | C19-C14-P1 | $118.6(2)$ |
| C12-O5-C13 | $118.0(3)$ | C2-C1-C6 | $118.3(3)$ | C2-C1-P1 | $119.2(2)$ |
| C6-C1-P1 | $122.5(2)$ | C15-C16-C17 | $119.5(3)$ | C15-C16-H16 | 120.2 |
| C17-C16-H16 | 120.2 | O1-C19-C18 | $124.2(3)$ | O1-C19-C14 | $114.8(3)$ |
| C18-C19-C14 | $121.0(3)$ | C16-C15-C14 | $120.9(3)$ | C16-C15-H15 | 119.5 |
| C14-C15-H15 | 119.5 | C19-C18-C17 | $119.5(3)$ | C19-C18-H18 | 120.2 |
| C17-C18-H18 | 120.2 | C8-C7-C12 | $119.2(3)$ | C8-C7-P1 | $123.0(2)$ |
| C12-C7-P1 | $117.7(2)$ | C10-C9-C8 | $119.4(4)$ | C10-C9-H9 | 120.3 |
| C8-C9-H9 | 120.3 | C4-C3-C2 | $120.4(3)$ | C4-C3-H3 | 119.8 |
| C2-C3-H3 | 119.8 | O1-C20-H20A | 109.5 | O1-C20-H20B | 109.5 |
| H20A-C20-H20B | 109.5 | O1-C20-H20C | 109.5 | H20A-C20-H20C | 109.5 |
| H20B-C20-H20C | 109.5 | C9-C10-C11 | $121.2(3)$ | C9-C10-H10 | 119.4 |
| C11-C10-H10 | 119.4 | O5-C12-C11 | $124.8(3)$ | O5-C12-C7 | $115.1(3)$ |
| C11-C12-C7 | $120.1(3)$ | C18-C17-C16 | $120.6(3)$ | C18-C17-H17 | 119.7 |
| C16-C17-H17 | 119.7 | C3-C2-C1 | $120.9(3)$ | C3-C2-H2 | 119.5 |
| C1-C2-H2 | 119.5 | C12-C11-C10 | $119.1(3)$ | C12-C11-H11 | 120.4 |
| C10-C11-H11 | 120.4 | O5-C13-H13A | 109.5 | O5-C13-H13B | 109.5 |
| H13A-C13-H13B | 109.5 | O5-C13-H13C | 109.5 | H13A-C13-H13C | 109.5 |
| H13B-C13-H13C | 109.5 | C7-C8-C9 | $121.1(3)$ | C7-C8-H8 | 119.5 |
| C9-C8-H8 | 119.5 | C21-C22-C23 | $141.7(10)$ | C21-C22-H22 | 109.2 |
| C23-C22-H22 | 109.2 |  |  |  |  |
|  |  |  |  |  |  |

## C. 3 X-ray diffraction data for crotylpalladium complex $15.2 \mathrm{CHCl}_{3}$

A yellow, cubical shaped crystal of complex $15 \cdot 2 \mathrm{CHCl}_{3}\left(\mathrm{C}_{26} \mathrm{H}_{25} \mathrm{Cl}_{6} \mathrm{O}_{5} \mathrm{PPdS}\right)$ with approximate dimensions of $0.24 \times 0.36 \times 0.38 \mathrm{~mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at $298(2) \mathrm{K}$ on a Bruker smart apex cci area detector system equipped with a graphite monochromator and a Mo K $\alpha$ fine-focus sealed tube ( $\lambda=0.71073 \AA$ ) operated at 1600 W power ( 50 kV , $32 \mathrm{~mA})$. The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of $0.3^{\circ}$ in $\omega$ and an exposure time of 5 s per frame. The total data collection time was about 6 h . The frames were integrated with the Bruker saint software package using a narrow-frame integration algorithm. The integration of the data using an Orthorhombic unit cell yielded a total of 20727 reflections to a maximum $\theta$ angle of $28.35^{\circ}(0.90 \AA$ resolution), of which 7864 were independent, completeness $=97.8 \%, R_{\text {int }}=0.0528, R_{\text {sig }}=0.0716$ and 5960 were greater than $2 \sigma(\mathrm{I})$. The final cell constants: $a=14.9431(19) \AA, b=10.2521(13) \AA, c=21.630(3) \AA, \alpha=90^{\circ}$, $\beta=90^{\circ}, \gamma=90^{\circ}$, volume $=3313.7(7) \AA^{3}$, are based upon the refinement of the XYZ-centroids of 3723 reflections above $20 \sigma(\mathrm{I})$ with $2.409^{\circ}<\theta<21.132^{\circ}$. Data were corrected for absorption effects using the multiscan technique (sADABS). The ratio of minimum to maximum apparent transmission was 0.045216 .

The structure was solved and refined using the Bruker shelxtl (Version 6.1) software package, using the space group Pna2(1), with $Z=4$ for the formula unit, $\mathrm{C}_{26} \mathrm{H}_{25} \mathrm{Cl}_{6} \mathrm{O}_{5} \mathrm{PPdS}$. The final anisotropic fullmatrix least-squares refinement on $F^{2}$ with 366 variables converged at $R_{1}=5.35 \%$, for the observed data and $w R 2=12.86 \%$ for all data. The goodness-of-fit was 1.024 . The largest peak on the final difference map was $0.928 \mathrm{e} \AA^{-3}$ and the largest hole was $-0.437 \mathrm{e} \AA^{-3}$. Based on the final model, the calculated density of the crystal is $1.603 \mathrm{gcm}^{-3}$ and $F(000)$ amounts to 1600 electrons.

Table C.11: Crystal data and structure refinements of complex $15 \cdot 2 \mathrm{CHCl}_{3}$.

| Empirical formula | $\mathrm{C}_{26} \mathrm{H}_{25} \mathrm{Cl}_{6} \mathrm{O}_{5} \mathrm{PPdS}$ |  |
| :--- | :--- | :--- |
| Formula weight | 799.59 |  |
| Temperature | $298(2) \mathrm{K}$ |  |
| Wavelength | $0.71073 \AA$ |  |
| Crystal size | $0.38 \times 0.36 \times 0.24 \mathrm{~mm}$ |  |
| Crystal habit | yellow cubical |  |
| Crystal system | Orthorhombic |  |
| Space group | Pna2(1) |  |
| Unit cell dimensions | $a=14.9431(19) \AA$ | $\alpha=90^{\circ}$ |
|  | $b=10.2521(13) \AA$ | $\beta=90^{\circ}$ |
|  | $c=21.630(3) \AA$ | $\gamma=90^{\circ}$ |
| Volume | $3313.7(7) \AA^{3}$ |  |
| $Z$ | 4 |  |
| Density (calculated) | $1.603 \mathrm{gcm}^{-3}$ |  |
| Absorption coefficient | $1.189 \mathrm{~mm}^{-1}$ |  |
| $F(000)$ | 1600 |  |

Table C.12: Data collection and structure refinement for complex $15 \cdot 2 \mathrm{CHCl}_{3}$.

| Diffractometer | CCD area detector |
| :--- | :--- |
| Radiation source | fine-focus sealed tube, Mo K $\alpha$ |
| Generator power | $1600 \mathrm{~W}(50 \mathrm{kV}, 32 \mathrm{~mA})$ |
| Detector distance | 5.8 cm |
| Data collection method | phi and omega scans |
| Theta range for data collection | $1.88^{\circ}$ to $28.35^{\circ}$ |
| Index ranges | $-19 \leq h \leq 13,-12 \leq k \leq 13,-28 \leq l \leq 28$ |

Table C.13: Atomic coordinates and equivalent isotropic atomic displacement parameters $\left(\AA^{2}\right)$ for complex $15 \cdot 2 \mathrm{CHCl}_{3}$.

|  | X | Y | Z | $U_{\text {(eq) }}{ }^{a}$ |
| :---: | :---: | :---: | :---: | :---: |
| C1 | 0.7833(4) | -0.0436(4) | 0.9181(2) | 0.0397(11) |
| C2 | 0.7227(4) | 0.0338(6) | 0.8872(3) | 0.0580(17) |
| C3 | 0.6307(4) | 0.0107(8) | 0.8915(4) | 0.081(2) |
| C4 | 0.5993(4) | -0.0919(7) | 0.9250(4) | 0.0724(19) |
| C5 | 0.6583(4) | -0.1694(6) | 0.9568(3) | 0.0596(16) |
| C6 | 0.7502(3) | -0.1471(5) | 0.9535(2) | 0.0399(11) |
| C7 | 0.9063(3) | 0.1567(5) | 0.8829(3) | 0.0423(11) |
| C8 | 0.9269(5) | 0.1841(6) | 0.8216(3) | 0.0583(15) |
| C9 | 0.9281(6) | 0.3111(8) | 0.8004(4) | 0.082(2) |
| C10 | 0.9096(5) | 0.4097(7) | 0.8392(5) | 0.079(2) |
| C11 | 0.8881(4) | 0.3877 (5) | 0.9000(4) | 0.0643(18) |
| C12 | 0.8860(4) | 0.2614(5) | 0.9214(3) | 0.0519(14) |
| C13 | 0.8595(8) | 0.3304(9) | 1.0254(5) | 0.132(4) |
| C14 | 0.9408(4) | -0.1072(5) | 0.8477(3) | 0.0472(13) |
| C15 | 0.8810(5) | -0.1786(6) | 0.8104(3) | 0.0660(18) |
| C16 | 0.9120(8) | -0.2516(8) | 0.7622(3) | 0.088(3) |
| C17 | 0.9966(10) | -0.2624(8) | 0.7515(4) | 0.100(3) |
| C18 | 1.0598(6) | -0.1926(9) | 0.7849(4) | 0.091(3) |
| C19 | 1.0318(5) | -0.1131(7) | 0.8330(3) | 0.0661(19) |
| C20 | 1.1793(6) | -0.0287(13) | 0.8546(6) | 0.141(5) |
| C21 | 1.0741(5) | 0.0964(8) | 1.0015(4) | 0.084(2) |
| C22 | 1.0683(8) | 0.0589(10) | 1.0622(6) | 0.146(6) |
| C23 | 1.0506(8) | -0.0280(14) | 1.0955(5) | 0.166(6) |
| C24 | 1.0282(7) | -0.0763(11) | 1.1541(5) | 0.098(3) |
| C25 | 0.6756(7) | 0.0966(10) | 0.6667(4) | 0.102(3) |
| C26 | 0.7751(7) | 0.5162(9) | 0.6079(4) | 0.093(3) |
| Cl1 | 0.56604(19) | 0.0588(3) | $0.64704(14)$ | 0.1083(8) |
| Cl 2 | 0.7351(3) | -0.0428(4) | 0.6834(2) | 0.1632(15) |
| Cl3 | 0.6726(3) | 0.2065(4) | 0.73075(16) | 0.1667(15) |
| Cl 4 | 0.7014(3) | 0.5792(4) | $0.66152(16)$ | 0.1512(12) |
| Cl5 | 0.8414(3) | 0.6327(4) | 0.5770(2) | 0.1682(15) |
| Cl6 | 0.8385(3) | 0.3945(4) | 0.6386(3) | 0.200(2) |
| O1 | 0.8823(3) | -0.3087(3) | 0.95091(19) | 0.0563(10) |
| O2 | 0.7651(3) | -0.3493(4) | $1.02632(19)$ | 0.0636(12) |
| O3 | 0.8679(2) | -0.1718(3) | 1.04108(17) | 0.0476(9) |
| O5 | 1.0846(3) | -0.0403(6) | 0.8694(3) | 0.0887(17) |
| O6 | 0.8645(4) | 0.2286(4) | 0.9810(2) | 0.0749(14) |
| P5 | 0.90352(9) | -0.00910(11) | $0.91268(6)$ | 0.0348(3) |
| Pd1 | 0.96822(2) | -0.03756(3) | 1.00847(2) | $0.04315(11)$ |
| S1 | 0.82193(9) | -0.25543(11) | $0.99493(6)$ | 0.0421(3) |

${ }^{a} U_{(\text {eq })}$ is defined as one third of the trace of the orthogonalized $U_{i j}$ tensor.

Table C.14: Bond lengths ( ${ }^{\circ}$ ) for complex $15 \cdot 2 \mathrm{CHCl}_{3}$.

| C1-C2 | $1.377(8)$ | C1-C6 | $1.398(7)$ | C1-P5 | $1.835(5)$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| C2-C3 | $1.397(10)$ | C2-H2 | 0.9300 | C3-C4 | $1.362(10)$ |
| C3-H3 | 0.9300 | C4-C5 | $1.372(9)$ | C4-H4 | 0.9300 |
| C5-C6 | $1.394(7)$ | C5-H5 | 0.9300 | C6-S1 | $1.786(5)$ |
| C7-C8 | $1.390(8)$ | C7-C12 | $1.393(8)$ | C7-P5 | $1.818(5)$ |
| C8-C9 | $1.380(9)$ | C8-H8 | 0.9300 | C9-C10 | $1.343(12)$ |
| C9-H9 | 0.9300 | C10-C11 | $1.374(11)$ | C10-H10 | 0.9300 |
| C11-C12 | $1.376(8)$ | C11-H11 | 0.9300 | C12-O6 | $1.369(8)$ |
| C13-O6 | $1.421(9)$ | C13-H13A | 0.9600 | C13-H13B | 0.9600 |
| C13-H13C | 0.9600 | C14-C19 | $1.398(9)$ | C14-C15 | $1.408(9)$ |
| C14-P5 | $1.817(6)$ | C15-C16 | $1.365(10)$ | C15-H15 | 0.9300 |
| C16-C17 | $1.290(14)$ | C16-H16 | 0.9300 | C17-C18 | $1.387(15)$ |
| C17-H17 | 0.9300 | C18-C19 | $1.386(11)$ | C18-H18 | 0.9300 |
| C19-O5 | $1.342(9)$ | C20-O5 | $1.455(10)$ | C20-H20A | 0.9600 |
| C20-H20B | 0.9600 | C20-H20C | 0.9600 | C21-C22 | $1.371(14)$ |
| C21-Pd1 | $2.100(6)$ | C21-H21A | 0.9300 | C21-H21B | 0.9300 |
| C22-C23 | $1.175(13)$ | C22-Pd1 | $2.136(7)$ | C23-C24 | $1.402(15)$ |
| C23-Pd1 | $2.251(8)$ | C24-H24A | 0.9600 | C24-H24B | 0.9600 |
| C24-H24C | 0.9600 | C25-Cl2 | $1.722(11)$ | C25-C11 | $1.736(10)$ |
| C25-Cl3 | $1.787(10)$ | C25-H25 | 0.9800 | C26-C15 | $1.690(10)$ |
| C26-Cl6 | $1.701(10)$ | C26-Cl4 | $1.724(11)$ | C26-H26 | 0.9800 |
| O1-S1 | $1.421(4)$ | O2-S1 | $1.452(4)$ | O3-S1 | $1.484(4)$ |
| O3-Pd1 | $2.154(4)$ | P5-Pd1 | $2.3048(14)$ |  |  |

Table C.15: Bond angles $\left({ }^{\circ}\right)$ for complex $15 \cdot 2 \mathrm{CHCl}_{3}$.

| C2-C1-C6 | 118.0(5) | C2-C1-P5 | 120.1(4) | C6-C1-P5 | 121.8(4) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| C1-C2-C3 | 121.1(6) | C1-C2-H2 | 119.4 | C3-C2-H2 | 119.4 |
| C4-C3-C2 | 120.4(6) | C4-C3-H3 | 119.8 | C2-C3-H3 | 119.8 |
| C3-C4-C5 | 119.5(6) | C3-C4-H4 | 120.2 | C5-C4-H4 | 120.2 |
| C4-C5-C6 | 120.8(6) | C4-C5-H5 | 119.6 | C6-C5-H5 | 119.6 |
| C5-C6-C1 | 120.1(5) | C5-C6-S1 | 117.6(4) | C1-C6-S1 | 122.3(4) |
| C8-C7-C12 | 117.6(5) | C8-C7-P5 | 122.2(4) | C12-C7-P5 | 120.2(4) |
| C9-C8-C7 | 120.7(7) | C9-C8-H8 | 119.7 | C7-C8-H8 | 119.7 |
| C10-C9-C8 | 120.0(7) | C10-C9-H9 | 120.0 | C8-C9-H9 | 120.0 |
| C9-C10-C11 | 121.5(6) | C9-C10-H10 | 119.2 | C11-C10-H10 | 119.2 |
| C10-C11-C12 | 118.9(6) | C10-C11-H11 | 120.6 | C12-C11-H11 | 120.6 |
| O6-C12-C11 | 123.6(6) | O6-C12-C7 | 115.1(4) | C11-C12-C7 | 121.3(6) |
| O6-C13-H13A | 109.5 | O6-C13-H13B | 109.5 | H13A-C13-H13B | 109.5 |
| O6-C13-H13C | 109.5 | H13A-C13-H13C | 109.5 | H13B-C13-H13C | 109.5 |
| C19-C14-C15 | 117.7(6) | C19-C14-P5 | 119.9(5) | C15-C14-P5 | 122.4(5) |
| C16-C15-C14 | 120.5(8) | C16-C15-H15 | 119.8 | C14-C15-H15 | 119.8 |
| C17-C16-C15 | 121.1(9) | C17-C16-H16 | 119.5 | C15-C16-H16 | 119.5 |
| C16-C17-C18 | 122.0(8) | C16-C17-H17 | 119.0 | C18-C17-H17 | 119.0 |
| C19-C18-C17 | 119.2(8) | C19-C18-H18 | 120.4 | C17-C18-H18 | 120.4 |
| O5-C19-C18 | 126.1(7) | O5-C19-C14 | 114.5(5) | C18-C19-C14 | 119.4(8) |
| O5-C20-H20A | 109.5 | O5-C20-H20B | 109.5 | H20A-C20-H20B | 109.5 |
| O5-C20-H20C | 109.5 | H20A-C20-H20C | 109.5 | H20B-C20-H20C | 109.5 |
| C22-C21-Pd1 | 72.6(4) | C22-C21-H21A | 120.0 | Pd1-C21-H21A | 57.1 |
| C22-C21-H21B | 120.0 | Pd1-C21-H21B | 147.3 | H21A-C21-H21B | 120.0 |
| C23-C22-C21 | 144.4(11) | C23-C22-Pd1 | 79.9(6) | C21-C22-Pd1 | 69.7(4) |
| C22-C23-C24 | 151.1(15) | C22-C23-Pd1 | 69.1(6) | C24-C23-Pd1 | 127.6(7) |
| C23-C24-H24A | 109.5 | C23-C24-H24B | 109.5 | H24A-C24-H24B | 109.5 |
| C23-C24-H24C | 109.5 | H24A-C24-H24C | 109.5 | H24B-C24-H24C | 109.5 |
| $\mathrm{Cl} 2-\mathrm{C} 25-\mathrm{Cl} 1$ | 110.7(5) | $\mathrm{Cl} 2-\mathrm{C} 25-\mathrm{Cl} 3$ | 111.9(5) | $\mathrm{Cl} 1-\mathrm{C} 25-\mathrm{Cl} 3$ | 107.9(6) |
| $\mathrm{Cl} 2-\mathrm{C} 25-\mathrm{H} 25$ | 108.8 | Cl1-C25-H25 | 108.8 | Cl3-C25-H25 | 108.8 |
| Cl5-C26-Cl6 | 110.3(6) | Cl5-C26-Cl4 | 112.0(5) | Cl6-C26-Cl4 | 111.6(6) |
| Cl5-C26-H26 | 107.6 | C16-C26-H26 | 107.6 | C14-C26-H26 | 107.6 |
| S1-O3-Pd1 | 118.1(2) | C19-O5-C20 | 119.2(7) | C12-O6-C13 | 117.9(6) |
| C14-P5-C7 | 103.6(3) | C14-P5-C1 | 104.0(3) | C7-P5-C1 | 103.0(2) |
| C14-P5-Pd1 | 119.82(19) | C7-P5-Pd1 | 115.30(18) | C1-P5-Pd1 | 109.21(17) |
| C21-Pd1-C22 | 37.7(4) | C21-Pd1-O3 | 164.9(3) | C22-Pd1-O3 | 127.2(4) |
| C21-Pd1-C23 | 67.6(4) | C22-Pd1-C23 | 30.9(3) | O3-Pd1-C23 | 97.8(3) |
| C21-Pd1-P5 | 99.7(2) | C22-Pd1-P5 | 136.4(3) | O3-Pd1-P5 | 94.78(10) |
| C23-Pd1-P5 | 167.3(3) | O1-S1-O2 | 115.5(2) | O1-S1-O3 | 112.3(2) |
| O2-S1-O3 | 109.8(2) | O1-S1-C6 | 106.5(2) | O2-S1-C6 | 107.2(2) |
| O3-S1-C6 | 104.8(2) |  |  |  |  |





## APPENDIX D

## Copolymerization of Ethene with Functional Styrenes



Figure D.1: Eyring plot for styrene insertion into the palladium-carbon bond of $\mathrm{P} \sim \mathrm{SO}_{3} \mathrm{PdCH}_{3}($ py $), 2$.






${ }_{8 \vdash 6} 0 \varepsilon 6 \cdot 1=$

$802 . \varepsilon=$
$82 Z^{\prime} \varepsilon=$
$9+2 \cdot \varepsilon=$
$\varepsilon 9 Z^{2} \varepsilon$

$00 \varepsilon \cdot \mathrm{~S}$
$0 \varepsilon \varepsilon$
S
${ }_{8}^{68 \%} \cdot \mathrm{~S}=$


Figure D.6: ${ }^{1} \mathrm{H}$ NMR spectrum of $\left(\mathrm{P}^{\sim}-\mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}(\mathrm{py}), \mathbf{2}$ with three equivalents of triphenylboron and one equivalent of styrene in dichloromethane- $d_{2}$ after 2.5 h at ambient temperature.
802.01

> Figure D.7: ${ }^{31} \mathrm{P}$ NMR spectrum of $\left(\mathrm{P}^{\sim} \mathrm{SO}_{3}\right) \mathrm{PdCH}_{3}(\mathrm{py}), 2$ with three equivalents of triphenylboron and one equivalent of styrene in dichloromethane- $d_{2}$ after 2.5 h at ambient temperature.







Vita

David K. Newsham was born in 1980 to Jane Nowaczyk and Kevin Newsham in San Diego, California. David moved with his mother to Brockport, New York in 1984 and lived with his grandparents, Robert and Sally Nowaczyk until 1991, when he moved with his mother and father, Glenn Slingerland, to Guilderland, New York. David attended Guilderland High School, where he met his future wife, Eden Carnes, and was introduced to Chemistry by Ms. Christine Cameron. After enrolling in The State University of New York College at Potsdam, David investigated ab initio computational techniques with respect to halogenated aldehydes under the direction of Dr. Jaime Martell and earned a B.A. in Chemistry in 2003. David then enrolled in The Pennsylvania State University and investigated palladium-based catalysts for copolymerization of polar and nonpolar monomers under the direction of Dr. Ayusman Sen and earned a Ph.D. in Chemistry in 2009. Afterwards, David accepted a position as a postdoctoral associate under Dr. Rory Waterman at The University of Vermont. David received no honors or awards in the field of Chemistry, but his family still loved him.


[^0]:    ${ }^{a}$ Imine insertion was not observed, even after heating to $50^{\circ} \mathrm{C}$.
    ${ }^{b}$ Imine insertion was not observed due to decomposition.

[^1]:    ${ }^{a}$ The anisotropic atomic displacement factor exponent takes the form: $-2 p^{2}\left[h^{2} a^{2} U_{11}+\ldots+2 h k a * b * U_{12}\right]$.

[^2]:    ${ }^{a} U_{(\text {eq) }}$ is defined as one third of the trace of the orthogonalized $U_{i j}$ tensor.

[^3]:    ${ }^{a}$ The anisotropic atomic displacement factor exponent takes the form: $-2 p^{2}\left[h^{2} a *^{2} U_{11}+\ldots+2 h k a * b * U_{12}\right]$.

