

STUDIES OF SOLUBLE POLYMER-SUPPORTED ORGANOCATALYSTS

A Dissertation

by

YUN-CHIN YANG

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

August 2012

Major Subject: Chemistry

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ABSTRACT

Studies of Soluble Polymer-supported Organocatalysts. (August 2012)

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Chair of Advisory Committee: Dr. David E. Bergbreiter

Polymer-supported reagents and catalysts have been extensively studied in the past few decades as they not only facilitate separation and isolation of products after reactions but also enable reuse of reagents/catalysts. In particular, chemistry using polymer-supported organocatalysts has the advantage of avoiding the use of sometimes toxic transition metals. Since organocatalysts are often used at high mol% loading in catalytic reactions, immobilizing organocatalysts on polymers for recycling and reusing makes chemistry using organocatalysts attractive in larger scale syntheses. Chapter II of this dissertation focuses on using variable temperature ^{31}P NMR spectroscopy to study and compare the dynamic behavior of silver complexes prepared from soluble polymer-supported phosphines and electronically similar low molecular weight phosphine ligands. The phosphine-silver complexes supported on terminally functionalized polyisobutylene (PIB) and poly(ethylene glycol) show similar kinetic behavior compared to their low molecular weight counterparts. However, the dynamic behavior of phosphine-silver complexes supported as pendent groups on a linear polystyrene is difficult to study because of significant line-broadening on ^{31}P NMR spectra. Chapter III of this dissertation aims at examining the recyclability and reusability of PIB-

supported phosphines as organocatalysts and reagents. PIB-supported alkyldiphenyl- and aryldiphenylphosphines were prepared and used as recyclable organocatalysts in addition and allylic amination reactions. The PIB-bound phosphines were useful reagents in aza-Wittig and Mitsunobu reactions. The PIB-bound phosphine oxides formed either from adventitious oxidation or during the course of reactions can be reduced to PIB-phosphines for reuse. Chapter IV of this dissertation describes preliminary studies on soluble polymer-supported *N*-heterocyclic carbene (NHC) organocatalysts. PIB- and polyethylene oligomer (PE_{Olig})-supported NHC adducts were synthesized and the corresponding polymer-supported NHC catalysts were generated *in situ* in lactide polymerization and phenyl isocyanate trimerization reactions. The PIB-bound NHC catalyst generated *in situ* was not recyclable in a lactide polymerization. However, PIB- and PE_{Olig}-bound NHC precatalysts showed modest recyclability in lactide polymerization and phenyl isocyanate trimerizations.

DEDICATION

To my family, especially my wife for her love and support throughout this process.

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First of all, I would like to thank Prof. David E. Bergbreiter for being a great mentor and teacher. I really thank him for the opportunity to work in his group for five years and his support for me to go to conferences. In his group, I learned how to analyze problems critically and propose useful solutions promptly. I also want to thank him for being fair and supportive to every student in a way which is never seen anywhere else.

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CHAPTER I

INTRODUCTION

In the past few decades, numerous important ligands, catalysts, and reagents have been developed to fulfill synthetic chemists' needs for reagents and/or catalysts for bond formation, functional group transformation, and the construction of complex organic frameworks. However, reuse of reagents or separation, reuse, and recycling of catalysts remain an unresolved issue in most cases. For example, although many ligand/catalyst combinations have been developed to demonstrate high activity and good selectivity with low catalyst loading, some concerns regarding the use of these reactions in industrial applications still remain. These include: (1) the high cost of many transition metals, (2) the high cost incurred in the synthesis and purification of ligands, and (3) the toxicity of ligands and catalysts. These economic, environmental, and safety concerns can pose problems in the application and use of these reagents and catalysts in industry. Therefore, studies that address the reuse and recovery of these ligands/catalysts/reagents have attracted much attention.

While there are many different types of reagents and catalysts, organocatalysts have recently received heightened attention because they avoid the use of expensive and sometimes toxic transition metals. In many cases, their mode of action mimics that of catalysts nature uses. However, these catalysts often are used at high mol% loading.

This dissertation follows the style of *Journal of the American Chemical Society*.

Moreover, while their toxicity can be less than that of metal-containing catalysts, their separation, recovery, and reuse remains of interest. There are literally thousands of examples of organocatalysts. Many examples have also been described where such catalysts are immobilized on divinylbenzene (DVB) crosslinked polystyrene resins. A representative but not comprehensive list of such polymer-bound organocatalysts bound to Merrifield resin or similar insoluble supports is provided in Figure 1.¹⁻¹⁸

The Merrifield^{19,20} and Letsinger²¹ concept of using insoluble polymer supports for synthesis, using insoluble polymer supports as handles to recycle and reuse ligands/catalysts/reagents has attracted wide attention.²²⁻²⁴ Such supports allow for facile separation of polymer-supported ligands/catalysts from product(s) by simple filtration. However, there are disadvantages associated with the insolubility of these species too. For example, detailed characterization of ligands, catalysts, or reagents bound to insoluble polymer supports by conventional solution state spectroscopic techniques, e.g. NMR spectroscopy, is more difficult. In addition, the reactivity and selectivity of ligand/catalyst combinations are sometimes different than the reactivity and selectivity of non-polymer-supported species due to the heterogeneous reaction conditions necessarily present during the use of species on a crosslinked polymer support. In order to keep the advantage of simple separation and at the same time solve the problems arising from insoluble supports, methods that use soluble polymer-supported ligands/catalysts/reagents have been developed.^{17,25,26} However, separation of these polymer-supported species from a reaction mixture can also be problematic. For example, while PEG supports are readily available in many organic solvents, the solvent

precipitation recovery techniques often used to separate/recover such supported species generate significant solvent waste.

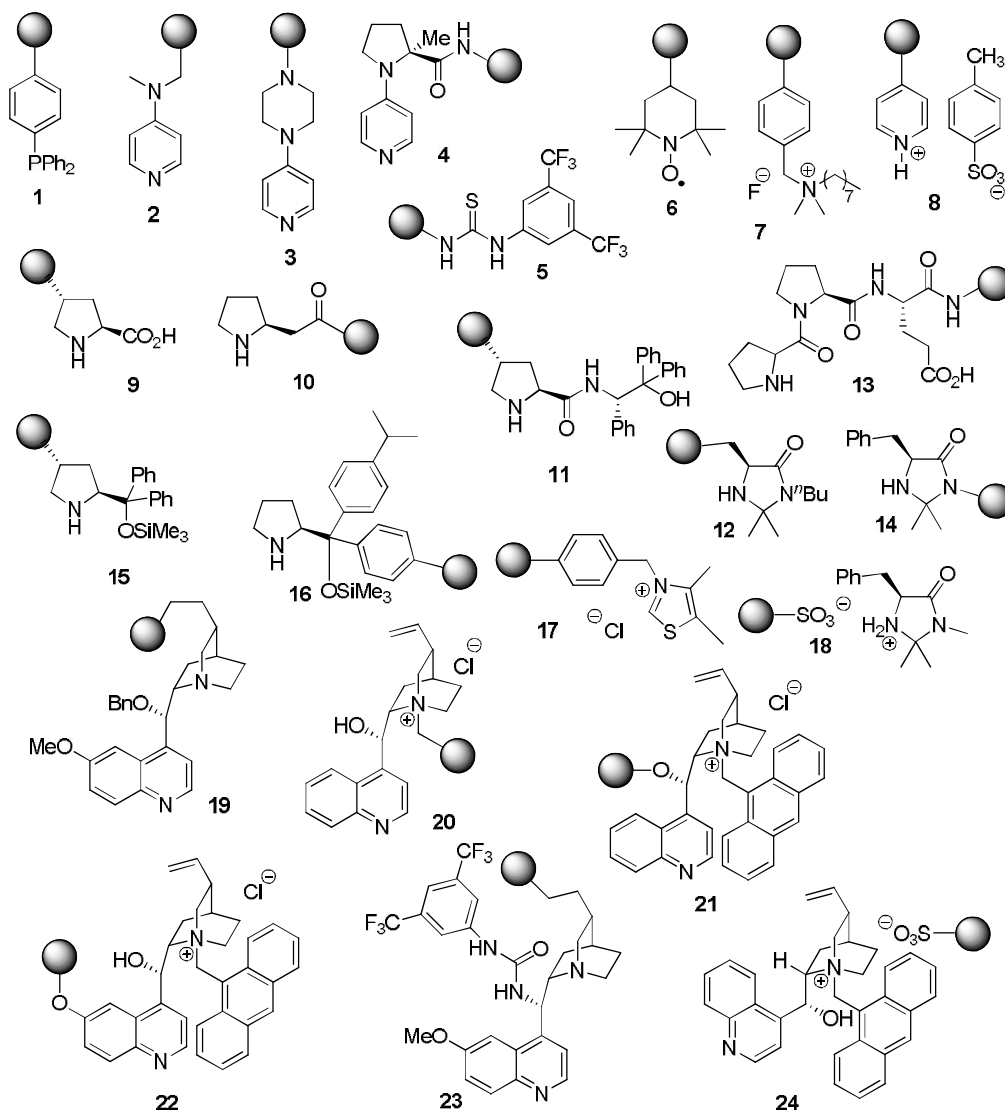


Figure 1. Examples of insoluble polymer-supported organocatalysts

The Bergbreiter group is among a number of groups that have studied strategies that facilitate separation of polymer-bound species from products. There are two systems heavily employed by our group: (a) thermomorphic separations, and (b) latent biphasic separations. Thermomorphic systems can be divided into solid/liquid and liquid/liquid separation systems as shown in Figure 2.

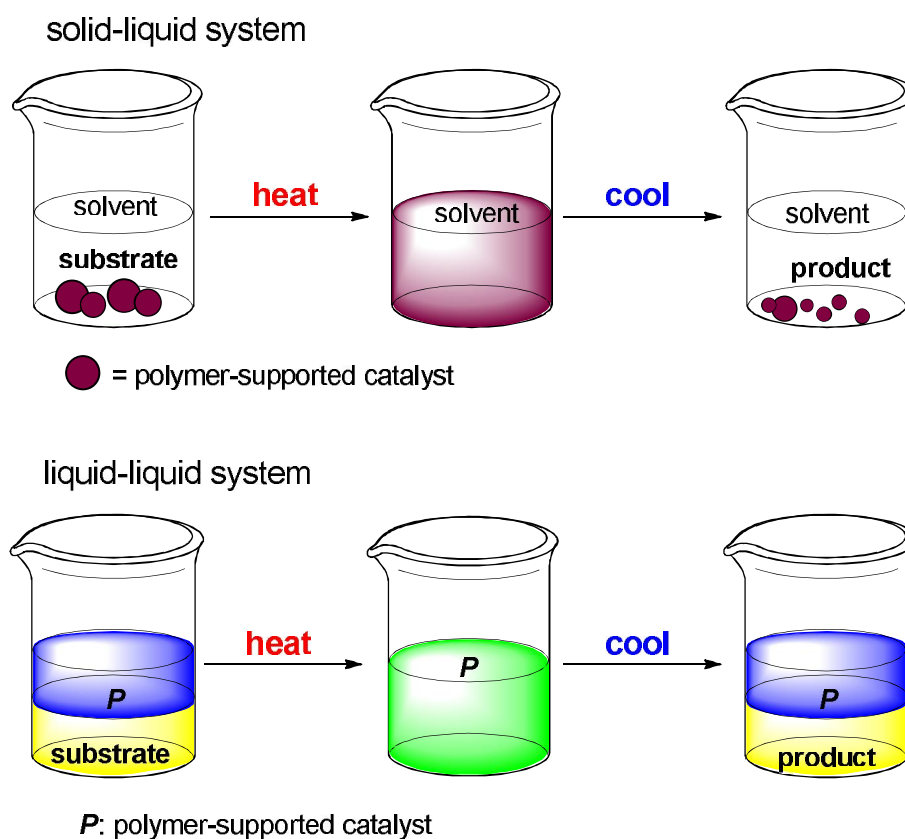


Figure 2. Thermomorphic systems

In a solid/liquid system, the polymer support is usually insoluble at lower temperature and becomes soluble at higher temperature. By raising the temperature,

reactions can thus be carried out under homogeneous reaction conditions. Then upon cooling, the polymer-supported catalyst precipitates while the products stay in solution. The polymer-supported catalyst can then be separated from the product solution by a simple filtration and then can be reused in the following cycle. Alternatively, one can use a liquid/liquid system comprised of a mixture of a nonpolar and a polar solvent which is immiscible at some temperature, but becomes monophasic at another temperature. In a liquid-liquid thermomorphic system, the polymer-supported catalyst is designed such that it is selectively soluble in one phase of the biphasic solvent mixture at room temperature but soluble in the hot monophasic system. This makes it possible for reactions to occur under homogeneous reaction conditions. Then, after the reaction is complete, the system is cooled to regenerate a biphasic mixture. A simple gravity separation can then separate the catalyst-containing solution from the product solution when the product solubility is such that it is mostly present in the phase that does not contain the catalyst.

Using a latent biphasic system is another way to separate soluble polymer-bound catalysts as shown in Figure 3. It requires the use of at least two solvents that form a single phase that is at its cusp of miscibility. By introducing a perturbation, this solvent mixture separates into two separate phases. In the case, it is possible to carry out a reaction at room temperature or below under homogeneous conditions and then to perturb the system into two phases: one containing the product and the other containing

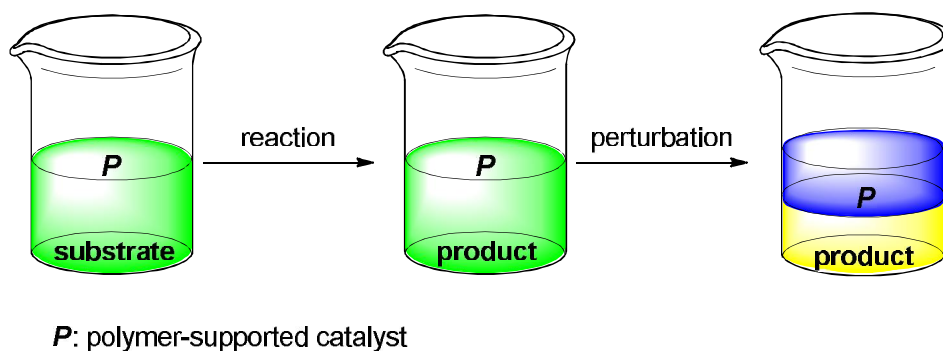


Figure 3. Latent biphasic system

the polymer-supported catalyst. For example, when using heptane and 95% ethanol-water as the solvent mixture, the addition of <5 vol% water is enough to produce a biphasic mixture.

While others have focused on insoluble cross-linked polymer supports, a goal in my work was to use soluble polymers. There are many different soluble polymer supports that have been studied to facilitate catalyst separation. Some of the polymers that have been used are shown in Figure 4 and include polyisobutylene (PIB) **25**, poly(ethylene glycol) (PEG) **26**, polystyrene (PS) **27**, poly(*tert*-butylstyrene) (PTBS) **28**, polyethylene (PE) **29**, dendrimer **30**, addition polymers with pendent groups **31**, and peptide **32**.

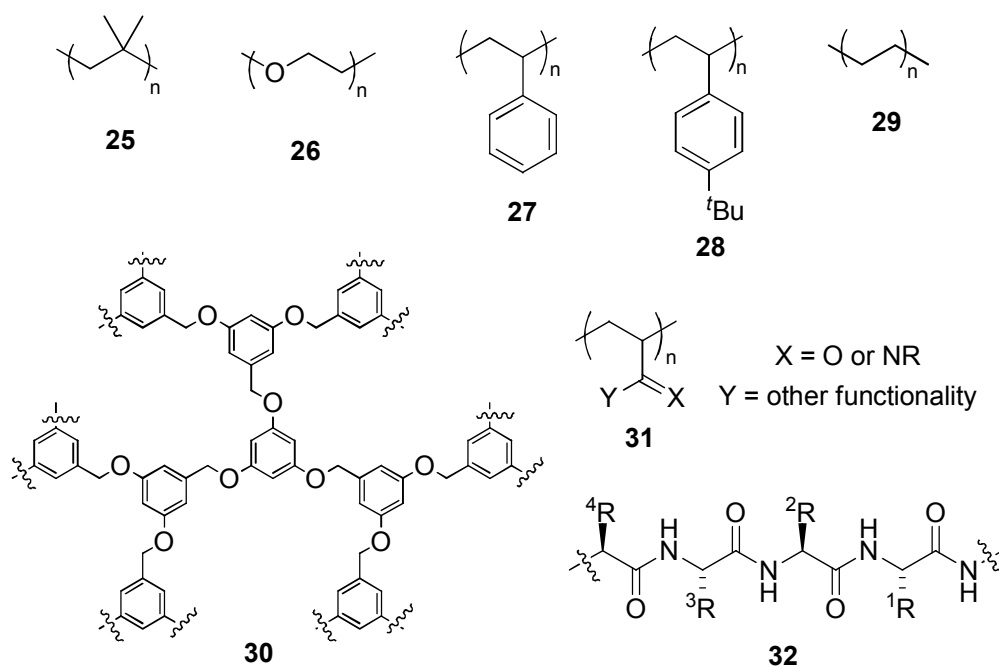
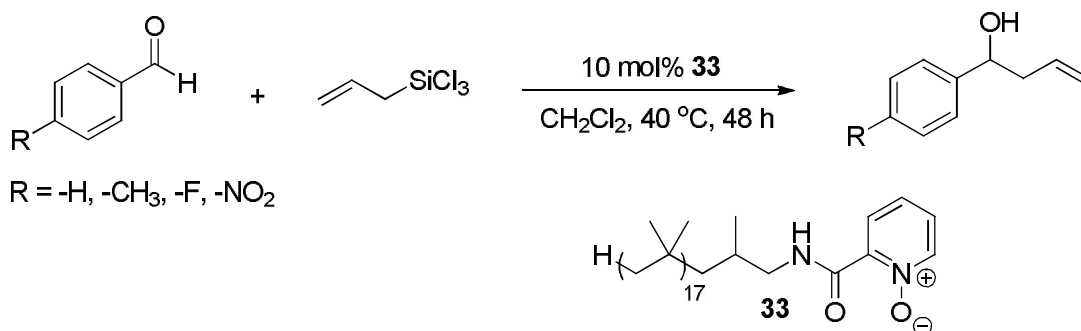


Figure 4. Common soluble polymer supports

As noted above, organocatalysts are currently of intensive interest as metal-free alternatives to commonly used organometallic catalysts. Although many organocatalysts have the advantages of air- and moisture-stability, column chromatography is typically used to separate these catalysts from the products. Therefore, immobilization of organocatalysts on polymer supports for easy recovery and reuse is highly attractive. There are many recent reports of insoluble polymer-supported organocatalysts as illustrated by the examples in Figure 1. However, my work was focused on soluble polymer supports and I will only discuss background work where organocatalysts immobilized on soluble polymer supports in the balance of this introduction.

Some work from our group on organocatalysts preceded my work. In that work, Bergbreiter and Ortiz-Acosta²⁷ synthesized a PIB-supported pyridine *N*-oxide catalyst (Scheme 1) that was used in allylation of benzaldehydes. After the reaction, the PIB-bound catalyst/product mixture was dissolved in a biphasic mixture of hexane/90% EtOH-H₂O. A gravity separation then isolated the hexane phase which contained the PIB-bound catalyst **33** which was isolated after hexane removal and reused in the following cycles. This catalyst was reused for five cycles with good conversions without significant loss of activity. This report suggests that hydrocarbon polymers like PIB should be generally useful as supports for recoverable organocatalysts.

Scheme 1. PIB-pyridine *N*-oxide catalyzed allylation



Since 2005 when Jørgensen^{28,29} and Hayashi³⁰ independently reported diarylprolinol silyl ethers as effective organocatalysts for a variety of transformations, efforts have been made to immobilize these catalysts onto polymers to provide better separation of the catalysts from the product mixtures. In 2010, Mager and Zeitler³¹ reported a PEG-supported Jørgensen-Hayashi catalyst **34** (Figure 5) prepared through a

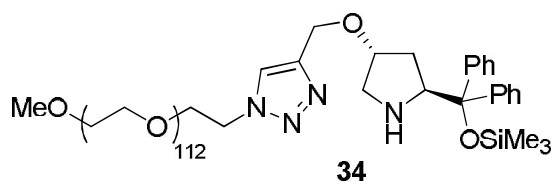
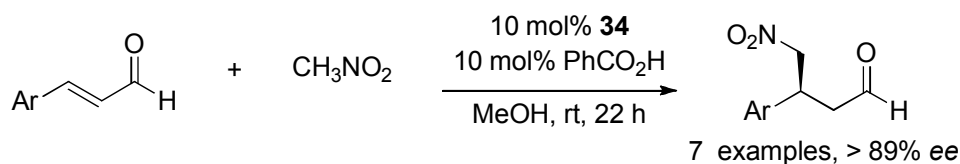


Figure 5. PEG-supported Jørgensen-Hayashi catalyst

copper-catalyzed Folkin-Huisgen reaction of a PEG-azide and a propargyl diarylprolinol silyl ether. The catalyst **34** was then tested in an asymmetric Michael addition of nitromethane to α,β -unsaturated aldehydes in methanol (Scheme 2). The yields and enantioselectivity of the products are comparable to those of products prepared with low

Scheme 2. Asymmetric Michael addition catalyzed by **34**



molecular weight catalysts. In addition, the polymer-bound catalyst **34** can be precipitated and recovered by adding the reaction mixture into ether, which allows separation of **34** from the products.

To examine the recyclability of catalyst **34**, nitromethane and cinnamaldehyde were chosen as the substrates. The catalyst was reused four times in this Michael reaction providing products in good enantioselectivity. However, the yields of the product were decreasing over the cycles. Such catalyst deactivation was attributed to the

formation of a species stemmed from the catalyst with non-released product. The authors found that stirring of the recovered catalyst **34** with a solution of cinnamaldehyde (substrate to be used for the following cycle) can release the trapped product and restore the catalytic activity.

Several reports have described polystyrene-supported organocatalysts. Toy³² reported a styrene copolymer **35** containing DMAP and piperazine moieties as shown in Figure 6. This bifunctional polymer was used as an organocatalyst in Doebner-Knoevenagel reactions as shown in Scheme 3. A variety of substrates were examined in

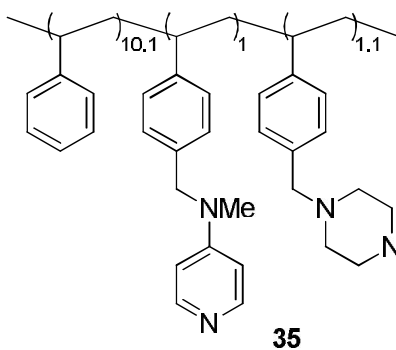
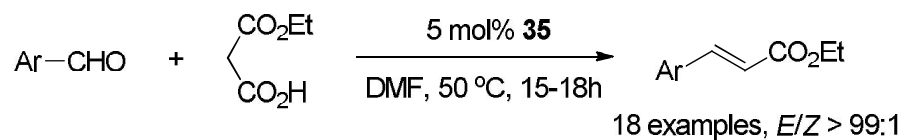


Figure 6. Styrene copolymer **35** containing DMAP and piperazine moieties

these condensation reactions and in most cases good yields were obtained along with good *E/Z* selectivity. However, attempts to recover and reuse **35** failed due to difficulty in precipitating **35** from the reaction mixtures, which precluded recycling.

Scheme 3. Doebner-Knoevenagel Condensation Reactions Catalyzed by **35**



Toy³³ also synthesized the styrene copolymer **36** containing trialkylamine and thiourea moieties as shown in Figure 7. In this case, the trialkylamino group on polymer can serve as a base while the thiourea moiety can serve as the nitroalkene activating

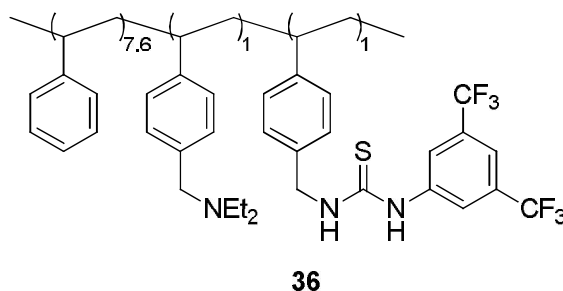
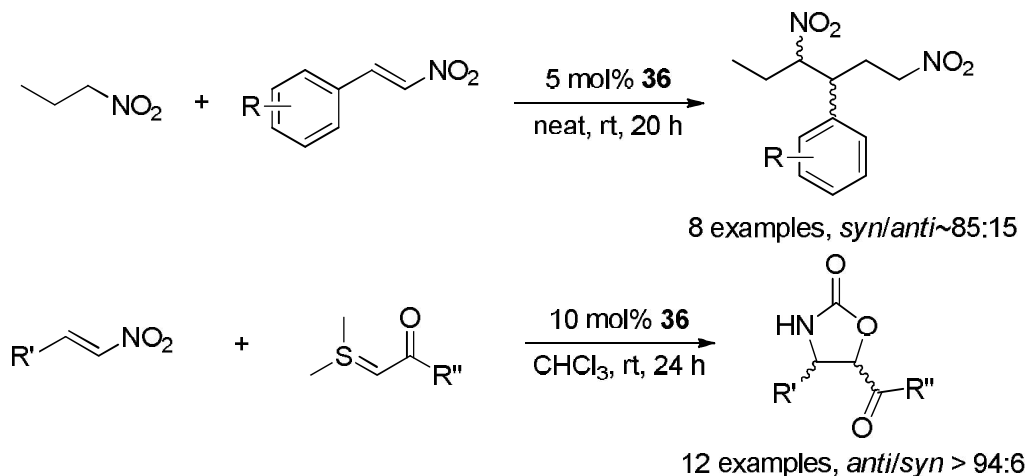


Figure 7. Styrene copolymer containing amine and thiourea moieties

group. This bifunctional polymer **36** was used as a catalyst in addition reactions of nitrostyrenes and sulfur ylides as shown in Scheme 4. These addition reactions proceeded in good yields with good *syn/anti* selectivity. In the addition reaction of sulfur ylides, a variety of cyclized products with moderate yields and good stereoselectivity were prepared. However, recycling experiment using **36** was not described.

Scheme 4. Addition Reactions Catalyzed by **36**



While polymers like polyisobutylene are achiral, polymers like polystyrene contain chiral centers. The general assumption with soluble polymer supports is the same as that with insoluble polystyrene supports and is that the chiral centers on polymer have little or no influence on an asymmetric catalytic reaction. However, this assumption is not always true as shown by work by Miyake and coworkers³⁴ who used cinchona alkaloid catalysts supported on poly(phenylacetylene)s as shown in Figure 8 as chiral catalysts in asymmetric synthesis. The chiral monomers were polymerized with a rhodium catalyst to form helical polymers **37** and **38**. These polymers have helical conformation and the helical conformation of the support was believed to enhance enantioselectivity of cinchona alkaloid catalysts compared to catalysts not attached to a helical polymer supports. The catalytic activity of the polymer-supported cinchona alkaloids were studied in Michael additions and Henry reactions as shown in Scheme 5. In the Michael addition reactions, **37a** and **38a** were successful in catalyzing the reaction

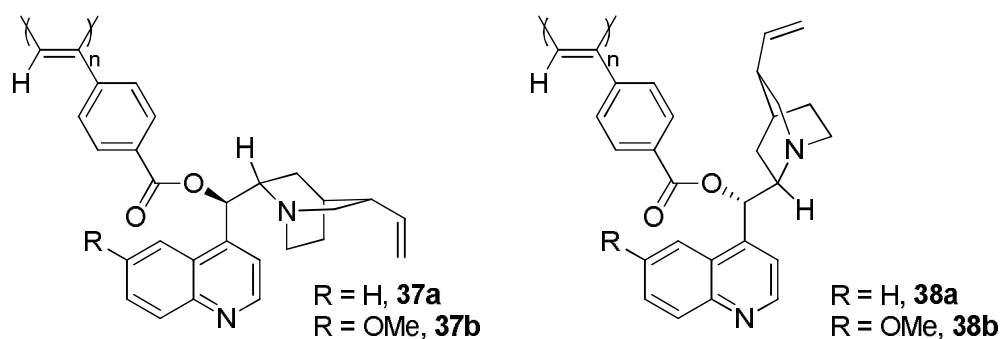
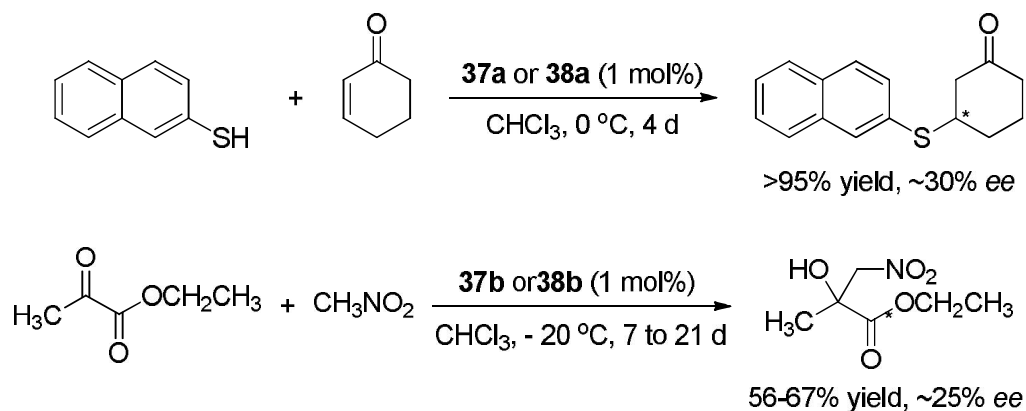


Figure 8. Poly(phenylacetylene)-supported cinchona alkaloids

and to provide the desired product with good yields with ~30% *ee*. In the case of **37a**, it can be recovered and reused twice affording products in similar yields and stereoselectivity in cycles 2 and 3. It is noteworthy in this case that the polymer served two roles – separation and enhancement of catalyst activity since the low molecular weight catalyst was less stereoselective under similar conditions. In the Henry reactions, polymer-bound catalysts **37b** and **38b** were able to catalyze the reactions with moderate

Scheme 5. Asymmetric Michael and Henry reactions catalyzed by **37** or **38**



yields. Similarly, only **37b** provided better enantioselectivity than its low molecular weight counterpart.

Dendrimers are another class of functional soluble polymers that can be used as supports for catalysts and reagents.³⁵ In 2009, Lo and Chow³⁶ reported synthesis of a series of pyrrolidines with different generations of aliphatic dendrons **39-44** (Figure 9).

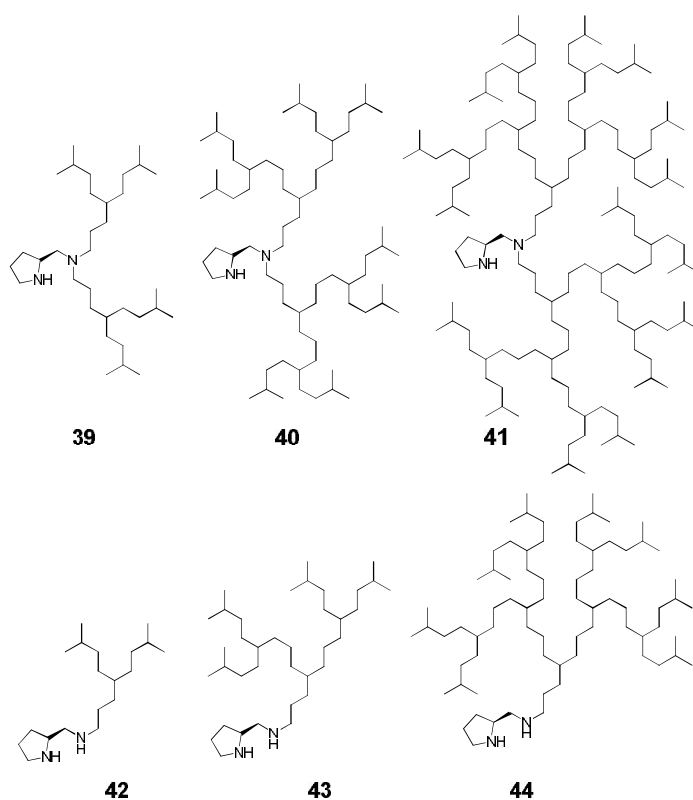
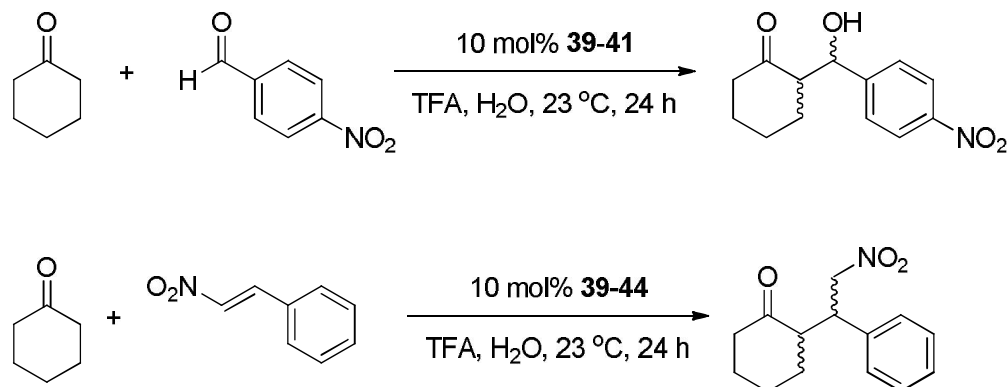


Figure 9. Dendrimer-supported diamino catalysts

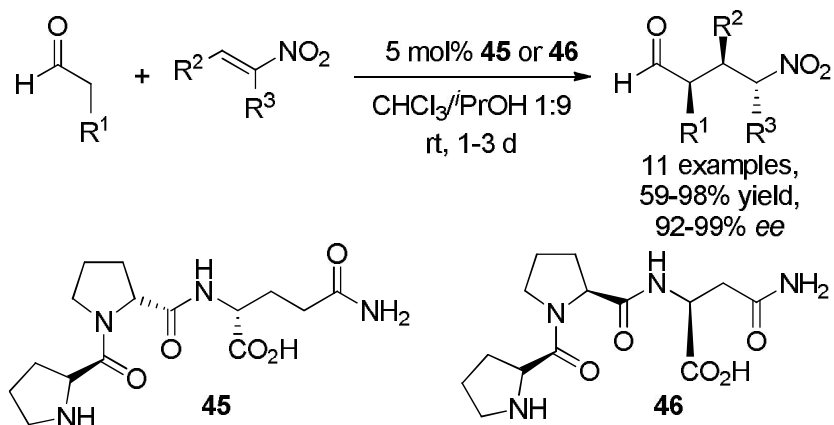
The authors used these dendrimer-supported diamino organocatalysts for aldol reactions and nitro-Michael reactions under emulsified reaction conditions (Scheme 6).

Scheme 6. Aldol and nitro-Michael reactions catalyzed by **39-44**

In the aldol reactions, a mixture of products (four isomers) was obtained in moderate yields. In this chemistry, the *anti* products were the major products and were formed with good stereoselectivity (>85% *ee*). In the nitro-Michael reactions, the *syn* products were the major products and were formed with moderate enantioselectivity. The authors found that the dendrimers **40** and **41** are phase selectively soluble in heptane phase in a biphasic heptane/MeOH mixture. Therefore, recycling dendrimers **40** and **41** was possible in a nitro-Michael reaction in which the crude product mixture was dissolved in a mixture of heptane and MeOH and the catalyst was selectively soluble in the heptane phase and the product mixture was selectively soluble in the MeOH phase. This group found that both **40** and **41** could be reused four times providing a mixture of products with similar yields and stereoselectivity comparable to that of the first cycle. Catalysts **40** and **41** were also examined in aldol reactions. In these cases, similar yields and stereoselectivity were also observed in the product mixtures throughout five cycles.

Enzymes are of course polymers and serve as useful soluble catalysts. While enzymes per se are outside the province of this literature survey, it is worth noting that smaller soluble synthetic peptides can also be used as catalysts for asymmetric catalysis. While examples of such catalysts have been known for some time, the use of these types of soluble polymers as organocatalysts has received more attention recently.^{15,37,38} For example, Duschmalé and Wennemers³⁹ reported success in using various tripeptides for asymmetric conjugate addition reactions of aldehydes to α,β -disubstituted nitroolefins. Among the screened tripeptides, **45** and **46** provided the best catalytic activity and stereoselectivity (Scheme 7). Recycling of **45** and **46** was not described.

Scheme 7. Addition reactions of aldehydes to α,β -disubstituted nitroolefins



While the most common approach to immobilization of a catalyst on a polymer is via covalent bonds, ionically linked catalysts have also been studied. Several examples of this approach have been reported recently with soluble linear organic polymers. This

is illustrated by work by Zlotin⁴⁰⁻⁴² and coworkers who used poly(styrene sulfonate) salts as the support for ionically-attached Jørgensen-Hayashi catalysts **47** (Figure 10). A low molecular weight analog **48** was also prepared for comparison.

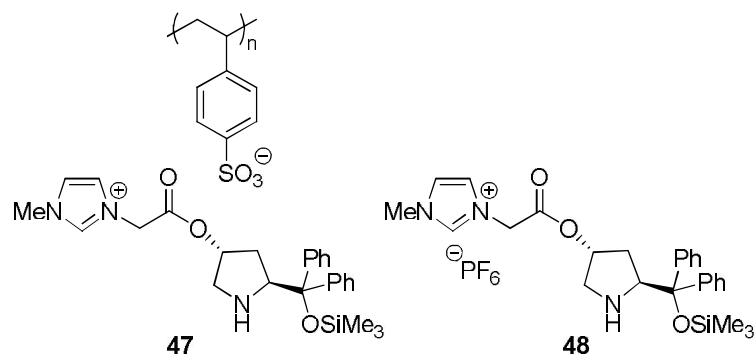
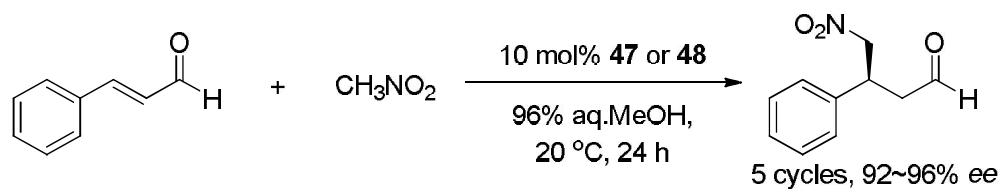


Figure 10. Ionic Jørgensen-Hayashi catalysts

Polymer-bound ionically linked catalyst **47** was examined in a Michael addition reaction in which cinnamaldehyde and nitromethane were chosen as the substrates (Scheme 8). The Jørgensen-Hayashi catalyst **48** without polymer support was also

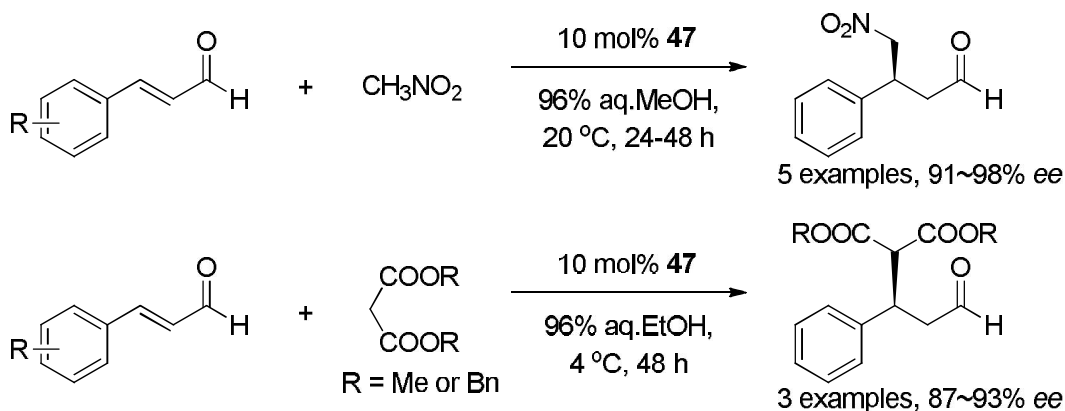
Scheme 8. Michael addition reactions catalyzed by **47** or **48**



studied. Both of these catalysts catalyze the transformation with excellent conversions along with good enantioselectivity. Besides, these catalysts can be recovered by removal of the solvents and the product can be extracted by ether. The recovered catalysts were reused four times providing products with good enantioselectivity. In this case too decreasing conversion was seen in the fourth and fifth runs. The authors attributed the decrease in conversion to physical losses of catalyst during workup in which **48** was an ionic liquid and it lost ~20% of its original mass. On the other hand, the catalyst **47**, which had the highest turnover number in five cycles, was a solid during recovery and had less than 5% loss of mass after five cycles.

The catalytic activity of polymer-supported catalyst **47** was also examined in asymmetric Michael additions with a variety of substrates (Scheme 9). By using similar reaction conditions, a variety of products were prepared with moderate to good yields and good enantioselectivity comparable to that of products prepared with **48**.

Scheme 9. Asymmetric Michael additions catalyzed by **47**



Soluble polymeric organocatalysts can also be prepared by using the organocatalyst as a monomer and have been successfully used as catalysts even when they are insoluble in the reaction mixture. This is illustrated by work by Itsuno and coworkers^{43,44} who prepared several quaternary ammonium sulfonate polymers **49** as shown in Figure 11. These polymers were not soluble in water and common organic

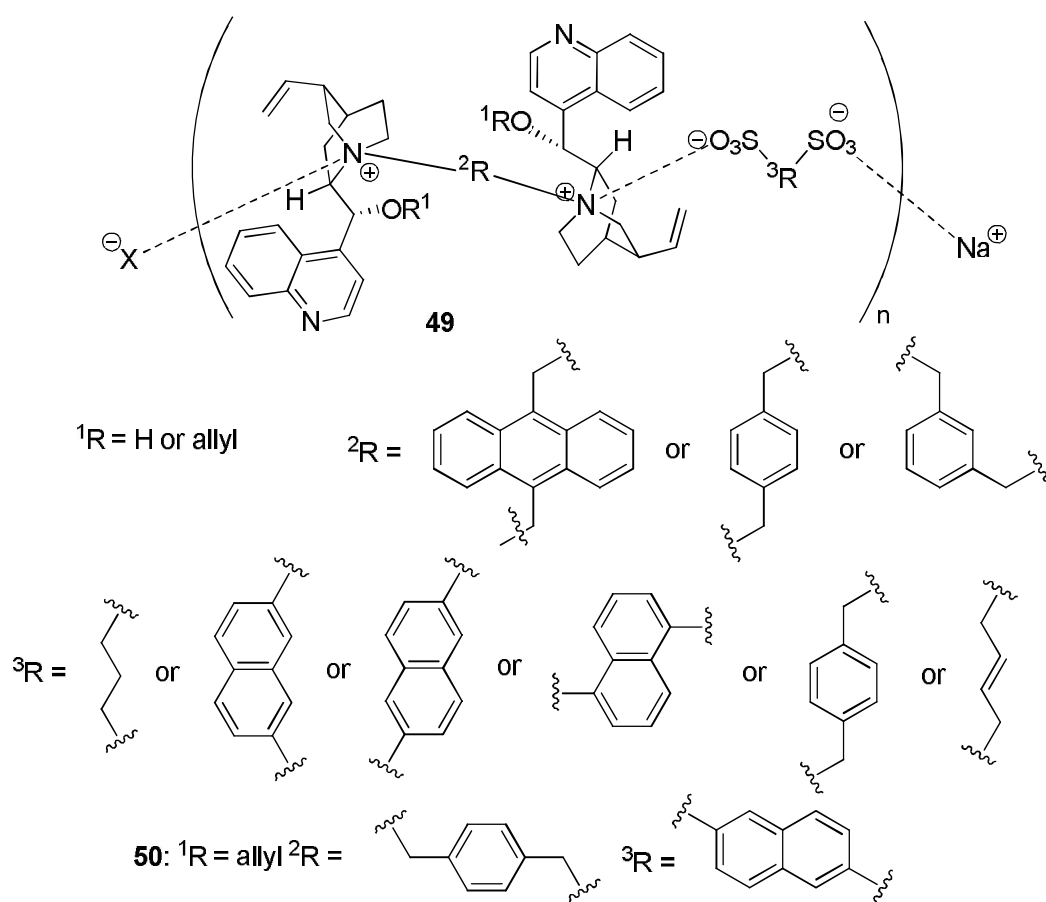
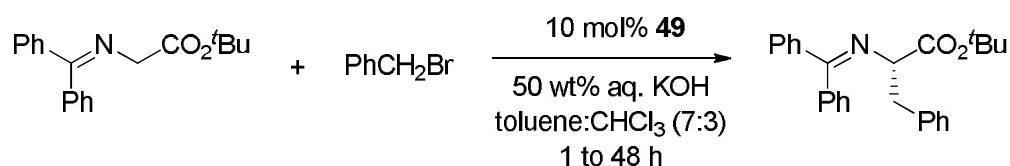


Figure 11. Ionic polymer bearing chiral quaternary ammonium salts

solvents but soluble in DMF and DMSO. Therefore these catalysts like other soluble polymer-bound catalysts can be characterized by conventional solution state spectroscopic techniques. The authors examined the catalytic activity of these polymers in an asymmetric benzylation of *N*-diphenylmethylene glycine *tert*-butyl ester as shown in Scheme 10. The reactions were carried out in a biphasic system containing an aqueous phase and an organic phase (a mixture of toluene and chloroform). The polymer was present as a solid suspension in the organic phase during the course of reactions. When the reactions were finished, the polymers were recovered by filtration and the recovered polymers did not show change of their intrinsic viscosity values and NMR spectra. One of the polymers, **50**, was found to be reusable for three cycles giving the similar yields and *ee* values of the product.

Scheme 10. Asymmetric benzylation of *N*-diphenylmethylene glycine *tert*-butyl ester



A MacMillan imidazolidinone catalyst was also incorporated into ionic polymers **51** by Haraguchi and coworkers⁴⁵ as shown in Figure 12. These polymers have solubility properties like those of **49** but their molecular weight distribution and degree of polymerization can be further analyzed by GPC. The low molecular weight analogs **52** were also prepared. Both ionic polymers **51** and their low molecular weight analogs

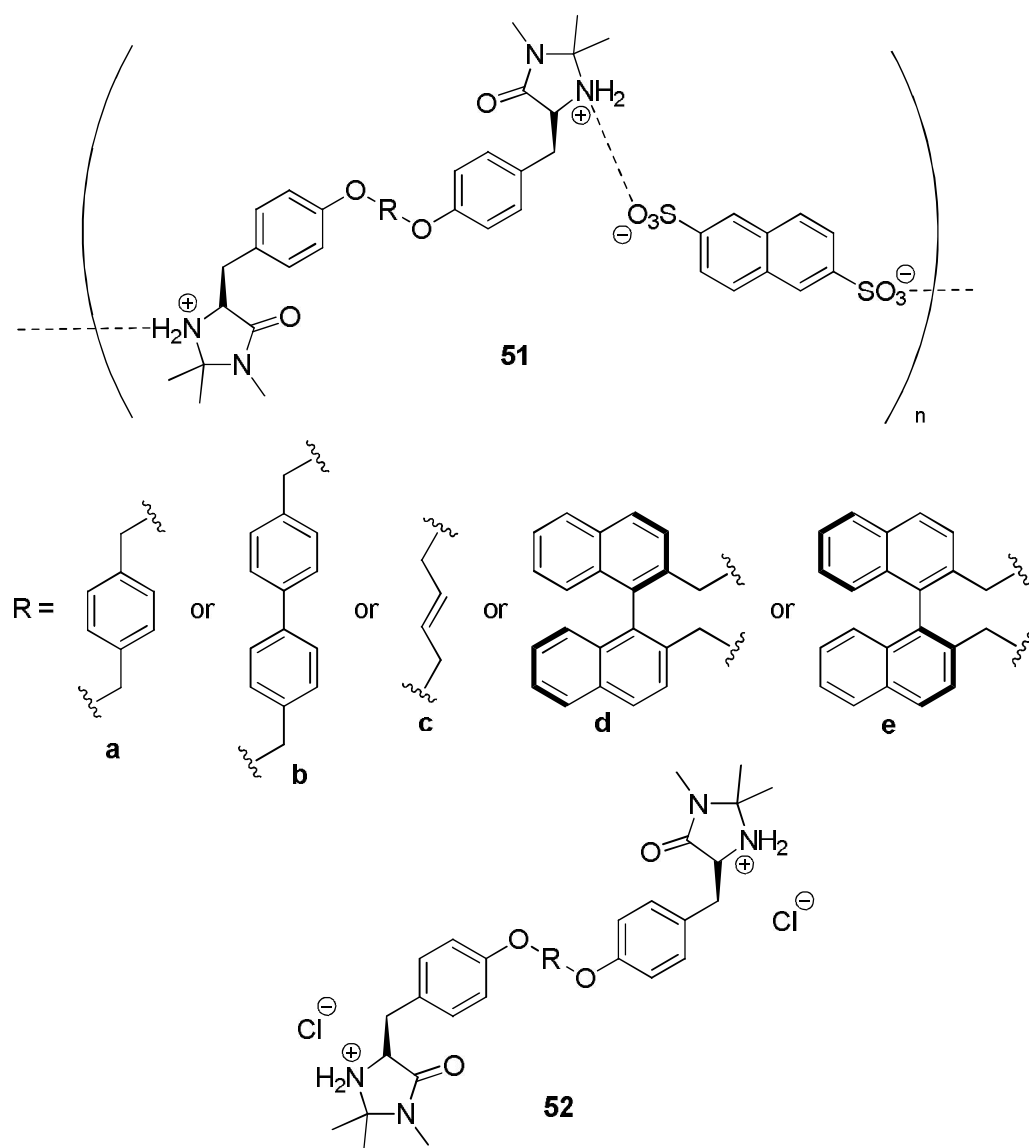
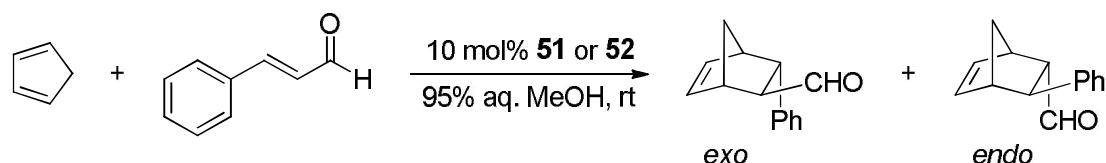


Figure 12. Ionic polymers bearing imidazolidinium salts

52 were used in an asymmetric Diels-Alder reaction of cyclopentadiene and cinnamaldehyde (Scheme 11). The low molecular weight analogs **52** were soluble in the reaction mixture and were able to catalyze the reaction to provide >90% conversions

with good *ee* values of the *endo* and *exo* product mixtures. Particularly, the *exo/endo* ratios of product mixtures were similar (~55/45) in all cases. When insoluble ionic polymers **51** were examined in the same reaction, longer reaction time was required to achieve good conversion but the *exo/endo* ratios and *ee* values of the product mixtures were very similar to those of product mixtures obtained from **52**.

Scheme 11. Asymmetric Diels-Alder reaction



One ionic polymer **51c** was recovered and reused for two cycles. Although the *exo/endo* ratios and *ee* values of the product mixtures were very similar to those obtained in the first cycle, elongated reaction time (two and three days for cycle two and three compared to one day for cycle one) was required. GPC analysis of the recovered **51c** after cycle three did not show significant change in terms of PDI and degree of polymerization. In this instance, the catalyst deactivation was ascribed to partial decomposition of the catalyst.

Much of the work in our laboratory in recent years has focused on the use of soluble polymer supports with thermomorphic and latent biphasic systems for catalyst recovery. My work has included both the design and synthesis of catalysts as well as studies that attempt to demonstrate the similarity between polymer-supported and low

molecular weight ligands. The design and synthesis of polymer-supported phosphine-silver complexes will be described first. These complexes' dynamic behavior was then examined by variable temperature (VT) ^{31}P NMR spectroscopy and has been compared to that of their low molecular weight analogs. Later I will describe the applications of PIB-supported phosphines as recyclable and regenerable organocatalysts and reagents. I will also describe immobilization of another organocatalyst, an *N*-heterocyclic carbene, on soluble polymer-supports and its application for lactide polymerization and isocyanate trimerization.

CHAPTER II
VARIABLE TEMPERATURE NMR STUDIES OF SOLUBLE POLYMER-
SUPPORTED PHOSPHINE-SILVER COMPLEXES*

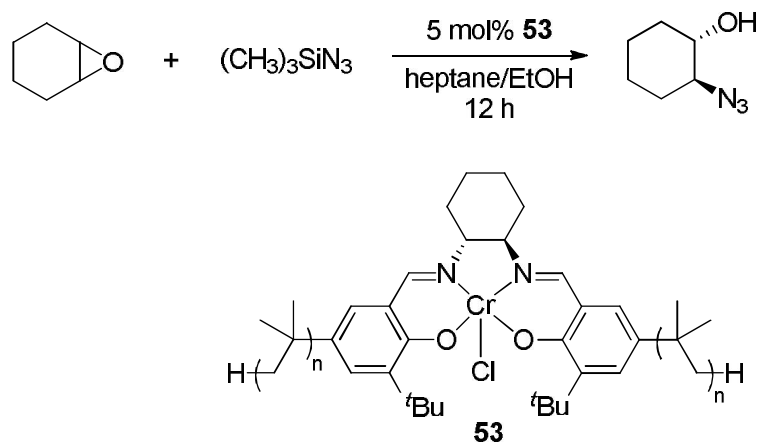
Introduction

Strategies that use ligands on polymer supports to immobilize and recover homogeneous transition metal catalysts have attracted attention ever since Merrifield introduced the concept of solid phase synthesis.^{17,24,46,47} While much of this work has involved insoluble cross-linked polymer supports, soluble supports have received attention as well.⁴⁸⁻⁵⁴ In recent years, interest in these supports has increased as new procedures have been developed that facilitate separation of soluble polymer-bound catalysts from products.^{25,26,55} For example, our group has emphasized the advantages of terminally functionalized nonpolar polyisobutylene (PIB) supports that readily separate in a liquid/liquid biphasic system after a homogeneous reaction.⁵⁶⁻⁶³ These supports are analogous to established more polar end-functionalized poly(ethylene glycol) (PEG) supports. We and others have argued that these soluble polymer supports lead to polymer-supported metal catalysts that have reactivity directly analogous to that of a more conventional low molecular weight catalyst. This argument has been substantiated

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in a number of studies where the yields of product or product selectivity for reactions of soluble polymer-bound catalysts have been compared with low molecular weight homogeneous catalysts. For example, Hobbs and coworkers⁶¹ recently reported a PIB-bound salen Cr(III) complex **53** which is able to catalyze an asymmetric ring-opening reaction of cyclohexene oxide (Scheme 12). The PIB-bound catalyst was recycled 5 times using the latent biphasic separation conditions providing the desired product with an average yield of 76% and 14% of *ee* value. The control experiment using a low molecular weight salen Cr(III) catalyst provided the product with 66% yield and 19% *ee* under similar reaction conditions.

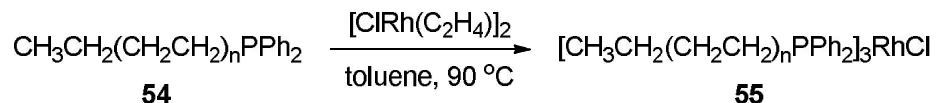
Scheme 12. Asymmetric epoxide ring-opening catalyzed by **53**



^{31}P NMR spectroscopy is generally useful as a tool to study ligand metal interactions in phosphine complexes of transition metals. The Bergbreiter group⁶⁴

reported a polyethylene oligomer(PE_{Olig})-supported phosphine **54** and its rhodium catalyst **3** for hydrogenation of olefins under thermomorphic conditions (Scheme 13).

Scheme 13. PE_{Olig}-bound phosphine **54** and its rhodium complex **55**



The design of the PE_{Olig}-bound phosphine complex **54** was based on the idea that **54** when in solution would have the same reactivity as a ligand as the low molecular weight ligand octadecyldiphenylphosphine **56** under similar reaction conditions (Figure 13).

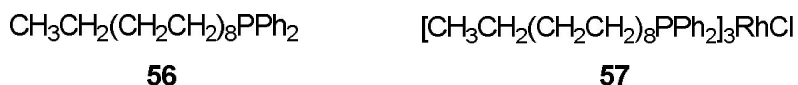
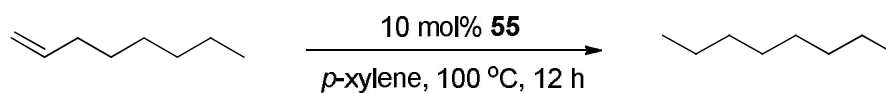


Figure 13. Octadecyldiphenylphosphine **56** and its rhodium complex **57**

The chemical shifts in ³¹P NMR spectra of **54** and its rhodium complex **55** (-14.3 and 29 ppm, respectively) were similar to those of low molecular weight phosphine **56** and its corresponding complex **57** (-16.3 and 29 ppm, respectively). Spin-lattice relaxation times (*T*₁) of **54** and **56** were also examined to see if the phosphine group in **54** has the similar steric and electronic environment as a similar phosphine group in **56** does. It was found that **54** and **56** have *T*₁ values of 5 and 8 s, respectively, in contrast to one order of difference between *T*₁ values for the phosphine atoms of phosphine ligands immobilized

on crosslinked polystyrene and ligands in solution as reported by Stille.⁶⁵ In the hydrogenation reaction of 1-octene, **55** and **57** also had similar turnover frequency in the given reaction conditions (Scheme 14). However, the polymer-bound catalyst **55** can be recycled and reused for 17 times with similar hydrogenation rate and conversion cycle to cycle while the catalyst **57** can only be used once. On the other hand, the hydrogenation reaction with insoluble crosslinked polystyrene-bound phosphine-rhodium catalyst proceeded much slower and gave the product with low yield under similar reaction conditions.

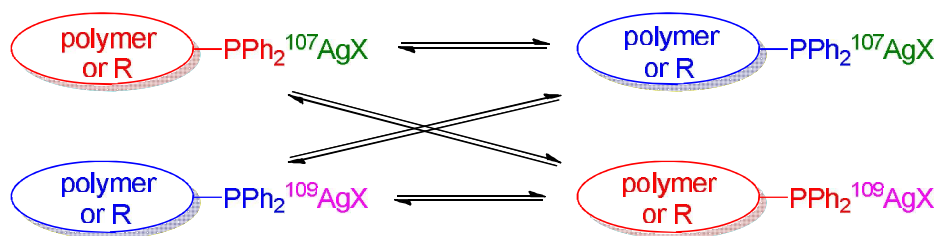
Scheme 14. Hydrogenation of olefins catalyzed by **55**



In this study, we examined the similarity of low molecular weight and high molecular weight phosphine ligands by studying the dynamics of phosphine ligand exchange at an NMR-active silver metal center. Phosphine-silver complexes are particularly useful subjects in this regard because the phosphine ligand exchange can often be studied by variable temperature (VT) dynamic NMR spectroscopy.⁶⁶⁻⁶⁸ Specifically, at low temperature, the ³¹P NMR spectrum of a slowly exchanging phosphine ligand in a silver-phosphine complex is seen as a doublet of doublets because silver exists as a nearly equally abundant mixture of ¹⁰⁷Ag and ¹⁰⁹Ag isotopes each with nuclear spin quantum number (I) of 1/2. In such cases, exchange of a phosphine ligand

from a ^{107}Ag to a ^{109}Ag or of a ^{107}Ag or ^{109}Ag from one phosphine to another as shown in Scheme 15 can then be studied in detail as a function of temperature. In the case of

Scheme 15. Polymer- or alkyldiphenylphosphine-silver exchange processes



complexes like Bu_3PAgI , this temperature-dependent ligand exchange can be monitored by ^{31}P NMR spectroscopy (Figure 14). These spectra show a temperature-dependent chemical shift for the phosphine ligand. More importantly, the kinetics of the phosphine ligand exchange process can be analyzed by line shape analysis because the low temperature ($-87\text{ }^\circ\text{C}$) doublet of doublets (Figure 14b) evolves to a singlet (Figure 14a) at higher temperature ($52\text{ }^\circ\text{C}$) due to the rapid exchange of phosphine from one silver to another.⁶⁹ The rate of the exchange as a function of temperature can then be used to determine the Gibbs energy of activation for the ligand exchange with the Eyring equation (eq 1).

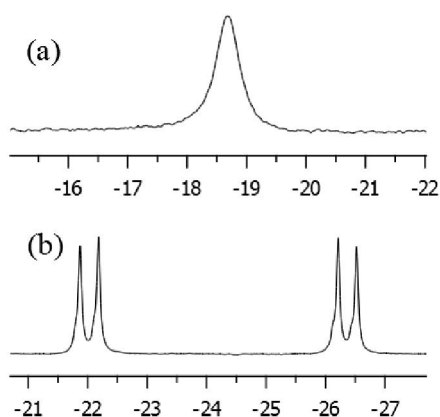


Figure 14. ^{31}P NMR spectra of Bu_3PAgI in THF at (a) $52\text{ }^\circ\text{C}$ and (b) $-87\text{ }^\circ\text{C}$

$$\ln\left(\frac{k}{T}\right) = \frac{\Delta S^\ddagger}{R} + \ln\left(\frac{k_B}{h}\right) - \frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} \quad (1)$$

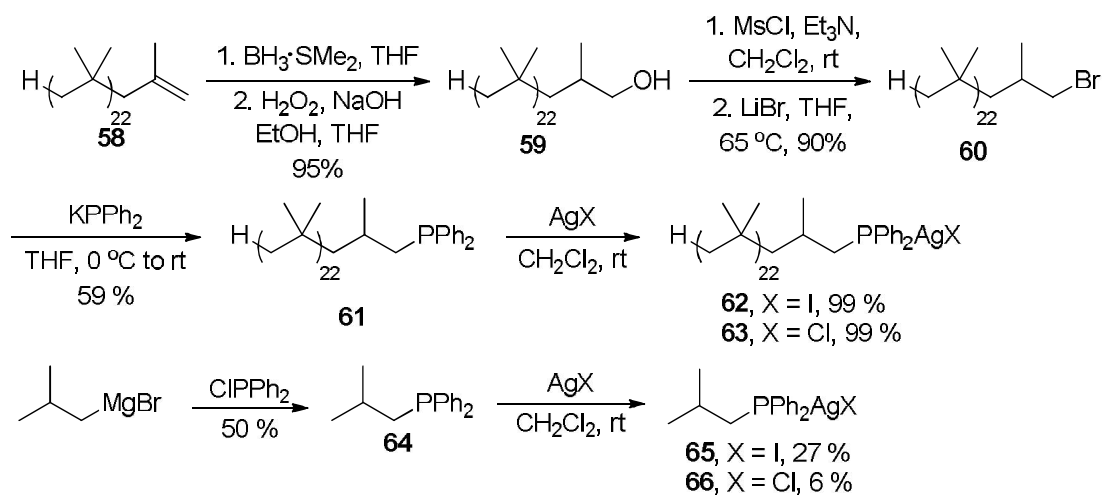
The studies reported below use variable temperature ^{31}P NMR spectroscopy to study and compare the dynamic behavior of silver complexes of both terminally functionalized PIB- PPh_2 and PEG- PPh_2 ligated silver complexes with silver complexes prepared from electronically similar low molecular weight phosphine ligands. The results of these studies show that both terminally functionalized soluble PIB- PPh_2 and PEG- PPh_2 phosphine ligands behave like electronically similar low molecular weight phosphine ligands in phosphine metal exchange. This similarity of a soluble polymeric ligand and a low molecular weight ligand is consistent with the idea that solutions of these homogeneous catalysts bound to these soluble ligands will generally behave like solutions of their low molecular weight analogs in catalytic processes. A silver complex

from a phosphine ligand immobilized as a pendent group on a linear alkylated polystyrene were also studied. However, broad line shape due to short T_1 of the phosphine peak on ^{31}P NMR spectra precluded detailed study.

Results and Discussion

Synthesis of the PIB-bound phosphine ligand started from functionalizing alkene-terminated polyisobutylene **58** using hydroboration-oxidation chemistry to give PIB-alcohol **59**. **59** was further transformed into the corresponding PIB- CH_2Br **60** and then to the desired PIB-alkyldiphenyl phosphine **61** (Scheme 16).^{70,71} The PIB-bound The similar AgI and AgCl complexes (**65** and **66**, respectively) were in turn prepared from **64** under similar reaction conditions.

Scheme 16. Syntheses of PIB-bound phosphine-silver complexes and their analogs



Polyisobutyldiphenyl- and isobutyldiphenylphosphine (**61** and **64**, respectively) had identical ^{31}P NMR spectra with a singlet at - 19.5 ppm in C_6D_6 (Figure 15). The AgI complexes (**62** and **65**) had similar more complex NMR spectra at room temperature in C_6D_6 . The ^{31}P NMR spectra of the AgCl complexes **63** and **66** were likewise similar in C_6D_6 at room temperature.

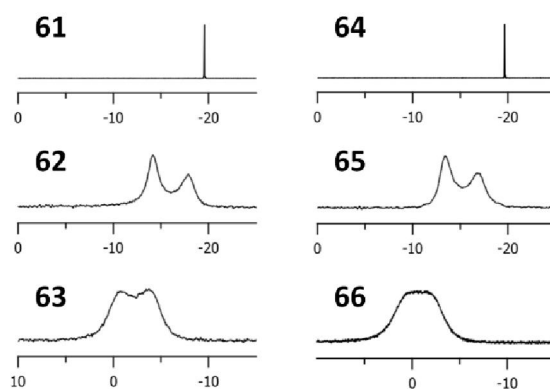


Figure 15. ^{31}P NMR spectra of phosphines (**61** and **64**) and corresponding silver complexes **62**, **63**, **65**, and **66** in C_6D_6 at room temperature

The AgI complexes **62** and **65** so formed were then dissolved in CD_2Cl_2 and their ^{31}P NMR spectra were recorded from - 64 °C to 30 °C as shown in Figure 16. Because the $\text{PIBCH}_2\text{PPh}_2$ ligand **61** is soluble at low temperature, high quality spectra were obtained even at - 64 °C. As shown, these $\text{PIBCH}_2\text{PPh}_2\text{AgI}$ and $(\text{CH}_3)_2\text{CHCH}_2\text{PPh}_2\text{AgI}$ complexes have nearly identical dynamic NMR behavior with both the changes in line shape and the temperature-dependent chemical shifts being very similar.

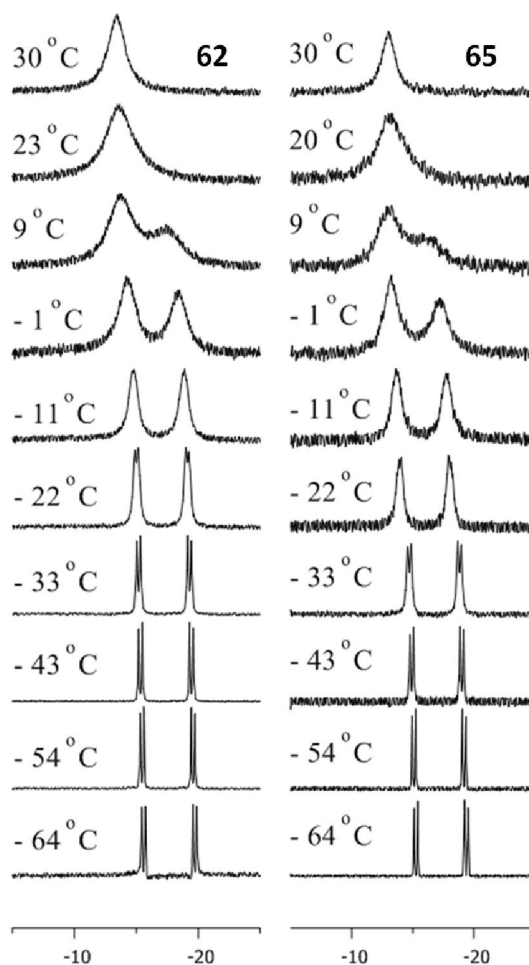


Figure 16. VT ^{31}P NMR spectra of **62** and **65** in CD_2Cl_2 from - 64 to 30 $^\circ\text{C}$

Below - 33 $^\circ\text{C}$, the exchange process is slow on the NMR time scale and a doublet of doublets was observed. The coupling constant of 464 Hz of inner doublet corresponds to ^{107}Ag - ^{31}P coupling, and the outer doublet has a coupling constant of 536 Hz due to ^{109}Ag - ^{31}P as shown in Figure 17. The ratio of these coupling constants is 0.866 which corresponds to gyromagnetic ratio of $^{107}\text{Ag}/^{109}\text{Ag}$ of 0.870. Integration of

inner/outer doublets is 52/48, which corresponds to the isotopic ratio of $^{107}\text{Ag}/^{109}\text{Ag}$ of 51.8/48.2. Using line shape analysis,⁷² the rate of phosphine ligand exchange for **62** and

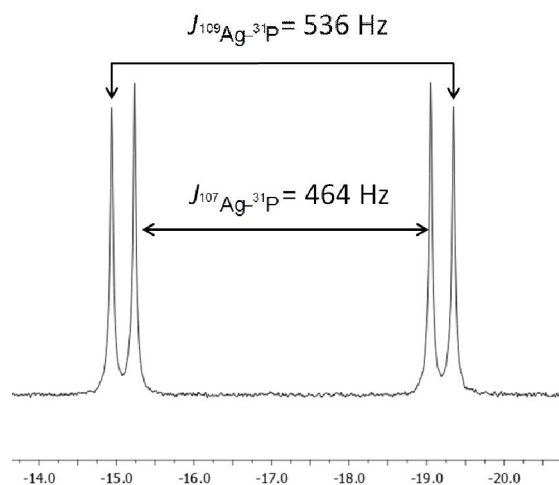


Figure 17. ^{31}P NMR spectrum of **65** at $-54 \text{ }^\circ\text{C}$

65 was then calculated at each temperature. The variable temperature NMR spectra for **62** and **65** can be used to calculate the rate of silver and phosphine exchange (Table 1). Similar VT NMR experiments of **62** were also carried out in THF and heptane with 10% C_6D_6 as internal lock and the spectra were shown in Figure 18. Since **65** is not soluble in heptane, further VT NMR experiments of **65** were only carried out in THF. As was found by comparing VT NMR spectra of **62** and **65** in CD_2Cl_2 , the similarity of kinetic behavior was also observed when THF was used as the solvent. Kinetic behavior was also studied for silver chloride complexes **63** and **66** in THF, CD_2Cl_2 , and heptane.

Similar to **65**, **66** was insoluble in heptane therefore VT NMR experiments were not performed.

Table 1. Calculated rate constants for phosphine exchange in **62** and **65** in CD₂Cl₂ at various temperatures

| | 62 | 65 |
|---------|-----------|-----------|
| 30 °C | 4331 | 5215 |
| 20 °C | 2598 | 3012 |
| 9 °C | 1352 | 1731 |
| - 1 °C | 743 | 865 |
| - 11 °C | 361 | 510 |
| - 22 °C | 163 | 238 |
| - 33 °C | 57 | 124 |
| - 43 °C | 24 | 56 |
| - 54 °C | 9 | 21 |
| - 64 °C | 3 | 8 |

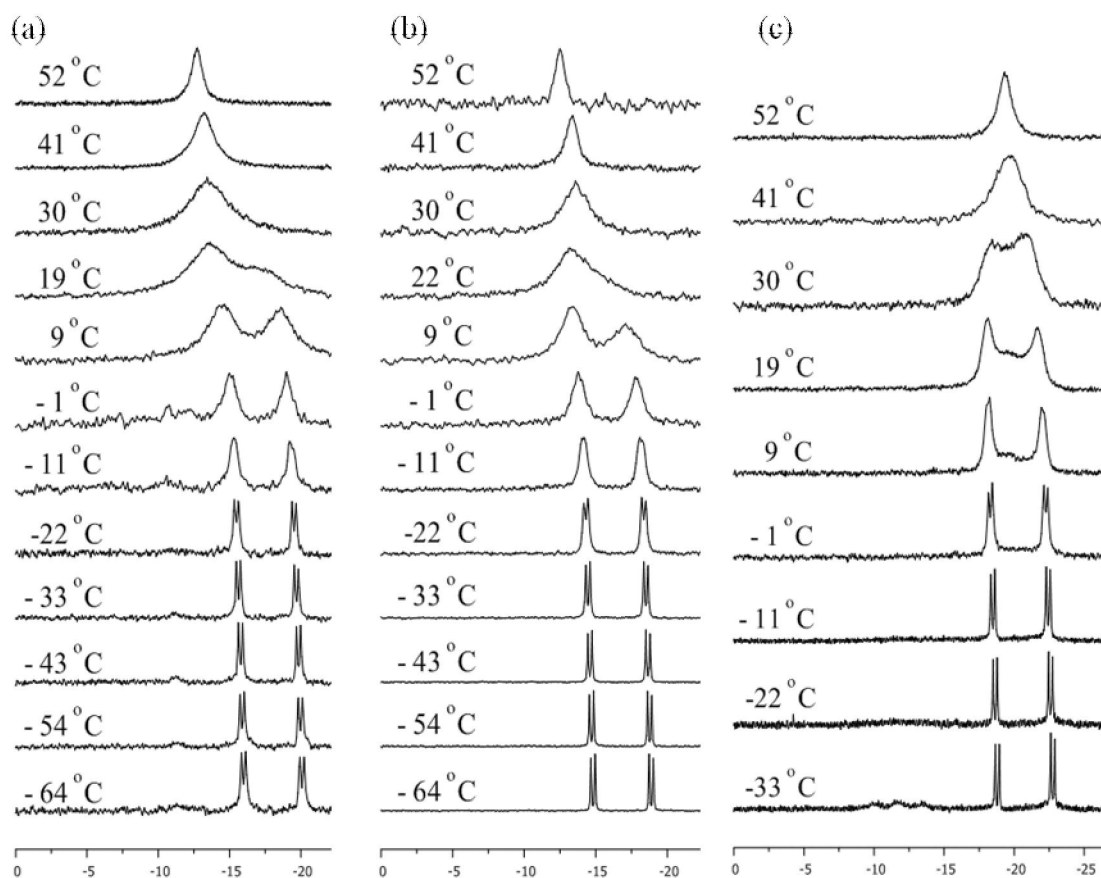


Figure 18. VT NMR spectra of (a) **62** in THF, (b) **65** in THF, and (c) **62** in heptane

These rate constants calculated from VT NMR spectra over a range of - 64 °C to 52 °C were then used to calculate the ΔG^\ddagger for the exchange process in different solvents at 20 °C using the Eyring equation (Table 2). A slightly higher Gibbs energy of activation is seen in the less polar solvent heptane for both **62** and **63**. However, the differences in energy of activation between the PIB- and the isobutylphosphine-silver complexes are minimal. While the observed differences were often within experimental

error, in most cases the calculated ΔG^\ddagger of the low molecular weight phosphine complex was consistently less than or equal to the ΔG^\ddagger of the polymer-bound species.

Table 2. Activation energies* (kcal/mol, 20 °C) for PIB- and isobutylphosphine-Ag(I) exchange in various solvents

| | 62 | 65 | 63 | 66 |
|---------------------------------|-----------|-----------|-----------|-----------|
| THF* | 12.9 | 12.7 | 12.3 | 11.9 |
| CD ₂ Cl ₂ | 12.6 | 12.5 | 11.5 | 11.5 |
| Heptane* | 13.4 | | 13.0 | |

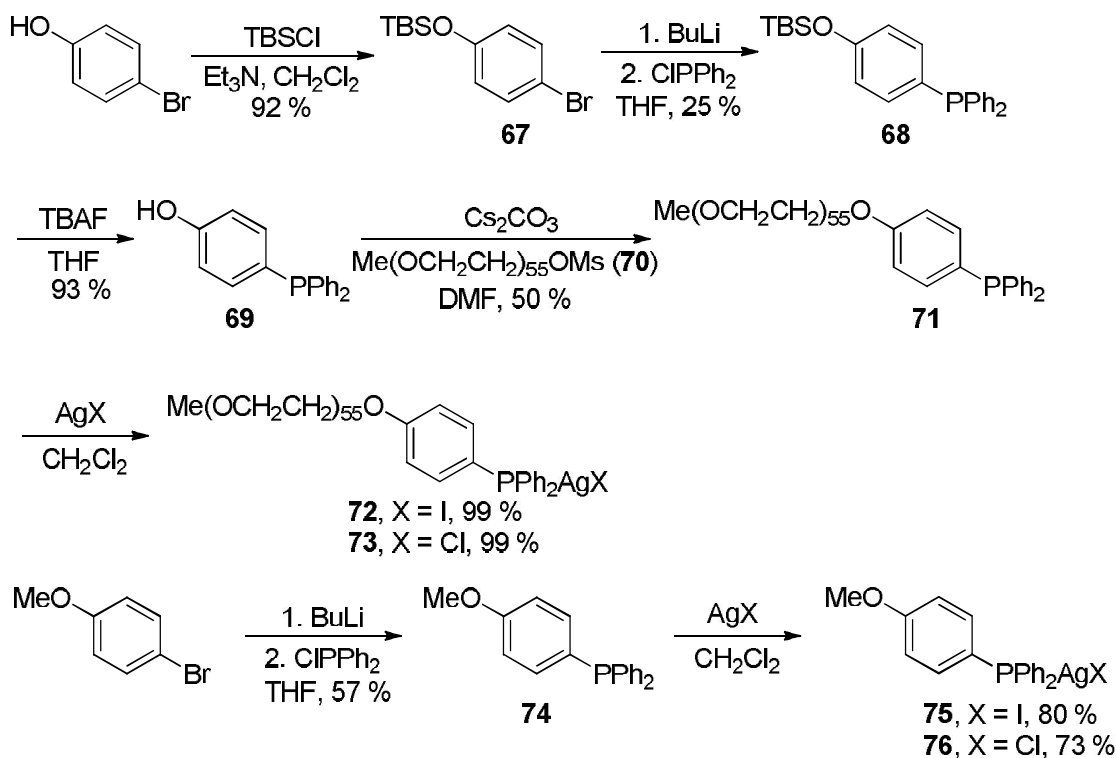
*10 % C₆D₆ was added.

While our recent work has focused on using soluble nonpolar PIB-bound ligands as catalyst supports, PEG derivatives are more common as soluble polymer supports.⁴⁹ Thus, we extended our studies of phosphine ligand exchange to include PEG-triarylphosphine-bound silver halide complexes too. These ³¹P NMR spectroscopy studies showed that phosphine-silver halide complexes bound to the terminus of a polar polymer, PEG, also have VT NMR behavior and exchange kinetics that is similar to an electronically analogous low molecular weight phosphine ligand.

In these studies, we first synthesized PEG-supported phosphine-silver halide complexes (Scheme 17). The syntheses started with protection of hydroxyl group of 4-bromophenol with TBS group. The protected aryl bromide **67** was treated with *n*-butyl lithium and then chlorodiphenylphosphine to give the triarylphosphine **68**. The silyl

protecting group on **68** was removed by TBAF to give hydroxytriarylphosphine **69**, which was then reacted with a PEG-mesylate **70** to give the desired PEG-triarylphosphine **71**. The corresponding PEG-phosphine-silver iodide and chloride (**72** and **73**, respectively) were prepared in similar conditions as described for the preparation of PIB-bound phosphine-silver salts.

Scheme 17. Synthesis of PEG-bound Ag complexes and their low molecular weight analogs



Electronically similar low molecular weight phosphine **74** and silver complexes **75** and **76** were then also prepared. The ^{31}P NMR spectra of PEG-bound species are also

very similar to those of low molecular weight analogs as shown in Figure 19. The comparative dynamic variable temperature ^{31}P NMR spectra of these polymeric and low molecular weight silver phosphine complexes were again found to be very similar.

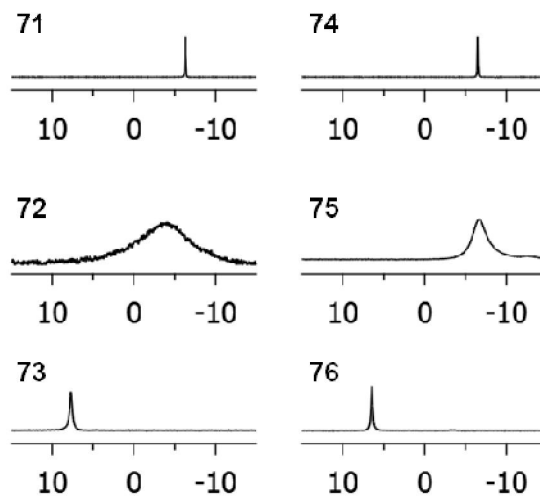


Figure 19. ^{31}P NMR spectra of phosphines (**71** and **74**) and corresponding silver complexes **72**, **73**, **75**, and **76** in CD_2Cl_2 at room temperature

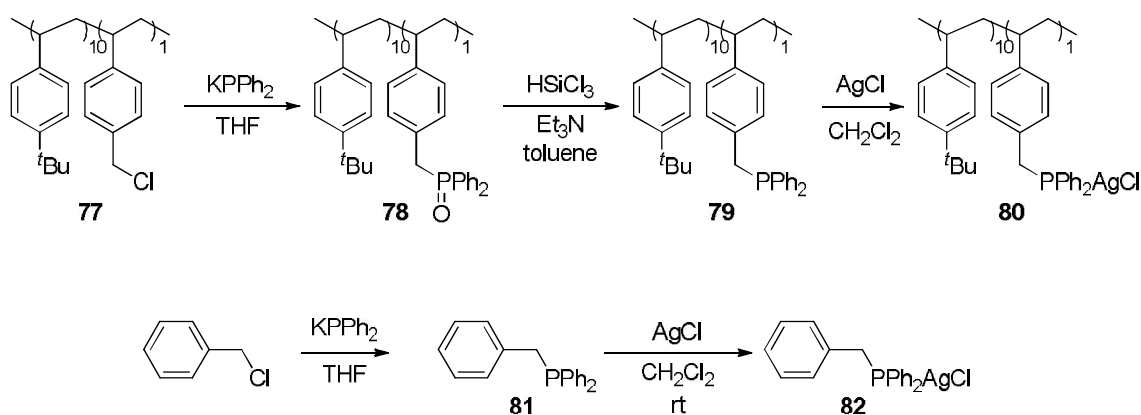
The free energies of activation for phosphine exchange at 20 °C were again calculated from the rate constants measured by line shape analysis at various temperatures over a -76 °C to 30 °C range. The calculated Gibbs energy of activation of silver complexes **72**, **73**, **75**, and **76** are shown in Table 3. As was true for the less polar terminally-substituted PIB-phosphines, the PEG-bound phosphine and low molecular weight phosphine ligands have similar kinetic behavior.

Table 3. Gibbs energy of activation (kcal/mol, 20 °C) for phosphine-Ag(I) exchange in CD₂Cl₂

| | 72 | 75 | 73 | 76 |
|---------------------|------|------|------|------|
| ΔG^\ddagger | 12.6 | 12.5 | 11.5 | 11.5 |

After examining the kinetic behavior of phosphine-silver complexes attached at the terminus of linear polymers, we extended our study to complexes attached to polymers as pending groups. Since polystyrene is the most frequently used support for catalysts, we prepared a PtBS-supported phosphine-silver chloride complex as shown in Scheme 18. The styrene copolymer **77** was prepared by radical polymerization of 4-*tert*-butylstyrene and 4-vinylbenzyl chloride. Treating **77** with a THF solution of potassium

Scheme 18. Synthesis of PtBS-bound phosphine-silver chloride and its low molecular weight analog



diphenylphosphide yielded **78**. The phosphine group on polymer **78** was found to be oxidized during the workup. Therefore, reduction of the phosphine oxide on the polymer successfully provided the desired polymer-bound phosphine **79**. It is noteworthy that a similar PtBS-supported triarylphosphine has been used as a soluble polymer-supported catalyst for Michael addition in a latent biphasic system.⁷³ The phosphine chloride complex **80** was prepared under similar reaction conditions as those used for preparing PIB-bound phosphine-silver complexes.

The low molecular weight analogous phosphine **81** and its silver chloride complex **82** were also prepared. The ³¹P NMR spectra of these complexes are shown in Figure 20. Unlike the ³¹P spectra seen in Figures 15 and 19, the polymer-bound complex

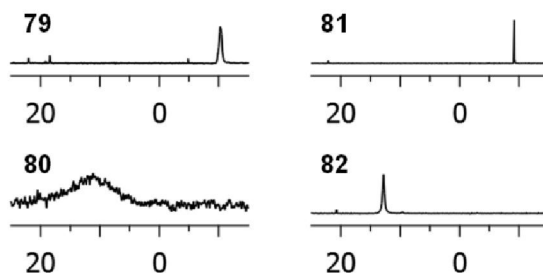


Figure 20. ³¹P NMR spectra of phosphines (**79** and **81**) and corresponding silver chlorides (**80** and **82**) in CD₂Cl₂ at room temperature

80 has much wider peak width compared to low molecular weight complex **82**. Furthermore, the line shape of VT ³¹P NMR spectra of **80** (Figure 21) recorded over a range of 20 to 60 °C didn't show significant change as observed in the cases in which

PIB- and PEG-phosphine-silver complexes were studied. Such phenomenon may arise from the slower molecular motion of phosphorous species attached on the polymer. In this case, the temperature-dependent change in line shape cannot be easily studied with the phosphine-silver complexes as pendent groups on alkylated polystyrene.

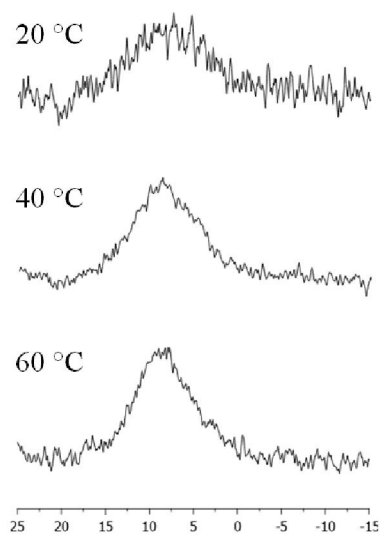


Figure 21. VT ^{31}P NMR spectra of **80** in C_6D_6

Conclusions

Dynamic NMR studies of phosphine-silver exchange in PIB-bound, PEG-bound, and low molecular weight phosphine-silver halide complexes show that terminal phosphine ligands on polar and nonpolar polymers have exchange behavior that is very similar to that seen with low molecular weight phosphine ligands. Line shape analyses show that the rates and Gibbs energy of activation are nearly the same. This similar dynamic behavior in a ligand exchange process for either a polymer or a non-polymer

silver complex supports the assumption that soluble end-functionalized polymer-supported ligands can be used to prepare soluble polymer-bound organometallic catalysts whose reactivity and selectivity will be exactly like that of low molecular weight analogs. Applying similar line shape analysis to phosphine-silver complexes immobilized on soluble polymer supports as pendent groups was not successful due to significant line-broadening on ^{31}P NMR spectra.

CHAPTER III
POLYISOBUTYLENE-SUPPORTED PHOSPHINES AS RECYCLABLE AND
REGENERABLE CATALYSTS AND REAGENTS*

Introduction

Phosphines are commonly used as reagents and catalysts in modern organic chemistry in reactions like Baylis-Hillman, Wittig, and Mitsunobu reactions.⁷⁴⁻⁸³ However, a drawback of using phosphines is the difficulty in separating phosphines or their phosphine oxide byproducts from desired products after a reaction. For example, triphenylphosphine oxide, which is generated in Mitsunobu reactions that use triphenylphosphine as a reagent, usually has to be separated from products by chromatography. The toxicity of phosphines and phosphine oxides can also pose concerns.⁸⁴ These Green chemistry issues have led to several methods being developed to facilitate product purification after reactions that use phosphines as reagents or catalysts. For example, the use of water soluble phosphines allows phosphines or phosphine byproducts to be separated from products with an aqueous wash. In the case, phosphines with pyridine or amine groups **83**⁸⁵ and **84**⁸⁶ have been used as alternatives to triphenylphosphine in Mitsunobu conditions and the corresponding phosphine oxides can be removed from the reaction mixture with an acidic aqueous wash (Figure 22).

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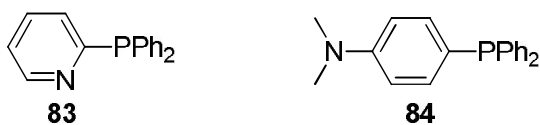


Figure 22. Phosphines soluble in acidic aqueous solutions

Another strategy involves attaching phosphines onto insoluble polymer supports that allow products and phosphine species to be separated by filtration. For example, crosslinked polystyrene-supported triphenylphosphine analogs **85** are now commercially available with different extent of crosslinking and different crosslinkers (Figure 23). Such phosphines have been used in Wittig^{87,88} and Mitsunobu^{89,90} reactions and the phosphine oxide byproducts can be separated from the reaction mixture by a filtration. The recovered polymer-bound phosphine oxides can be reduced to phosphines for reuse.

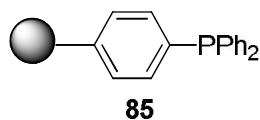
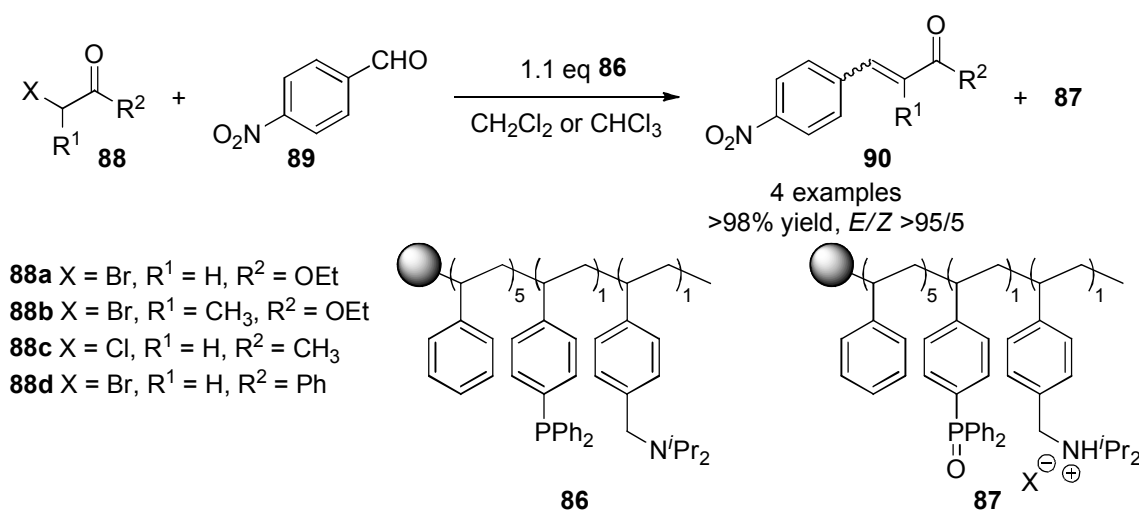


Figure 23. Insoluble polymer-supported triphenylphosphine analog

Recently, Toy⁸⁸ reported a phosphine- and tertiary amine-containing catalyst supported on crosslinked polystyrene. The amine group on the bifunctional catalyst **86** served as a base to deprotonate the phosphonium salts formed on the polymer in Wittig reactions (Scheme 19). After a Wittig reaction, the polymer-supported phosphine oxide-ammonium halide **87** was separated from the reaction mixture and treated with

trichlorosilane and then Hunig's base to regenerate **86** for reuse. This strategy is illustrated by chemistry where **88d** and **89** were chosen as the substrates for a Wittig reaction. In this instance, **86** was recycled, regenerated, and reused for 5 cycles providing the product **90** with good yields and *E/Z* ratios. However, prolonged reaction time was required to achieve good yields after cycle 1.

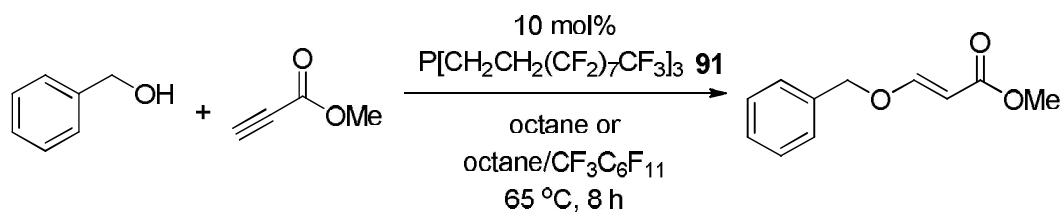
Scheme 19. Wittig reactions mediated by **86**



There have been limited studies where soluble polymers have been used as phase handles to support phosphine reagents or catalysts during a homogeneous reaction with a biphasic separation of phosphines or phosphine oxide byproducts after the reaction.^{25,26} Such phase separation strategies can also include chemistry using fluororous tags for fluororous biphasic separations. Examples of soluble polymers that have been used include polyethylene (PE), poly(ethylene glycol) (PEG), or linear polystyrene supports.

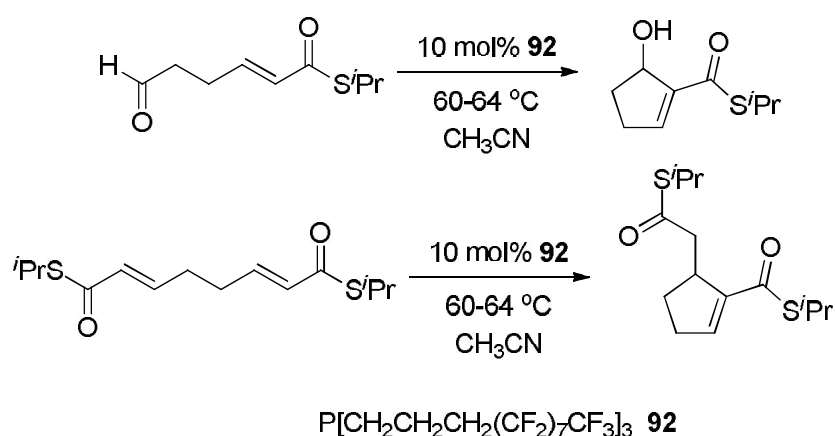
Fluorous phosphines and their byproducts can be separated from desired products both by a liquid/liquid phase separation using fluorous solvents or by a thermomorphic strategy. The latter strategy is illustrated by work by the Gladysz group who reported syntheses of a variety of fluorous trialkylphosphines and described their roles as recyclable catalysts in addition reaction^{91,92} of alcohols to alkynes, in Baylis-Hillman reactions, in Rauhut-Currier reactions,⁹³ and in Michael addition reactions.⁹⁴ The Baylis-Hillman reaction can be carried out under using either a liquid/liquid or solid/liquid separation to isolate the fluorous phosphines or fluorous phosphine byproducts. An example of a thermomorphic liquid/liquid strategy is a reaction where a mixture of *n*-octane and perfluoro(methylcyclohexane) was used as the solvent mixture (Scheme 20). In this case, the reaction was carried out at 65 °C as a single phase mixture. After the reaction was completed, the reaction mixture was cooled to -30 °C and a liquid/liquid biphasic mixture was formed. The catalyst-containing fluorous phase was recovered after separation of the less-dense *n*-octane-rich phase containing the product. By adding fresh solvent and substrates to the fluorous phase, the reaction could

Scheme 20. Catalysis of fluorous phosphine catalyst under thermomorphic conditions



be repeated. Recycling experiments were successful for 4 runs with an average yield of 72% per run. The Gladysz group also carried out the reaction in the absence of fluororous solvent under thermomorphic solid/liquid conditions. Catalyst **91** has temperature-dependent solubility in *n*-octane with very low solubility (0.104 mM) at -20 °C but much higher solubility (19.6 mM) at 50 °C. Therefore, when an alcohol addition reaction was carried out using *n*-octane as the only solvent under similar reaction conditions at 65 °C, a homogeneous reaction mixture was formed. When the reaction was completed, the reaction mixture was cooled to -30 °C and the supernatant was removed from the solid catalyst. This separation strategy allowed the catalyst **91** to be recycled and reused for 4 times with an average yield of 80% per run. Similar thermomorphic solid/liquid separations were also used in Baylis-Hillman and Rauhut-Currier reactions catalyzed by another fluororous phosphine **92** (Scheme 21). Similar temperature-dependent solubility

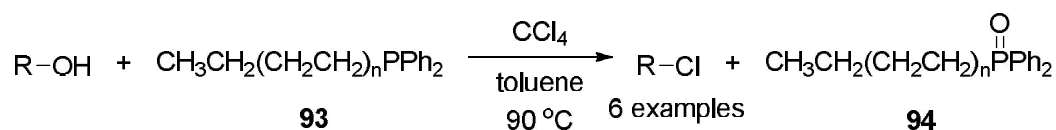
Scheme 21. Baylis-Hillman and Rauhut-Currier reactions catalyzed by **92**



of **92** in acetonitrile was also observed. Thus, the reactions could be carried out at 60-64 °C as homogeneous mixtures and then the catalyst could be separated from the product solutions as a solid at -30 °C. Catalyst **92** was shown recyclable and reusable for 5 runs. The yields of products of Baylis-Hillman reaction ranged from 95-96%. Rauhut-Currier reactions catalyzed by **92** produced products with 71-73% yields per cycle.

Soluble polymer-bound phosphines are an alternative to fluorous phosphines like **91** or **92**. Such polymer-supported phosphines and their byproducts have been classically separated from products by a solid/liquid separation. This can involve simply using thermomorphic conditions like those used with **92** or can involve solvent precipitation of the polymeric species after a reaction. For example, a polyethylene oligomer (PE_{Olig})-supported alkyl-diphenylphosphine **93** was reported by the Bergbreiter group⁹⁵ to be useful as a recyclable and regenerable reagent for converting alkyl alcohols to alkyl chlorides (Scheme 22). This terminally functionalized polyethylene oligomer **93** has temperature-dependent solubility like that of polyethylene itself. Indeed, linear PE_{Olig}-supported species like **93** as well as other PE_{Olig} derivatives with other reagents or catalysts are insoluble in all organic solvents at room temperature. However, PE itself as well as these PE oligomers are not covalently crosslinked. Thus, a PE oligomer like

Scheme 22. Synthesis of alkyl chlorides mediated by **93**

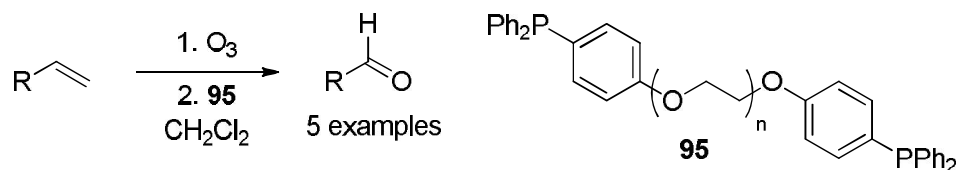


polyethylene itself is soluble in suitable solvents on heating. In the case of PE oligomers, this solubility can be achieved by heating in toluene above 80 °C. Thus **93** can be used in a mixture of toluene and carbon tetrachloride at 90 °C to form a homogeneous reaction mixture. In this case, after the reaction was finished, cooling the reaction mixture to room temperature led to quantitative precipitation of the PE_{Olig}-bound phosphine oxide **94** which can be recovered as a solid by a filtration from the product mixture. The recovered **94** was then reduced by trichlorosilane. However, in this instance the regenerated PE_{Olig}-bound phosphine **93** did not show the same activity as freshly prepared **93**. This was ascribed to partial formation of the phosphonium salt from **93** and alkyl chlorides.

PEG as supports for reagents and catalysts have a much longer history as soluble polymer supports. These polymers and their derivatives have the advantage of good solubility in many polar solvents, e.g. H₂O, DMF, EtOH. They also dissolve in solvents like toluene and dichloromethane. They are typically recovered by solvent precipitation where a concentrated solution of a PEG derivative in a “good” solvent is added to a large excess of an appropriate “poor” solvent, e.g. diethyl ether. The precipitated PEG derivative is then recovered by a filtration. This process can lead to high yields of recovered PEG species but at the expense of using a large amount of precipitating solvent. An example of this chemistry is illustrated by work by the Janda group⁹⁶ who reported using a PEG-bound triarylphosphine reagent **95** for ozonide reduction (Scheme 23). After the completion of the reactions, reaction mixtures were concentrated and added dropwise to vigorously stirring excess amount of diethyl ether to induce

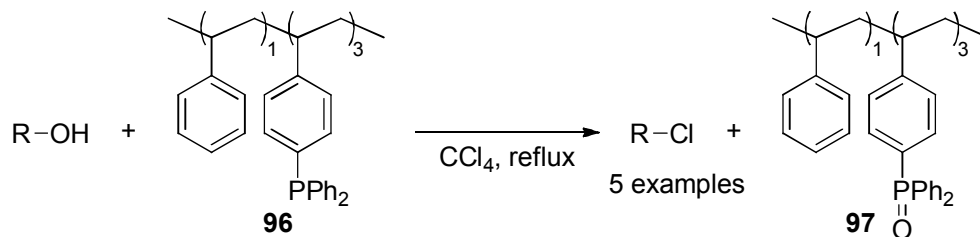
precipitation of the oxidized **95**. In the case, oxidized **95** was isolated by a filtration and reduction using AlH_3 reformed **95** which could be reused.

Scheme 23. PEG-bound phosphine **95** mediated ozonide reduction



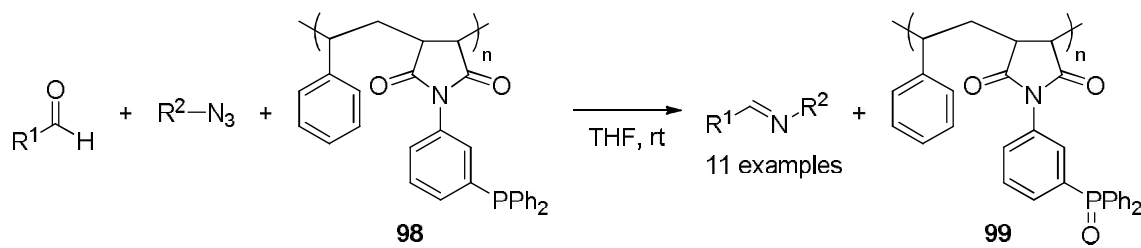
Non-crosslinked polystyrene (NCPS) is another soluble polymer that received attention for supporting reagents and catalysts. The Hodge group⁹⁷ for example described using a triarylphosphine supported on NCPS **96** to convert alkyl alcohols to alkyl chlorides (Scheme 24). In this case, the reaction was carried in refluxing carbon tetrachloride. Since the polymer **96** was soluble in carbon tetrachloride, the reaction mixture was initially homogeneous. However, as the reaction proceeded, the polymeric phosphine oxide **97** precipitated. At the end of the reaction, **97** was collected as a solid by filtering the cooled reaction mixture.

Scheme 24. NCPS-supported triarylphosphine **96** as a reagent for Wittig reactions



Recently, Mahdavi and Amani⁹⁸ reported using a linear styrene copolymer **98** containing triarylphosphine groups as a reagent for aza-Wittig reactions (Scheme 25).

Scheme 25. Aza-Wittig reactions mediated by **98**



The styrene copolymer **98** is soluble in THF while its phosphine oxide **99** is not. Therefore aza-Wittig reactions were carried in THF as homogeneous solutions in the beginning and turned into suspensions at the end. The products were isolated in good yields by filtration of the reaction mixture and evaporation of the solvent. The recovered **99** was successfully converted back to **98** with trichlorosilane and reused for four times without loss of efficiency.

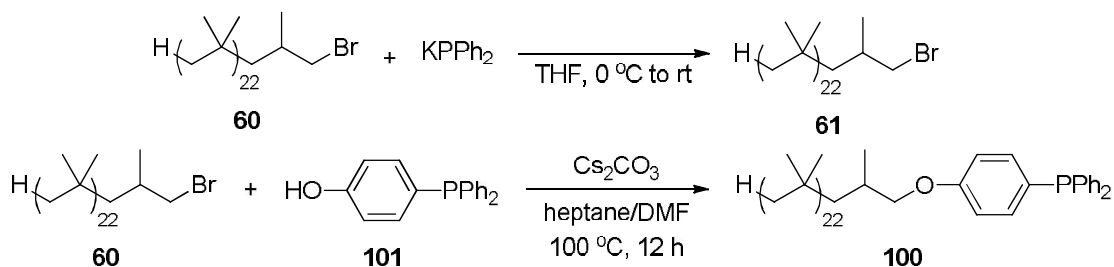
In our work, we have been using terminally functionalized polyisobutylene (PIB) oligomers as nonpolar phase selective supports for ligands and catalysts. PIB supports are readily soluble in many nonpolar or modestly polar solvents but can be separated in the heptane phase of liquid/liquid biphasic mixtures after a homogeneous reaction. As shown in the examples below, the heptane phase selective solubility properties of PIB enable PIB-bound phosphines and phosphine oxides to be easily separated from products by a liquid/liquid separation that avoids the requirements of higher temperature used

with PE oligomers or the requirements of a large excess of a precipitation solvent used often with poly(ethylene glycol) or polystyrene supports. As shown by the work below, these PIB-bound phosphines can be recovered, regenerated, and reused in a variety of chemistry.

Results and Discussion

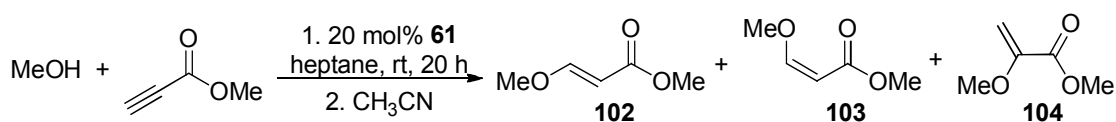
PIB-alkyldiphenylphosphine **61** was synthesized by reaction of PIB-CH₂Br **60** with potassium diphenylphosphide using chemistry described in chapter II (Scheme 26). The PIB-triarylphosphine **100** was prepared by allowing (4-diphenylphosphino)phenol **101** to react with **60** and a base under thermomorphic reaction conditions. These two PIB-supported phosphines have ³¹P NMR spectra similar to their low-molecular weight analogs. Chemical shifts of **61** and **100** on ³¹P NMR spectra are -19.6 and -6.5 ppm, respectively. The low molecular weight analogs isobutyldiphenylphosphine **64** and 4-methoxyphenyldiphenylphosphine **74** have chemical shifts of -19.5 and -6.5 ppm, respectively.

Scheme 26. Synthesis of PIB-phosphines **61** and **100**



PIB-alkyldiphenylphosphine **61** was first examined for its use as a catalyst for an addition reaction of methanol to methyl propiolate, a known reaction that generates a product mixture consisting mainly of *cis*- and *trans*-1,4 addition products (Scheme 27).⁹⁹ Methyl propiolate, methanol, and **61** were dissolved in heptane and allowed to react for 20 h. Acetonitrile was then added to the reaction mixture to form a biphasic mixture where **61** was in the heptane-rich phase and the products were in the polar acetonitrile

Scheme 27. Methanol addition of methyl propiolate catalyzed by **61**

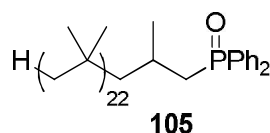


phase. The heptane solution of **61** was then separated from the product phase by a gravity separation. Addition of fresh substrates to this recovered heptane phase allowed **61** to be reused. This strategy allowed **61** to be recycled for up to six cycles with an average yield of 85% per cycle (Table 4). In this set of experiments, the yield of products decreased in the last cycle. ³¹P NMR spectroscopy showed that this was the result of the adventitious oxidation of **61** to form a phosphine oxide **105** (Figure 24). At this point the heptane solution of **61** could still be reused but only after reduction of the **105** (*vide infra*).

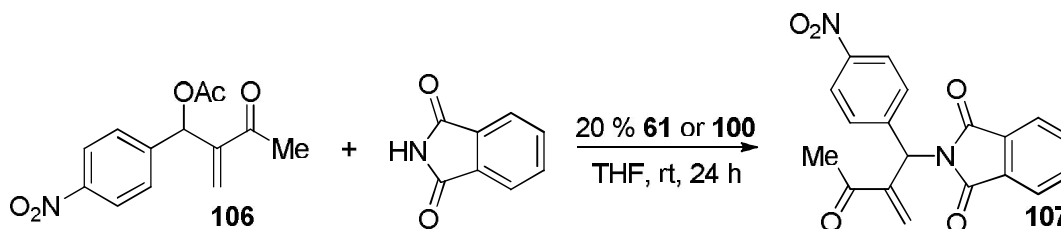
Table 4. Alcohol addition catalyzed by **61**^a

| run | yield (%) ^b | | | combined yield |
|-----|--------------------------------|------------------------------|------------------------------|----------------|
| | <i>trans</i> (102) | <i>cis</i> (103) | <i>gem</i> (104) | |
| 1 | 64 | 20 | 6 | 90 |
| 2 | 62 | 18 | 5 | 85 |
| 3 | 68 | 25 | 3 | 96 |
| 4 | 66 | 22 | 4 | 92 |
| 5 | 59 | 21 | 3 | 82 |
| 6 | 48 | 15 | 3 | 65 |

^aThe reaction was conducted with 0.2 mmol of methyl propiolate, 0.6 mmol of methanol, and 0.04 mmol of **61** in 2 mL of heptane. ^bGC yields.

**Figure 24.** PIB-alkyldiphenylphosphine oxide **105**

PIB-alkyldiphenylphosphine **61** can also function as a catalyst in allylic aminations (Scheme 28).¹⁰⁰ In this reaction, the allylic acetate **106**, phthalimide, and 20 mol% of **61** were allowed to react for 24 h at room temperature in THF. Then most of

Scheme 28. Allylic amination reaction catalyzed by **61** or **100**

the solvent was removed and an equivolume mixture of heptane and acetonitrile was added to the residue. The resulting biphasic mixture consisted of a heptane-rich solution of **61** and an acetonitrile solution of the product **107**. The acetonitrile product phase was separated and the product was further purified to give the expected product in an isolated yield of 96%. The catalyst **61** in the heptane solution was reused 2 times with yields of 62% and 10% in cycles 2 and 3. Adventitious oxidation of **61** to form **105** was again shown to account for the low yields in the failed recycling experiment. Later we turned our attention to the use of the triarylphosphine **100** as a more air-stable phosphine catalyst in the allylic amination reaction to evaluate the recyclability of **100**. It was found that **100** could be recycled and reused 5 times under similar reaction conditions affording the product with an average yield of 87% per run (Table 5).

Table 5. Allylic amination catalyzed by **100**^a

| run | yield (%) ^b |
|-----|------------------------|
| 1 | 96 |
| 2 | 95 |
| 3 | 93 |
| 4 | 94 |
| 5 | 87 |
| 6 | 54 |

^aThe reaction was conducted with 0.2 mmol of **106**, 0.4 mmol of phthalimide, and 0.04 mmol of **100** in 2 mL of THF. ^bIsolated yields.

In this case, adventitious oxidation of **100** to form **108** (Figure 25) was also observed after analyzing the heptane phase after cycle 6. ^1H NMR spectra of residues of the heptane and acetonitrile phases showed that neither **106** nor **107** were present in the heptane phase and that no PIB-phosphine or phosphine oxide was present in the acetonitrile phase.

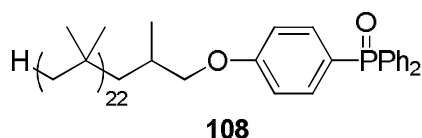
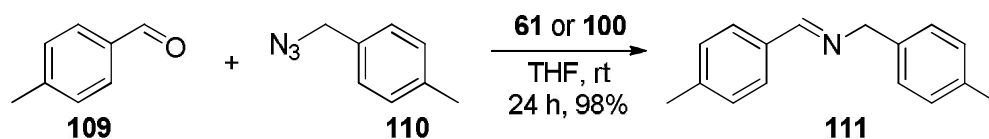


Figure 25. Oxidized PIB-triarylphosphine **108**

PIB-bound phosphines can also be used as reagents in reactions like an aza-Wittig reaction. This application of **61** or **100** used 4-methylbenzaldehyde **109** and 4-methylbenzyl azide **110** and formed the *N*-4-methylbenzyl aldimine **111** using either **61** or **100** as a phosphine reducing agent (Scheme 29). The use of **61** or **100** in this aza-Wittig reaction simplified separation of the product from the oxidized phosphine

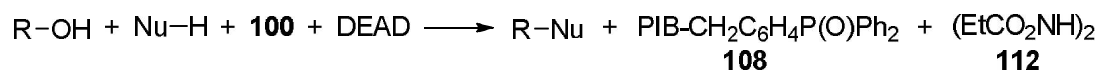
Scheme 29. Aza-Wittig reaction mediated by **61** or **100**



byproduct since the phosphine oxides **105** and **108** formed during the course of the reaction were selectively soluble in heptane phase in a biphasic mixture of heptane and acetonitrile. After removal of the reaction solvent, the reaction mixture was redissolved in a biphasic mixture of heptane and acetonitrile to separate the acetonitrile-soluble aldimine product from the heptane-soluble PIB-bound oxidized phosphine byproduct **105** or **108**.


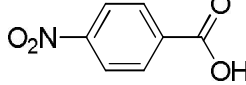
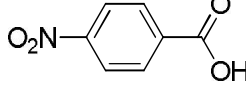
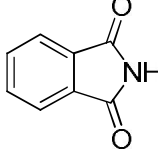
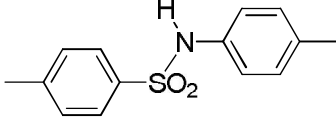
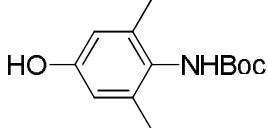
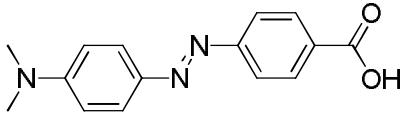
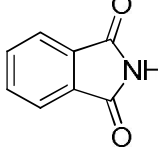
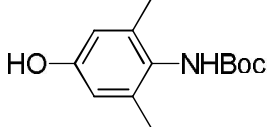
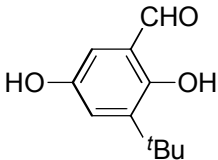
One of the more common reactions that use a triarylphosphine as a reagent is the Mitsunobu reaction. PIB-triarylphosphine **100** was shown to be useful in a variety of Mitsunobu reactions with a wide range of substrates (Scheme 30 and Table 6). In these

Scheme 30. Mitsunobu reactions mediated by **100**



cases, using the PIB-bound phosphine **100** simplified the isolation of products free of phosphine oxide byproducts. For example, when 2-propanol was allowed to react with 4-nitrobenzoic acid (entry 1), the phosphine oxide **108** could be easily removed from the ester product by a liquid/liquid extraction. The ease of separation of **108** from Mitsunobu products was also useful in functionalizing polymers. For instance, poly(ethylene glycol) monomethyl ether ($M_n = 5000$) was used as the alcohol substrate (entries 2-6) with a wide range of nucleophiles to provide high yields of terminally-substituted poly(ethylene glycol)s. In these cases, the functionalized PEG products

Table 6. Mitsunobu reactions mediated by **100**^a

| | alcohol | nucleophile | Isolated yield(%) |
|---|--|--|-------------------|
| 1 |  |  | 95 |
| 2 | Me(OCH ₂ CH ₂) ₁₁₃ OH (M _n = 5000) |  | 95 |
| 3 | Me(OCH ₂ CH ₂) ₁₁₃ OH (M _n = 5000) |  | 94 |
| 4 | Me(OCH ₂ CH ₂) ₁₁₃ OH (M _n = 5000) |  | 93 |
| 5 | Me(OCH ₂ CH ₂) ₁₁₃ OH (M _n = 5000) |  | 92 |
| 6 | Me(OCH ₂ CH ₂) ₁₁₃ OH (M _n = 5000) |  | 90 |
| 7 | Me(CH ₂ CH ₂) ₁₉ OH (M _n = 550) |  | 99 |
| 8 | Me(CH ₂ CH ₂) ₁₉ OH (M _n = 550) |  | 99 |
| 9 | Me(CH ₂ CH ₂) ₁₉ OH (M _n = 550) |  | 90 |

^aThe reactions were generally carried out with a 1:1:1 molar ratio of nucleophile:**100**:DEAD using with the alcohol as the limiting reagent in toluene at 80 °C. Entry 1 used THF at rt and excess alcohol.

could be isolated by precipitation after adding the reaction mixture to cold ether. Since the PIB-bound phosphine oxide **108** and the DEAD byproduct **112** are soluble in ether, no further purification was required. This was in contrast to a similar experiment using triphenylphosphine. When triphenylphosphine was used to prepare PEG derivatives, the first precipitation of PEG led to PEG products containing ca. 20% triphenylphosphine oxide as indicated by the integration of peaks from 7.35 to 7.70 ppm in the ^1H NMR spectrum. In addition, we were also able to separate **108** from **112** by concentrating the filtrate and redissolving the residue in a heptane/acetonitrile mixture. As was true in the above examples, a gravity separation of the biphasic mixture afforded a heptane phase containing only **108**. In this case the phosphine oxide **108** could be reduced and reused.

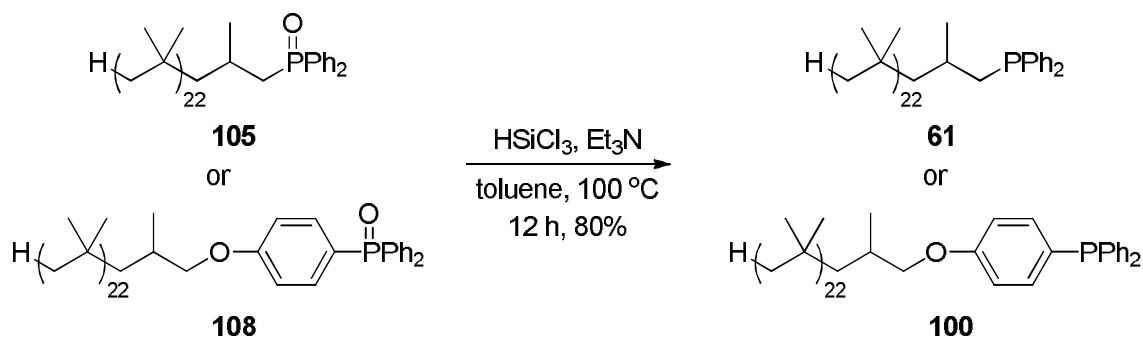
The use of these PIB-bound phosphines to modify polymers via Mitsunobu chemistry was also extended to the synthesis of terminally functional polyethylene oligomers (PE_{Olig}). As noted above, polyethylene oligomers have thermomorphic solubility and are completely insoluble in all solvents at room temperature but soluble in solvents like toluene on heating. In the case of some commercially available PE oligomers, dissolution can even be achieved in toluene at temperatures of 65-70 °C. The temperature differential in solubility and the current commercial availability of PE oligomers increases the potential utility of functional PE_{Olig} as ligands for thermomorphic catalysts.^{55,59,64,101-105} However, syntheses of ligands with PE_{Olig} groups still can be complicated because separation techniques like chromatography are impractical and because PE oligomers are insoluble in the polar aprotic solvents often favored for nucleophilic substitution reactions. Thus we were pleased to find that PIB-

phosphine reagents are a viable alternative to ordinary phosphines in Mitsunobu reactions of hydroxyl-terminated polyethylene oligomers. For example, when a commercially available PE_{Olig} ($M_n = 550$) with a terminal hydroxyl group¹⁰⁶ was used in Mitsunobu reactions like those in entries 7 to 9, the PE_{Olig}-derivatives formed in a nucleophilic substitution can be isolated as solids by filtration after simply cooling the reaction mixture to room temperature. The filtrate was then concentrated and the residue was redissolved in a mixture of heptane and acetonitrile. The PIB-bound phosphine oxide **108** was then isolated in a heptane solution by a liquid/liquid separation of the heptane-acetonitrile mixture. These Mitsunobu reactions of polyethylene oligomers were used to advantage in syntheses of other ligands in our group because they take advantage of the regioselectivity inherent in Mitsunobu chemistry. For example, when the substituted hydroquinone was used as the nucleophile (entry 9), the less hindered phenolic group was selectively functionalized to form PE_{Olig}-salicylaldehyde, a precursor for the synthesis of a PE_{Olig}-salen ligand.⁵⁹

Trichlorosilane is a common reagent used to reduce phosphine oxides to phosphines as shown in the previous examples of polymer-supported phosphines. However, our experience is that the use of trichlorosilane to reduce phosphine oxides to phosphines is experimentally complicated because of separation problems involving the solid siliceous side products produced after an aqueous workup.⁶⁴ For example, these byproducts make reduction of an insoluble polymer-bound phosphine oxide and reduction of PEG-bound phosphine oxides experimentally difficult.⁹⁶ However, this is not the case with phosphine oxides formed in reactions of **61** or **100**. Since PIB is

soluble in a nonpolar solvent, we could carry out reduction of phosphine oxides **105** or **108** with trichlorosilane in toluene and easily separate the toluene solution of **61** or **100** from the silicon-containing byproducts formed in an aqueous workup (Scheme 31).

Scheme 31. Reduction of PIB-phosphine oxides to PIB-phosphines



Removal of toluene from the **61** or **100** regenerated from **105** or **108** produced phosphines that were identical to those prepared initially based on ^{31}P NMR spectroscopy. More importantly, these regenerated phosphines **61** and **100** could be reused in both the catalytic and stoichiometric reactions described above (Schemes 27 to 30) with reactivity equivalent to freshly prepared **61** and **100**.

Conclusions

In summary, PIB-bound alkyldiphenylphosphine **61** and triarylphosphine **100** were synthesized and examined as catalysts and reagents. The PIB-bound alkyldiphenylphosphine **61** can be used as a catalyst and recycled/reused repeatedly in

methanol addition of methyl propiolate and the PIB-bound triarylphosphine **100** can be used as a reusable catalyst in allylic amination. Both PIB-bound phosphines **61** and **100** were used successfully as reagents in aza-Wittig and Mitsunobu reactions that use the nonpolar phase selective solubility of the phosphine oxide byproducts to facilitate product purification. Finally, the phosphine oxides **105** and **108** formed either by adventitious oxidation or in the course of a stoichiometric reaction can be separated as heptane solutions and can easily be recycled to form the starting phosphine catalysts/reagents by reduction with trichlorosilane.

CHAPTER IV
POLYMER-SUPPORTED N-HETEROCYCLIC CARBENES AS RECYCLABLE
AND REUSABLE CATALYSTS

Introduction

N-Heterocyclic carbenes (NHCs) have been widely used as ligands in organometallic chemistry (Figure 26). The tunable electronic and steric properties of these ligands have led to the syntheses of a variety of NHC-metal complexes whose reactivity as catalysts have been evaluated.¹⁰⁷⁻¹¹³ The use of NHCs in their own right as organocatalysts has also been studied. For example, the use of NHCs as catalysts has been reported for benzoin condensations, Stetter reactions, aza-Baylis-Hillman reactions, isocyanate trimerizations, cyanosilylation, transesterification, lactide polymerizations, carbonate formation, amide formation, and hydrosilylation reactions.¹¹⁴⁻¹¹⁸

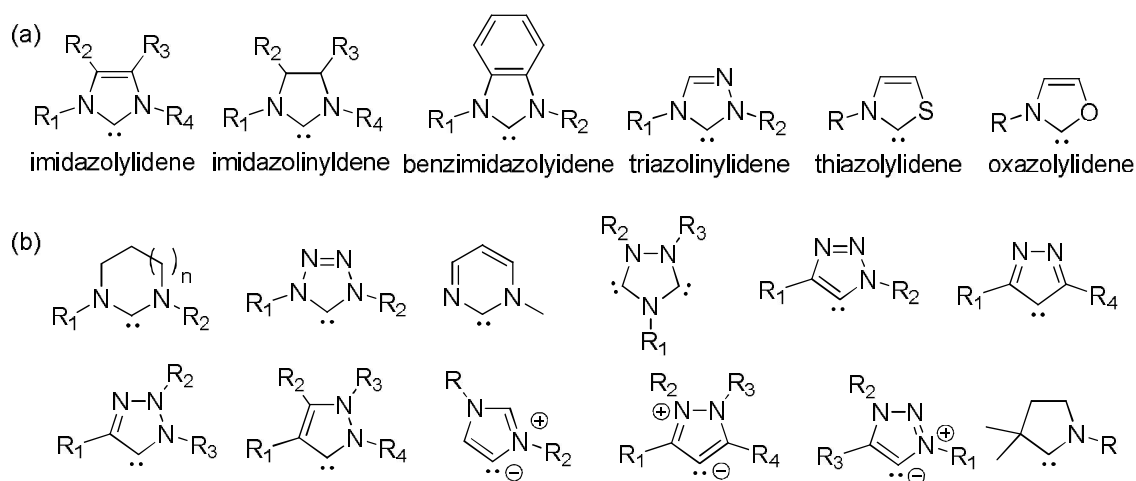
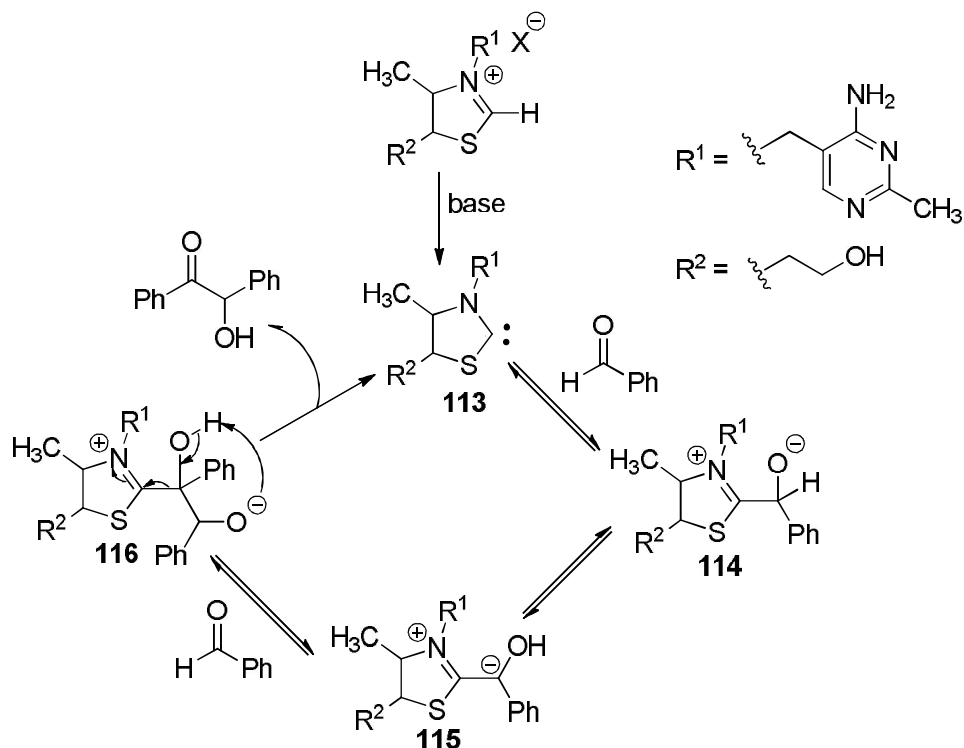


Figure 26. Examples of (a) commonly used NHCs and (b) less commonly used NHCs

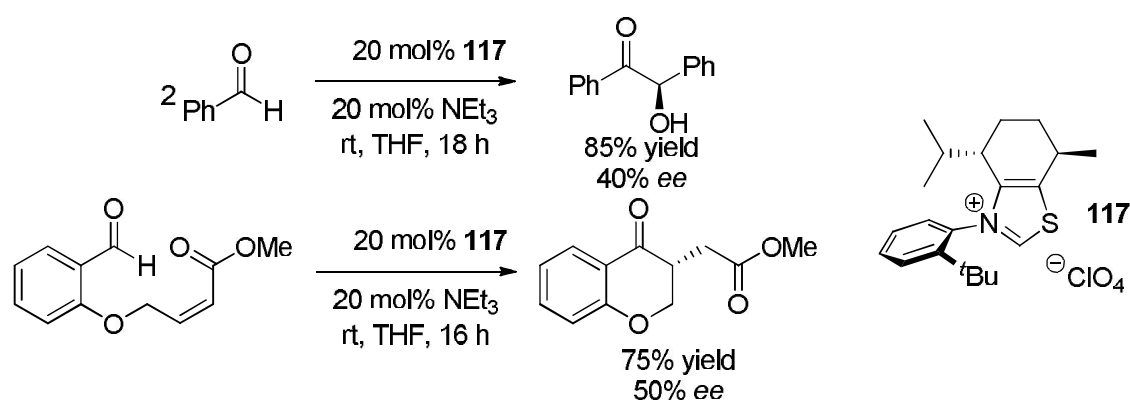
The benzoin condensation reaction has attracted much attention for several decades notably because of its use in C-C bond formation. The widely accepted mechanism of NHC-catalyzed benzoin condensation was proposed by Breslow¹¹⁹ in 1958 (Scheme 32). In this mechanism, the conjugate base **113** of the thiazolium salt in thiamin acts as a nucleophile leading to **114**. Base promoted isomerization then affords **115**, which reacts with another molecule of benzaldehyde to form **116**. Intermediate **116** eliminates benzoin and regenerates **113**. In addition to the formation of a new C-C bond,

Scheme 32. Proposed mechanism for benzoin condensation



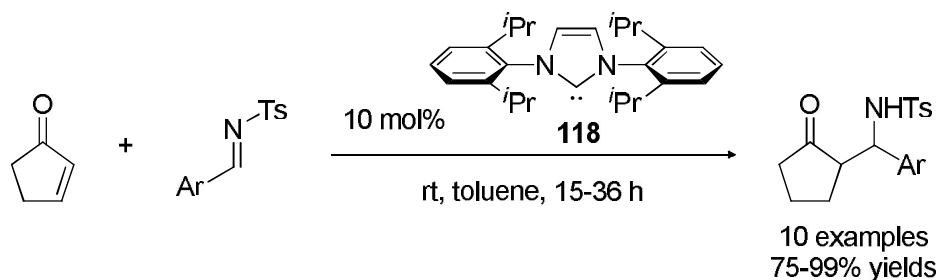
the benzoin condensation features the creation of a stereogenic center in the product. It thus now serves as an important reaction to evaluate the potential of new chiral heterazolium salts. For example, Pesch¹²⁰ et al. reported an asymmetric benzoin condensation catalyzed by a chiral thiazolium salt **117** (Scheme 33). The same catalyst was also used in an intramolecular Stetter reaction providing the product with a moderate yield and moderate *ee*.

Scheme 33. Asymmetric benzoin condensation and Stetter reaction using **117**



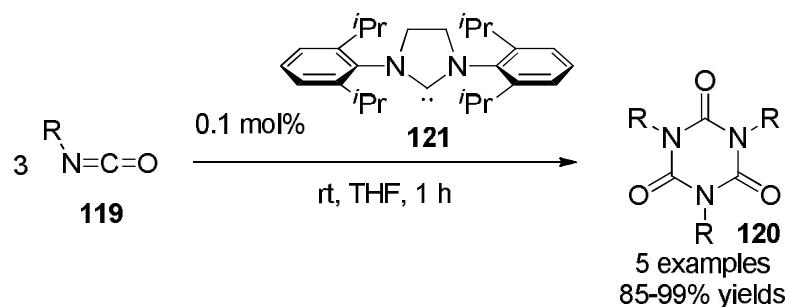
The following discussion focuses on various chemistry that uses NHCs generated from imidazolium derivatives—chemistry most related to my work. For example, the Ye¹²¹ group (Scheme 34) described aza-Baylis-Hillman chemistry where various *N*-tosylaldimines were reacted with cyclopentenone in the presence of catalytic amount of NHC **118** to form β -aminoketones in moderate to good yields.

Scheme 34. Aza-Baylis-Hillman reactions catalyzed by **118**



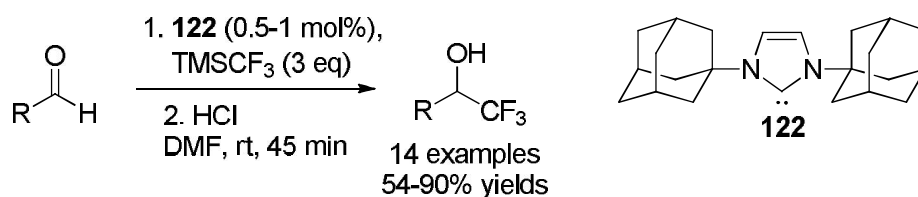
Another interesting approach in applying NHC catalysts for the formation of heterocyclic compounds was reported by Louie and co-workers.¹²² Her research group developed a straightforward cyclotrimerization method to convert a variety of isocyanates **119** to isocyanurates **120** in excellent yields with low catalyst loadings (Scheme 35). Among the different NHC catalysts tested in this reaction, **121** was the most suitable one for this reaction. With phenyl isocyanate was used as the substrate, the catalyst loading could be as low as 0.001 mol% and the reaction still proceeded to completion in a reasonable time.

Scheme 35. Isocyanate trimerization catalyzed by NHCs



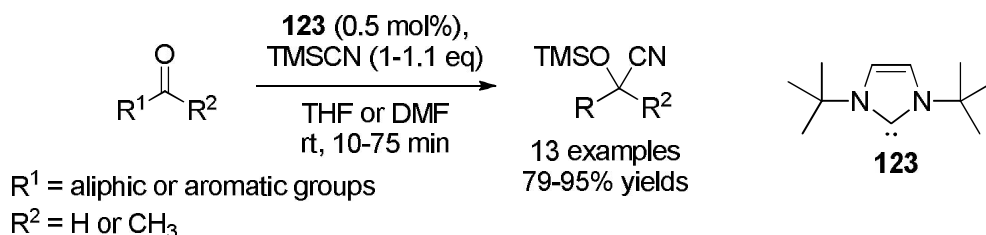
In 2005, Song¹²³ et al. reported a NHC-catalyzed trifluoromethylation reaction of carbonyl compounds (Scheme 36). In this case, the NHC catalyst **122** successfully transformed several aliphatic and aromatic aldehydes forming CF₃-substituted tertiary

Scheme 36. Trifluoromethylation of aldehydes catalyzed by NHCs



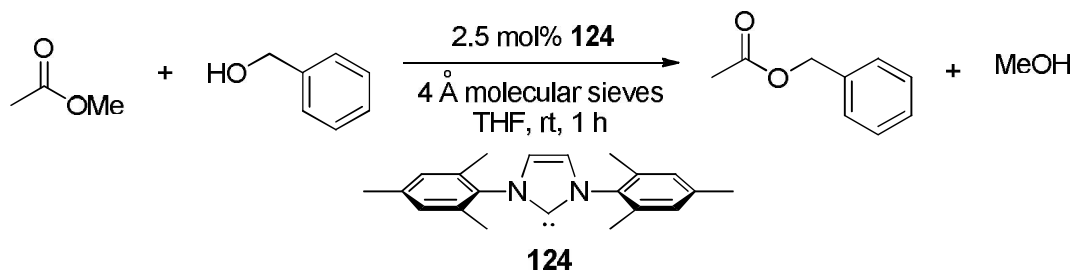
alcohols in moderate to good yields under mild reaction conditions with 0.5 to 1 mol% catalyst loading. The same group¹²⁴ later reported the cyanosilylation of carbonyl compounds with a NHC catalyst **123** (Scheme 37). In this report, various aldehydes and ketones were converted into the trimethylsilylated cyanohydrins in good yields with 0.5 mol% of catalyst loading.

Scheme 37. Cyanosilylation of carbonyl compounds catalyzed by **123**



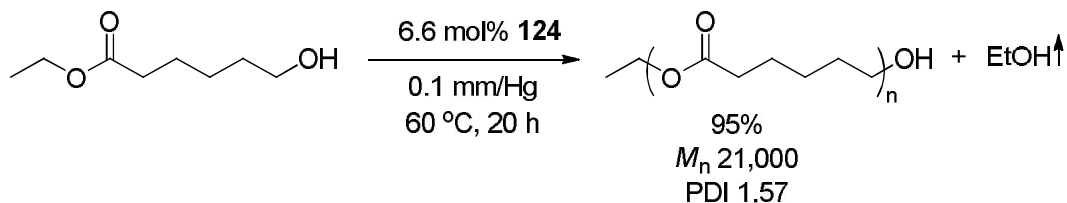
In 2002, the Nolan group¹²⁵ described chemistry using NHCs to catalyze transesterification of methyl acetate and benzyl alcohol (Scheme 38). In this particular

Scheme 38. Transesterification catalyzed by **124**



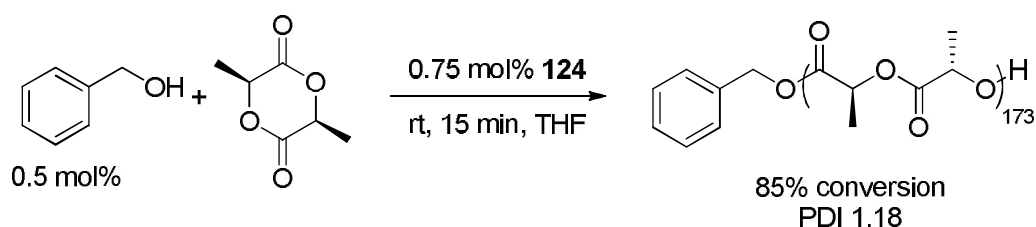
case, 2.5 mol% of NHC catalyst **124** formed a 93% yield of benzyl acetate under conditions where nucleophilic catalysts such as DMAP and DBU were inefficient. The Waymouth and Hedrick groups¹²⁶ also reported similar chemistry with NHC catalyst **124** for preparing high yields of polyesters by condensation polymerizations (Scheme 39).

Scheme 39. Polymerization of ethyl 6-hydroxyhexanoate catalyzed by **124**



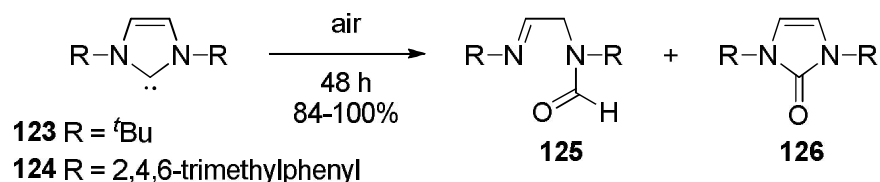
Poly lactides are an important class of biodegradable polymers.¹²⁷ NHC-catalyzed ring-opening polymerizations of lactides and other cyclic lactones were first reported by the Hedrick group.^{128,129} It was found that the carbene catalyst **124** is a very reactive catalyst that can polymerize lactide in 92% conversion in 15 min with 0.75 mol% catalyst (Scheme 40).

Scheme 40. Lactide polymerization catalyzed by **124**



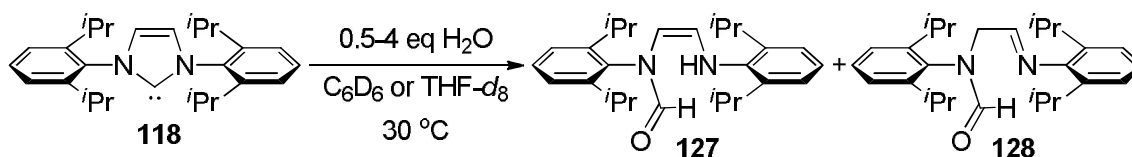
A problem with NHC catalysts is that they can decompose in the presence of moisture and air. This is illustrated by work by the Baceiredo group¹³⁰ who studied the decomposition of NHC carbenes **123** and **124** in air (Scheme 41). These carbenes were

Scheme 41. Decomposition of carbenes **123** and **124** in air

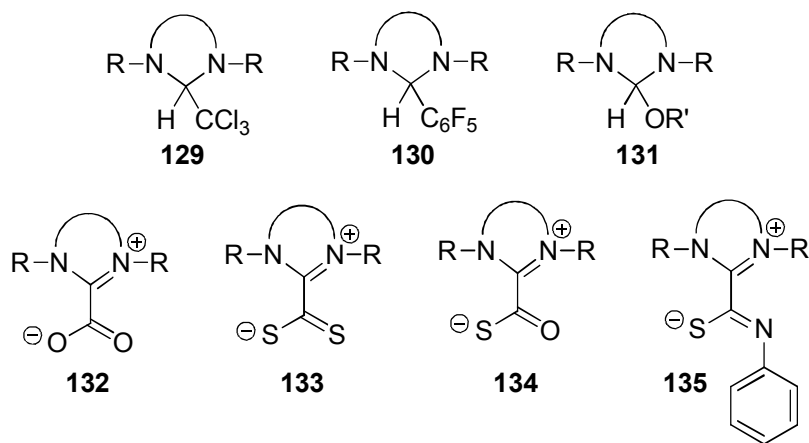


allowed to stand in air for 48 h and the residue of these materials were dissolved in C_6D_6 and analyzed by 1H NMR spectroscopy. Most of these carbenes decomposed and form a mixture of formamide **125** and imidazolone **126**. Decomposition of NHC carbenes were also reported by Hollóczy¹³¹ et al. who studied hydrolysis of NHC **118** in C_6D_6 and THF- d_8 by NMR spectroscopy (Scheme 42). Upon addition of 0.5-4 eq. of water to a

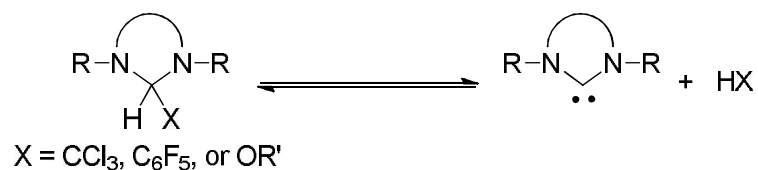
Scheme 42. Hydrolysis of NHC **118** in C_6D_6 and THF- d_8



C_6D_6 or a THF- d_8 solution of carbene **118**, a mixture of formamides **127** and **128** formed and were observed by 1H NMR spectroscopy. The decomposition of carbene **118** was completed in a few hours at 30 °C in both solutions. Thus, NHCs are generally stored and used in an inert atmosphere or generated *in situ* by treating the corresponding imidazolium salts with bases. There are also other methods to generate NHCs in the reaction mixture based on the use of NHC adducts. Several different types of NHC adducts have been prepared in prior work for this sort of process (Scheme 43).

Scheme 43. Common NHC precatalysts

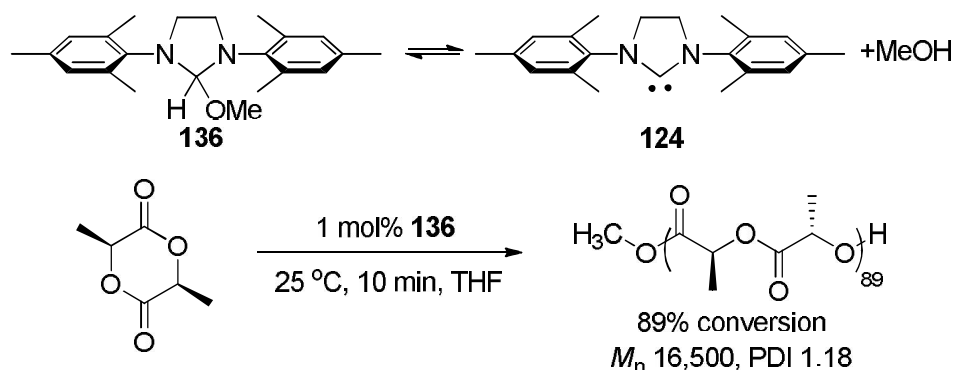
Chloroform, pentafluorobenzene, and alcohol adducts of NHCs (**129**, **130**, and **131**, respectively) are efficient NHC precursors which can liberate free NHCs in the reaction mixture. These adducts are commonly used as organocatalysts directly as shown in Scheme 44 or as precursors to prepare NHC-metal complexes.¹³²⁻¹³⁵

Scheme 44. Free NHCs from adducts

The Waymouth and Hedrick groups¹³³ found that the alcohol adducts of carbene **124** can serve as latent NHC catalysts in lactide polymerization. Unlike the unstable NHCs, these adducts can be easily purified and characterized by spectroscopic methods.

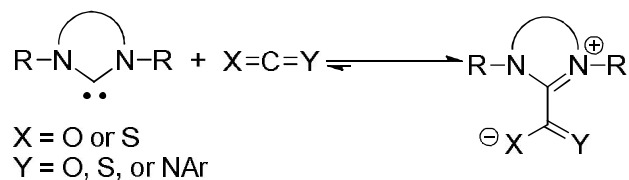
The utility of these adducts as precatalysts is illustrated by the use of the NHC-methanol adduct **136** (Scheme 45). Here, the adduct **136** serves as a latent catalyst as it is in equilibrium with the free carbene **124** and methanol. Thus, when added to lactide, polylactide can form and in this case the polymer was prepared with a degree of polymerization and PDI like that achieved using **124** in the presence of methanol.

Scheme 45. Lactide polymerization catalyzed by NHC-alcohol adduct **136**



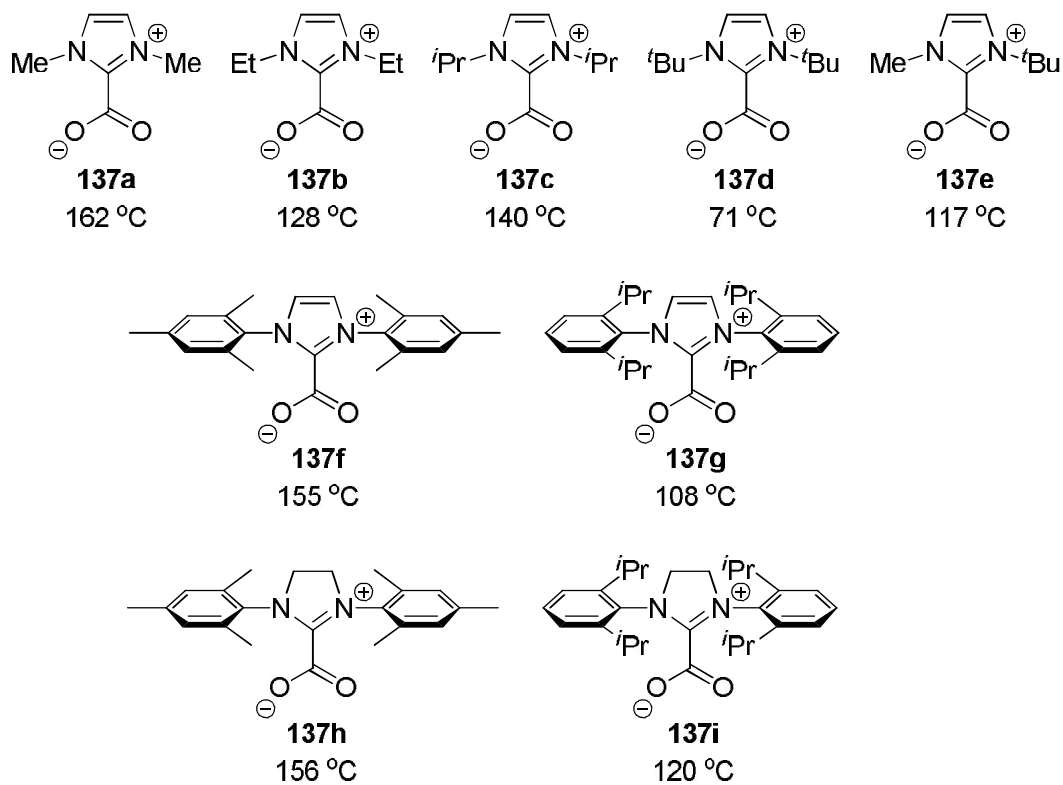
CO_2 , CS_2 , COS , and phenyl isothiocyanate adducts of NHCs (**132**, **133**, **134**, and **135**, respectively) have also been synthesized and characterized both by spectroscopic methods and thermogravimetric analysis (TGA) (Scheme 46).^{136,137} It was found that most of these CS_2 adducts are thermally stable to 200 °C as indicated by TGA studies. Thus, they need to be heated to higher temperatures in order to decompose and release free NHCs. Their CO_2 and COS counterparts decompose at lower temperatures. Therefore the applications of using these adducts to generate NHCs under thermolysis conditions have been more focused on CO_2 and COS adducts.

Scheme 46. Syntheses of adducts **132** to **135**



The Louie group synthesized NHC-CO₂ adducts like **137** and analyzed these adducts by spectroscopy and TGA (Scheme 47).^{138,139} These adducts decompose between 71-162 °C as shown by TGA with loss of CO₂ based on the measured weight loss. The behavior of these adducts in solution was also studied. Louie¹³⁸ also showed

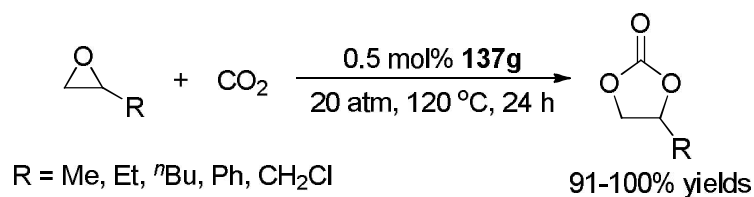
Scheme 47. NHC-CO₂ adducts and their decomposition temperatures



that when a CD_2Cl_2 solution of NHC- CO_2 adduct **137g** was placed under 1 atm of ^{13}C , the intensity of carbonyl resonance in the ^{13}C NMR spectrum increased. Similarly, reintroduction of CO_2 (1 atm) to ^{13}C -labeled **137g** attenuated the carbonyl signal. These results suggest that the CO_2 adduct **137g** is in equilibrium with carbene **118** and CO_2 in solution. The Lu group¹⁴⁰ also studied the thermal stability of **137g** in CH_2Cl_2 using *in situ* monitoring of the 1692 cm^{-1} region (the $\nu(\text{CO}_2)$ region) of the IR spectrum of **137g** utilizing a temperature-controlled high pressure liquid cell. At $12\text{ }^\circ\text{C}$, no obvious decomposition of CO_2 adduct **137g** was observed over 4 h. However, on heating to $100\text{ }^\circ\text{C}$, most of **137g** decomposed in 1 h. Such decomposition was significantly suppressed if a high CO_2 pressure (20 atm) was present. These results confirmed that the CO_2 adduct **137g** is in equilibrium with the free carbene **118** and that the amount of free carbene present becomes more significant on heating.

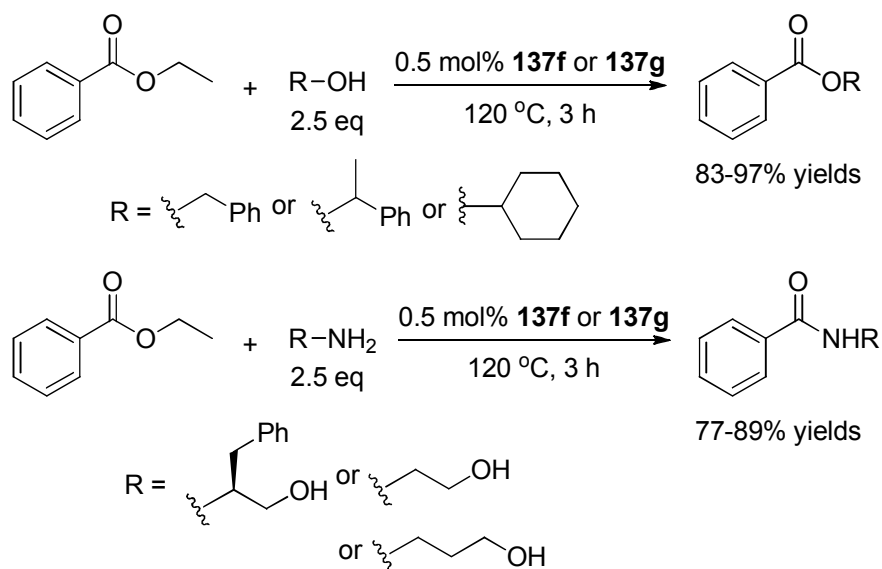
This dynamic behavior of the NHC- CO_2 adducts also allows these adducts to be used as latent organocatalysts. The Lu group¹⁴⁰ tested this idea by studying the catalytic activity of several NHC- CO_2 adducts in a coupling reaction of carbon dioxide and epoxides to afford cyclic carbonates (Scheme 48). Among the catalysts examined, CO_2 adduct **137g** showed the best catalytic activity affording good yields of carbonate

Scheme 48. Carbonate formation using **137g** as a catalyst precursor



products in 24 h at 120 °C. Recently, the chemistry using NHC-CO₂ adducts as NHC precursors was also described by Wang and Li¹⁴¹ (Scheme 49). Transesterification and amide formation reactions were used to examine the catalytic activity of several adducts. In this case, 0.5 mol% of NHC precatalysts **137f** and **137g** successfully promoted these two reactions providing the benzoate and benzamide products in good yields.

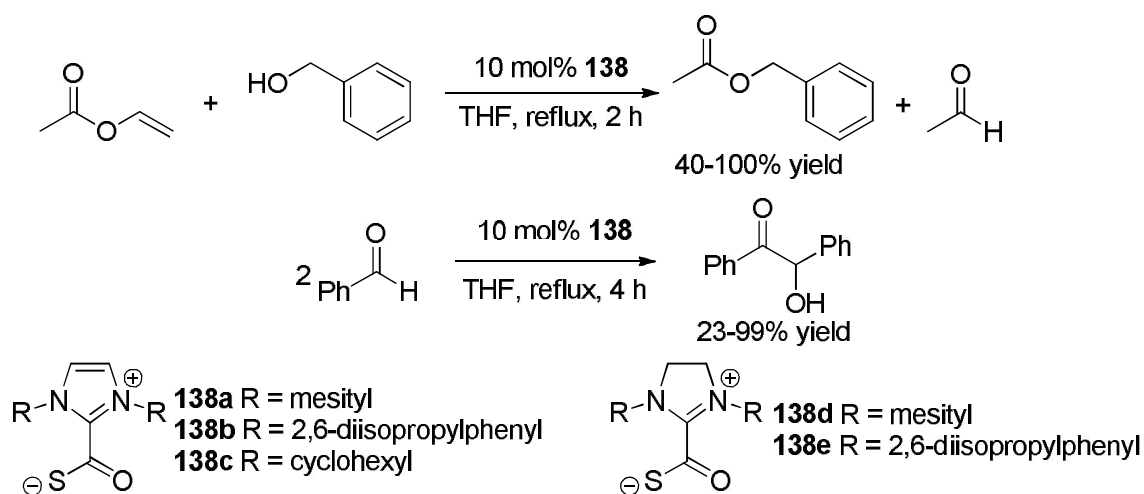
Scheme 49. Transesterification and amide formation reactions using **137f** and **137g**



Recently, Hans¹³⁷ et al. synthesized NHC-COS adducts **138** and used these adducts as latent organocatalysts for transesterification of vinyl acetate and benzyl alcohol (Scheme 50). Among the NHC-COS adducts screened, the authors found that adducts **138a**, **138b**, and **138c** were efficient to produce the benzyl acetate product in good yields. In particular, the NHC-COS adduct **138c** was able to catalyze the

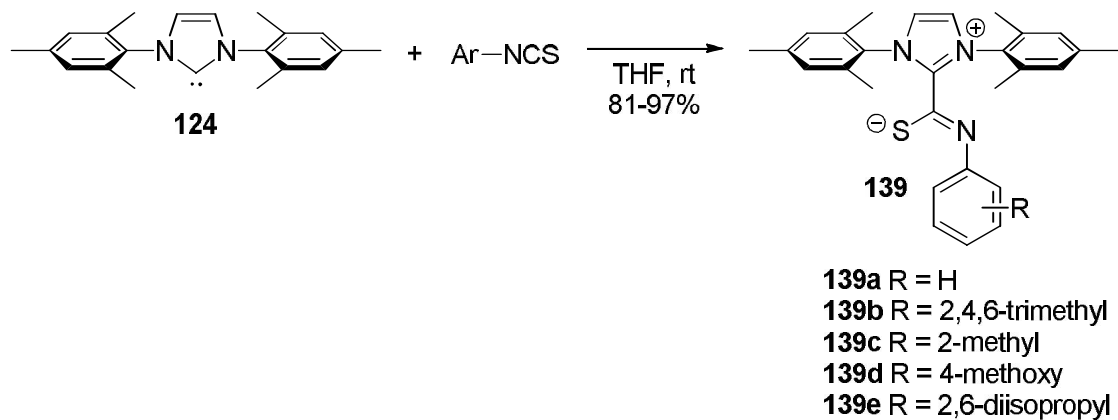
transesterification reaction even at room temperature affording benzyl acetate in quantitative yield. Such results indicate the existence of equilibrium between NHC-COS adducts and the free carbenes and COS in solutions like those observed from NHC-CO₂ adducts. NHC-COS adducts **138** were also used as catalyst precursors in benzoin condensation reactions but only **138d** was able to provide benzoin product with a good yield.

Scheme 50. Transesterification and benzoin condensation reactions with **138**



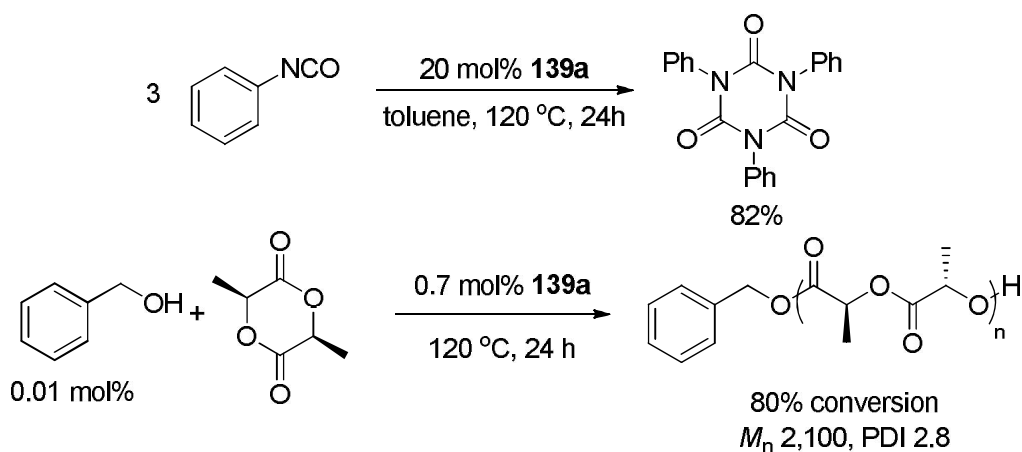
In 2011, the Bielawski group¹⁴² reported synthesis of NHC-isothiocyanate (NHC-NCS) adducts **139** from NHC **124** and aryl isothiocyanates (Scheme 51). The equilibrium constant of forming NHC-NCS adduct **139a** was estimated to be $5.94 \times 10^{14} \text{ M}^{-1}$ at 25 °C. The activation energy for the adduct **139a** to revert to carbene **124** and phenyl isothiocyanate is 28.5 kcal/mol. Thus, in order to generate carbene **124**, the

Scheme 51. NHC-isothiocyanate adduct formation



NHC-NCS adduct **139a** has to be heated to elevated temperatures in solutions. The NHC-NCS adduct **139a** was used as a latent catalyst for isocyanate trimerization and lactide polymerization at elevated temperatures (Scheme 52). In the isocyanate trimerization reaction, the adduct **139a** and phenyl isocyanate were heated in toluene to 120 °C in a sealed tube for 24 h and the product isocyanurate was isolated in 82% yield.

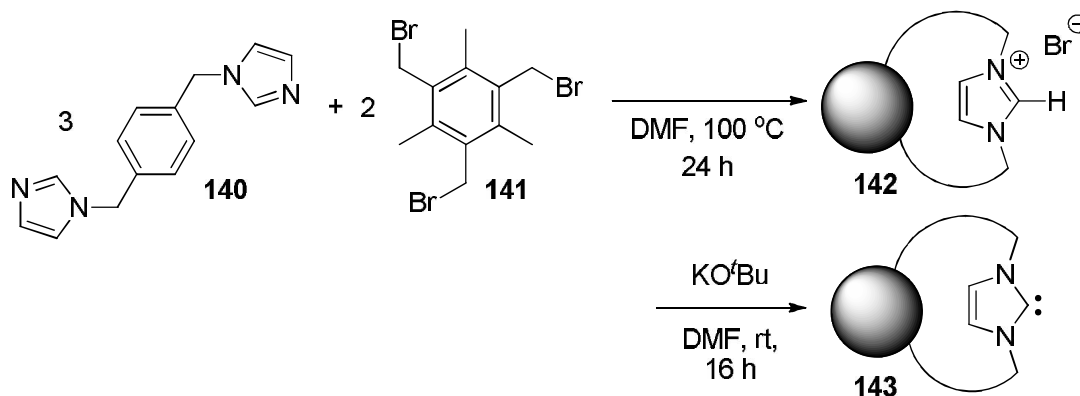
Scheme 52. Phenyl isocyanate trimerization and lactide polymerization



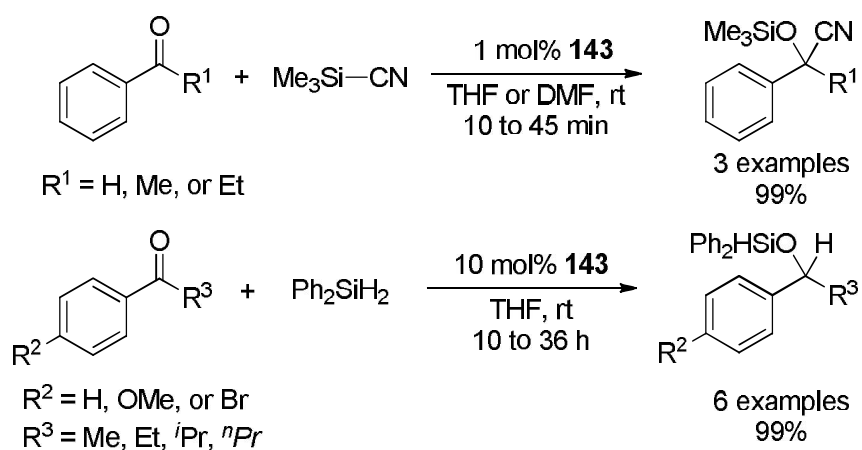
Lactide polymerization was also carried out in the presence of **139a** using benzyl alcohol as the initiator at 120 °C converting 80% of lactide to polylactide. Reactivity of NHC-NCS adducts with different substituents **139a-e** were studied by carrying out phenyl isocyanate trimerization reactions with 0.05 mol% of NHC-NCS adducts **139** in toluene for 2 h in reactions at 70-120 °C. After analyzing the reaction mixtures by IR spectroscopy, **139c** and **139d** with substituents on *ortho* and *para* positions on the phenyl ring of the aryl isothiocyanate moiety were shown to provide higher conversions in this trimerization reaction than **139a**. These results showed that NHC-NCS adducts **139** could be alternative NHC precatalysts for reactions carried out at elevated temperatures.

Owing to the high price of NHCs and the high mol% loading of these catalysts in catalytic reactions, immobilizing NHCs on polymers for recycling and reusing makes NHC-catalyzed chemistry attractive in large scale syntheses. Efforts to recycle NHC-ligated metal complexes or NHC catalysts have been developed. For example, studies where NHCs or NHC adducts are immobilized on insoluble polymer supports have been reported. However, in addition to the problems often seen with immobilization NHCs or NHC adducts on insoluble supports, problems with the air and moisture sensitivity of NHCs still make recycling NHCs difficult.

In 2009, the Ying group¹⁴³ reported synthesis of a polymer-supported imidazolium bromide from condensation of bisimidazole **140** and tris(bromomethyl)-mesitylene **141** in DMF (Scheme 53). The resulting solid polymeric imidazolium bromide **142** was deprotonated by potassium *tert*-butoxide to form a polymer-supported

Scheme 53. Synthesis of polymer-supported NHC **143**

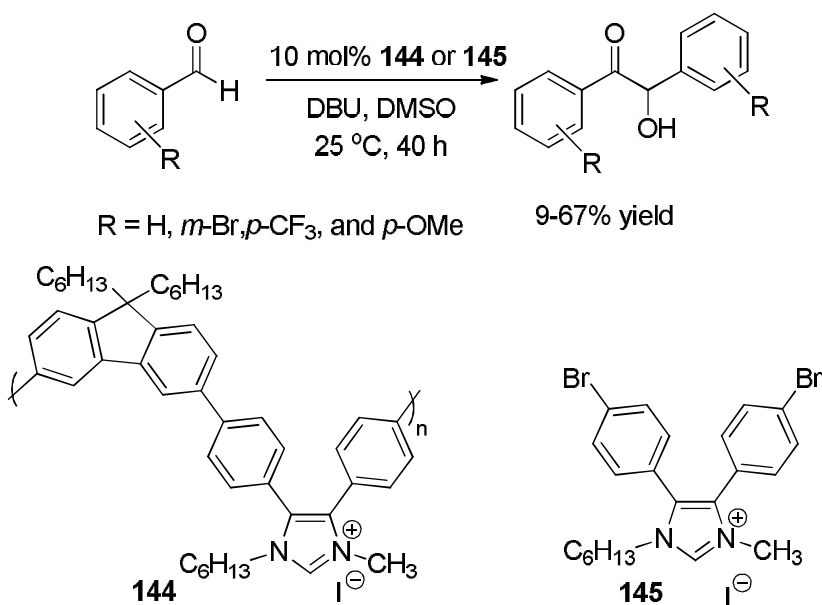
NHC **143** which was characterized by IR and solid-state NMR spectroscopy. The solid polymeric NHC **143** was used as a solid-supported catalyst in formation of silylated cyanohydrins and siloxanes of carbonyl compounds (Scheme 54). Both of these reactions proceeded smoothly at room temperature with 1-10 mol% loading of the NHC catalyst **143**. In the case when benzaldehyde was used for cyanohydrin formation,

Scheme 54. Reactions catalyzed by polymeric carbene catalyst **143**

catalyst **143** was recycled by filtration and reused for two times without loss of catalytic activity. Similar recyclability of catalyst **143** was also observed when acetophenone was used as the substrate in the hydrosilylation reaction and catalyst **143** was recycled and reused for 2 times affording the siloxane product with quantitative yields.

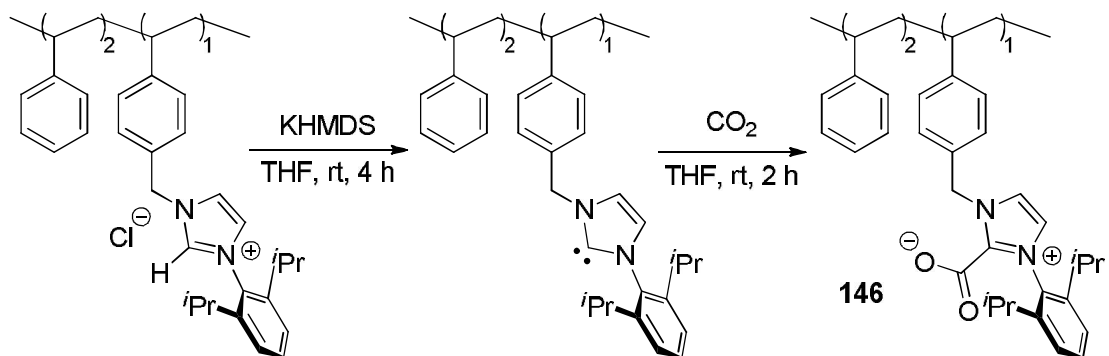
Soluble polymeric NHC catalysts can be prepared by incorporating NHC precursors into main chain of a linear soluble polymer. This is illustrated by work by the Bielawski group¹⁴⁴ who synthesized a polymeric imidazolium salt **144** and its low molecular weight analog **145**. These imidazolium salts **144** and **145** were used as precursors for NHC catalysts in benzoin condensations under basic conditions (Scheme 55). When benzaldehyde was used as the substrate, NHCs generated *in situ* from **144**

Scheme 55. Benzoin condensation catalyzed by NHCs generated from **144** and **145**

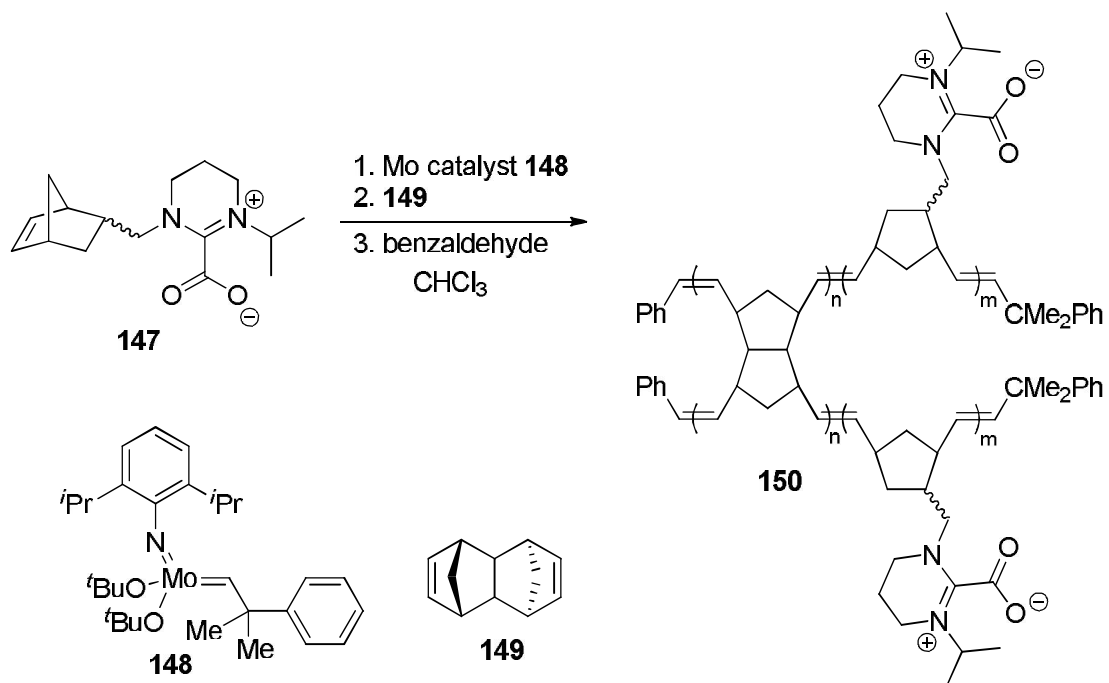


and **145** had similar catalytic activity and the benzoin products were isolated in 67% yield in both cases. Furthermore, the recyclability and reusability of **144** was also studied. When a benzoin condensation reaction using benzaldehyde as the substrate was finished, a dioxane solution of HCl and excess ethyl acetate were added to the reaction mixture to precipitate **144** as a polymeric imidazolium salt. Thus the polymeric imidazolium salt **144** was collected by a filtration and reused twice giving the benzoin product in 66% and 64% yields in cycle 2 and 3, respectively.

Polymer-supported NHC-CO₂ adducts as NHC precursors have also been reported. This is illustrated by work by the Lu group¹⁴⁵ who reported synthesis of a polystyrene-supported NHC-CO₂ adduct **146** and studied its CO₂ release using TGA (Scheme 56). The TGA studies showed this polymer started to lose CO₂ between 120 to 160 °C. This ability of the polymeric NHC-CO₂ adduct **146** to release CO₂ (140 °C in N₂) is reversible and the free NHC could recapture CO₂ at 40 °C under CO₂. These release-capture experiments were carried out for four cycles without significant decrease in CO₂ capturing efficiency. These results suggest that NHC-CO₂ adducts supported on polymers behave like their low molecular weight counterparts in terms of generating NHCs at elevated temperatures. However, the application of polymeric NHC-CO₂ adduct **146** as a NHC precatalyst was not described.

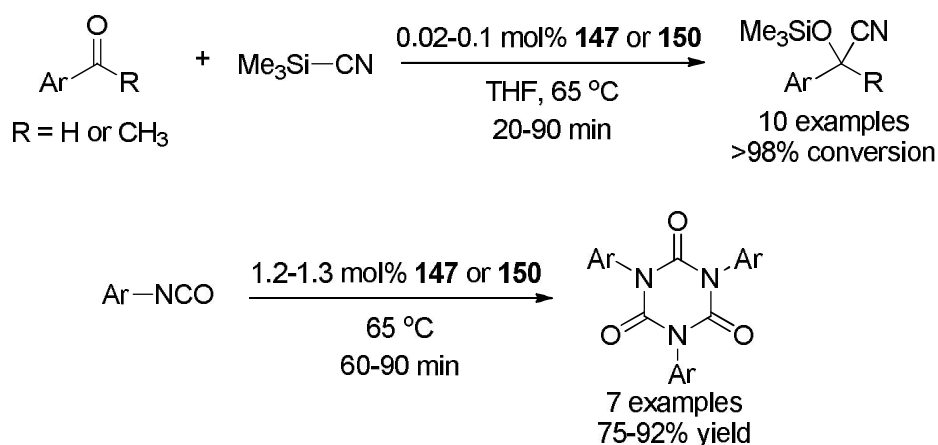
Scheme 56. Polystyrene-supported NHC-CO₂ adduct **146**

In 2010, Pawar and Buchmeiser¹⁴⁶ described synthesis of a polymer-supported NHC-CO₂ adduct by ring-opening metathesis polymerization (ROMP) (Scheme 57).

Scheme 57. ROMP of norbornene-containing monomer **147** to form **150**

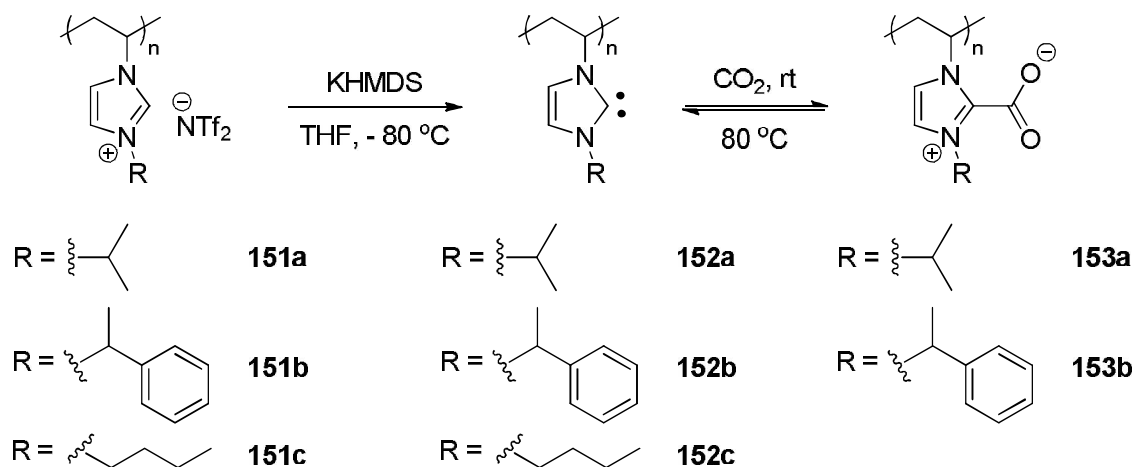
The norbornene monomer **147** containing NHC-CO₂ moiety was polymerized by a molybdenum catalyst **148** followed by crosslinking with **149** to form an insoluble polymer-supported NHC-CO₂ adduct **150**. The activities of **147** and **150** as latent NHC catalysts were then examined in cyanosilylation of ketones and aryl isocyanate trimerization reactions (Scheme 58). Both reactions proceeded smoothly with 0.02-1.3 mol% loading of the NHC-CO₂ precatalysts **147** and **150** affording the silylated cyanohydrins and isocyanurates products in moderate to good yields. The turnover numbers of the polymeric NHC precatalyst **150** were similar to those of the low molecular weight analog **147** in both reactions. Although used **150** can be separated from product solutions by a simple filtration, recycling experiments using **150** were not described.

Scheme 58. Cyanosilylation and isocyanate trimerization using **147** and **150**



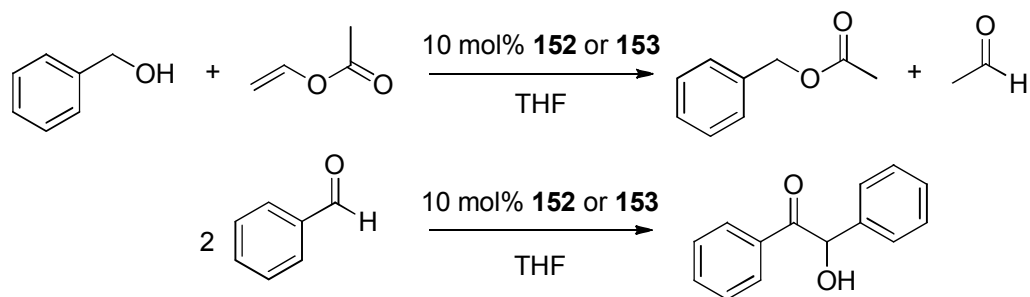
Pinaud¹⁴⁷ and coworkers reported syntheses of poly(vinylimidazolium salt) **151** (Scheme 59). These imidazolium salts form corresponding NHCs **152** on deprotonation

Scheme 59. Polymer-bound imidazolium salts, NHCs, and CO₂ adducts



that lead in turn form CO₂ adducts **153** on exposure to CO₂. On heating, the polymers **153** could be used as organocatalysts for transesterification and benzoin condensation reactions as shown in Scheme 60. The free carbene **152** itself was also used as a

Scheme 60. Benzoin condensation and transesterification catalyzed by **152** and **153**



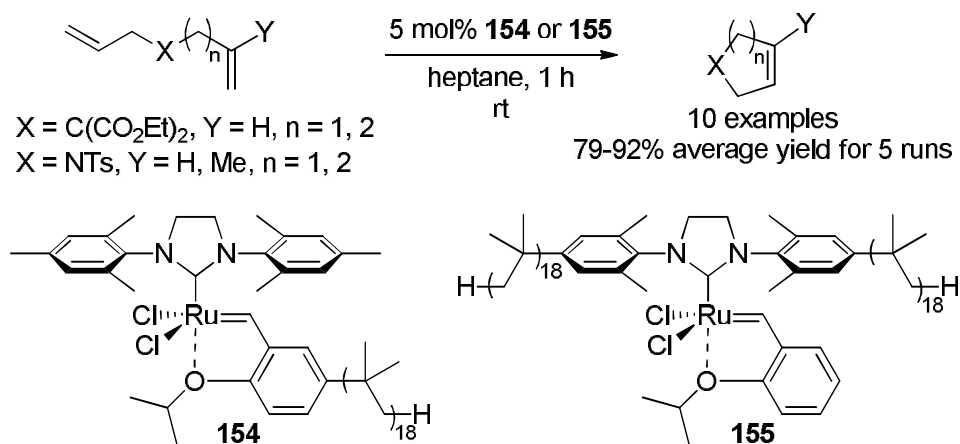
polymer-bound catalyst. In this case, recycling the polymer-bound catalyst involved precipitating **152** by adding the reaction mixture to excess ether. In the case of **153**, the CO₂ adduct serves as a latent NHC catalyst that can be recovered at the end of a reaction by bubbling CO₂ through the cooled reaction mixture to reform the polymer-bound CO₂ adduct which precipitated. A simple filtration was used to recover the CO₂ adduct. This latter procedure has the advantage that it avoids the use of excess ether solvent.

While **152** and **153** can catalyze a transesterification providing the products in good yields in the first run, the product yields decreased significantly after the first run when the free carbene **152** was used. This could be due to the air and moisture sensitivity of **152** or dimerization of these NHC organocatalysts. Catalysis using the CO₂ adduct **153** showed better recyclability and **153b** was successfully recycled and reused for 7 runs in the transesterification reaction providing an average yield of 76% per run. In the benzoin condensation reaction, moderate to good yields were obtained with catalysts **152** and **153** in the first runs except for **152c**. However, recycling **152** and **153** were not successful as much lower yields of the product were obtained in the following cycles. The modest recyclability and the solvent inefficiencies associated with solvent precipitation suggest studies of other recycling strategies merit attention.

Of the modest success to date with polymer-supported NHCs as recyclable and reusable organocatalysts suggested that there was an opportunity for us to explore this chemistry with the soluble polymer supports that have been extensively studied by our group. We specifically thought that we could prepare PIB- and PE_{Olig}-bound NHC (pre)catalysts and use liquid/liquid and solid/liquid separation strategies to separate them

from products after a catalytic reaction. Precedent for this notion is our success in using PIB-bound NHC-ligated ruthenium complexes as recyclable and reusable catalysts in metathesis reactions. Two PIB-supported Hoveyda-Grubbs catalysts **154** and **155** were previously reported as recyclable and reusable catalysts in ring-closing metathesis (RCM) reactions of diallylmalonates and *N,N*-diallyltosylamides (Scheme 61).^{62,148} The RCM reactions were carried out in heptane at room temperature. Once the reaction was completed, acetonitrile was added to the reaction mixture to form a biphasic mixture.

Scheme 61. Ring-closing metathesis reactions catalyzed by **154** and **155**

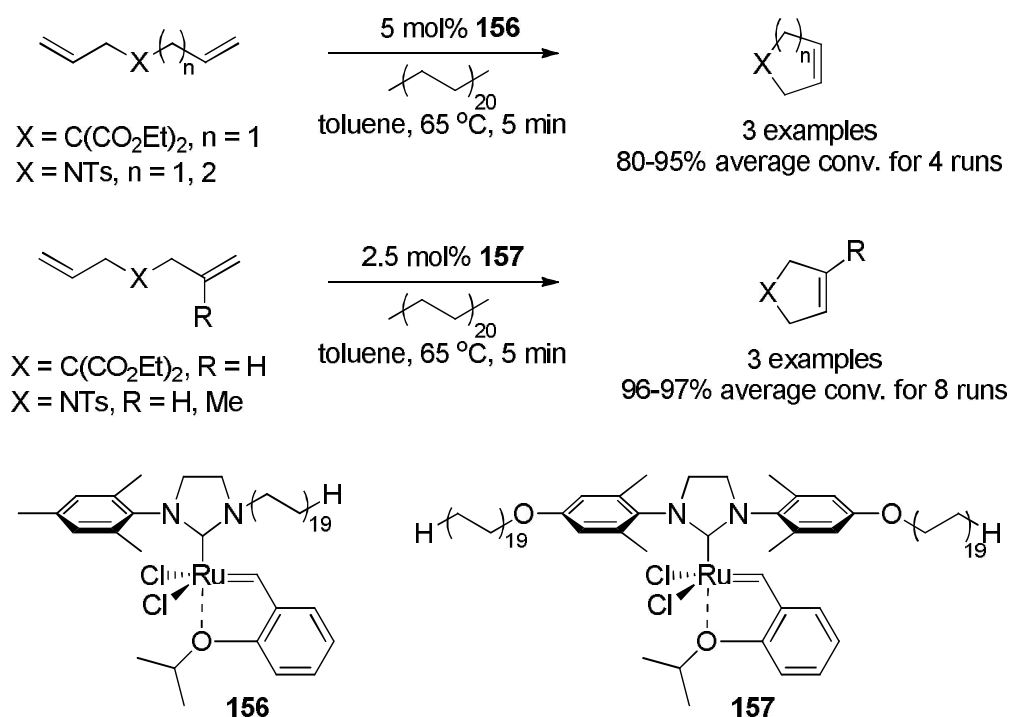


Since these PIB-bound Ru catalysts have the heptane phase selective solubility, they could be separated in the heptane phase from a heptane/acetonitrile mixture. Thus, simply adding fresh substrate to the heptane solution of the recycled catalysts allows reuse of these catalysts. In one case, the substrates are soluble in heptane but the product dihydropyrrole derivative is insoluble. In this instance, the heptane solutions containing

catalysts **154** or **155** can be separated from solid products by a filtration. ICP-MS analysis of the Ru content in the products showed that Ru leaching into products was minimal especially when **155** was used as the catalyst. Such data implies high recyclability of the PIB-supported NHC-Ru catalysts in the heptane phase. In fact, when *N,N*-diallyllysylamide was used as the substrate, **155** was recycled and reused for 20 cycles with an average yield of 97% per cycle and 0.37-0.63% of the starting Ru observed in the product phases in the first four runs.

Similar NHC-Ru metathesis catalysts were also prepared with PE_{Olig} supports. Recently, two PE_{Olig}-supported NHC-Ru catalysts **156** and **157** were reported as recyclable and reusable catalysts for ring-closing metathesis reactions (Figure 62).¹⁰⁶

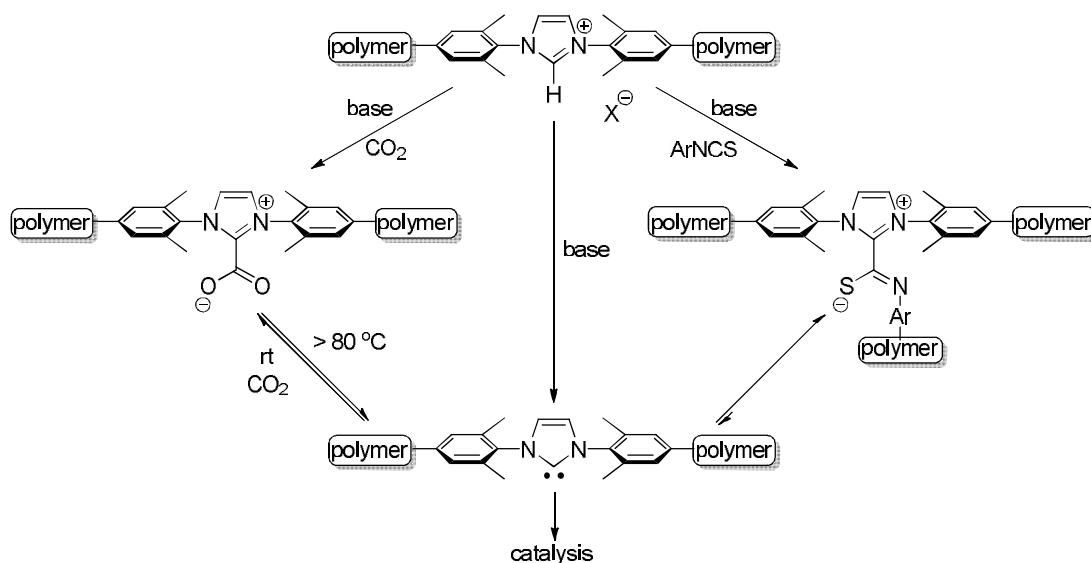
Scheme 62. Ring-closing metathesis reactions catalyzed by **156** and **157**



These PE_{Olig} NHC-Ru catalysts were successfully recycled and reused in RCM reactions with a number of substrates using thermomorphic solid/liquid separation techniques. In these RCM reactions, unfunctionalized polyethylene oligomer was added to the reaction mixtures to facilitate precipitation of PE_{Olig}-bound catalysts after a reaction. Catalyst **157** showed superior performance in recycling experiments especially when diethyl 2,2-diallylmalonate was used as the substrate. PE_{Olig} catalyst **157** was recycled and reused for 10 cycles providing the RCM product with an average conversion of 96% per cycle.

Given the success of preparing PIB- and PE_{Olig}-bound NHC ruthenium catalysts for facile catalyst/product separation, I undertook to synthesize PIB- and PE_{Olig}-bound (latent) NHC catalysts and to examine their catalytic activity and recyclability in lactide polymerization and phenyl isocyanate trimerization reactions (Scheme 63). In this work,

Scheme 63. Polymer-supported NHCs

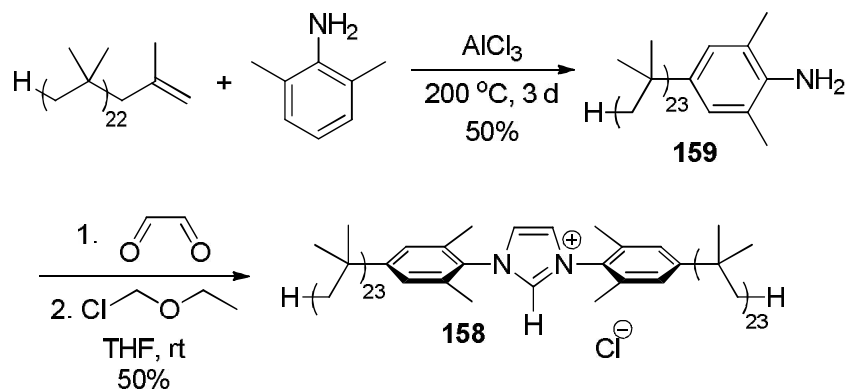


the heptane phase selective solubility of PIB was to serve as a handle to separate PIB-bound NHC (latent) catalysts from products using liquid/liquid or solid/liquid biphasic separation strategies. The PE_{Olig}-bound (latent) NHC catalysts in these instances would function as homogeneous catalysts in hot toluene solutions and precipitate when the reaction mixture is finished and cooled to room temperature. The PE_{Olig}-bound material would be separated by a simple filtration and recovered for recycling experiments. In addition, the use of hydrophobic PE_{Olig} support should also minimize reaction of water with catalysts entrapped in a solid PE_{Olig}-matrix during workup, which was thought to improve the recyclability of these NHC catalysts.

Results and Discussion

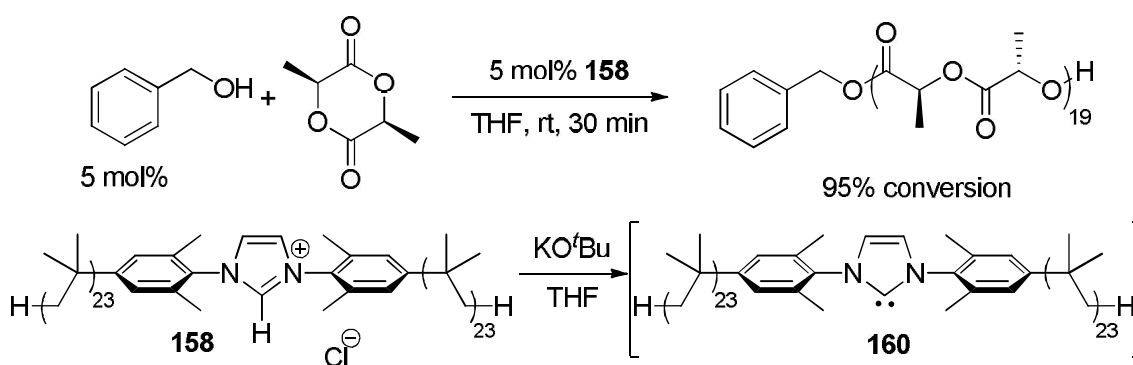
Preparation of a PIB-bound imidazolium salt **158** was accomplished as shown in Scheme 64.⁶² An alkene-terminated PIB oligomer was allowed to react with 2,6-dimethylaniline and aluminum chloride at 200 °C for 3 d to form PIB-dimethylaniline **159**.

Scheme 64. Synthesis of PIB-bound imidazolium salt **158**



The resulting PIB-bound aniline **159** was allowed to react with glyoxal and then chloromethyl ethyl ether to give PIB-bound imidazolium chloride **158**. With this PIB-bound NHC precursor in hand, we first examined the catalytic activity of PIB-NHC **160** generated *in situ* from **158** in a lactide polymerization (Scheme 65).

Scheme 65. PIB-NHC **160** catalyzed lactide polymerization

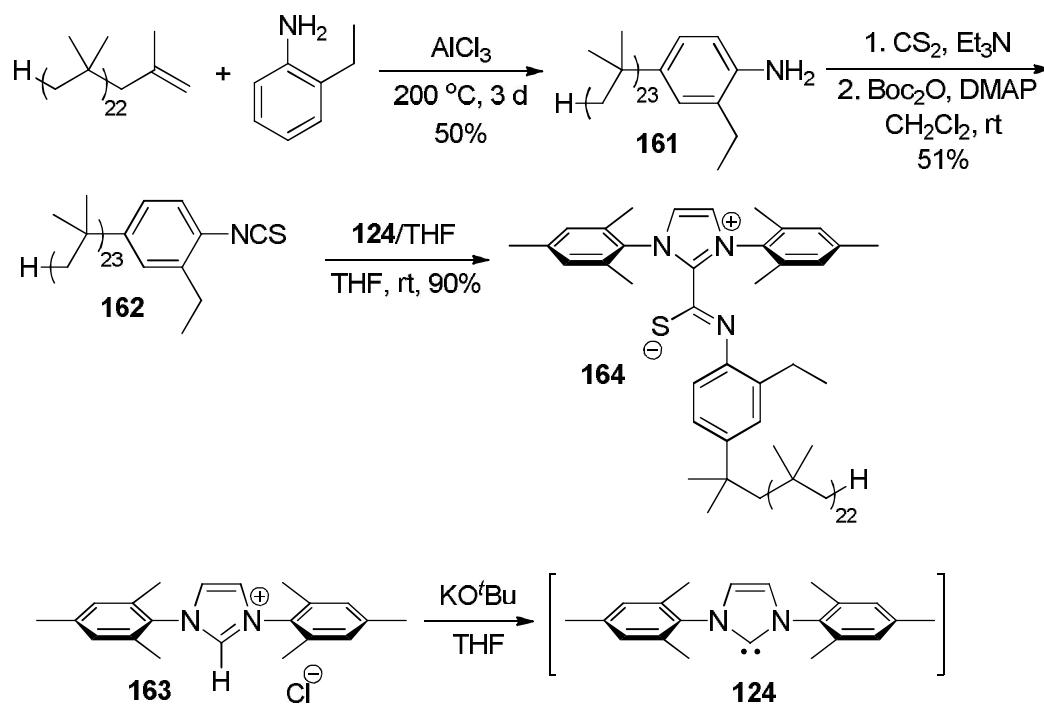


PIB-bound imidazolium salt **158** was first dissolved in THF and deprotonated by potassium *tert*-butoxide to form a THF solution of PIB-NHC **160**. A THF solution of L-lactide and benzyl alcohol was added to the THF solution of **160** and the reaction mixture was stirred for 30 min. The solvent was removed under reduced pressure and a mixture of heptane and DMF was added to the residue to form a biphasic mixture. A gravity separation separated the heptane-rich phase from the DMF phase. It is noteworthy that only polylactide was observed in the DMF phase by ^1H NMR spectroscopy indicating a good conversion of the lactide to polylactide was achieved. However, removal of solvent of the heptane-rich phase afforded a complicated mixture

based on the ^1H NMR spectrum of the residue. The failure to cleanly isolate **160** was presumed to be a result of decomposition of PIB-NHC **160**. Such decomposition may arise from the exposure of **160** to moisture and air during workup. Therefore, we turned our attention to using a PIB-NHC adducts as latent NHC catalysts. In this case, we prepared a PIB-bound NHC-NCS adduct from a PIB-functionalized aryl isothiocyanate and NHC **124** generated *in situ*. This PIB-bound NHC-NCS adduct would have substituents at *ortho* and *para* positions of the phenyl ring of phenyl isothiocyanate moiety.

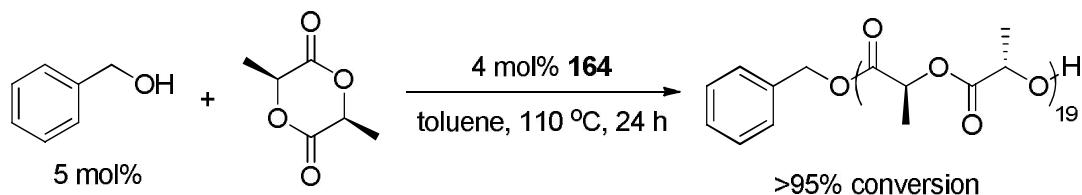
A PIB-NHC-NCS adduct was prepared as shown in Scheme 66. A PIB-bound 2-ethylaniline **161** was prepared using conditions similar to those used for preparing PIB-

Scheme 66. Synthesis of PIB-NHC-NCS adduct **164**

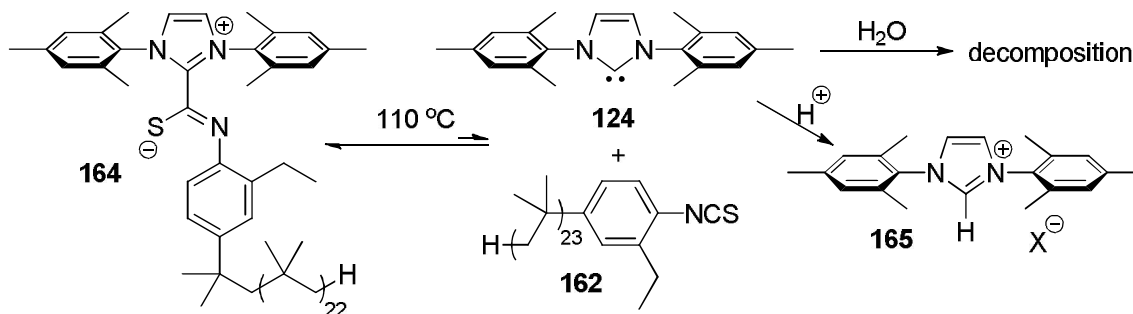


dimethylaniline **159** following a reported procedure.⁵⁸ The aniline **161** was then allowed to react with carbon disulfide and triethylamine. Treatment of this product with Boc-anhydride and DMAP formed a PIB-bound isothiocyanate **162**. A THF solution of NHC**124** which was generated in situ by deprotonation of imidazolium chloride **51** with potassium *tert*-butoxide in THF was then added to a THF solution of PIB-isothiocyanate **162** to form the PIB-bound NHC-NCS adduct **164**. The PIB-isothiocyanate adduct **164** was purified by silica gel column chromatography as a yellow viscous liquid and characterized by ¹H and ¹³C NMR spectroscopy. When NHC-NCS adduct **164** was added a mixture of heptane and DMF, a biphasic mixture formed with yellow color observed in both phases. This indicated a poor phase selective solubility of **164** with partial solubility of PIB-NHC-NCS adduct **164** in the DMF-rich phase. Indeed, when an aliquot of the DMF-rich phase was analyzed by ¹H NMR spectroscopy, presence of **164** was observed. The partial solubility of PIB-NHC-NCS adduct **164** arises because **164** consists of a segment of nonpolar PIB oligomer ($M_n \sim 1300$) and a segment (the polar end group) that contains a similar-sized zwitterionic NHC-isothiocyanate adduct ($M_n \sim 460$).

The catalytic activity and recyclability of PIB-NHC-NCS adduct **164** as a NHC precatalyst was examined in a lactide polymerization using benzyl alcohol as the initiator (Scheme 67). The reaction was carried out in anhydrous toluene using 4 mol% of the latent catalyst **164** at 110 °C as a homogeneous reaction mixture. After 24 h, the reaction mixture was added to a mixture of heptane and DMF and cooled to roomtemperature. The resulting biphasic mixture was separated and aliquots of the two phases were analyzed by ¹H NMR spectroscopy. In the less-dense phase, neither lactide

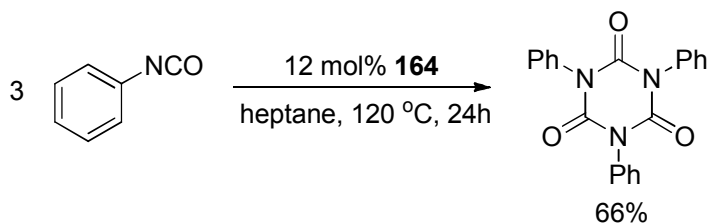
Scheme 67. Lactide polymerization using PIB-NHC-NCS adduct **164**

nor polylactide was observed. The polylactide and some PIB-NHC-NCS adduct **164** containing lower ($M_n \sim 400$) molecular weight PIB were both present in the DMF-rich phase. The conversion of lactide to polylactide was calculated based on integral of methine protons on lactide (5.0 ppm) and on polylactide (5.2 ppm). In this case, a 95% conversion was obtained. A control reaction carried out in the absence of NHC-NCS adduct **164** under similar conditions gave 2% of conversion. The less-dense phase solvents were removed under reduced pressure and fresh substrates and toluene were added to the residue in a recycling experiment. A 65% conversion of lactide to polylactide was achieved in the second run. The loss of some of the PIB-NHC-NCS adduct **164** into the DMF-rich phase during the first phase workup may partially account for the lower conversion in the second run. In addition, trace amount of water present in the reaction mixture may hydrolyze lactide into lactic acid which may serve as the proton source for carbene **124** to form an imidazolium salt **165** (Scheme 68). Hydrolysis of carbene **124** in the presence of water is also a possible pathway to consume **124** in the reaction mixture and could also account for inefficient recycling of PIB-NHC-NCS adduct **164**.

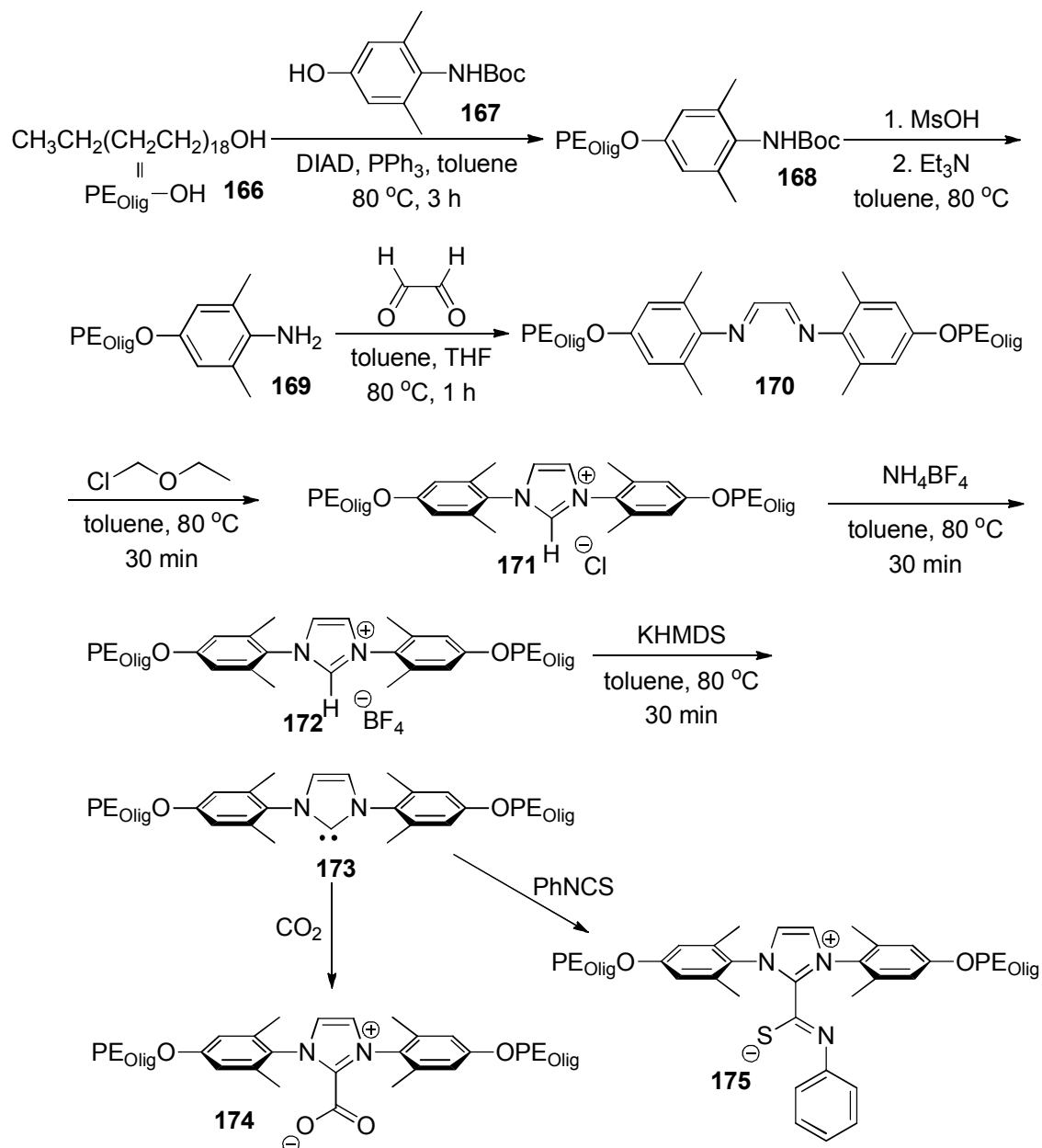
Scheme 68. Possible pathways to consume **124**

Phenyl isocyanate trimerization was also chosen to examine the catalytic activity and recyclability of PIB-bound NHC-NCS adduct **164** (Scheme 69). Since phenyl isocyanate is soluble in heptane, the reaction mixture was initially a homogeneous mixture in heptane at 120 °C. However, as the reaction proceeded, the desired product isocyanurate precipitated. At the end of the reaction, the product was collected as a solid in 66% yield by filtering the cooled reaction mixture and purified by recrystallization. A control reaction carried out in the absence of NHC-NCS adduct **164** in similar conditions showed no detectable conversion observed by ¹H and ¹³C NMR spectroscopy. The heptane solution containing PIB-NHC-NCS adduct **164** and unreacted phenyl isocyanate was then allowed to react with fresh phenyl isocyanate. The isocyanurate product of the second run was isolated in 60% yield.

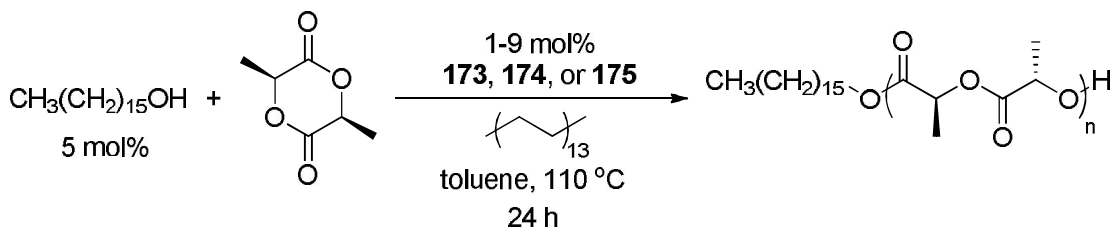
Scheme 69. Phenyl isocyanate trimerization using **164**



We then turned our attention to use solid/liquid thermomorphic strategies as a way to separate and recover PE_{Olig} -supported NHC (pre)catalysts after a reaction. Preparation of the desired PE_{Olig} -NHC (pre)catalysts began with a Mitsunobu reaction of PE_{Olig} -OH **166** with *N*-Boc-4-amino-3,5-xyleneol **167** to form a Boc-protected PE_{Olig} -dimethylaniline **168** (Scheme 70).¹⁰⁶ Deprotection of the Boc group on **168** with methanesulfonic acid afforded the PE_{Olig} -supported aniline **169**. Coupling of this PE_{Olig} -bound aniline **169** with glyoxal in a mixture of toluene and THF (4:1) at 80 °C formed the bisimine **170** as a bright yellow solid. The PE_{Olig} -bound imidazolium chloride **171** was then formed by treating bisimine **170** with chloromethyl ethyl ether. The imidazolium chloride **171** was then treated with ammonium tetrafluoroborate to generate PE_{Olig} -imidazolium tetrafluoroborate **172**. Deprotonation of **172** by KHMDS in a toluene solution at 80 °C formed PE_{Olig} -NHC **173**. Treating this toluene solution of PE_{Olig} -NHC **173** with CO_2 or phenyl isothiocyanate provided corresponding adducts **174** and **175**. The PE_{Olig} -bound NHC **173** can also be isolated as a solid. The catalytic activity and recyclability of PE_{Olig} NHC **173**, and the adducts **174** and **175** as latent NHC catalysts were then examined in lactide polymerization and phenyl isocyanate trimerization reactions.

Scheme 70. Synthesis of PE_{Olig} imidazolium chloride

In lactide polymerizations, the PE_{Olig} (latent) catalysts were used at loadings that varied from 1 to 9 mol% with respect to L-lactide (Scheme 71). Hexadecanol was

Scheme 71. Lactide polymerization using PE_{Olig} (latent) catalysts

used as the initiator and extra unfunctionalized PE_{Olig} was added to the reaction mixture to facilitate precipitation and isolation of the PE_{Olig} material after a reaction. The reaction mixture was heated to 110 °C for 24 h in anhydrous toluene and then cooled to room temperature. At this point, the reaction mixture was a viscous slurry as the PE_{Olig} material was swollen in toluene. Filtration of this slurry was inefficient and resulted in physical loss of PE_{Olig} material as PE_{Olig} material strongly stuck to the filter paper. Therefore the workup procedures were modified that excess acetone was added to cooled reaction mixture after a reaction to de-swell the PE_{Olig} material so PE_{Olig} material could be recovered by a filtration as a fine powder and recovered in 99% yield. In the case when PE_{Olig} NHC-CO₂ adduct **174** was used as the latent catalyst, CO₂ was bubbled through the reaction mixture when the reaction mixture was cooled to room temperature. The recovered fine powder of PE_{Olig} material after a filtration was then added to fresh substrates and toluene for recycling experiments. An aliquot of the filtrate was analyzed by ¹H NMR spectroscopy to determine the conversion of lactide to polylactide (Table 7). The PE_{Olig} carbene **173** gave a moderate conversion in run 1. Recycling and reusing **173** for 4 more times provided polylactide with decreased conversion after each run. When

PE_{Olig} NHC-CO₂ adduct **174** and NHC-NCS adduct **175** were used as catalyst precursors, good conversions were achieved in the first run. However, decreased conversions in recycling experiments was observed when precatalysts **174** and **175** were used.

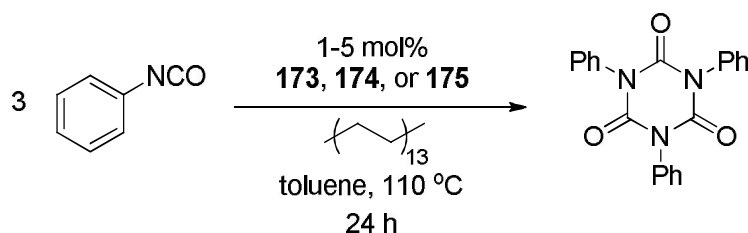
Table 7. Lactide polymerization using **173**, **174**, and **175**^a

| run | conversion (%) ^b | | |
|-----|-----------------------------|------------------------|------------------------|
| | 173 (1 mol%) | 174 (4 mol%) | 175 (9 mol%) |
| 1 | 69 | 95 | 95 |
| 2 | 61 | 80 | 89 |
| 3 | 54 | 69 | 85 |
| 4 | 42 | 61 | 77 |
| 5 | 31 | 58 | 67 |

^aThe reaction was conducted with 5 mmol of L-lactide, 0.25 mmol of hexadecanol, and 0.80 g of PE_{Olig} material in 5 mL of toluene. ^banalyzed by ¹H NMR spectroscopy.

We next examined the catalytic activity and recyclability of these PE_{Olig} NHC (latent) catalysts in phenyl isocyanate trimerization (Scheme 72). The trimerization

Scheme 72. Phenyl isocyanate trimerization using **173**, **174**, and **175**^a



reaction was carried out in toluene for 24 h at 110 °C as a homogeneous reaction mixture. By using similar workup procedures as those describe for lactide polymerizations, these PE_{Olig} materials were recycled and reused for 4 more runs. In this case, all three PE_{Olig} (latent) NHC catalysts provided quantitative yields of the isocyanurate product in the first runs (Table 8). However, the yield of product started to decrease from run 4 when PE_{Olig} NHC **173** was used as the catalyst. When PE_{Olig} NHC-CO₂ adduct **174** was used, incomplete conversion was observed from run 3. In the case when PE_{Olig} NHC-NCS adduct **175** was used as the catalyst precursor, quantitative yields of the isocyanurate product were obtained through run 5.

Table 8. Yields of Phenyl isocyanate trimerization using **173**, **174**, and **175**^a

| run | yield (%) ^b | | |
|-----|------------------------|------------------------|------------------------|
| | 173 (1 mol%) | 174 (5 mol%) | 175 (5 mol%) |
| 1 | 99 | 99 | 99 |
| 2 | 99 | 99 | 99 |
| 3 | 99 | 81 | 99 |
| 4 | 73 | 61 | 99 |
| 5 | 55 | 44 | 99 |

^aThe reaction was conducted with 3 mmol of phenyl isocyanate and 0.80 g of PE_{Olig} material in 2 mL of toluene. ^bisolated yield.

Based on the results shown above, modest recyclability was seen when PE_{Olig}-supported carbene was used in lactide polymerization and phenyl isocyanate trimerization reactions while the catalytic activity gradually decreases in recycling

experiments. Although the way PE_{Olig} NHC- CO_2 adduct **174** and NHC-NCS adduct **175** generate free carbene in reaction mixtures is different, they both served as recyclable and reusable NHC catalyst precursors in the lactide polymerization and phenyl isocyanate trimerization reactions.

Conclusions

PIB- and PE_{Olig} -bound NHC and their CO_2 and phenyl isothiocyanate adducts were prepared. PIB-bound NHC catalyst **160** was found active in lactide polymerization reaction but was not recyclable. PIB-NHC-isocyanate adduct **164** was used as a latent NHC catalyst in lactide polymerization and phenyl isocyanate trimerization reactions with modest recyclability. Physical loss of the PIB-NCS adduct **164** during workup and adventitious decomposition of free carbene generated *in situ* are the possible reasons for lower catalytic activity in recycling experiments. PE_{Olig} -bound NHC **173** and its CO_2 and isothiocyanate adducts **174** and **175** were used as recyclable catalysts or latent catalysts for 5 runs in lactide polymerization and phenyl isocyanate trimerization reactions. Modest recyclability was observed in most cases when PE_{Olig} -bound (pre)catalysts were used.

CHAPTER V
EXPERIMENTAL SECTION

Vinyl-terminated PIB oligomers (Glissopal[®] 1300, M_n of 1300) were obtained from BASF. The hydroxyl-terminated polyethylene oligomer (UNILIN[®] 550, M_n of 550) and unfunctionalized polyethylene oligomer (POLYWAX[®] 400, M_n of 400) were gifts from Baker-Hughes. All other reagents and solvents were purchased from commercial sources and used without further purification unless otherwise specified. CH_2Cl_2 was degassed with three freeze-pump-thaw cycle before used in preparation of silver complexes. ^1H NMR spectra were obtained on Varian Inova 300 or 500 MHz spectrometers operating at 299.96 and 499.71 MHz, respectively. ^{13}C NMR spectra were measured on these spectrometers operating at 75.433 and 125.66 MHz. Chemical shifts of ^1H and ^{13}C NMR spectra are reported in parts per million (δ) relative to residual proton resonances in the deuterated solvents (CDCl_3 , CD_2Cl_2 , C_6D_6 , or acetone- d_6). ^{31}P NMR spectra were recorded on spectrometers operating at Varian Inova 300 MHz spectrometers operating at 121.43 MHz. Chemical shifts of ^{31}P NMR spectra were reported in ppm and were referenced to external 85% H_3PO_4 aqueous solution at room temperature. When THF or heptane was used for VT NMR experiments, 10% C_6D_6 was added as internal lock. Coupling constants (J values) were reported as Hertz (Hz) and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), br (broad), and m (multiplet). All reactions were carried out under nitrogen atmosphere unless otherwise noted. Temperatures

recorded for VT NMR experiments were calibrated with 100% MeOH. High resolution MS data were collected from Applied Biosystems Voyager STR MALDI/TOF mass spectrometer using 2,4,6-trihydroxyacetophenone (THAP) as the matrix. Melting points were measured by Stanford Research Systems OptiMelt apparatus and uncorrected. Gel permeation chromatography (GPC) data were collected using a Viscotek I-MBMMW-3078 mixed bed column (30 °C) in DMF. The Viscotek instrument was equipped with a VE 3210 UV-Vis detector, a 270 Viscometer and Light Scattering Dual Detector, and a VE 3580 RI detector. The molecular weights and polydispersity index (PDI) of polymers were calculated using the OmniSEC software (v. 4.6.1) based on polystyrene standards.

Polyisobutyldiphenylphosphine (61). A 100-mL round-bottomed flask containing a THF solution of polyisobutylbromide **60** (6.54 g, 4.77 mmol in 25 mL THF) was immersed in an ice-water bath. After 30 min, a THF solution of potassium diphenylphosphide (10.0 mL, 0.5 M in THF, 5.0 mmol) was added to the flask via a syringe. Ice-water bath was removed and the resulting reaction mixture was stirred at room temperature for 14 h. Then saturated aqueous NH₄Cl (50 mL) and hexanes (50 mL) were added to the reaction mixture and the aqueous phase was separated. The nonpolar phase was washed with H₂O (50 mL x 2), 90 % aqueous EtOH (50 mL x 3), acetonitrile (20 mL x 7), and dried over anhydrous MgSO₄. The solvents were evaporated under reduced pressure to afford a crude product that was purified by silica gel column chromatography using hexanes as the eluting solvent to afford a colorless oil (4.13 g, 2.80 mmol, 59% yield). ¹H NMR (300 MHz, C₆D₆): δ 0.80-1.90 (m, 183 H),

1.90-2.00 (dd, $J = 13.4, 8.1$ Hz, 1 H), 2.06-2.18 (dd, $J = 13.4, 5.5$ Hz, 1 H), 7.02-7.13 (m, 6 H), 7.43-7.54 (m, 4 H). ^{13}C NMR (125 MHz, C_6D_6): δ 14.4, multiple peaks between 20-41 and 55-61, 128.4, 128.6 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 6.2$ Hz), 128.7 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 5.1$ Hz), 133.0 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 18.5$ Hz), 133.6 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 19.3$ Hz), 140.0 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 15.2$ Hz), 140.2 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 14.4$ Hz). ^{31}P NMR (121 MHz, C_6D_6): δ - 19.5.

Polyisobutyldiphenylphosphine Silver Iodide (62). The PIB-alkyldiphenylphosphine **61** (0.0414 g, 0.0280 mmol) and silver iodide (0.0134 g, 0.0571 mmol) were placed in a 25-mL round-bottomed flask equipped with a magnetic stir bar. Then CH_2Cl_2 (3 mL) was added to the flask and the reaction mixture was stirred at room temperature for 54 h in dark. The suspension was filtered and the solvent was evaporated under reduced pressure to afford a colorless oil (0.0476 g, 0.0278 mmol, 99% yield). ^1H NMR (300 MHz, C_6D_6): δ 0.77-2.38 (m, 185 H), 7.03-7.25 (m, 6 H), 7.74-8.00 (m, 4 H). ^{13}C NMR (75 MHz, C_6D_6): δ 14.4, 15.2, multiple peaks between 24-41, 55-60, and 128-136. ^{31}P NMR (121 MHz, C_6D_6): δ - 15.6.

Polyisobutyldiphenylphosphine Silver Chloride (63). The same procedure used to prepare **62** was used substituting AgCl (0.0102 g, 0.0698 mmol) for AgI . The product was isolated as a colorless oil (0.0451 g, 0.0278 mmol, 99% yield). ^1H NMR (300 MHz, C_6D_6): δ 0.70-1.97 (m, 183 H), 2.00-2.43 (m, 2 H), 6.98-7.14 (m, 6 H), 7.75-8.09 (m, 4 H). ^{13}C NMR (75 MHz, C_6D_6): δ multiple peaks between 24-38, 55-60, and 128-134. ^{31}P NMR (121 MHz, C_6D_6): δ - 2.0.

Isobutyldiphenylphosphine (64). Isobutylmagnesium bromide (30 mL, 1.25 M in THF, 37.5 mmol) was cooled to 0 °C and chlorodiphenylphosphine (6.9 mL, 37.6 mmol)

was added dropwise via a syringe. The reaction mixture was warmed to room temperature and stirred for 24 h. Then saturated aqueous NH_4Cl (50 mL) was added to quench reaction mixture followed by addition of ethyl acetate (50 mL). The organic layer was separated and washed with H_2O (50 mL), brine (50 mL) and dried over anhydrous MgSO_4 . The solvent was evaporated under reduced pressure to afford the crude product which was further purified by vacuum distillation to give a colorless liquid (4.55 g, 18.8 mmol, 50% yield). ^1H NMR (300 MHz, C_6D_6): δ 0.98 (d, $J = 6.3$ Hz, 6 H), 1.55-1.77 (m, 1 H), 1.89 (d, $J = 7.0$ Hz, 2 H), 7.00-7.12 (m, 6 H), 7.39-7.47 (m, 4 H). ^{13}C NMR (75 MHz, C_6D_6): δ 24.3 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 9.6$ Hz), 26.4 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 14.0$ Hz), 38.9 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 13.8$ Hz), 128.5, 128.6 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 6.6$ Hz), 133.1 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 18.8$ Hz), 140.2 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 14.3$ Hz). ^{31}P NMR (121 MHz, C_6D_6): δ - 19.5.

Isobutyldiphenylphosphine Silver Iodide (65). The same procedure used to prepare **62** was used. The product was recrystallized from a mixture of EtOH and CH_2Cl_2 to give a white solid (0.514 g, 1.08 mmol, 27% yield). ^1H NMR (500 MHz, C_6D_6): δ 1.02 (dd, $J = 6.7, 0.5$ Hz, 6 H), 2.15 (t, $J = 7.0$ Hz, 2 H), 2.31-2.46 (m, 1 H), 7.01-7.06 (m, 2 H), 7.06-7.12 (m, 4 H), 7.81-7.88 (m, 4 H). ^{13}C NMR (125 MHz, C_6D_6): δ 25.2 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 9.2$ Hz), 26.9 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 9.2$ Hz), 31.9 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 8.9$ Hz), 128.7 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 9.2$ Hz), 129.6 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 1.5$ Hz), 133.9 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 15.3$ Hz), 135.3 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 20.1$ Hz). ^{31}P NMR (121 MHz, C_6D_6): δ - 15.3. M.P.: 260-264 °C. HRMS calcd for $[(\text{C}_{16}\text{H}_{19}\text{P}\text{Ag})_2\text{I}]^+$ 824.9595, found 824.9785.

Isobutyldiphenylphosphine Silver Chloride (66). The same procedure used to prepare **65** was used substituting AgCl (0.722 g, 5.04 mmol) for AgI. The product was recrystallized from an EtOH/CH₂Cl₂ mixture to give a white solid (0.101 g, 0.262 mmol, 6% yield). ¹H NMR (500 MHz, C₆D₆): δ 0.99 (d, *J* = 6.6 Hz, 6 H), 1.97 (t, *J* = 7.4 Hz, 2 H), 2.22-2.34 (m, 1 H), 6.94-7.04 (m, 6 H), 7.91-7.97 (m, 4 H). ¹³C NMR (125 MHz, C₆D₆): δ 24.8 (d, *J*_{31P-13C} = 10.0 Hz), 27.2 (d, *J*_{31P-13C} = 10.0 Hz), 37.1 (d, *J*_{31P-13C} = 13.7 Hz), 128.8 (d, *J*_{31P-13C} = 9.8 Hz), 129.8, 133.9 (d, *J*_{31P-13C} = 16.7 Hz), 135.2 (d, *J*_{31P-13C} = 26.1 Hz). ³¹P NMR (121 MHz, C₆D₆): δ - 0.7. M.P.: 191-193 °C. HRMS calcd for [(C₁₆H₁₉PAg)₂Cl]⁺ 733.0239, found 733.0394.

Poly(ethylene glycol)triarylphosphine (71). This phosphine was prepared by a literature procedure.^{96,149} The product was precipitated using diethyl ether (500 mL) and was characterized by ¹H and ³¹P NMR spectroscopy. The product was collected by filtration as a white solid and contaminated with 20 % phosphine oxide. ¹H NMR (500 MHz, CDCl₃): δ 3.32, (s, 3 H), 3.42-3.83 (m, 218 H), 4.04-4.08 (m, 2H), 6.79-6.85 (m, 2 H), 7.16-7.28 (m, 12 H). ³¹P NMR (121 MHz, CDCl₃): δ - 6.5.

Poly(ethylene glycol)triarylphosphine Complexes of Silver Iodide and Silver Chloride (72 and 73, respectively) were prepared from the phosphine **71** and AgI or AgCl using a procedure analogous to that used to prepare PIB-bound phosphine silver complexes **62** and **63**. The silver halide complexes so formed were characterized by ¹H and ³¹P NMR spectroscopy and were contaminated with up to 25 % phosphine oxide. **72:** ¹H NMR (500 MHz, CD₂Cl₂): δ 3.33, (s, 3 H), 3.42-3.86 (m, 218 H), 4.06-4.10 (m, 2H), 6.83-6.88 (m, 2 H), 7.26-7.33 (m, 4 H), 7.35-7.41 (m, 2 H), 7.43-7.51 (m, 6 H). ³¹P

NMR (121 MHz, CD₂Cl₂): δ - 3.4. **73**: ¹H NMR (300 MHz, CD₂Cl₂): δ 3.32, (s, 3 H), 3.32-3.84 (m, 218 H), 4.02-4.09 (m, 2 H), 6.80-6.88 (m, 2 H), 7.24-7.50 (m, 12 H). ³¹P NMR (121 MHz, CD₂Cl₂): δ 7.7.

(4-Methoxyphenyl)diphenylphosphine (74). To a 250-mL round-bottomed flask equipped with a magnetic stirrer was added 4-bromoanisole (5.61 g, 30.0 mmol) and THF (100 mL). The flask was immersed in a dry ice-acetone bath for 30 min before BuLi (20.0 mL, 1.6 M in hexanes, 32.0 mmol) was added. The reaction mixture was stirred at - 78 °C for 60 min at which point chlorodiphenylphosphine (7.20 mL, 40.1 mmol in 20 mL THF) was added. The reaction mixture was stirred at - 78 °C for 3 h and warmed to room temperature and stirred overnight. Then saturated aqueous NH₄Cl (50 mL) and H₂O (50 mL) were added to quench the reaction and the organic phase was separated. The organic phase was washed with H₂O (50 mL), brine (50 mL) and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to afford a crude product that was purified by silica gel column chromatography using hexanes and CH₂Cl₂ (hexanes : CH₂Cl₂ = 4 : 1) to afford a colorless oil which turned into a solid on standing. The solid was further recrystallized from ethanol to give colorless prisms (5.04 g, 17.2 mmol, 57% yield). ¹H NMR (500 MHz, CDCl₃): δ 3.82, (s, 3 H), 6.89-6.95 (m, 2 H), 7.28-7.43 (m, 12 H). ¹³C NMR (75 MHz, CDCl₃): δ 55.1, 114.2 (d, $J_{^{31}\text{P}-^{13}\text{C}}$ = 8.1 Hz), 127.3 (d, $J_{^{31}\text{P}-^{13}\text{C}}$ = 6.8 Hz), 128.4 (d, $J_{^{31}\text{P}-^{13}\text{C}}$ = 6.8 Hz), 128.5, 133.4 (d, $J_{^{31}\text{P}-^{13}\text{C}}$ = 19.0 Hz), 135.6 (d, $J_{^{31}\text{P}-^{13}\text{C}}$ = 21.3 Hz), 137.6 (d, $J_{^{31}\text{P}-^{13}\text{C}}$ = 9.3 Hz), 160.4. ³¹P NMR (121 MHz, CDCl₃): δ - 6.5. M.P.: 65-66 °C (lit¹⁵⁰ 64.5-65.5 °C).

(4-Methoxyphenyl)diphenylphosphine Silver Iodide and Silver Chloride (75 and 76)

were prepared from (4-methoxyphenyl)diphenylphosphine **74** and AgI or AgCl. The product $\text{CH}_3\text{OC}_6\text{H}_4\text{PPh}_2\text{AgI}$ **75** was isolated as white needles in 80% yield. ^1H NMR (300 MHz, CD_2Cl_2): δ 3.80 (s, 3 H), 6.86-6.93 (m, 2 H), 7.31-7.39 (m, 4 H), 7.40-7.47 (m, 2 H), 7.54-7.64 (m, 6 H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 55.8, 114.8 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 10.8$ Hz), 123.3 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 28.7$ Hz), 129.1 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 9.5$ Hz), 130.3 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 1.6$ Hz), 133.8 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 24.9$ Hz), 134.5 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 15.7$ Hz), 136.7 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 17.6$ Hz), 161.9 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 1.5$ Hz). ^{31}P NMR (121 MHz, CD_2Cl_2): δ -6.5. M.P.: 188-189 °C. HRMS calcd for $[(\text{C}_{19}\text{H}_{17}\text{OPAg})_2\text{I}]^+$ 924.9181, found 924.8835. The product $\text{CH}_3\text{OC}_6\text{H}_4\text{PPh}_2\text{AgCl}$ **76** was isolated as a white solid in 73% yield. ^1H NMR (300 MHz, CD_2Cl_2): δ 3.75 (s, 3 H), 6.81-6.88 (m, 2 H), 7.27-7.35 (m, 4 H), 7.36-7.44 (m, 2 H), 7.50-7.62 (m, 6 H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 55.7, 114.9 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 11.2$ Hz), 123.1 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 32.6$ Hz), 129.2 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 9.8$ Hz), 130.4 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 1.7$ Hz), 133.6 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 28.7$ Hz), 134.2 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 16.5$ Hz), 136.5 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 18.5$ Hz), 161.9 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 1.4$ Hz). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 6.5. M.P.: 97-100 °C. HRMS calcd for $[(\text{C}_{19}\text{H}_{17}\text{OPAg})_2\text{Cl}]^+$ 832.9824, found 833.0092.

Polyisobutyltriarylphosphine (100). To a 250-mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser was added polyisobutylbromide **61** (11.6 g, 8.45 mmol), 4-(diphenylphosphino)phenol **101** (2.50 g, 8.98 mmol), and Cs_2CO_3 (5.54 g, 17.0 mmol). The apparatus was first flushed with N_2 and then heptane (50 mL) and

DMF (50 mL) were added. The flask was immersed in an oil bath regulated at 100 °C and the reaction mixture was stirred for 12 h. At this point, the reaction mixture was allowed to cool to room temperature and was transferred to a separation funnel. The heptane phase was separated and washed with H₂O (50 mL x 2), 90 % aqueous ethanol (50 mL), acetonitrile (50 mL x 2) and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to give a crude product that was then purified by silica gel column chromatography (hexanes:CH₂Cl₂ = 4 : 1) to afford a colorless, viscous liquid (8.62 g, 5.49 mmol, 65% yield). ¹H NMR (500 MHz, CDCl₃): δ 0.76-1.82 (m, 182 H), 1.97-2.11 (m, 1 H), 3.61-3.68 (m, 1 H), 3.79 (dd, *J* = 8.8, 5.6 Hz, 1 H), 6.87-6.92 (m, 2 H), 7.25-7.37 (m, 12 H). ¹³C NMR (125 MHz, CDCl₃) δ 20.4, multiple peaks between 29-33, 35.9, multiple peaks between 37-39, 49.6, 56.7, 58.2, 58.8, multiple peaks between 59-60, 74.2, 114.8 (d, *J*_{31P-13C} = 8.4 Hz), 126.9 (d, *J*_{31P-13C} = 6.3 Hz), 128.4 (d, *J*_{31P-13C} = 6.8 Hz), 128.5, 133.4 (d, *J*_{31P-13C} = 19.0 Hz), 135.6 (d, *J*_{31P-13C} = 21.5 Hz), 137.8 (d, *J*_{31P-13C} = 10.1 Hz), 160.1. ³¹P NMR (121 MHz, CDCl₃) δ - 6.5.

Polyisobutyldiphenylphosphine oxide (105). ¹H NMR (500 MHz, CDCl₃): δ 0.65-1.80 (m, 182 H), 2.01-2.12 (m, 1 H), 2.18 (ddd, *J* = 15.0, 11.7, 9.2 Hz, 1 H), 2.32 (ddd, *J* = 15.0, 10.3, 4.0 Hz, 1 H), 7.38-7.56 (m, 6 H), 7.69-7.82 (m, 4 H). ¹³C NMR (125 MHz, CDCl₃) δ 24.6, multiple peaks between 29-33, 36.2, multiple peaks between 37-40, 55.5, 55.6, 57.0, multiple peaks between 58-60, 128.5 (d, *J*_{31P-13C} = 11.7 Hz), 130.6 (d, *J*_{31P-13C} = 8.9 Hz), 130.8 (d, *J*_{31P-13C} = 9.3 Hz), 131.5 (d, *J*_{31P-13C} = 2.7 Hz), 131.5

(d, $J_{^{31}\text{P}-^{13}\text{C}} = 2.9$ Hz), 133.5 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 97.2$ Hz), 134.3 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 97.3$ Hz).

^{31}P NMR (121 MHz, CDCl_3) δ 31.5.

Polyisobutylaryldiphenylphosphine oxide (108). ^1H NMR (500 MHz, CDCl_3): δ 0.65-1.90 (m, 182 H), 1.93-2.00 (m, 1 H), 3.60-3.68 (m, 1 H), 3.77 (dd, $J = 8.7, 5.7$ Hz, 1 H), 6.85-6.98 (m, 2 H), 7.32-7.42 (m, 4 H), 7.42-7.50 (m, 2 H), 7.50-7.59 (m, 2 H), 7.59-7.69 (m, 4 H). ^{13}C NMR (125 MHz, CDCl_3) δ 20.3, multiple peaks between 28-33, 35.7, multiple peaks between 37-39, 49.4, 56.5, multiple peaks between 58-60, 74.1, 114.4 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 13.1$ Hz), 123.0 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 110.6$ Hz), 128.2 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 12.0$ Hz), 131.5 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 2.3$ Hz), 131.9 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 9.8$ Hz), 133.0 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 104.2$ Hz), 133.7 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 11.2$ Hz), 162.0 (d, $J_{^{31}\text{P}-^{13}\text{C}} = 2.6$ Hz). ^{31}P NMR (121 MHz, CDCl_3) δ 29.3.

General procedure for alkyne addition. (Table 4) Methyl propiolate (17.8 μL , 0.200 mmol), **61** (0.0548 g, 0.0371 mmol), MeOH (24.3 μL , 0.600 mmol) and heptane (2.0 mL) were added to a 10-mL flask equipped with a magnetic stirrer. The mixture was stirred for 20 h, at which time, acetonitrile (2.0 mL) was added to reaction mixture to form a biphasic mixture. The polar phase was removed from the flask and analyzed by GC using 1,4-dichlorobenzene as an internal standard. Recycling experiments involved addition of methyl propiolate (17.8 μL , 0.200 mmol) and MeOH (24.3 μL , 0.60 mmol) to the heptane solution of **61** for the next cycle.

General procedure for allylic amination. (Table 5) Phthalimide (0.0589 g, 0.400 mmol), PIB-bound phosphine **61** (0.0590 g, 0.0400 mmol) or **100** (0.0621 g, 0.0395

mmol), **106** (0.0527g, 0.201 mmol), and THF (2 mL) were added to a 10-mL flask equipped with a magnetic stirrer and the reaction mixture was stirred at room temperature for 24 h. At this point, the solvent was removed under reduced pressure and heptane (5 mL) and acetonitrile (5 mL) were added to reaction flask to form a biphasic mixture. The polar acetonitrile phase was removed from the flask. The acetonitrile was removed under reduced pressure to give a crude product which was then purified by silica gel column chromatography (CH₂Cl₂) to afford **107** as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 2.41 (s, 3 H), 5.75 (s, 1 H), 6.43 (s, 1 H), 6.51 (s, 1 H), 7.55 (d, *J* = 8.8 Hz, 2 H), 7.70-7.75 (m, 2 H), 7.79-7.84 (m, 2 H), 8.18 (d, *J* = 8.8 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 25.9, 53.0, 123.5, 123.8, 129.3, 129.5, 131.4, 134.3, 144.6, 144.9, 147.4, 167.7, 197.7. M.P.: 154-156 °C (lit.¹⁰⁰ 137-139 °C). In recycling experiments, the heptane of the remaining nonpolar phase was removed under reduced pressure and 2 mL of a THF solution containing **106** (0.0527g, 0.201 mmol) and phthalimide (0.0589 g, 0.400 mmol) was added to the reaction flask for the next cycle.

General procedure for aza-Wittig reaction. The PIB-bound phosphine **61** (6.50 g, 4.40 mmol) or **100** (6.89 g, 4.39 mmol) in THF (40 mL) was added to a 100-mL round-bottomed flask equipped with a magnetic stirrer. A 10-mL THF solution containing 4-methylbenzaldehyde **109** (0.481 g, 4.00 mmol) and 1-(azidomethyl)-4-methylbenzene **110** (0.586 g, 3.98 mmol) was added to the reaction flask. The reaction mixture was stirred at room temperature for 24 h at which time the evolution of bubbles had ceased. The solvent was removed under reduced pressure and heptane (100 mL) and acetonitrile (20 mL) were added. The heptane phase was separated and washed with acetonitrile (20

mL x 5) and then the heptane was removed under reduced pressure. The residue from the heptane phase was analyzed by ^1H and ^{31}P NMR spectroscopy which showed that the residue was the PIB-phosphine oxide **105** or **108**. The acetonitrile phases were combined and the solvent was removed under reduced pressure to give a white solid which was purified by recrystallization from MeOH to give **111** as white plates (0.875 g, 3.92 mmol, 98% yield). ^1H NMR (500 MHz, CDCl_3): δ 2.34 (s, 3 H), 2.39 (s, 3 H), 4.77 (s, 2 H), 7.13-7.18 (m, 2 H), 7.19-7.25 (m, 4 H), 7.65-7.69 (m, 2 H), 8.34 (s, 1 H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.1, 21.5, 64.8, 127.9, 128.2, 129.1, 129.3, 133.6, 136.3, 136.5, 141.0, 161.7. M.P.: 84-86 °C (lit.¹⁵¹ 83.5-84.5 °C).

General procedure for Mitsunobu reactions (Table 6) Alcohol (0.40 mmol), nucleophile (0.80 mmol), PIB-bound aryldiphenylphosphine **100** (1.25 g, 0.797 mmol) and toluene (4 mL) were added to a 25-mL round-bottomed flask equipped with a magnetic stirrer. DEAD (126 μL , 0.800 mmol) was added to reaction mixture. The flask was immersed in an oil bath regulated at 80 °C and the reaction mixture was stirred for 15 h. In the case of entry 1, the reaction was carried out in THF at room temperature using 4-nitrobenzoic acid (0.0669 g, 0.400 mmol) as the limiting reagent. Workup procedures varied as follows. For entry 1, the solvent was removed under reduced pressure and a mixture of heptane (40 mL) and acetonitrile (40 mL) was added to the reaction residue. The heptane phase containing **100** and its phosphine oxide byproduct **108** was separated from the acetonitrile phase and was washed with acetonitrile (10 mL x 4). The acetonitrile solutions were combined and the solvent was removed under reduced pressure to give a crude product which was purified by silica gel column

chromatography (hexanes: $\text{CH}_2\text{Cl}_2 = 4:1$) to afford isopropyl 4-nitrobenzoate as a white solid (0.0795 g, 0.380 mmol, 95% yield). ^1H NMR (500 MHz, CDCl_3): δ 1.39 (d, $J = 6.2$ Hz, 6 H), 5.28 (hept, $J = 6.2$ Hz, 1 H), 8.17-8.22 (m, 2 H), 8.25-8.29 (m, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.8, 69.7, 123.4, 130.6, 136.2, 150.4, 164.1. M.P.: 104-106 °C (lit.¹⁵² 104-106 °C).

Workup for the reactions yielding polymeric products was slightly different. For entries 2-6, the reaction mixture was cooled to room temperature and then added, in a dropwise fashion, to ice-cold Et_2O (50 mL). The product PEG polymer precipitate was isolated and characterized by ^1H and ^{13}C NMR spectroscopy. Concentrating the filtrate solutions, addition of heptane (15 mL) and acetonitrile (15 mL) followed by separation and washing of the heptane phase led to a heptane solution that contained a mixture of **100** and **108** based on ^1H and ^{31}P NMR spectroscopy. This mixture could be reduced and reused as described below.

For entries 7-9, a slightly different workup procedure was used. In the case of entries 7 and 8, the crude PE_{Olig} product precipitated on cooling. In the case of entry 8, this crude product was dissolved in toluene at 80 °C and was allowed to react with methanesulfonic acid for 1 h. After neutralization with triethylamine the reaction mixture was cooled and the product aniline was isolated by filtration. In the case of entry 9, the initial PE_{Olig} precipitate appeared to be an adduct of the aldehyde with the diethyl hydrazine-1,2-dicarboxylate based on the appearance of two $-\text{OCH}_2\text{CH}_3$ groups in the ^1H NMR spectrum of this initial adduct.¹⁵³ This product was not further characterized but was simply hydrolyzed by dissolving it in toluene, adding *p*-TsOH, and adding triethylamine

and water to the 80 °C toluene solution of the PE_{Olig} product. Most of the water was removed from this mixture by a pipette. Cooling formed an isolable precipitate of the desired PE_{Olig}-modified salicylaldehyde derivative which was characterized by ¹H and ¹³C NMR spectroscopy and was identical to the PE_{Olig}-derivative of salicylaldehyde prepared earlier.⁶¹

Poly(ethylene glycol) 4-nitrobenzoate (Table 6, entry 2) The product was isolated as a white powder (0.245 g, 0.0475 mmol, 95% yield). ¹H NMR (500 MHz, CDCl₃): δ 3.36 (s, 3 H), 3.46-3.88 (m, 450 H), 4.49-4.53 (m, 2 H), 8.20-8.24 (m, 2 H), 8.26-8.30 (m, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 58.8, 64.7, 67.2, 68.7, multiple peaks between 69-74, 123.3, 130.6, 135.2, 150.3, 164.4.

N-Poly(ethylene glycol)phthalimide (Table 6, entry 3) The product was isolated as a white powder (0.242 g, 0.0477 mmol, 94% yield). ¹H NMR (500 MHz, CDCl₃): δ 3.36 (s, 3 H), 3.46-3.91 (m, 452 H), 7.69-7.74 (m, 2 H), 7.80-7.86 (m, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 58.7, 67.1, 67.6, multiple peaks between 68-74, 122.9, 131.8, 133.7, 167.9.

4-Methyl-N-(4-methylphenyl)-N-poly(ethylene glycol)benzenesulfonamide (Table 6, entry 4) The product was isolated as a white powder (0.244 g, 0.0464 mmol, 93% yield). ¹H NMR (500 MHz, CDCl₃): δ 2.33 (s, 3 H), 2.42 (s, 3 H), 3.37 (s, 3 H), 3.47-3.80 (m, 452 H), 6.89-6.94 (m, 2 H), 7.06-7.11 (m, 2 H), 7.21-7.25 (m, 2 H), 7.47-7.51 (m, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 58.7, multiple peaks between 64-76, 127.4, 128.4, 129.0, 129.3, 135.1, 136.5, 137.6, 143.0.

***N*-Boc-2,6-dimethyl-4-poly(ethylene glycol)aniline** (Table 6, entry 5) The product was isolated as a white powder (0.241 g, 0.0461 mmol, 92% yield). ^1H NMR (500 MHz, CDCl_3): δ 1.48 (s, 9 H), 3.36 (s, 3 H), 3.44-3.84 (m, 450 H), 4.03-4.09 (m, 2 H), 6.59 (s, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ multiple peaks between 66-76, 79.0, 113.5, 126.8, 136.8, 153.7, 156.6.

Poly(ethylene glycol) 4-(4-(dimethylamino)phenylazo)benzoate (Table 6, entry 6) The product was isolated as an orange powder (0.237 g, 0.0450 mmol, 90% yield). ^1H NMR (500 MHz, CDCl_3): δ 3.10 (s, 6 H), 3.35 (s, 3 H), 3.42-3.88 (m, 450 H), 4.40-4.52 (m, 2 H), 6.72-6.81 (m, 2 H), 7.80-7.97 (m, 4 H), 8.08-8.16 (m, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ multiple peaks between 65-76, 111.3, 121.7, 125.5, 129.8, 130.4, 134.4, 152.7, 155.6, 166.0.

***N*-Polyethylphthalimide**¹⁰² (Table 6, entry 7) The product was isolated as a white powder (0.252 g, 0.371 mmol, 99% yield). ^1H NMR (500 MHz, C_6D_6 , 70 °C) δ 0.91 (t, J = 6.6 Hz, 5 H), 1.20-1.49 (brs, 140 H), 1.64 (m, 2 H), 3.58 (t, J = 6.8 Hz, 2 H), 6.96 (m, 2 H), 7.49 (m, 2 H). ^{13}C NMR (125 MHz, C_6D_6 , 70 °C) δ 12.2, 22.6, 26.8, 28.5, 29.1, 29.3, 29.7, 31.8, 37.8, 122.6, 132.6, 132.9, 167.6.

2,6-Dimethyl-4-polyethylaniline (Table 6, entry 8) The product was isolated as a light brown powder (0.249 g, 0.372 mmol, 99% yield). ^1H NMR (500 MHz, C_6D_6 , 70 °C) δ 0.91 (t, J = 6.6 Hz, 5H), 1.20-1.49 (brs, 164 H), 1.72 (m, 2 H), 1.94 (s, 6 H), 3.82 (t, J = 6.7 Hz, 2 H), 6.66 (s, 2 H). ^{13}C NMR (125 MHz, C_6D_6 , 70 °C) δ 14.0, 22.5, 26.1, 28.9, 29.2, 29.3, 29.7, 31.9, 34.8, 68.0, 103.0, 114.0, 136.5, 157.0.

3-*tert*-Butyl-5-polyethylsalicylaldehyde⁶¹ (Table 6, entry 9) The product was isolated as a light orange powder (0.251 g, 0.345 mmol, 90% yield). ¹H NMR (500 MHz, C₆D₆, 70 °C) δ 0.91 (t, *J* = 6.6 Hz, 5 H), 1.30-1.49 (brs, 230 H), 1.71 (m, 1 H), 3.71 (t, *J* = 6.3 Hz, 2 H), 6.43 (d, *J* = 1.9 Hz, 1 H), 7.26 (d, *J* = 3.1 Hz, 1H), 9.38 (s, 1H), 11.87 (s, 1 H). ¹³C NMR (125 MHz, C₆D₆, 70 °C) δ 13.9, 22.5, 26.1, 28.9, 29.2, 29.3, 29.7, 31.9, 34.8, 68.6, 113.1, 120.1, 123.9, 139.9, 151.7, 155.9, 196.0.

***N*-Boc-4-amino-3,5-xyleneol**. To a 100-mL round-bottomed flask equipped with a magnetic stirrer was added 4-amino-3,5-xyleneol (5.02 g, 45.8 mmol) and acetone (46 mL). The suspension was stirred under N₂. Upon dissolution, Boc₂O (11.0 g, 50.4 mmol) was added to reaction flask and the reaction mixture was stirred for 24 h at room temperature. After this time, the solvent was removed under reduced pressure. To the solid residue was added hexanes (150 mL) and the product was isolated by filtration as a light brown powder (8.04 g, 33.7 mmol, 74% yield) which was used without further purification. ¹H NMR (300 MHz, acetone-*d*₆) δ: 1.44 (s, 9H), 2.18 (s, 6H), 6.50 (s, 2H), 7.21 (brs, 1H), 8.11 (brs, 1H). ¹³C NMR (75 MHz, acetone-*d*₆) δ: 17.7, 27.8, 78.0, 114.3, 127.0, 137.3, 154.4, 155.5. IR (neat, cm⁻¹) 3306, 3200, 2945, 1680, 1599, 1500, 1483, 1443. HRMS calcd for [C₁₃H₁₈NO₃]⁺ 236.1287, found 236.1290. M.P.: 165 °C (dec.).

General procedure for PIB-phosphine oxide reduction. PIB-phosphine oxide **105** or **108** (4.40 mmol), triethylamine (12.3 mL, 88.2 mmol), and degassed toluene (80 mL) were added to a 250-mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser. Trichlorosilane (4.40 mL, 43.6 mmol) was added to reaction flask

dropwise using a syringe. The reaction flask was then immersed in an oil bath regulated at 100 °C and the reaction mixture was stirred for 12 h. At this time, the system was allowed to cool to room temperature, and hexanes (50 mL) and saturated aqueous Na₂CO₃ (100 mL) were added to reaction mixture. The mixture was then filtered through a pad of Celite which was then washed with an additional portion of hexanes (100 mL). The combined filtrate was transferred to a separation funnel. The organic layer was separated and washed with H₂O (50 mL), brine (50 mL), and then dried over anhydrous MgSO₄. The solvents were evaporated under reduced pressure to give a viscous liquid which was shown to be **61** or **100** based on ¹H and ³¹P NMR spectroscopy.

Lactide polymerization catalyzed by PIB-NHC (160) generated *in situ* PIB-imidazolium chloride **158**⁶² (0.722 g, 0.250 mmol) and THF (10 mL) was added to a 50-mL round-bottomed flask equipped with a magnetic stirrer. A THF solution of potassium *tert*-butoxide (0.250 mL, 1.0 M, 0.250 mmol) was added to the flask and the reaction mixture was stirred at room temperature for 30 min. A THF solution (10 mL) of benzyl alcohol (26 μL, 0.251 mmol) and L-lactide (0.721g, 5.00 mmol) was added to reaction flask and the reaction mixture was stirred for 30 min at room temperature. Solvent was removed under reduced pressure and the residue was dissolved in a mixture of heptane (5 mL) and DMF (5 mL) to form a biphasic mixture. The less-dense phase was separated and the solvent was removed under reduced pressure and the residue was analyzed by ¹H NMR spectroscopy. An aliquot of DMF-phase was analyzed by ¹H NMR spectroscopy to determine the conversion of L-lactide to polylactide.

2-Ethyl-1-isothiocyanato-4-polyisobutylbenzene (162) PIB-ethylaniline⁵⁸ **161** (1.406 g, 0.996 mmol) and dichloromethane (5 mL) were added to a 25-mL round-bottomed flask equipped with a magnetic stirrer. After dissolution of PIB-ethylaniline **161**, triethylamine (0.150 mL, 1.08 mmol) and carbon disulfide (0.600 mL, 9.98 mmol) were added to the flask. The reaction mixture was stirred at room temperature for 4 h. Boc-anhydride (0.222 g, 1.02 mmol) and DMAP (0.0060 g, 0.0491 mmol) were added to the flask and the reaction mixture was stirred for 2 h at room temperature. Solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexanes as the eluent solvent. The product was obtained as a colorless viscous liquid (0.734 g, 0.505 mmol, 51 % yield). ¹H NMR (500 MHz, CDCl₃): δ 0.89-1.52 (m, 187 H), 2.72 (q, *J* = 7.6 Hz, 2 H), 7.10-7.22 (m, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 14.4, 25.8, multiple peaks between 30-39 and 58-60, 124.8, 125.6, 126.6, 127.1, 134.3, 139.7, 150.3.

PIB-NHC-isothiocyanate adduct (164) A THF solution of NHC carbene **124** (5.0 mL, 0.1 M, 0.499 mmol) was prepared by allowing 1,3-bis(2,4,6-trimethylphenyl)-imidazolium chloride (**163**) (0.172 g, 0.505 mmol) to react with potassium *tert*-butoxide (0.0560 g, 0.499 mmol) in THF (5 mL) for 30 min at room temperature. To the THF solution of carbene **124**, a THF solution (5 mL) of PIB-isothiocyanate **162** (0.734 g, 0.505 mmol) was added and the reaction mixture turned into a yellow solution. The reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using a mixture of hexanes and acetone (4:1) as the eluent mixture to

give a yellow viscous liquid (0.786 g, 0.447 mmol, 90% yield). ^1H NMR (300 MHz, CDCl_3): δ 0.80-1.53 (m, 187 H), 2.37 (s, 6 H), 2.39 (s, 12 H), 6.15 (d, $J = 8.2$ Hz, 1 H), 6.92 (d, $J = 8.2$ Hz, 1 H), 7.00 (m, 5 H), 7.04 (s, 2 H). ^{13}C NMR (75 MHz, CDCl_3) δ 14.4, 25.8, multiple peaks between 30-39 and 58-60, 119.0, 120.0, 123.3, 125.5, 129.3, 131.3, 133.0, 135.9, 140.4, 144.0, 147.1, 147.6, 165.2.

Lactide polymerization catalyzed by PIB-NHC-NCS (164) Benzyl alcohol (26 μL , 0.251 mmol), L-lactide (0.721g, 5.00 mmol), and PIB-NHC-NCS **164** (0.351 g, 0.200 mmol) were placed in a 10-mL pear-shaped flask equipped with a magnetic stirrer. The flask was flushed with N_2 and then added anhydrous toluene (2 mL). The flask was placed in an oil bath regulated at 110 $^\circ\text{C}$ and the reaction mixture was stirred for 24 h. Reaction mixture was added a mixture of heptane (3mL) and DMF (3 mL) cooled to room temperature to form a biphasic mixture. The less-dense phase was separated and the solvents were removed under reduced pressure. The residue of less dense-phase was added fresh substrates for recycling experiments. An aliquot of DMF-phase was analyzed by ^1H NMR spectroscopy to determine the conversion of L-lactide to polylactide.

Phenyl isocyanate trimerization catalyzed by PIB-NHC-NCS (164) Phenyl isocyanate (0.381 g, 3.20 mmol) and PIB-NHC-NCS **164** (0.740 g, 0.421 mmol) were placed in a 10-mL pear-shaped flask equipped with a magnetic stirrer. The flask was flushed with N_2 and then added heptane (2 mL). The flask was placed in an oil bath regulated at 120 $^\circ\text{C}$ and the reaction mixture was stirred for 24 h. White precipitate was observed as the reaction proceeded. The reaction mixture was cooled to room

temperature and added heptane (3 mL) and then filtered. Solvent of combined heptane filtrates was removed and the residue was added fresh phenyl isocyanate for recycling experiments. Solid product was further washed with heptane (5 mL) and then dried under vacuum. The crude product was recrystallized from acetone to form white prisms (0.251 g, 0.702 mmol, 66% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.38-7.42 (m, 6 H), 7.43-7.47 (m, 3 H), 7.47-7.52 (m, 6 H). ^{13}C NMR (125 MHz, CDCl_3) δ 128.4, 129.4, 133.5, 148.67. M.P.: 278-280 °C (lit.¹⁵⁴ 279-280 °C).

PE_{Olig}-bound imidazolium Chloride (171) PE_{Olig}-bound bisimine¹⁰⁶ (0.551 g, 0.404 mmol) was placed in a 10-mL round-bottomed flask equipped with a magnetic stirrer. The flask was flushed with N_2 and then added anhydrous toluene (5 mL). The flask was immersed in an oil bath regulated at 80 °C and the reaction mixture was stirred until complete dissolution of PE_{Olig}-bound bisimine was observed. At this point chloromethyl ethyl ether (74 μL , 0.798 mmol) was added to the flask via a syringe. Reaction mixture was further stirred for 30 min and then cooled to room temperature. The product PE_{Olig}-bound imidazolium chloride **171** was isolated by vacuum filtration and washed with acetone (10 mL) to yield a brown powder (0.550 g, 0.390 mmol, 97% yield). ^1H NMR (500 MHz, C_6D_6 , 70 °C) δ 0.90 (t, $J = 5.6$ Hz, 10H), 1.15-1.53 (brs, 328 H), 1.74 (m, 4 H), 2.06 (s, 12 H), 3.79 (t, $J = 6.0$ Hz, 4 H), 6.46 (s, 2 H), 6.68 (s, 4 H), 11.3 (s, 1 H). ^{13}C NMR (125 MHz, C_6D_6 , 70 °C) δ , 14.2, 18.5, 23.0, 26.6, 29.7, 29.8, 30.0, 32.3, 68.8, 115.3, 124.7, 126.7, 136.7, 141.4, 160.9.

PE_{Olig}-bound imidazolium Tetrafluoroborate (172) PE_{Olig}-bound imidazolium chloride (0.550 g, 0.390 mmol) and ammonium tetrafluoroborate (0.0840 g, 0.802 mmol

were placed in a 10-mL round-bottomed flask equipped with a magnetic stirrer. The flask was flushed with N₂ and then added anhydrous toluene (5 mL). The flask was placed in an oil bath regulated at 80 °C and the reaction mixture was stirred for 30 min. The reaction mixture was cooled to room temperature. The solid product was isolated by vacuum filtration and washed with methanol (10 mL) and acetone (10 mL) to yield a brown powder (0.562 g, 0.384 mmol, 98% yield). ¹H NMR (500 MHz, C₆D₆, 70 °C) δ 0.90 (t, *J* = 6.4 Hz, 10H), 1.15-1.53 (brs, 328 H), 1.74 (m, 4 H), 1.89 (s, 12 H), 3.83 (t, *J* = 6.4 Hz, 4 H), 6.57, (s, 2 H), 6.64 (s, 4 H), 8.41 (s, 1 H). ¹³C NMR (125 MHz, C₆D₆, 70 °C) δ, 14.2, 17.5, 23.0, 26.6, 29.7, 29.8, 30.0, 32.3, 68.7, 115.2, 125.6, 126.5, 136.6, 138.3, 161.0.

PE_{Olig}-bound NHC (173) PE_{Olig}-bound imidazolium tetrafluoroborate **172** (0.152 g, 0.104 mmol) and KHMDS (0.0401 g, 0.201 mmol) were placed in a 10-mL round-bottomed flask equipped with a magnetic stirrer. The flask was flushed with N₂ and then added anhydrous toluene (2 mL). The flask was placed in an oil bath regulated at 80 °C and the reaction mixture was stirred for 30 min. The reaction mixture was cooled to room temperature. The solid product was isolated by vacuum filtration and washed with acetone (10 mL) to yield a brown powder (0.131 g, 0.0953 mmol, 95% yield).

PE_{Olig}-bound NHC-CO₂ adduct (174) PE_{Olig}-bound imidazolium tetrafluoroborate **172** (0.152 g, 0.104 mmol) and KHMDS (0.0401 g, 0.201 mmol) were placed in a 10-mL round-bottomed flask equipped with a magnetic stirrer. The flask was flushed with CO₂ and then added anhydrous toluene (2 mL). The flask was placed in an oil bath regulated at 80 °C and the reaction mixture was stirred for 30 min under a CO₂ atmosphere. The

reaction mixture was cooled to room temperature. The solid product was isolated by vacuum filtration and washed with acetone (10 mL) to yield a brown powder (0.139 g, 0.0980 mmol, 94% yield). ^1H NMR (500 MHz, C_6D_6 , 70 °C) δ 0.90 (s, 10H), 1.15-1.53 (brs, 328 H), 1.74 (m, 4 H), 2.03 (s, 12 H), 3.81 (m, 4 H), 6.24, (s, 2 H), 6.66 (s, 4 H).

PE_{Olig}-bound NHC-NCS adduct (175) PE_{Olig}-bound imidazolium tetrafluoroborate **172** (0.152 g, 0.104 mmol), KHMDS (0.0401 g, 0.201 mmol), and phenyl isothiocyanate (24 μL , 0.201 mmol) were placed in a 10-mL round-bottomed flask equipped with a magnetic stirrer. The flask was flushed with N_2 and then added anhydrous toluene (2 mL). The flask was placed in an oil bath regulated at 80 °C and the reaction mixture was stirred for 30 min. The reaction mixture was cooled to room temperature. The solid product was isolated by vacuum filtration and washed with acetone (10 mL) to yield a brown powder (0.131 g, 0.0868 mmol, 83% yield). ^1H NMR (500 MHz, C_6D_6 , 60 °C) δ 0.90 (s, 10H), 1.15-1.53 (brs, 328 H), 1.66 (m, 4 H), 2.37 (s, 12 H), 3.64 (t, $J = 5.6$ Hz, 4 H), 5.87, (s, 2 H), 6.61 (s, 4 H), 6.83 (t, $J = 7.5$ Hz, 1 H), 7.51 (d, $J = 7.5$ Hz, 2 H). ^{13}C NMR (125 MHz, C_6D_6 , 70 °C) δ 14.2, 18.9, 23.0, 26.5, 29.7, 30.0, 32.3, 68.3, 114.7, 119.6, 122.7, 123.2, 137.9, 138.3, 139.8, 148.0, 152.3, 160.7, 166.6.

General procedure for lactide polymerization catalyzed by PE_{Olig}-bound NHC (pre)catalysts (Table 7) The PE_{Olig} material used in lactide polymerization was consisted of either **173** (0.0691 g, 0.0502 mmol) with polywax (0.731 g) or **174** (0.284 g, 0.200 mmol) with polywax (0.522 g) or **175** (0.680 g, 0.450 mmol) with polywax (0.120 g). Hexadecanol (0.0603 g, 0.247 mmol), L-lactide (0.721g, 5.00 mmol), and PE_{Olig} material were placed in a 10-mL round-bottomed flask equipped with a magnetic stirrer.

The flask was flushed with N₂ and then added anhydrous toluene (5 mL). The flask was placed in an oil bath regulated at 110 °C and the reaction mixture was stirred for 24 h. The reaction mixture was cooled to room temperature and added to a 50-mL Erlenmeyer flask containing acetone (25 mL). The resulting mixture was stirred vigorously for 5 min. In the case when **174** was used as the NHC precatalyst, CO₂ was bubbled through the reaction mixture when the reaction mixture was cooled to room temperature. Reaction mixture was filtered and an aliquot of the filtrate was analyzed by ¹H NMR spectroscopy to determine the conversion of L-lactide to polylactide. The PE_{Olig} material collected by filtration and washed with acetone (10 mL) and dried under vacuum. Recycled PE_{Olig} material was added fresh substrates for recycling experiments.

General procedure for phenyl isocyanate trimerization catalyzed by PE_{Olig}-bound NHC (pre)catalysts (Table 8) The PE_{Olig} material used in lactide polymerization was consisted of either **173** (0.0411 g, 0.0299 mmol) with polywax (0.181 g) or **174** (0.213 g, 0.150 mmol) or **175** (0.226 g, 0.150 mmol). PE_{Olig} material was placed in a 5-mL pear-shaped flask equipped with a magnetic stirrer. The flask was flushed with N₂ and then added phenyl isocyanate (0.330 mL, 3.04 mmol) and anhydrous toluene (2 mL). The flask was placed in an oil bath regulated at 110 °C and the reaction mixture was stirred for 24 h. The reaction mixture was cooled to room temperature and added to a 50-mL Erlenmeyer flask containing acetone (25 mL). The resulting mixture was stirred vigorously for 5 min. In the case when **174** was used as the NHC precatalyst, CO₂ was bubbled through the reaction mixture when the reaction mixture was cooled to room temperature. Reaction mixture was filtered and the solvent of the filtrate was removed

under reduced pressure. The residue of filtrate was weighed and analyzed by ^1H and ^{13}C NMR spectroscopy to confirm the identity of desired isocyanurate product. The PE_{Olig} material collected by filtration and washed with acetone (10 mL) and dried under vacuum. Recycled PE_{Olig} material was added fresh substrates for recycling experiments.

CHAPTER VI

CONCLUSIONS

Research presented in this dissertation includes VT NMR studies of soluble polymer-supported phosphine-silver complexes, the use of soluble polymer-supported phosphines as recyclable and reusable catalysts and reagents, and preliminary studies of the use of polymer-bound NHC adducts as catalysts. Chapter II of this dissertation shows that terminally functionalized PIB- and PEG-bound phosphine-silver complexes have exchange behavior similar to that of their low molecular weight analogues as shown by variable temperature NMR studies. Comparison of line shape analyses of ^{31}P NMR spectra of polymer-bound and low molecular weight phosphine-silver complexes undergoing temperature dependent exchange show that the exchange rates and Gibbs energy of activation of PIB- and PEG-supported phosphine silver complexes and their low molecular weight counterparts are nearly the same. This similar dynamic behavior in a ligand exchange process for either a polymer-bound or a low molecular weight phosphine-silver complex supports the assumption that soluble terminally-functionalized polymer-supported metal complexes can be used to prepare soluble polymer-bound catalysts whose reactivity and selectivity will be similar to that of their low molecular weight counterparts.

Chapter III of this dissertation describes the use of PIB-bound alkyldiphenyl- and triarylphosphines as recyclable and reusable organocatalysts in an addition reaction of methyl propiolate and an allylic amination reaction. This chapter also shows that these

PIB-bound phosphines are useful reagents in aza-Wittig and Mitsunobu reactions. An advantage of these phosphines is that nonpolar phase selective solubility of the PIB-bound phosphine catalysts or the phosphine oxide byproducts of a stoichiometric reaction facilitates isolation and separation of products. In addition, when PIB-bound phosphine oxides are formed either by adventitious oxidation or in the course of a stoichiometric reaction, the heptane solutions they form can be treated with trichlorosilane to reform the PIB-phosphines. This reduction to regenerate PIB-bound phosphines is also simplified by the heptane solubility of the product phosphines that avoids a more complicated workup. The regenerated phosphines as expected have reactivity equivalent to freshly prepared PIB-phosphines.

Chapter IV of this dissertation describes the syntheses and the use of PIB- and PE_{Olig}-bound NHC (pre)catalysts that have reported utility in lactide polymerization and phenyl isocyanate trimerization reactions. The results show that a PIB-NHC catalyst generated *in situ* from PIB-bound imidazolium salt is an efficient catalyst in a lactide polymerization. However, this PIB-NHC catalyst was not recyclable. A PIB-NHC-NCS precatalyst however was somewhat recyclable in lactide polymerization and phenyl isocyanate trimerizations. PE_{Olig}-bound NHC and its CO₂ and isothiocyanate adducts were also prepared and used as in lactide polymerization and phenyl isocyanate trimerizations. Modest recyclability of these PE_{Olig}-bound NHC (pre)catalysts was also observed.

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