The Pennsylvania State University

The Graduate School

Eberly College of Science

PALLADIUM CATALYZED COPOLYMERIZATIONS OF POLAR AND NON-POLAR MONOMERS

A Dissertation in

Chemistry

by

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Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

December 2009

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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-*co*carbon monoxide) with carbon monoxide content ranging from 0–50 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

Atomic symbols and SI units are omitted for brevity.

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 (cal mol ^{-1} K ^{-1})
FT-IR	Fourier transform infrared spectroscopy
GPC	gel-permeation chromatography
Hex	hexyl
HMQC	heteronuclear multiple quantum coherence
IR	infrared spectroscopy
$M_{ m n}$	number average molecular weight
M^tBE	methyl tert-butyl ether
$M_{ m w}$	weight average molecular weight
NMR	nuclear magnetic resonance spectroscopy
PDI	polydispersity index (M_w/M_n)
PE	polyethene
phen	1,10-phenanthroline (ligand)
РК	polyketone
ppm	parts per million
psig	pounds per square inch gauge (above ambient pressure)
P^SO ₃ H	$\label{eq:linear} 2\mbox{-}[bis(2\mbox{-}methoxyphenyl) phosphino] benzene sulfonic acid$
Py (py)	pyridine (ligand)
SADABS	Siemens area detector absorption correction program
SEC	size-exclusion chromatography
THF	tetrahydrofuran
T _m	melt-transition temperature
TMEDA (tmeda)	N, N, N', N'-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 $(P^SO_3)PdCH_3(py)$ 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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Acknowledgements

The completion of this dissertation would not have been possible without the assistance of many people whose contributions I would like to acknowledge. First, I would like to thank my fellow researchers, especially my preceptor, Dr. Ayusman Sen, for giving me the opportunity to sink or swim, and for sharing his knowledge and experience, which have been an invaluable resource; my collaborators, Dr. Sachin Borkar, Paul Chiarulli, Dr. Jeffrey Funk, Dr. Shengsheng Liu, and Dr. Rong Luo, without whom this work would be much impoverished; the other Sen group catalysis researchers, Ying Chen, Dr. Minren Lin, Dr. Megan Nagel, Weiran Yang, and Hua Zhang, for their helpful advice; and the rest of the Sen group for their affable character. Also, I would like to thank Dr. John Badding, Dr. Alan Benesi, Dr. T. C. Mike Chung, and Dr. Xumu Zhang for their time and guidance as members of my committee; Dr. Bernie O'Hare, Dr. C. J. Thode, and Dr. Hemant Yennawar for maintaining the department instruments and training me in their use; and Betty Jo Houser for protecting me from all the paperwork. Furthermore, I would like to thank my parents Glenn and Jane Slingerland as well as the rest of my family for supporting me in my foolish endeavor and my good friends, Dr. Matthew Dirmyer, Dr. Lisa Quimby, and Dr. Benjamin Unger for helping me to maintain my sense of perspective and for sharing in my madness. Finally, I owe an immeasurable debt to my long-suffering wife, Eden Carnes for her patience, understanding, and support, which have made all the difference.

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."

-Dr. Albert Hofmann (1906-2008)

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*-PK) is problematic due to its insolubility in common solvents and its very high melting point (~ 265 °C), both of which result from high crystallinity brought about by dipolar interactions between carbonyl groups present at 50 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 mol% to 10 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 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*-PK) with as little as 35 mol% carbon monoxide has been reported and it employs the anionic phosphine ligand bis(2-methoxyphenyl)phosphinobenzenesulfonic acid (P^SO_3H), **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 mol% to 50 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 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*-PK, thereby allowing the synthesis of the block copolymer: polyethene-*block*-poly(ethene-*alt*-carbon monoxide).



Phosphine-sulfonate ligand (P^SO_3H), 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 $P^SO_3^-$ -based system caused a dramatic reduction in activity despite the system's ability to produce PE, *nonalt*-PK and *alt*-PK. However, it was possible to produce *nonalt*-PK incorporating as little as 10 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 °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 (**A** \rightarrow **D**), a requirement for sequential ethene insertions; note that this issue does not arise in ethene *homo*polymerization. However, carbon monoxide binding is strong enough to disrupt the chelate leading to further insertions (**A** \rightarrow **B** \rightarrow **C** \rightarrow **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 Pd(OAc)₂ and P^{SO₃}H) was not well-defined.² Therefore, we used a model compound with a methyl group and pyridine occupying two coordination sites, *cis*-(P^{SO₃})PdCH₃(py), **2**. This species was synthesized and characterized by ¹H and ³¹P NMR spectroscopy, IR spectroscopy and single-crystal X-ray diffraction. The oRTEP structure of **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 °C, PE was produced. The ethene polymerization has living characteristics under these conditions and the chain-growth was monitored by ¹H 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 β-hydrogen abstraction. Also, methylene groups α and β 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 (**■**) and composition (\diamond). Curves are presented only to guide the eye. Reaction conditions: Pd₂(DBA)₃, 10 µmol; P^{SO}₃H, 10 µmol; C₂H₄, 300 psig; dichloromethane-*d*₂, 20 mL; 75 °C; 3h.



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



Figure 1.3: Crystal structure of $(P^SO_3)PdCH_3(py)$, **2**, and $(P^SO_3)PdC(O)CH_3(py)$, **3**. Hydrogen atoms are omitted for clarity.

When 2 was exposed to a mixture of 50 psig carbon monoxide and 50 psig ethene in dichloromethane- d_2 at 25 °C, *alt*-PK was formed. As with ethene homopolymerization, it was possible to observe stepwise insertion of carbon monoxide (or ¹³CO for ¹³C 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-(P SO_3)PdC(O)CH₃(py), **3**. The ¹H NMR signal for Pd–CH₃ at 0.2 ppm was replaced by the Pd–C(O)CH₃ signal at 1.8 ppm. Also, the 31 P signal at 23 ppm was replaced by a signal at 11 ppm and a ¹³C carbonyl signal appeared at 227 ppm. The infrared spectrum showed a carbonyl absorption at 1695 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 2 and 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 2 was found to be reversible as shown by the following experiment. First, $(P^SO_2)Pd^{13}C(O)CH_2(py)$ was formed by the insertion of ${}^{13}CO$ as confirmed by a strong carbonyl ¹³C NMR signal at 227 ppm. The solvent and excess ¹³CO were removed under vacuum and the product was re-dissolved in dichloromethane- d_2 before being exposed to 50 psig of regular ¹²CO. After 18h, ¹³C NMR analysis showed a lack of ¹³C enrichment in the palladium complex, indicating slow decarbonylation of ¹³CO followed by rapid insertion of ¹²CO as predicted by Ziegler.⁵

When a solution of **3** in dichloromethane- d_2 was exposed to 100 psig ethene at 0 °C, slow insertion of ethene into the palladium-acyl bond occurred to give a mixture of (P^SO₃)PdCH₂CH₂C(O)CH₃, **4**, and unreacted **3** but not PE. NMR analysis showed a new terminal methyl ¹H NMR signal at 1.9 ppm and the methylene groups α and β 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 ³¹P signal appeared at 25 ppm and a broad ¹³C carbonyl signal appeared at 216 ppm. A new carbonyl absorption was seen at at 1643 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 ¹H NMR analysis suggests that the five-membered chelate **4** is likely in equilibrium with the open-chain, pyridine-coordinated analogue, **4**·py, and that the former is favored at low temperatures. At 80 °C, a doublet due to the *ortho*-hydrogens of the free pyridine is observed at 8.7 ppm. Additionally, the doublet of triplets at 1.3 ppm and the multiplet at 2.1 ppm from the methylene groups α and β to the metal, respectively, split into unique proton signals at 0.80 ppm, 1.01 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 **3**, the chelated species **4** was unreactive towards ethene alone at 100 psig and 25 °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*-PK. However, unlike *alt*-PK formation, the yield of *nonalt*-PK is low because of the slowness of this step. We hypothesize that the step $A \rightarrow D$ of Scheme 1.2 does proceed in the present *neutral* system, albeit slowly, because the carbonyl group in species 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 °C, formed (P^SO_3)PdC(O)CH₂CH₂C(O)CH₃, **5**, which corresponds to either structure **C** in Scheme 1.2 or its open-chain pyridine-coordinated analogue. The ¹H NMR signals for the CH₂ groups α and β to the metal in **5** were shifted to 1.9 ppm and 2.5 ppm, respectively. The ³¹P signal at 25 ppm was replaced by a peak at 12 ppm and the ¹³C 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 °C for 18 h. The ³¹P 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, **2** in dichloromethane- d_2 was exposed to ethene at 100 psig and 25 °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*-PK block. The PE and *alt*-PK blocks were identified by their characteristic ¹H NMR chemical shifts at 1.3 ppm and 2.7 ppm, respectively. The connectivity between the two blocks was observed as two CH₂ signals at 1.5 ppm and 2.4 ppm. The assignment of the connecting CH₂ groups was established by comparing with the ¹H NMR shifts of 3-hexanone. The protons labeled *a* and *b* in CH₃CH₂C(O)-CH₂^{*a*}-CH₂^{*b*}-CH₃ 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 ¹H, 121.49 MHz for ³¹P or 75.4 MHz for ¹³C NMR spectra. ³¹P and ¹³C NMR experiments were conducted with proton decoupling.

1.4.1 Synthesis of (tmeda)PdCl₂

(tmeda)PdCl₂ was synthesized under air by modifying the literature procedure.¹ Potassium tetrachloropallidate (SI2g, 6.12mmol) was dissolved in distilled water (20mL) and filtered through a fine-porosity frit. TMEDA (3.55g, 30.6mmol) was added to the filtrate and the mixture was stirred for 15min and then cooled to 0°C. The resulting yellow precipitate was collected by filtration and washed with cold water followed by diethyl ether. Yield = 1.5g (83%).

1.4.2 Synthesis of (tmeda)Pd(CH₃)₂

(tmeda)Pd(CH₃)₂ was synthesized by following literature procedure.⁸

1.4.3 Synthesis of Phosphine-Sulfonate Ligand P^{SO}₃H, 1

The P^SO₃H ligand, 1 was synthesized by following literature procedure.²

1.4.4 Synthesis of Methylpalladium Complex (P^SO₃)PdCH₃(py), 2

To a single-neck round-bottom flask 0.3 g (0.75 mmol) of **1** was suspended in 10 mL of dry tetrahydrofuran. To this 0.22 g (0.75 mmol) of (tmeda)Pd(CH₃)₂ was added and the reaction mixture was stirred for 30 min. To this five equivalents of pyridine (0.29g, 3.73 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 g (95%). ¹H NMR (CD₂Cl₂): 0.26 ppm (d, 3H), 3.69 ppm (s, 6H), 6.98 ppm to 7.09 ppm (m, 4H), 7.32 ppm (m, 2H), 7.49 ppm to 7.60 ppm (m, 7H), 7.92 ppm (t, 1H), 8.01 ppm (t, 1H), 8.8 ppm (d, 2H). ³¹P NMR (CD₂Cl₂): 22.76 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 $0.010 \text{ g Pd}_2(\text{dba})_3$ (Strem Chemicals), 0.010 g1 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 °C (75 °C internal autoclave temperature) with magnetic stirring for 3h. 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 ¹H NMR analysis using 5 mm sample tubes (Norell). Carbon monoxide incorporation was determined from the following equation

$$[CO] = \frac{A}{2A+B} \tag{1.1}$$

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 $5 \,^{\circ}$ Cmin⁻¹ from 40 $^{\circ}$ C to 280 $^{\circ}$ 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, $5 \text{ mg} (P^SO_3)PdCH_3(py)$ 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 °C. (13 C-enriched carbon monoxide was used for 13 C NMR experiments and normal carbon monoxide was used for 1 H and 31 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 °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 °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 5kHz 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 cm^{-1} to 900 cm^{-1} with a resolution of 1 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** ($C_{26}H_{26}NO_5PPdS$) with approximate dimensions of 0.02 × 0.07 × 0.10 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 α fine-focus sealed-tube (l = 0.71073Å) operated at 1600W power (50 kV, 32 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° in ω 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° (0.90Å resolution), of which 6269 were independent, completeness = 98.0%, $R_{intv} = 0.0535$, $R_{sig} = 0.0803$ and 4561 were greater than 2σ (I). The final cell constants: a = 11.484(5)Å, b = 13.828(6)Å, c = 16.239(6)Å, $\alpha = 90^{\circ}$, $\beta = 97.515(8)^{\circ}$, $\gamma = 90^{\circ}$, volume = 2556.5(18)Å³, are based upon the refinement of the XYZ-centroids of 3550 reflections above 20σ (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 P2(1)/c, with Z = 4 for the formula unit, $C_{26}H_{26}NO_5PPdS$. 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 eÅ⁻³ and the largest hole was -1.398 eÅ⁻³. Based on the final model, the calculated density of the crystal is 1.564 g cm⁻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** ($C_{27}H_{26}NO_6PPdS$) with approximate dimensions of $0.05 \times 0.13 \times 0.17$ 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 α fine-focus sealed tube (l = 0.71073Å) operated at 1600W power (50 kV, 32 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° in ω and an exposure time of 10s per frame. The total data collection time was about 8h. 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° (0.90 Å resolution), of which 6396 were independent, completeness = 97.3%, $R_{\rm int} = 0.0693$, $R_{\rm sig} = 0.0924$ and 4577 were greater than 2σ (I). The final cell constants: a = 11.567(2)Å, b = 14.097(3)Å, c = 16.198(3)Å, $\alpha = 90^{\circ}$, $\beta = 96.68(3)^{\circ}$, $\gamma = 90^{\circ}$, volume = 2623.5(9)Å³, are based upon the refinement of the XYZ-centroids of 3462 reflections above 20σ (I) with 2.286° < $q < 27.834^{\circ}$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (saddes). 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, $C_{27}H_{26}NO_6PPdS$. 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 eÅ⁻³ and the largest hole was $-0.818 eÅ^{-3}$. Based on the final model, the calculated density of the crystal is 1.595 g cm^{-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 °C. The sample was allowed to equilibrate for 5 min before ¹H- and ³¹P NMR spectra were taken. The sample was then warmed by 10 °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 ℃ increment from −80 ℃ to 20 ℃. 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 $0.005 \text{ g} (P^SO_3)PdCH_3(py)$ 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 °C for 2 h. The solvent and excess ethene were removed under vacuum. The system was re-dissolved in CD_2Cl_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 $(P^SO_3)Pd^{13}C(O)CH_3(py)$ complex was prepared by exposing $(P^SO_3)PdCH_3(py)$ to 50 psig ¹³CO as described in Section 1.4.6. The solvent and excess ¹³CO were removed under vacuum before the product was re-dissolved in CD_2Cl_2 and exposed to un-enriched carbon monoxide at 50 psig overnight at ambient temperature. The ¹³C NMR spectra of the $(P^SO_3)Pd^{13}C(O)CH_3)(py)$ before and after exposure to un-enriched carbon monoxide are shown in Section A.1. Note the carbonyl signal at 227 ppm and the free carbon monoxide signal at 185 ppm.

1.5 References

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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 (~ 260 °C) brought about by the interchain dipolar interaction between carbonyl groups present at 50 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 $\sim 5-10 \text{ mol }\%$ 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 oligomerizing⁶ or polymerizing⁷ 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 Drent¹⁵ and then we⁸ and others¹⁶ have reported on neutral palladium complexes with anionic phosphine-sulfonate ligands ($P^SO_3^-$) 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 ethene¹⁵ and to decarbon-ylation 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 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.



 $\label{eq:scheme 2.1: Catalytic cycle for alternating copolymerization of ethene with carbon monoxide. R represents the growing polymer chain and L^L represents a bidentate ligand.$



 $P^{-}SO_{3}^{-}$ ligand.

2.2 Results and Discussion

2.2.1 Bulk Polymerization

The combination of P^SO_3H and palladium acetate $(Pd(OAc)_2)$ 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 mol% to 32 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 °C to 110 °C decreased the carbon monoxide content of the copolymer from 28 mol% to 8 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.⁴

Entry	Temperature (℃)	CO (psig)	Yield (g)	$\begin{array}{c} Activity \\ (gmmol_{Pd}^{-1}h^{-1}) \end{array}$	CO incorporation (mol%) ^b	Т _т (°С)	M _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 psig; Pd(OAc)₂, 0.1 mmol; P^{SO}₃H, 0.1 mmol; CH₂Cl₂, 10 mL; 1.5 h.

^b Determined by ¹H 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 ¹H- and ¹³C NMR spectroscopy as shown in Figure 2.2 and Figure 2.3. In the ¹H NMR spectra, the peak at 2.7 ppm was assigned to CH_2 in alternating copolymer segments. The peaks at 2.4 ppm and 1.6 ppm were assigned to the CH_2 groups α and β 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 ¹³C 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: ¹H NMR spectrum of non-alternating polyketone with 10 mol% carbon monoxide incorporation in tetrachloroethane- d_2 .



Figure 2.3: ¹³C NMR spectrum of non-alternating polyketone with 10 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 mol% to 28 mol% decreased the melting point from 125.3 °C to 115.9 °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 ($v_{C=0} \approx 1695 \text{ cm}^{-1}$).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 mol% to 49 mol%. The corresponding carbonyl stretching frequency was observed to decrease from 1717 cm⁻¹ to 1689 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 (P^{SO_3})PdCH₃(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 **3** in dichloromethane- d_2 to ethene at 80 psig and 50 °C for 5 min resulted in slow insertion of ethene into the palladium-acyl bond to give a mixture of the five-membered chelate (P^{SO}₃)PdCH₂CH₂C(\overrightarrow{O})CH₃, **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 ¹H 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 CH₂ groups α and β to the metal center shifted from 1.3 ppm and 2.1 ppm to broad peaks at 0.8–1.1 ppm and 1.5–1.7 ppm, respectively. As expected, ⁹ coordinated ethene was not observed in the presence of excess monomer. The ³¹P NMR signal at 23.6 ppm was shifted to 27.0 ppm, and the ¹³C 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 ¹³C NMR spectroscopy from –90 °C to –70 °C. The van 't Hoff plot (see Appendix B) gives $\Delta H^{\circ} = 0.68(7)$ kcal mol⁻¹ and $\Delta S^{\circ} = -1.1(3)$ eu. The calculated equilibrium constant *K*₁ at 25 °C is

 0.548 Lmol^{-1} . Because impure **4** was used as a starting material, it is possible that residual **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 **8** was confirmed by ¹H 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 CH₂ groups α and β to the metal center shifted from 1.3 ppm and 2.1 ppm to broad peaks at 0.8–1.1 ppm and 1.5–1.7 ppm, respectively. The ³¹P NMR signal at 23.6 ppm was shifted to 26.6 ppm and the ¹³C 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 ¹³C NMR spectroscopy from –90 °C to –70 °C. The van 't Hoff plot (see Appendix B) gives $\Delta H^\circ = 3.2(2)$ kcal mol⁻¹ and $\Delta S^\circ = 17.2(12)$ eu. The calculated equilibrium constant K_2 at 25 °C is 27.4 Lmol⁻¹. In this case, although impure **4** was used as a starting material, the presence of palladium-acyl complex **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 **2**, $k_{\rm E}$, to give palladiumpropyl complex **9** was determined by ¹H NMR spectroscopy. The presence of **9** was confirmed by ¹H NMR spectroscopy, which showed that the PdCH₃ signal shifted from 0.2 ppm to 1.0 ppm and was accompanied by the appearance of CH₂ groups α and β to the metal center at 0.8 ppm and 1.3 ppm, respectively. The ³¹P 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 $\Delta H^{\ddagger} = 17.7(1)$ kcalmol⁻¹ and $\Delta S^{\ddagger} = -13.6(4)$ eu, which are somewhat higher than those reported by Brookhart and co-workers for the analogous cationic dppp-ligated system ($\Delta H^{\ddagger} =$ 15.2(7)kcalmol⁻¹, $\Delta S^{\ddagger} = -6.2(29)$ eu). 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, β -H elimination of propene was not observed.



The rate of migratory insertion of carbon monoxide into palladium-methyl complex **2**, k_{CO} , to give palladium-acyl complex **10** was also determined by ¹H NMR spectroscopy. The presence of **10** was confirmed by ¹H NMR spectroscopy, which showed that the PdCH₃ signal at 0.2 ppm was replaced by PdC(O)-CH₃ at 1.8 ppm. The ³¹P NMR 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 $\Delta H^{\ddagger} = 16.6(8)$ 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 ($\Delta H^{\ddagger} = 14.8(7)$ kcalmol⁻¹ and $\Delta S^{\ddagger} = 0.1(4)$ eu). 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 $(K_2 : K_1)$ is ~ 50 : 1 at 25 °C, compared to ~ 10⁴ : 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_{eq} , and the relative rates of migratory insertion for these two species, K_{CO} and K_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_{eq} , was estimated from the ratio of [11] to [12] multiplied by the ratio of [CO] to $[C_2H_4]$ in dichloromethane at 25 °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_{eq} is offset by the slow rate of ethene insertion since one would expect a double ethene insertion to occur only once for every 6.4×10^4 alternating insertions under these conditions. Although this is more frequent than either the $\sim 10^5$ reported for the bidentate diphosphine system¹⁹ or the $\sim 10^6$ reported for the bidentate dimine 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 P^O represents the phosphine-sulfonate ligand.

$$\begin{aligned} \frac{\text{Alternation}}{\text{Non-alternation}} &= K_{\text{eq}} \left(\frac{k_{\text{CO}}}{k_{\text{E}}} \right) \\ &\approx \left(\frac{[11]}{[12]} \right) \left(\frac{k_{\text{CO}}}{k_{\text{E}}} \right) \\ &= \left(\frac{K_2 \times [\text{CO}]}{K_1 \times [\text{C}_2\text{H}_4]} \right) \left(\frac{(1730 \,\text{Lmol}^{-1} \,\text{s}^{-1}) \times [\text{CO}]^1}{(6.11 \times 10^{-4} \,\text{s}^{-1}) \times [\text{C}_2\text{H}_4]^0} \right) \\ &= \left(\frac{(27.4 \,\text{Lmol}^{-1}) \times (7.3 \times 10^{-3} \,\text{mol} \text{L}^{-1})}{(0.584 \,\text{Lmol}^{-1}) \times (0.11 \,\text{mol} \text{L}^{-1})} \right) \left(\frac{(1730 \,\text{Lmol}^{-1} \,\text{s}^{-1}) \times (7.3 \times 10^{-3} \,\text{mol} \text{L}^{-1})}{(6.11 \times 10^{-4} \,\text{s}^{-1})} \right) \\ &= 6.4 \times 10^4 \end{aligned}$$

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 °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_{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 Pd–CH₃ 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 (PdC(O)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 (P^SO_3)PdC(O)CH₂CH₂C(O)CH₃ 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, (P^SO_3)Pd¹³C(O)-CH₃(py), and its cationic analogue, (dppp)Pd¹³C(O)CH₃(py)+BF₄⁻, was performed. The rate of decarbonylation, $k_{obs(CO)}^{-1}$, was measured by using ¹³C NMR spectroscopy to observe the loss of ¹³C 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 $k_{obs(CO)}^{-1}$ of $5.6 \times 10^{-6} s^{-1}$ while the cationic diphosphine system was found to have an approximate $k_{obs(CO)}^{-1}$ of $2.8 \times 10^{-5} s^{-1}$. Thus, the classic cationic system actually undergoes decarbonylation with exchange more readily than the phosphine-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 ΔH^{\ddagger} . Furthermore, because a decarbonylation event can affect the copolymer composition only if it is followed by exchange between carbon monoxide and ethene ($11 \rightarrow 12$) and the subsequent insertion of the latter, the higher relative binding affinity of ethene in the phosphine-sulfonate system (i.e., low K_{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 attenuates²³ 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 **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 palladium–carbon bond *trans* to the phosphine, (b) isomerization to the complex with the palladium–carbon bond *trans* 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^CL 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 Pd–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 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 Pd–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 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 ¹³CO 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 ¹H, 121.49 MHz for ³¹P, or 75.4 MHz for ¹³C NMR spectra. ³¹P and ¹³C spectra were obtained with proton decoupling. Quantitative ¹³C 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.

NMR data: **2** ¹H NMR (CD₂Cl₂): δ (ppm) 0.22 (d, 3H, PdCH₃); 3.68 (s, 6H, OCH₃); 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, 2H, Py). ³¹P NMR (CD₂Cl₂): δ 23.4 ppm. **3** ¹H NMR (CD₂Cl₂): δ (ppm) 1.84 (s, 3H, PdC(O)CH₃); 3.78 (s, 6H, OCH₃); 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 (t, 1H, Ar); 8.09 (dd, 1H, Ar); 8.81 (d, 2H, Py). ³¹P NMR (CD₂Cl₂): δ 11.0 ppm. ¹³C NMR (CD₂Cl₂): δ 227 ppm (PdC(O)CH₃). 4 ¹H NMR (CD₂Cl₂): δ (ppm) 1.30 (m, 2H, PdCH₂CH₂C(O)CH₃); 1.89 (s, 3H, PdCH₂CH₂C(O)CH₃); 2.11 (b, 2H, PdCH₂CH₂C(O)CH₃); 3.70 (s, 6H, OCH₃); 7.02 (dd, 2H, Ar); 7.09 (dd, 2H, Ar); 7.34 (m, 2H, Ar); 7.50 (dd, 3H, Ar); 7.59 (t, 2H, Ar); 7.67 (b, 2H, Ar); 7.90 (t, 1H, Ar); 8.09 (m, 1H, Ar); 8.79 (d, 2H, Py). ³¹P NMR (CD₂Cl₂): δ 23.6 ppm. ¹³C NMR (CD₂Cl₂): δ 216 ppm (PdCH₂CH₂C(O)CH₃). **7** ¹H NMR (CD₂Cl₂, -70°C): δ (ppm) 0.8-1.1 (b, 2H, (PdCH₂CH₂C(O)CH₃); 1.4 (s, 3H, PdCH₂CH₂C(O)CH₃); 1.5- $1.7 (b, 2H, PdCH_2CH_2C(O)CH_3); 3.6 (b, 3H, OCH_3); 3.8 (b, 3H, OCH_3); 5.4 (s, free ethene); 6.7-8.0 (17H, Ar); 7.7-8.0 (17$ 8.7 (b, 1H, Py); 8.8 (b, 1H, Py). ³¹P NMR (CD₂Cl₂, -70 °C): δ 27.0 ppm. ¹³C NMR (CD₂Cl₂, -70 °C): δ 201 ppm (PdCH₂CH₂C(O)CH₃). **8** ¹H NMR (CD₂Cl₂, -70 °C): δ (ppm) 0.8-1.1 (b, 2H, (PdCH₂CH₂C(O)CH₃); 1.4 (s, 3H, PdCH₂CH₂C(O)CH₃); 1.5–1.7 (b, 2H, PdCH₂CH₂C(O)CH₃); 3.6 (b, 3H, OCH₃); 3.8 (b, 3H, OCH₃); 6.7–8.0 (17H, Ar); 8.7, 8.8 (b, 2H, Py). ³¹P NMR (CD₂Cl₂, -70 °C): δ 26.6 ppm. ¹³C NMR (CD₂Cl₂, -70 °C): δ 201 ppm (PdCH₂CH₂C(O)CH₃). **9** ¹H NMR (CD₂Cl₂): δ (ppm) 0.8 (b, 2H, PdCH₂CH₂CH₃) 1.0 (b, 3H, PdCH₂CH₂CH₃) 1.3 (b, 2H, PdCH₂CH₂CH₂) 3.7 (s, 6H, OCH₂); 5.5 (s, free ethene); 6.9–8.2 (17H, Ar); 8.8, 8.9 (b, 2H, Py). ³¹P NMR (CD₂Cl₂): δ 27.1 ppm. **10** ¹H NMR (CD₂Cl₂): δ (ppm) 1.76 (s, 3H, PdC(O)CH₃); 3.73 (s, 6H, OCH₃); 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, 1H, Ar); 8.73 (d, 2H, Py). ³¹P NMR (CD₂Cl₂): δ 11.4 ppm. ¹³C NMR (CD₂Cl₂): δ 227 ppm (PdC(O)CH₃).

Differential scanning calorimetry was performed using a TA Instruments model DSC Q100 and heating 3 mg copolymer samples at a rate of 20 °C min⁻¹ from 40 °C to 300 °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 5kHz laser modulation frequency. The sample chamber was flushed with dry nitrogen, and data was collected from 4000 cm^{-1} to 900 cm^{-1} with a resolution of 1 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 mg (0.10 mmol) of Pd(OAc)₂ and 40 mg (0.10 mmol) of P^{SO}₃H 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 1.5h. 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 °C for NMR analysis. Carbon monoxide incorporation was determined by the integration of the CH₂ protons using the formula

$$[CO] = \frac{A+B}{2A+2B+C+D}$$
(2.2)

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 CH_2 protons α and β 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 β -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 β -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 mol%). Herein, we report on catalyst systems based on palladium complexes incorporating anionic P^SO_3H ligands. Two π -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 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 P^SO₂H 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 13 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) [Pd(dba),] 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 ¹³C NMR resonance at 28ppm and a $T_{\rm m}$ of 127.8 °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, $Pd(dba)_2/ligand 1$ catalyst produced copolymers with 37.7 mol% of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (Entry 4) and 22.6 mol% of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (Entry 6) while Pd(dba)₂/ligand 13 catalyst only generated copolymers with 31.2 mol% of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (Entry 8) and 13.3 mol% of bicyclo[2.2.1]hept-5enyl-2-methyl acetate (Entry 10). On the other hand, there is little effect on copolymer molecular weight (e.g., Entry 6: $M_n = 47000$, $M_w/M_n = 2.1$. Entry 10: $M_n = 49700$, $M_w/M_n = 1.8$). The structures of the obtained copolymers were analyzed by ¹H and ¹³C 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, norborneneethene-ethene, and ethene-norbornene-ethene triads are present. The ¹³C NMR 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 CH₂ 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 (CH₂=CHR) into palladium-alkyl bonds in cationic complexes decreases with increasing donor ability of the substituent ($R = CO_2R > H > alkyl$).²⁶ An alkene with an electronwithdrawing substituent coordinates less strongly to the electrophilic metal (i.e. σ -donation is more important than π -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: $Pd(dba)_{2}$, 13.5 µmol; ligand 1, 16.2 µmol; sodium dodecylsulfate, 0.9 g; ethene, 500 psig; bicyclo[2.2.1]hept-5-enyl-2methyl acetate, 3 g; toluene, 10 mL; water, 90 mL; 95 °C, 3 h. Yield, 7.1 g; activity, 175 kg mol_{pd}⁻¹h⁻¹); norbornene, 13.4 mol % $M_{\rm n}$ = 42000; $M_{\rm w}/M_{\rm n}$ = 1.9). The lower activity is expected due to significantly reduced

Entry	Ligand or Complex	Pd (امسما)	Ethene (psig)	Time (h)	Norbornene functional group	Norbornene (mmol)	Incorporation (mol%)	Activity (kgmol ⁻¹ h ⁻¹)
1ª	-	4.5	500	-				520
2^a	1	4.5	500	1	Н-	11.7	22.6	618
3^{a}	1	4.5	500	1	-CH ₃ OC(0)CH ₃	12.0	14.9	816
4^a	1	4.5	150	з	-CH ₂ OC(0)CH ₃	18.1	37.7	221
5^a	1	4.5	150	3	$-C(0)OCH_2CH_3$	18.1	43.9	241
e^{a}	1	4.5	250	3	$-0C(0)CH_3$	12.0	22.6	268
7a	1	4.5	250	3	-CH ₂ OH	12.0	34.2	48
8a	13	4.5	150	3	$-0C(0)CH_3$	18.1	31.2	194
θ^a	13	4.5	250	3	-C(0)OCH ₂ CH ₃	12.0	16.7	73
10^{a}	13	4.5	250	3	-0C(0)CH ₃	12.0	13.3	233
11^{a}	13	7.8	250	2	-CH ₂ OH	12.0	24.2	67
12^{b}	14	4.5	500	1	Н-	11.7	31.0	167
13^{b}	15	4.5	500	I	Н-	11.7	18.5	528

Table 3.1: Copolymerization of ethene with functional norbornenes.

^{*a*} Conditions: 1.2 equivalents of ligand, 10 mL toluene, 95 °C. ^{*b*} Conditions: 2 equivalents of $B(C_6F_5)_3$, 10 mL toluene, 95 °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; Pd(dba)₂, 4.5 µmol; ligand 1, 5.4 µmol; toluene, 10 mL; 1,1,2,2-tetrachloroethane, 50 µL;95 °C.

solubility of ethene in water. In an attempt to better define the catalysts, π -allyl (14) and π -1-methallyl (15) complexes incorporating the P^{SO}₃H ligand 1 were synthesized by the reaction of the chloro-bridged π -allyl or π -1-methallyl dimer with the sodium salt of 1 in dichloromethane at -20 °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, 2.22Å versus 2.09Å; 15, 2.25Å versus 2.10Å).

Neither complex **14** nor **15** showed significant activity towards the copolymerization of ethene and norbornene, presumably because the η^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 $B(C_6F_5)_3$ were added (Table 3.1). Under these conditions, the polymerization activity of **15** 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 $B(C_6F_5)_3$ in activating **14** and **15** is currently under investigation. In conclusion, we have described catalyst systems based on palladium complexes incorporating anionic P SO_3H ligands. Two new π -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 mol%). Second, the system is so highly tolerant of reactive functionalities that the copolymerization can even be carried out in the presence of water.

Run	Solvent	Yield	Activity	Norbornene incorporation	$M_{\mathrm{n}}{}^{b}$	$M_{\rm w}/M_{\rm n}{}^b$
		(g)	$(kg mol_{Pd}^{-1} h^{-1})$	(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

Table 3.2: Solvent effect.^a

 a Conditions: solvent, 10 mL; bicyclo[2.2.1]hept-5-enyl-2-methyl acetate, 2g; ethene, 150 psig; Pd(dba)_2, 4.5 μ mol; ligand 1, 5.4 μ mol; 95 °C; 3 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. Pal-ladium(II) acetate, and Bis(dibenzylideneacetone)palladium(0) [Pd(dba)₂], 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 °C in 1,1,2,2-tetrachloroethane- d_2 on a Bruker DPX-300 spectrometer at 300.15 MHz for ¹H NMR and 75.4 MHz for ¹³C 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 mLmin⁻¹ and a three-column bed (Styragel HR 7.8 × 300 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 CHCl₃ 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(2-methoxyphenyl)methoxyphosphine (1.89 g, 6.85 mmol) in THF (10 mL) was added drop wise a solution of PCl₃ (4.71 g, 34.3 mmol) in THF (10 mL) at 0 °C. The reaction was then allowed to stand for 5 h at room temperature. The unreacted PCl₃ was removed under vacuum. The bis(2-methoxyphenyl)chlorophosphine solution in THF was added slowly to the lithium salt of benzenesulfonic acid at -40 °C. The reaction was allowed to stand at room temperature for 16 h. Water (40 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 HCl (37%). The precipitate was filtered off and the filtrate was washed with tert-butyl methyl ether (15 mL). After extracting three times with CH₂Cl₂ (20 mL), the crude product was dried over anhydrous MgSO₄. Solvent was removed under vacuum to afford a white powder (1.05 g, 38.2%). ¹H NMR (CD₂Cl₂): 9.1 ppm (1H, P–H), 6.8 ppm to 8.4 ppm (m, 12H, phenyl), 3.8 ppm (s, 6H, OCH₃); ³¹P NMR (CDCl₃): -9.6 ppm.



Scheme 3.4: Outline of ligand synthesis.

3.3.4 Synthesis Ligand 13

To a solution of benzenesulfonic acid (1.08g, 6.84 mmol) in THF (15 mL) was added drop-wise n-butyl lithium (15 mmol, 2.5 mol dm⁻³ in hexane) at 0 °C. After stirring at room temperature for 18 h a solution of bis(2,6-dimethoxyphenyl)methoxyphosphine (2.30 g, 6.86 mmol) in THF (50 mL) was added at -40 °C and the reaction was allowed to stand for further 12 h. Water (40 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 HCl (37%). The precipitate was filtered off and the filtrate was washed with *tert*-butyl methyl ether (15 mL). After extracting three times with CH_2Cl_2 (20 mL), the crude product was dried over anhydrous MgSO₄. Solvent was removed under vacuum to afford a white powder (1.25g, 39.6%) The crystal for X-ray analysis was obtained at -10 °C from a mixture of CH_2Cl_2 and hexane. ¹H NMR (CD_2Cl_2): 10.3 ppm (1H, P–H), 6.6 ppm to 8.4 ppm (m, 10H, phenyl), 3.6 ppm (s, 12H, OCH₃); ³¹P NMR ($CDCl_3$): -29.3 ppm.

3.3.5 Synthesis of Allylpalladium Complex 14

Sodium carbonate (Na_2CO_3) (0.315g, 2.97 mmol) was added to a flask containing ligand **1** (1g, 2.48 mmol) and 15 mL dichloromethane. The solution was stirred until it formed a white precipitate (approx. 4h). To this was added dichloromethane solution of allylpalladium chloride dimer (0.45g, 1.24 mmol) at -20 °C, and stirring continued overnight. The reaction mixture was filtered and the filtrate was recrystallized using pentane as a non-solvent. Yield: 1.09g (80%). ¹H NMR (CD₂Cl₂): 8.19 ppm (1H, m, aromatic), 7.53 ppm (2H, m, aromatic), 7.39 ppm (1H, m, aromatic), 6.9 ppm to 7.2 ppm (8H, m, aromatic), 5.66 ppm (1H, m, *CH*), 4.74 ppm (1H, m, HC*H*), 3.80 ppm (1H, m, HC*H*), 3.14 ppm (1H, m, HC*H*), 2.65 ppm (1H, d, HC*H*), 3.80 ppm (6H, m, OCH₃). ³¹P NMR (CD₂Cl₂): -2.9 ppm (s). Because of general instability of this class of palladium compounds, elemental analysis was not attempted. However, **14** 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: 1.1g (78%). ¹H NMR (CD₂Cl₂): 6.9 ppm to 8.4 ppm (12H, m, aromatic), 5.45 ppm (1H, m, $CH=CHCH_3$), 4.62 ppm (1H, m, $CH=CHCH_3$), 3.74 ppm (6H, s, OCH_3), 3.10 ppm (1H, br, HCH-CH=CH), 2.51 ppm (1H, br, HCH-CH=CH), 1.76 ppm (3H, m, $CH=CHCH_3$). ³¹P NMR (CD₂Cl₂): -4.87 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 N₂-filled glovebox, charged with toluene (10 mL), Pd(dba)₂ (4.5 μ mol), ligand **1** (5.4 μ 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 °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 ¹H NMR peaks from 3.60–4.20 ppm for the CH₂OCO unit of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate and 1.2 ppm for the CH₂ units of ethene. Yield: 2.98 g. Bicyclo[2.2.1]hept-5-enyl-2-methyl acetate incorporation: 37.7 mol%.

3.3.8 Determination of the Relative Uptake of endo and exo Isomers

In a N₂-filled glovebox, a 300 mL, glass-lined, stainless-steel autoclave equipped with a magnetic stir bar was charged with 10 mL of toluene, $4.5 \,\mu$ mol of Pd(dba)₂, $5.4 \,\mu$ mol of ligand **1** (pre-dissolved in 1 mL of toluene), 12 mmol of bicyclo[2.2.1]hept-5-enyl-2-methyl acetate, and $50 \,\mu$ 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 °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 N₂-filled glovebox, a 600 mL glass-lined, stainless-steel autoclave equipped with a magnetic stir-bar was charged with toluene (7 mL), Pd(dba)₂ (13.5 µmol), ligand **1** (16.2 µmol pre-dissolved in 3 mL toluene), and bicyclo[2.2.1]hept-5-enyl-2-methyl acetate (3.0 g, 18.1 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 °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 mol%. $M_n = 42000$; $M_w/M_n = 1.9$.

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), **14** or **15** (4.5 μ mol), tris(pentafluorophenyl)borane (9 μ mol) and norbornene (1.1 g, 11.7 mmol) inside a N₂-filled glovebox. The autoclave was charged to 500 psig with ethene and immersed in a preheated oil bath at 95 °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) K for **15**, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo K α fine-focus sealed tube ($\lambda = 0.71073$ Å) 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.

3.4 References

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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, few⁷⁻⁹ have been shown to be effective for copolymerization of ethene with styrene; insertion of styrene typically leads to chain termination through β -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 phosphine-sulfonate ligands described by Drent and Pugh.⁶ In those studies, we found that the well-defined, square-planar model compound (P^SO_3)PdCH₃(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 (P^SO_3H) and bis(dibenzylideneacetone)palladium(0), Pd(dba)₂ or palladium(II) acetate [Pd(OAc)₂]. 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 (η^3 -phenylprop-yl)palladium complex, **16**, followed by β -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 **16** was attempted by adapting the procedure used previously for the synthesis of (η^3 -crotyl)palladium complex **15** via an (η^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 (η^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 (η^3 -phenylethyl)palladium complex, **17**. The structure of the η^3 -phenylethyl moiety was confirmed by a cosy NMR experiment and ¹H NMR splitting in an isolated sample of **17** which showed a doublet of doublets for the CH₃ group, which is consistent with the complex splitting observed in the analogous (η^3 -crotyl)palladium complex **15** we reported previously¹¹ (see Chapter 3). Also, the formation of η^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 **17** at ambient temperature to give styrene and palladium black.

The insertion of styrene into the palladium-carbon bond of **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 BPh₃ as confirmed by ¹H NMR signals at 6.5 ppm (1H, d), 6.3 ppm (1H, m) and 1.9 ppm (3H, d). This is consistent with a 2,1-insertion of styrene into the Pd–C bond followed by rapid β -H elimination to give a palladium hydride and 1-phenyl-1-propene. Additionally, the conversion of styrene to **17** was shown by ¹H NMR signals at 3.2 ppm (1H, q) and 0.7 ppm (3H, dd) along with the replacement of the ³¹P 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 Pd–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 ¹H and ²H 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 ³¹P NMR spectrum. The reaction is first-order in styrene and the Eyring plot shows a ΔH^{\ddagger} of 64.3(6)kJ mol⁻¹ and a ΔS^{\ddagger} of -60(20)J mol⁻¹ K⁻¹.



 $(\eta^{3}$ -phenylethyl)palladium complex 17.



Scheme 4.1: Conversion of methylpalladium complex **2** and styrene to (η³-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 Pd–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 $12800 \text{ gmol}_{Pd}^{-1} \text{ h}^{-1}$, and $16100 \text{ gmol}_{Pd}^{-1} \text{ h}^{-1}$, and the comonomer incorporations were 2.8 mol%, 6.7 mol%, and 4.5 mol%, respectively. The hydrolysis of 4-acetoxystyrene and 4-vinylmethylbenzoate-containing copolymers afforded materials bearing hydroxyl and carboxylic acid functionalities,

respectively.

entry	comonomer	amount (g)	ethene (psig)	time (h)	$M_{ m w}$	PDI ^b	$\begin{array}{c} activity \\ (gmol_{Pd}^{-1}h^{-1}) \end{array}$	incorporation ^c (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 ^f
8	1-hexene	2	50	15	2200	1.7^e	4310	47 ^f
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

Table 4.1: Copolymerization of ethene with polar vinyl monomers using complex 2 and triphenylboron.^a

^{*a*} Conditions: complex **2**, 0.005 g (8.30×10^{-6} mol); BPh₃, 0.004 g (1.66×10^{-5} mol); CH₂Cl₂, 5 mL; 80 °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 °C.

 d In the presence of one equivalent of galvinoxyl.

^e By GPC analysis in THF at 35 °C using polystyrene standards.

^{*f*} By ¹H 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 mol% of styrene exhibits an advancing contact angle of 101° and a receding contact angle of 89°. The introduction of 4-acetoxystyrene and 4-vinylmethylbenzoate into the copolymer results in the contact angle dropping to 92° (advancing) and 82° (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° (advancing) and 96° (receding).

The copolymerization of ethene with other vinyl monomers such as vinylcyclohexane (VCH), propene, 1-hexene, and methyl vinyl ketone (Μνκ) 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 mol% of 1-hexene, as determined by ¹H NMR spectroscopy. The structures of all the copolymer materials were confirmed by ¹H and ¹³C 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 $-CH_2CH=CHPh$ chain-ends formed by styrene insertion and subsequent β -H elimination. The formation of poly(ethene-*co*-styrene) was further confirmed by ${}^{13}C{}^{1}H$ NMR spectroscopy in 1,1,2,2-tetrachloroethane- d_2 at 110 °C. Both ¹H and ¹³C NMR analysis revealed the formation of linear copolymers. The ¹³C resonance at 28.6 ppm suggests the presence of ethene-ethene sequences, whereas resonances at 45 ppm, 36 ppm, and 28 ppm represent [-(Ph)CHCH₂CH₂-] 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 lowmolecular-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 β -H elimination following styrene insertion. The unsaturated carbons next to the aromatic ring show ¹³C 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 β -H elimination following ethene insertion occur to a much lower extent than the styrenic end groups.



Figure 4.2: Assignment of ¹³C{¹H} NMR spectrum of poly(ethene-*co*-styrene). (The Copolymer was dissolved in 1,1,2,2-tetrachloroethane- d_2 at 110 °C. Chemical shifts are assigned on the basis of literature values and are given in ppm. ^{13,17})

The ¹H NMR spectrum of poly(ethene-*co*-vinylcyclohexane) at 110 °C in 1,1,2,2-tetrachloroethane- d_2 shows resonances at 5.1 ppm and 5.5 ppm, suggesting $-CH_2CH=CHC_6H_{11}$ chain-ends, which were further confirmed by ¹³C 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 ¹³C NMR spectroscopy (2 s delay) are close to those calculated by ¹H NMR spectroscopy. ¹⁸ Furthermore, the ¹³C 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 β -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 ¹H NMR spectra of both poly(ethene-*co*-propene) and poly(ethene-*co*-1-hexene) show vinyl chain-ends. The predominant ¹H NMR resonances for poly(ethene-*co*-1-hexene) (~ 50 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) (4.3 mol% styrene) showed a T_m value of 106 °C, which is 23 °C



Figure 4.3: Assignment of ¹³C{¹H} NMR spectrum of poly(ethene-*co*-vinylcyclohexane). (The Copolymer was dissolved in 1,1,2,2-tetrachloroethane- d_2 at 110 °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 $T_{\rm m}$ value can be attributed to a drop in polyethene crystallinity due to incorporation of styrene units. The $T_{\rm m}$ values for poly(ethene-*co*-4-acet-oxystyrene) and poly(ethene-*co*-4-fluorostyrene) were 114 °C and 118 °C, respectively. Similarly, the DSC analysis of poly(ethene-*co*-vinylcyclohexane) containing 5.2 mol % of vinylcyclohexane shows a $T_{\rm m}$ value of 109 °C, whereas the copolymer with 11.8 mol % vinylcyclohexane does not show a $T_{\rm m}$ value but has a $T_{\rm g}$ value of -9 °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 5g of styrene and 200 psig of ethene giving 0.3g of copolymer with 5.8 mol % of styrene incorporation. The high-temperature GPC analysis of the polymer shows a monomodal peak with a M_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 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) [Pd(dba)₂] was obtained from Strem Chemicals and used as received. The phosphine sulfonate ligand ^{6,11} 2-[bis(2-methoxyphenyl)phosphino]benzenesulfonic acid (P SO_3H) 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 ¹H-, 121.49 MHz for ³¹P- or 75.4 MHz for ¹³C NMR spectra. ³¹P- and ¹³C 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 °C in tetrachloroethane- d_2 except for polyethene, which was analyzed at 80 °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_g) and melt-transition temperature (T_m) of the polymers were obtained using a differential scanning calorimeter, TA Instruments DSC Q100, in the temperature range of -70 °C to 200 °C, with a heating rate of 10 °C min⁻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 mLmin^{-1} and a three-column bed (Styragel HR $7.8 \times 300 \text{ mm}$ columns with 5 mm bead size: 100Da to 10000Da; 500Da to 30000Da; and 5000Da to 600000Da), a

Shimadzu RID 10A differential refractometer and SPD 10A UV-Vis detector. SEC samples were run in tetrahydrofuran at 35 °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 803S and two Shodex AT 806MS columns or Polymer Laboratories model 220 high-temperature chromatograph using polystyrene standards at 135 °C or 140 °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%(m/m) to 5%(m/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° C with an accuracy of 2° . 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 8.3×10^{-6} mol of 2, 1.66×10^{-5} mol of BPh₃, 10 mL of dichloromethane and 5g of styrene. The autoclave was charged with ethene to 100 psig and then placed in a preheated oil bath at 80 °C for 7h. 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 8.30×10^{-6} mol of **2**, 1.66×10^{-5} mol of BPh₃, 10 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 °C for 16h. 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 mg (8.30×10^{-6} mol) of **2**, 4 mg (1.66×10^{-5} mol) of BPh₃, 5 mL of dichloromethane and 6.16×10^{-3} 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 °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 mg $(1.35 \times 10^{-5} \text{ mol})$ of Pd(dba)₂, 6.5 mg $(1.61 \times 10^{-5} \text{ mol})$ of P^{SO}₃H ligand, 10 mg $(2.37 \times 10^{-5} \text{ mol})$ of galvinoxyl, 7.2 mg $(2.96 \times 10^{-5} \text{ mol})$ of BPh₃, 5.6 mg $(2.96 \times 10^{-5} \text{ mol})$ of 2,6-di-*tert*-butylpyridine, 10 mL of toluene and 5g 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 °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 7h. 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 ¹H NMR spectroscopy and showed the disappearance of the methyl resonance.

4.3.7 Synthesis of η^3 -Phenylethylpalladium Complex 17

First, the synthesis of (η^3 -phenylpropyl)palladium complex **16** was attempted by adapting the procedure we reported previously for η^3 -allyl- and (η^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 g, 0.1 mol); selenium oxide (0.222 g, 0.002 mol); and 1-phenyl-1-hydroxypropane (6.810 g, 0.05 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 ¹H 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 ¹H 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 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 Na₂PdCl₄ (0.883g, 294.21gmol⁻¹, 0.003mol) was dissolved in hot, degassed water (1.5mL) and filtered. The Pd solution was then added to a solution of PhCH(Cl)CH₂CH₃ (1.389g, 154.37gmol⁻¹, 0.009mol) in degassed methanol (30mL). 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 (η^3 -allyl)palladium chloride dimer as expected. This indicated that the (η^3 -phenylpropyl)palladium chloride dimer is not sufficiently stable for isolation. The most likely route of decomposition is through β -elimination to give β -methylstyrene and a palladium hydride species that is then reduced to 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 (P SO_3)PdCH₃(py) (0.2 mmol, 601.95 g mol⁻¹) and 0.145 g of BPh₃ (0.6 mmol, 242.12 g mol⁻¹) with 0.020 g of styrene (0.2 mmol, 104.15 g 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 BPh₃ and the yellow product. The product was re-precipitated with diethyl ether and dried. ¹H NMR analysis showed only signals at 8.1 ppm to 6.9 ppm (\sim 17H, aromatic), 3.9 ppm (OCH₃, s), 3.6 ppm (OCH₃, s), 3.2 ppm (CH, q) and 0.64 ppm (CH₃, dd). ³¹P 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 CH₃ 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 µmol), 0.015 g of BPh₃ (60 µmol) and 0.004 g of styrene (40 µmol) 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 ¹H- and ³¹P NMR and, after 18 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 BPh₃ 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 ¹H- and ³¹P NMR.

4.4 References

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CHAPTER FIVE

Copolymerization of Imines with Carbon Monoxide

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 atom-economical 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 $(L^L)PdCH_3^+BF_4^-$ systems, which undergo rapid insertion of carbon monoxide at 5 atm followed by slow insertion of PhCH=NPh or PhCH=NCH₃ to form the inactive palladicycles, $(L^L)PdCH(Ph)N(Ph)C(O)CH_3$ and $(L^L)PdCH(Ph)N(CH_3)C(O)CH_3$, 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'*,*N'*-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 PhCH=NCH₃ 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 carbon¹⁰ 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- α -amino acids.

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



 $\label{eq:scheme 5.1: Proposed catalytic cycle for the copolymerization of imines with carbon monoxide where L^L is a bidentate ligand, R is the growing polymer chain, R' is an aryl or alkyl group, and R'' is an aryl group.$

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 electron-withdrawing 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)PdCH₃⁺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)PdC(O)CH₃⁺BF₄⁻ 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)PdC(O)CH₃⁺BF₄⁻ was observed as shown in Table 5.1. Insertion was monitored by ¹H NMR and thermodynamics of insertion were measured for select imines by variable-temperature ¹H NMR. Also, it was possible to compare the relative palladium-amide 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.

Entry	Imine	ΔH^{\ddagger}	ΔS^{\ddagger}	$v_{c=0}$
		$(kJ mol^{-1})$	$(kJ K^{-1} mol^{-1})$	(cm^{-1})
1	PhCH=N-(<i>p</i> -Tol)	100.9	-0.1759	1672.9
2	PhCH=N-Ph	111.1	0.0548	1681.6
3	$PhCH=N-(p-C_6H_4CF_3)$	99.27	-0.1769	1673.8
4	$PhCH=N-(p-C_6H_4F)$	107.7	-0.1737	1659.8
5	PhCH=N $-C_6F_5^a$	N/A	N/A	
6	PhCH=N-OCH ₃ ^a	N/A	N/A	
7	PhCH=N-CH ₃			
8	PhCH=N-CF ₃			
9	PhCH=N-CN ^a	N/A	N/A	
10	PhCH=N-S(O) ₂ CH ₃ ^a	N/A	N/A	
11	PhCH=N-Cl ^b	N/A	N/A	
12	$PhCH=N-H^{b}$	N/A	N/A	

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

^a Imine insertion was not observed, even after heating to 50 °C.

^b Imine insertion was not observed due to decomposition.

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 Beller¹⁰ and Kacker¹ 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)PdCH₃⁺X⁻ complexes with anions of varying coordination strength were synthesized ($BF_4^- < Tf^- < Tos^- < NO_3^- < Br^- < Cl^-$), dissolved in dichloromethane- d_2 (1g) with PhCH=NPh, exposed to carbon monoxide at 5 atm, and heated to 80 °C. The reaction progress was monitored by ¹H NMR as shown in Table 5.2.

Entry	Anion	Solvent	Result
1	BF_4^-	tetrahydrofuran	CO, imine insertion
2	BF_4^-	dichloromethane	CO, imine insertion
3	BF_4^{-a}	dichloromethane	CO, imine insertion
4	Tf^{-}	tetrahydrofuran	CO insertion
5	Tf⁻	dichloromethane	CO, imine insertion
6	Tos-	tetrahydrofuran	CO insertion
7	Tos-	dichloromethane	CO, imine insertion
8	NO_3^-	tetrahydrofuran	no insertion
9	Br-	tetrahydrofuran	CO insertion
10	Br ⁻	dichloromethane	CO insertion
11	Cl^-	tetrahydrofuran	CO insertion
12	Cl^{-}	dichloromethane	CO insertion

Table 5.2: Effect of anions on imine 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 °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*-(PPh₃)₂PdCH₃Br was synthesized by addition of two equivalents of PPh₃ to (cod)PdCH₃Br. This was then dissolved in *N*,*N*-dimethylformamide- d_7 with five equivalants of lithium bromide and 5 atm carbon monoxide. After heating to 80 °C overnight, no imine insertion was observed.

Finally, the neutral, phosphine-sulfonate ligated palladium complex $(P^SO_3)PdCH_3$, **18**, 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 PhCH=NPh or PhCH=NCH₃, charging to 30 psig with carbon monoxide and heating to 90 °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 coworkers¹³ that PhCH=NCN, and to a lesser extent PhCH=NS(O)₂CH₃, 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 PhCH=NCN or PhCH=NS(O)₂CH₃ was dissolved in 4.1 mL (100 mmol) of acetonitrile with 20 μ mol of AIBN. The mixture was then charged with carbon monoxide to 20 atm and heated in a 100 °C bath for 3 days. The reaction mixtures were dissolved in dichloromethane- d_2 and analyzed by ¹H 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 °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 PhCH=NCN and PhCH=NS(O)₂CH₃, 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 3h. 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 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 Birkofer¹⁴ 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 (65 °C at 1 atm) to give ((CH₃)₃Si)₂NCN as a colorless liquid, which was pure by ¹H NMR. ((CH₃)₃Si)₂NCN and one equivalent of benzaldehyde were cooled to 0 °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 PhCH=NCN or PhCH=NS(O)₂CH₃, (dppp)PdCH₃(imine)⁺BF₄⁻ complexes were synthesized in the absence of light by dissolving (dppp)PdCH₃Cl (0.114 g, 200 μ mol) with three equivalents of imine in dichloromethane (5 mL). A solution of silver tetrafluoroborate (0.039 g, 200 μ 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.

PhCH=NCN and PhCH=NS(O)₂CH₃ 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)PdCH₃Cl 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.

 $(dppp)PdCH_3(OEt_2)^+BF_4^-$ was prepared using a method similar to that employed by Brookhart and coworkers for the synthesis of (phen)PdCH_3(OEt_2)(BArF).¹⁵ First, (dppp)Pd(CH_3)₂ was prepared in quantitative yield by dissolving (tmeda)Pd(CH_3)₂ (see Chapter 1) in a minimal amount of dichloromethane, adding one equivalent of DPPP, and precipitating with pentane. Next, 0.944 g (2 mmol) of (dppp)Pd(CH_3)₂ was dissolved in a 3:2 (v:v) mixture of dichloromethane and diethyl ether. In a separate container, 0.324 g (2 mmol) of HBF₄ · OEt₂ 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 °C until use. Yield = 1.044 g (84.5%).

In each trial, $20 \,\mu\text{mol}$ of $(\text{dppp})\text{PdCH}_3(\text{imine})^+\text{BF}_4$ 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. ¹H NMR spectra were then recorded every 10 min at 25 °C, 35 °C, and 45 °C to generate first-order kinetics plots and Eyring plots.

In all cases except for Br⁻ and Cl⁻, substitution of the anion was performed by dissolving (dppp)PdCH₃-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)PdCH₃Br was synthesized by dissolving palladium(II) bromide in concentrated hydrobromic acid followed by addition of excess 1,5-cyclooctadiene to precipitate (cod)PdBr₂ as a bright orange solid. Dissolving the solid in dichloromethane and adding excess tetramethyltin gave (cod)PdCH₃Br, which was reduced under vacuum and washed with diethyl ether to remove tin compounds. Finally, adding one equivalent of pppp gave the desired product.

5.5 References

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APPENDIX A

Copolymerization of Ethene with Carbon Monoxide: Mechanism

A.1 Nuclear magnetic resonance spectroscopy data






Figure A.3: ³¹P NMR spectrum of $(P \cap SO_3)$ PdCH₃ (py), **2**.

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Figure A.5: ^{31}P NMR spectrum of $(P^{\frown}SO_3)PdC(O)CH_3(py),$ 3.

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A.2 Low-temperature NMR spectroscopy data



Figure A.19: Low-temperature ${}^{1}H$ NMR spectra of (P ${}^{\circ}SO_{3}$)PdCH₂CH₂C(O)CH₃, 4.



 $\label{eq:Figure A.20: Low-temperature 1H NMR spectra of $(P^SO_3)PdCH_2CH_2COCOCH_3, 4$, (detail).}$



Figure A.21: Low-temperature ³¹P NMR spectra of (P^{SO}₃)PdCH₂CH₂C(O)CH₃, 4.





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 mol% carbon monoxide.

A.5 X-ray diffraction data

A.5.1 X-ray diffraction data for $(P^SO_3)PdCH_3(py)$, 2.



Figure A.25: Crystal structure for $(P^SO_3)PdCH_3(py)$, **2**.

Identification code	svb12s	
Crystallization solvents	Dichloromethane and pentane	
Crystallization method	Diffusion chamber	
Empirical formula	C ₂₆ H ₂₆ NO ₅ PPdS	
Formula weight	601.91	
Temperature	103(2)K	
Wavelength	0.71073Å	
Crystal size	$0.10\times0.07\times0.02\mathrm{mm}$	
Crystal habit	Colorless plate	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.484(5)Å	$\alpha = 90^{\circ}$
	b = 13.828(6)Å	$\beta = 97.515(8)^{\circ}$
	c = 16.239(6)Å	$\gamma = 90^\circ$
Volume	$2556.5(18)\text{\AA}^3$	
Ζ	4	
Density (calculated)	$1.564\mathrm{gcm^{-3}}$	
Absorption coefficient	$0.907{ m mm^{-1}}$	
F(000)	1224	

Table A.1: Sample and crystal data for $(P^SO_3)PdCH_3(py)$, **2**.

Table A.2: Data collection and structure refinement for $(P^SO_3)PdCH_3(py)$, **2**.

Diffractomator	con area detector
Dimactometer	
Radiation source	fine-focus sealed tube, Mo Kα
Generator power	1600W (50kV, 32mA)
Detector distance	5.8 cm
Data collection method	phi and omega scans
Theta range for data collection	1.94° to 28.38°
Index ranges	$-15 \le h \le 13, -17 \le k \le 18, -21 \le l \le 19$

	Х	Y	Z	$U_{(\mathrm{eq})}{}^a$
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)
01	0.5588(3)	0.7291(2)	0.20185(18)	0.0247(7)
02	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)
03	0.3978(3)	0.6219(2)	0.15974(17)	0.0217(7)
04	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)
05	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 $U_{\rm (eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Pd1-C1	2.027(5)	Pd1-N1	2.108(3)
Pd1-O3	2.165(3)	Pd1-P3	2.2317(12)
S1-O2	1.438(3)	S1-O1	1.449(3)
S1-O3	1.472(3)	S1-C13	1.786(4)
P3-C2	1.810(5)	P3-C14	1.821(4)
P3-C8	1.831(4)	N1-C25	1.331(6)
N1-C21	1.344(6)	O4-C19	1.375(6)
O4-C20	1.423(5)	C2-C3	1.385(6)
C2-C7	1.423(6)	C9-C10	1.389(6)
C9-C8	1.394(6)	C9-H9	0.9500
C8-C13	1.405(6)	C13-C12	1.397(6)
C14-C19	1.388(6)	C14-C15	1.391(6)
C12-C11	1.364(6)	C12-H12	0.9500
O5-C7	1.360(5)	O5-C26	1.440(6)
C11-C10	1.376(6)	C11-H11	0.9500
C4-C5	1.379(7)	C4-C3	1.392(6)
C4-H4	0.9500	C19-C18	1.394(6)
C3-H3	0.9500	C22-C23	1.354(6)
C22-C21	1.376(6)	C22-H22	0.9500
C7-C6	1.383(6)	C1-H1A	0.9800
C1-H1B	0.9800	C1-H1C	0.9800
C21-H21	0.9500	C5-C6	1.380(7)
C5-H5	0.9500	C23-C24	1.377(7)
C23-H23	0.9500	C10-H10	0.9500
C15-C16	1.375(7)	C15-H15	0.9500
C17-C18	1.358(8)	C17-C16	1.385(8)
C17-H17	0.9500	C16-H16	0.9500
C20-H20A	0.9800	C20-H20B	0.9800
C20-H20C	0.9800	C24-C25	1.368(7)
C24-H24	0.9500	C18-H18	0.9500
C25-H25	0.9500	C6-H6	0.9500
C26-H26A	0.9800	C26-H26B	0.9800
C26-H26C	0.9800		

Table A.4: Bond lengths (Å) for $(P^SO_3)PdCH_3(py)$, .

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)	01-S1-O3	110.38(17)
O2-S1-C13	106.96(17)	01-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)
С10-С9-Н9	119.0	С8-С9-Н9	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)	С2-С3-Н3	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.5: Bond angles (°) for $(P^SO_3)PdCH_3(py)$, **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.6: Torsion angles (°) for $(P^SO_3)PdCH_3(py)$, **2**.

_	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)
01	0.0196(17)	0.0277(17)	0.0280(16)	-0.0018(13)	0.0076(13)	-0.0034(13)
02	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)
03	0.0231(17)	0.0195(15)	0.0235(15)	-0.0034(12)	0.0065(13)	-0.0027(13)
04	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)
05	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)

 Table A.7: Anisotropic atomic displacement parameters (Å²) for $(P^SO_3)PdCH_3(py)$, 2.^a

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

	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
H1C	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
H10	0.1651	0.9728	0.2972	0.031
H15	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

Table A.8: Hydrogen atom coordinates and
isotropic atomic displacement parameters ($Å^2$) for
 $(P^SO_3)PdCH_3(py)$, 2.

A.5.2 X-ray diffraction data for $(P^SO_3)PdC(O)CH_3(py)$, 3



Figure A.26: Crystal structure for $(P^SO_3)PdC(O)CH_3(py)$, **3**.

Identification code	svb13				
Crystallization solvents	Dichloromethane and pentane				
Crystallization method	Diffusion chamber				
Empirical formula	C ₂₇ H ₂₆ NO ₆ PPdS				
Formula weight	629.92				
Temperature	293(2)K				
Wavelength	0.71073Å				
Crystal size	$0.17 \times 0.13 \times 0.05 \mathrm{mm}$				
Crystal habit	yellow plate				
Crystal system	Monoclinic				
Space group	P2(1)/c				
Unit cell dimensions	a = 11.567(2)Å	$\alpha = 90^{\circ}$			
	b = 14.097(3)Å	$\beta = 96.68(3)^{\circ}$			
	c = 16.198(3)Å	$\gamma = 90^{\circ}$			
Volume	2623.5(9)Å				
Ζ	4				
Density (calculated)	$1.595{ m gcm^{-3}}$				
Absorption coefficient	$0.891{ m mm^{-1}}$				
F(000)	1280				

Table A.9: Sample and crystal data for $(P^SO_3)PdC(O)CH_3(py)$, **3**.

Table	A.10:	Data	collection	and	structure	refinement	for
		($(P^SO_3)PdC(0)$	0)CH ₃ (ру), З .		

Diffractometer	CCD area detector
Radiation source	fine-focus sealed tube, Mo Kα
Generator power	1600W (50kV, 32mA)
Detector distance	5.8 cm
Data collection method	phi and omega scans
Theta range for data collection	1.77 to 28.36°
Index ranges	$-15 \le h \le 15, -18 \le k \le 17, -15 \le l \le 21$

	Х	Y	Ζ	$U_{(eq)}$
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)
01	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)
04	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)
06	0.5097(3)	0.2928(2)	0.16075(18)	0.0260(7)
05	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)

Table A.11: Atomic coordinates and equivalent isotropic atomicdisplacement parameters (Å²) for (P^SO₃)PdC(O)CH₃(py), **3**.

 $a U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.12: Bond lengths (Å) for $(P^SO_3)PdC(O)CH_3(py)$, **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)	С9-Н9	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		

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)	03-S1-O1	112.38(18)	02-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)	С10-С9-Н9	119.4
С8-С9-Н9	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	С11-С10-Н10	120.4	C7-C6-C5	119.5(4)
С7-С6-Н6	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	С22-С23-Н23	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.13: Bond angles (°) for $(P^SO_3)PdC(O)CH_3(py)$, **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.14: Torsion angles (°) for $(P^SO_3)PdC(O)CH_3(py)$, **3**.
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	<i>U</i> 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)
01	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)
04	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)
06	0.0204(16)	0.0364(19)	0.0199(16)	-0.0076(14)	-0.0037(13)	-0.0088(14)
05	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)

Table A.15: Anisotropic atomic displacement parameters (Å2) for (P^SO3)PdC(O)CH3(py), **3**.

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

	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

Table A.16: Hydrogen atom coordinates and
isotropic atomic displacement parameters (Å2)
for $(P^SO_3)PdC(O)CH_3(py)$, **3**.

APPENDIX B

Copolymerization of Ethene with Carbon Monoxide: Kinetics and Thermodynamics



Figure B.1: Van 't Hoff plot for the equilibrium $\mathbf{4} + C_2 H_4$.



Figure B.2: Van 't Hoff plot for the equilibrium 4 + CO $\xrightarrow{K_2}$ 8.



Figure B.3: Eyring plot for the migratory insertion reaction $\mathbf{2} + C_2 H_4 \xrightarrow{k_E} \mathbf{9}$.



Figure B.4: Eyring plot for the migratory insertion reaction $2 + CO \xrightarrow{k_{CO}} 10$.



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



Figure B.6: $^1\mathrm{H}$ NMR spectrum of 2 with carbon monoxide.





Figure B.8: ¹H NMR spectrum of $3 + C_2 H_4 \xrightarrow{K_1} 4$ at 50 °C.



Figure B.9: ¹H NMR spectrum of $\mathbf{1} + CO \xrightarrow{k_{CO}} \mathbf{7}$ at $-30 \,^{\circ}C$.

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APPENDIX C

Copolymerization of Ethene with Functional Norbornenes

C.1 X-ray diffraction data for ligand 13·CH₂Cl₂

A total of 1850 frames were collected with a scan width of 0.3° in ω and an exposure time of 10s per frame. The total data collection time was about 8h. 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 θ angle of 28.31° (0.90 Å resolution), of which 5915 were independent, completeness = 95.9%, $R_{int} = 0.0277$, $R_{sig} = 0.0304$ and 5190 were greater than 2σ (I). The final cell constants: a = 13.979(2)Å, b = 11.9196(17)Å, c = 15.071(2)Å, $\alpha = 90^{\circ}$, $\beta = 99.700(2)^{\circ}$, $\gamma = 90^{\circ}$, volume = 2475.2(6)Å³, are based upon the refinement of the XYZ-centroids of 5313 reflections above 20σ (I) with 2.189° < θ < 28.271°. 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 P2(1)/c, with Z = 4 for the formula unit, $C_{23}H_{25}Cl_2O_7PS$. 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 $wR_2 = 10.36\%$ for all data. The goodness-of-fit was 1.070. The largest peak on the final difference map was 0.559 eÅ^{-3} and the largest hole was -0.428 eÅ^{-3} . Based on the final model, the calculated density of the crystal is 1.469 g cm⁻³ and F(000) amounts to 1136 electrons.

Empirical formula $C_{23}H_{25}Cl_2O_7PS$ Formula weight547.36Temperature98(2) KWavelength0.71073ÅCrystal size0.43 × 0.39 × 0.36 mmCrystal habitClear brickCrystal systemMonoclinicSpace groupP2(1)/cUnit cell dimensions $a = 13.979(2)$ Å $a = 15.071(2)$ Å $\gamma = 90^{\circ}$ Volume2475.2(6)Å ³ Z4Density (calculated)1.469 g cm^{-3}			
Formula weight547.36Temperature98(2) KWavelength0.710 73 ÅCrystal size $0.43 \times 0.39 \times 0.36 \mathrm{mm}$ Crystal habitClear brickCrystal systemMonoclinicSpace groupP2(1)/cUnit cell dimensions $a = 13.979(2)$ Å $a = 90^{\circ}$ $b = 11.9196(17)$ Å $\beta = 99.700(2)^{\circ}$ $c = 15.071(2)$ Å $\gamma = 90^{\circ}$ Volume2475.2(6)Å^3Z4Density (calculated) $1.469 \mathrm{g cm^{-3}}$	Empirical formula	C ₂₃ H ₂₅ Cl ₂ O ₇ PS	
Temperature98(2) KWavelength 0.71073 Å Crystal size $0.43 \times 0.39 \times 0.36 \text{ mm}$ Crystal habitClear brickCrystal systemMonoclinicSpace groupP2(1)/cUnit cell dimensions $a = 13.979(2) \text{ Å}$ $a = 90^{\circ}$ $b = 11.9196(17) \text{ Å}$ $\beta = 99.700(2)^{\circ}$ $c = 15.071(2) \text{ Å}$ $\gamma = 90^{\circ}$ Volume2475.2(6) \text{ Å}^3Z4Density (calculated) 1.469 g cm^{-3}	Formula weight	547.36	
Wavelength 0.71073 ÅCrystal size $0.43 \times 0.39 \times 0.36$ mmCrystal habitClear brickCrystal systemMonoclinicSpace groupP2(1)/cUnit cell dimensions $a = 13.979(2)$ Å $a = 13.979(2)$ Å $\beta = 99.700(2)^{\circ}$ $c = 15.071(2)$ Å $\gamma = 90^{\circ}$ Volume2475.2(6)Å ³ Z 4Density (calculated) 1.469g cm^{-3}	Temperature	98(2)K	
Crystal size $0.43 \times 0.39 \times 0.36 \mathrm{mm}$ Crystal habitClear brickCrystal systemMonoclinicSpace groupP2(1)/cUnit cell dimensions $a = 13.979(2)$ Å $a = 90^{\circ}$ $b = 11.9196(17)$ Å $\beta = 99.700(2)^{\circ}$ $c = 15.071(2)$ Å $\gamma = 90^{\circ}$ Volume2475.2(6)Å^3 Z 4Density (calculated)1.469 g cm^{-3}	Wavelength	0.71073Å	
Crystal habitClear brickCrystal systemMonoclinicSpace group $P2(1)/c$ Unit cell dimensions $a = 13.979(2)$ Å $a = 90^{\circ}$ $b = 11.9196(17)$ Å $\beta = 99.700(2)^{\circ}$ $c = 15.071(2)$ Å $\gamma = 90^{\circ}$ Volume $2475.2(6)$ Å ³ Z4Density (calculated) $1.469 {\rm g cm^{-3}}$	Crystal size	$0.43\times0.39\times0.36\mathrm{mm}$	
Crystal systemMonoclinicSpace group $P2(1)/c$ Unit cell dimensions $a = 13.979(2)$ Å $\alpha = 90^{\circ}$ $b = 11.9196(17)$ Å $\beta = 99.700(2)^{\circ}$ $c = 15.071(2)$ Å $\gamma = 90^{\circ}$ Volume $2475.2(6)$ Å ³ Z4Density (calculated) $1.469 {\rm g cm^{-3}}$	Crystal habit	Clear brick	
Space group P2(1)/c Unit cell dimensions $a = 13.979(2)$ Å $\alpha = 90^{\circ}$ $b = 11.9196(17)$ Å $\beta = 99.700(2)^{\circ}$ $c = 15.071(2)$ Å $\gamma = 90^{\circ}$ Volume 2475.2(6)Å ³ Z 4 Density (calculated) 1.469 g cm ⁻³	Crystal system	Monoclinic	
Unit cell dimensions $a = 13.979(2)$ Å $\alpha = 90^{\circ}$ $b = 11.9196(17)$ Å $\beta = 99.700(2)^{\circ}$ $c = 15.071(2)$ Å $\gamma = 90^{\circ}$ Volume 2475.2(6)Å ³ Z 4 Density (calculated) 1.469 g cm ⁻³	Space group	P2(1)/c	
$b = 11.9196(17) \text{\AA} \qquad \beta = 99.700(2)^{\circ}$ $c = 15.071(2) \text{\AA} \qquad \gamma = 90^{\circ}$ Volume 2475.2(6) \text{\AA}^{3} Z 4 Density (calculated) 1.469 g cm ⁻³ the size 26 is a 2.152 set b	Unit cell dimensions	a = 13.979(2)Å	$\alpha = 90^{\circ}$
$c = 15.071(2) \text{\AA} \qquad \gamma = 90^{\circ}$ Volume 2475.2(6) \AA^3 Z 4 Density (calculated) 1.469 g cm ⁻³		b = 11.9196(17)Å	$\beta = 99.700(2)^{\circ}$
Volume $2475.2(6)$ Å ³ Z4Density (calculated) $1.469 {\rm g cm^{-3}}$		c = 15.071(2)Å	$\gamma = 90^{\circ}$
Z 4 Density (calculated) 1.469 g cm ⁻³	Volume	$2475.2(6)\text{\AA}^3$	
Density (calculated) $1.469 \mathrm{g cm^{-3}}$	Ζ	4	
	Density (calculated)	$1.469{ m gcm^{-3}}$	
Absorption coefficient $0.453 \mathrm{mm}^{-1}$	Absorption coefficient	$0.453{ m mm^{-1}}$	
F(000) 1136	<i>F</i> (000)	1136	

Table C.1: Sample and crystal data for ligand $13\cdot \mathrm{CH}_2\mathrm{Cl}_2.$

Table C.2: Data collection and structure refinement of ligand $13\cdot \mathrm{CH_2Cl_2}.$

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

	Х	Y	Z	$U_{ m (eq)}{}^a$
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)
06	0.03110(8)	0.45539(10)	0.37571(7)	0.0205(2)
04	0.23379(8)	0.72778(10)	0.49748(7)	0.0200(2)
05	0.01396(8)	0.66359(10)	0.23357(7)	0.0201(2)
03	0.20821(8)	0.45847(10)	0.14166(7)	0.0207(2)
02	0.25387(8)	0.36488(9)	0.28523(7)	0.0211(2)
07	0.35477(8)	0.52601(10)	0.50028(7)	0.0217(2)
01	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	0.304 44(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)
Cl2	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)

 $\label{eq:table_c.3:} \mbox{ Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) of ligand 13 \cdot CH_2Cl_2.$

 a $U_{\rm (eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

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)	07-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.4: Bond lengths (Å) of ligand $13 \cdot CH_2Cl_2$.

Table C.5: Bond angles (°) of ligand $13 \cdot \text{CH}_2\text{Cl}_2$.

O1-S1-O3	113.69(7)	01-S1-O2	114.44(7)	O3-S1-O2	112.37(7)
01-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)	Cl2-C21-Cl1	111.02(11)

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

A yellow, cuboidal shaped crystal of complex 14 ($C_{23}H_{22}O_5PPdS$) with approximate dimensions of 0.11 × 0.14 × 0.20 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 α fine-focus sealed tube ($\lambda = 0.71073$) operated at 1600 W power (50 kV, 32 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° in ω and an exposure time of 20 s per frame. The total data collection time was about 10h. 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 θ angle of 28.30° (0.90 Å resolution), of which 5208 were independent, completeness = 96.1%, $R_{int} = 0.0207$, $R_{sig} = 0.0297$ and 4486 were greater than 2σ (I). The final cell constants: a = 10.8667(11)Å, b = 17.0383(18)Å, c = 11.8080(13)Å, $\alpha = 90^{\circ}$, $\beta = 95.365(2)^{\circ}$, $\gamma = 90^{\circ}$, volume = 2176.7(4)Å³, are based upon the refinement of the XYZ-centroids of 5300 reflections above 20σ (I) with 2.230° < θ < 28.148°. 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, $C_{23}H_{22}O_5PPdS$. 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 $wR_2 = 11.34\%$ for all data. The goodness-of-fit was 1.066. The largest peak on the final difference map was $1.872 \text{ e}^{A^{-3}}$ and the largest hole was $-1.480 \text{ e}^{A^{-3}}$. Based on the final model, the calculated density of the crystal is 1.672 g cm^{-3} and F(000) amounts to 1108 electrons.

Empirical formula	C ₂₃ H ₂₃ O ₅ PPdS	
Formula weight	547.84	
Temperature	SI108(2)K	
Wavelength	0.71073Å	
Crystal size	$0.20\times0.14\times0.11\text{mm}$	
Crystal habit	yellow cuboidal	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.8667(11)Å	$\alpha = 90^{\circ}$
	b = 17.0383(18)Å	$\beta = 95.365(2)^{\circ}$
	c = 11.8080(13)Å	$\gamma = 90^{\circ}$
Volume	$2176.7(4)\text{\AA}^3$	
Ζ	4	
Density (calculated)	$1.672{ m g}{ m cm}^{-3}$	
Absorption coefficient	$1.055{ m mm^{-1}}$	
<i>F</i> (000)	1108	

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

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

CCD area detector
fine-focus sealed tube, Mo Ka
1600W (50kV, 32mA)
5.8 cm
phi and omega scans
2.10° to 28.30°
$-14 \le h \le 13, -22 \le k \le 21, -11 \le l \le 15$

	Х	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)
02	0.4966(2)	0.32904(13)	0.7657(2)	0.0254(5)
01	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)
04	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)
05	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)
C20	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)
C12	0.7150(3)	0.0673(2)	0.7499(3)	0.0266(7)
C17	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)	-0.02145(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)

Table C.8: Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for complex 14.

 a $U_{\rm (eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table C.9: Bond lengths (Å) for complex 14.

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	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)				

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)	С10-С9-Н9	120.3
С8-С9-Н9 120.3 С4-С3-С2 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)	С7-С8-Н8	119.5
С9-С8-Н8 119.5 С21-С22-С23 141.7(10)	C21-C22-H22	109.2
C23-C22-H22 109.2		

 Table C.10:
 Bond angles (°) for complex 14.

C.3 X-ray diffraction data for crotylpalladium complex 15.2 CHCl₃

A yellow, cubical shaped crystal of complex 15.2 CHCl_3 ($\text{C}_{26}\text{H}_{25}\text{Cl}_6\text{O}_5\text{PPdS}$) with approximate dimensions of $0.24 \times 0.36 \times 0.38$ mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 298(2)K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo K α fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 1600W power (50kV, 32 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° in ω and an exposure time of 5s per frame. The total data collection time was about 6h. 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 θ angle of 28.35° (0.90Å resolution), of which 7864 were independent, completeness = 97.8%, $R_{int} = 0.0528$, $R_{sig} = 0.0716$ and 5960 were greater than 2σ (I). The final cell constants: a = 14.9431(19)Å, b = 10.2521(13)Å, c = 21.630(3)Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, volume = 3313.7(7)Å³, are based upon the refinement of the XYZ-centroids of 3723 reflections above 20σ (I) with 2.409° < $\theta < 21.132^\circ$. 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, $C_{26}H_{25}Cl_6O_5PPdS$. The final anisotropic full-matrix least-squares refinement on F^2 with 366 variables converged at $R_1 = 5.35\%$, for the observed data and wR2 = 12.86% for all data. The goodness-of-fit was 1.024. The largest peak on the final difference map was $0.928 \text{ e}\text{Å}^{-3}$ and the largest hole was $-0.437 \text{ e}\text{Å}^{-3}$. Based on the final model, the calculated density of the crystal is 1.603 g cm⁻³ and F(000) amounts to 1600 electrons.

Empirical formula	C ₂₆ H ₂₅ Cl ₆ O ₅ PPdS	
Formula weight	799.59	
Temperature	298(2)K	
Wavelength	0.71073Å	
Crystal size	$0.38\times0.36\times0.24\text{mm}$	
Crystal habit	yellow cubical	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 14.9431(19)Å	$\alpha = 90^{\circ}$
	b = 10.2521(13)Å	$\beta = 90^{\circ}$
	c = 21.630(3)Å	$\gamma = 90^{\circ}$
Volume	3313.7(7)Å ³	
Ζ	4	
Density (calculated)	$1.603{ m gcm^{-3}}$	
Absorption coefficient	$1.189{ m mm^{-1}}$	
F(000)	1600	

Table C.11: Crystal data and structure refinements of complex 15.2 CHCl_3 .

Table C.12: Data collection and structure refinement for complex 15.2 CHCl₃.

Diffractometer	CCD area detector
Radiation source	fine-focus sealed tube, Mo Ka
Generator power	1600W (50kV, 32mA)
Detector distance	5.8 cm
Data collection method	phi and omega scans
Theta range for data collection	1.88° to 28.35°
Index ranges	$-19 \le h \le 13, -12 \le k \le 13, -28 \le l \le 28$

	Х	Y	Z	$U_{(\mathrm{eq})}{}^a$
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)
Cl2	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)
Cl4	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)
01	0.8823(3)	-0.3087(3)	0.95091(19)	0.0563(10)
02	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)
06	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)
	. ,	. ,		

 $\label{eq:conditional} \begin{array}{l} \textbf{Table C.13:} \ Atomic \ coordinates \ and \ equivalent \ isotropic \ atomic \ displacement \ parameters \ (\text{\AA}^2) \ for \ complex \ \textbf{15.2 \ CHCl}_3. \end{array}$

 a $U_{\rm (eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

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)
С9-Н9	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-Cl1	1.736(10)
C25-Cl3	1.787(10)	C25-H25	0.9800	C26-Cl5	1.690(10)
C26-Cl6	1.701(10)	C26-Cl4	1.724(11)	C26-H26	0.9800
01-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.14: Bond lengths (°) for complex 15.2 CHCl_3 .

Table C.15: Bond angles (°) for complex $15 \cdot 2 \text{ CHCl}_3$.

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)	С9-С8-Н8	119.7	С7-С8-Н8	119.7
C10-C9-C8	120.0(7)	С10-С9-Н9	120.0	С8-С9-Н9	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
Cl2-C25-Cl1	110.7(5)	Cl2-C25-Cl3	111.9(5)	Cl1-C25-Cl3	107.9(6)
Cl2-C25-H25	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	Cl6-C26-H26	107.6	Cl4-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)	01-S1-O2	115.5(2)	01-S1-O3	112.3(2)
O2-S1-O3	109.8(2)	O1-S1-C6	106.5(2)	O2-S1-C6	107.2(2)
03-81-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 $P^SO_3PdCH_3(py)$, **2**.
































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.