Phosphonium Ionic Liquid Based Salen Ligands for Use in Catalysis

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Abstract

Salen ligands and their corresponding complexes are well known in the field of asymmetric catalysis due to their success in stereoselective reactions. A method that easily allows for recycling of the catalyst without degradation of catalytic activity would make them more industrially viable. The generation of a Task Specific Ionic Liquid (TSIL) by attaching tributylphosphonium moieties to Jacobsen's ligand could promote the entrainment of the catalyst in an ionic liquid (IL). This would potentially create a recyclable system where the desired product can be extracted, leaving the IL/catalyst layer behind ready for reuse. The racemic and asymmetric versions of the ligand, 5,5'-(1E,1'E)-(cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(3-tert-butyl-4-hydroxy-5,1-phenylene)bis(methylene)bis(tributylphosphonium)
hexafluoridophosphate, as well as their respective copper complexes were successfully synthesized and characterized. These were applied to aziridinations of styrene, using tosyliminophenyliodinane (PhINTs) as a nitrene source, in both acetonitrile and three different ILs. Acetonitrile generated yields of up to 88%, however no product was extracted from 1-butyl-3-methylimidazolium hexafluoridophosphate, tetradecyl(trihexyl) phosphonium hexafluoridophosphate and chloride.

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Abbreviations

ILs	ionic liquids
RT	room temperature
NMR	nuclear magnetic resonance
[emim]$^+$	ethylmethylimidazolium
[PF$_6$]$^-$	hexafluoridophosphate
[BF$_4$]$^-$	tetrafluoridoborate
[NTf$_2$]$^-$	bis(trifluoromethanesulfonimide)
[bmim]$^+$	1-butyl-3-methylimidazolium
TSILs	task specific ionic liquids
salen	N,N'-bis(salicylidene)ethylenediamine
saldach	*N, N'*-bis(salicylidene)diaminocyclohexane
e.e.	enantiomeric excess
PhINTs	*N*-tosyliminophenyliodinane
GC	gas chromatography
ppm	parts per million
HR-ESI-MS	high resolution mass spectrometry electrospray ionization
PILs	phosphonium ionic liquids
DMSO-d^6	deuterated dimethylsulfoxide
CDCl$_3$	deuterated chloroform
(CD$_3$)$_2$CO	deuterated acetone
TMS	tetramethylsilane
MS-ESI	electrospray ionization- mass spectrometry
CCD	charge-coupled-device
m.p.	melting point
IR	infrared
VOC	volatile organic compound
RTIL	room temperature ionic liquid

1.0 Introduction

1.1.0   Ionic Liquids

Ionic liquids (ILs) have more than a century of history but have recently emerged as a popular research topic due to their wide variety of applications. The last eighteen years have shown a significant increase from approximately twenty publications in 1995, to more than 1500 in 2005.[1] Their unique characteristics, such as the ability to solvate a wide variety of organic molecules, have intrigued many researchers.

Ionic liquids are defined as salts with melting temperatures below 100°C.[1] A significant number are liquids at room temperature and are therefore referred to as room temperature ionic liquids (RTILs). They were previously referred to as "molten salts" before the recent boom in literature, however this term has a connotation of a high melting, corrosive and viscous species.[2] There are many other synonyms such as room temperature molten salt, low temperature molten salt, ambient temperature molten salt, ionic fluid, and liquid organic salt.[3]

ILs often consist of a bulky organic cation and a relatively smaller inorganic anion. Low melting points can be attributed to the presence of unsymmetrical alkyl groups on the cation.[2] Common examples of cations composing ILs are tetraalkylammonium, tetraalkylphosphonium, N-alkylpyridinium, 1,3-and dialkylimidazolium, while halides, hexafluoridophosphate, tetrafluoridoborate, and bis(trifluoromethanesulfonimide) are all typical anions (Figure 1).

N-alkylpyridinium   N,N'-dialkylimidazolium   tetra-alkylammonium   tetra-alkylphosphonium

Halide   tetrafluoroborate   bis(trifluoromethanesulfonimide)   hexafluorophosphate
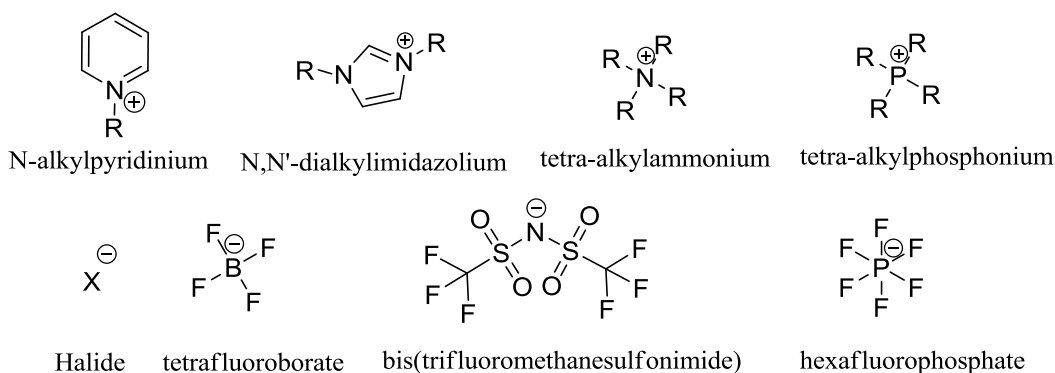
Figure 1. Common cations and anions used in ionic liquids.

1.1.1 History of Ionic Liquids

While it is only within the past two decades that ionic liquids have become very popular within scientific literature, their history goes back almost two centuries. The first recorded observation of an ionic liquid was reported in the mid-19th century as a "red oil" separating from the reactants through the progression of a Friedel-Crafts reaction.[3] The classic example of this reaction employs a benzene ring with chloromethane, which requires a Lewis acid to successfully synthesize toluene. The red oil that separated from the reaction was discovered to be an organic cation, resulting from the nucleophillic π-electrons attack on the methyl carbon, and the Lewis acid anion. This was observed upon early application of Nuclear Magnetic Resonance (NMR) Spectroscopy.[3]
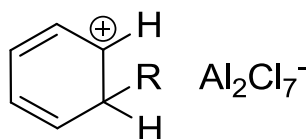
Figure 2. An example of the first ionic liquid synthesized through the Friedel-Crafts Reaction (R=CH$_3$).

The early 20th century brought the discovery of additional room temperature ionic liquids, the alkylammonium nitrates.[3] The first variation was ethylammonium nitrate, which was reported in 1914.[1] It was formed by the addition of concentrated nitric acid to ethylamine; water was then removed by distillation, resulting in a room temperature ionic liquid salt. Wilkes and coworkers reported the first examples of dialkylimidazolium based ionic liquids, which contained chloroaluminate anions ($AlCl_4^{2-}$ or $Al_2Cl_7^{2-}$). These were proven to be useful in Friedel-Crafts acylations as both a solvent and a catalyst.[4] However these anions are very air and water sensitive and therefore difficult to use in the open atmosphere.

The first water stable ionic liquid, ethylmethylimidazolium, [emim], tetrafluoridoborate, was reported by Wilkes *et al* in 1992[5], followed by [emim][PF_6].[6] It was thought that these species could be used as battery electrolytes, but they also proved to be useful for a wide range of applications.[1]

1.1.2 Properties of Ionic Liquids

Ionic liquids have many unique characteristics such as negligible vapor pressure, thermal stability, and other tunable properties. The low volatility of ILs gives the potential for them to be used as a recyclable solvent, and do not contribute to volatile organic compounds, VOCS. It may also be problematic in regards to purification because they cannot be distilled and therefore must be synthesized in high purity.[2] Generally ILs have a large range of thermal stability, although there are some existing exceptions. The salts [emim][BF_4] and [emim][NTf_2] are reported to be stable up to 300°C and 400°C, respectively, however the tetraalkylammonium salts are an exception

to this general characteristic because they can decompose *via* the Hoffman elimination.[2]

The cation and anion can be manipulated in order to achieve the desired properties of the ionic liquid.[2]   For instance, anion selection is extremely important when determining the species' desired interaction with water. For example, [bmim][BF_4] and halide anions are miscible with water, whereas [PF_6]⁻ salts are immiscible with water. The hydrophobicity can be controlled by the length of the alkyl chains on the organic cation, increasing with longer alkyl chain length.[7]

1.1.3 Synthesis of Ionic Liquids

Ionic liquids are often synthesized by the protonation with a free acid or by quaternization of an amine, phosphine or sulfide with a haloalkane or dialkylsulfate.[1] The former method is only applicable to a small number of ionic liquids whereas the latter can be applied to a much wider range of ILs. Salts formed by alkylation possess two major advantages: a variety of cheap haloalkanes are available and the substitution reactions are completed under ambient conditions. While all halides, with the exception of fluorine, are common leaving groups in such reactions, there are others that can be used such as methyl fluoroacetate, methyl tosylate and octyl tosylate. An example of a quaternization reaction is shown in Figure 3.[12]
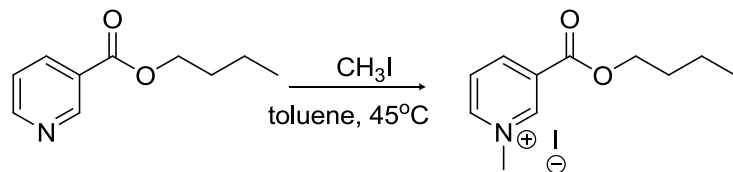
Figure 3. Quaternization of 3-(*n*-butoxycarbonyl)pyridinium with methyliodide.[12]

The desired anions can be introduced by one of two methods, the reaction of the halide salt with a Lewis acid or direct anion metathesis.[1] The former is accomplished by mixing the halide salt with the Lewis acid, resulting in the desired ionic liquid. Salts such as [Rmim]$_2$[MCl$_4$] (M=Co, Ni) can be formed in this manner. Water immiscible ionic liquids can be synthesized by metathesis. The dissolved halide salt, corresponding to the desired cation, is reacted with a free acid, such as hexafluoridophosphoric acid, resulting in the precipitation of the desired ionic liquid from the aqueous solution. An example of a metathesis with lithium bis(trifluoromethanesulfonyl)imide being the desired anion is shown in Figure 4 below.[12]
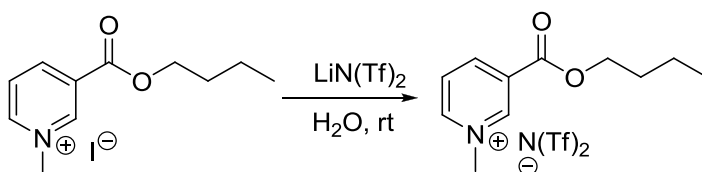
Figure 4. Metathesis of 3-(*n*-butoxycarbonyl)-1-methylpyridinium iodide for the bis(trifluoromethanesulfonyl)imide anion.[12]

1.1.4 Ionic Liquids as Solvents

Many features of ionic liquids make them attractive green solvents compared to VOCs. They are typically non-flammable and show chemical inertness to a wide variety of organic and organometallic compounds[8], which are usually highly soluble in a variety of salts.[2] Gases such as H$_2$, CO and O$_2$ are generally soluble in ionic liquids as well, making them attractive for catalytic hydrogenations, carbonylations, hydroformylations and aerobic oxidations.[2]

The purity of an ionic liquid used as a solvent is essential. Impurities in an IL solvent may result in the formation of unwanted side products. As previously stated, ILs

are often synthesized by the quaternization of a halomethylated species, resulting in a halide counter ion. If the metathesis from the halide to the desired anion is not properly purified and still contains residual halide, it may impede subsequent reactions such as in transition metal catalysis due to possible coordination of the halide to the transition metal.[2]

The anions of the ionic liquids, such as $[BF_4]^-$ and $[PF_6]^-$, are typically weakly coordinating. This characteristic is desirable because it allows them to be highly polar yet non-coordinating solvents. This would stabilize the transition state leading to the intermediate through its high polarity without competing for coordination sites, resulting in a faster rate of reaction.[2] These anions have been increasingly used in transition metal catalyzed reactions because they can immobilize the catalyst and preserve its activity due to the ionic liquid's non-coordinating nature. The nature of the interaction between the solute and ionic liquid remain uncertain but the ability of ILs to support and retain the catalyst after extraction of the desired product makes them recyclable.[2]

One of the major advantages of using ILs as solvents is their negligible vapor pressure, making them greener in comparison to VOCs such as toluene, ether and acetonitrile because they are non-volatile and therefore have the potential to be recycled.[9] This recyclability would ideally lead to less waste compared to the massive volumes of solvents used in industrial processes completed in typical VOCs. The waste, in kilograms, to the mass of desired product ratio is measured by the Sheldon E factor.[10] A higher E factor corresponds to more waste, which negatively impacts the environment, while an ideal E factor is zero. The pharmaceutical industry is an extremely wasteful

one, giving an E factor of up to over 100 times. This waste arises due to the large volumes of solvent used for synthesis.[11] Alternative solvents, such as ionic liquids, could be recycled and hence reduce this large waste to product ratio.

1.1.5 Task Specific Ionic Liquids

The functional groups of ionic liquids can be manipulated in order to perform specific functions, which gives rise to the category of task specific ionic liquids (TSILs). The design of particular cations and anions create suitable ionic liquids that can be used for specific applications, such as catalysis, lubricants, electro-chemistry, catalyst anchoring, metal ion separation, and ion conducting materials.[13] TSILs have also been determined to be beneficial for metal ion extraction, with ions such as U(VI), Am(III), Hg^{2+}, and Cd^{2+}.

Metal ions in aqueous solutions can be extracted using ionic liquid functionalized ligands.[13] These TSILs can be manipulated in order to alter their properties, promoting their use in the removal of metal ions, such as copper. One method used to enhance the ligand's capability to extract ions was to change the length of the alkyl chains. Increasing the length of the alkyl chain on the imidazole substituent increases the hydrophobicity of the complexes, allowing it to be a distinct, separate phase from aqueous solutions.[13]

In addition to the ion extracting TSILs, there are also Co(salen) complexes utilizing imidazolium cores that have been synthesized.[14] These complexes were shown to selectively oxidize the lignin model compound, veratryl alcohol, to veratraldehyde. This is an important application because it succeeded without further oxidation to the carboxylic acid (3,4-dimethoxybenzoic acid); this potentially could be applied to

depolymerize lignin, offering a prospective source of aromatic functionality.[14]

1.2.0 Salen Ligands

Salen ligands are a specific type of Schiff base that are prepared by a condensation reaction between two equivalents of a salicylaldehyde derivative and one equivalent of diamine, the simplest being ethylenediamine.[15] The resulting Schiff base, which contains a carbon-nitrogen double bond attached to a non-hydrogen R group, known as an imine, arises from the reaction between the carbonyl group on the salidicylaldehyde derivative and the free amine. The abbreviation "salen" arises from this basic Schiff base and is short for N,N'-bis(salicylidene)ethylenediamine, which is a tetradentate ligand, shown in Figure 5.
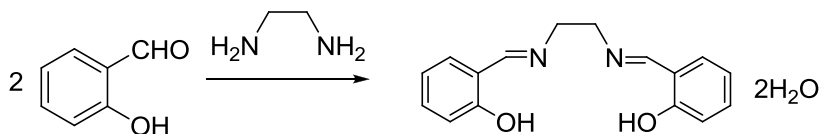
Figure 5. Condensation reaction to form N,N'-bis(salicylidene)ethylenediamine.[16]

Although less Lewis basic than a free amine, the sp^2-hybridized nitrogen on salen ligands is a relatively good base and readily available to donate its lone pair of electrons to a metal ion, forming stable complexes.[17] Without complexation, the salicylidene imine group has a tendency to revert to its corresponding salicylaldehyde and diamine *via* acid-catalyzed hydrolysis in the presence of water. The complexation to a metal ion significantly increases the stability of the imine functionality.[17] This allows the salen metal complex to be used in wet solvents or aqueous media without the risk of hydrolysis.

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1.2.1 Saldach Complexes as Asymmetric Catalysts

Salen ligands can be modified to be effective ligands for asymmetric catalysts through the addition of a chiral diamine backbone. There is no chirality within the simple salen ligands with an ethylenediamine moiety and therefore when complexed to a metal and used in catalysis, a racemic mixture will result. If ethylenediamine is replaced with a chiral diamine backbone, such as *trans*-1,2-diaminocyclohexane, the ligand has the potential to catalyze reactions enantioselectively.[15] This gives rise to the class of saldach ligands, which is an abbreviation for *N, N'*-bis(salicylidene)diaminocyclohexane. These ligands are often complexed to first and second row transition metals, as well as main group metals.

Saldach ligands are known to be effective in the preparation of asymmetric catalysts that are to be used to produce enantiomerically pure products.[17] Saldach ligands can be complexed to a variety of metals, which are chosen based on the desired reactivity. In addition to varying the metal, the structure of the ligand itself can be manipulated to achieve the desired steric and electronic properties through adjustment of the chiral diamine or salicylaldehyde starting material.[17, 18] Although a large number of ligand structures are possible, the ligand of Jacobsen's catalyst, presented in Figure 6, has been reviewed in Baleizão *et al* to be the optimum ligand for a wide range of stereoselective reactions.[17]
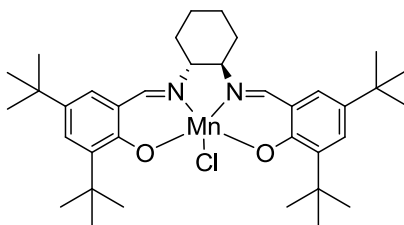
Figure 6. Chiral salen ligand complexed to Mn(III), known as Jacobsen's Catalyst**,** used for epoxidations.[17]

Jacobsen's catalyst was first utilized in the manganese (III)-catalyzed asymmetric epoxidation of alkenes in 1990.[17] It yielded high enantioselectivites up to 86% enantiomeric excess (ee) for terminal epoxides. High enantioselectivites were often observed with *cis*-1,2-disubstituted olefins, in addition to selected tri- and tetrasubstituted olefins as well.[17]

Although there have been many variations of saldach ligands reported in the literature, Jacobsen's catalyst has remained one of the most effective catalysts due to its balance between high stereoselectivity and inexpensive starting materials.[17] Its *tert*-butyl groups in the 3,3'- and 5,5'- positions force the substrate to approach the chiral diamine portion of the ligand, where its *trans*-diaxial α-protons promote enantioselctivity within the products. The success of Jacobson's catalyst led to its modification to include different metal cations and the investigation of various other asymmetric catalyzed reactions, such as epoxide ring opening, cyclopropanations, aziridinations, and selective hydrogenations.[19] Many structural variations of the ligand were explored in the search for new catalysts and these involved 1,2-, 1,3- and 1,4-diamines, chiral tertiary 1,2-diamines, chiral salicylaldehydes and hydroxyacetophones.[17]

Asymmetric catalysts are important in drug synthesis. There have been many

observations concluding the human body is extremely stereoselective and will only react with molecules possessing the proper absolute configuration. The use of enantiomerically pure drugs is, in many cases, a necessity and an incident that highlights this statement is the tragic thalidomide case in the 1960s. Many women were given the drug, produced in the form of a racemic mixture, to treat morning sickness and the R-enantiomer (structure **a** in Figure 7 below), did just this. However its S- enantiomer, **b,** induced fetal deformities.[19]

<center>a   b</center>
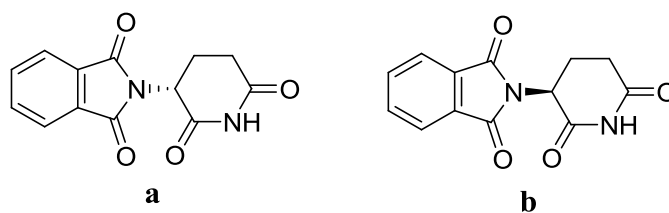
Figure 7. The structures of the R-enantiomer, **a**, and S-enantiomer, **b**, of thalidomide.

1.2.3 Development of Asymmetric Catalysis in Industry

Asymmetric catalysts are extremely attractive to the pharmaceutical industry[19] because they amplify chirality within products of the reactions they catalyze.[17] They offer a much simpler approach to synthesize chiral drugs as they often eliminate the need for the expensive and tedious process of separating racemic mixtures and diminish reliance on naturally occurring chiral compounds such as amino acids, carbohydrates and others.[19] Even with the success seen in asymmetric catalysis, such as the case of Jacobsen's catalyst, the rate at which this single enantiomer synthesis technique is introduced into industrial processes is much slower than originally anticipated. The huge limitation to these successful techniques that are reported in literature is the inability to reuse the catalysts, due to the frequent use of homogeneous reaction conditions.[17] This

requires the catalyst and chiral product to be separated upon completion, which often requires tedious and wasteful processes such as extraction to be incorporated into the process. In order to sustain this method within industry, a convenient technique must be developed to separate the expensive catalysts for reuse, while retaining high selectivity and yields.

The shift from homogenous conditions to recoverable catalyst systems has been the reasonable solution to the recyclability problem. A recoverable catalyst would promote the use of asymmetric catalysis within industry.[17] Many industrial strategies have utilized methods involving heterogeneous conditions and catalyst immobilization. However heterogeneous catalysts often suffer from deactivation, manifested with decreased catalytic efficiency, which may arise because the catalyst center is a separate phase and it is not as readily available to the reagents.[20] Many heterogeneous reactions involving salen metal complexes also require costly additives added in excess to act as axial bases, such as pyridine to promote coordination of dioxygen to cobalt metal complexes.[20, 21] This has caused many research groups to investigate catalyst immobilization as an alternative. Recently within the literature, salen catalysts have been immobilized on inorganic-organic hybrid materials due to their consistent distribution of functional organic groups. This allows the density, chemical reactivity and thermal stability of the framework to be easily manipulated. Zou *et al* investigated the immobilization of a Jacobsen-like catalyst on phenoxy-modified zirconium poly(styrene-phenylvinylphosphonate)phosphate and achieved high enantioselectivities in the epoxidation of α-methylstyrene.[20]

Another potential alternative to homogeneous catalysts in volatile organic solvents is the use of "green liquids".[17] The principle of this method is to retain the catalyst in the liquid phase while the chiral products can easily be separated by physical processes such as extraction, distillation, precipitation, and membrane filtration. The high molecular weight of the salen metal complexes make liquid-liquid extraction extremely viable with an immiscible solvent with low solubility power, such as an ether or a hydrocarbon.[17] Such organic solvents easily dissolve organic products and leave the catalyst behind in the non-volatile liquid. Green liquids thereby follow some of the principles of Green Chemistry, which aims to avoid or reduce the use of auxillary solvents, use of catalysts to increase reaction efficiency and prevent waste.[22] Such green liquids include water, supercritical fluids, and ionic liquids.[13] Although a reaction would ideally be completed without any organic solvents, this is unrealistic because there is a trade off with product yields; separation of products and starting materials would also be difficult, hazardous or even environmentally unfriendly.[17] If a successful and recoverable green liquid method for asymmetric catalysis were developed, this could then be applied to industry to lower costs and achieve high enantioselectivities of products.

1.2.4 Enantiomeric Excess

The goal of asymmetric catalysis is to produce one enantiomeric form of the chiral product, however reactions rarely behave ideally and typically generate both forms of enantiomers.[17, 23] If neither a racemic nor enantiomerically pure mixture is produced, there will be net excess of one of the enantiomers. This principle generates the need for a measurement of enantiomeric purity, which is measured by enantiomeric excess.

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Enantiomeric excess is expressed as a percentage of purity within the mixture and is calculated by subtracting the minor enantiomer from the major.[24]

The polarimeter is a commonly used instrument to measure enantiomeric excess of a non-racemic mixture. Polarimetry measures the rotation of a plane of monochoromatic polarized light after it has been passed through a sample, a scheme is shown in Figure 8.[25]
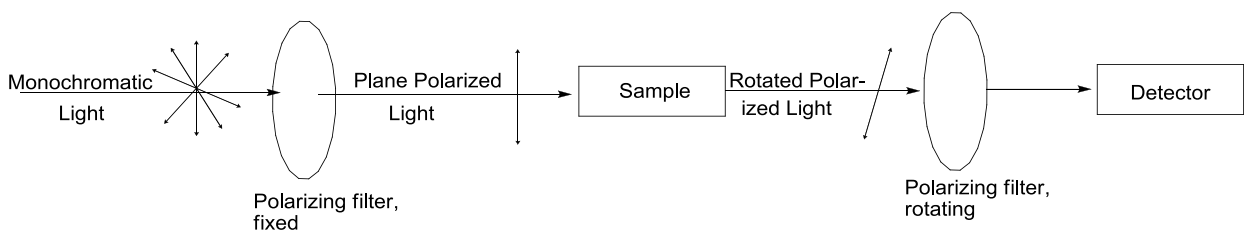
Figure 8. The scheme of monochromatic light of a polarimeter passing through a chiral sample.[25]

A linear plane of light is the resultant of two components, right and left circularly polarized light. The two wave components, each possessing a unique refractive index, superimpose and produce a linear plane of light. When the mixture is non-racemic and contains a higher ratio of one enantiomer, the net vector will favor one of the two components and result in rotation of the plane of light. Achiral and racemic mixtures do not rotate the plane of light because they have equal refractive indexes of the left and right circular components.[25]

The enantiomeric excess is calculated by finding the observed rotation, α, of plane polarized light traveling through the sample and relating it to the specific rotation, α value *via* the following equation:

$$ \overline{\qquad} \tag{1} $$

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In order to find α_{obs}, the concentration, c, in g/mL and path length of the light, l, in dm, must be known. α_{obs} can then be calculated as follows, with a reference temperature of 25˚C:

$$[a]_D^{25} = \frac{a}{l*c} \qquad (2)$$

The ratio of enantiomers can be found by using other instrumental methods, which can then be used to calculate enantiomeric excess. Alternative methods include chiral chromatography and NMR spectroscopy. One of the major techniques used in NMR studies is a chiral shift agent.[25] The principle of chiral shift reagents is that enantiotopic groups will react differently with a chiral reagent, forming distinct diastereoisomeric products, a ratio of which may be determined.

1.3.0 Aziridines

1.3.1 Properties of Aziridines

Aziridines are a class of compounds consisting of a heterocyclic, three membered ring containing a nitrogen atom that have many properties that can be applied in a variety of fields.[26] They are often considered to be the nitrogenous equivalent to epoxides. The simplest aziridine, also referred to as ethyleneimine, consists of a non-substituted nitrogen and two carbon atoms. It is a colorless, water soluble, distillable liquid that undergoes polymerization *via* nucleophilic ring opening. The bond strain within aziridines cause them to deviate from the typical properties of a standard secondary amine; their trigonal ring significantly increases the barrier to inversion which creates potential for stereoisomers when an electronegative substituent is present on the nitrogen.[26]

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There are many naturally occurring aziridines such as the mitosanes, shown in Figure 9.[26] These compounds were originally isolated from soil isolates of *Streptomyces verticillatus*. Studies have demonstrated that the anti-tumor and antibiotic activity of these compounds is related to the presence of the aziridine ring. This has therefore increased interest in aziridines, especially their use in the pharmaceutical industry.
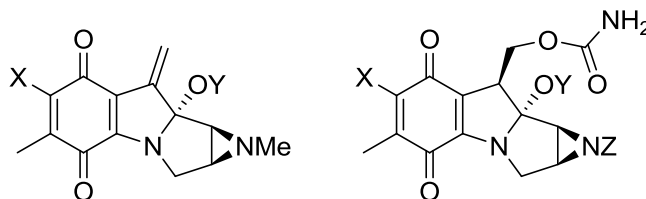
Figure 9. The mitosanes. (X,Y and Z represent various functional groups).

The azinomycin family and nitrogen mustards are two other classes of compounds that have aziridine formation that exhibit activity against tumor growth. Aziridines can also be utilized to produce important chemical species that may not be accessible, such as unique amino acids and β-lactams which are a key element in the synthesis of many effective antiobiotics, like (+)-thienamycin.[27]

1.3.2 Applications of Aziridines

Chiral aziridines are extremely useful in the field of synthesis because they readily undergo a wide variety of reactions. These reactions are both predictable and yield excellent stereo- and regiocontrol within the ring opened or ring expanded chiral amines.[28] With respect to reactivity, aziridines may be divided broadly into two general classes, activated and unactivated. The former is a substituted aziridine, which can stabilize the developing negative charge on the nitrogen when the ring is attacked by a nucleophile. The latter species is an unsubstituted aziridine that usually requires an acid

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catalyst to encourage ring opening. Different synthetic uses for chiral aziridines including stereoselective ring opening, rearrangements and ring expansions, chiral ligands and auxillaries were reported by McCoull and Davis. [28]

Stereoselective ring opening occurs with a variety of chiral aziridines. Some of the most common aziridine reagents have a C-carboxylate substituent because this is an efficient way to synthesize a chiral amino acid derivative upon ring opening. The nucleophile can either attack the C2 or C3 on the aziridine to give a β- or an α-amino acid derivative, respectively. The majority of nucleophiles attack the C3 position.
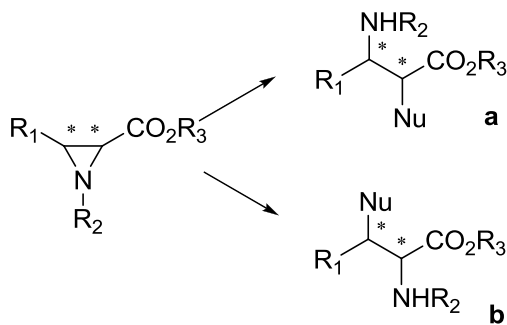
Figure 10. Reaction scheme for ring opening of carboxylate aziridine. Nucleophile attack at carbon C2 yields product **a**, at carbon C3 product **b**.[28]

The nucleophiles and substituents can be altered depending on the structure of the desired product. For example, one of the utilized methods is the hydrogenolysis of aryl substituted aziridines; this reaction does not affect the C2 stereochemistry in the α-amino acid derivative and often involves unactivated or sulfonyl activated phenyl aziridine carboxylates. There are many other nitrogen, halogen, and carbon based nucleophiles that are commonly used for stereoselective ring opening for carboxylate and non-carboxylate containing aziridines.[28]

Many non-carboxylate aziridine derivatives have been used as replacement of

aziridine-2-carboxylates, as in their reactions often frequently encounter regio- and chemoselectivity problems.[28] Reductive ring opening reactions are one of the alternative methods, along with other ones, frequently described in literature, involving an attack at the benzylic position of the aziridine structure using species such as di-tert-butyl dicarbonate, (Boc)$_2$O, and lithium with catalytic amounts of naphthalene. Another alternative method is to use heteronucleophiles such as hydroxyl[29], chloro[29] and azide[30] groups, which often require Lewis acids or nitrogen activation, while some thiols have been successful without the use of either activation.[31] These heteronucleophiles will generally attack the least sterically hindered aziridine carbon.[28] One example of a heteronucleophile attack, with a thiol, is shown in Figure 11[32], an alkoxy nucleophile reacts in a similar fashion.[33]
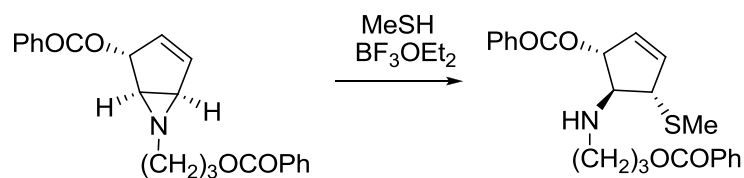
Figure 11. Reaction of an aziridine with a Lewis acid and a thiol.[32]

Aziridines are useful in a wide variety of other applications in synthesis, chiral catalysis and as chiral auxiliaries.[28] A synthetic application of aziridines is to form β-lactams *via* carbonylative ring expansion reactions.[28] Aziridine-2-carbinols have been tested as catalysts for the enatioselective addition of diethylzinc to aldehydes and the chiral aziridine ligand, giving up to 97% ee and good yields of the alcohol product.[34] The reaction scheme is shown in Figure 12. Aziridines can also be used as chiral auxiliaries if they are symmetric.[35]

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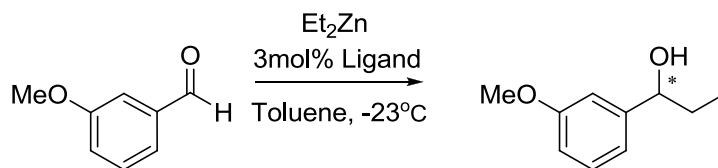
Figure 12. Catalytic scheme using a chiral aziridine and diethylzinc to form chiral alcohols.[34]

1.3.3 Synthesis of Aziridines

Aziridines are comparatively more difficult to synthesize than epoxides due to the relative inertness of the N–O and N–N bonds compared to the highly reactive peroxide bond.[26] One of the most successful routes to aziridines is the addition of a nitrene source to an alkene.[27] These species are reactive intermediates, where an electroneutral, electron deficient nitrogen atom has only one substituent.[26] There are two different forms of nitrenes, singlet nitrenes and triplet nitrenes. A singlet nitrene has two paired sets of free electrons whereas triplet nitrenes have one pair and two electrons with parallel spins. In the case of alkyl and aryl nitrenes the triplet state is lower in energy and deemed the ground state.[36] The singlet nitrene must be used in order to achieve a stereospecific reaction because it reacts in a concerted mechanism, whereas the triplet state-involving reaction occurs in a two step process with a diradical intermediate; this allows rotation to occur before the ring is formed.[27] These two states are represented in the Figure 13 below.

Singlet   Triplet

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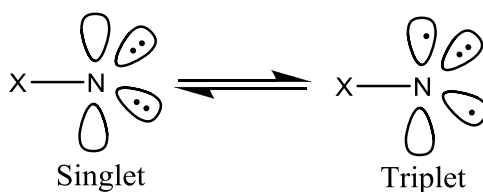
Figure 13. The singlet nitrene state versus the triplet state.[26]

Common nitrene sources include *N*-tosyliminophenyliodinane (PhINTs)[26] and chloramine-T[37]: the former has been used extensively in many studies. These nitrenes are known as metal-stabilized and have been coupled with salen catalysts to aziridinate alkenes.[26] Jacobsen and coworkers used chiral salen ligands in enantioselective aziridinations and they suspected the transition state to consist of a copper-nitrene complex, which is analogous to the well known mechanism of cyclopropanation.[38] Similar to the copper(II)-carbene intermediate, studies showed that the nitrene in aziridinations react *via* a copper(II)-nitrene intermediate, represented in the scheme in Figure 14.[16]
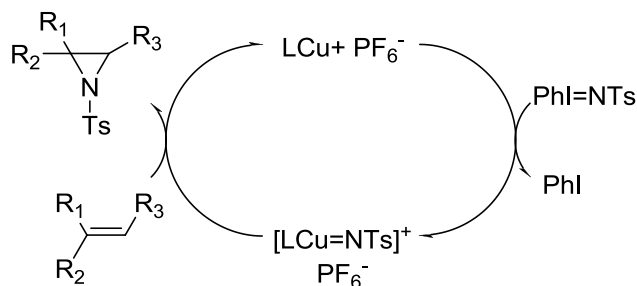
Figure 14. The reaction scheme for the proposed mechanism for the nitrene-Cu-complex intermediate.[26]

Both Cu(I) and Cu(II) species have been shown to catalyze the reaction; however it is suggested that the Cu(II) oxidation state is the catalytically active one as opposed to Cu(I) and that PhINTs likely acts as an oxidant, promoting oxidation of Cu(I) to the Cu(II) species.[39]

There are limitations that arise when using a nitrene source. One of the major drawbacks is that a large excess of alkenes, upwards of five equivalents, is required for

optimal yields.[26] There can also be unpredictable enantiocontrol and it is difficult to remove the arylsulfonyl group from the substituent position on the nitrogen, often requiring harsh conditions that potentially destroy the newly formed ring.[40] Additional synthetic pathways to aziridines that were described in literature include the use of compounds such as 1,2-aminoalcohols, 1,2-aminohalides, and α-bromoacrylates as starting materials.[26]

1.4.0 Previous Work

The Singer Group at Saint Mary's University has used a variety of TSILs for a variety of applications. TSILs have been synthesized for catalysis by adding IL moieties to commonly used catalysts. For example, methylimidazolium moieties have been added to salen ligands to generate recyclable catalysts in ionic liquid solvents.[41, 42] Naik *et al* synthesized a methylimidazolium tagged ligand with an ethylenediamine backbone and complexed it to both copper (II) and manganese (III) chloride.[42] The manganese (III) chloride complex was used with a 10% catalyst loading to investigate its ability to catalyze epoxidations in [bmim][PF$_6$]. A variety of substrates were reacted with the oxidant iodosobenzene, including styrene, *trans*-stilbene, and 6-cyano-2,2-dimethylchromene. Reaction times ranged from 1 to 24 hours and gas chromatography (GC) yields up to 100% were obtained.
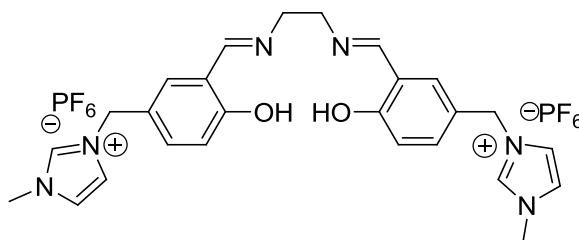
Figure 15. Structure of methylimidazolium salen ligand.[42]

The most recent study investigated the synthesis of an asymmetric saldach copper complex with methylimidazolium moieties in the 5-5' positions of the aryl ring (the ligand is shown in Figure 16) in anticipation that this would entrain the catalyst in a similar ionic liquid, such as [bmim][PF$_6$] and be recycled.[41]   The copper complex was successfully synthesized in both the racemic and R,R- forms; both of these proved to be a useful catalyst in traditional solvents such as acetonitrile, but no efficient protocols were established for catalytic reactions in ionic liquid solvents. A more sterically hindered analogue was synthesized by adding *tert*-butyl groups to the 3,3' positions, but required further purification.[41]
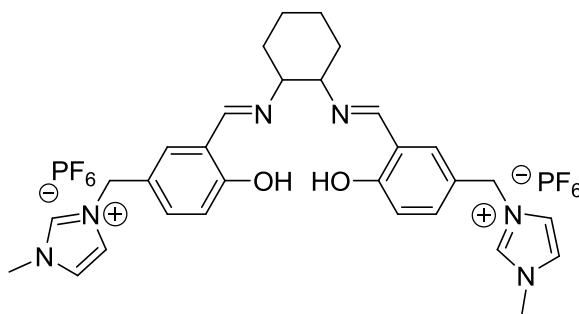
Figure 16. Previously synthesized imidazolium-based saldach ligand.

1.5.0 Objectives

The overall goal of the project was to synthesize an asymmetric phosphonium ion based saldach copper(II) complex, shown in Figure 17, and evaluate its catalytic potential in an ionic liquid solvent. It was expected that the tributylphosphonium salen ligand would generate higher enantiomeric excess than the methylimidazolium salen ligand due to an increase in its steric bulk. Unlike the sp^2 hybridized methylimidizolium, the sp^3 hybridized tributylphosphonium groups and additional *tert*-butyl groups would provide the necessary steric bulk to direct the olefin substrate to the chiral 1,2-diaminocyclohexane backbone. The aziridination of styrene was first performed in acetonitrile to test the complex's ability to catalyze the reaction and then apply it to an ionic liquid solvent, preferably one with a phosphonium cation. It was hypothesized that the ionic liquid will easily entrain the salen ligand due to the presence of the phosphonium moieties on the complex. This would promote recyclability and prevent leaching of the catalyst to the extracting solvent. Ideally the product could be extracted, leaving the catalyst and ionic liquid behind and ready to re-use. These goals would result in a system with a significantly lower volume of solvent waste, and possibly a more sustainable system than previous ones.
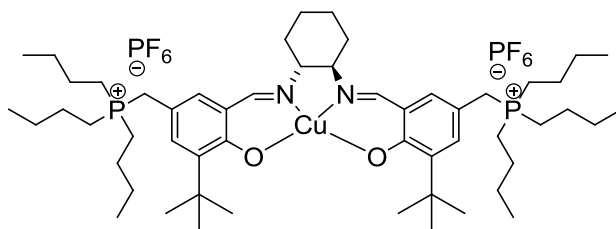
Figure 17. Proposed saldach phosphonium copper complex.

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2.0 Results and Discussion

2.1 Synthesis of Copper Saldach Complex, **5a,b**

The synthesis of both the asymmetric and racemic copper complexes consisted of a five step synthetic sequence beginning with the reagent 3-*tert*-butyl-2-hydroxybenzaldehyde. The chloromethylation of the starting material afforded 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde, **1**. Compound **1** was used to alkylate tributylphosphine yielding 3-tert-butyl-5-formyl-4-hydroxybenzyl)phosphonium chloride, **2**. Subsequent metathesis with hexafluoridophosphoric acid gave the hexafluoridophosphate salt, **3**, which then underwent a condensation reaction with 1,2-diaminocyclohexane to afford racemic and asymmetric 5,5'-cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(3-tert-butyl-4-hydroxy-5,1-phenylene)bis(methylene)bis(tributylphosphonium), saldach phosphonium ligand, **4a** and **4b**, respectively. The ligand, **4a,b**, was then refluxed with copper (II) acetate monohydrate to form the racemic and asymmetric copper (II) complex, **5a,b**.
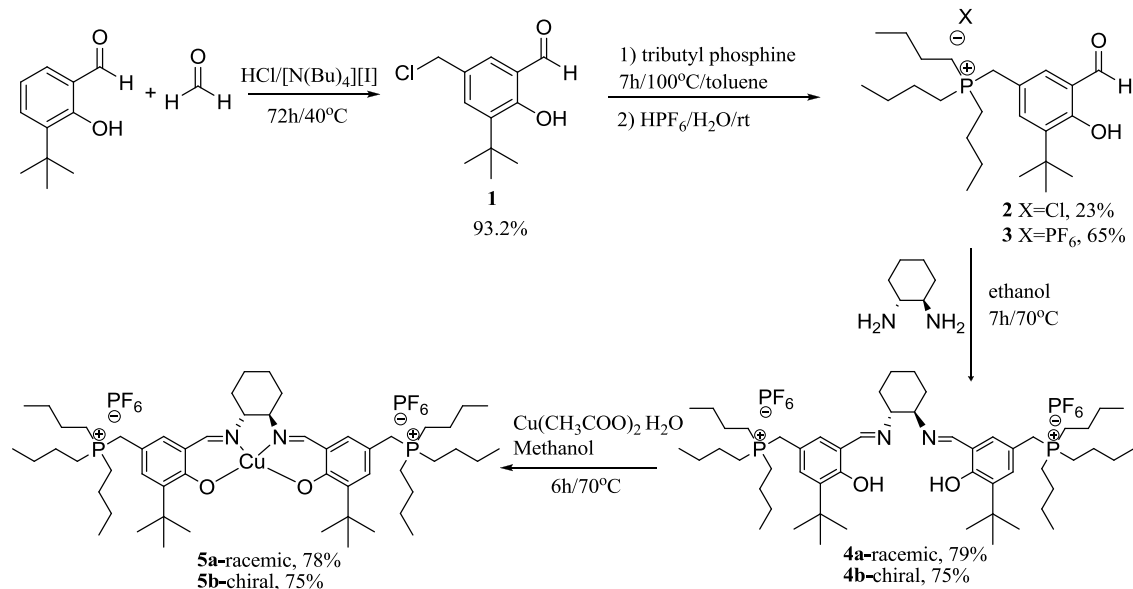
Figure 18. The reaction scheme for the synthesis of phosphonium saldach copper(II) complex.

The chloromethylation of 3-*tert-* butyl-2-hydroxybenzaldehyde is the first step in the synthesis of **5a,b**. The procedure of Durand[41] was followed, this procedure, a modification of Canali *et al* using paraformaldehyde, tetrabutylammonium iodide and concentrated hydrochloric acid.[43] Tetrabutylammonium iodide was chosen for the reaction as opposed to tetrabutylammonium bromide, which was used in the original procedure due to availability. The iodide salt acts as a phase transfer catalyst. A phase transfer catalyst, originally introduced by Starks, permits the reaction of two substances in two immiscible phases.[44] This procedure yielded a red oil separating from the aqueous layer, which was subsequently determined to contain molecular iodine.[41] The aqueous layer was extracted with portions of diethyl ether and the red oil was removed by washing the organic layer with sodium bisulfite, leaving the ether solution a pale yellow color. Sodium bisulfite acts as a mild reducing agent, reducing the iodine to iodide, which is soluble and colourless in aqueous solution. The ether was evaporated, leaving

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the yellow crystalline product, 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde, **1**. Identity of this product was confirmed both by ^{1}H and ^{13}C NMR.

The associated mechanism for the chloromethylation of the salicylaldehyde derivative is likely two subsequent steps consisting of aromatic electrophilic substitution and S_N1 due to the use of a polar protic solvent and the stability of the carbocation intermediate. Water can stabilize the positive charge that develops in the transition state leading to the intermediate and a benzylic carbocation is extremely stable due to mesomeric effects. The acidic conditions are necessary to protonate the carbonyl group on formaldehyde. This allows the π electrons of the benzene ring to attack the electrophilic carbon which eliminates the aromaticity. The aromaticity is quickly re-established by the removal of a hydrogen by an available Lewis base, such as chloride. The acidic conditions also promote protonation of the hydroxymethylated salicylaldehyde derivative, which creates an ideal leaving group. The resulting benzylic carbocation is readily attacked by the chloride to achieve the chloromethylated product.
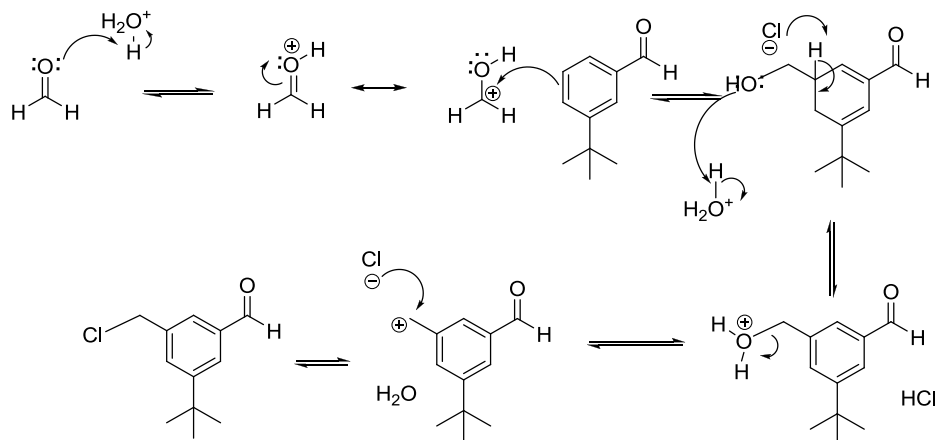
Figure 19. Chloromethylation mechanism of 3-*tert*-butyl-2-hydroxybenzaldehyde, **1**.

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The next step in the synthesis of the copper saldach phosphonium complex is a quaternization of 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde, **1**, to afford 3-*tert*-butyl-5-formyl-4-hydroxybenzyl)phosphonium chloride, **2**. Tributylphosphonium was transferred to a dried round bottom with dry toluene in an inert atmosphere glove box due to its sensitivity to moisture in the atmosphere. This was then transferred to a Schlenk line under nitrogen. 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde was previously dissolved in dry toluene and was added *via* syringe. After 7 hours at reflux, the reaction was cooled and a white precipitate formed. This immediately became pale green when exposed to air. The precipitate was filtered using a Büchner funnel in order to attempt to isolate the product. However this was problematic due to the hygroscopic nature of chloride salts. The sticky solid could not be removed from the Büchner funnel, which required it to be dissolved in hot toluene. The toluene was subsequently evaporated to afford 23% yield of the desired product, **2**. An alternative method improved the overall yield from Compound **1** to **3** to 65% by simple evaporation of the toluene to afford the crude Compound **2**. This could then be directly metathesized to the hexafluoridophosphate salt, **3,** without further purification.

Characterization of the chloride salt was difficult due to its hygroscopic nature; however, phosphorus-proton decoupled NMR shows a single strong singlet at 31.55ppm corresponding to the newly formed phosphonium moiety. The emergence of a doublet at 4.43ppm on the proton NMR of Compound **2** shows the methylene protons coupling to the newly formed phosphonium moiety with a coupling constant, $^2J_{H-P}$, of 14.8Hz.
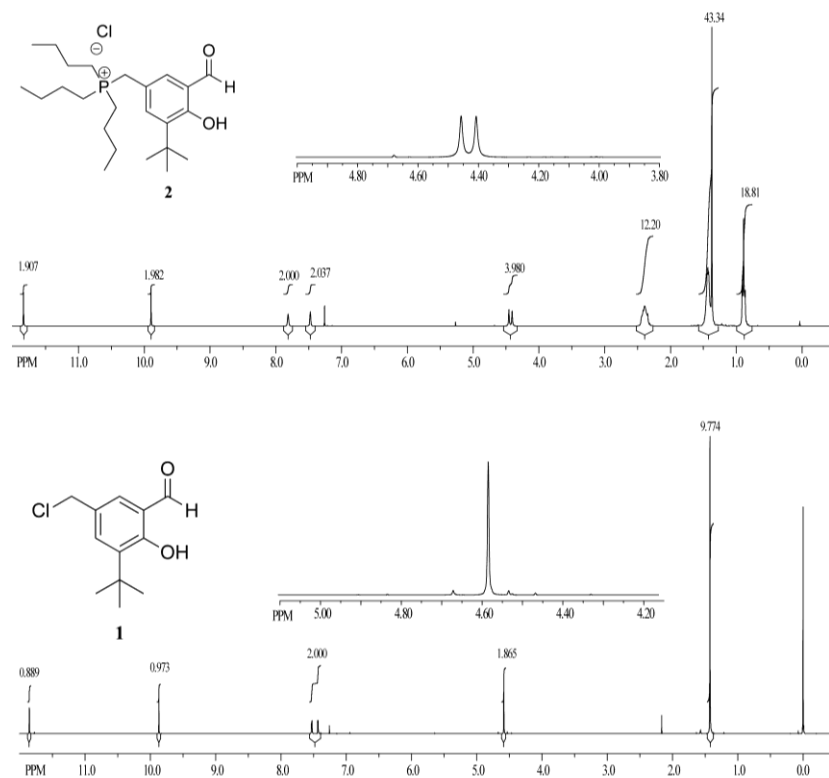
Figure 20. ^{1}H NMR of compound **1** and compound **2** showing the emergence of a doublet in **2** due to $^2J_{P-H}$ coupling at 4.45 ppm.

Metathesis from the chloride, **2**, to the hexafluoridophosphate salt was attempted without further purification because the chloride salt was difficult to work with. The hexafluoridophosphate salt was obtained by adding further diluted 65% w/w hexafluoridophosphoric acid dropwise to a solution of Compound **2** and water. The acid was further diluted in order to avoid the hexafluoridophosphate product from precipitating too rapidly from the aqueous solution and entrapping chloride impurities. After the addition of the hexafluoridophosphoric acid, a yellow-green solid precipitated out of solution, which was difficult to isolate because it had a sticky consistency. It was left to stir for an additional 24 hours and then isolated using a Büchner funnel, leaving a

mixture of green and white solid. The isolated solid was dried *in vacuo,* ground using a mortar and pestle and re-suspended in water. An additional 1.0 mL of hexafluoridophosphoric acid was added dropwise and the suspension was stirred for 24 hours. A white solid was isolated and confirmed to be the desired product, **3**, by X-ray Crystallography, HR-ESI MS, ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} NMR. The phosphorus NMR shows the emergence of an additional signal, a heptet at -144ppm, resulting from the ^{1}J coupling of the fluorine to phosphorous with a coupling constant of 713 Hz. The original singlet at 31.55ppm is still present indicating the presence of the phosphonium cation. The crystal structure, Figure 21, confirms the structure of **3**, for example it can be seen that the hexafluoridophosphate anion balances the positive charge on the phosphorus atom. The *tert*-butyl group is also evident on C3 of the benzene ring. The structure also shows successful alkylation of the tributylphosphosphonium group on C5 of the aromatic ring.
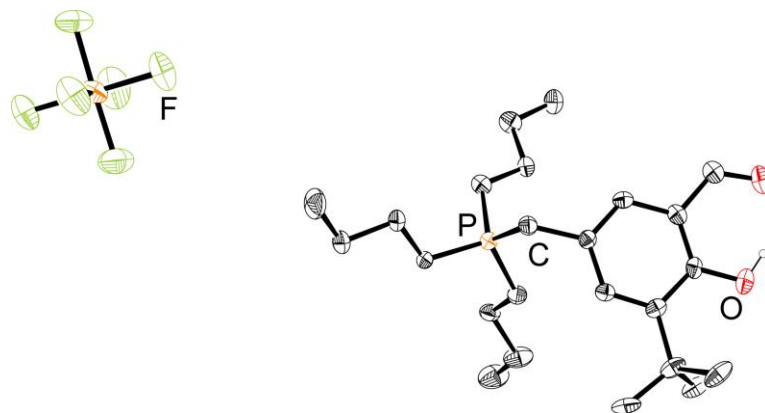
Figure 21. Xray crystal structure of structure 3-tert-butyl-5-formyl-4-hydroxybenzyl)phosphonium hexafluoridophosphate, **2**.

The mechanism of the alkylation of tributylphosine is likely an S_N2 like mechanism involving tributylphosphine acting as the nucleophile and the

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chloromethylated reagent as the electrophile. The lone pair of electrons on the phosphorus attacks the methylene carbon, which possess a partial positive charge compared to its electronegative chlorine neighbour. The phosphine acts as a strong Lewis base due to its readily available lone pair. Toluene was chosen as the solvent because it dissolves the reactants but the desired product is insoluble and therefore precipitates out of solution. According to Le Chatelier's Principle this would push the equilibrium forward, towards products, because there is consistent removal of the product, which increases the overall yield.

Once 3-tert-butyl-(5-formyl-4-hydroxybenzyl) phosphonium hexafluorido phosphate, **3**, was successfully synthesized and characterized, the ligand, **4a,b**, was synthesized *via* a condensation reaction. The procedure reported in Maio *et al*[45] was followed, however *trans*-1,2-diaminocyclohexane was used instead of ethylenediamine in order to potentially generate a chiral ligand. Racemic *trans*-1,2-diaminocyclohexane was used initially to synthesize racemic 5,5'-cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(3-tert-butyl-4-hydroxy-5,1-phenylene)bis(methylene)bis(tributylphosphonium), **4a**. Addition of the diamine reagent resulted in an immediate change of solution color to yellow. After 7 hours of refluxing and cooling to room temperature, a bright, transparent, yellow solution remained. The solution was concentrated and placed in the freezer in an unsuccessful attempt to precipitate the desired ligand. The ethanol was then evaporated affording a yellow-orange solid. Re-crystallization utilizing the method described by Maio *et al* with 4:3 dichloromethane: ethyl acetate by slow evaporation was attempted in order to purify this

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product.[45] No solid crystallized out of solution after a day so it was left to evaporate to complete dryness for 2 days, yielding a sticky solid. This solid was placed under a vacuum to remove the residual solvent, leaving the crude material.

Flash column chromatography was used to purify the ligand using silica gel and nitrogen gas. Many solvent systems were tested by thin layer chromatography (TLC), but it was determined that 5% methanol in dichloromethane achieved the best separation. Eluent was collected in a series of test tubes, content of which were analyzed by TLC with UV light detection. The test tubes containing product were combined and concentrated *in vacuo*, leaving a yellow solid. The ^{31}P NMR of this product displayed a strong singlet at 31.55 ppm and the anion heptet was displayed at -144ppm relative to an external H_3PO_4 standard. HR-ESI MS confirmed the presence of the racemic phosphonium saldach ligand, **4a**. The data contains mass/charge ratios of 1009.6 and 432.3, corresponding to a +1 and +2 charge, respectively. The +1 charge corresponds to the cation with one $[PF_6]$ anion, whereas the +2 charge does not contain any anions.

The asymmetric phosphonium based saldach ligand, **4b,** was synthesized by using the same method as the racemic version, **4a**, however the reactant R, R-*trans*-1,2-diaminocyclohexane was used as opposed to its racemic analog. The reactant is a hygroscopic solid so it was dissolved in ethanol before addition to **3**. Similar to the synthesis of **4a**, addition of the reactant resulted in a bright yellow solution, however after refluxing and cooling to room temperature, a light brownish yellow solution remained that contained a precipitate was obtained. This solution was placed in the freezer overnight then filtered and washed with cold absolute ethanol, leaving an off-white

precipitate. A bright yellow solid was expected, similar to the racemic version of the ligand as well as other salen ligands[46], which caused some doubt as to whether the ligand had actually formed. Upon dissolution in chloroform, a bright yellow solution was seen and ^{1}H, ^{13}C and ^{31}P NMR spectroscopy confirmed the presence and purity of the phosphonium based saldach ligand, **4b**. When the solvent was evaporated, a bright yellow solid remained, which was further characterized by HR-ESI MS, confirming the formation of the chiral ligand, **4b**.

The racemic ligand, **4a**, and asymmetric ligand, **4b**, were both successfully complexed to copper (II). Initially the less expensive racemic ligand was used to synthesize the copper (II) complex by refluxing it with methanol and copper (II) acetate monohydrate. The copper (II) acetate monohydrate was difficult to dissolve in methanol and light heating was required before adding the methanolic solution dropwise to the solution containing the ligand **4a** or **4b**. After 6 hours of refluxing, the solution was cooled to room temperature, resulting in some precipitate, and then placed in the freezer overnight yielding additional precipitate. A purple fluffy solid afforded a 78% yield after filtration and washing with ice-cold methanol. The asymmetric ligand was later synthesized using the same method and afforded a similar yield of 75%. The formation of both complexes was confirmed by HR-ESI MS.

2.2 Aziridinations

The catalytic ability of the newly synthesized copper (II) complexes **5a,b** in stereoselective aziridination reactions was investigated. This investigation is based on results of many previous catalytically active salen copper (II) complexes reported in

scientific literature.[26, 38, 47] The typical scheme for the series of aziridinations performed is presented in Figure 22.
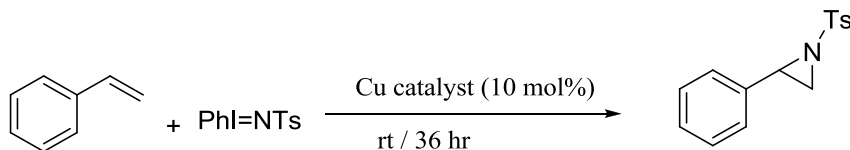
Figure 22. Typical aziridination of styrene using Cu(II) catalysts **5a,b** using PhINTs as a nitrene source.

The olefin has four side-on approaches to the metal complex, which are shown in Figure 23. Approach "c" of the substrate is disfavored because of the *tert*-butyl groups on position 3 of the salicylaldehyde ring. Approaches "a" and "b" are not favored due to the steric bulk of the phosphonium groups, similar to the *tert*-butyl groups in Jacobsen's catalyst, leaving the alkene favoring approach "d". This would favor an orientation of the least substituted face of the alkene, giving a stereoselective reaction.[48] The phosphonium groups provide three major advantages. The tri-n-butylphosphonium moieties are sp^3 hybridized, creating more steric bulk than previously synthesized planar, sp^2 hybridized imidazolium moieties.[41] This would ideally direct the substrate to the axial hydrogens on the 1,2-diaminocyclohexane backbone as opposed to a side on attack and result in a higher percentage of molecules with the desired chiral orientation.
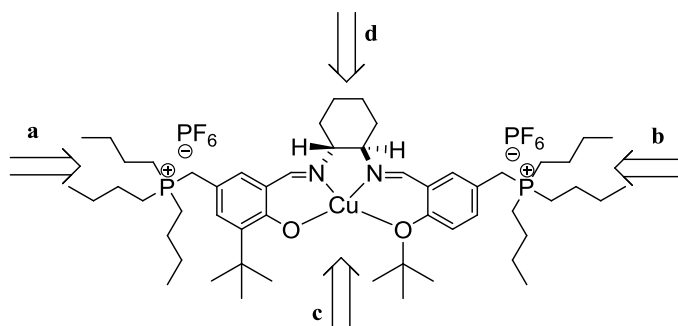
Figure 23. Side on approaches of an olefin towards the phosphonium Cu(II) complex, **5a,b**.

The functionalities also give ionic liquid character to the salen complex, facilitating the entrainment of it into IL solvents, promoting recycling of the catalyst-IL system. The third advantage is attributed to the tributyl groups on the phosphorus, which promote hydrophobicity of the complex, making it immiscible with water, preventing the hydrolysis of the ligand and/or catalytic complex.[17]

2.2.1 Aziridination of Styrene in Acetonitrile

Aziridinations of the unfunctionalized olefin, styrene, involving complexes **5a** and **5b** (Figure 22) were conducted in acetonitrile, a typical organic solvent, to determine its catalytic activity using 10% catalyst loading. The nitrene source chosen was n-tosyliminophenyliodinane (PhINTs) with a five-fold excess of styrene, under conditions successfully applied in reported work.[26] PhINTs was synthesized according to literature[49], however it is difficult to purify due to its ease of decomposition, and was used without purification. After reacting for a minimum of 18 hours at room temperature, the acetonitrile was concentrated and a wet brown solid remained. This was then extracted with portions of diethyl ether. The combined extracts were concentrated *in vacuo* affording a white solid. The phosphonium based copper complexes, **5a** and **5b**,

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were shown to effectively catalyze the aziridination presented in Figure 22 with yields of 84% and 88%, of 2-phenyl-1-tosylaziridine, respectively. The yields are slightly under the 89-95% yields achieved by a series of copper catalysts reported by Evans *et al*[50], however this is an improvement from the 56% yields reported with the imidazolium saldach copper complex (Figure 16).[41]

The grey solid that remained after the ether extractions was analyzed by low resolution mass spectrometry and the parent ion, 1071, corresponding to compound **5a** without a hexafluoridophosphate anion was present. This would suggest that unaltered copper (II) complex, **5a** remains intact and increases the likelihood of success in recycling experiments.

Table 2. Series of aziridinations performed using various Cu(II) Catalysts, PhINTs as a nitrene source and styrene.

mmol styrene	mmol PhINTs	Solvent	Catalyst	Yield
5	1	CH_3CN	Racemic	84%
5	1	PIL^*PF_6	Racemic	-
5	1	PIL^*Cl	Racemic	-
5	1	CH_3CN	Asymmetric	88%
5	1	[bmim][PF_6]	Asymmetric	-

2.2.2 Azirination of Styrene in Ionic Liquids

The initial goal was to investigate the catalytic activity of the Cu(II) saldach phosphonium complexes, **4a,b**, in an IL containing similar functionality to the phosphonium moieties on the ligand, specifically tetradecyl(trihexyl)phosphonium (PIL)

hexafluoridophosphate. The similarity of the structure between the ligand and the PIL would encourage entrainment of the catalyst into the IL solvent. The phosphonium moiety on the salen ligand would be attracted to the long alkyl chains on the PIL cation through intermolecular dispersion forces. This would produce a recyclable system, encouraging the reuse of the catalyst and reducing the amount of solvent waste associated with a reaction conducted in VOCs. [PIL][PF$_6$] for the aziridination reactions was synthesized *via* a metathesis from the chloride analogue, which was obtained from CYTEC, using hexafluoridophosphoric acid. The resulting [PIL][PF$_6$] ionic liquid had a melting point of 49˚C, with a reported melting point of 50˚C[51] and was therefore a solid at room temperature. This is a limitation because an ideal solvent should be liquid at room temperature.

The ability to perform aziridinations in both [PIL][PF$_6$] and [PIL][Cl] was investigated. The aziridination in the former IL had to be performed at 50˚C, however this is a downfall because elevated temperatures have been shown to decrease the enantioselectively of a reaction.[25] This is because with increasing temperature, the separation between the activation energies of the two enantiomers decreases, thus making the unwanted enantiomer more feasible. It was discovered if styrene was added prior to the nitrene source, PhINTs, the mixture remained liquid at room temperature, and the nitrene source could then be added. This technique is much more ideal than increasing the reaction temperature because this should theoretically increase the enantiomeric excess obtained. The limitation to this method is the high viscosity of the ionic liquid-styrene solution which could result in low yields of aziridine due to a reduced probability

of collisions between reactants and therefore a reduced probability to achieve correct collision symmetry. This led to the investigation of tetradecyl(trihexyl)phosphonium chloride as a solvent because it is a RTIL and possesses the desired cation, therefore will have similar interactions to the hexafluoridophosphate version with copper complexes, **5a** and **5b**.

Extracting the potential aziridine product from both phosphonium based ionic liquids (PILs), tetradecyl(trihexyl)phosphonium chloride and hexafluoridophosphate, was difficult due to solubility issues. Although the copper complexes, **5a**,**b**, are soluble in only a small range of solvents, the PILs are extremely soluble in a wide range of solvents. The initial solvent chosen for extraction was diethyl ether because it was previously used to extract aziridines from 1-butyl-3-methylimidazolium hexafluoridophosphate, [bmim][PF$_6$], leaving the ionic liquid layer and catalyst behind.[41] Unfortunately although the catalyst was not soluble in diethyl ether, the PILs were soluble, making this solvent impractical to use for extraction. The solubility of the PILs was then investigated to find a solvent in which 2-phenyl-N-tosylaziridine was soluble in but left the ionic liquid and catalyst layer undissolved. The PILs were found to be soluble in toluene, ethyl acetate, ethanol, dichloromethane, chloroform, and 1-butanol. It was therefore necessary to consider other ionic liquids as potential solvents for the aziridinations due to the solubility issues of the PILs.

[Bmim][PF$_6$] was chosen as the alternative ionic liquid to perform the aziridinations due to its recognition within the literature as a useful solvent.[18] The Cu (II) saldach phosphonium complex is soluble in [bmim][PF$_6$] and the aziridine product can be

extracted with diethyl ether. This diminishes the amount of necessary VOCs because a minimal amount is required for extraction. 3 mL of previously synthesized [bmim][PF$_6$][52] was dried under vacuum before addition of the catalyst and similar conditions to the acetonitrile reactions were applied. However the reaction had to be stirred overnight in order for PhINTs to dissolve. After extraction with diethyl ether, decantation and collection of the organic layer, it was passed through a silica-gel plug and a small amount of brown-orange solid remained upon evaporation. There was no aziridine product observed in the ^{13}C and ^{1}H NMR. These poor results are similar to those found in previous aziridinations with the methylimidizolium based Cu(II) catalyst.[41] This could be attributed to the high viscosity of [bmim][PF$_6$] compared to acetonitrile, being 450 mPa•s[7] and 0.346 mPa•s[53] at 25˚C, respectively. Although heating would result in a lower viscosity, and potentially yield the desired product, this would defeat the purpose of the experiment, which is to obtain enantiomerically pure aziridine from styrene. Heating would be unfavorable because the transition state of the undesired enantiomer would become more feasible, resulting in a poor enantiomeric excess. The reaction can also be reacted for a longer time to encourage the chance of correct collisions, however this is not efficient and thus an alternative solvent must be chosen. One possible variation, which shows a significantly lower viscosity relative to [bmim][PF$_6$], is dicynamide anion, $N(CN)_2^-$ or NTf_2, based ILs. For example, the RTIL 1-ethyl- 3-methylimidazolium dicyanamide is reported to have a viscosity of 21mPa•s.[54]

2.3 Polarimetry

The chirality of the asymmetric ligand, **4b**, was investigated using a polarimeter and associated Logger Pro software. A dichloromethane blank was used to generate a reference sinusoidal curve using 589nm monochromatic light. A solution of known concentration was prepared by dissolving 0.674g of the ligand **4b** in 10.00mL of dichloromethane. The solution's sinusoidal curve was tested against the blank curve and there was a 1.95° horizontal shift between the values at which the maximum occurs (shown in Figure 24). This horizontal shift between the blank and sample solution indicates the presence of an optically active species, **4b**. From this angle, the specific rotation was calculated, using equation 2, to be -67.4°cm^{3}g^{-1}dm^{-1}. This specific rotation shows there is chirality within the ligand, **4b**, which gives the potential to prepare chiral aziridine products using the copper (II) complex, **5b**. The difference in amplitude of the sinusoidal curves arises because the ligand absorbs wavelengths in the violet region[55], whereas the blank dichloromethane does not absorb in this region. Since the ligand absorbs light, there is less intense light reaching the detector, resulting in a smaller amplitude.
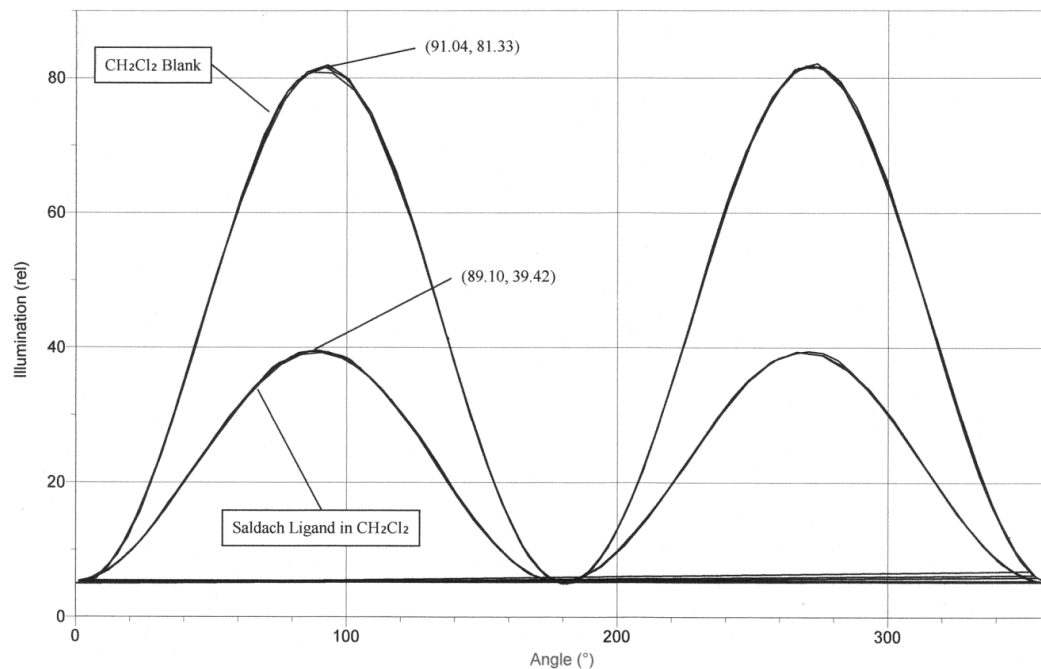
Figure 24. The Vernier Logger Pro graph corresponding to the polarimeter measurements of the IL-saldach phosphonium ligand.

The specific rotation of the asymmetric copper complex is difficult to measure by polarimetry due to the nature of the solid and the technique used. The complex forms a dark purple solution that absorbs the monochromatic light of the polarimeter. Since the light cannot reach the detector, the rotation of its plane cannot be measured.

3.0 Conclusion

The racemic and R,R- *tert*-butyl saldach phosphonium Cu(II) complexes, **5a** and **5b**, respectively were successfully synthesized and characterized. A series of aziridinations were conducted in acetonitrile and different ionic liquids using N-tosylphenyliodinane as the nitrene source. Both complexes, **5a** and **5b** were catalytically active in the aziridination of styrene in acetonitrile, affording a 84% and 88% yield, respectively. The application of the catalyst system to an ionic liquid solvent proved to be problematic with the phosphonium based ionic liquids, tetradecyl(trihexyl)phosphonium chloride and hexafluoridophosphate. This was because the PILs are soluble in a wide range of solvents, making a suitable extracting solvent difficult to find. 1-butyl-3-methyl-imidizolium hexafluoridophosphate was also used as a solvent for the reaction, however no aziridine product was obtained. This is possibly due to the high viscosity of the IL compared to acetonitrile. Ligand **4b** was confirmed to be optically active as determined using polarimetry, resulting in a specific rotation of -67.4°cm^{3}g^{-1}dm^{-1}. The application of the chiral catalyst, **4b**, in a successful recyclable system still requires further investigation.

4.0 Future Work

The application of the copper complex **4b** requires further investigation regarding both a suitable ionic liquid (IL) solvent for recycling experiments and additional olefin substrates to assess its universality. A relatively non-viscous ionic liquid that does not require an increase in temperature and can produce high yields while retaining good enatiomeric excess is the ultimate goal of this research. One possible IL reported, 1-ethyl- 3-methylimidazolium dicyanamide, should be investigated as a potential aziridination solvent.[54] This would ideally entrain the copper complex, allowing for recycling experiments.

An alternative nitrene source to n-tosyliminophenyliodinane should also be considered. The tosyl group on the nitrogen requires harsh conditions to remove, usually destroying the aziridine ring. A substituent that can be removed in mild conditions would allow the unsubstituted aziridine to be synthesized more easily.

The application of the asymmetric copper phosphonium complex, **5b**, to other olefins should be investigated and eventually applied to di- and tri- substituted alkenes as well. Some commonly reported alkenes, such as 3-phenylpropene, and *trans*-stilbene would be potential substrates due to their moderate to high yielding reactions described in the literature.[56]

One of the future goals is to complex the *tert*-butyl phosphonium based ligand to Mn(III), which would mimic Jacoben's catalyst[17]. The complex would then be entrained in a suitable ionic liquid for epoxidations and recyclability of the system would be tested.

5.0 Experimental

5.1 General Procedures

All glassware used in the experiments was washed with soap and water and rinsed with acetone before being placed in the oven to dry at 120˚C. The round bottom flasks and condenser used in each reaction were then put under vacuum to cool and were kept under a nitrogen atmosphere for all synthesis reactions using a Schlenk line. All aziridinations were completed using the same technique; only the aziridination with the tetradecyl(trihexyl)phosphonium hexafluoridophosphate was conducted with a condenser because it required heating due to the fact that the melting point of the IL is above room temperature.

Transfer of tri-n-butylphosphine, purchased from Sigma-Aldrich, into a round bottom flask was performed in an mBraun Labmaster SP inert atmosphere glovebox. Toluene used in this reaction was purified by Grubbs'-type solvent purification system manufactured by Innovative Technology. Purification grade acetonitrile was purchased from Sigma-Aldrich and was purified using a Pure Solv PS-400-4 System prior to use. Hydrochloric acid, ethyl ether, absolute ethanol, dichloromethane, n-hexane and methanol were purchased from Sigma-Aldrich and used without further purification. The ionic liquid, [bmim][PF$_6$], was previously synthesized according to literature and stored appropriately, and dried *in vacuo* before use.[52] Tetradecyl(trihexyl)phosphonium chloride was donated by CYTEC and dried *in vacuo* before use as a solvent and in an anion exchange reaction to the hexafluoridophosphate anion.

Sodium bicarbonate, sodium chloride, and sodium bisulfate solutions used in extraction of 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde, **1**, were used as purchased from Sigma Aldrich and were prepared in deionized water. 3-*tert*-Butyl-2-hydroxybenzaldehyde, paraformaldehyde, tetra-butylammonium iodide, hexafluoridophosphoric acid (65% w/w), racemic-*trans*-1,2-diaminocyclohexane, (1*R*,2*R*)-(−)-1,2-diaminocyclohexane (99% ee), *para*-toluenesulfonamide, potassium hydroxide, diacetoxyiodobenzene and styrene were all purchased from Sigma-Aldrich. All NMR solvents, DMSO-d[6], CDCl$_3$, and (CD$_3$)$_2$CO, were purchased from Cambridge Isotope Laboratories. Copper (II) acetate monohydrate was purchased from Fischer.

Dalhousie University Facilities, Nuclear Magnetic Resonance Research Resource (NMR[3]), were used to analyze samples by nuclear magnetic spectroscopy (NMR). A Bruker AV 300 MHz Spectrometer and a Bruker AV 500 MHz Spectrometer were used to collect all data and spectra were processed using the software program Topspin 1.3. All chemical shifts were reported in parts per million (ppm). ^{13}C and ^{1}H NMR were reported with respect to an internal standard, tetramethylsilane (TMS). ^{31}P NMR was reported relative to the external standard H$_3$PO$_4$.

All polarimetry experiments were performed on the Vernier "Chemical Polarimeter" using Vernier's Logger Pro software 3.8.5 to analyze the data. A cosine squared regression was applied to the 360 degree range of the signal profile to determine the angle of rotation of the polarized 589 nm LED source. Melting points were determined using an Electrothermal Mel-Temp 3.0 apparatus. Infrared spectra were recorded in KBr pellets using a Bruker Vertex 2.2 Infrared Spectrometer and were

44

processed using OPUS software. The electrospray ionization mass spectrometry (ESI-MS) was performed at the Center for Environmental Analysis and Remediation at Saint Mary's University. ESI-MS was performed using an Agilent 1100 LC/MSD Trap. All of the high resolution ESI-MS were performed using a Bruker microTOF Focus Mass Spectrometer at the Maritime Mass Spectrometry Laboratory at Dalhousie University.

Crystallographic data was collected on a Siemens/Bruker APEX II charged-coupled device (CCD) diffractometer with an Oxford KRYO-FLEX cooling device. The instrument was equipped with graphite-monochromated Mo Kα radiation (λ =0.71073 Å), with MonoCap X-ray source optics. A hemisphere of data was collected using ω scans, with frame exposures of 45 seconds and 0.5˚ frame widths. Data collection and initial indexing and cell refinement were handled using APEX II software.[57] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.[57] The data had been corrected for absorption using the SADABS program.[57] The structures were solved using direct methods and difference Fourier techniques. Structure solution, refinement, and creation of publication materials were performed using SHELXL.[58] All hydrogen atom positions were idealized using a riding model. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. The figure was made using ORTEP-3 for Windows.[59]

5.2 Synthesis of the IL-saldach Phosphonium Copper Complex

Preparation of 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde, **1**
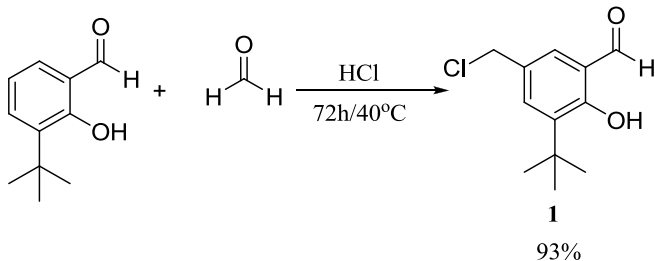
Paraformaldehyde (0.240g, 8.0mmol) was added to concentrated hydrochloric acid (7.1mL) and the resulting solution stirred for 10 minutes. Tetrabutylammonium iodide (0.145g) was added and dissolved in the solution. 3-*tert*-butyl-2-hydroxybenzaldehyde (0.714g, 4.0mmol) was added dropwise over a period of 25 minutes. The resulting solution stirred at 40˚C for 72 hours. A dark orange solution resulted in a red oil. The aqueous solution was extracted with ether (5x8mL). The organic layer was combined and washed with sodium bicarbonate (2x5mL) and brine (2x5mL). The resulting dark red-brown solution was washed with sodium bisulfite (3x5mL), which resulted in a pale yellow solution, which was dried with anhydrous magnesium sulphate. The ether was removed, affording a beige solid (0.845g, 93%). m.p. 58˚C ^{1}H NMR (300 MHz, CDCl$_3$): δ 11.86 (s, 1H), 9.87 (s, 1H), 7.53 (d, ^{2}J=2.27, 1H), 7.44 (d, ^{2}J=2.27, 1H), 4.58 (s, 2H), 1.43 (s, 9H) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 196.75, 161.31, 139.20, 134.56, 131.76, 128.30, 120.36, 45.90, 34.97, 29.12 ppm. IR (KBr): 2874, 1657, 1580, 1484, 1375, 1284, 1189, 1110, 942, 905, 798 cm^{-1}.

Preparation of tributyl(3-*tert*-butyl-5-formyl-4-hydroxybenzyl)phosphonium chloride, **2**.

2
23%
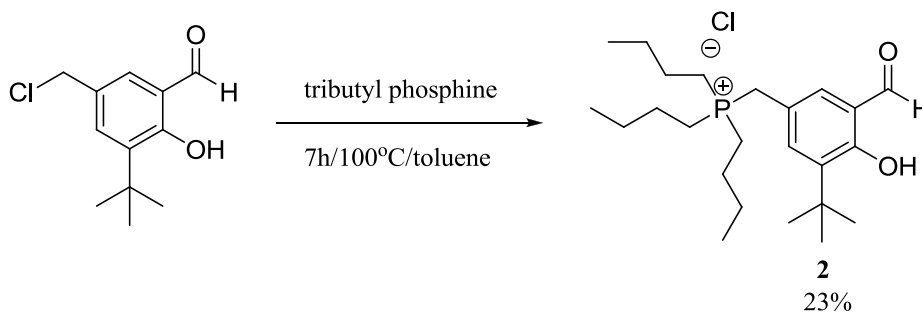
Tri-n-butylphosphine (1.06g, 5.25mmol) was dissolved in 35mL of dry toluene, under a nitrogen atmosphere in a glovebox. A solution of compound **1** (0.895g, 5.26mmol) in dry toluene (15mL) was added dropwise *via* syringe, turning the solution light yellow. The resulting solution was refluxed at 100˚C for 7 hours. Upon cooling, a white solid appeared to have precipitated out, however it turned to a green-yellow oily substance when exposed to air. The toluene was evaporated, leaving a green-yellow solid (1.8891g, 84%). m.p. 112-116˚C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.90 (s, 1H), 9.87 (s, 1H), 7.46 (t, ^{1}J=2.30Hz, 1H), 7.40 (t, J=1.97Hz, 1H), 3.67 (d, ^{2}J$_{H-P}$ =13.80Hz, 2H), 2.17-2.01 (m, 6H), 1.51-1.41 (m, 2H), 1.39 (s, 18H) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 197.21, 161.18, 140.26, 135.14, 133.13, 121.03, 118.27, 118.16, 35.03, 29.09, 26.22 (d, ^{1}J$_{C-P}$ =46.26Hz), 24.01 (d, ^{2}J$_{C-P}$= 15.67Hz), 23.37 (d, ^{3}J$_{C-P}$=4.84Hz), 18.55 (d, ^{1}J$_{C-P}$=47. 09Hz), 13.18 ppm. ^{31}P{^{1}H} (121 MHz, CDCl$_3$) δ 31.55 (s), -144.03 (sep, 713 Hz) ppm. ESI-MS: Positive mode: m/z 393.7 ([C$_{24}$H$_{42}$O$_2$P]$^+$).   HR ESI MS: Positive mode: m/z 393.2902 ([C$_{24}$H$_{42}$F$_6$O$_2$P]$^+$) amu. Calculated to be 393.2917 amu.

Preparation of (3-tert-butyl-5-formyl-4-hydroxybenzyl)phosphonium hexaflurophosphate, **3**.

3
84%
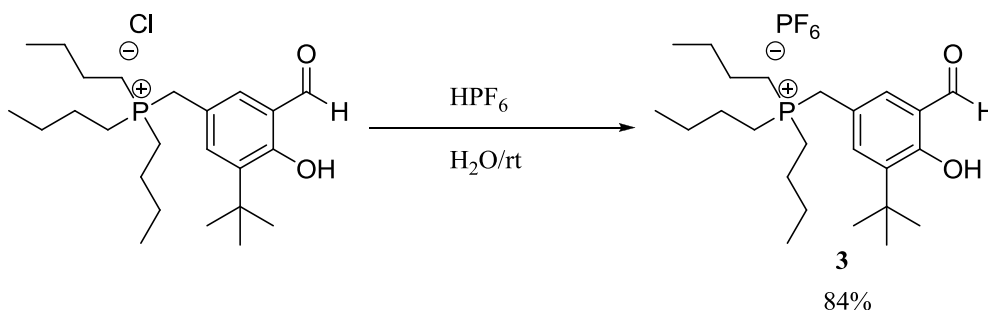
The crude tributyl(3-tert-butyl-5-formyl-4-hydroxybenzyl)phosphonium chloride, **2** (1.8891g, 3.5mmol) was dissolved in water (75mL), which proved to be difficult due to the hygroscopic nature of compound **2** because the chloride impurities precipitated out with the hexafluoriodophosphate product. Once **2** was dissolved in water, HPF$_6$ (0.67g, 4.56mmol) was added dropwise to the solution. A white precipitate formed immediately, but residual green solid remained. This was allowed to stir at room temperature over night. The green/white solid was isolated and dried *in vacuo* before grinding it with a mortar and pestle. This was re-suspended in water with an additional 1.0mL of HPF$_6$ and stirred for 24 hours. The white precipitate was isolated by filtration and washed with water (3x10mL), which afforded the white solid (1.350g, 71.4%). m.p. 152-153°C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 11.84 (s, 1H), 9.90 (s, 1H), 7.81 (t, J=2.30Hz, 1H), 7.48 (t, ^{2}J=1.97Hz, 1H), 4.46 (d, ^{1}J$_{P-H}$ =14.94Hz, 2H), 2.47-2.30 (m, 6H), 1.50-1.34 (m, 2H), 1.37 (s, 18H) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ 197.21, 161.18, 139.90, 135.34, 133.79, 121.01, 119.43, 119.31, 118.16, 35.10, 29.31, 24.18 (d, ^{1}J$_{C-P}$= 15.22Hz), 23.93

($^2J_{C-P}$= 5.01Hz), 19.21, 18.59, 13.54 ppm. ^{31}P{^{1}H} (121 MHz, CDCl$_3$) δ 31.55 (s), -

144.03 (sep, $^1J_{P-F}$= 713 Hz) ppm.   IR (KBr): 2962, 2876, 2747, 1655, 1618, 1466, 1442,

1414, 1330, 1238, 1099, 844, 577 cm^{-1}.   ESI-MS: Positive mode: m/z 393.3

([C$_{24}$H$_{42}$O$_2$P]$^+$) Negative mode: m/z 144.6 (100%, [PF$_6$]$^-$) amu.   HR ESI MS: Positive

mode: m/z 393.2909 ([C$_{24}$H$_{42}$F$_6$O$_2$P]$^+$) amu.   Calculated to be 393.2917 amu.   See

Appendix 7.0 for Crystallographic data.

Preparation of racemic 5,5'-cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methane-1-

yl-1-ylidene)bis(3-tert-butyl-4-hydroxy-5,1-

phenylene)bis(methylene)bis(tributylphosphonium),   racemic   saldach   phosphonium

ligand, **4a**.
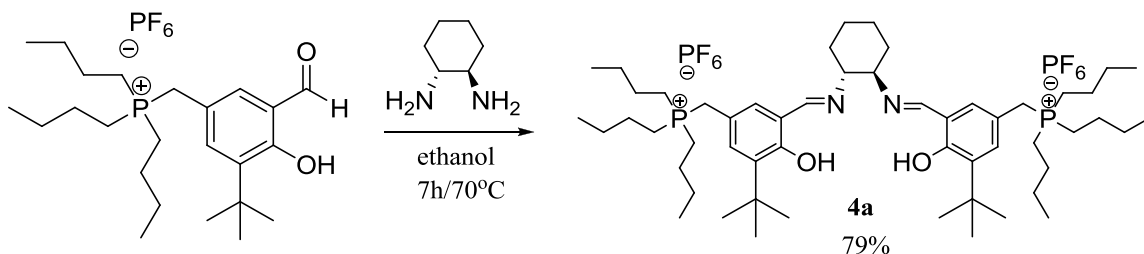
(3-tert-butyl-5-formyl-4-hydroxybenzyl)phosphonium   hexaflurophosphate,   **3**   (0.62g,

1.15mmol) was dissolved in absolute ethanol (40mL) and heated to 70˚C to ensure

complete dissolution.   1,2-diaminocyclohexane (0.066g, 0.575mmol) was first dissolved

in absolute ethanol (5mL) and added dropwise to the solution, which immediately turned

yellow.   The mixture was refluxed for 7 hours at 70˚C.   The ethanol was evaporated and

the crude solid was run through a silica column with 5% methanol in dichloromethane to

obtain the final product (0.5252g, 79%). m.p. 125-128˚C. ^{1}H (500 MHz, CDCl$_3$): δ 14.19

(s, 1H), 8.34 (s, 1H), 7.11 (s, 1H), 7.04 (s, 1H), 3.63-3.36 (m, 12H), 2.12-1.96 (m, 32H) ppm. ^{13}C {^1H} (126 MHz, CDCl$_3$): δ 164.79, 161.31, 160.88, 139.12, 131.08, 130.3712, 119.16, 116.02, 115.95, 69.99, 34.88, 33.38, 29.21, 24.44 (d, $^1J_{C-P}$=37.98Hz), 23.85 (d, $^2J_{C-P}$=15Hz), 23.24 (d, $^3J_{C-P}$=4.79Hz), 18.14 (d, $^1J_{C-P}$=47. 95Hz), 13.18 ppm. ^{31}P{^1H} (202 MHz, CDCl$_3$): δ 31.28 (s), -144.11 (sep, $^1J_{P-F}$= 713 Hz) ppm. IR (KBr): 3433, 2962, 2874, 2363, 1633, 1467, 1443, 839, 710, 557. ESI MS: Positive mode: m/z 1009.8 ([C$_{54}$H$_{94}$F$_6$N$_2$O$_2$P$_3$]$^+$) Negative mode: m/z 144.6 (100%, [PF$_6$]$^-$) amu.   HR ESI MS: Positive mode: m/z 1009.6444 ([C$_{54}$H$_{94}$F$_6$N$_2$O$_2$P$_3$]$^+$) amu. Calculated to be 1009.6427 amu.

Preparation of racemic 5,5'-cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(3-tert-butyl-4-hydroxy-5,1-phenylene)bis(methylene)bis(tributylphosphonium) bis(hexafluoridophosphate) copper (II) complex, racemic saldach phosphonium copper complex, **5a**.
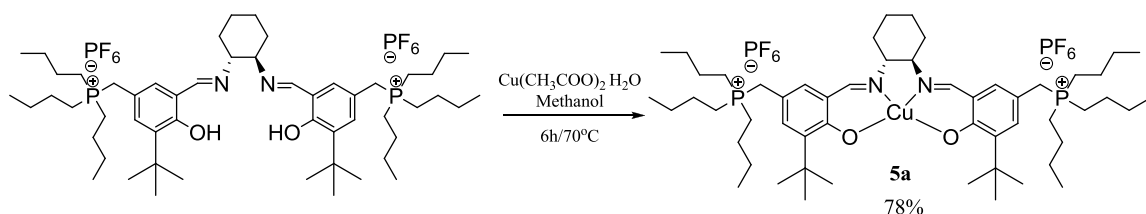
Compound **4a** (0.1962g, 0.17mmol) was dissolved in methanol (20mL). Cupric acetate monohydrate (0.037g, 0.19mmol) was also dissolved in methanol (20mL), with slight heating. The latter solution was added dropwise to the compound **4a** in methanol solution. When all of the cupric acetate monohydrate was added, the solution became

purple. The resulting solution was refluxed at 70˚C for 5.5 hours. Upon completion of the reaction, the solution was cooled and concentrated to 20mL. This solution was placed in the freezer overnight to afford a precipitate, which was isolated by filtration and washed with ice cold methanol (3x5mL). A purple solid product remained (0.154g, 78%). m.p. decomposed at 289˚C. IR (KBr): 2960, 2873, 1627, 1537, 1466, 1439, 1422, 1385, 1351, 1320, 1245, 1206, 1168, 1098, 839, 558 cm^{-1}. ESI MS: Positive mode: m/z 1071.6 ([$C_{54}H_{92}CuF_6N_2O_2P_3$]$^+$) Negative mode: m/z 144.6 (100%, [PF_6]$^-$) amu. HR-ESI MS: Positive mode: 462.7966 ([$C_{54}H_{92}CuN_2O_2P_2$]$^{2+}$) amu. Calculated to be 462.7939 amu.

**Synthesis of the IL-saldach R,R-Phosphonium Copper Complex**

Preparation of R,R-5,5'-cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(3-tert-butyl-4-hydroxy-5,1-phenylene)bis(methylene)bis(tributylphosphonium), racemic saldach phosphonium ligand, Compound **4b**.
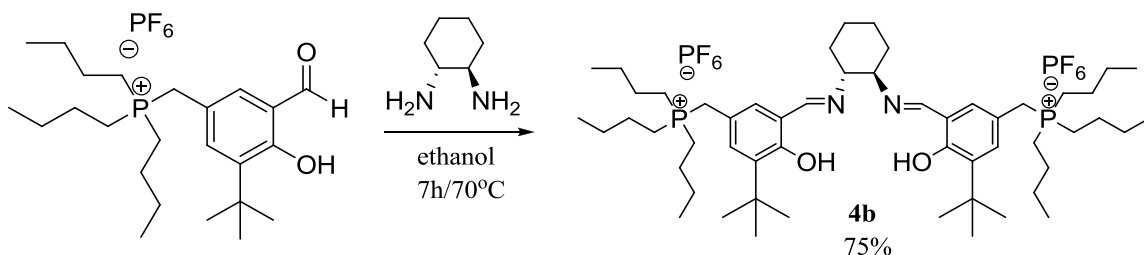
The previously synthesized (3-tert-butyl-5-formyl-4-hydroxybenzyl)phosphonium hexaflurophosphate, **3** (0.62g, 1.15mmol) was dissolved in absolute ethanol (40mL) with heating at 70˚C. R,R-diaminocyclohexane (0.066g, 0.575mmol) was first dissolved in absolute ethanol (5mL) was added dropwise to the solution of **3**. This mixture was

refluxed for 7 hours at 70˚C and stirred over night at room temperature. The resulting

precipitate was filtered, yielding white solid (0.4978g, 75%).   m.p. 128-130˚C. ^{1}H

(500MHz, CDCl$_3$): δ 14.19 (s, 2H), 8.34 (s, 2H), 7.15 (t, ^{1}J=2.27Hz, 2H), 7.02 (t,

^{1}J=1.81Hz, 2H), 3.74-3.36 (m, 12H), 2.15-1.85 (m, 18H), 1.68-1.23 (m, 60H), 0.85 (t,

^{1}J=7.0Hz, 18H) ppm. ^{13}C{^{1}H} (126 MHz, CDCl$_3$): δ 164.79, 161.31, 160.88, 139.12,

131.08, 130.3712, 119.16, 116.02, 115.95, 69.99, 34.88, 33.38, 29.21, 24.44 (d, ^{1}J$_{C-}$
$_P$=37.98Hz), 23.85 (d, ^{2}J$_{C-P}$=15Hz), 23.24 (d, ^{3}J$_{C-P}$=4.79Hz), 18.14 (d, ^{1}J$_{C-P}$=47. 95Hz),

13.18 ppm. ^{31}P{^{1}H} (202 MHz, CDCl$_3$): δ 31.17 (s), -144.11 (sep, ^{1}J$_{P-F}$= 713 Hz). IR

(KBr): 2962, 2937, 2874, 1631, 1594, 1467, 1444, 1387, 1276, 1100, 909, 839. ESI MS:

Positive mode: m/z 1009.8 ([C$_{54}$H$_{94}$F$_6$N$_2$O$_2$P$_3$]$^+$) Negative mode: m/z 144.6 (100%, [PF$_6$]$^-$

) amu. HR-ESI MS: Positive mode: m/z 432.3368 ([C$_{54}$H$_{94}$N$_2$O$_2$P$_2$]$^{2+}$) amu. Calculated

to be 432.3390 amu.

Preparation of R,R-5,5'-cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-

ylidene)bis(3-tert-butyl-4-hydroxy-5,1-

phenylene)bis(methylene)bis(tributylphosphonium) bis(hexafluoridophosphate) copper

(II) complex, R,R- saldach phosphonium copper complex, **5b**.
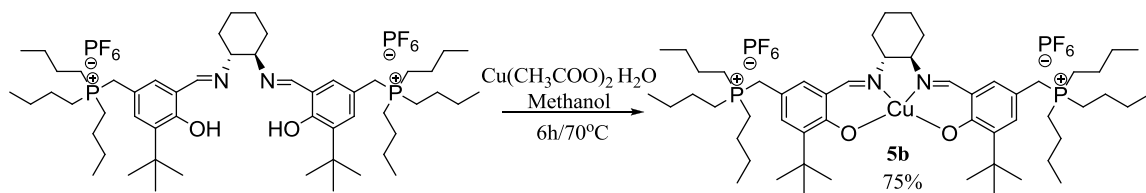
Compound **4b** (0.1962g, 0.17mmol) was dissolved in methanol (30mL). Cupric acetate

monohydrate (0.037g, 0.19mmol) was also dissolved in methanol (10mL), which

required slight heating. The latter was added dropwise to the compound **4b** in methanol solution. When all of the cupric acetate monohydrate was added, the solution became purple. The solution was refluxed at 70˚C for 6 hours, this then was removed from heat and cooled to room temperature before placing in the freezer. Purple precipitate was isolated by filtration, and was washed with 3x5mL of ice cold methanol. The methanol filtrate was concentrated to 15mL and left in the freezer overnight but yielded no additional product (0.1557g, 75%). m.p. decomposed at 297˚C. IR (KBr): 2961, 2873, 1626, 1538, 1465, 1422, 1386, 1351, 1320, 839, cm^{-1}. ESI MS: Positive mode: m/z 1071.3 ($[C_{54}H_{92}CuF_6N_2O_2P_3]^+$) Negative mode: m/z 144.6 (100%, $[PF_6]^-$) amu. HR ESI MS: Positive mode: 462.7939 ($[C_{54}H_{92}CuN_2O_2P_2]^{2+}$) amu. Calculated to be 462.7939 amu.

5.3 Aziridinations

Preparation of N-tosyliminophenyliodinane
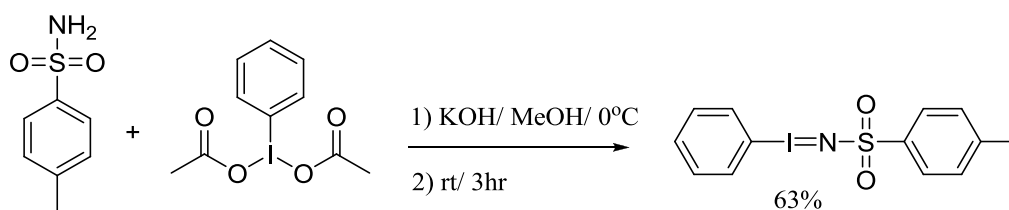
para-toluenesulfonamide (1.71g, 10mmol) and potassium hydroxide (1.43g, 25mmol) were dissolved in methanol (40mL) and the solution was placed in a rock salt-ice bath at 0˚C. Diacetoxyiodobenzene (3.20 g, 10mmol) was added slowly in portions over 15 minutes to ensure the temperature did not rise above 5˚C. The solution which was initially cloudy, became a clear yellow and was then stirred at room temperature for 3

hours. The solution was poured into 100mL of ice cold water, which was left still at room temperature overnight. The precipitate was isolated by filtration and washed with ether, leaving a pale yellow solid (2.33 g, 62.4%). m.p. decomposed at 103˚C. ^{1}H NMR (300 MHz, DMSO-d^6) δ: 7.76-7.04 (m, 9H), 2.27 (s, 3H) ppm.

Aziridination of Styrene in Acetonitrile with the Racemic/Asymmetric IL-saldach Phosphonium Copper Complex.
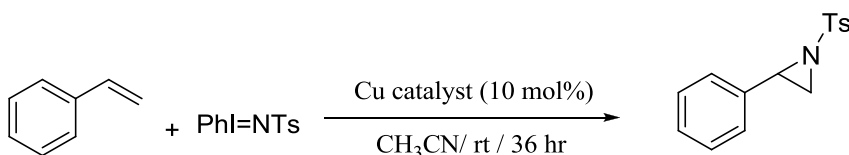
  The racemic/asymmetric copper catalyst (0.1216g, 0.10mmol) Compound **5a/b** was dissolved in acetonitrile (3mL). Styrene (0.55mL, 5.0mmol) was added against a positive pressure of nitrogen. PhINTs (0.3728g, 1mmol) was then added in one portion and it did not dissolve right away. The mixture was stirred for 36 hours at room temperature. The acetonitrile was evaporated *in vacuo* to leave a wet, brown solid, which was extracted with ether (4x8mL), allowing each portion to stir for 15 minutes. The combined ether extracts were concentrated *in vacuo* to afford a white solid (**5a:** 0.2284g, 83.6%, **5b:** 0.239g, 87.5%). m.p. 87-89˚C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.88 (d, J=8.33 Hz, 2H), 7.34-7.19 (m, 7H), 3.78 (dd, J=4.48, 7.15 Hz, 1H), 2.99 (d, J=7.21 Hz, 1H), 2.43 (s, 3H), 2.39 (d, J=4.46 Hz, 1H) ppm. ^{13}C{^{1}H} (75 MHz, CDCl$_3$): δ 144.65, 135.08, 129.77, 128.58, 128.31, 127.96, 126.58, 41.06, 35.93, 21.64 ppm. All spectral data agree with those found in the literature.[56]

Aziridination of Styrene with the racemic Cu-catalyst in tetradecyl(trihexyl)phosphonium hexafluoridophosphate/chloride
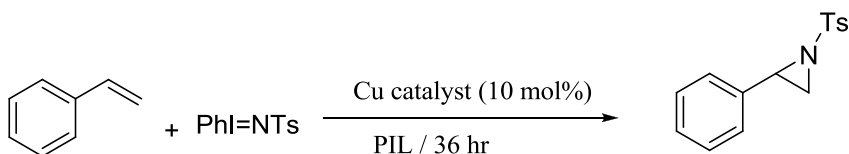
Both procedures involving the tetradecyl(trihexyl)phosphonium hexafluoridophosphate and chloride were similar to those performed in acetonitrile except that the hexafluoridophosphate salt had to be heated to 50°C because it is not a RTIL. The racemic copper catalyst (0.1216g, 0.10mmol) Compound **5a/b**, was dissolved in the ionic liquid. Styrene (0.55mL, 5.0mmol) was added under a positive pressure of nitrogen. PhINTs (0.3728g, 1mmol) was then added in one portion. It did not dissolve right away, but was dissolved upon stirring overnight. It was stirred for a total of 36 hours at room temperature. Diethyl ether was used in an attempt to extract the product, but the PILs are soluble in ether. Other solvents were tested but no suitable solvent was found for these systems.

Aziridination of Styrene in [bmim][PF$_6$] with the R,R- Saldach Phosphonium Copper Complex.
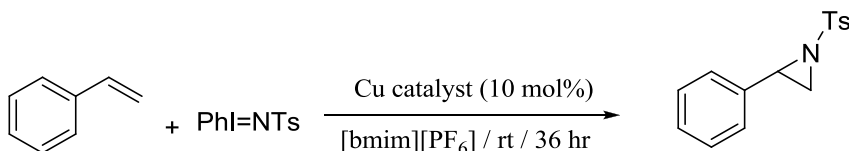
3mL of [bmim][PF$_6$] that was previously synthesized according to literature[52] was dried under vacuum in a 50mL 2 neck round bottom for 3 hours while stirring. The asymmetric copper catalyst (0.1216g, 0.10mmol) was added against a positive pressure of nitrogen and dissolved in the ionic liquid. PhINTs (0.3728g, 1mmol) was then added in the same manner and styrene (0.55mL, 5.0mmol) was added *via* a syringe. This mixture was stirred for 36 hours and then extracted with 4x10mL of ethyl ether. The combined ether portions were run through a silica plug and evaporated. This afforded a dark orange, sticky solid. No product was observed by proton NMR.

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7.0 Appendix: X-ray Crystallographic Data

Table 2. Crystal data and structure refinement for Compound **2**.

Identification code	CP064_0m
Empirical formula	C24.50 H41.25 Cl1.50 F6 O2 P2
Formula weight	596.94
Temperature	197(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 14.567(3) Å $\quad$ α= 90°.
	b = 23.664(5) Å $\quad$ β= 92.011(2)°.
	c = 17.704(4) Å $\quad$ γ = 90°.
Volume	6099(2) Å^3
Z	8
Density (calculated)	1.300 Mg/m^3
Absorption coefficient	0.330 mm^{-1}
F(000)	2510
Crystal size	0.42 x 0.22 x 0.20 mm^3
Theta range for data collection	1.72 to 24.90°.
Index ranges	-17<=h<=17, -22<=k<=28, -20<=l<=14
Reflections collected	28667
Independent reflections	17080 [R(int) = 0.1036]
Completeness to theta = 24.90°	99.1 %
Absorption correction	Multiscan
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	17080 / 1055 / 1325
Goodness-of-fit on F^2	0.940
Final R indices [I>2sigma(I)]	R1 = 0.0823, wR2 = 0.1713
R indices (all data)	R1 = 0.2558, wR2 = 0.2593
Absolute structure parameter	0.39(13)
Largest diff. peak and hole	0.320 and -0.301 e.$\mathring{A}^{-3}$

Table 3. Bond lengths [Å] and angles [°] for Compound **2**.

P(13)-C(65)	1.781(12)	F(12)-P(2)-F(11)	179.4(6)
P(13)-C(57)	1.789(12)	F(10)-P(2)-F(11)	91.5(6)
P(13)-C(61)	1.792(12)	F(7)-P(2)-F(11)	89.0(6)
P(13)-C(56)	1.808(12)	F(9)-P(2)-F(11)	91.1(6)
P(3)-F(14)	1.511(10)	F(1)-P(1)-F(6)	89.9(5)
P(3)-F(16)	1.543(9)	F(1)-P(1)-F(4)	90.3(5)
P(3)-F(18)	1.546(10)	F(6)-P(1)-F(4)	90.7(5)
P(3)-F(17)	1.552(9)	F(1)-P(1)-F(3)	178.7(6)
P(3)-F(13)	1.582(10)	F(6)-P(1)-F(3)	90.8(5)
P(3)-F(15)	1.591(10)	F(4)-P(1)-F(3)	90.7(5)
P(12)-C(33)	1.741(12)	F(1)-P(1)-F(2)	90.2(5)
P(12)-C(37)	1.793(13)	F(6)-P(1)-F(2)	90.1(5)
P(12)-C(41)	1.807(14)	F(4)-P(1)-F(2)	179.0(5)
P(12)-C(32)	1.841(12)	F(3)-P(1)-F(2)	88.7(5)
P(2)-F(8)	1.542(10)	F(1)-P(1)-F(5)	91.6(5)
P(2)-F(12)	1.546(9)	F(6)-P(1)-F(5)	177.5(6)
P(2)-F(10)	1.547(9)	F(4)-P(1)-F(5)	91.2(5)
P(2)-F(7)	1.569(9)	F(3)-P(1)-F(5)	87.6(5)
P(2)-F(9)	1.589(9)	F(2)-P(1)-F(5)	87.9(5)
P(2)-F(11)	1.593(9)	C(79)-P(14)-C(88)	113.1(6)
P(1)-F(1)	1.560(8)	C(79)-P(14)-C(80)	114.3(7)
P(1)-F(6)	1.579(9)	C(88)-P(14)-C(80)	107.7(7)
P(1)-F(4)	1.587(9)	C(79)-P(14)-C(84)	107.7(6)
P(1)-F(3)	1.588(8)	C(88)-P(14)-C(84)	106.5(7)

P(1)-F(2)	1.598(9)	C(80)-P(14)-C(84)	107.2(7)
P(1)-F(5)	1.597(8)	C(17)-P(11)-C(21)	107.5(11)
P(14)-C(79)	1.763(13)	C(17)-P(11)-C(13)	113.1(10)
P(14)-C(88)	1.766(12)	C(21)-P(11)-C(13)	107.3(11)
P(14)-C(80)	1.803(13)	C(17)-P(11)-C(12)	111.3(7)
P(14)-C(84)	1.824(14)	C(21)-P(11)-C(12)	109.7(8)
P(11)-C(17)	1.716(15)	C(13)-P(11)-C(12)	107.8(8)
P(11)-C(21)	1.763(19)	F(22)-P(4)-F(21)	93.1(9)
P(11)-C(13)	1.778(18)	F(22)-P(4)-F(23)	92.5(8)
P(11)-C(12)	1.819(13)	F(21)-P(4)-F(23)	174.1(8)
P(4)-F(22)	1.511(11)	F(22)-P(4)-F(20)	90.3(6)
P(4)-F(21)	1.512(10)	F(21)-P(4)-F(20)	90.0(6)
P(4)-F(23)	1.548(12)	F(23)-P(4)-F(20)	88.1(7)
P(4)-F(20)	1.553(10)	F(22)-P(4)-F(19)	91.1(7)
P(4)-F(19)	1.549(10)	F(21)-P(4)-F(19)	91.1(7)
P(4)-F(24)	1.615(9)	F(23)-P(4)-F(19)	90.7(7)
Cl(4)-C(151)	1.729(15)	F(20)-P(4)-F(19)	178.2(7)
C(30)-C(31)	1.365(16)	F(22)-P(4)-F(24)	178.9(9)
C(30)-C(29)	1.405(15)	F(21)-P(4)-F(24)	85.9(6)
C(30)-C(32)	1.503(16)	F(23)-P(4)-F(24)	88.5(8)
O(1)-C(1)	1.208(16)	F(20)-P(4)-F(24)	89.4(6)
O(4)-C(23A)	1.348(15)	F(19)-P(4)-F(24)	89.2(5)
C(24A)-C(23A)	1.376(17)	C(31)-C(30)-C(29)	118.5(12)
C(24A)-C(29)	1.402(17)	C(31)-C(30)-C(32)	123.5(12)
C(24A)-C(25)	1.511(17)	C(29)-C(30)-C(32)	117.8(12)
Cl(2)-C(150)	1.715(16)	C(23A)-C(24A)-C(29)	116.0(12)

C(2)-C(11)	1.385(17)	C(23A)-C(24A)-C(25)	122.4(13)
C(2)-C(3)	1.399(16)	C(29)-C(24A)-C(25)	121.7(12)
C(2)-C(1)	1.468(18)	C(24A)-C(29)-C(30)	123.2(12)
C(46)-C(47)	1.395(17)	C(11)-C(2)-C(3)	118.6(12)
C(46)-C(55)	1.418(17)	C(11)-C(2)-C(1)	119.6(13)
C(46)-C(45)	1.441(18)	C(3)-C(2)-C(1)	121.9(14)
C(12)-C(10)	1.483(17)	C(47)-C(46)-C(55)	121.7(13)
C(9)-C(10)	1.388(15)	C(47)-C(46)-C(45)	121.4(14)
C(9)-C(4)	1.388(15)	C(55)-C(46)-C(45)	116.8(13)
C(47)-O(6)	1.328(14)	C(10)-C(12)-P(11)	114.8(9)
C(47)-C(48)	1.435(17)	C(10)-C(9)-C(4)	125.9(11)
Cl(6)-C(151)	1.717(14)	O(6)-C(47)-C(46)	121.8(13)
O(3)-C(21A)	1.238(15)	O(6)-C(47)-C(48)	119.8(13)
O(8)-C(71)	1.339(14)	C(46)-C(47)-C(48)	118.3(13)
C(53)-C(48)	1.344(16)	C(48)-C(53)-C(54)	124.3(13)
C(53)-C(54)	1.385(15)	C(4)-C(5)-C(7)	109.4(10)
C(5)-C(4)	1.504(16)	C(4)-C(5)-C(8)	111.8(10)
C(5)-C(7)	1.524(17)	C(7)-C(5)-C(8)	109.3(12)
C(5)-C(8)	1.532(17)	C(4)-C(5)-C(6)	109.3(11)
C(5)-C(6)	1.576(18)	C(7)-C(5)-C(6)	110.4(11)
C(89)-C(88)	1.516(17)	C(8)-C(5)-C(6)	106.6(11)
C(89)-C(90)	1.519(16)	C(88)-C(89)-C(90)	113.1(11)
C(78)-C(60A)	1.375(15)	C(30)-C(32)-P(12)	117.9(9)
C(78)-C(77)	1.379(15)	C(60A)-C(78)-C(77)	117.3(12)
C(78)-C(79)	1.525(16)	C(60A)-C(78)-C(79)	121.2(12)
C(3)-O(2)	1.374(14)	C(77)-C(78)-C(79)	121.5(12)

C(3)-C(4)	1.392(16)	O(2)-C(3)-C(4)	119.7(11)
C(55)-C(54)	1.367(16)	O(2)-C(3)-C(2)	117.5(11)
C(48)-C(49)	1.529(17)	C(4)-C(3)-C(2)	122.9(13)
C(23A)-C(22A)	1.399(17)	C(54)-C(55)-C(46)	118.0(12)
C(10)-C(11)	1.387(16)	C(53)-C(48)-C(47)	117.7(12)
C(70)-C(60A)	1.379(16)	C(53)-C(48)-C(49)	121.6(13)
C(70)-C(69)	1.407(17)	C(47)-C(48)-C(49)	120.7(13)
C(70)-C(71)	1.446(17)	O(4)-C(23A)-C(24A)	118.8(12)
O(7)-C(69)	1.234(15)	O(4)-C(23A)-C(22A)	120.1(13)
C(49)-C(52)	1.512(19)	C(24A)-C(23A)-C(22A)	121.0(13)
C(49)-C(51)	1.560(18)	C(9)-C(10)-C(11)	116.2(12)
C(49)-C(50)	1.560(18)	C(9)-C(10)-C(12)	120.8(11)
C(31)-C(22A)	1.366(17)	C(11)-C(10)-C(12)	123.0(12)
C(28)-C(25)	1.538(18)	C(60A)-C(70)-C(69)	120.7(13)
C(61)-C(62)	1.491(16)	C(60A)-C(70)-C(71)	118.8(12)
C(90)-C(91)	1.507(18)	C(69)-C(70)-C(71)	120.5(14)
C(27)-C(25)	1.535(17)	C(52)-C(49)-C(48)	113.2(13)
C(71)-C(72)	1.390(17)	C(52)-C(49)-C(51)	104.8(12)
C(45)-O(5)	1.236(15)	C(48)-C(49)-C(51)	110.0(11)
C(72)-C(77)	1.359(17)	C(52)-C(49)-C(50)	110.6(12)
C(72)-C(73)	1.544(17)	C(48)-C(49)-C(50)	109.2(12)
C(62)-C(63)	1.524(16)	C(51)-C(49)-C(50)	108.9(12)
C(73)-C(76)	1.523(19)	C(2)-C(11)-C(10)	121.8(12)
C(73)-C(74)	1.551(17)	C(22A)-C(31)-C(30)	119.6(13)
C(73)-C(75)	1.568(18)	C(78)-C(60A)-C(70)	121.0(12)
C(25)-C(26)	1.551(17)	C(62)-C(61)-P(13)	119.0(10)

Cl(1)-C(150)	1.685(17)	C(91)-C(90)-C(89)	115.9(12)
C(56)-C(54)	1.539(16)	O(8)-C(71)-C(72)	119.9(13)
C(22A)-C(21A)	1.484(17)	O(8)-C(71)-C(70)	119.5(12)
C(41)-C(42)	1.520(17)	C(72)-C(71)-C(70)	120.6(13)
C(43)-C(42)	1.478(17)	O(5)-C(45)-C(46)	123.3(15)
C(43)-C(44)	1.545(18)	C(77)-C(72)-C(71)	115.8(12)
C(33)-C(34)	1.551(17)	C(77)-C(72)-C(73)	122.5(13)
C(37)-C(38)	1.434(17)	C(71)-C(72)-C(73)	121.8(13)
C(63)-C(64)	1.511(18)	C(61)-C(62)-C(63)	109.7(11)
Cl(5)-C(151)	1.703(16)	C(76)-C(73)-C(72)	111.8(12)
C(81)-C(80)	1.473(17)	C(76)-C(73)-C(74)	106.2(12)
C(81)-C(82)	1.537(18)	C(72)-C(73)-C(74)	110.1(11)
C(67)-C(68)	1.444(18)	C(76)-C(73)-C(75)	111.2(12)
C(67)-C(66)	1.541(17)	C(72)-C(73)-C(75)	108.8(11)
C(57)-C(58)	1.500(15)	C(74)-C(73)-C(75)	108.8(12)
C(59)-C(60)	1.436(19)	C(24A)-C(25)-C(27)	110.0(11)
C(59)-C(58)	1.552(18)	C(24A)-C(25)-C(28)	111.1(11)
C(38)-C(39)	1.55(2)	C(27)-C(25)-C(28)	107.0(12)
C(39)-C(40)	1.508(18)	C(24A)-C(25)-C(26)	108.2(11)
C(15)-C(16)	1.38(3)	C(27)-C(25)-C(26)	113.1(12)
C(15)-C(14)	1.53(3)	C(28)-C(25)-C(26)	107.4(11)
C(14)-C(13)	1.42(2)	C(54)-C(56)-P(13)	114.3(8)
C(66)-C(65)	1.548(16)	C(31)-C(22A)-C(23A)	121.6(13)
C(84)-C(85)	1.521(19)	C(31)-C(22A)-C(21A)	117.2(13)
C(83)-C(82)	1.472(18)	C(23A)-C(22A)-C(21A)	121.3(13)
C(18)-C(17)	1.36(2)	C(42)-C(41)-P(12)	114.9(9)

C(18)-C(19)	1.52(2)	C(72)-C(77)-C(78)	126.4(12)
C(19)-C(20)	1.34(2)	C(9)-C(4)-C(3)	114.6(11)
C(85)-C(86)	1.57(2)	C(9)-C(4)-C(5)	123.1(11)
C(150)-Cl(3)	1.751(15)	C(3)-C(4)-C(5)	122.3(12)
C(35)-C(36)	1.433(19)	C(42)-C(43)-C(44)	111.9(12)
C(35)-C(34)	1.530(18)	C(55)-C(54)-C(53)	119.9(13)
C(86)-C(87)	1.26(2)	C(55)-C(54)-C(56)	120.2(12)
C(21)-C(22)	1.23(2)	C(53)-C(54)-C(56)	119.9(12)
C(22)-C(23)	1.37(3)	C(43)-C(42)-C(41)	114.1(11)
C(24)-C(23)	0.98(2)	C(34)-C(33)-P(12)	118.3(10)
C(65)-P(13)-C(57)	108.4(6)	C(38)-C(37)-P(12)	118.0(11)
C(65)-P(13)-C(61)	107.4(6)	C(64)-C(63)-C(62)	111.9(12)
C(57)-P(13)-C(61)	112.9(6)	O(1)-C(1)-C(2)	125.5(15)
C(65)-P(13)-C(56)	107.6(6)	C(89)-C(88)-P(14)	116.5(10)
C(57)-P(13)-C(56)	109.1(6)	C(78)-C(79)-P(14)	117.8(9)
C(61)-P(13)-C(56)	111.3(6)	C(80)-C(81)-C(82)	112.0(12)
F(14)-P(3)-F(16)	178.3(8)	O(7)-C(69)-C(70)	126.9(16)
F(14)-P(3)-F(18)	91.1(8)	C(68)-C(67)-C(66)	110.7(12)
F(16)-P(3)-F(18)	90.7(7)	C(58)-C(57)-P(13)	116.9(9)
F(14)-P(3)-F(17)	89.9(7)	C(81)-C(80)-P(14)	117.9(11)
F(16)-P(3)-F(17)	88.4(6)	C(60)-C(59)-C(58)	114.1(14)
F(18)-P(3)-F(17)	178.5(7)	C(37)-C(38)-C(39)	111.1(13)
F(14)-P(3)-F(13)	88.7(6)	C(40)-C(39)-C(38)	109.8(14)
F(16)-P(3)-F(13)	91.3(6)	C(16)-C(15)-C(14)	114(2)
F(18)-P(3)-F(13)	91.0(6)	C(13)-C(14)-C(15)	123(2)
F(17)-P(3)-F(13)	90.2(6)	C(67)-C(66)-C(65)	112.2(10)

F(14)-P(3)-F(15)	90.3(6)	O(3)-C(21A)-C(22A)	123.1(14)
F(16)-P(3)-F(15)	89.7(6)	C(14)-C(13)-P(11)	117.7(16)
F(18)-P(3)-F(15)	89.2(6)	C(85)-C(84)-P(14)	115.0(10)
F(17)-P(3)-F(15)	89.6(5)	C(17)-C(18)-C(19)	120(2)
F(13)-P(3)-F(15)	179.0(6)	C(83)-C(82)-C(81)	111.7(13)
C(33)-P(12)-C(37)	107.3(7)	C(57)-C(58)-C(59)	110.8(11)
C(33)-P(12)-C(41)	107.5(7)	C(66)-C(65)-P(13)	115.0(8)
C(37)-P(12)-C(41)	111.5(6)	C(20)-C(19)-C(18)	113(2)
C(33)-P(12)-C(32)	110.8(6)	C(84)-C(85)-C(86)	111.8(14)
C(37)-P(12)-C(32)	113.1(7)	Cl(5)-C(151)-Cl(6)	109.5(10)
C(41)-P(12)-C(32)	106.6(7)	Cl(5)-C(151)-Cl(4)	112.3(8)
F(8)-P(2)-F(12)	90.3(6)	Cl(6)-C(151)-Cl(4)	111.5(8)
F(8)-P(2)-F(10)	177.8(7)	C(18)-C(17)-P(11)	128.3(18)
F(12)-P(2)-F(10)	88.6(6)	Cl(1)-C(150)-Cl(2)	112.6(10)
F(8)-P(2)-F(7)	89.3(6)	Cl(1)-C(150)-Cl(3)	110.1(9)
F(12)-P(2)-F(7)	91.6(5)	Cl(2)-C(150)-Cl(3)	110.4(9)
F(10)-P(2)-F(7)	88.9(6)	C(36)-C(35)-C(34)	113.9(14)
F(8)-P(2)-F(9)	90.9(6)	C(35)-C(34)-C(33)	111.6(12)
F(12)-P(2)-F(9)	88.3(5)	C(87)-C(86)-C(85)	121(2)
F(10)-P(2)-F(9)	91.0(6)	C(22)-C(21)-P(11)	140(2)
F(7)-P(2)-F(9)	179.8(7)	C(21)-C(22)-C(23)	149(3)
F(8)-P(2)-F(11)	89.7(6)	C(24)-C(23)-C(22)	144(5)

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Symmetry transformations used to generate equivalent atoms: