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DEVELOPMENT OF PHOSPHINIMINE-SULFONATE LIGANDS
FOR LATE METAL CATALYSIS

By

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M.Med., Guangxi Medical University

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A Dissertation

Submitted to the Faculty of the

College of Arts and Sciences of the University of Louisville

in Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

Department of Chemistry

University of Louisville

Louisville, Kentucky

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A Dissertation Approved on

August 9, 2013

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ABSTRACT

DEVELOPMENT OF PHOSPHINIMINE-SULFONATE LIGANDS FOR LATE METAL CATALYSIS

Suisheng Shang

August 9, 2013

Transition metal complexes are widely used as homogeneous catalysts mediating a variety of organic reactions, such as σ -bond activation/formation, regio-/ enantio-selective reactions, oxygen transfer, homo-/co-polymerization, etc. Among miscellaneous supporting ligands, bidentate ligands bearing a sulfonate donor have drawn considerable attention. Phosphine sulfonate ligands have been successfully developed for neutral palladium alkyls that promote incorporation of polar vinyl monomers into polyethylene chains producing highly linear copolymers. In the past decade, extensively investigated sulfonate ligands are mainly three types, phosphine-sulfonate, NHC-sulfonate, and olate-sulfonate. Phosphine-sulfonate ligands support palladium(II) for catalysis of ethylene copolymerization with polar vinyl monomers. They also support ruthenium(II) and (IV) forming complexes that are catalysts in regioselective alkylation reactions. NHC-sulfonate ligands form copper(I) complexes promoting asymmetric conjugate addition with high enantioselectivity. One olate-sulfonate ligand is known. It can stabilize Ru(II) to form a Ru(II) alkenylidene complex to perform ring closure metathesis (RCM). The literature has shown that sulfonate ligands have unique catalytic properties.

Pursuing enhanced donor capability and tunable electronic and steric properties while retaining the unique catalytic properties of the sulfonate donor, we have developed a series of phosphinimine-sulfonate ligands which employ phosphinimine as a co-donor. The phosphinimine-sulfonate ligands are synthesized in their zwitterionic forms from commercially available toluidine-sulfonic acid and in 7 steps. The synthetic steps include chlorination of sulfonic acid, formation of alkyl sulfonate esters, diazotization of amines, azidation of diazonium salts, formation of phosphazene group via Staudinger reaction, and protonation-deprotection of the phosphazene. The zwitterionic ligands are air-stable and convenient for creation of a ligand library. The desired anionic ligands can be readily generated by deprotonation with sodium hydride. Phosphinimine-sulfonate ligands show good coordination ability with palladium precursors such as (cod)PdMeCl or Py₂PdMeCl to form corresponding palladium methyl complexes. Palladium methyl complexes containing triphenyl, methyldiphenyl, di-*n*-butylphenyl, and tri-*n*-butylphosphinimine-sulfonate ligands have been synthesized.

A thermal behavior study of the synthesized palladium methyl complexes showed that 2,6-positions of the phosphiniminobenzene rings are subjected to orthopalladation. An ethylene reactivity test showed that phosphinimine sulfonate palladium methyl complexes can oligomerize ethylene forming alkanes and are catalyst candidates for polymerization. A study on the introduction of ortho-bulky groups to maintain proper steric properties required for blocking axial faces of the palladium's coordination plane in ethylene polymerization and copolymerization will be required to develop the phosphinimine motif further.

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CHAPTER ONE

INTRODUCTION

Transition metal complexes are widely used as homogeneous catalysts mediating a variety of organic reactions, such as σ -bond activation/formation, regio-/ enantio-selective reactions, oxygen transfer, homo-/co-polymerization, etc.¹ Compared with heterogeneous catalysis, homogeneous catalysis has the most important advantage in its mechanism study, which rationalizes reaction processes so that reaction selectivity can be realized and product structures can be controlled.² In transition metal-mediated catalysis, the metal center plays an important role in catalysts' ability to survive polar environments. Early metals prefer to adopt high oxidation states and intrinsically have high oxophilicity; late metals prefer to be at low oxidation states and have low oxophilicity. As a result, late transition metals have excellent tolerance to heteroatoms. For example, early metal based Ziegler-Natta catalysts are used in polymerization of non-polar olefins, whereas late metal based α -diimine and phosphine-sulfonate complexes are catalysts for copolymerization of polar vinyl monomers.^{3,4} In an organometallic catalyst, the most important determinant is its ligand environment which determines catalyst activity and product structures. A transition metal complex ligand environment includes two types of ligands, the spectator and the actor. As a rule, a spectator ligand does not change its structure during catalytic processes but intrinsically defines catalytic reactivity by providing the metal center with proper electronic and steric properties. In

organometallic catalysis, miscellaneous spectator ligands have been developed for reactions. The following discussion is limited to sulfonate and phosphinimine ligands which are related to late transition metal catalysis.

1.1 Sulfonate Ligands Related to Late Metal Catalysis

The sulfonate group is based on a 6-valence sulfur species. In a sulfonate group, the lone pair of electrons on an oxygen atom resonates among the three oxygen atoms through the sulfur $p\pi$ - $d\pi$ conjugation (Figure. 1.1). This feature relates to Berry's pseudo-

Figure 1.1 Mesomeric structures of sulfonate group

rotation, an important concept in ethylene polymerization. The three oxygen atoms may exchange their positions to bind to the metal center, causing isomerization of sulfonate complexes.⁵ Since the conjugate acid SO_3H is a strong acid (ArSO_3H , $\text{pK}_a = -6.5$),⁶ the sulfonate donor is a weak anionic lone pair donor when bound to a transition metal in the monodentate mode. Very few sulfonate complexes, except those using the sulfonate

Figure 1.2 Bidentate mode of sulfonate group

donor as an actor ligand,⁷ are known. Instead, the sulfonate donor has been used in a bidentate ligand mode whose binding strength can be enhanced through the resonance

effect provided by a strong donor like N, P, or O donors (Figure 1.2). Bidentate sulfonate complexes can exist in three complexation fashions, $(\text{Nu}, \text{SO}_3)\text{M}$, $(\text{Nu}, \text{SO}_3)_2\text{M}$, and $[(\text{Nu}, \text{SO}_3)\text{M}]_2$ ($\text{Nu} = \text{N}, \text{P}, \text{O}$). Bidentate sulfonate ligands coordinate with metal centers to form 5-7 membered rings, of which, the 6 and 7 membered coordinating rings take the puckered conformation. Late transition metals like Pd, Ni, Ru, Rh, Cu, Ag, etc. can form complexes with bidentate sulfonate ligands. Tridentate sulfonate ligands are also known for stabilizing transition metals (Figure 1.3).⁸

Figure 1.3 Tridentate Sulfonate Copper(II) Complex

Relevant to late metal catalysis, there are three important types of bidentate sulfonate ligands, phosphine-sulfonate ($\text{P}^{\wedge}\text{SO}$) (Figure 1.4, a), NHC-sulfonate ($\text{NHC}^{\wedge}\text{SO}$) (Figure 1.4, b), and olate-sulfonate ligands ($\text{O}^{\wedge}\text{SO}$) (Fig. 1.4, c).⁹ In a phosphine-sulfonate ligand, the chelating sulfonate donor works with a neutral coordinating phosphine co-donor to stabilize late metals like Pd(II), Ni(II), Ru(II), Ru(IV), and Rh(I) forming a 6-membered coordination ring.^{5c, 10} The electronic and steric factors can be tuned through placing different substituents on phosphorus. In an NHC-sulfonate ligand, N-heterocyclic carbene is the neutral lone pair co-donor. NHC-sulfonate ligand can stabilize silver(I) or copper(I) forming a 7-membered coordinative ring.^{9b} The electronic and steric factors can be tuned through placing different substituents on a nitrogen atom in the NHC ring. In the olate-sulfonate ligand, the co-donor is an anionic oxido donor.

This ligand stabilizes Ru(II) to form a 6-membered coordinative ring.^{9c} The electronic and steric factors cannot be tuned through modification to the oxido co-donor. They are reached through modification to another spectator ligand. Phosphine-sulfonate complexes

Figure 1.4 Three types of sulfonate ligands

are catalysts for ethylene polymerization and copolymerization, regioselective alkylation and allylation. NHC-sulfonate complexes catalyze enantioselective reactions including chiral conjugation addition, allylic addition, hydroboration, boration, and diboration. The olate-sulfonate complex is a catalyst for olefin metathesis.

Phosphine-sulfonate (P^{SO}) Ligands

Being a first catalytically significant bidentate sulfonate ligand, P^{SO} was initially developed by Drent and co-workers as palladium catalysts performing insertion chemistry to form linear copolymers of ethylene and alkyl acrylates.¹³ This work is based on an ill-defined P^{SO} Pd catalyst. The combination of the zwitterionic phosphine-sulfonate ligand (Figure 4a) and a Pd precursor, Pd(dba)₂ or Pd(OAc)₂ can *in situ* generate a (P^{SO})Pd complex, which proves active in incorporating alkyl acrylates into polyethylene chains. As is shown in scheme 1.1, the product is an ethylene- initiated, acrylate-terminated random copolymer. P^{SO} Pd hydride is initially formed by the oxidative addition of Pd to PH bond in the P^{SO} zwitterion. The catalytic cycle starts by

association and insertion of the ethylene molecule to the Pd-H. Repetition of this step results in a polyethylene chain to grow on Pd, forming a palladium alkyl species

Scheme 1.1 Catalytic cycle of $[P^{\wedge}SO]Pd$ complex

($[P^{\wedge}SO]Pd-P_x$). Randomly, methyl acrylate (MA) associates to this species and inserts into the Pd-C bond. Since MA is an unsymmetrical vinyl species, the insertion can be in 1,2- or 2,1-fashion. However, due to a reduced steric repulsion between the migrating group and the substituent on the olefin and a lowered energy barrier, the acrylate unit prefers to insert into the growing polyethylene chain in 1,2-insertion.^{5c, 9a} At the end of catalytic cycling, β -hydride elimination releases the copolymer chain and regenerates the catalyst $P^{\wedge}SO$ Pd hydride species.

$P^{\wedge}SO$ Pd alkyl complexes can take two geometries, *cis*-isomer and *trans*-isomer. The *cis*-isomer reflects the geometry where the alkyl group lies on the side of the phosphine donor, whereas the *trans*-isomer shows that it is on the side of the sulfonate donor. Because of the strong trans influence of the phosphine functional group, however, the alkyl group is not allowed to stand on its *trans* position. A *cis*-isomer is therefore the preferred and stable geometry.¹¹ In ethylene polymerization, both isomers are possible for

chain growth by insertion chemistry. However, because of its more labile character, the *trans*-isomer is preferred over the *cis*-isomer.^{5b} This requires a fast equilibrium between the two isomers. The sulfonate group in the P[^]SO ligand plays a unique role in the isomerization process. As is shown in Scheme 1.2, the sulfonate group can use its second

Scheme 1.2 Berry's pseudo-rotation

oxygen to coordinate the Pd metal center, forming a 5-membered associative intermediate. The two coordinated oxygen atoms can exchange, undergoing the so-called Berry's pseudo-rotation to result in *cis-trans* isomerization of the complex.^{5a} Further studies comparing Pd complexes bearing phosphine-sulfonate, imine-phenolate, and diphosphine ligands showed that the anionic sulfonate can destabilize the κ -chelating mode of the comonomer like acrylonitrile and increase the population of π -complexes.¹² The sulfonate donor is important in the copolymerization process.

Based on the ill-defined P[^]SO Pd catalyst, well-defined P[^]SO Pd alkyl complexes have been designed and synthesized. Modifications to the P[^]SO Pd complex structures were carried out by changing the alkyl group and labile ligand on the metal and placing different bulk on the phosphorus (Fig. 1.5). In polymerization, the alkyl group (R as in Fig. 1.5) is the initiating carbon source where the polymer chain can grow via insertion of ethylene or vinyl units. R can be CH₃, CH₂SiMe₃, CH₂^tBu, CH₂Ph, or Ph.¹³ The labile ligand (L as in Fig. 1.5) is used for generation of a coordination open site. This

Figure 1.5 [P^{SO}]Pd Complexes

can be an amine base like pyridine, lutidine, or pyridazine, or a phosphine like PPh₃.¹³ It can also be an anionic species like the chloride ion.^{11, 14} An important observation is that the use of DMSO as a labile ligand can significantly increase the catalyst activity.¹⁵ Steric bulk on phosphorus (R' as in Fig. 1.5) can be realized by placing substituents like Ph, 2-EtPh, 2-MeOPh, 2-EtOPh, 2-ⁱPrOPh, and 2-(2,6-MeO₂Ph)Ph.¹⁶ Cyclohexyl group is also a choice for this purpose.^{15c} Successfully incorporated to polyethylene have been polar vinyl monomers including alkyl acrylates, vinyl acetate, vinyl fluoride, alkyl vinyl ether, vinyl ketone, vinyl cyclohexane, acrylonitrile, vinyl sulfone, styrene derivatives, N-isopropylacrylamide, and N-vinylpyrrolidinone, norbornene derivatives, and allyl monomers.¹³⁻¹⁷ Generally, the catalyst activity is low (< 40 gmmol⁻¹h⁻¹), the incorporation ratios are low (<20% vinyl comonomers) and polymer molecular weight is low (M_n<15,000).

In addition to linear copolymerization, regioselective reactions are important applications of phosphine-sulfonate ligands. Arene ruthenium(II) complexes containing a P^{SO} ligand mediate the sp³ CH bond activation at the 3(C) position of N-protected cyclic aliphatic amines such as N-benzylpyrrolidine facilitating regioselective alkylation with an aldehyde species such as benzaldehyde.^{10d} As is shown in scheme 1.3, P^{SO} Ru(II) complex A or B catalyzes the conversion of N-benzylpyrrolidine to C-3 benzylated species (**a**) at a high conversion ratio 99% with an olefinated species (**b**) as

the minor. It shows that 88-89% of the 3(C)-alkylated species (**a**) can be obtained using catalyst A and B. On the phosphorus atom, a phenyl group can be replaced with a *tert*-butyl group. The catalytic process involves nonoxidative dehydrogenation, C-C bond

Scheme 1.3 Regioselective Alkylation

Scheme 1.4 Regioselective Alkylation Mechanism

formation, and hydrogen transfer. As is shown in Scheme 1.4, $[P^{\wedge}SO]Ru$ abstracts hydride to convert amine to a cationic iminium species followed by the formation of azomethine ylide promoted by the ruthenium hydride species. In the presence of acid, the ylide is isomerized to enamine, which can undergo a Michael-type addition with

benzaldehyde forming an enolate intermediate. The following acid-assisted dehydration is supposed to afford a conjugate iminium which can be reduced by ruthenium hydride giving C(3) alkylated amine.^{10d}

P[^]SO ruthenium(IV) complex can mediate O-allylation of *p*-MeOC₆H₄OH with allyl chloride and C-allylation of indole with allylic alcohols to selectively form branched products (Scheme 1.5).^{10e} In the presence of P[^]SO Ru(IV) catalyst (C), O-allylation of

Scheme 1.5 Regioselective allylation by [P[^]SO]Ru(IV)

p-MeOC₆H₄OH can be carried out in acetonitrile and dichloromethane to yield 98:2 and 97:3 branched and linear products. Compared to phosphine-carbonate ligand supported complex (D), P[^]SO ruthenium complex (C) shows higher activity (room temperature, no heating necessary) and regioselectivity (higher branched/linear ratio). This demonstrates that the electron deficient sulfonate donor tends to give high reactivity and selectivity. In

Scheme 1.6 Catalytic cycle in hydroformylation of 1-hexene

the C-allylation of indole, a high selectivity for the branched products can be obtained at a branched/linear ratio 95:5 using catalyst C. Interestingly, “poor regioselectivity” has been observed for carbonyl rhodium(I) featuring a P^+SO^- chelating ligand. The complex catalyzes hydroformylation of 1-hexene to give a mixture primarily consisting of n-septanal (35-60%) and 2-methylhexanal (15-35%) along with a minority of isomerized products 2-hexenes.^{10f} As a rule of thumb, catalysts supported by firmly chelating ligands tend to selectively form linear products.¹⁸ In this case, poor regioselectivity can be ascribed to the relatively weak chelating effect of the P^+SO^- ligand – the nature of P^+SO^-

ligand. Based on this important understanding, P⁺SO ligand has probably lost its chelating state to rhodium metal to allow formation of both linear and branched aldehydes during the catalytic cycle. As is shown in scheme 1.6, hydrogen gas splitting results in O-chelating monodentate sulfonate Rh(I) intermediate. There are two pathways to undergo hydroformylation. On the one hand, monodentate sulfonate Rh(I) undergoes association and migratory insertion of hexene and CO to form linear or branched septanals and regenerates the P,O-chelating bidentate sulfonate Rh(I) catalyst. On the other hand, the sulfonate ligand can be replaced by CO to generate the zwitterionic ligand species and RhH(CO)_nL complexes. The later can catalyze the formation of linear or branched septanals.^{10f}

NHC-Sulfonate (NHC⁺SO)

Chiral NHC-sulfonate (NHC⁺SO) Cu(I) complex derived from a dimeric NHC⁺SO Ag(I) complex and (CuOTf)₂ catalyzes the asymmetric conjugate addition of organozinc reagents such as Me₂Zn or Ph₂Zn to cyclic γ -keto ester creating all-carbon quaternary stereogenic centers in high enantioselectivity (up to 84% ee) and high efficiency (>98% yield) (Scheme 1.7).^{9b} This compares to the low enantioselectivity (<30% ee) and inefficiency (<25% yield) of its NHC-phenolate analogs. The significant

Scheme 1.7 Enantioselective conjugation addition by [NHC⁺SO]Cu(I)

differences derive from steric and electronic differences between monomeric copper(I) complexes containing NHC-phenolate and NHC-sulfonate. NHC-phenolate ligands chelate in an 8-membered ring, whereas NHC-sulfonate forms Cu(I) complex in a 7-membered ring, which is more geometrically constrained. In addition, sulfonate donor is less basic than the phenolate donor. Similarly, replacement of sulfonate with carbonate donor immediately lowers the enantioselectivity to less than 30% ee. The donor capability is apparently a determinant of selectivity. The chiral NHC^{SO} Cu(I) complex also promotes hydroboration of styrene derivatives and boration/diboration of terminal alkynes in high regioselectivity (99:1 er and 97:3 er).¹⁹

Scheme 1.8 Asymmetric allylic addition by [NHC^{SO}]Cu(II)

Cu(II) complex derived from a chiral NHC-sulfonate ligand promotes asymmetric allylic addition, in which vinylaluminum can add to the benzylic position of a styrene derivative forming a vinylated product with 98% enantioselectivity, 98% $\text{S}_{\text{N}}2'$ and E

selectivity, and 98% conversion (Scheme 1.8). This compares to the inactivity profiles for its corresponding NHC-phenolate and NHC-naphtholate analogs.²⁰

Scheme 1.9 Ring closure metathesis by [O[^]SO]Ru(II)

Olate-Sulfonate (O[^]SO) Ligands

One olate-sulfonate (O[^]SO) ligand is known.^{9c} It can stabilize Ru(II) to form a Ru(II) alkenylidene complex to perform ring closure metathesis (RCM). As is shown in scheme 1.9, the di-terminal alkene ester species can be converted to a cyclic alkene species in the presents of O[^]SO Ru(II) alkylidene as a catalyst. The conversion ratio is 95%.

1.2 Phosphinimine Ligands Related to Late Metal Catalysis

Phosphinimines, sp^2 nitrogen based ligands are attractive donors in coordination chemistry. Phosphinimines possess a highly polarized $\text{P}=\text{N}$ bond because of the mesomeric effect (Figure 1.6). It forms a coordinative bond with transition metals and

Figure 1.6 Mesomeric structure of phosphinimine ligands

has tunable electronic and steric properties.²¹ In phosphinimine complexes, a dual coordination sphere is present since the steric bulk has been slightly removed from the metal center. The inner sphere can be used for catalytic reaction, whereas the outer sphere provides protection for the inner sphere catalysis.²² Bidentate phosphinimine ligands are reported to stabilize a wide scope of late transition metal species including Fe(II)/Fe(III), Co(II), Rh(I), Pd(II), Ni(II), Zn(II).²³ Tridentate phosphinimine ligands are known to for palladium and nickel complexes.^{23f}

Relevant to late metal catalysis, phosphinimine donor is primarily developed for zinc complexes which can promote formation of polylactide via ring open polymerization.^{23f} The ligand employs dibenzo[b,d]furan as the backbone and has a phosphinimine donor tethered on its 4 position or two on its 4,6-positions constituting bidentate ($P=N^{\wedge}O$) or tridentate ($P=N^{\wedge}O^{\wedge}N=P$) chelating mode (Figure 1.7, a and b).

Figure 1.7 Mono and bisphosphinimine ligands and Zinc complex

Due to unwanted side reactions such as inter- and intramolecular esterification and chain transfer, P=N⁺O ligand supported cationic zinc complexes can only form low molecular weight (up to Mn = 5000) polylactide. Some P=N⁺O⁺N=P supported zinc complexes are active for polymerization with high molecular weight (up to Mn = 50,000) products. The pinched cationic zinc complex (Figure 1.7, c) shows high activity in polymerization of *rac*-lactide. At the ambient condition, it can convert 200 equivalents of *rac*-lactide into polylactide in 50 minutes. The process has a living polymerization character. The mechanism is coordination and insertion polymerization.^{23g}

1.3 Dissertation Objective

In P⁺SO ligands, the tertiary phosphine moiety provides tunable electronic and steric properties. Triarylphosphines act as σ donors.² The steric bulk is provided by placing different aryl groups on phosphorus such as phenyl, *o*-tolyl, *o*-ethylphenyl, *o*-propylphenyl, *o*-anisyl, and *o*-(2,6-dimethoxy)phenyl groups.^{10b, 16c} In the NHC⁺SO ligands, the NHC moiety works as the source for electronic and steric properties. The imidazole nitrogen atoms donate electrons to increase the donor strength of the singlet carbene. Bulky groups on imidazole's 3-nitrogen contribute steric bulk required for

Figure 1.8 Phosphininimine-sulfonate ligand and PNSO Pd Complex

catalytic reactivity.^{9b} Pursuing enhanced donor capability and tunable electronic and steric properties while retaining the unique catalytic properties of the sulfonate donor, we have designed and synthesized a series of phosphinimine-sulfonate (PN[^]SO) ligands (Figure 1.8, a). As a modification to the P[^]SO ligand system, a phosphinimine motif has been built to replace the phosphine functionality. We have already synthesized the palladium complexes (Figure 1.8, b) using discrete PN[^]SO ligands and studied their thermal behavior and ethylene reactivity. The development of PN[^]SO ligands will be discussed in chapter two. The synthesis and reactivity of phenyl-based PN[^]SO Pd complexes will be described in chapter three and that of alkyl-based PN[^]SO Pd complexes will be detailed in chapter four.

CHAPTER TWO

SYNTHESIS OF ZWITTERIONIC PHOHSPHINIMINIUM ARENESULFONATES

2.1 Introduction

Bidentate ligands are an important category of ligands supporting organometallic complexes acting as homogeneous catalysts. However, those containing a sulfonate donor are few. Very recently, Drent and co-workers developed phosphine-sulfonate bidentate ligands for palladium catalysts which are capable of incorporating polar vinyl monomers such as methyl acrylate, vinyl acetate, acrylonitrile, etc. into polyethylene chains in high linearity.^{9a} Based on Drent's work, some other bidentate ligands containing a sulfonate donor have been designed and synthesized for catalysis in late metal regioselective and enantioselective reactions. For instance, Bruneau and coworkers utilized phosphine-sulfonate ligands to form Ru(II) complexes to mediate the sp^3 CH bond activation at the C(3) position of N-protected cyclic aliphatic amines such as N-benzylpyrrolidine facilitating regioselective alkylation with an aldehyde species such as benzaldehyde.^{10d} Hoveyda and co-worker have developed N-heterocyclic carbene/sulfonate bidentate ligands which are useful copper catalysts for enantioselective reactions.^{9b, 19b}

Synthesis of phosphinimine-arenesulfonate involves constructing the phosphinimine functionality *ortho* to a sulfonic acid group. One challenge for this chemistry is that the hydrophilic nature of the sulfonic acid group usually complicates the organic solvent based synthesis.^{9a} In the synthesis of phosphine-arenesulfonates, the

solubility issue was addressed by Drent and coworkers using a dilithiated species, 2-lithiobenzenesulfonate lithium salt.²⁴ This allows a manipulation of substitution reaction with diarylmethoxyphosphines [(2-ROC₆H₄)₂P(OMe), R = Me, Et, ⁱPr] in THF with ease. Functionalization of phosphinimine can be achieved through Staudinger, Kirsanov, or Mitsunobu reactions.²⁵ However, all three types of reactions require amine derivatives as starting materials. The challenge is that an incoming basic group like the amino or imino group can cause compatibility problems with the neighboring acidic group. A common practice to avoid incompatibility between the acidic and the basic groups is to start the synthesis with a 2-halo or 2-nitro sulfonic acid. Protection of the sulfonic acid group with its isobutyl or neopentyl esters allows introduction of an amino group into its *ortho* position by either amination of the *ortho* halogen group or reduction of the *ortho* nitro group. To build an *ortho* amido unit, Howery and coworkers converted 2-fluorobenzenesulfonic acid to its neopentyl ester for the protection purpose.²⁶ This allowed them to manipulate the nucleophilic substitution of amine for the fluoro group to form the *ortho* amino sulfonic acid species, which can be readily amidated. Similarly, when they synthesized the NHC-sulfonate ligands, Hoveyda and coworkers protected 2-bromobenzenesulfonic acid with its isobutyl ester for the manipulation of amination of the *ortho* bromo group so that a chiral ethylenediamine functionality can be introduced into the *ortho* position of the sulfonic acid group.^{9b, 19b} Under the protection of the sulfonate ester, nitro group has also been used as an amino precursor in the realization of the *ortho* amine-sulfonate scaffold. This can be exemplified by the formation of aryl 2-acylaminobenzenesulfonates.²⁷

p-Toluidine-2-sulfonic acid, available commercially, is the most ready-to-go

ortho amine-sulfonate scaffold. This synthon allows us to work on the phosphinimine structure in two ways. For simplicity, can we run the Staudinger reaction without protecting the sulfonic acid group to obtain a phosphinimino-benzenesulfonate sodium salt? This will be similar to Drent's strategy for the PSO ligand synthesis. Or, should we protect the sulfonic acid group before carrying out the Staudinger reaction to phosphoranylate the *ortho* amino group? If this is a have-to-do choice, it needs a clean conversion of the *ortho* amine-sulfonic acid to its sulfonyl chloride for esterification and a neat transformation of the sulfonate esters without touching the *ortho* basic amine group. The literature shows that *p*-toluidine-2-sulfonic acid can be chlorinated to its sulfonyl chloride with chlorosulfuric acid.²⁸ Synthesis of sulfonyl chloride is critical for the protection of the sulfonate group, making the protecting strategy promising. A retroanalysis (Scheme 2.1) illustrates the two synthetic strategies, the sulfonate-unprotected and the sulfonate-protected.

Scheme 2.1 Retroanalysis for two synthetic strategies

2.2 Results and Discussion

Attempted Synthesis of Sodium Phosphinimine-sulfonate

To apply a straightforward synthetic strategy, we attempted to prepare the anionic ligand sodium phosphinimine-sulfonate by directly functionalizing sodium toluidine-2-sulfonate. As is shown in Scheme 2.2, toluidine-2-sulfonic acid (**1**) was converted to sodium toluidine-2-sulfonate (**2**) with a yield of 98%.²⁹ The deprotonation of the sulfonic acid was performed by boiling **1** in diluted aqueous solution of NaOH. Compound **2** was diazotized with NaNO₂ and H₂SO₄ in water at 0 °C. In the reaction, 20 mol% urea was to destroy the excess nitrous acid (HONO); charcoal to adsorb non-polar impurities; filtration to remove solid trashes.³⁰ Due to its solubility in water, the diazonium bisulfate salt stayed in the filtrate. The obtained aqueous diazonium bisulfate salt (**2-N₂⁺HSO₄⁻**) was subjected to azidation with NaN₃ in water at 0 °C to form

Scheme 2.2 Synthesis and complexation of Sodium Phosphinimine-sulfonate

sodium 2-azido-5-methylbenzenesulfonate (**3**).³¹ Azide **3** was isolated in low yield (20-50%) and contained water. In anhydrous THF, the Staudinger reaction of **3** with PPh₃ was

run to afford sodium 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate (**4**) in 86% yield.^{25a} Crude **4** was a white solid and further treated with hexanes-benzene, 3:1 to remove impurities. Based on ³¹P NMR, **4** was completely free of excess starting triphenylphosphine and a reaction by-product triphenylphosphine oxide. However, other non-interpretable impurities were observed in the ¹H NMR spectrum. Also surprising to us, all proton resonances, as well as the ³¹P resonance for the phosphinimine peak at $\delta_P = 2.8$ ppm, were broadened. Any solvent effect was excluded by running ¹H and ³¹P NMR experiments with different deuterated solvents such as dichloromethane-d₂, chloroform-d, and THF-d₈.

Complexation of **4** was attempted by reacting it with (cod)PdCl₂ in CH₂Cl₂ in the presence of pyridine. An orange precipitate was isolated from the reaction. Unfortunately, the ¹H NMR was more complicated than expected even though the ³¹P NMR showed one single peak and we were unable to obtain a well characterized [NP⁺SO]PdCl(py) complex (**4a**).

Development of Zwitterionic Phosphiniminium-Sulfonates

Alternately, we developed a synthetic route involving protection and deprotection the sulfonic acid group.³² It includes 5 steps: 1) chlorination of the starting toluidine-2-sulfonic acid to its sulfonyl chloride; 2) esterification to form alkyl sulfonates; 3) conversion of the sulfonate ester protected amines to diazonium salts for azidation; 4) P=N double bond formation to prepare the sulfonate ester protected phosphinimine; 5) deprotection of the phosphinimine-sulfonate esters to produce zwitterionic phosphiniminium-sulfonate. The synthesis is successful and provides clean ligands in the

form of zwitterion. Basing on this success, we also developed a one-pot synthetic route, a combination of step 4 and 5. It proves an efficient and versatile pathway for a facile access to the proligand library.

Preparation of Toluidine-2-sulfonyl Chloride

Toluidine-2-sulfonic acid (**1**) is commercial available chemical. As is mentioned in the introduction, it can be converted to its sulfonyl chloride by chlorination with chlorosulfuric acid (ClSO_3H) with the *ortho*-amine untouched. A 1933 patent shows that the reaction was performed by dissolving 1 part of the sulfonic acid **1** in 5 parts of ClSO_3H at 0 °C in 1 hour and heating the solution for 8 hours, followed by quenching the reaction by pouring the hot solution onto a large amount of ice to yield the crude product as a pale yellow solid.²⁹ We tried to reproduce the reaction as described in the patent. However, it gave us a mixture consisting not only the desired monosulfonyl chloride, toluidine-2-sulfonyl chloride (**5**) and the unwanted disulfonyl chloride, toluidine-2,6-disulfonyl chloride (**6**) as well (Scheme 2.3). Based on the literature,³³ the chlorination process is initiated first by protonation of the anionic sulfonate with 2 equivalents of ClSO_3H to generate the ammonium-sulfonyloxonium dichlorosulfate intermediate (**7**) (Scheme 2.3a). The nucleophilic attack on the sulfonyloxonium sulfur by the chloride

Scheme 2.3 Chlorination in 8 hours

Scheme 2.3a Proposed mechanism for **5-HO₃SCI**

anion that is released from the $\text{S}=\text{O}$ double bond formation produces the protonated species of **5** (**5-HO₃SCI**) and sulfuric acid. The neutral species **5** is resulted from the quenching workup. Understandably, the 5 position of **5-HO₃SCI** is reluctant in reactivity due to the presence of electron withdrawing group ortho- NH_3^+ . But long time exposure to hot ClSO_3H may have largely increased the reactivity of this position. Mechanistically, we proposed that in an extended heating environment, another equivalent of ClSO_3H reacted with **5-HO₃SCI** via the electrophilic aromatic substitution to form the σ -complex

Scheme 2.4 Mechanism for **6-HO₃SCI**

(**8**) (Scheme 2.4). Intramolecular lone pair rearrangement extruded an HCl to form intermediate **9**. The 4th equivalent of ClSO_3H performed the reaction showing in Scheme 2.3 to chlorinate **9** to **6-HO₃SCI**, which could be neutralized to the disulfonyl chloride **6** in the quenching workup.

With this understanding, we reinvestigated the reaction by performing it in different reaction times, 2, 4, 6, and 8 hours. Because of the symmetrical structure of **6**, ^1H NMR spectra were used for its differentiation from **5**. ^1H NMR spectra showed that the 6- and 8-hour reactions contained **6** in a significant amount. The 4-hour reaction contained very little **6**. The best is the 2-hour reaction and there are no seeable peaks of **6** on the ^1H NMR spectrum. Optimally, the chlorination of toluidine-2-sulfonic acid (**1**) can be run by dissolving the starting **1** in ClSO_3H in 1 hour at $0\text{ }^\circ\text{C}$ and heating the solution to $80\text{ }^\circ\text{C}$ for 2 hours (Scheme 2.5). After the reaction is quenched with ice, the sulfonyl chloride (**5**) can precipitate out as a yellow solid. The product can be dried in the vacuum oven at $40\text{ }^\circ\text{C}$. A typical scale is of 4 grams and with a yield of 80%.

Scheme 2.5 Synthesis of **5**

Synthesis of Alkyl Toluidine-2-sulfonates

In literature, neopentyl and isobutyl sulfonate esters are most encountered protecting groups. Neopentyl sulfonates are usually formed by esterification of the neopentyl alcohol with a sulfonyl chloride species and can tolerate a variety of robust reagents including Grignard reagent like vinyl-MgBr, CrO_3 , NBS/benzoyl peroxide, H_2/RaNi , DIBAL, NaI, aqueous NaOH or HBr, HONH_2 , and NaH.³⁴ The cleavage can be completed by heating the neopentyl sulfonate ester in the presence of tetramethylammonium iodide (Me_4NI) in a polar aprotic solvent like DMF at $160\text{ }^{\circ}\text{C}$ for 16 hours.³⁴ Isobutyl sulfonates are also available from the esterification of the corresponding isobutyl alcohol with a sulfonyl chloride species and can survive reagents like SOCl_2 , TFA, NaBH_4 , H_2/Pd , etc.³⁵ The protective groups can be readily cleaved with Bu_4NI . The deprotection is usually manipulated in acetone and by heating to $55\text{ }^{\circ}\text{C}$ for 12 hours.³⁵ In addition to these two sulfonates, candidate protecting groups widely screened include isopropyl, n-butyl, difluoroethyl, hexafluoroisopropyl, trifluoroethyl, and α -(trifluoromethyl)benzyl, phenyl, tetrahydropyran-2-methyl, 3-methyl-3-oxetane-methyl groups.²⁴ Deprotecting conditions are 1) 1M NaI in acetone refluxing for 16 hours; 2) 20% piperidine in DMF at room temperature for 16 hours; 3) 0.3 M NaN_3 in DMSO at $70\text{ }^{\circ}\text{C}$ for 16 hours; 4) excess $\text{Fe}(0)$ in 2:2:1 EtOH/HOAc/ H_2O at $50\text{ }^{\circ}\text{C}$ for 1 hour; 5) 9:1 $\text{CH}_2\text{Cl}_2/2\text{ M NaOH}$ in MeOH at room temperature for 16 hours; 6) 48% HBr refluxing

for 2 hours, and 7) 0.1 M BBr₃ in CH₂Cl₂ at room temperature for 2 hours.²⁴ These protecting groups displays different abilities to tolerate different conditions. To reach our chemistry, we looked for a proper protecting group which is compatible with the subsequent reactions including diazotization, azidation, and Staudinger reaction and whose cleavage condition does not affect the phosphinimine group. For this purpose, we successfully prepared alkyl esters including neopentyl, isobutyl, n-butyl, and n-propyl sulfonates. We also attempted to make more robust esters like methyl and allyl sulfonates but did not obtain them as isolated products due to their thermal instability.

The synthesis of neopentyl, isobutyl, n-butyl, and n-propyl toluidine-2-sulfonates (**10-13**) were carried out by sulfonylation of the corresponding alkyl alcohols with the sulfonyl chloride (**5**) in CH₂Cl₂ in the presence of 1.2 equivalents of DABCO as a proton scavenger (Scheme 2.6). A pure sulfonate ester can be obtained by running the

Scheme 2.6 Synthesis of alkyl toluidine-2-sulfonates

reaction mixture through a silica gel plug. The typical yield is above 80% at a 2-4 gram product scale. The characterization of **10-13** has been finished using ¹H NMR. In comparison to **5**, aliphatic signals demonstrate the introduction of alkyl groups.

Reminiscent of sulfonate ester bond formation, the neopentyl sulfonate **10** gave a singlet

at $\delta_{\text{H}} = 3.63$ ppm; the isobutyl sulfonate **11** a doublet at $\delta_{\text{H}} = 3.77$ ppm; the n-butyl and n-propyl sulfonates **12** and **13** triplets at $\delta_{\text{H}} = 3.97$ ppm. All esters had a broad singlet around $\delta_{\text{H}} = 4.80$ ppm with a 2H integration number, showing that the *ortho*-amino group was innocent during the esterification.

Synthesis of Alkyl 2-Azido-5-methybenzenesulfonates

Azides are useful reagents for a couple of organic transformations.³⁶ N-Heterocyclic carbene (NHC) can couple with an aryl or alkyl azide species to form imidazole-2-triazene compounds which are monomers for polytriazene.³⁷ Azides provides access to aza-ylide reagents by performing the Staudinger reaction with triphenylphosphine.^{25a} Through aza-ylides, some important functionalities like amine and amide can be realized.³⁸ However, azide chemistry is infamous for its explosive potential. Due to formation of diazidomethane, combination of sodium azide and dichloromethane can result in explosion.³⁹ For the laboratory safety, converting the nucleophilic inorganic azide to an electrophilic organic one is a strategy for the manipulation of this chemistry. Following Sharpless' "Rule of Six" and the mechanism of diazotransfer proposed by Wong,⁴⁰ different research groups have developed three types of stable azide precursors including triflyl azide (**14**), imidazole-1-sulfonyl azide (**15**), and benzotriazole-1-sulfonyl azide (**16**) (Figure 2.1).⁴¹ These azide precursors are sulfonyl azide derivatives and their delivery of the azide unit is catalyzed by CuSO_4 . With this

Figure 2.1 Azide precursors

knowledge, we attempted using the azide precursors **15** and **16** to convert the sulfonate ester protected amine (**10**) to its azide derivative. Unfortunately, none of them worked for unknown reasons.

In the foregoing context, when we made the sodium 2-azido-5-methylbenzenesulfonate (**3**) we followed Blackburn's method to add the NaN₃ solution into the filtrate of the diazonium bisulfate salt (**2-N₂⁺HSO₄⁻**).³¹ The problem here is that the filtrate contained unreacted H₂SO₄. Excess strong acid could acidify NaN₃ to hydrazoic acid (HN₃). Since HN₃ is a highly volatile, toxic and explosive liquid,⁴² its generation and evolution causes stringent health and safety issues. Further, the formation of the volatile HN₃ lowers the concentration of the nucleophile NaN₃ in water. This explains why the yield of azide-sulfonate was low (20-50%). Clearly, an HN₃ free synthetic methodology will avoid these adverse factors. Instead of the aqueous filtrate, an isolated diazonium salt species, if used for the azidation step, is apparently one choice. For isolation, the diazonium salt must be stable in air enough to allow at least a simple separation manipulation like filtration. In the Schiemann reaction, as we know, heating dry diazonium fluoroborate is a method to fluorinate an aromatic ring.⁴³ Diazonium fluoroborate is precipitated from water and usually stable to allow being dried in air. Specific to our reaction portfolio, a quick filtration to wash away the excess acid will help address the above mentioned problems. A stable diazonium fluoroborate is usually

prepared by diazotizing an arylamine with sodium nitrite and HCl, then precipitating the diazonium chloride with HBF₄ or NaBF₄. In our practice, we directly employed HBF₄ as the acid to run the diazotization reaction. After completion of diazotization, we performed a quick filtration in air and washed the collected orange solid with water, ethanol and water to remove the residual HBF₄. The obtained wet diazonium fluoroborate salt was suspended into cold water for the azidation with NaN₃. In this way, we have successfully prepared neopentyl, isobutyl, n-butyl, and n-propyl toluene-4-azide-3-sulfonates (**17-20**) at reasonably high yields (53-83%) (Scheme 2.7). All the azide-sulfonates **17-20** are ether soluble and worked up by extracting the aqueous mixture with ether. The neopentyl azide-sulfonate **17** is isolated as a yellow solid and the others **18-20** as brown oils.

Scheme 2.7 Synthesis of alkyl 2-azido-5-methylbenzenesulfonates

To verify the structure of the isolated diazonium fluoroborate, we took a ¹H NMR spectrum for **11-N₂⁺BF₄⁻** using dmsO-d₆ as the deuterated solvent. The three aromatic signals had shifted to downfield in comparison to its amine-sulfonate **11**. The diazonium fluoroborate **11-N₂⁺BF₄⁻** turned to a red solution and decomposed shortly after the NMR experiment. The azide-sulfonates **17-20** were characterized by interpreting ¹H and ¹³C NMR spectra. Compared with their corresponding amine-sulfonates **11-13**, **17-20** did not

show peaks around $\delta_{\text{H}} = 4.80$ ppm. This demonstrates the success of the conversion of the NH_2 group to the N_3 group. Aliphatic signals matched the corresponding neopentyl, isobutyl, n-butyl, and n-propyl substituents. This demonstrated all alkyl sulfonates survived the acidic condition (HONO and HBF_4) during the diazotization and the nucleophilic condition (NaN_3) during the azidation.

Synthesis of Alkyl 2-(Triaryl/alkyldiarylphosphiniminino)-5-methylbenzenesulfonates

As is shown in Scheme 2.8, alkyl 2-azido-5-methylbenzenesulfonates **17-20** were successfully converted to different phosphinimine-sulfonates (**21-26**) by Staudinger

Scheme 2.8 Synthesis of phosphinimine-sulfonate esters

reaction using a specific triarylphosphine like triphenylphosphine (Ph_3P) and tri-*p*-tolylphosphines ($(p\text{-tolyl})_3\text{P}$) or alkyldiarylphosphine like methyldiphenylphosphine (MePh_2P) in 1.05-1.2 equivalents.³ Respectively, **17** formed neopentyl 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate (**21**); **18** formed isobutyl 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate (**22**), 2-(tri-*p*-tolylphosphiniminino)-5-methylbenzenesulfonate (**25**) and 2-

(methyldiphenylphosphinimino-5-methylbenzenesulfonate (**26**); **19** formed n-butyl 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate (**23**); and **20** formed n-propyl 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate (**24**). The reactions were pretty straightforward. All were run in toluene at room temperature and completed in 4 hours. Yields are good to excellent except that for **26**. After completion, a typical Staudinger reaction resulted in a green solution. In the workup, toluene was removed and the resulting viscous residue was treated with hexanes-benzene 3:1 to remove the unreacted phosphine and the by-product phosphine oxide. This yields the desired solid product at a relatively high yield for each of phosphinimine-sulfonates (**21-23**, **25**, and **26**). In the case of **26**, derived from MePh₂P, the obtained viscous residue was still a viscous state in the mixture of hexanes-benzene 3:1. This made precipitation of **26** from the solution difficult. Decantations of the solvents had taken away relatively a large portion of the product. The actual isolated yield of **26** became low. The tough workup relates to the nature of the alkyl group in the phosphinimine motif.

The characterization of **21-26** was accomplished by ¹H, ³¹P, and ¹³C NMR spectra. ³¹P chemical shifts are particularly useful in determining product purity. Typically, a reaction mixture contains the desired phosphinimine-sulfonate, unreacted phosphine, and by-product phosphine oxide. They have characteristic ³¹P chemical shifts. NMR experiments showed that all the phosphinimine-sulfonates (**21-26**) resonate at 2-3 ppm on ³¹P NMR spectra. Phosphines have negative chemical shifts, $\delta_p = -5.0$ ppm for Ph₃P and $\delta_p = -28.0$ ppm for MePh₂P, whereas their oxides have positive chemical shifts, $\delta_p = 28.0$ ppm for Ph₃PO and $\delta_p = 30.0$ ppm for MePh₂PO. These experimental data for phosphines and phosphine oxides are identical to those in literature.⁴⁴ In addition, ¹H

NMR spectra clearly showed the incorporated phosphine units. For phosphinimine-sulfonates **21-24** bearing a $\text{Ph}_3\text{P}=\text{N}$ fragment, two typical sets of doublet of doublets in the aromatic area showed that the 2,6- and 3,5-proton signals were split by both the phenyl proton and the phosphorus nuclei. For phosphinimine-sulfonate **26**, the upfield doublet at $\delta_{\text{H}} = 30.0$ ppm demonstrated the presence of a $\text{MePh}_2\text{P}=\text{N}$ unit.

To diversify the steric bulk, we attempted coupling two *ortho*-bulky phosphines, (*o*-tolyl) $_3\text{P}$ and (1-naphthyl) $_3\text{P}$ with isobutyl toluene -4-azide-3-sulfonate **18** via the Staudinger route. We did not obtain desired phosphinimine-sulfonate products from the two *ortho*-bulky phosphines. Non-reactivity apparently relates to the disfavored steric

Scheme 2.9 Mechanism of Staudinger Reaction

hindrance from either (*o*-tolyl) $_3\text{P}$ or (1-naphthyl) $_3\text{P}$. Mechanistically, Staudinger reaction is initiated by the nucleophilic attack of triarylphosphine on the terminal nitrogen with partial positive charge (Scheme 2.9).⁴⁵ The resulting phosphonium-amide zwitterions (**27**) ring-closes presumably to form a 4-membered ring intermediate (**28**), which can undergo 2,2- σ migration to extrude N_2 and form the $\text{P}=\text{N}$ double bond which can resonate to its aza-ylide structure (**29**). However, in the case of (*o*-tolyl) $_3\text{P}$ or (1-naphthyl) $_3\text{P}$, too much

steric bulk on P and N atoms can hinder from forming 4-membered intermediate **28**, subsequently stop producing the desired phosphinimine structure **29**.

The steric bulk of phosphines can be quantitatively described using Tolman cone angles.⁴⁶ The larger the cone angle, the more hindered the steric bulk of a phosphine species. Steric hindrance is a limit of Staudinger reaction. Therefore, a phosphinimine's reactivity toward Staudinger reaction can be correlated to its cone angle. Tolman cone angles of some phosphines we are interested are listed in Table 2.1. Among the listed phosphines, (*o*-tolyl)₃P has the largest cone angle $\theta = 195^\circ$, therefore it is the most hindered phosphine species and does not react toward Staudinger reaction. PPh₃ and

Table 2.1 Tolman cone angles of phosphines

Phosphine	θ ($^\circ$)	Phosphine	θ ($^\circ$)
Ph ₃ P	145	BnPh ₂ P	152
MePh ₂ P	136	Bn ₃ P	165
Me ₂ PhP	122	(<i>o</i> -tolyl) ₃ P	195

MePh₂ have relatively small cone angles, they do react toward Staudinger reaction. Predictably, Me₂PhP, whose cone angle is the smallest, should be active in this reaction. Our further investigation also indicates that BnPh₂P and Bn₃P are workable phosphines. These three phosphine species will be introduced in later discussion. Currently, 165° (Bn₃P) is the largest cone angle to allow a phosphine to couple with an amine-sulfonate ester via the Staudinger route.

As a ligand to metal, the steric bulk is frequently demanded to be placed at the *ortho* position. For instance, *ortho*-methoxyphenyl is used in P[^]SO ligand. In the

ethylene copolymerization with methyl acrylate using $P^{\wedge}SO$ Pd complexes, two *ortho*-methoxy groups assist suppress the formation of Pd enolate complexes through an intermittent chelating effect to the metal center.^{9a} In the Brookhart α -diimine palladium polymerization, high polymers are possible due to a retarded chain transfer, which is realized by placing two 2,6-diisopropylphenyl groups on the α -diimine scaffold to block the axial faces of the metal center.⁴⁷ With the expectation to introduce *ortho*-bulky phosphines into our ligand backbone, we explored Kirsanov reaction.^{25b} Neopentyl and isobutyl toluidine-2-sulfonates (**10**, **11**) were respectively reacted with dibromotriphenylphosphorane (Ph_3PBr_2) in the presence of triethylamine in toluene at

Scheme 2.10 Kirsanov Reactions

room temperature (Scheme 2.10). After 16 hours, the desired neopentyl 2-(triphenylphosphinimino-5-methylbenzenesulfonate (**21**) from the starting amine-sulfonate **10** was isolated as a solid at a 55% yield. However, the other Kirsanov reaction resulted in a 3-component mixture primarily consisting of Ph_3PO and the starting amine-sulfonate **11**. The desired isobutyl 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate (**22**) was only a minor component in the mixture. The ^{31}P NMR spectrum indicated there were 6% phosphorus nuclei from **22** ($\delta_p = 2.2$ ppm) and all the

rest from Ph_3PO ($\delta_{\text{p}} = 29.0$ ppm). The attempted Kirsanov reaction did not show a more promising scenario than did the Staudinger route.

Deprotection of Alkyl 2-(Triphenylphosphiniminino)-5-methylbenzenesulfonates

Sulfonate esters are usually deprotected using iodides such as tetrabutylammonium iodide (Bu_4NI), tetramethylammonium iodide (Me_4NI), N,N-dimethylmethaniminium iodide ($[\text{Me}_2\text{NCH}_2]\text{I}$), and sodium iodide (NaI).^{9b, 24, 34-35} For example, 2 equivalents of Bu_4NI were used to deblock isobutyl sulfonates in the synthesis of nucleoside sulfonate derivatives (Scheme 2.11).³⁵ Acetone was used as the

Scheme 2.11 Isobutyl sulfonate cleaved by Bu_4NI

solvent and the deprotecting reaction was done at $55\text{ }^\circ\text{C}$ and in 12 hours. N,N-dimethylmethaniminium iodide, $[\text{Me}_2\text{NCH}_2]\text{I}$ was uniquely selected as a deprotecting reagent in the synthesis of NHC-sulfonate ligands.^{9b} As shown in Scheme 2.12, $[\text{Me}_2\text{NCH}_2]\text{I}$ played dual roles in the reaction. On the one hand,

Scheme 2.12 Isobutyl sulfonate cleaved by iminium iodide

the iodide anion worked to cleave the sulfonate ester bond; on the other hand, the N,N-dimethylmethaniminium cation provided a one-carbon unit to cyclize the imidazoline ring. The reaction was run in acetic acid and at 110 °C. In our experiments, we attempted using 2 equivalents of Bu₄NI to deblock isobutyl 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate **22**. The experiments were carried out by refluxing **22** in the presence of 2 equivalents of Bu₄NI in three different of solvents including benzene, CH₂Cl₂ and THF. None of the three conditions worked (Scheme 2.13). In consideration of potential unwanted aza-Wittig reaction between the substrate and acetone,⁴⁸ we did not select acetone as a solvent in these experiments. This could be one reason for non-

Scheme 2.13 ⁿBu₄I to cleave phosphinimine-sulfonate ester

reactivity. Compared to the substrates showing in scheme 2.11, the steric hindrance arisen from the *ortho* relationship of the sulfonate and phosphinimine groups may disfavor the reaction.

Piperidine is a nitrogen-based protic amine. Neopentyl sulfonate esters can tolerate piperidine.^{24, 49} In literature, it indicated that 6% piperidine in CDCl₃ was able to cleave isobutyl sulfates at room temperature (Scheme 2.14). In 24 hours, a 100%

Scheme 2.14 Isobutyl sulfate cleaved by piperidine

conversion was observed. Taking this strategy, we tried the deprotection of isobutyl phosphinimine-sulfonate **25** using piperidine as a deprotecting reagent. In a series of NMR experiments, 1 and 3 equivalents of piperidine were used. Two different temperatures, room temperature and 64 °C were tested. After 6 and 24 hours no reactions were observed for all the experiments (Scheme 2.15). As is shown in schem 2.14, the

Scheme 2.15 Piperidine to cleave isobutyl phosphinimine sulfonate

sulfate substrate reactive toward piperidine is not hindered at the *ortho* position. In contrast, our phosphinimine-sulfonate is hindered at the *ortho* position. Steric hindrance is apparently a factor affecting deprotection reactivity. Basing on these observations, we believed that a less bulky, more robust protecting group is necessary for the ease of deprotection. Logically, our deprotection work was moved to using n-propyl phosphinimine-sulfonate as a substrate.

n-Propyl 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate **24** was subjected to deprotecting experiments using two nitrogen bases, the protic piperidine and aprotic DABCO. In the piperidine experiments (Scheme 2.16), different piperidine

Scheme 2.16 Piperidine to cleave *n*-propyl phosphinimine sulfonate

<i>n</i>	30 (%)				Ph_3PO (%)
	1 day	2 days	3 days	4 days	
5	31	55	67	80	3
10	49	74	83		9
20	72	87			12

concentrations in CDCl_3 were used and the temperature was set at 68°C . Under these conditions, 1 and 2 equivalents of piperidine could cleave the sulfonate ester, but the reactions were slow. To reach above 80% conversion, 5, 10, and 20 equivalents of piperidine are required. During a 4-day experiment, the fastest cleavage of **24** by 20 equivalents of piperidine could be completed within 2 days with the best conversion ratio of $[\text{}^n\text{PrP}][\text{NP}^+\text{SO}]$ ($\text{}^n\text{PrP}$ = *N*-propylpiperidinium) (**30**) at 87%. In the cleavage reactions, the employment of 5, 10, 20 equivalents of piperidine caused oxidation of **30** to generate 3%, 9%, and 12% of $\text{Ph}_3\text{P}=\text{O}$ respectively. These data showed that the cleavage by piperidine followed an $\text{S}_\text{N}2$ mechanism, i.e., the reaction rate is as a function of piperidine concentration. It deserves to note that the amount of by product $\text{Ph}_3\text{P}=\text{O}$ relates to piperidine concentration but not time. Namely, for a given piperidine concentration, the $\text{Ph}_3\text{P}=\text{O}$ level is constant regardless of reaction time.

In the DABCO experiments, 2 and 5 equivalents of DABCO were used for cleavage of **24**. In 2 days, we observed 51% and 70% conversion to [ⁿPrD][NP⁺SO] (ⁿPrD = N-propyl-DABCO) (**31**) (Scheme 2.17) along with formation of

Scheme 2.17 DABCO to cleave phosphinimine sulfonate ester

n	day(s)	31 (%)	Ph ₃ PO (%)
2	1	32	8
	2	51	18
5	1	60	15
	2	70	28

triphenylphosphine oxide, whose content depended not only on DABCO concentration, but also on time. For the 2 equivalent DABCO reaction, 1 day caused 8% Ph₃P=O; 2 days caused 18% Ph₃P=O. For the 5 equivalent DABCO reaction, 1 day caused 15% Ph₃P=O; 2 days caused 28% Ph₃P=O. Compared with the protic base piperidine, the aprotic base DABCO deblocked the n-propyl sulfonates in a slow fashion but accompanying high level of Ph₃P=O. What reasons have made the two types of bases different in their reaction profiles?

Scheme 2.18 Proposed mechanism for DABCO experiments

a. Sulfonic acid oxidizes Ph_3P to $\text{Ph}_3\text{P=O}$

b. Observed sultam formation

c Proposed mechanism for DABCO experiments

In the DABCO experiments, we believed that decomposition of the sulfonate species (**31**) after deprotection of the phosphinimine-sulfonate ester **24** resulted in generation of $\text{Ph}_3\text{P=O}$. Literature shows that sulfonic acid can be an oxidant oxidizing Ph_3P to $\text{Ph}_3\text{P=O}$ (Scheme 2.18, a).⁵⁰ In a separate experiment, we found that heating isobutyl amine-sulfonate (**11**) in acetonitrile resulted in sultam (**32**) (Scheme 2.18, b). Sultam is a subliming compound and has been synthesized from toluidine-2-sulfonic acid (**1**) by Wu, *et al.*⁵¹ Thus, we proposed a decomposition mechanism involving sultam formation for the cleavage of **24** using DABCO as a nucleophile (Scheme 2.18, c). In

this proposed mechanism, the *in situ* formed anionic sulfonate species **31** undergoes nucleophilic attacking on phosphorus, where the P=N double bond can be reduced to P-N single bond generating an amide intermediate (**33**). Subsequently, the anionic amide attacks the electron positive sulfur to cleave the S-O(P) bond. Rearrangement of lone pair forms a 4-membered ring species, an anionic sultam species (**34**), releasing the byproduct Ph_3PO .

This important understanding led us to rationale that the structural difference between **30** and **31**, the existence of proton in **30** not in **31**, had made the reactivity of the piperidine experiments different than the DABCO experiments. Unlike the aprotic species **31**, the protic species **30** was stabilized by intermolecular hydrogen bonding (Scheme 2.19). The hydrogen bonding effect in **30** must have protected **30** from being further decomposed to **34** and $\text{Ph}_3\text{P}=\text{O}$ via the sultam route as is shown in Scheme 18c. In a word, both aprotic and protic bases can cleave the n-propyl phosphinimine- sulfonate ester but behave differently. Protonation is necessary to avoid forming Ph_3PO .

Scheme 2.19 Hydrogen bonding effect in piperidine experiments

Based on these observations, pyridinium tetrafluoroborate ([HPy][BF₄]) was chosen to react with **24**. The idea was that since pyridine has a lower pK_a (5.2) than phosphinimine (~9), [HPy][BF₄] could be able to protonate n-propyl phosphinimine-sulfonate **24** and release free pyridine, which can act as a nucleophile to cleave the ester bond. The *in situ* generated n-propyl phosphiniminium-sulfonate ester intermediate would be stable enough to avoid the proposed sultam route when the sulfonate ester bond was cleaved by the ‘aprotic’ pyridine. Pyridinium tetrafluoroborate was prepared by

Scheme 2.20 Pyridinium tetrafluoroborate to cleave phosphinimine sulfonate ester

protonating pyridine with tetrafluoroboric acid diethyl ether complex in diethyl ether.⁴² In a J. Young tube, pyridinium tetrafluoroborate and **24** were combined in a 1:1 ratio and dissolved with deuterated dichloromethane (Scheme 2.20). In 30 minutes, ¹H and ³¹P NMR showed complete protonation of **24** to n-propyl toluene-4-triphenylphosphoniminium-3-sulfonate (**35**). The ³¹P NMR showed a sharp peak at 25.5 ppm (**35**), downfield shifted from 2.2 ppm (**24**). The solution was heated to 44 °C for 24 hours and 88% cleavage was observed. On the ¹H NMR spectrum, a sharp doublet at δ_H = 10.27 ppm demonstrated the formation of a zwitterionic species, toluene-4-

phosphininium-3-sulfonate (**36**). The much downfield shifted chemical shift proves the presence of intramolecular hydrogen bonding and the doublet shows the presence of a germinal P atom ($^2J_{\text{PH}} = 9.6 \text{ Hz}$). $^{52,31}\text{P}$ NMR chemical shift for **36** appeared at 31.5 ppm. To speed up the cleavage, we added 1.5 equivalent of free pyridine to the reaction. The cleavage reached 95% after 8 hours (Scheme 2.21). These NMR based reactions

Scheme 2.21 Pyridinium tetrafluoroborate to cleave phosphininium sulfonate ester in the presence of pyridine

indicated that 1) protonation occurs before cleavage of sulfonate ester bond; 2) *in situ* generated free pyridine can cleave the sulfonate ester bond; 3) additional pyridine can boost the cleavage. Directed by these NMR scale reactions, a scaled up reaction was run. A solution of pyridinium tetrafluoroborate and **24** in dichloromethane was refluxed for 16

Scheme 2.22 Synthesis of phosphininium-sulfonate

hours. Purification by ether wash, silica gel chromatography, and precipitation using $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ afforded the zwitterionic species **36** (Scheme 2.22). Compound **36**, isolated cleanly, in a 96% yield and on a 1.6 g scale, is stable in air.

Compound **36** had been fully characterized using ^1H , ^{31}P , ^{13}C NMR spectra and 2D NMR including HSQC and HMBC. As is shown in the ^1H NMR spectra (Figure 2.2), A sharp doublet at $\delta_{\text{H}} = 10.27$ ppm (e) with a coupling constant $J_{\text{PH}} = 9.6$ Hz is

Figure 2.2 ^1H NMR of **36**

Table 2.2 ^{13}C , ^1H and 2D NMR Data of **36** (δ_{C} and δ_{H} in ppm; J in Hz)

Position	δ_{C} (J)	δ_{H} (J)	HSQC	HMBC
1	130.8	7.74s	CH	
2	135.8		C	H-3

3	22.2	2.24s	CH ₃	
4	133.2	6.81dd (8.0,1.2)	CH	
5	121.0d (3.9)	6.43d (8.0)	CH	
6	139.3d (8.5)		C	H-5
7	134.0d (1.5)		C	NH
8	122.5d (102.2)		C	NH; H-10
9	135.5d (10.9)	7.91m	CH	
10	132.0d (13.9)	7.68m	CH	
11	137.2d (3.1)	7.80m	CH	
		10.27d (10.0)	NH	

characteristic of the P=NH functionality. The aliphatic region gives only a methyl peak at $\delta_{\text{H}} = 2.26$ ppm (b), showing the deprotection is complete and clean. In the aromatic region, except the toluene backbone (a, c, and d), it is clear the phosphino phenyl groups (f, g, and h) are present in the structure. Their splitting patterns indicate the coupling from both proton and phosphorus nuclei. ¹H and ¹³C chemical shifts were assigned by aid of HSQC and HMBC (Table 2.2). As shown in Table 2.2, HSQC correlations allowed determination of the multiplicities of C-1(CH), C-3(CH₃), C-4(CH), C-5(CH), C-9(CH), C-10(CH), and C-11(CH). Quaternary carbons C-8, a doublet which has a uniquely large coupling constant (102.2 Hz), showed the connectivity directly with phosphorus. On HMBC, important correlations of C-2 to H-3, C-6 to H-5, C-7 to NH, and C-8 to NH and H-10 helped assignments of quaternary carbons.

One-Pot Synthesis of Zwitterionic Phosphiniminium-sulfonates

We have clearly demonstrated that triphenylphosphiniminium-sulfonate zwitterion is readily available through a series of synthetic manipulations like protecting the sulfonic acid, preparing the azide derivative, forming P=N double bond via Staudinger reaction, and deprotecting of the sulfonate ester. Our practice showed that, however, running Staudinger reaction to introduce some phosphines other than triaryarylphosphines frequently encountered difficulty in the workup which significantly lowered the yield of phosphinimine products. For instance, isobutyl 2-(methyldiphenylphosphiniminino)-5-methylbenzenesulfonate (**26**) was obtained by coupling MePh₂P with isobutyl 2-azido-5-methylbenzenesulfonate (**18**) at a low yield (22%) (Scheme 2.8). For removal of the starting MePh₂P and side product MePh₂PO, the reaction was treated with 3:1 hexanes-benzene. This work up did very good job in all triarylphosphine-related reactions, but not in this one. The mixture revealed high viscosity. Washing it with any solvent combinations (we tried ether-hexanes 1:3 and ether-benzene too 1:1) would take away too much products. Unfortunately, due to air sensitivity, washing the reaction mixture with certain solvents is the only way to pure products. In the workup of the zwitterions **36**, however, we easily obtained a satisfactory yield by chromatographic purification. The big point is the stability of the zwitterionic structure of **36**. To simple the workup and obtain a high yield, we developed a one-pot route for the zwitterion synthesis. As is shown in

Scheme 2.23 One-pot synthesis of phosphiniminium-sulfonates

Scheme 2.23, starting with n-propyl toluene-azide-sulfonate **17**, one-pot synthesis proceeds in tandem of three steps, phosphine coupling by Staudinger reaction, protonation of phosphinimine with pyridinium fluoroborate, and deprotection of n-propyl sulfonate ester with free pyridine. The Staudinger was performed in toluene. After 4 hours, toluene was removed and the obtained solid residue was dissolved in methylene chloride. Pyridinium fluoroborate and additional free pyridine were introduced. An overnight reflux readily produced the desired phosphiniminium-sulfates (**36-40**). Purification was performed using silica gel chromatography. The one-pot synthesis has been successfully applied but not limited to the coupling of phosphines including Ph_3P ($\theta = 145^\circ$), MePh_2P ($\theta = 136^\circ$), Me_2PhP ($\theta = 122^\circ$), BnPh_2P ($\theta = 152^\circ$), and Bn_3P ($\theta = 165^\circ$). In this way, zwitterionic **36-40** can be synthesized with good isolated yields (65-70%) from silica gel chromatography.

X-Ray Crystallography of 36 and 37

For understanding the structural features of **36** and **37**, X-ray crystallography study was conducted.³² For X-ray diffraction, single crystal of **36** was grown by slow

diffusion of benzene into a CH₂Cl₂ solution of **36**; that of **37** was grown by slow diffusion of pentane into a MeOH solution of **37**. The temperature for growing single crystals is at room temperature. Crystals were inspected carefully for their suitability for X-ray crystallography.

ORTEP plots generated from X-Ray crystallographic data, have confirmed the structures of **36** and **37** (Figure 2.3).

Figure 2.3. ORTEP plots of **36** and **37** (ellipsoids with 50% probability).

2.3 Conclusions

To obtain clean, stable phosphinimine-sulfonate ligands, we designed and practiced two synthetic methods using commercially available toluidine-2-sulfonic acid as the starting material. Targeting sodium phosphinimine-sulfonate, a 4-step synthesis without protection of the sulfonic acid does not successfully furnish a clean product. Taking the strategy of protecting the sulfonic acid group, we converted the starting amine-sulfonic acid to its alkyl esters such as neopentyl, isobutyl, n-butyl, and n-propyl amine-sulfonates for the purpose of protecting group screening. These alkyl amine-

sulfonates were transformed to alkyl azide-sulfonates for the Staudinger reaction to form alkyl phosphinimine-sulfonates. Deprotection experiments showed that neopentyl and isobutyl phosphinimine-sulfonates cannot be deblocked by Bu_4NI and piperidine due to the steric hindrance between the ester group and the bulky phosphinimino group. Further experiments demonstrated that n-propyl sulfonate is the proper protecting group which can accommodate the reaction conditions and the ease of deprotection. Initial deprotection experiments showed that both aprotic base DABCO and protic base piperidine worked to cleave the n-propyl triphenylphosphinimine-sulfonate along with Ph_3PO formation. In the DABCO experiments, The Ph_3PO level is relatively high and depends on the DABCO concentration. In the piperidine experiments, the Ph_3PO level is relatively low and unrelated to the piperidine concentration. To explain the difference between using DABCO and piperidine, we proposed two different mechanisms for them. DABCO cleaved the ester to produce an anionic triphenylphosphinimine-sulfonate species which can form Ph_3PO via a sultam route. However, the anionic triphenylphosphinimine-sulfonate species produced in the piperidine cleavage was stabilized by an intramolecular hydrogen bonding effect from the counter cation piperidinium species. This protected the anionic triphenylphosphinimine-sulfonate species from forming Ph_3PO via the sultam route. As a result, pyridinium fluoroborate was chosen as the deprotecting reagent. Pyridinium fluoroborate played dual roles in the cleavage reaction. It protonated phosphinimine to phosphiminium and released free pyridine. The phosphiminium form worked to inhibit the sultam route and the free pyridine cleaved the ester bond. The cleavage provided a zwitterionic ligand triphenylphosphiminium-sulfonate, which is sufficiently stable in air and can be

purified using silica gel chromatography. For the simplicity and ease of workup in the Staudinger reaction, a one-pot synthetic protocol has been created for zwitterionic phosphiniminium-sulfonates. One pot synthesis is a tandem reaction of Staudinger reaction, protonation, and deprotection. It provides a neat synthetic pathway for prolignands from a variety of phosphines including Ph_3P , MePh_2P , Me_2PhP , BnPh_2P , and Bn_3P .

In the study of phosphiniminium-sulfonate prolignand synthesis, a new methodology for protecting sulfonic acid groups has been developed. For the first time we successfully employed n-propyl sulfonate as a protecting group and used pyridinium fluoroborate as a deprotecting reagent. Protected by n-propyl sulfonates, sulfonate substrates can cleanly undergo a series of manipulations involving diazotization, azidation, and Staudinger reaction. Compared to commonly encountered neopentyl and isobutyl sulfonate esters, however, n-propyl sulfonates are more facile toward deprotection due to the reduced steric hindrance. Pyridinium tetrafluoroborate is proven to be an efficient deprotecting reagent for cleavage of n-propyl phosphiniminium-sulfonates. We believe that the methodology we developed for protection of sulfonic acid will find its new applications in organic synthesis.

2.4 Experimental Section

General Procedures. All manipulations were performed under N_2 or vacuum using standard Schlenk or high vacuum techniques or in N_2 -filled drybox unless otherwise specified. N_2 was purified by passage through columns containing activated molecular

sieves and Q-5 oxygen scavenger. Pentane, hexanes, toluene, benzene, and dichloromethane were purified by passage through columns of activated 4 Å molecular sieves. Diethyl ether and tetrahydrofuran were distilled from Na/benzophenone ketyl. CDCl_3 and CD_2Cl_2 were dried over CaH_2 for 24 hours, degassed by freeze-pump-thaw cycles, and vacuum transferred to a storage vessel. Ethylene (research grade) was obtained from Matheson and used as received. Chlorosulfonic acid from Alfa Aesar, toluidine-2-sulfonic acid from TCI America, PPh_3 , PMePh_2 , Bu_4NI , and NaN_3 from Aldrich, PMe_2Ph from Strem, $\text{P}(\text{C}_6\text{H}_5\text{CH}_2)\text{Ph}_2$ from Acros, and NaNO_2 from J.T. Baker were purchased and used as received. 1-Propanol was purchased from Aldrich and distilled from I_2 /magnesium granules. Piperidine was obtained from Aldrich and distilled before using. Dibromotriphenylphosphorane (Ph_3PBr_2) and pyridinium tetrafluoroborate ($[\text{HPy}][\text{BF}_4]$) were prepared as described in the literature.⁵¹ All other solvents were purchased from Aldrich and used without further purification. ^1H , ^{13}C , ^{31}P , ^{19}F , ^{11}B NMR spectra were recorded in Teflon valve sealed tubes on Varian 400 and 500 spectrometers at ambient probe temperature unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported versus SiMe_4 and were determined by reference to the residual ^1H and ^{13}C solvent peaks. ^{31}P , ^{19}F , and ^{11}B chemical shifts were referenced to external 85% aqueous H_3PO_4 , CF_3COOH , and $\text{BF}_3\cdot\text{Et}_2\text{O}$, respectively. All the ligands and their precursors bear a sulfonated toluidine parental structure which has an atom-labeling scheme as follows:

2-NH₂-5-CH₃C₆H₃SO₂Cl (5). To a flask containing ClSO₃H (20 mL, 300.89 mmol) cooled to 0 °C, toluidine-2-sulfonic acid (4 g, 21.36 mmol) was added portionwise (This and all other following manipulations in this reaction were performed in air). The reaction mixture was stirred for 1 hour at 0 °C and 2 hours at 80 °C. A brown solution was obtained. The brown solution was quickly poured onto a large amount of crushed ice in a 500 mL Erlenmeyer flask affording a yellow precipitate. The precipitate was then filtered and washed with water (3 x 50 mL) to give **5** as a bright yellow solid (3.08 g, 70%). ¹H NMR (CD₂Cl₂): δ 7.56 (s, 1H, 6-CH), 7.28 (dd, *J* = 8.0, 1.6, 1H, 4-CH), 6.78 (d, *J* = 8.0, 1H, 3-CH), 5.30 (bs, 2H, NH₂), 2.27 (s, 3H, 5-CH₃C₆H₃). ¹³C NMR (CD₂Cl₂): δ 143.5, 138.3, 127.9, 127.3, 125.1, 118.3, 19.7. Anal. Calcd for C₇H₈ClNO₂S: C, 40.88; H, 3.92; N, 6.81. Found: C, 40.56; H, 3.84; N, 6.61.

2-NH₂-5-CH₃C₆H₃SO₂OCH₂C(CH₃)₃ (10). To a solution of DABCO (1.09 g, 9.44 mmol) and neo-pentyl alcohol (0.69 g, 7.87 mmol) in CH₂Cl₂ (40 mL), toluidine-2-sulfonyl chloride (1.62 g, 7.87 mmol) was added portionwise at 0 °C. The clear yellow solution rapidly turned turbid. After 30 minutes, the reaction mixture was warmed to 25 °C and stirred for 16 hours, affording a white suspension. The suspension was separated using a silica gel plug (20 g) and CH₂Cl₂ (200 mL). The fractions (50 mL) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum yielding **10** as a greenish solid (1.65 g, 86%). ¹H NMR (CDCl₃): δ 7.49 (s, 1H, 6-CH), 7.16 (dd, *J* = 8.5, 2, 1H, 4-CH), 6.66 (d, *J* = 8.5, 1H, 3-CH), 4.80 (bs, 2H, NH₂), 3.63 (s, 2H, CH₂C(CH₃)₃), 2.26 (s, 3H, 5-CH₃), 0.91 (s, 9H, CH₂C(CH₃)₃). ¹³C NMR (CDCl₃): δ 143.9, 136.1, 129.9,

126.5, 117.4, 116.5, 79.4, 31.6, 26.0, 20.1. Anal. Calcd for C₁₂H₁₉NO₃S: C, 56.01; H, 7.44; N, 5.44. Found: C, 55.88; H, 7.37; N, 5.44.

2-NH₂-5-CH₃C₆H₃SO₂OCH₂CH(CH₃)₂ (11). To a solution of DABCO (2.02 g, 17.99 mmol) and 1-propanol (1.38 mL, 14.99 mmol) in CH₂Cl₂ (87 mL), toluidine-2-sulfonyl chloride (3.08 g,

14.99 mmol) was added portionwise at 0 °C. The clear yellow solution rapidly turned turbid. After 30 minutes, the reaction mixture was warmed to 25 °C and stirred for 16 hours, affording a white suspension. The suspension was separated using a silica gel plug (20 g) and CH₂Cl₂ (350 mL). The fractions (50 mL) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum yielding **11** as a colorless oil (2.64 g, 72%). ¹H NMR (CDCl₃): δ 7.49 (s, 1H, 6-CH), 7.16 (d, *J* = 8.0, 1H, 4-CH), 6.66 (d, *J* = 8.0, 1H, 3-CH), 4.80 (bs, 2H, NH₂), 3.77 (d, *J* = 6.4, 2H, CH₂CH(CH₃)₂), 2.26 (s, 3H, 5-CH₃), 1.95 (m, 1H, CH₂CH(CH₃)₂), 0.90 (d, *J* = 6.8, 6H, CH₂CH(CH₃)₂). ¹³C NMR (CDCl₃): δ 144.1, 136.3, 130.0, 126.8, 117.7, 116.9, 76.4, 28.2, 20.3, 18.8. Anal. Calcd for C₁₁H₁₇NO₃S: C, 54.30; H, 7.04; N, 5.76. Found: C, 54.68; H, 7.37; N, 5.44.

2-NH₂-5-CH₃C₆H₃SO₂O(CH₂)₃CH₃ (12). To a solution of DABCO (1.43 g, 12.79 mmol) and 1-buanol (0.98 mL, 10.65 mmol) in CH₂Cl₂ (60 mL), toluidine-2-sulfonyl chloride (**5**)

(2.19 g, 10.65 mmol) was added portionwise at 0 °C. The clear yellow solution rapidly turned turbid. After 30 minutes, the reaction mixture was warmed to 25 °C and stirred for 16 hours, affording a white suspension. The suspension was separated using a silica gel plug (25 g) and CH₂Cl₂ (350 mL). The fractions (50 mL) were analyzed by UV-Vis, and

those that contained the product were combined and dried under vacuum yielding **12** as a colorless oil (2.05 g, 80%). ^1H NMR (CDCl_3): δ 7.49 (s, 1H, 6-CH), 7.17 (d, $J = 8.0$, 1H, 4-CH), 6.67 (d, $J = 8.0$, 1H, 3-CH), 4.81 (bs, 2H, NH_2), 4.00 (t, $J = 6.4$, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.25 (s, 3H, 5- CH_3), 1.64 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.35 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.86 (t, $J = 7.6$, 3H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

2-NH₂-5-CH₃C₆H₃SO₂OCH₂CH₂CH₃ (13). To a solution of DABCO (2.88 g, 25.65 mmol) and 1-propanol (1.6 mL, 21.38 mmol) in CH_2Cl_2 (112 mL), toluidine-2-sulfonyl chloride (4.40 g, 21.68

mmol) was added portionwise at 0 °C. The clear yellow solution rapidly turned turbid. After 30 minutes, the reaction mixture was warmed to 25 °C and stirred for 16 hours, affording a white suspension. The suspension was separated using a silica gel plug (25 g) and CH_2Cl_2 (350 mL). The fractions (50 mL) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum yielding **13** as a colorless oil (3.98 g, 80%). ^1H NMR (CDCl_3): δ 7.50 (d, $J = 2.0$, 1H, 6-CH), 7.17 (dd, $J = 8.0$, 2.0, 1H, 4-CH), 6.67 (d, $J = 8.0$, 1H, 3-CH), 4.81 (bs, 2H, NH_2), 3.97 (t, $J = 6.5$, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.25 (s, 3H, 5- CH_3), 1.67 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.90 (t, $J = 7.0$, 3H, $\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (CDCl_3): δ 144.1, 136.3, 130.0, 126.8, 117.7, 116.9, 72.2, 22.4, 20.3, 10.2. Anal. Calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_3\text{S}$: C, 52.38; H, 6.59; N, 6.11. Found: C, 52.77; H, 6.30; N, 6.03.

2-N₃-5-CH₃C₆H₃SO₃CH₂C(CH₃)₃ (17). (a) *Diazotization using H₂SO₄ as the acid.* To a solution of concentrated H_2SO_4 (1.4 mL) and water (8 mL), **10** (2.06 g, 8.00 mmol) was added. The obtained suspension was cooled to 0 °C (This and all other following manipulations in this reaction

were performed in air). After 15 minutes, a solution of NaNO_2 (0.66g, 9.60 mmol) in water (8 mL) precooled to 0 °C was added dropwise with vigorous stirring. An orange foam formed immediately. After 1 hour stirring at 0 °C, urea (96 mg, 1.6 mmol) was added. After 15 minutes, charcoal (48 mg) was added. After 15 minutes, the reaction mixture was filtered. The clear colorless filtrate was cooled down to 0 °C. With vigorous stirring, a 0 °C solution of NaN_3 (0.88 g, 13.60 mmol) in water (8 mL) was added dropwise. A white precipitate was observed immediately. The mixture was stirred for 1 hour at 0 °C and 12 hours at 25 °C. The white precipitate was filtered off and dried in a vacuum oven at 35 °C for 12 hours, yielding **17** as a white solid (1.60 g, 71%). (b) *Diazotization using HBF_4 as the acid.* To a flask containing **10** (0.71 g, 2.50 mmol) cooled to 0 °C, a mixture of 2 mL water and 0.9 mL HBF_4 (48% aqueous solution) precooled to 0 °C was added (This and all other following manipulations in this reaction were performed in air). After 15 minutes, a solution of NaNO_2 (0.19 g, 2.70 mmol) in water (2 mL) precooled to 0 °C was added dropwise with vigorous stirring. An orange foam formed immediately. After 20 minutes, the orange foam was filtered and washed with a limited amount of 0 °C water (5 mL), 0 °C ethanol (5 mL), and 0 °C water (5 mL), affording an orange solid. Quickly after filtration, the collected solid was added to a flask containing 5 mL of 0 °C water resulting in an orange suspension. With vigorous stirring, a 0 °C solution of NaN_3 (0.28 g, 4.25 mmol) in water (2 mL) was added dropwise to the orange suspension. An orange precipitate was observed immediately. The mixture was stirred for 1 hour at 0 °C and 1 hour at 25 °C. The reaction mixture was extracted with Et_2O (3 x 25 mL). The organic layers were combined and dried over Na_2SO_4 . The Na_2SO_4 was filtered off and the volatiles were removed under vacuum

affording a brown oil. The oil was separated by column chromatography using silica gel (70 g) and hexanes. The column was eluted with hexanes (200 mL), hexanes-Et₂O 90:10 (200 mL), and hexanes-Et₂O 80:20 (600 mL). The fractions (50 mL) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum, yielding **17** as a white solid (0.38 g, 53%). ¹H NMR (CDCl₃): δ 7.80 (s, *J* = 1.5, 1H, 6-CH), 7.59 (dd, *J* = 8.0, 1.5, 1H, 4-CH), 7.22 (d, *J* = 8.0, 1H, 3-CH), 3.75 (s, 2H, CH₂C(CH₃)₃), 2.40 (s, 3H, 5-CH₃C₆H₃), 0.96 (s, 9H, CH₂C(CH₃)₃). ¹³C NMR (CDCl₃): δ 135.3, 134.6, 133.9, 130.8, 125.0, 118.9, 79.3, 30.7, 25.0, 19.7, 14.2. Anal. Calcd for C₁₂H₁₇N₃O₃S: C, 50.87; H, 6.05; N, 14.83. Found: C, 50.98; H, 5.94; N, 14.61.

2-N₃-5-CH₃C₆H₃SO₃CH₂CH(CH₃)₂ (18). To a flask containing **11** (2.00 g, 8.22 mmol) cooled to 0 °C, a mixture of 3 mL water and 3 mL HBF₄ (48% aqueous solution) precooled to 0 °C was added

(This and all other following manipulations in this reaction were performed in air). After 15 minutes, a solution of NaNO₂ (0.60 g, 8.63 mmol) in water (3 mL) precooled to 0 °C was added dropwise with vigorous stirring. An orange foam formed immediately. After 20 minutes, the orange foam was filtered and washed with a limited amount of 0 °C water (15 mL), 0 °C ethanol (15 mL), and 0 °C water (15 mL), affording an orange solid. Quickly after filtration, the collected solid was added to a flask containing 7 mL of 0 °C water resulting in an orange suspension. With vigorous stirring, a 0 °C solution of NaN₃ (0.91 g, 13.95 mmol) in water (3 mL) was added dropwise to the orange suspension. An orange precipitate was observed immediately. The mixture was stirred for 1 hour at 0 °C and 12 hour at 25 °C. The solid was filtered off and washed with 0 °C water (3x15 mL), then dried in a vacuum oven at 35 °C for 12 hours, yielding **18** as a yellowish solid (1.93

g, 87%). ^1H NMR (CDCl_3): δ 7.79 (s, 1H, 6-CH), 7.44 (dd, J = 8.4, 0.8, 1H, 4-CH), 7.21 (d, J = 8.4, 1H, 3-CH), 3.88 (d, J = 6.4, 2H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 2.39 (s, 3H, 5- $\text{CH}_3\text{C}_6\text{H}_3$), 2.01 (m, 2H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 0.94 (d, J = 6.8, 6H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3): δ 136.4, 135.5, 134.9, 131.8, 126.1, 119.9, 77.1, 28.1, 20.7, 10.6. Anal. Calcd for

$\text{C}_{11}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$: C, 49.06; H, 5.61; N, 15.60. Found: C, 49.30; H, 5.57; N, 15.42.

2-N₃-5-CH₃C₆H₃SO₃(CH₂)₃CH₃ (19). To a flask containing **12**

(2.05 g, 8.42 mmol) cooled to 0 °C, a mixture of 3 mL water and 3 mL HBF_4 (48% aqueous solution) precooled to 0 °C was added (This and all other following manipulations in this reaction were performed in air). After 15 minutes, a solution of NaNO_2 (0.61g, 8.84 mmol) in water (3 mL) precooled to 0 °C was added dropwise with vigorous stirring. An orange foam formed immediately. After 20 minutes, the orange foam was filtered and washed with a limited amount of 0 °C water (10 mL), 0 °C ethanol (10 mL), and 0 °C water (10 mL), affording an orange solid. Quickly after filtration, the collected solid was added to a flask containing 6 mL of 0 °C water resulting in an orange suspension. With vigorous stirring, a 0 °C solution of NaN_3 (0.93 g, 14.31 mmol) in water (3 mL) was added dropwise to the 0 °C orange suspension. An orange oil was observed immediately. The mixture was stirred for 1 hour at 0 °C and 1 hour at 25 °C. The reaction mixture was extracted with Et_2O (3 x 10 mL). The organic layers were combined and dried over Na_2SO_4 . The Na_2SO_4 was filtered off and the volatiles were removed under vacuum yielding **19** as a brownish oil (1.76 g, 77%). ^1H NMR (CDCl_3): δ 7.79 (s, 1H, 6-CH), 7.44 (dd, J = 8.4, 0.8, 1H, 4-CH), 7.21 (d, J = 8.4, 1H, 3-CH), 4.13 (t, J = 6.4, 2H,

$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.40 (s, 3H, 5- $\text{CH}_3\text{C}_6\text{H}_3$), 1.69 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.41 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.89 (t, $J = 7.6$, 3H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

2-N₃-5-CH₃C₆H₃SO₃CH₂CH₂CH₃ (20). To a flask containing **13** (3.98 g, 17.34 mmol) cooled to 0 °C, a mixture of 6 mL water and 6 mL HBF₄ (48% aqueous solution) precooled to 0 °C was added

(This and all other following manipulations in this reaction were performed in air). After 15 minutes, a solution of NaNO₂ (1.26g, 18.21 mmol) in water (6 mL) precooled to 0 °C was added dropwise with vigorous stirring. An orange foam formed immediately. After 20 minutes, the orange foam was filtered and washed with a limited amount of 0 °C water (15 mL), 0 °C ethanol (15 mL), and 0 °C water (15 mL), affording an orange solid.

Quickly after filtration, the collected solid was added to a flask containing 12 mL of 0 °C water resulting in an orange suspension. With vigorous stirring, a 0 °C solution of NaN₃ (1.92 g, 29.48 mmol) in water (6 mL) was added dropwise to the 0 °C orange suspension. An orange oil was observed immediately. The mixture was stirred for 1 hour at 0 °C and 1 hour at 25 °C. The reaction mixture was extracted with Et₂O (3 x 20 mL). The organic layers were combined and dried over Na₂SO₄. The Na₂SO₄ was filtered off and the volatiles were removed under vacuum yielding **20** as a brownish oil (3.65 g, 82%). ¹H NMR (CDCl₃): δ 7.80 (s, 1H, 6-CH), 7.44 (dd, $J = 8.4$, 0.8, 1H, 4-CH), 7.21 (d, $J = 8.4$, 1H, 3-CH), 4.09 (t, $J = 6.4$, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.40 (s, 3H, 5- $\text{CH}_3\text{C}_6\text{H}_3$), 1.74 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.96 (t, $J = 7.6$, 3H, CH₃). ¹³C NMR (CDCl₃): δ 136.4, 135.6, 134.9, 131.7, 126.2, 119.9, 72.9, 22.4, 20.7, 15.2, 10.0. Anal. Calcd for C₁₀H₁₃N₃O₃S: C, 47.05; H, 5.13; N, 16.46. Found: C, 47.34; H, 5.06; N, 16.22.

2-((C₆H₅)₃P=N)-5-CH₃C₆H₃SO₃CH₂C(CH₃)₃ (21**). (a) via**

Staudinger Reaction. To a solution of PPh₃ (1.78 g, 6.79 mmol) in

toluene (15 mL), a solution of **17** (1.60 g, 5.66 mmol) in toluene

(15 mL) was added via cannula. After stirring for 4 hours, a white precipitate formed.

The solid was filtered and washed with a mixture of 1:3 benzene-hexanes (3 x 15 mL),

yielding an off-white solid **21** (2.79 g, 95%). (b) via *Kirsanov Reaction*. To a solution of

10 (0.26 g, 1.00 mmol) in CH₂Cl₂ (5 mL), a solution of PPh₃Br₂ (0.42 g, 1.00 mmol) in

CH₂Cl₂ (5 mL) was added via cannula. Et₃N (0.14 mL, 1.0 mmol) was added.

Immediately, a green solution was observed. After stirring for 16 hours, the solution was pumped down and the resulting residue was dissolved in THF (15 mL) to result in a white precipitate. The solid was filtered onto a layer of Celite and washed down with CH₂Cl₂

(15 mL). Evaporation of the CH₂Cl₂ solution afforded a solid, which was dried in a

vacuum oven yielding **21** as an off-white solid (0.26 g, 50%). ¹H NMR (CD₂Cl₂): δ 7.83

(m, 6H, 2,6-CH of (C₆H₅)₃P=N-), 7.63 (s, 1H, 6-CH of -C₆H₃SO₃-), 7.55 (m, 3H, 4-CH

of (C₆H₅)₃P=N-), 7.48 (m, 6H, 3,5-CH of (C₆H₅)₃P=N-), 6.88 (d, *J* = 8.4, 1H, 4-CH of -

C₆H₃SO₃-), 6.40 (d, *J* = 8.4, 1H, 3-CH of -C₆H₃SO₃-), 3.61 (s, 2H, CH₂C(CH₃)₃), 2.20 (s,

3H, 5-CH₃ of -C₆H₃SO₃-), 0.81 (s, 9H, CH₂C(CH₃)₃). ³¹P NMR (CD₂Cl₂): δ 2.3. ¹³C

NMR (CD₂Cl₂): δ 148.7, 134.6, 132.7 (d, *J*_{PC} = 10.1, *ortho*-CH of (C₆H₅)₃P=N-), 131.9

(d, *J*_{PC} = 3.1, *para*-CH of (C₆H₅)₃P=N-), 131.5 (d, *J* = 2.3), 130.3 (d, *J*_{PC} = 99.9, ipso C

of (C₆H₅)₃P=N-), 128.7 (d, *J*_{PC} = 12.4, *meta*-CH of (C₆H₅)₃P=N-), 126.6 (d, *J* = 24.8),

124.9, 122.7 (d, *J* = 10.9), 78.9, 30.6, 25.9, 19.9. Anal. Calcd for C₃₀H₃₂NO₃PS: C, 69.61;

H, 6.23; N, 2.71. Found: C, 69.27; H, 6.09; N, 2.74.

2-((C₆H₅)₃P=N)-5-CH₃C₆H₃SO₃CH₂CH(CH₃)₂ (22). To a

solution of PPh₃ (1.29 g, 4.91 mmol) in toluene (15 mL), a solution of **18** (1.10 g, 4.09 mmol) in toluene (15 mL) was added via cannula. After stirring for 4 hours, a white precipitate formed. The

solid was filtered and washed with a mixture of 1:3 benzene-hexanes (3 x 15 mL),

yielding an off-white solid **22** (1.84 g, 89%). ¹H NMR (CD₂Cl₂): δ 7.82 (m, 6H, 2,6-CH

of (C₆H₅)₃P=N-), 7.63 (s, 1H, 6-CH of -C₆H₃SO₃-), 7.58 (m, 3H, 4-CH of (C₆H₅)₃P=N-),

7.49 (m, 6H, 3,5-CH of (C₆H₅)₃P=N-), 6.89 (d, *J* = 7.6, 1H, 4-CH of -C₆H₃SO₃-), 6.40 (d,

J = 7.6, 1H, 3-CH of -C₆H₃SO₃-), 3.70 (d, *J* = 6.4, 2H, CH₂CH(CH₃)₂), 2.20 (s, 3H, 5-

CH₃ of -C₆H₃SO₃-), 1.81 (m, 2H, CH₂CH(CH₃)₂), 0.78 (d, *J* = 6.4, 3H, CH₂CH(CH₃)₂).

³¹P NMR (CD₂Cl₂): δ 2.5. ¹³C NMR (CD₂Cl₂): δ 148.6, 134.6, 132.6 (d, *J*_{PC} = 10.1,

ortho-CH of (C₆H₅)₃P=N-), 131.9 (d, *J*_{PC} = 2.3, *para*-CH of (C₆H₅)₃P=N-), 131.4 (d, *J* =

3.1), 130.3 (d, *J*_{PC} = 100.6, ipso C of (C₆H₅)₃P=N-), 128.7 (d, *J*_{PC} = 12.4, *meta*-CH of

(C₆H₅)₃P=N-), 126.6 (d, *J* = 24.7), 125.1, 122.7 (d, *J* = 10.8), 75.6, 28.11, 19.9, 18.5.

Anal. Calcd for C₂₉H₃₀NO₃PS: C, 69.17; H, 6.00; N, 2.78. Found: C, 69.06; H, 5.99; N,

2.77.

2-((C₆H₅)₃P=N)-5-CH₃C₆H₃SO₃(CH₂)₂CH₃ (23). To a

solution of PPh₃ (2.06 g, 7.84 mmol) in toluene (10 mL), a

solution of **19** (1.76 g, 6.53 mmol) in toluene (10 mL) was

added via cannula. After 4 hours, a brown solution was observed. The solution was

pumped down to give a gluey residue. The residue was treated with 1:3 benzene-hexanes

(24 mL), affording a precipitate. The solid was filtered and washed with a mixture of 1:3

benzene-hexanes (3 x 15 mL) and hexanes, yielding an off-white powder **23** (1.95 g, 59%). ^1H NMR (CDCl_3): δ 7.83 (m, 6H, 2,6-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 7.68 (s, 1H, 6-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 7.53 (m, 3H, 4-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 7.46 (m, 6H, 3,5-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 6.86 (d, $J = 8.0$, 1H, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 6.40 (d, $J = 8.0$, 1H, 3-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 3.95 (t, $J = 6.4$, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.20 (s, 3H, 5- CH_3 of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 1.47 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.22 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.71 (t, $J = 7.6$, 3H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (CDCl_3): δ 2.2. ^{13}C NMR (CDCl_3): δ 148.7, 134.7, 132.7 (d, $J_{\text{PC}} = 10.1$, *ortho*-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 131.9 (d, $J_{\text{PC}} = 2.4$, *para*-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 131.6 (d, $J = 2.4$), 130.5 (d, $J_{\text{PC}} = 100.0$, ipso C of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 128.7 (d, $J_{\text{PC}} = 12.3$, *meta*-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 126.6 (d, $J = 24.0$), 124.9, 122.7 (d, $J = 10.8$), 69.5, 31.0, 20.2, 18.7, 13.5.

2-((C_6H_5) $_3\text{P}=\text{N}$)-5-

$\text{CH}_3\text{C}_6\text{H}_3\text{SO}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (24**).** To a solution of PPh_3 (1.95 g, 7.43 mmol) in toluene (20 mL), a solution of **20** (1.58 g, 6.20 mmol) in toluene (10 mL) was added via cannula. After 4 hours, a white

precipitate formed. The solid was filtered and washed with a mixture of 1:3 benzene-hexanes (3 x 15 mL), yielding an off-white solid **24** (1.90 g, 63%). ^1H NMR (CDCl_3): δ 7.83 (m, 6H, 2,6-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 7.69 (s, 1H, 6-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 7.53 (m, 3H, 4-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 7.46 (m, 6H, 3,5-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 6.86 (dd, $J = 8.0$, 1.6, 1H, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 6.40 (d, $J = 8.0$, 1H, 3-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 3.91 (t, $J = 6.4$, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.20 (s, 3H, 5- CH_3 of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 1.52 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.77 (t, $J = 7.6$, 3H, $\text{CH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (CDCl_3): δ 2.3. ^{13}C NMR (CDCl_3): δ 148.7, 134.7, 132.7 (d, $J_{\text{PC}} = 10.1$, *ortho*-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 131.9 (d, $J_{\text{PC}} = 3.1$, *para*-CH of

(C₆H₅)₃P=N-), 131.6 (d, $J = 2.3$), 131.0 (d, $J_{PC} = 154.9$, ipso C of (C₆H₅)₃P=N-), 128.7 (d, $J_{PC} = 12.4$, *meta*-CH of (C₆H₅)₃P=N-), 126.7 (d, $J = 24.0$), 125.0, 122.6 (d, $J = 10.9$), 71.2, 22.4, 20.2, 10.1. Anal. Calcd for C₂₈H₂₈NO₃PS: C, 68.69; H, 5.76; N, 2.86. Found: C, 68.53; H, 5.70; N, 2.87.

2-((*p*-Tolyl)₃P=N)-5-

CH₃C₆H₃SO₃CH₂CH(CH₃)₂ (25). To a solution of (*p*-tolyl)₃P (1.34 g, 4.40 mmol) in toluene (10 mL), a solution of **18** (1.12 g, 4.19 mmol) in toluene (15 mL) was added via cannula. After stirred for a while at 25 °C, the mixture was heated to 60 °C and stirred for 6 hours to give brown solution. Toluene was removed under vacuum, resulting in a viscous residue. Trituration of this residue twice with 1:3 benzene-hexanes (25 mL) and evaporation of the remaining solvents under vacuum yielded **25** as a white solid (1.69 g, 74%). ¹H NMR (CDCl₃): δ 7.68 (m, 6H, 2,6-CH of (*p*-tolyl)₃P=N-), 7.60 (s, 1H, 6-CH of -C₆H₃SO₃-), 7.29 (m, 6H, 3,5-CH of (*p*-tolyl)₃P=N-), 6.86 (d, $J = 8.4$, 1H, 4-CH of -C₆H₃SO₃-), 6.41 (d, $J = 8.4$, 1H, 3-CH of -C₆H₃SO₃-), 3.68 (d, $J = 6.8$, 2H, CH₂CH₂(CH₃)₂), 2.39 (s, 9H, CH₃ of *p*-tolyl), 2.19 (s, 3H, 5-CH₃ of -C₆H₃SO₃-), 1.80 (m, 2H, CH₂CH₂(CH₃)₂), 0.79 (d, $J = 6.8$, 3H, CH₂CH₂(CH₃)₂). ³¹P NMR (CDCl₃): δ 3.1. ¹³C NMR (CDCl₃): δ 149.1, 142.1, 134.5, 132.7 (d, $J_{PC} = 10.8$, *ortho*-CH of (*p*-tolyl)₃P=N-), 131.5 (d, $J_{PC} = 3.1$), 129.3 (d, $J_{PC} = 12.4$, *ortho*-CH of (*p*-tolyl)₃P=N-), 127.5 (d, $J_{PC} = 102.2$, ipso C of (*p*-tolyl)₃P=N-), 126.5, 124.4, 122.6 (d, $J_{PC} = 10.8$), 75.5, 28.1, 21.5, 20.2, 18.8.

2-(CH₃(C₆H₅)₂P=N)-5-CH₃C₆H₃SO₃CH₂CH(CH₃)₂ (26).

To a solution of 2-N₃-5-CH₃C₆H₃SO₃CH₂CH(CH₃)₂ (0.81 g, 3.00

mmol) in toluene (20 mL), MePh₂P (0.59 mL, 3.15 mmol) was added via a syringe. After stirring for 4 hours at 25 °C, the mixture was heated to 60 °C and stirred for 6 hours to give a brown solution. Toluene was removed under vacuum, resulting in a viscous residue. Trituration of this residue twice with 2:1 Et₂O-hexanes (25 mL) and evaporation of the solvent under vacuum yielded **26** as a beige solid (0.29 g, 22%). ¹H NMR (CD₂Cl₂): δ 7.88 (m, 4H, 2,6-CH of -(C₆H₅)₂P=N-), 7.63 (s, 1H, 6-CH of -C₆H₃SO₃-), 7.44-7.58 (m, 6H, 3,5- and 4-CH of -(C₆H₅)₂P=N-), 6.93 (dd, *J* = 8.4, 1.6, 1H, 4-CH of -C₆H₃SO₃-), 6.33 (d, *J* = 8.4, 1H, 3-CH of -C₆H₃SO₃-), 3.81 (d, *J* = 6.4, 2H, CH₂CH(CH₃)₂), 2.20 (s, 3H, 5-CH₃ of -C₆H₃SO₃-), 2.16 (d, *J*_{PH} = 12.8, 3H, -CH₃P=N-), 1.93 (m, 1H, CH₂CH(CH₃)₂), 0.88 (d, *J* = 6.8, 6H, CH₂CH(CH₃)₂). ³¹P NMR (CD₂Cl₂): δ 2.8. ¹³C NMR (CD₂Cl₂): δ 149.1, 134.7, 132.2, 131.8 (d, *J*_{PC} = 2.3, *para*-CH of -(C₆H₅)₂P=N-), 131.3 (d, *J*_{PC} = 10.0, *ortho*-CH of (C₆H₅)₂P=N-), 128.8 (d, *J*_{PC} = 11.6, *meta*-CH of -(C₆H₅)₂P=N-), 126.8, 126.7 (d, *J*_{PC} = 50.9, ipso-C of -(C₆H₅)₂P=N-), 124.8, 122.5 (d, *J* = 13.2), 75.8, 28.2, 19.8, 18.6, 13.7 (d, *J*_{PC} = 62.0). Anal. Calcd for C₂₄H₂₈NO₃PS: C, 65.29; H, 6.39; N, 3.17. Found: C, 65.55; H, 5.02; N, 2.87.

Attempted Synthesis of [ⁿBu₄N] [2-(Ph₃P=N)-5-CH₃C₆H₃SO₃] by Deprotection of 2-(Ph₃P=N)-5-CH₃C₆H₃SO₃ⁱBu (22**) with [ⁿBu₄N][I]**

(a) *In Benzene.* To a 100 mL single neck round bottom flask containing two solids 2-(Ph₃P=N)-5-CH₃C₆H₃SO₃ⁱBu (**22**) (504 mg, 1 mmol) and [ⁿBu₄N][I] (369 mg, 1 mmol), a H₂O condenser was attached and dry benzene (15 mL) was added via syringe. The mixture was stirred under N₂ and refluxed. After 30 minutes, a brown solution was observed. The reaction was monitored by taking a 0.2 mL aliquot after 4 hours and 12 hours. Each aliquot was placed in a valved NMR tube and the C₆H₆ was removed under

vacuum. The resulting oily residue was redissolved using CD₂Cl₂ (0.7 mL) which was added via vacuum transfer at -196 °C. The tube was sealed and warmed to 25 °C and shaken to produce a clear light yellow solution. The ¹H NMR spectra obtained in CD₂Cl₂ of the 4 and 12 hour intervals showed only unreacted starting material and no reaction had occurred.

(b) In THF. To a 100 mL single neck round bottom flask containing two solids 2-(Ph₃P=N)-5-CH₃C₆H₃SO₃ⁱBu (**22**) (504 mg, 1 mmol) and ⁿBu₄NI (369 mg, 1 mmol), a H₂O condenser was attached and dry THF (15 mL) was added via syringe. The mixture was stirred under N₂ and refluxed for 12 hours, resulting in yellow solution. The reaction was monitored by taking a 0.2 mL aliquot. The aliquot was placed in a valved NMR tube and the THF was removed under vacuum. The resulting oily residue was redissolved using CD₂Cl₂ (0.7 mL) which was added via vacuum transfer at -196 °C. The tube was sealed and warmed to 25 °C and shaken to produce a clear pale yellow solution. The ¹H NMR spectrum obtained in CD₂Cl₂ showed only unreacted starting material **22** and no reaction had occurred.

Generation of [ⁿPrPip][2-(Ph₃P=N)-5-CH₃C₆H₃SO₃] (ⁿPrPip = 1- n-Propylpiperidinium) (30**) by Deprotection of 2-(Ph₃P=N)-5-CH₃C₆H₃SO₃ⁿPr (**24**) with Piperidine**

With 1 Equivalent of Piperidine. A valved NMR tube was loaded with **24** (49 mg, 0.1 mmol) and CDCl₃ (0.5 mL) was added via vacuum transfer at -196 °C. After flushed with N₂ gas, the tube was sealed and warmed to 25 °C and shaken to produce a clear colorless solution. Via a microsyringe, piperidine (10 µL, 0.1 mmol) was added quickly after opening the

valve of the sealed tube. The NMR tube was resealed immediately and subjected to a freeze-pump-thaw cycle. The tube was flushed with N₂ and warmed to 25 °C to produce a clear colorless solution. ¹H and ³¹P NMR spectra established that **30** had not formed. The solution was heated to 64 °C for 5 hours. ¹H and ³¹P NMR spectra established that **30** had not formed. The solution was heated to 68 °C for 24 hours, 48 hours, 68 hours, 90 hours, and 120 hours. ¹H and ³¹P NMR spectra were obtained for each time interval. The integration of ³¹P NMR spectra established that after 24 hours at 68 °C, 4.2% **30** and 1.1% Ph₃PO had formed. It was observed that after 48 hours at 68 °C, 22.7% **30** and 1.7% Ph₃PO had formed; after 68 hours, 54.6% **30** and 3% Ph₃PO had formed; after 90 hours, 55.8% **30** and 2.5% Ph₃PO had formed; after 120 hours, 57.1% **30** and 2.8% Ph₃PO had formed. ¹H and ³¹P NMR data from the 120 hour experiment are as follows: ¹H NMR (CDCl₃): δ 7.71-7.90 (m, 16.1H, 2,6-CH of (C₆H₅)₃P=N- in **24** and **30**), 7.26-7.70 (m, 24.3H, 6-CH of -C₆H₃SO₃-, 4-CH of (C₆H₅)₃P=N-, and 3,5-CH of (C₆H₅)₃P=N- in **24** and **30**), 6.83 (dd, *J* = 8.0, 1.2, 1.0H, 4-CH of -C₆H₃SO₃- in **24**), 6.72 (dd, *J* = 8.4, 1.2, 1.5H, 4-CH of -C₆H₃SO₃- in **30**) 6.34-6.40 (m, 2.4H, 3-CH of -C₆H₃SO₃- in **24** and **30**), 3.86 (t, *J* = 6.8, 2.0H, CH₂CH₂CH₃ in **24**), 2.86 (t, *J* = 5.6, 4.6H, CH₂CH₂CH₃ in 1-n-propylpiperidinium), 2.35 (bs, 5.1H, NH in piperidine and 1-n-propylpiperidinium), 2.17(d, 7.3H, 5-CH₃ of -C₆H₃SO₃- in **30** and **24**), 1.30-1.70 (m, 20.9H, CH₂CH₂CH₃ in **24** and **30**; -(CH₂)₅- in piperidine and 1-n-propylpiperidinium), 0.87(t, *J* = 7.6, 3.9H, CH₂CH₂CH₃ in **30**), 0.74(t, *J* = 7.6, 3H, CH₂CH₂CH₃ in **24**). ³¹P NMR (CDCl₃): δ 29.0 (2.8%, Ph₃PO), 22.9 (57.1%, **30**), 2.4 (40.1%, **24**).

With 2 Equivalents of Piperidine. A valved NMR tube was loaded with **24** (49 mg, 0.1 mmol) and CDCl₃ (0.5 mL) was added via vacuum transfer at -196 °C. After flushed with

N_2 gas, the tube was sealed and warmed to 25 °C and shaken to produce a clear colorless solution. Via a microsyringe, piperidine (20 μL , 0.2 mmol) was added quickly after opening the valve of the sealed tube. The NMR tube was resealed immediately and subjected to a freeze-pump-thaw cycle. The tube was flushed with N_2 and warmed to 25 °C to produce a clear colorless solution. ^1H and ^{31}P NMR spectra established that **30** had not formed. The solution was heated to 64 °C for 5 hours. ^1H and ^{31}P NMR spectra established that **30** had not formed. The solution was heated to 68 °C for 24 hours, 48 hours, 68 hours, 90 hours, and 120 hours. ^1H and ^{31}P NMR spectra were obtained for each time interval. The integration of ^{31}P NMR spectra established that after 24 hours at 68 °C, 12.3% **30** and 2.3% Ph_3PO had formed. It was observed that after 48 hours at 68 °C, 43.8% **30** and 3.2% Ph_3PO had formed; after 68 hours, 80.1% **30** and 4.4% Ph_3PO had formed; after 90 hours, 80.9% **30** and 3.7% Ph_3PO had formed; after 120 hours, 82.2% **30** and 4.7% Ph_3PO had formed. ^1H and ^{31}P NMR data from the 120 hour experiment are as follows: ^1H NMR (CDCl_3): δ 7.74-7.90 (m, 8.0H, 2,6-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$ in **24** and **30**), 7.28-7.70 (m, 11.8H, 6-CH of $-\text{C}_6\text{H}_3\text{SO}_3-$, 4-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$, and 3,5-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$ in **24** and **30**), 6.81 (m, 0.1H, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3-$ in **24**), 6.70 (dd, $J = 8.4, 1.2, 1.5\text{H}$, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3-$ in **30**), 6.34-6.40 (m, 1.1H, 3-CH of $-\text{C}_6\text{H}_3\text{SO}_3-$ in **24** and **30**), 3.84 (t, $J = 6.8, 2.0\text{H}$, $\text{CH}_2\text{CH}_2\text{CH}_3$ in **24**), 2.87 (t, $J = 5.6, 4.6\text{H}$, $\text{CH}_2\text{CH}_2\text{CH}_3$ in 1-n-propylpiperidinium), 2.34 (bs, 5.1H, NH in piperidine and 1-n-propylpiperidinium), 2.15(bs, 3.6H, 5-CH₃ of $-\text{C}_6\text{H}_3\text{SO}_3-$ in **30** and **24**), 1.40-1.70 (m, 18.8H, $\text{CH}_2\text{CH}_2\text{CH}_3$ in **24** and **30**; $-(\text{CH}_2)_5-$ in piperidine and 1-n-propylpiperidinium), 0.84(t, $J = 7.6, 3.0\text{H}$, $\text{CH}_2\text{CH}_2\text{CH}_3$ in **30**), 0.74(t, $J = 7.6, 0.5\text{H}$, $\text{CH}_2\text{CH}_2\text{CH}_3$ in **24**). ^{31}P NMR (CDCl_3): δ 29.0 (4.7%, Ph_3PO), 15.4 (82.3%, **30**), 2.4 (13.0%, **24**).

With 5 Equivalents of Piperidine. A valved NMR tube was loaded with **24** (49 mg, 0.1 mmol) and CDCl₃ (0.5 mL) was added via vacuum transfer at -196 °C. After flushing with N₂ gas, the tube was sealed and warmed to 25 °C and shaken to produce a clear colorless solution. Via a microsyringe, piperidine (50 µL, 0.5 mmol) was added quickly after opening the valve of the sealed tube. The NMR tube was resealed immediately and subjected to a freeze-pump-thaw cycle. The tube was flushed with N₂ and warmed to 25 °C to produce a clear colorless solution. ¹H and ³¹P NMR spectra established that **30** had not formed. The solution was heated to 68 °C for 24 hours, 48 hours, 72 hours, and 96 hours. ¹H and ³¹P NMR spectra were obtained for each time interval. The integration of ³¹P NMR spectra established that after 24 hours at 68 °C, 31.2% **30** and 3.0% Ph₃PO had formed. It was observed that after 48 hours at 68 °C, 54.8% **30** and 3.1% Ph₃PO had formed; after 72 hours, 67.2% **30** and 3.2% Ph₃PO had formed; after 96 hours, 78.3% **30** and 3.2% Ph₃PO had formed. ¹H and ³¹P NMR data from the 96 hour experiment are as follows: ¹H NMR (CDCl₃): δ 7.20-7.90 (m, 21 H, 2,6-CH of (C₆H₅)₃P=N-, 6-CH of -C₆H₃SO₃-, 4-CH of (C₆H₅)₃P=N-, and 3,5-CH of (C₆H₅)₃P=N- in **24** and **30**; Ph₃PO), 6.65 (d, *J* = 8.0, 1.0H, 4-CH of -C₆H₃SO₃- in **30**), 6.35(d, *J* = 8.0, 1.0H, 4-CH of -C₆H₃SO₃- in **30**), 2.76(bs, 22H), 2.30(bs, 4 H), 2.19 (m, 2.3H), 2.11(s, 3.8H, 5-CH₃ of -C₆H₃SO₃- in **30**), 1.30-1.70 (m, 43H, CH₂CH₂CH₃ in **24** and **30**; -(CH₂)₅- in piperidine and 1-n-propylpiperidinium), 0.81(m, 3.0H, CH₂CH₂CH₃ in **30**), 0.70(m, 0.4H, CH₂CH₂CH₃ in **24**). ³¹P NMR (CDCl₃): δ 28.9 (3.2%, Ph₃PO), 2.7 (78.3%, **30**), 2.2 (18.5%, **24**).

With 10 Equivalents of Piperidine. A valved NMR tube was loaded with **24** (49 mg, 0.1 mmol) and CDCl₃ (0.5 mL) was added via vacuum transfer at -196 °C. After flushed with N₂ gas, the tube was sealed and warmed to 25 °C and shaken to produce a clear colorless

solution. Via a microsyringe, piperidine (100 μ L, 1.0 mmol) was added quickly after opening the valve of the sealed tube. The NMR tube was resealed immediately and subjected to a freeze-pump-thaw cycle. The tube was flushed with N_2 and warmed to 25 $^{\circ}$ C to produce a clear colorless solution. 1H and ^{31}P NMR spectra established that **30** had not formed. The solution was heated to 68 $^{\circ}$ C for 24 hours, 48 hours and 72 hours. 1H and ^{31}P NMR spectra were obtained for each time interval. The integration of ^{31}P NMR spectra established that after 24 hours at 68 $^{\circ}$ C, 48.7% **30** and 8.3% Ph_3PO had formed. It was observed that after 48 hours at 68 $^{\circ}$ C, 74.2% **30** and 8.5% Ph_3PO had formed; after 72 hours, 83.2% **30** and 8.8% Ph_3PO had formed. 1H and ^{31}P NMR data from the 72 hour experiment are as follows: 1H NMR ($CDCl_3$): δ 7.20-7.90 (m, 33.1H, 2,6-CH of $(C_6H_5)_3P=N^-$, 6-CH of $-C_6H_3SO_3^-$, 4-CH of $(C_6H_5)_3P=N^-$, and 3,5-CH of $(C_6H_5)_3P=N^-$ in **24** and **30**; Ph_3PO), 6.59 (d, J = 8.0, 1.0H, 4-CH of $-C_6H_3SO_3^-$ in **30**), 6.30 (d, J = 8.0, 1.0H, 4-CH of $-C_6H_3SO_3^-$ in **30**), 3.30 (bs, 1.7H), 2.69 (bs, 60H), 2.24 (bs, 4.8H), 2.10 (s, 3.0H, 5-CH₃ of $-C_6H_3SO_3^-$ in **30**), 1.30-1.70 (m, 105.1H, $CH_2CH_2CH_3$ in **24** and **30**; $-(CH_2)_5-$ in piperidine and 1-n-propylpiperidinium), 0.76 (t, J = 6.8, 3.0H, $CH_2CH_2CH_3$ in **30**), 0.64 (t, J = 7.6, 0.3H, $CH_2CH_2CH_3$ in **24**). ^{31}P NMR ($CDCl_3$): δ 28.8 (8.8%, Ph_3PO), 2.1 (8.1%, **24**), 1.7 (83.1%, **30**).

With 20 Equivalents of Piperidine. A valved NMR tube was loaded with **24** (49 mg, 0.1 mmol) and $CDCl_3$ (0.5 mL) was added via vacuum transfer at -196 $^{\circ}$ C. After flushed with N_2 gas, the tube was sealed and warmed to 25 $^{\circ}$ C and shaken to produce a clear colorless solution. Via a microsyringe, piperidine (200 μ L, 2.0 mmol) was added quickly after opening the valve of the sealed tube. The NMR tube was resealed immediately and subjected to a freeze-pump-thaw cycle. The tube was flushed with N_2 and warmed to 25

°C to produce a clear colorless solution. ^1H and ^{31}P NMR spectra established that **30** had not formed. The solution was heated to 68 °C for 24 hours, 48 hours and 72 hours. ^1H and ^{31}P NMR spectra were obtained for each time interval. The integration of ^{31}P NMR spectra established that after 24 hours at 68 °C, 72.2% **30** and 11.6% Ph_3PO had formed. It was observed that after 48 hours at 68 °C, 86.8% **30** and 12.9% Ph_3PO had formed; after 72 hours, 88.0% **30** and 12.0% Ph_3PO had formed. ^1H and ^{31}P NMR data from the 72 hour experiment are as follows: ^1H NMR (CDCl_3): δ 7.20-7.90 (m, 34.3H, 2,6-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}^-$, 6-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$, 4-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}^-$, and 3,5-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}^-$ in **24** and **30**; Ph_3PO), 6.49 (d, $J = 8.0$, 1.0H, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$ in **30**), 6.20(d, $J = 8.0$, 1.0H, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$ in **30**), 3.21(bs, 1.7H), 2.58(bs, 60H), 2.17(bs, 5.3H), 2.10(s, 3.0H, 5-CH₃ of $-\text{C}_6\text{H}_3\text{SO}_3^-$ in **30**), 1.30-1.70 (m, 141.5H, $\text{CH}_2\text{CH}_2\text{CH}_3$ in **24** and **30**; - $(\text{CH}_2)_5^-$ in piperidine and 1-n-propylpiperidinium), 0.67(t, $J = 7.6$, 0.3H, $\text{CH}_2\text{CH}_2\text{CH}_3$ in **30**). ^{31}P NMR (CDCl_3): δ 28.6 (12.0%, Ph_3PO), 1.3 (88.0%, **30**).

Generation of [2-($\text{Ph}_3\text{P}=\text{NH}$)-5- $\text{CH}_3\text{C}_6\text{H}_3\text{SO}_3^-\text{Pr}$][BF_4] (35**) by**

Protonation of 2-($\text{Ph}_3\text{P}=\text{N}$)-5- $\text{CH}_3\text{C}_6\text{H}_3\text{SO}_3^-\text{Pr}$ (7**) with**

[PyH][BF_4]. A valved NMR tube was charged with 2-($\text{Ph}_3\text{P}=\text{N}$)-5- $\text{MeC}_6\text{H}_3\text{SO}_3^-\text{Pr}$ (**24**) (49 mg, 0.1 mmol) and pyridinium

tetrafluoroborate (16.7 mg, 0.1 mmol), and dry CDCl_3 (0.5 mL) was added by vacuum transfer at -196 °C. The resulting suspension was flushed with N_2 and warmed to 25 °C while being shaken. After 30 minutes, ^1H , ^{31}P , ^{11}B , and ^{19}F NMR spectra were recorded. ^1H and ^{31}P NMR spectra showed that 2-($\text{Ph}_3\text{P}=\text{N}$)-5- $\text{MeC}_6\text{H}_3\text{SO}_3^-\text{Pr}$ was completely protonated to generate [2-($\text{Ph}_3\text{P}=\text{NH}$)-5- $\text{MeC}_6\text{H}_3\text{SO}_3^-\text{Pr}$][BF_4] (**35**) and release free pyridine. ^1H NMR (CDCl_3): δ 8.61 (d, $J = 3.6$, 2H, 2,6-CH of pyr) 7.80 (m, 6H, 2,6-CH

of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 7.71 (m, 5H, 6-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$, 4-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$, and 4-CH of pyr), 7.29 (m, 2H, 3,5-CH of pyr), 7.13 (d, $J = 8.4$, 1H, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 6.77 (d, $J = 8.4$, 1H, 3-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 4.00 (t, $J = 6.4$, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.28 (s, 3H, 5- CH_3 of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 1.63 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.85 (t, $J = 7.6$, 3H, $\text{CH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (CDCl_3): δ 25.5 (broad). ^{31}F NMR (CDCl_3): δ -152.8. ^{11}B NMR (CDCl_3): δ -1.1.

Generation 2-($\text{Ph}_3\text{P}=\text{NH}$)-5- $\text{CH}_3\text{C}_6\text{H}_3\text{SO}_3$ Zwitterion (12**) by Deprotection of [2-($\text{Ph}_3\text{P}=\text{NH}$)-5- $\text{CH}_3\text{C}_6\text{H}_3\text{SO}_3$] $^{\text{n}}\text{Pr}$][BF_4](**35**).**

Without Additional Pyridine. The NMR tube containing **35**

generated from **24** by reaction with $[\text{PyrH}][\text{BF}_4]$ in CDCl_3 was

spinned at 25 °C for 19 hours, 24 hours, 48 hours and 96 hours. ^1H and ^{31}P NMR spectra were obtained for each time interval. ^1H and ^{31}P NMR spectra showed the deprotection had occurred to generate 2-($\text{Ph}_3\text{P}=\text{NH}$)-5-Me $\text{C}_6\text{H}_3\text{SO}_3$ Zwitterion (**36**). ^{31}P NMR spectra established that after 19 hours, 21.6% **36** had formed; after 24 hours, 27.1% **36** had formed; after 48 hours 43.4% **36** had formed; after 96 hours, 63.5% **36** had formed. It needs to note that for an unknown reason, along with time, ^{31}P chemical shifts had gradually shifted to downfield from δ_{P} 25.5 ppm to δ_{P} 32.2 ppm. ^1H and ^{31}P NMR data from the 96 hour experiment are as follows: ^1H NMR (CDCl_3): δ 10.19 (bs, 1.5H, $(\text{C}_6\text{H}_5)_3\text{P}=\text{NH}-$), 8.96 (d, $J = 6.4$, 3.0H, 2,6-CH of 1-propylpyridinium), 8.62 (d, $J = 4.0$, 2H, 2,6-CH of pyr), 8.43 (m, 1.4H, 4-CH of 1-propylpyridinium), 8.02 (t, $J = 7.2$, 3.0H, 3,5-CH of 1-propylpyridinium), 7.70-7.90 (m, 24.0H), 7.55-7.66 (m, 16.0H), 7.42 (m, 3.0H), 7.20 (d, $J = 8.4$, 1H, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$ in **35**), 6.85 (d, $J = 8.4$, 1H, 3-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$ in **35**), 6.79 (d, $J = 8.0$, 1.5H, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$ in **36**), 6.38 (d, $J = 8.0$, 1H, 3-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$ in **36**), 4.59 (t, $J = 7.6$, 3.0H, $\text{CH}_2\text{CH}_2\text{CH}_3$ in 1-propylpyridinium),

4.00 (t, $J = 6.8$, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$ in **35**), 2.31 (s, 3H, 5- CH_3 of $-\text{C}_6\text{H}_3\text{SO}_3^-$ in **35**), 2.28 (s, 4.5H, 5- CH_3 of $-\text{C}_6\text{H}_3\text{SO}_3^-$ in **36**), 2.0 (m, 3.0H, $\text{CH}_2\text{CH}_2\text{CH}_3$ in 1-propylpyridinium), 1.63 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$ in **35**), 0.93 (t, $J = 7.2$, 4.5H, $\text{CH}_2\text{CH}_2\text{CH}_3$ in 1-propylpyridinium), 0.85 (t, $J = 7.2$, 3H, $\text{CH}_2\text{CH}_2\text{CH}_3$ in **35**). ^{31}P NMR (CDCl_3): δ 32.2 (34.4%, **35**), 31.5 (63.5%, **36**), 29.1 (2.1%, unknown). *With 1.5 equivalents of additional pyridine.* A valved NMR tube was charged with 2-($\text{Ph}_3\text{P}=\text{N}$)-5-Me $\text{C}_6\text{H}_3\text{SO}_3^{\text{nPr}}$ (**24**) (49 mg, 0.1 mmol) and pyridinium tetrafluoroborate (16.7 mg, 0.1 mmol), and dry CDCl_3 (0.5 mL) was added by vacuum transfer at -196°C . The resulting suspension was flushed with N_2 and warmed to 25°C while being shaken. The NMR tube was uncapped. Quickly, pyridine (15 μL , 0.15 mmol) was added. Immediately, the NMR tube was resealed and shaken. The resulting suspension was subjected to a cycle of freeze-pump-thaw and flushed with N_2 . After 30 minutes, ^1H , ^{31}P , ^{11}B , and ^{19}F NMR spectra were recorded. ^1H and ^{31}P NMR spectra showed the protonation was complete with partial deprotection, generating 96.2% of 3-n-propoxysulfonyltoluene-4-triphenylphosphiniminium tetrafluoroborate (**35**) and 3.8% of **36**. Characteristically, the phosphazeno proton ($\text{P}=\text{NH}$) resonated at $\delta_{\text{H}} = 9.40$ ppm in a broad singlet. ^{11}B and ^{19}F NMR data showed that the anion $[\text{BF}_4^-]$ was innocent during the experiment. The NMR tube was heated to 44°C for 4 and 24 hours. ^1H and ^{31}P NMR spectra were collected at each time interval. ^1H and ^{31}P NMR spectra showed the deprotection had occurred. ^{31}P NMR spectra established that after 4 hours, 86.1% **36** had formed; after 24 hours, 97.9% **36** had formed. In both cases, the phosphazeno proton ($\text{P}=\text{NH}$) resonated at $\delta_{\text{H}} = 10.11$ ppm in a broad singlet, 0.71 ppm downfield shifted relative to that of **35**. ^1H , ^{31}P , ^{19}F , and ^{11}B NMR data from room temperature experiment are as follows: ^1H NMR (CD_2Cl_2): δ 9.40 (bs, 1H, $\text{P}=\text{NH}$), 8.59

(d, $J = 3.6$, 5H, 2,6-CH of pyr), 7.60-7.90 (m, 19H, 6-CH of $\text{-C}_6\text{H}_3\text{SO}_3^-$, 4-CH of $(\text{C}_6\text{H}_5)_3\text{P=N-}$, and 4-CH of pyr), 7.35 (m, 5H, 3,5-CH of pyr), 7.20 (dd, $J = 8.0$, 2, 1H, 4-CH of $\text{-C}_6\text{H}_3\text{SO}_3^-$), 6.80 (d, $J = 8.0$, 1H, 3-CH of $\text{-C}_6\text{H}_3\text{SO}_3^-$), 3.92 (t, $J = 6.4$, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.32 (s, 3H, 5- CH_3 of $\text{-C}_6\text{H}_3\text{SO}_3^-$), 1.56 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.83 (t, $J = 7.2$, 3H, $\text{CH}_2\text{CH}_2\text{CH}_3$). ^{31}P NMR (CD_2Cl_2): δ 32.1 (**36**, 3.8%), 27.7(**35**, 96.2%). ^{31}F NMR (CD_2Cl_2): δ -152.6. ^{11}B NMR (CDCl_3): δ -1.1. ^1H and ^{31}P NMR data from the 24 hour experiment are as follows: ^1H NMR (CDCl_3): δ 10.11 (bs, 1H, P=NH), 8.96 (d, $J = 5.6$, 2H, 2,6-CH of 1-propylpyridinium), 8.58 (d, $J = 4.0$, 3H, 2,6-CH of pyr), 8.48 (t, $J = 8.0$, 1H, 4-CH of 1-propylpyridinium), 8.05 (t, $J = 7.2$, 3.0H, 3,5-CH of 1-propylpyridinium), 7.90 (m, 6H, 2,6-CH of $(\text{C}_6\text{H}_5)_3\text{P=NH-}$ in **36**), 7.84(m, 3H, 4-CH of $(\text{C}_6\text{H}_5)_3\text{P=NH-}$ in **36**), 7.69 (m, 9H, 6-CH of $\text{-C}_6\text{H}_3\text{SO}_3^-$ in **36**, 3,5-CH of $(\text{C}_6\text{H}_5)_3\text{P=NH-}$ in **36** and 4-CH of pyr), 7.28 (m, 3H, 3,5-CH of pyr), 6.85 (dd, $J = 8.0$, 1.6, 1H, 4-CH of $\text{-C}_6\text{H}_3\text{SO}_3^-$ in **36**), 6.47(d, $J = 8.0$, 1H, 3-CH of $\text{-C}_6\text{H}_3\text{SO}_3^-$ in **36**), 4.60 (t, $J = 7.6$, 2.0H, $\text{CH}_2\text{CH}_2\text{CH}_3$ in 1-propylpyridinium), 2.22 (s, 3, 5- CH_3 of $\text{-C}_6\text{H}_3\text{SO}_3^-$ in **36**), 2.03 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$ in 1-propylpyridinium), 0.96 (t, $J = 7.2$, 3H, $\text{CH}_2\text{CH}_2\text{CH}_3$ in 1-propylpyridinium). ^{31}P NMR (CD_2Cl_2): δ 31.9 (**36**, 97.9), 27.4(**35**, 2.12%).

2-((C₆H₅)₃P=NH)-5-CH₃C₆H₃SO₃ (36**).** (a) By deprotection of *n*-propyl 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate (**24**).

In a dry 100 mL round bottom flask under N₂ equipped with a H₂O condenser, **24** (1.83 g, 3.73 mmol) and pyridinium tetrafluoroborate (0.62 g, 3.73 mmol) were added. Dichloromethane (40 mL) was added via a syringe to the two solids resulting in a clear solution with small amount of white precipitate which was stirred at 25 °C. After stirring for 5 minutes, pyridine (0.45 mL, 5.60 mmol) was

syringed into the stirring solution. The clear light green CH_2Cl_2 solution was refluxed for 16 hours. After cooling the reaction to 25 °C, a clear light green solution was observed and the volatiles were removed under vacuum. The resulting gelatinous residue was triturated with Et_2O (40 mL) to afford a tough off-white solid. The solid was separated by column chromatography using silica gel (180 g) and CH_2Cl_2 . The column was eluted with CH_2Cl_2 (700 mL), followed by 95:5 CH_2Cl_2 -MeOH (1500 mL) and 8:2 CH_2Cl_2 -MeOH (1500 mL). The fractions (100 mL) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum, affording a white solid. The solid was dissolved in 40 mL CH_2Cl_2 and precipitated with 120 mL Et_2O . Filtration of the precipitate afforded **36** (1.60 g, 96%) as a white solid. (b) *Via one-pot synthesis.*

To a clear brown solution of **17** (6.09 g, 23.9 mmol) in toluene (80 mL) in a 300 mL Kjeldahl flask PPh_3 (6.57 g, 25.0 mmol) was added dropwise at 25 °C. Effervescence was observed immediately after addition of PPh_3 . The solution was stirred for 2 hours and became a clear yellow solution. Removal of the solvent under vacuum afforded a yellow viscous material which was redissolved with CH_2Cl_2 (40 mL). The resulting clear yellow solution was transferred via cannula over to a suspension of pyridinium tetrafluoroborate ($[\text{PyrH}][\text{BF}_4]$) (3.98 g, 23.9 mmol) in CH_2Cl_2 (40 mL). The Kjeldahl flask was rinsed with CH_2Cl_2 (40 mL) and the rinsing solution was transferred to the reaction flask via cannula. Pyridine (2.9 mL, 35.8 mmol) was added to the white suspension in CH_2Cl_2 and the reaction mixture was refluxed for 12 hours. After cooling the reaction to 25 °C, a clear pale green solution was observed and the volatiles were removed under vacuum. The resulting viscous residue was treated with CH_2Cl_2 (20 mL) and diethyl ether (100 mL) followed by filtration to give a white solid. The solid was separated by column

chromatography using silica gel (160 g) and CH₂Cl₂. The column was eluted with CH₂Cl₂-MeOH 95:5 (2000 mL). The fractions (100 mL) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum, affording a white foam. The foam was treated with CH₂Cl₂ (40 mL) and diethyl ether (80 mL) to afford a white precipitate. Filtration of the precipitate followed by diethyl ether washes (3 x 20 mL) afforded **36** (8.95g, 84%) as a white powder. ¹H NMR (CD₂Cl₂): δ 10.27 (d, *J* = 10.0, 1H, (C₆H₅)₃P=NH-), 7.92 (m, 6H, 2,6-CH of (C₆H₅)₃P=NH-), 7.82 (m, 3H, 4-CH of (C₆H₅)₃P=NH-), 7.74 (s, 1H, 6-CH of -C₆H₃SO₃-), 7.67 (m, 6H, 3,5-CH of (C₆H₅)₃P=NH-), 6.82 (dd, *J* = 8.0, 1.2, 1H, 4-CH of -C₆H₃SO₃-), 6.44 (d, *J* = 8.0, 1H, 3-CH of -C₆H₃SO₃-), 2.24 (s, 3H, 5-CH₃ of -C₆H₃SO₃-). ³¹P NMR (CD₂Cl₂): δ 31.6. ¹³C NMR (CD₂Cl₂): δ 139.3 (d, *J* = 8.5), 137.2 (d, *J*_{PC} = 3.1, *para*-CH of (C₆H₅)₃P=NH-), 135.8, 135.5 (d, *J*_{PC} = 10.9, *ortho*-CH of (C₆H₅)₃P=NH-), 134.1 (d, *J* = 1.5), 132.2, 132.0 (d, *J*_{PC} = 13.9, *meta*-CH of (C₆H₅)₃P=NH-), 130.8, 122.5 (d, *J*_{PC} = 102.2, ipso C of (C₆H₅)₃P=NH-), 121.0 (d, *J* = 3.9), 22.2.

Crystal data and structure refinement for **36**.

Identification code	CCDC 867295	
Empirical formula	C ₃₁ H ₂₈ N O ₃ P S	
Formula weight	525.57	
Temperature	99.95(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	<i>a</i> = 10.3622(7) Å	<i>α</i> = 90°.
	<i>b</i> = 17.9827(18) Å	<i>β</i> = 95.113(4)°.
	<i>c</i> = 14.6795(6) Å	<i>γ</i> = 90°.
Volume	2724.5(3) Å ³	
<i>Z</i>	4	
Density (calculated)	1.281 Mg/m ³	
Absorption coefficient	0.210 mm ⁻¹	

F(000)	1104
Crystal size	0.48 x 0.10 x 0.02 mm ³
Theta range for data collection	3.24 to 27.57°
Index ranges	-13 ≤ h ≤ 13, -23 ≤ k ≤ 23, -18 ≤ l ≤ 19
Reflections collected	32299
Independent reflections	6298 [R(int) = 0.0384]
Completeness to theta = 27.57°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.85663
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6298 / 0 / 427
Goodness-of-fit on F ²	1.045
Final R indices [I > 2σ(I)]	R1 = 0.0466, wR2 = 0.0984
R indices (all data)	R1 = 0.0727, wR2 = 0.1097
Largest diff. peak and hole	0.632 and -0.425 e.Å ⁻³

Single Pot Synthesis of 2-(CH₃(C₆H₅)₂P=NH)-5-CH₃C₆H₃SO₃

(**37**). To a clear brown solution of **17** (3.65 g, 14.3 mmol) in toluene (40 mL) in a 200 mL Kjeldahl flask PMePh₂ (2.8 mL, 15.0 mmol)

was added dropwise at 25 °C. Effervescence was observed immediately after addition of PMePh₂. The solution was stirred for 2 hours and became a clear yellow solution.

Removal of the solvent under vacuum afforded a yellow viscous material which was redissolved with CH₂Cl₂ (40 mL). The resulting clear yellow solution was transferred via cannula over to a suspension of pyridinium tetrafluoroborate ([PyrH][BF₄]) (2.39 g, 14.3 mmol) in CH₂Cl₂ (40 mL). The Kjeldahl flask was rinsed with CH₂Cl₂ (40 mL) and the rinsing solution was transferred to the reaction flask via cannula. Pyridine (1.8 mL, 21.5 mmol) was added to the white suspension in CH₂Cl₂ and the reaction mixture was refluxed for 12 hours. After cooling the reaction to 25 °C, a clear pale green solution was observed and the volatiles were removed under vacuum. The resulting viscous residue

was treated with CH₂Cl₂ (20 mL) and diethyl ether (100 mL) followed by filtration to give a white solid. The solid was separated by column chromatography using silica gel (160 g) and CH₂Cl₂. The column was eluted with CH₂Cl₂-MeOH 95:5 (2000 mL). The fractions (100 mL) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum, affording a white foam. The foam was treated with CH₂Cl₂ (40 mL) and diethyl ether (80 mL) to afford a white precipitate. Filtration of the precipitate followed by diethyl ether washes (3 x 20 mL) afforded **37** (3.86g, 70%) as a white powder. ¹H NMR (CD₃OD): δ 7.97 (m, 4H, 2,6-CH of CH₃(C₆H₅)₂P=NH-), 7.78 (m, 2H, 4-CH of CH₃(C₆H₅)₂P=NH-), 7.66 (m, 5H, 6-CH of C₆H₃SO₃⁻ and 3,5-CH of CH₃(C₆H₅)₂P=NH-), 6.96(dd, *J* = 8.0, 1.2, 1H, 4-CH of -C₆H₃SO₃⁻), 6.59 (d, *J* = 8.0, 1H, 3-CH of -C₆H₃SO₃⁻), 2.72 (d, *J*_{PH} = 14.0, 3H, CH₃P), 2.21 (s, 3H, 5-CH₃ of -C₆H₃SO₃⁻). ³¹P NMR (CD₃OD): δ 39.0. ¹³C NMR (CD₃OD): δ 136.3 (d, *J*_{PC} = 7.7), 135.0 (d, *J*_{PC} = 3.1, *para*-CH of CH₃(C₆H₅)₂P=NH-), 134.2, 132.3 (d, *J*_{PC} = 11.6, *ortho*-CH of CH₃(C₆H₅)₂P=NH-), 132.0, 131.5, 129.9 (d, *J*_{PC} = 13.9, *meta*-CH of CH₃(C₆H₅)₂P=NH-), 128.4, 122.2 (d, *J*_{PC} = 101.5, ipso C of CH₃(C₆H₅)₂P=NH-), 120.5 (d, *J* = 3.9), 19.2, 9.3 (d, *J*_{PC} = 4.2). Anal. Calcd for C₂₀H₂₀NO₃PS: C, 62.23; H, 5.23; N, 3.63. Found: C, 62.50; H, 5.15; N, 3.67.

Crystal data and structure refinement for **37**

Identification code	CCDC 867296	
Empirical formula	C ₂₁ H ₂₄ N O ₄ P S	
Formula weight	417.44	
Temperature	99.95(10) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	<i>a</i> = 7.9985(4) Å	<i>α</i> = 81.985(7)°.
	<i>b</i> = 9.9206(10) Å	<i>β</i> = 81.187(5)°.
	<i>c</i> = 13.1626(9) Å	<i>γ</i> = 74.604(7)°.
Volume	989.72(13) Å ³	

Z	2
Density (calculated)	1.401 Mg/m ³
Absorption coefficient	0.272 mm ⁻¹
F(000)	440
Crystal size	0.36 x 0.22 x 0.21 mm ³
Theta range for data collection	3.25 to 27.56°
Index ranges	-10<=h<=10, -12<=k<=12, -17<=l<=17
Reflections collected	18333
Independent reflections	4576 [R(int) = 0.0267]
Completeness to theta = 27.56°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.90148
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4576 / 0 / 349
Goodness-of-fit on F ²	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0772
R indices (all data)	R1 = 0.0396, wR2 = 0.0806
Largest diff. peak and hole	0.423 and -0.368 e.Å ⁻³

Single Pot Synthesis of 2-((CH₃)₂C₆H₅P=NH)-5-CH₃C₆H₃SO₃ (**38**).

To a clear brown solution of **17** (2.37 g, 9.26 mmol) in toluene (40 mL) in a 200 mL Kjeldahl flask PMe₂Ph (1.5 mL, 11.1 mmol) was added dropwise at 25 °C. Effervescence was observed immediately after addition of PMe₂Ph. The solution was stirred for 2 hours and became a clear yellow solution. Removal of the solvent under vacuum afforded a yellow viscous material which was redissolved with CH₂Cl₂ (40 mL). The resulting clear yellow solution was transferred via cannula over to a suspension of [PyrH][BF₄] (1.55 g, 9.26 mmol) in CH₂Cl₂ (40 mL). The Kjeldahl flask was rinsed with CH₂Cl₂ (40 mL) and the rinsing solution was transferred to the reaction flask via cannula. Pyridine (1.2 mL, 14.0 mmol) was added to the white suspension in CH₂Cl₂ and the reaction mixture was stirred at 25 °C for 48 hours. A clear pale green solution was observed and the volatiles were removed under vacuum. The resulting viscous residue was treated diethyl ether (4 x 60 mL)

followed by filtration to give a light yellow solid. The solid was separated by column chromatography using silica gel (160 g) and CH₂Cl₂. The column was eluted with CH₂Cl₂-MeOH 95:5 (500 mL), CH₂Cl₂-MeOH 90:10 (1000 mL), CH₂Cl₂-MeOH 80:20 (1000 mL). The fractions (100 mL) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum, affording a white solid. The solid was treated with CH₂Cl₂ (20 mL) and diethyl ether (100 mL) to afford a white precipitate. Filtration of the precipitate followed by diethyl ether washes (3 x 20 mL) afforded **38** (3.86g, 70%) as a white powder. ¹H NMR (CD₂Cl₂): δ 8.83 (d, ²J_{PH} = 7.6, 1H, P=NH), 7.97 (m, 2H, 2,6-CH of (CH₃)₂C₆H₅P=NH-), 7.82 (m, 1H, 4-CH of (CH₃)₂C₆H₅P=NH-), 7.77 (s, 1H, 6-CH of C₆H₃SO₃-), 7.71 (m, 2H, 3,5-CH of (CH₃)₂C₆H₅P=NH-), 6.97 (dd, J = 8.0, 1.6, 1H, 4-CH of -C₆H₃SO₃-), 6.59 (dd, J = 8.0, 1.2, 1H, 3-CH of -C₆H₃SO₃-), 2.72 (d, J_{PH} = 13.6, 6H, (CH₃)₂P), 2.30 (s, 3H, 5-CH₃ of -C₆H₃SO₃-). ³¹P NMR (CD₂Cl₂): δ 43.6. ¹³C NMR (CD₂Cl₂): δ 138.9 (d, J_{PC} = 6.2), 135.0 (d, J_{PC} = 3.1, *para*-CH of (CH₃)₂C₆H₅P=NH-), 134.8 (d, J_{PC} = 1.6), 131.9 (d, J_{PC} = 3.1), 131.3 (d, J_{PC} = 11.6, *ortho*-CH of (CH₃)₂C₆H₅P=NH-), 130.8, 130.2 (d, J_{PC} = 13.2, *meta*-CH of (CH₃)₂C₆H₅P=NH-), 128.7, 123.2 (d, J_{PC} = 99.9, ipso C of (CH₃)₂C₆H₅P=NH-), 120.7 (d, J = 3.8), 20.4, 11.8 (d, J_{PC} = 65.8). Anal. Calcd for C₁₅H₁₈NO₃PS: C, 55.72; H, 5.61; N, 4.33. Found: C, 55.60; H, 5.38; N, 4.06.

Single Pot Synthesis of 2-(C₆H₅CH₂(C₆H₅)₂P=NH)-5-

CH₃C₆H₃SO₃ (39). To a white suspension of P(C₆H₅CH₂)Ph₂ (2.08 g, 7.53 mmol) in toluene (20 mL) in a 300 mL Kjeldahl flask, added dropwise a yellow solution of **17** (1.83 g, 7.17 mmol) in toluene (20 mL) at 25 °C. The combined mixture became a clear yellow solution immediately. After

stirring for 15 minutes effervescence was observed. The solution was stirred for 4 hours and it remained a clear yellow solution. Removal of the solvent under vacuum afforded a yellow viscous material which was redissolved with CH₂Cl₂ (20 mL). The resulting clear yellow solution was transferred via cannula over to a suspension of pyridinium tetrafluoroborate ([PyrH][BF₄]) (1.29 g, 7.17 mmol) in CH₂Cl₂ (20 mL). The Kjeldahl flask was rinsed with CH₂Cl₂ (2x20 mL) and the rinsing solution was transferred to the reaction flask via cannula. Pyridine (0.9 mL, 10.8 mmol) was added to the white suspension in CH₂Cl₂ and the reaction mixture was refluxed for 12 hours. After cooling the reaction to 25 °C, a clear yellow solution was observed and the volatiles were removed under vacuum. The resulting viscous residue was washed with diethyl ether (4 x 40 mL) to give a yellow gum. The gum was purified by column chromatography using silica gel (80 g) and CH₂Cl₂. The column was eluted with CH₂Cl₂ (200 mL), CH₂Cl₂-MeOH 98:2 (500 mL), CH₂Cl₂-MeOH 95:5 (500 mL), CH₂Cl₂-MeOH 90:10 (500 mL), and CH₂Cl₂-MeOH 80:20 (500 mL). The fractions (100 mL) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum, affording a white foam. The foam was treated with CH₂Cl₂ (100 mL) and diethyl ether (300 mL) to afford a white precipitate. Filtration of the precipitate followed by diethyl ether washes (40 mL) afforded **39** (2.17g, 66%) as a white powder. ¹H NMR ((CD₃)₂SO): δ 9.66 (d, *J*_{PH} = 10.4, 1H, -P=NH-), 7.97 (m, 4H, 2,6-CH of -(C₆H₅)₂P=NH-), 7.82 (m, 2H, 4-CH of -(C₆H₅)₂P=NH-), 7.70 (m, 4H, 3,5-CH of -(C₆H₅)₂P=NH-), 7.54 (s, 1H, -CH of C₆H₃SO₃), 7.20-7.28 (m, 3H, 2,6- and 4-CH of -C₆H₅CH₂P=NH-), 7.10 (m, 3,5-CH of -C₆H₅CH₂P=NH-), 6.91 (dd, *J* = 8.0, 1.6, 1H, 4-CH of -C₆H₃SO₃-), 6.64 (d, *J* = 8.0, 1H, 3-CH of -C₆H₃SO₃-), 5.00 (d, *J*_{PH} = 14.0, -CH₂P=NH-), 2.21 (s, 3H, 5-CH₃ of -C₆H₃SO₃-).

^1H NMR (CD_2Cl_2): δ 9.68 (d, $J_{\text{PH}} = 10.4$, 1H, $-\text{P}=\text{NH}-$), 7.71-7.85 (m, 7H, 6-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$, 3,5-CH of $-(\text{C}_6\text{H}_5)_2\text{P}=\text{NH}-$, and 2,6-CH of $-\text{C}_6\text{H}_5\text{CH}_2\text{P}=\text{NH}-$), 7.62 (, m, 4H, 2,6-CH of $-\text{C}_6\text{H}_5\text{CH}_2\text{P}=\text{NH}$), (m, 2H, 4-CH of $-(\text{C}_6\text{H}_5)_2\text{P}=\text{NH}-$), 7.28 (m, 1H, 4-CH of $-\text{C}_6\text{H}_5\text{CH}_2\text{P}=\text{NH}$), 7.20 (t, $J = 7.6$, 3,5-CH of $-\text{C}_6\text{H}_5\text{CH}_2\text{P}=\text{NH}-$), 6.79 (dd, $J = 8.4$, 2.0, 1H, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 6.34 (d, $J = 8.4$, 1H, 3-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 4.27 (d, $J_{\text{PH}} = 14.0$, $-\text{CH}_2\text{P}=\text{NH}-$), 2.23 (s, 3H, 5- CH_3 of $-\text{C}_6\text{H}_3\text{SO}_3^-$). ^{31}P NMR ($(\text{CD}_3)_2\text{SO}$): δ 35.9. ^{31}P NMR (CD_2Cl_2): δ 36.1. ^{13}C NMR (CD_3OD): δ 137.0 (d, $J_{\text{PC}} = 7.8$), 135.6 (d, $J_{\text{PC}} = 3.1$, *para*-CH of $-(\text{C}_6\text{H}_5)_2\text{P}=\text{NH}-$), 133.1 (d, $J_{\text{PC}} = 10.8$, *ortho*-CH of $-(\text{C}_6\text{H}_5)_2\text{P}=\text{NH}-$), 132.7, 132.4, 131.1, 131.0 (d, $J_{\text{PC}} = 3.1$), 130.4 (d, $J_{\text{PC}} = 10.8$, *meta*-CH of $-(\text{C}_6\text{H}_5)_2\text{P}=\text{NH}-$), 129.3 (d, $J_{\text{PC}} = 3.1$), 128.5, 128.4, 128.0 (d, $J_{\text{PC}} = 10.0$, ipso C of $-\text{C}_6\text{H}_5\text{CH}_2\text{P}=\text{NH}-$), 120.5 (d, $J_{\text{PC}} = 96.8$, ipso C of $-(\text{C}_6\text{H}_5)_2\text{P}=\text{NH}-$), 119.5 (d, $J_{\text{PC}} = 3.9$), 30.9 (d, $J_{\text{PC}} = 56.5$, $-\text{CH}_2\text{P}=\text{NH}-$), 20.5. Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{NO}_3\text{PS}$: C, 67.66; H, 5.24; N, 3.03. Found: C, 67.86; H, 5.33; N, 2.91.

Single Pot Synthesis of 2-(($\text{C}_6\text{H}_5\text{CH}_2$) $_3\text{P}=\text{NH}$)-5-Me $\text{C}_6\text{H}_3\text{SO}_3$ (**40**)

To a 200 mL pear-shaped flask containing a clear brown solution of **17** (2.76 g, 10.8 mmol) in toluene (10 mL) chilled to 0 °C for 15 minutes, a solution of $\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$ (3.60 g, 13.0 mmol) in toluene (30 mL) was added via cannula transfer by aid of rinsing with toluene (10 mL), resulting in a yellow solution. The mixture was allowed to return to 25 °C after stirred at 0 °C for 15 minutes. Effervescence was observed gradually after addition of the $\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$ solution. The reaction mixture was stirred for 4 hours until no effervescence was observed. A yellow solution was obtained and the solvent was removed under vacuum to afford a yellow frothy solid. The solid was dissolved in CH_2Cl_2 (20 mL). The resulting

yellow solution was transferred via cannula to a 300 mL Kjeldahl flask containing a suspension of [PyH][BF₄] (1.81 g, 10.8 mmol) in CH₂Cl₂ (20 mL). The 200 mL pear-shaped flask was rinsed with CH₂Cl₂ (3 x 20 mL) and the rinsing solutions were transferred to the reaction flask via cannula. Gradually, the yellow reaction mixture turned to red solution with some seeable white solid. The reaction mixture was stirred for 1 hour and the white solid almost disappeared. Pyridine (1.3 mL, 16.2 mmol) was added to the resulting reaction solution. The reaction was stirred at 25 °C for 72 hours. The resulting brown solution was pumped down under vacuum giving a glutinous residue, which was treated with CH₂Cl₂ (15 mL) and Et₂O (75 mL). A brown oily insoluble precipitate was observed. Decantation of the liquid layer afforded a gelatinous solid. Treatment with Et₂O (75 mL) and decantation of the ether layer were performed. The resulting viscous solid was pumped down to a brown foam. The frothy solid was separated by column chromatography using silica gel (150g) and CH₂Cl₂. The column was eluted with CHCl₃ (100 mL), CHCl₃-MeOH 98:2 (1500 mL), CHCl₃-MeOH 95:5 (500 mL), and CHCl₃-MeOH 90:10 (500 mL). The fractions (100 mL) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum, affording a brown foamed solid. The brown solid was treated with CHCl₃ (20 mL) and Et₂O (80 mL) to give a white precipitate with some viscous brown chunks. The chunks were broken down to a fine powder by trituration. The resulting suspension was filtered and washed with Et₂O (2 x 50 mL) affording a light brown solid (5.85 g). The light brown solid was trituated in a mixture of CHCl₃ (10 mL) and MeOH (20 mL). A powdery precipitate from a red solution was observed. The precipitate was filtered and washed with Et₂O (30 mL), yielding **40** as a white powder (2.00 g). The red filtrate was

evaporated to a gum which was triturated in a mixture of CHCl_3 (5 mL) and MeOH (10 mL). A powdery precipitate from a red solution was observed. The precipitate was filtered and washed with Et_2O (20 mL), yielding **40** as a white powder (1.20 g). Combination of the two harvests afforded **40** as a white powder in an overall yield of 3.20 g (60%). ^1H NMR (CD_2Cl_2): δ 7.90 (d, $J = 6.4$, 1H, $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{P}=\text{NH}-$), 7.82 (s, 1H, 6-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), δ 7.38 (m, 6H, *meta*-CH and 3H, *para*-CH of $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{P}=\text{NH}-$), 7.27 (m, 6H, *ortho*-CH of $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{P}=\text{NH}-$), 6.81 (d, $J = 7.8$, 1H, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 5.64 (d, $J = 7.8$, 1H, 3-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 5.68 (d, $J_{\text{PH}} = 14.4$, 6H, CH_2 of $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{P}=\text{NH}-$), 2.28 (s, 3H, 5- CH_3 of $-\text{C}_6\text{H}_3\text{SO}_3^-$). ^{31}P NMR (CD_2Cl_2): δ 48.9. ^{13}C NMR (CD_2Cl_2): δ 140.8 (d, $J_{\text{PC}} = 5.4$), 136.1, 131.0 (d, $J_{\text{PC}} = 4.7$), 130.8, (d, $J_{\text{PC}} = 6$), 130.6, (d, $J_{\text{PC}} = 5.4$), 129.6 (d, $J_{\text{PC}} = 3.1$), 128.7, 128.6 (d, $J_{\text{PC}} = 3.9$), 127.2 (d, $J_{\text{PC}} = 7.0$), 123.5 (d, $J_{\text{PC}} = 2.3$), 29.9 (d, $J_{\text{PC}} = 54.2$), 20.4. Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{NO}_3\text{PS} \cdot 0.9 \text{CHCl}_3$: C, 58.14; H, 4.88; N, 2.35. Found: C, 57.97; H, 4.83; N, 2.36.

CHAPTER THREE

SYNTHESIS AND REACTIVITY OF OF TRIPHENYLPHOSPHINIMINE-SULFONATE PALLADIUM METHYL PYRIDINE COMPLEX

3.1 Introduction

In the synthesis of P[^]SO palladium alkyl complexes, two methods are used. First, the zwitterionic phosphonium-sulfonate directly reacts with a dimethyl metal precursor. In the presence of a base like pyridine, replacement of tmeda ligand by the P[^]SO ligand followed by methane elimination generates the desired complexes. For instance, combination of zwitterion benzene-2-(di-*o*-anisylphosphonium)-1-sulfonate with (tmeda)PdMe₂ or (tmeda)NiMe₂ in the presence of excess pyridine can form P[^]SO palladium/nickel methyl pyridine complexes accompanied by methane elimination (Scheme 3.1).^{10c, 17b, 53}

Scheme 3.1 P[^]SO zwitterion reacts with Pd/Ni precursors

The other method to make P[^]SO palladium complexes involves using anionic phosphine-sulfonate to coordinate with a metal precursor. The deprotonation of

zwitterionic phosphonium-sulfonate is typically realized using an amine base like Et₃N or Hünig base.¹¹ In practice, the zwitterionic phosphonium-sulfonate was *in situ* deprotonated with the amine base to its anionic ligand, which can undergo complexation

Scheme 3.2 Synthesis of [P⁺SO]PdMeCl

with a palladium source. As shown in Scheme 3.2, benzene-2-(di-o-anisylphosphonium)-1-sulfonate is deprotonated with amines and interacts with (cod)PdMeCl to form phosphine-sulfonate palladium methyl chloride complexes.¹¹ The anionic palladium chloride complex can be further converted to a neutral palladium methyl lutidine complex in the presence of a large amount of lutidine and K₂CO₃ (Scheme 3.3).¹⁴ Lutidine can be

Scheme 3.3 Lutidine replaces chlorine

used for deprotonation of the zwitterionic phosphonium-sulfonate species and coordination to the metal center. Thus, a combination of di-o-anisylphosphonium-sulfonate with excess lutidine followed by the introduction of (cod)PdMeCl generates the desired complex (Scheme 3.4).¹⁴

Scheme 3.4 Synthesis of [P^{SO}]Pd(lutidine)Me

In this thesis research, *ortho*-phosphinimine-arenesulfonate Pd(II) complexes have been synthesized and studied. The modular nature of phosphinimine synthesis allows for the creation of a diverse ligand library where steric and electronic properties can be manipulated with ease.⁵⁴ Neutral phosphinimines are believed to be stronger donor ligands than phosphines due to the delocalization of electron lone pairs about the N=P double bond. The steric properties of phosphinimines are different than phosphines since the steric bulk is slightly removed from the metal center. A series of phosphinimine aryl sulfonate (NPSO) alkyl esters have been synthesized by simple azide oxidation (Staudinger reaction) of 2-azido aryl sulfonate esters with triaryl, diaryl(alkyl), aryl(dialkyl) and tri(alkyl)phosphines. Deprotection routes to liberate the sulfonate anion of the NPSO ligand have been explored and led to the formation of the desired zwitterionic ligands.^{25a, 32, 55} NPSO-based palladium complexes are synthesized and their thermal behavior and ethylene reactivity are investigated.

3.2 Results and Discussion

Attempted Zwitterion Complexation

For investigation of the reactivity of the synthesized zwitterionic PN⁺SO ligand, toluene-4-triphenylphosphiniminium-3-sulfonate (**36**) and the metal precursor (cod)PdMeCl was combined at 1:1 ratio for NMR acquisition. After 24 hours, it did not undergo complexation (Scheme 3.5). In comparison to the phosphonium-sulfonate zwitterion ($pK_a = 2.7$), phosphiniminium-sulfonate zwitterion **36** (estimated $pK_a = 8-10$) is apparently too weak an acid to be deprotonated via methane elimination.^{10b, 56} Deprotonation of the phosphiniminium-sulfonate zwitterions with a strong base is necessary for coordination.

Scheme 3.5 Phosphiniminium-sulfonate to react with (cod)PdMeCl

Generation and Synthesis of Sodium Phosphinimine-sulfonates

For deprotonation of phosphiniminium-sulfonate zwitterions, bases with pK_a values higher than phosphiniminium-sulfonate ($pK_a = 8-10$) such as potassium tert-butoxide (^tBuOK, $pK_a = 17$),⁵⁷ sodium hexamethyldisilazide ($\text{NaN}(\text{TMS})_2$, $pK_a = 25$),⁵⁸ and sodium hydride (NaH, $pK_a = 35$) were screened.⁵⁹ In an attempted NMR reaction, combination of zwitterion **36** and ^tBuOK in THF- d_8 generated a turbid mixture containing some chunks. The mixture was not suitable for NMR acquisition. Then

zwitterion **8** was combined with $\text{NaN}(\text{TMS})_2$ in THF-d_8 . This resulted in a clear yellowish solution. The phosphinio proton peak at $\delta_{\text{H}} = 10.25$ ppm reminiscent of the zwitterionic structure clearly disappeared from ^1H NMR spectrum. ^{31}P NMR showed a singlet at 0.0 ppm, about 31.0 ppm downfield shifted compared with the zwitterion. ^1H and ^{31}P NMR spectra supported the structure of sodium toluene-4-phosphinimine-3-sulfonate (**4**). (Scheme 3.6).

Scheme 3.6 Generation of Sodium Phosphinimine-sulfonate

Based on these data, sodium 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate (**4**) was synthesized successfully by reacting the corresponding zwitterion (**36**) with $\text{NaN}(\text{TMS})_2$ in THF at room temperature (Scheme 3.7).

Scheme 3.7 Synthesis of sodium phosphinimine-sulfonate: $\text{NaN}(\text{TMS})_2$ as a base

This method works to deprotonate the zwitterion, but one disadvantage is that the hexamethyldisilazane residue is usually observed on the ^1H NMR spectrum. Alternately,

deprotonation using NaH as a base was performed. The reaction was done in benzene and stirred for 4 hours. In this way, neat sodium 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate (**4**) could be prepared from the zwitterion **36** in high yield (89%, 2.09 grams) (Scheme 3.8).

Scheme 3.8 Synthesis of sodium phosphinimine-sulfonate: NaH as a base

Synthesis of Triphenylphosphinimine-sulfonate Palladium Methyl Pyridine Complexes

Scheme 3.9 Synthesis of Complex **41**

Table 3.1 1D and 2 D NMR Data of **41** (δ_C and δ_H in ppm; J in Hz)

Position	δ_C (J)	δ_H (J)	HMQC	HMBC	NOSEY
1	133.6d (1.6)	7.59-7.67m	CH		
2	25.1	2.21d (1.2)	CH ₃		
3	148.1d (1.6)		C	H-5	
4	135.3d (2.3)	6.97dd (8.0, 2.0)	CH		
5	131.6d (4.6)	6.85dd (8.0, 2.0)	CH		
6	147.0d (10.0)		C	H-4	
7	137.4d (2.3)		C		
8	133.3d (101.4)		C	H-9; H-10	
9	139.4d (10.1)	8.01dd (12.0, 7.2)	CH		H-12
10	133.0 (13.2)	7.52td (7.6, 3.2)	CH		
11	137.5d (3.1)	7.59-7.67m	CH	H-9	
12	0.0d (1.5)	0.19s	CH ₃		H-9; H-13
13	156.8	8.38dd (6.8, 1.6)	CH	H-14; H-15	H-12
14	129.7	7.26 td (6.4, 1.2)	CH	H-13	
15	142.2	7.72tt (8.0, 1.6)	CH	H-13	

Zwitterion **36** was deprotonated with $\text{NaN}(\text{TMS})_2$ in THF to generate compound **4**. In CH_2Cl_2 , **4** reacted with $(\text{cod})\text{PdMeCl}$ in the presence of 1.5 equivalents of pyridine to form the desired palladium methyl pyridine complex species **41** (Scheme 3.9).

Complex **41** was fully characterized by interpretation of ^1H , ^{31}P , and ^{13}C NMR spectra and 2D NMR spectra including HMQC and HMBC. On the ^1H NMR spectra of **41**, a high intensity sharp singlet $\delta_H = 0.19$ ppm in the upfield region demonstrates the presence of a methyl on palladium. The pyridine ligand coordinated to palladium gave a set of 3 typical peaks including a doublet of doublets at $\delta_H = 8.38$ ppm, a triplet of triplets

at $\delta_{\text{H}} = 7.72$ ppm, and a triplet of doublets at $\delta_{\text{H}} = 7.26$ ppm. Compared to free pyridine, an obvious change is that the chemical shift of the 2 and 6 position protons have increased by 0.25 ppm, while other protons showed similar chemical shifts. The combination of other 6 aromatic signals at 6.85-8.01 ppm and the singlet at 2.21 ppm showed the presence of triphenylphosphinimine-sulfonate ligand. The ^{31}P NMR showed a singlet at 31.7 ppm, downfield shifted by 33.3 ppm compared to that in sodium salt. All peaks are sharp and well split. This has been an apparent contrast to its precursor, sodium triphenylphosphinimine-sulfonate, which had a set of all broadened peaks in CD_2Cl_2 . ^{13}C NMR chemical shifts have been completely assigned by aid of 2D NMR including HMQC and HMBC (Table 3.1).

In the complex **41**, the relative positions between the methyl group and pyridine can form two types of isomers, *cis*- or *trans*- isomers (Figure 3.1). Based on the convention used for differentiation of the geometric isomers of phosphine-sulfonate palladium complexes, the *cis*-isomer defines that the labile ligand pyridine orients itself

Figure 3.1 Two possible isomers of **41**. Double arrows show possible NOESY correlations.

on the side of the sulfonate group, whereas the *trans*-isomer defines that the labile ligand pyridine orients itself opposite to the side of the sulfonate group.^{5b} The differentiation of

cis-**41** from *trans*-**41** was realized using NOESY. On a NOESY spectrum of *cis*-**41**, the methyl group is expected to have 2 correlation, one with the 2,6-protons of PPh₃, the other with the 2,6-protons of pyridine. On a NOESY spectrum of *trans*-**41**, only one correlation which is the methyl with the 2,6-protons of pyridine can be seen. Our experiment showed the scenario of the *cis*-**41**. The NOESY correlations are listed in Table 3.1.

In the preparation of **41**, aliquots of reaction mixtures were taken for NMR study. ¹H NMR clearly showed that 20% bispyridine palladium methyl chloride (Py₂PdMeCl) could be observed. Based on this important observation, a mechanism can be proposed that the complex **41** forms via an intermediate Py₂PdMeCl. As is shown in Scheme 3.10, ligand exchange between 2 equivalents of pyridine and the cod converts (cod)PdMeCl into Py₂PdMeCl as an intermediate. The phosphinimine-sulfonate ligand species **4** displaces a pyridine and the chloride in Py₂PdMeCl to produce complex **41**.

Scheme 3.10 Proposed mechanism for formation of **41**

By this mechanism, complex **41** was synthesized from a reaction between sodium salt (**4**) and Py₂PdMeCl in benzene at room temperature (Scheme 3.11). Similarly, triphenylphosphinimine-sulfonate palladium methyl 4-tert-butylpyridine complex (**42**)

was synthesized from a reaction between sodium salt (**4**) and (4-^tBuPy)₂PdMeCl in benzene at room temperature (Scheme 3.11). The reaction is neat and this is a

Scheme 3.11 Synthesis of **41** and **42**

reliable method to prepare phosphinimine-sulfonate palladium alkyl complexes. The advantages of this method for the synthesis of palladium methyl complexes using are: 1) instead of maintaining a cold condition at -20 °C, the reaction is run at room temperature; 2) the one-step reaction makes the stoichiometry more controllable; this improves the yield significantly from 55% to 86%; 3) In reactions using (cod)PdMeCl as a metal precursor, product quality is an issue. This could be due to the use of CH₂Cl₂ as a solvent, which leads to side reactions like formation of phosphinimine-sulfonate palladium pyridine chloride. Other impurities are zwitterions and unreacted intermediate Py₂PdMeCl. When using Py₂PdMeCl as a metal precursor, since the reaction is run in benzene, pure products can be obtained.

*Variable Temperature ¹H NMR of **42***

Variable temperature ¹H NMR has been studied for complex **42** using an array of temperatures, 20, -10, -30, -50, -60, -70, -90 °C. According to NMR spectra, coalescence occurs at -60 °C. Significant differences have been observed for 2,6-protons on PPh₃ and

2,6-protons of Pd(^tBuPy). At 20 °C, the 2,6-protons of PPh₃ show one apparent triplet at 8.01 ppm, whereas at -90 °C, they are split into three apparent triplets, one at 8.69 ppm, one at 7.83 ppm, and one at 7.76 ppm. The difference of NMR behavior of PPh₃ between the solution and solid structures results from conformational interchange, which is similar to that for 2,6-MeO groups in P[^]SO ligand.¹¹ Scheme 3.2 shows the two conformers of **42**.

Scheme 3.12 Conformational interchange of **42**.

*X-ray Crystallography of **42***

For understanding the solid structure of **42**, X-ray crystallography study was conducted. For X-ray diffraction, single crystals of **42** were grown by slow diffusion of pentane into a benzene solution of **42**. The temperature for growing single crystals was at 25 °C. Crystals were inspected carefully for their suitability for X-ray crystallography.

Figure 3.2 ORTEP plot of **42**.

ORTEP plots generated from X-Ray crystallographic data, have confirmed the structure of **42**, which was assigned from interpretation of NMR spectral data (Figure 3.2).

Thermal Behavior of Triphenylphosphinimine-sulfonate Palladium Methyl Pyridine Complexes

Orthopalladation is a known reaction of palladium complexes containing a phosphinimine donor.⁶⁰ In a phosphinimine supported palladium complex, palladium abstracts an *ortho* hydrogen from either a P attached arene ring to form a 5-membered *exo* orthopalladated species or an N-C linked arene ring to form a 5-membered *endo* orthopalladated species (Scheme 3.13).^{60g} In general, low temperature and chlorinated

Scheme 3.13 Endo/Exo orthopalladaion

solvents favor *exo* orthopallation and high temperature and non-halogenated solvents favor *endo* orthopalladation. Thus, the *endo* orthopalladated species can be converted from the *exo* orthopalladated species when heated in toluene.^{60g}

To understand how or if orthopalladation occurs in phosphinimine-sulfonate palladium complex, we studied the thermal behavior of complexes **41** and **42**. The experiment was carried out under different conditions including NMR solvents, temperature, and time. NMR solvents include halogenated solvents CDCl₃ and CD₂Cl₂ and non-halogenated solvents benzene-d₆ and toluene-d₈. Due to poor solubility in non-halogenated solvents, palladium pyridine complexes **41** was heated in CDCl₃. Palladium *t*-butylpyridine complex **42** is soluble in benzene and toluene. **42** was heated in 4

Scheme 3.14 Thermal behavior of **41** and **42**

different solvents, CDCl_3 , CD_2Cl_2 , C_6D_6 , and toluene- d_8 . As shown in scheme 3.14, endo-orthopalladated species **43** and **44** are formed from the corresponding palladium complexes **41** and **42**.

In our investigation, orthopalladation was determined using ^{31}P NMR. Based on ^{31}P NMR spectra, the orthopalladated products **43** and **44** are primary decomposition pathways. Other components present in the heating mixture include the starting complex **41** or **42**, palladium chloride complex, zwitterion, Ph_3PO , and an unknown intermediate. In CDCl_3 at room temperature, **41** remained unchanged after 2 hours and reacted to form 3.68% of orthopalladated product **43** after 24 hours. When heated to 68 °C, **41** reacted to form 71.41% and 76.52% of orthopalladated product **43** after 2 and 24 hours, respectively.

For complex **42**, when dissolved in CDCl_3 and heated to 70 °C for 2 and 24 hours, 28.19% and 51.21% orthopalladated products were observed; when dissolved in CD_2Cl_2 and heated to 46 °C for 2 and 24 hours, 0% and 1.64% orthopalladated products were observed; when dissolved in C_6D_6 and heated to 68 °C for 2 and 24 hours, 2.97% and 28.61% orthopalladated products were observed; when dissolved in toluene- d_8 and heated to 70 °C for 2 and 24 hours, 7.80% and 35.71% orthopalladated products were observed; when dissolved in toluene- d_8 and heated to 80 °C for 2 and 24 hours, 37.08% and 100% orthopalladated products were observed. The comprehensive data demonstrate that solvent, temperature, and time are determinants to govern orthopalladation behavior. In general, chlorinated solvents, high temperature, and extended time of heating promotes the orthopalladation process.

The ^1H NMR spectral data from these heating experiments of **42** has also provided information to allow us to elaborate the mechanism by which orthopalladation occurs. In the very upfield regions of ^1H NMR spectra, we observed signals of CH_4 , CDH_3 , and C_2H_6 . In CDCl_3 and CD_2Cl_2 , methane appeared with a singlet at 0.21 ppm, monodeuterated methane with a triplet at 0.19 ppm, ethane with a singlet at 0.85~0.86 ppm. In C_6D_6 and $\text{C}_6\text{D}_5\text{CD}_3$, methane appeared with a singlet at 0.16~0.17 ppm, ethane with a singlet at 1.00~1.02 ppm. The presence of CH_4 suggests that orthopalladation occur via elimination of a CH_4 molecule. Elimination of CH_4 can be either a free radical or ionic mechanism. However, the fact of formation of C_2H_6 proves the former, because the coupling of two methyl radicals generates C_2H_6 . During the heating process, thermal homolysis cleaved the Pd-CH_3 bond and generated the palladium and methyl radicals. From the appearance, it seems that the methyl radical abstracted an *ortho*-H from the benzene ring on the phosphorus to have caused the elimination of CH_4 and coupling of palladium radical and phenyl radical to have formed the orthopalladated product. But the fact that only *ortho*-H can be removed demonstrated that the palladium radical has attacked the benzene ring before the *ortho*-H was abstracted. Therefore, orthopalladation occurs via the homolytic aromatic substitution (HAS). In this mechanism (Scheme 3.15), the palladium radical substituted the *ortho*-H of a benzene

Scheme 3.15 Mechanism of orthopalladation

ring on phosphorous to form the orthopalladated production. Coupling of a methyl radical and a hydrogen radical afforded CH_4 . Monodeuterated methane results from H/D exchange.

For determination of the structure of **44**, a separate reaction of heating complex **42** has allowed isolation of 47 mg of **44**. Single crystals suitable for X-ray diffraction were obtained by diffusion of pentane into a benzene solution of **44**. The temperature for growing single crystals is at room temperature. Crystals were inspected carefully for their suitability for X-ray crystallography. As is shown in Figure 3.4, the crystal structure of

44 has proven orthopalladation at one of the 2,6-positions of the phosphiniminobenzene ring.

Figure 3.4 ORTEP plot of **44**

Ethylene Reactivity of Triphenylphosphinimine-sulfonate Palladium Methyl Pyridine Complexes

For the understanding of its catalytic properties, **42** was chosen for the ethylene reactivity test. Because of poor solubility in toluene, **41** was not tested for ethylene reactivity. In the experiments, toluene was the solvent, ethylene pressure was 5 atm (76 psi), and temperatures were 25 °C and 80 °C. After 6 hours, clear, yellowish solutions with some black materials were obtained. For quenching the catalyst, methanol was added to the solutions and the mixtures were stirred overnight. Volatiles were removed to result in white solid residues. Then the residues were tested with ^1H NMR. ^1H NMR spectra for both temperatures indicated presence of alkanes, suggesting oligomerization of ethylene occur during the catalytic test. Along with alkanes, we obtained the zwitterionic ligand (**36**) and free 4-*tert*-butylpyridine. Figure 3.5 is the ^1H NMR for ethylene reactivity of **42** at 80 °C. As labeled with z, peaks at 10.27d, 7.86m, 7.83m,

6.75d, 6.33d, and 2.20s prove the existence of **36**. Peaks, labeled with p, resonating 8.49m and 1.29s stand for free 4-*tert*-butylpyridine. Peaks, labeled with a, having chemical shifts 1.24m, 1.20m, and 0.86m are typical for alkane compounds.

Figure 3.5 ¹H NMR for ethylene reactivity of **42** at 80 °C

Ut supra, **42** can be converted to its orthopalladated species **44** at this experimental condition. To exclude possible participation of **44** in the catalytic process, we tested **44** for its ethylene reactivity. **44** was *in situ* generated in a J. Young NMR tube by heating a solution of 5 mg of **42** in toluene-*d*₈. 10 equivalents of ethylene gas were introduced into the tube by vacuum transfer. After 6 hours, ¹H NMR did not show any change. These experiments demonstrate that **42** is the only catalyst having promoted ethylene oligomerization.

3.3 Conclusions

Sodium triphenylphosphinimine sulfonate is the ligand form which can be generated from its zwitterionic form through deprotonation using a strong base such as $\text{NaN}(\text{TMS})_2$ and NaH . In order to obtain a neat complex, we have attempted complexation of the ligand with different palladium precursors, such as $(\text{COD})\text{PdMeCl}$ and $(\text{Py})_2\text{PdMeCl}$, of which the latter works ideally. In our investigations, we understood that $(\text{Py})_2\text{PdMeCl}$ is an intermediate involved in complexation using $(\text{COD})\text{PdMeCl}$ as a precursor. The thermal behavior study shows that the triphenylphosphinimine sulfonate palladium methyl pyridine complexes decompose at high temperature to their orthopalladated species. The catalytic reactivity study shows that triphenylphosphinimine sulfonate palladium methyl pyridine complexes can oligomerize ethylene to alkanes.

3.4 Experimental Section

General Procedures. All manipulations were performed under N_2 or vacuum using standard Schlenk or high vacuum techniques or in N_2 -filled gloveboxes unless otherwise specified. N_2 was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger. Pentane, hexanes, toluene, benzene, and dichloromethane were purified by passage through columns of activated 4 Å molecular sieves. Diethyl ether and tetrahydrofuran were distilled from Na/benzophenone ketyl. CDCl_3 and CD_2Cl_2 were dried over CaH_2 for 24 hours, degassed by freeze-pump-thaw cycles, and vacuum transferred to a storage vessel. Piperidine was obtained from Aldrich and distilled before using. All other solvents were purchased from Aldrich and used

without further purification. ^1H , ^{13}C , ^{31}P , and 2D NMR spectra were recorded in Teflon valve sealed tubes on Varian 400 and 500 spectrometers at ambient probe temperature unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported versus SiMe_4 and were determined by reference to the residual ^1H and ^{13}C solvent peaks. ^{31}P chemical shifts were referenced to external 85% aqueous H_3PO_4 . All the ligands and their precursors bear a sulfonated toluidine parental structure which has an atom-labeling scheme as follows:

Attempted Reaction of $(\text{C}_6\text{H}_5)_3\text{P}=\text{NH}$ -5- $\text{CH}_3\text{C}_6\text{H}_3\text{SO}_3$ (36**) and $(\text{COD})\text{PdMeCl}$.** A valved NMR tube was loaded with toluene-4-triphenylphosphiniminium-3-sulfonate **36** (25.7 mg, 0.057 mmol) and $(\text{COD})\text{PdMeCl}$ (15.1 mg, 0.057 mmol) and CD_2Cl_2 (0.5 mL) was added via vacuum transfer at $-196\text{ }^\circ\text{C}$. After flushed with N_2 gas, the tube was sealed and warmed to $25\text{ }^\circ\text{C}$ and shaken to result in a clear colorless solution. After sitting for 30 min and 24 hours at room temperature, ^1H and ^{31}P NMR spectra were acquired. From the two time intervals, ^1H and ^{31}P NMR spectra indicated that the zwitterion **36** and $(\text{COD})\text{PdMeCl}$ were unchanged and no free COD were observed. They established that no products had formed.

Generation of 2- $((\text{C}_6\text{H}_5)_3\text{P}=\text{N})$ -5- $\text{CH}_3\text{C}_6\text{H}_3\text{SO}_3\text{Na}$ (4**) by Deprotonation of $(\text{Ph}_3\text{P}=\text{NH})$ -5- $\text{CH}_3\text{C}_6\text{H}_3\text{SO}_3$ (**36**) with $\text{NaN}(\text{TMS})_2$ in THF-d_8 .** A valved NMR tube was loaded with **36** (22.4 mg, 0.05 mmol) and $\text{NaN}(\text{TMS})_2$ (9.2 mg, 0.05 mmol) and THF-d_8

(0.5 mL) was added via vacuum transfer at -196 °C. After flushed with N₂ gas, the tube was sealed and warmed to 25 °C and shaken to result in a clear yellowish to greenish solution. ¹H and ³¹P NMR spectra established that **4** had formed. ¹H NMR (THF-d₈): δ 8.00 (m, 6 H, 2,6-CH of (C₆H₅)₃P=N-), 7.74 (s, 1H, 6-CH of -C₆H₃SO₃-), 7.24-7.40 (m, 9H, 3,5-CH of (C₆H₅)₃P=N- and 4-CH of (C₆H₅)₃P=N-), 6.53 (dd, *J* = 2.4, 7.6, 1H, 4-CH of -C₆H₃SO₃-), 6.31 (d, *J* = 7.6, 1H, 3-CH of -C₆H₃SO₃-), 2.01 (s, 3H, 5-CH₃ of -C₆H₃SO₃-), 0.95 (bs, 1H, NH in HN(TMS)₂), 0.05 (s, 18H, CH₃ in HN(TMS)₂). ³¹P NMR (THF-d₈): δ -1.8.

2-((C₆H₅)₃P=N)-5-CH₃C₆H₃SO₃Na (4**).** *a. Using NaN(TMS)₂ as a Base.* A 100 mL Kjejdahl flask containing **36** (0.90 g, 2.00 mmol) and NaN(TMS)₂ (0.37 g, 2.00 mmol) was cooled down with ice bath for 15 minute and charged with THF (50 mL). After 15 minutes, the mixture was warmed up to 25 °C and stirred for 1 hour. A clear slightly yellow solution was obtained. The volume of the solution was reduced to around 10 mL and pentane (30 mL) was added. The mixture was stirred for 30 minutes to result in a white suspension. The suspension stood until 2 layers could be clearly observed. The liquid layer was syringed out. The remaining solid layer was washed with pentane (30 mL) once. After decantation of the solvent, the residue was pumped down to dryness under high vacuum for 2 hours, yielding **4** (0.57 g, 60%) as an amber solid.

b. Using NaH as a Base. To a flask loaded with (Ph₃P=NH)-5-CH₃C₆H₃SO₃ (**36**, 2.23 g, 5.00 mmol) and NaH (0.18 g, 7.50 mmol), THF (60 mL) was added while stirring. The turbid mixture was stirred for 4 hours to give a clear slightly yellow solution, which was filtered through Celite. Removal of THF afforded a yellow solid, which was stirred in

pentane (40 mL) for 30 minutes. The resulting suspension was filtered off and the collected solid was washed with pentane (2x10 mL) yielding **4** (2.09 g, 89%) as a pale yellow powder. ^1H NMR (CD_2Cl_2): δ 7.75 (bs, 6H, 2,6-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 7.45 (bs, 1H, 6-CH of $-\text{C}_6\text{H}_3\text{SO}_3-$), 7.24 (bs, 9H, 3,5-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$ and 4-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 6.60 (bd, $J = 6.4$, 1H, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3-$), 6.34 (bd, $J = 7.2$, 1H, 3-CH of $-\text{C}_6\text{H}_3\text{SO}_3-$), 1.98 (bs, 3H, 5-CH₃ of $-\text{C}_6\text{H}_3\text{SO}_3-$). ^1H NMR ($\text{THF}-d_8$): δ 7.99 (m, 6H, 2,6-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 7.73 (bs, 1H, 6-CH of $-\text{C}_6\text{H}_3\text{SO}_3-$), 7.23-7.48 (m, 9H, 3,5-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$ and 4-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 6.52 (d, $J = 7.5$, 1H, 4-CH of $-\text{C}_6\text{H}_3\text{SO}_3-$), 6.34 (d, $J = 7.5$, 1H, 3-CH of $-\text{C}_6\text{H}_3\text{SO}_3-$), 2.03 (s, 3H, 5-CH₃ of $-\text{C}_6\text{H}_3\text{SO}_3-$). ^{31}P NMR (CD_2Cl_2): δ 7.82 (bs). ^{31}P NMR ($\text{THF}-d_8$): δ -1.64. ^{13}C NMR ($\text{THF}-d_8$): 146.4 (2-C), 138.0 (d, $J_{\text{PC}} = 22.0$, 1-C), 133.0 (d, $J_{\text{PC}} = 9.9$, *ortho*-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 132.0 (d, $J_{\text{PC}} = 98.7$, ipso C of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}$), 130.8 (*para*-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 129.6 (overlapping of 4- and 6-C), 128.2 (d, $J_{\text{PC}} = 12.2$, *meta*-CH of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-$), 123.9 (5-C), 122.0 (3-C), 19.7 (5-CH₃).

[2-(Ph₃P=N)-5-MeC₆H₃SO₃]Pd(Py)Me (41**). a. *Using in situ***

Generated Ligand. A 125 mL Schlenk tube containing zwitterion toluene-4-triphenylphosphonium-3-sulfonate **36** (0.45 g, 1.0 mmol) and $\text{NaN}(\text{TMS})_2$ (0.18 g, 1.0 mmol) was chilled with an

ice bath for 15 minutes and charged with THF (20 mL). After 15 minutes, the mixture was warmed up to 25 °C and stirred for 1 hour. A clear slightly yellow solution was obtained. The solution was pumped down for 2 hours to result in a yellowish solid. The solid was redissolved in CH_2Cl_2 (15 mL) to generate a yellow solution, which was cooled down to -20 °C with an isopropanol-dry ice cold bath for 15 minutes. A solution of

(COD)PdMeCl (0.27 g, 0.1 mmol) in CH₂Cl₂ (5 mL) was introduced via cannula transfer. The reaction was stirred for 30 minutes at -20 °C and warmed up to room temperature for a 1 hour stirring to result in a dark orange solution. The solvent was removed from the reaction mixture to give a yellow solid. The solid was treated with a combination of CH₂Cl₂ (20 mL) and diethyl ether (60 mL), giving a yellow precipitate. The precipitate was collected onto a fritted funnel and washed with CH₂Cl₂-Et₂O 1:4 (20 mL) and Et₂O (3x20 mL). The resulting yellow solid dissolved into CH₂Cl₂ (20mL) to give a yellow solution. Filtration of the solution through Celite and evaporation of the resulting filtrate furnished **41** as a slightly yellow solid (0.33 g, 55%).

b. *Using Isolated Ligand.* A flask containing sodium 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate (**4**) (0.23 g, 0.5 mmol) and bispyridinepalladium (II) methyl chloride (Py₂PdMeCl) (0.16 g, 0.5 mmol) was charged with benzene (30 mL) while stirring. Shortly, an initially observed clear greenish solution turned turbid. The reaction proceeded for 2 hours, resulting in an off-white suspension. The precipitate was collected onto a celite layer and washed with benzene (2x10 mL). The collected solid revealed greenish color and was washed down into a flask with CH₂Cl₂ (3x20 mL). Evaporation of the filtrate afforded a yellowish residue, which was further treated with Et₂O (20 mL) to give a white suspension. The suspension was filtered and washed with Et₂O (2x10 mL) yielding **41** (0.28 g, 86%) as a greenish solid. ¹H NMR (CD₂Cl₂): δ 8.38 (dd, *J* = 6.8, 1.6, 2H, 2,6-CH of (C₅H₅N)Pd), 8.01 (dd, *J*_{PH} = 12.0, *J*_{HH} = 7.2, 6H, 2,6-CH of (C₆H₅)₃P=N-), 7.72 (tt, *J* = 8.0, 1.6, 1H, 4-CH of (C₅H₅N)Pd), 7.59-7.67 (m, 4H, 6-CH of -C₆H₃SO₃- and 4-CH of (C₆H₅)₃P=N-), 7.52 (td, *J*_{HH} = 7.6, *J*_{PH} = 3.2, 6H, 3,5-CH of (C₆H₅)₃P=N-), 7.26 (td, *J* = 6.4, 1.2, 2H, 3,5-CH of (C₅H₅N)Pd), 6.97 (dd, *J* = 8.0, 2.0, 1H, 4-CH of -

C₆H₃SO₃⁻), 6.85 (dd, *J* = 8.0, 2.0, 1H, 3-CH of -C₆H₃SO₃⁻), 2.21 (d, *J* = 1.2, 3H, 5-CH₃ of -C₆H₃SO₃⁻), 0.19 (s, 3H, Pd(CH₃)). ³¹P NMR (CDCl₃): δ 31.8. ¹³C NMR (CD₂Cl₂): δ 156.8, 148.1d (1.6), 147.0d (10.0), 142.2, 139.4d (10.1), 137.5d (3.1), 137.4d (2.3), 135.3d (2.3), 133.6d, 133.3d (101.4), 133.0 (13.2), 131.6d (4.6), (1.6), 129.7, 25.1, 0.0d (1.5). 2D NMR data are as shown in Table 3.1.

[2-(Ph₃P=N)-5-MeC₆H₃SO₃]Pd(4-^tBuPy)Me (42**).**

a. Using in situ Generated Ligand. A 125 mL Schlenk tube containing zwitterion **36** (0.24 g, 0.50 mmol) and NaN(TMS)₂ (0.09 g, 0.50 mmol) was chilled with an ice bath for 15 minutes and charged with benzene (30 mL). After 15 minutes, the mixture was warmed up to 25 °C and stirred for 1 hour. A clear slightly yellow solution was obtained. A solution of (4-^tBu)₂PdMeCl (0.21 g, 0.5 mmol) in benzene (10 mL) was introduced via cannula transfer. The reaction was stirred for 2 hours to result in a yellow solution. Filtration of the solution through Celite and evaporation of the resulting filtrate furnished a yellow solid. The solid was treated with a combination of benzene (5 mL) and pentane (20 mL) and resulting in a white precipitate. The precipitate was collected onto a fritted funnel and washed with pentane (2x10 mL), yielding **42** (0.34 g, 97%) as a white solid.

b. Using Isolated Ligand. A flask containing sodium 2-(triphenylphosphiniminino)-5-methylbenzenesulfonate (**4**) (0.23 g, 0.5 mmol) and bis(4-tert-butylpyridine)palladium (II) methyl chloride (4-^tBuPy₂PdMeCl) (0.21 g, 0.5 mmol) was charged with benzene (30 mL) while stirring. Shortly, an initially observed clear greenish solution turned to a clear

yellowish solution. The reaction proceeded for 2 hours, resulting in a clear yellow solution. The yellow solution was filtered through Celite along

Table 3.2 1D and 2 D NMR Spectral Data of **42** (δ_C and δ_H in ppm; J in Hz)

Position	δ_C (J)	δ_H (J)	HMQC	HMBC	NOSEY
1	142.8d (9.9)		CH		
2	133.1		C	H-4; H-6	
3	127.3	6.89dd (8.0, 2.0)	CH		H-9
4	131.2	6.78dd (8.0, 2.0)	CH	H-2	
5	144.0		C		
6	130.2	7.76s	CH		
7	21.5	2.19s	CH ₃		
8	125.9d(106.3)		CH	H-10	
9	135.5d (9.8)	8.03m	CH	H-11	H-12
10	129.1d (12.1)	7.50m	CH	H-8	
11	133.4	7.58m	CH	H-9	
12	-4.0	0.15s	CH ₃		H-9; H-3
13	152.3	8.24dd (5.2, 1.6)	CH		
14	122.7	7.14 dd (5.2, 1.6)	CH	H-13	
15	162.4		C	H-13	
16	35.7		C		
17	31.0	1.24s	CH ₃		

with 2x10 mL benzene rinsing. Evaporation of the filtrate afforded a yellowish solid residue, which was further treated with benzene (10 mL) and pentane (30 mL) to give a yellowish precipitate. The precipitate was filtered onto a Buchner funnel top and washed with pentane (3x10 mL) yielding **42** (0.28 g, 80%) as a greenish solid. ^1H NMR (CDCl_3): δ 8.24 (dd, J = 5.2, 1.6, 2H, 2,6-*CH* of $(\text{CH}_3)_3\text{C}(\text{C}_5\text{H}_5\text{N})\text{Pd}$), 8.03 (m, 6H, 2,6-*CH* of

(C₆H₅)₃P=N-), 7.76 (*s*, 1H, 6-CH), 7.58 (*m*, 3H, 4-CH of (C₆H₅)₃P=N-), 7.5 (*m*, 3H, 4-CH of (C₆H₅)₃P=N-), 7.14 (*dd*, *J* = 5.2, 1.6, 2H, 3,5-CH of 4-(CH₃)₃C(C₅H₅N)Pd), 6.89 (*dd*, *J* = 8.0, 2.0, 1H, 3-CH), 6.78 (*dd*, *J* = 8.0, 2.0, 1H, 4-CH), 2.19 (*s*, 3H, 5-CH₃), 1.24 (*s*, 9H, 4-(CH₃)₃C(C₅H₅N)Pd), 0.15 (*s*, 3H, CH₃Pd). ³¹P NMR (CDCl₃): δ 31.3. ¹³C NMR (CDCl₃): δ 162.4, 152.3, 144.0, 142.8 (*d*, *J*_{PC} = 9.9), 135.5 (*d*, *J*_{PC} = 9.8, *ortho*-CH of (C₆H₅)₃P=N-), 133.4 (*para*-CH of (C₆H₅)₃P=N-), 133.1, 131.2, 130.2, 130.4 (*d*, *J*_{PC} = 106.3, *ipso* C of (C₆H₅)₃P=N-), 129.1 (*d*, *J*_{PC} = 12.1, *meta*-CH of (C₆H₅)₃P=N-), 127.3, 122.7, 35.7, 34.0, 21.5, -4.0. 2D NMR data are as shown in Table 3.2.

VT NMR Experiments of [2-(Ph₃P=N)-5-

MeC₆H₃SO₃]Pd(4-^tBuPy)Me (42**). A valved NMR tube was loaded with **42** (20.0 mg, 28.4 μmol) and CD₂Cl₂ (0.5 mL) was added via vacuum transfer at -196 °C. After**

flushed with N₂ gas, the tube was sealed and warmed to 25 °C and shaken to result in a yellow solution. ¹H and ³¹P NMR spectra were acquired at temperatures 10, -10, -30, -50, -60, -70, and -90 °C. ¹H NMR (CD₂Cl₂, 10 °C): δ 8.22 (*d*, *J* = 5.2, 2H, 2,6-CH of 4-^tBuPy), 8.01 (*m*, 6H, 2,6-CH of (C₆H₅)₃P=N-), 7.62 (*t*, *J* = 6.0, 3H, 4-CH of (C₆H₅)₃P=N-), 7.58 (*s*, 1H, 6-CH), 7.52 (*m*, 6H, 3,5-CH of (C₆H₅)₃P=N-), 7.23 (*d*, *J* = 5.2, 2H, 3,5-CH of 4-^tBuPy), 6.97 (*d*, *J* = 6.80, 1H, 3-CH), 6.84 (*d*, *J* = 6.8, 1H, 4-CH), 2.20 (*s*, 3H, 5-CH₃), 1.25 (*s*, 9H, ^tBu), 0.15 (*s*, 3H, CH₃Pd). ³¹P NMR (CDCl₃): δ 31.6. ¹H NMR (CD₂Cl₂, -10 °C): δ 8.19 (*d*, *J* = 5.2, 2H, 2,6-CH of 4-^tBuPy), 8.00 (*bs*, 6H, 2,6-CH of (C₆H₅)₃P=N-), 7.63 (*m*, 4H, 4-CH of (C₆H₅)₃P=N- and 6-CH), 7.52 (*m*, 6H, 3,5-CH of (C₆H₅)₃P=N-), 7.23 (*d*, *J* = 5.2, 2H, 3,5-CH of 4-^tBuPy), 6.99 (*d*, *J* = 6.80, 1H, 3-CH), 6.88 (*d*, *J* = 6.8, 1H, 4-CH), 2.19 (*s*, 3H, 5-CH₃), 1.24 (*s*, 9H, ^tBu), 0.13 (*s*, 3H, CH₃Pd).

^{31}P NMR (CDCl_3): δ 31.7. ^1H NMR (CD_2Cl_2 , $-30\text{ }^\circ\text{C}$): δ 8.17 (d, $J = 5.2$, 2,6-CH of 4- $^t\text{BuPy}$), 7.41-8.10 (broadened by coalescence, 16H, 6-CH and $(\text{C}_6\text{H}_5)_3\text{P=N-}$), 7.23 (d, $J = 5.2$, 2H, 3,5-CH of 4- $^t\text{BuPy}$), 6.99 (d, $J = 6.80$, 1H, 3-CH), 6.85 (d, $J = 6.8$, 1H, 4-CH), 2.18 (s, 3H, 5- CH_3), 1.23 (s, 9H, ^tBu), 0.11 (s, 3H, CH_3Pd). ^{31}P NMR (CDCl_3): δ 31.8. ^1H NMR (CD_2Cl_2 , $-50\text{ }^\circ\text{C}$): δ 8.15 (d, $J = 5.2$, 2,6-CH of 4- $^t\text{BuPy}$), 7.44-7.96 (broadened by coalescence, 16H, 6-CH and $(\text{C}_6\text{H}_5)_3\text{P=N-}$), 7.21 (d, $J = 5.2$, 2H, 3,5-CH of 4- $^t\text{BuPy}$), 7.00 (d, $J = 6.80$, 1H, 3-CH), 6.85 (d, $J = 6.8$, 1H, 4-CH), 2.15 (s, 3H, 5- CH_3), 1.20 (s, 9H, ^tBu), 0.08 (s, 3H, CH_3Pd). ^{31}P NMR (CDCl_3): δ 31.9. ^1H NMR (CD_2Cl_2 , $-60\text{ }^\circ\text{C}$): δ 8.40-8.80 (broadened by coalescence), 8.07 (d, $J = 5.2$, 2,6-CH of 4- $^t\text{BuPy}$), 7.44-7.86 (broadened by coalescence), 7.41 (s, 3H, 6-CH), 7.15 (d, $J = 5.2$, 2H, 3,5-CH of 4- $^t\text{BuPy}$), 6.94 (d, $J = 6.80$, 1H, 3-CH), 6.77 (d, $J = 6.8$, 1H, 4-CH), 2.06 (s, 3H, 5- CH_3), 1.21 (s, 9H, ^tBu), 0.00 (s, 3H, CH_3Pd). ^{31}P NMR (CDCl_3): δ 32.0. ^1H NMR (CD_2Cl_2 , $-70\text{ }^\circ\text{C}$): δ 8.70 (bm, 2H, $(\text{C}_6\text{H}_5)_3\text{P=N-}$), 8.11 (d, $J = 5.2$, 2H, 2,6-CH of 4- $^t\text{BuPy}$), 7.60-7.95 (bm, 10H, $(\text{C}_6\text{H}_5)_3\text{P=N-}$), 7.32-7.52 (m, 6H, 6-CH and $(\text{C}_6\text{H}_5)_3\text{P=N-}$), 7.21 (d, $J = 5.2$, 2H, 3,5-CH of 4- $^t\text{BuPy}$), 7.00 (d, $J = 6.80$, 1H, 3-CH), 6.82 (d, $J = 6.8$, 1H, 4-CH), 2.12 (s, 3H, 5- CH_3), 1.17 (s, 9H, ^tBu), 0.06 (s, 3H, CH_3Pd). ^{31}P NMR (CDCl_3): δ 32.0. ^1H NMR (CD_2Cl_2 , $-90\text{ }^\circ\text{C}$): δ 8.67 (m, 2H, $(\text{C}_6\text{H}_5)_3\text{P=N-}$), 8.09 (d, $J = 5.2$, 2,6-CH of 4- $^t\text{BuPy}$), 7.85 (m, 2H, $(\text{C}_6\text{H}_5)_3\text{P=N-}$), 7.77 (m, 1H, $(\text{C}_6\text{H}_5)_3\text{P=N-}$), 7.67 (bm, 6H, $(\text{C}_6\text{H}_5)_3\text{P=N-}$), 7.38-7.46 (bm, 5H, $(\text{C}_6\text{H}_5)_3\text{P=N}$ and 6-CH), 7.21 (d, $J = 5.2$, 2H, 3,5-CH of 4- $^t\text{BuPy}$), 7.00 (d, $J = 6.80$, 1H, 3-CH), 6.82 (d, $J = 6.8$, 1H, 4-CH), 2.10 (s, 3H, 5- CH_3), 1.15 (s, 9H, ^tBu), 0.03 (s, 3H, CH_3Pd). ^{31}P NMR (CDCl_3): δ 32.0.

Crystal data and structure refinement for **42**

Empirical formula	C ₃₅ H ₃₇ N ₂ O ₃ P Pd S
Formula weight	703.10
Temperature	100.0 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P b c n
Unit cell dimensions	a = 17.86211(17) Å α = 90°. b = 17.52994(15) Å β = 90°. c = 21.0147(2) Å γ = 90°.
Volume	6580.15(11) Å ³
Z	8
Density (calculated)	1.419 Mg/m ³
Absorption coefficient	0.713 mm ⁻¹
F(000)	2896
Crystal color, habit	yellow prism
Crystal size	0.23 x 0.14 x 0.13 mm ³
Theta range for data collection	3.21 to 29.16°
Index ranges	0 ≤ h ≤ 24, 0 ≤ k ≤ 24, 0 ≤ l ≤ 28
Reflections collected	8871
Independent reflections	8871 [R(int) = 0.0000]
Completeness to theta = 29.16°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9103
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8871 / 0 / 344
Goodness-of-fit on F ²	1.079
Final R indices [I > 2σ(I)]	R1 = 0.0435, wR2 = 0.0957
R indices (all data)	R1 = 0.0649, wR2 = 0.1041
Largest diff. peak and hole	1.719 and -1.173 e.Å ⁻³

Thermal Behavior of [2-(Ph₃P=N)-5-MeC₆H₃SO₃]Pd(Py)Me (**41**): Formation of [2-

((C₆H₄)Ph₂P=N)-5-MeC₆H₃SO₃]Pd(Py) (**43**). In CDCl₃, at 25 °C. A valved NMR tube

was loaded with **41** (15.0 mg, 23 μmol) and CDCl₃ (0.5 mL) was added via vacuum

transfer at -196 °C. After flushed with N₂ gas, the tube was sealed and warmed to 25 °C

and shaken to result in a greenish solution. ¹H and ³¹P NMR spectra established that **43**

had not formed. The solution sat at room temperature for 2 hours and 24 hours. ¹H and

^{31}P NMR spectra were obtained for each time interval. ^1H and ^{31}P NMR spectra established that **43** had not formed. *In CDCl₃, at 68 °C.* A valved NMR tube was loaded with **41** (15.0 mg, 23 μmol) and CDCl_3 (0.5 mL) was added via vacuum transfer at -196 °C. After flushed with N_2 gas, the tube was sealed and warmed to 25 °C and shaken to result in a greenish solution. ^1H and ^{31}P NMR spectra established that **43** had not formed. The solution was heated to 68 °C for 2 hours and 24 hours. ^1H and ^{31}P NMR spectra were obtained for each time interval. After 2 hours, the integration of ^{31}P NMR spectra established that decomposition of **41** had proceeded to a significant degree and revealed a mixture with multiple phosphorous compounds, **43** (δ_{P} 46.7, 71.41%), [2-($\text{Ph}_3\text{P}=\text{N}$)-5-MeC₆H₃SO₃] $\text{Pd}(\text{Py})\text{Cl}$ (abbreviated as **Pd-Cl**) (δ_{P} 35.3, 7.95%), unknown intermediate (δ_{P} 33.5, 1.80%), **41** (δ_{P} 31.5, 6.05%), zwitterion **36** (δ_{P} 30.9, 9.38%), and Ph_3PO (δ_{P} 28.3, 1.65%). After 24 hours, the integration of ^{31}P NMR spectra established that decomposition of **41** had completed and revealed a mixture containing **43** (δ_{P} 46.7, 76.52%), **Pd-Cl** (δ_{P} 35.3, 5.08%), zwitterion **36** (δ_{P} 30.9, 16.4%), and Ph_3PO (δ_{P} 28.3, 1.99%). ^1H NMR shows presence of multiple components including **43**, **Pd-Cl**, $(\text{Py})_2\text{PdCl}_2$, and **36**. ^1H and ^{31}P NMR data from the 24 hour experiment are as follows:

^1H NMR (CDCl_3): δ 10.35 (d, $J = 12.0$, 0.17 H, **36**), 8.97 (d, $J = 4.8$, 2 H, 2,6-*CH* of Py of **43**), 8.84 (d, $J = 5.2$, 0.51H, $(\text{Py})_2\text{PdCl}_2$), 8.30 (d, $J = 8.0$, **Pd-Cl**), 7.80-8.00 (m, 7.83 H), 7.65 (m, 3.57H), 7.54 (m, 4.48H), 7.42 (t, $J = 8.0$, 2H, 3,5-*CH* of PdPy of **43**), 7.34 (t, $J = 7.6$, $(\text{Py})_2\text{PdCl}_2$), 6.90-7.10 (m, 3.02H), 6.78 (d, 0.31H), 6.56 (dd, $J = 8.4$, 2.4, 1H, 4-*CH* of **43**), 6.35-6.40 (m, 1.19H), 6.27 (d, $J = 6.8$, 3-*CH* of **43**), 2.22 (s, 1.03H, **36**), 2.18 (s, **41**), 2.14 (s, 3H, 5-*CH*₃ in **43**), 0.85 (s, 0.21H, C_2H_6), 0.21(s, 0.76H, CH_4). ^{31}P NMR

(CDCl₃): δ_P 46.7 (**43**, 76.52%), 35.3 (**Pd-Cl**, 5.08%), 30.9 (**36**, 16.4%), and δ_P 28.3 (Ph₃PO, 1.99%).

Thermal Behavior of [2-(Ph₃P=N)-5-MeC₆H₃SO₃]Pd(4-^tBuPy)Me (42**): Formation of [2-((C₆H₄)Ph₂P=N)-5-MeC₆H₃SO₃]Pd(4-^tBuPy) (**44**).** *In CDCl₃ at 70 °C.* A valved NMR tube was loaded with **42** (15.0 mg, 21 μ mol) and CDCl₃ (0.5 mL) was added via vacuum transfer at -196 °C. After flushed with N₂ gas, the tube was sealed and warmed to 25 °C and shaken to result in a greenish solution. ¹H and ³¹P NMR spectra established that **44** had not formed. The solution was heated to 68 °C for 2 and 24 hours. ¹H and ³¹P NMR spectra were obtained for each time interval. After 2 hours, ³¹P NMR spectra established that decomposition of **42** had proceeded to a significant degree and revealed a mixture with multiple phosphorous compounds, **44** (δ_P 46.5, 28.19%), [2-(Ph₃P=N)-5-MeC₆H₃SO₃]Pd(4-^tBuPy)Cl (abbreviated as ^tBu**Pd-Cl**) (δ_P 35.1, 5.84%), unknown intermediate (δ_P 33.3, 1.57%), **42** (δ_P 31.3, 40.56%), zwitterion **36** (δ_P 30.9, 21.17), and Ph₃PO (δ_P 28.9, 2.66%). After 24 hours, ³¹P NMR spectra established that decomposition of **42** had completed and revealed a mixture containing **44** (δ_P 46.4, 51.21%), ^tBu**Pd-Cl** (δ_P 35.1, 2.82%), zwitterion **36** (δ_P 30.9, 42.02%), and Ph₃PO (δ_P 28.3, 3.95%). ¹H NMR shows presence of multiple components including **44**, ^tBu**Pd-Cl**, **36**, and Ph₃PO. ¹H and ³¹P NMR data from the 24 hour experiment are as follows: ¹H NMR (CDCl₃): δ 10.33 (d, J = 12.0, 0.12H, **36**), 8.72 (d, J = 4.0, 2H, 2,6-CH of Py of **44**), 8.58 (d, J = 4.0, 0.87H, ^tBu**Pd-Cl**), 8.04 (m, 0.26H), 7.72-7.90 (m, 6.56 H), 7.67 (t, J = 6.4, 1.47H), 7.50-7.60 (m, 4.52H), 7.38-7.42 (m, 4.28H), 7.22-7.3 (m, 2.32H), 7.20 (d, J = 12.0, 0.87H, ^tBu**Pd-Cl**), 7.02 (d, J = 5.2, 0.20H), 6.80-6.90 (m, 2.30H), 6.65 (d, J = 5.6, 0.58H), 6.45 (d, J = 6.8, 0.84H), 6.23 (d, J = 6.4, 2H), 2.12 (s, 2.43H, **36**), 2.03(s, 2.51H, **42**), 1.25 (s, 7.28H),

1.15 (s, 6H), 0.11(s, 0.35H, CH₄). ³¹P NMR (CDCl₃): δ_P 46.4 (**44**, 51.21%), 35.1 (^tBuPd-Cl, 2.82%), 30.9 (**36**, 42.02%), and δ_P 28.3 (Ph₃PO, 3.95%). In CD₂Cl₂ at 46 °C. A valved NMR tube was loaded with **42** (15.0 mg, 21 μmol) and CD₂Cl₂ (0.5 mL) was added via vacuum transfer at -196 °C. After flushed with N₂ gas, the tube was sealed and warmed to 25 °C and shaken to result in a greenish solution. ¹H and ³¹P NMR spectra established that **44** had not formed. The solution was heated to 46 °C for 2, 24, 72, and 120 hours. ¹H and ³¹P NMR spectra were obtained for each time interval. After 2 hours, ³¹P NMR spectra established that decomposition of **42** had proceeded to a significant degree and revealed a mixture containing multiple phosphorous compounds, [2-(Ph₃P=N)-5-MeC₆H₃SO₃]Pd(4-^tBuPy)Cl (^tBuPd-Cl) (δ_P 35.2, 4.63%), unknown intermediate (δ_P 33.5, 10.76%), **42** (δ_P 31.5, 84.61%). The orthopalladated species [2-((C₆H₄)Ph₂P=N)-5-MeC₆H₃SO₃]Pd(4-^tBuPy) (**44**) had not formed at this stage. After 24 hours, ³¹P NMR spectra established that decomposition of **42** proceeded further, revealing a mixture that contains **44** (δ_P 47.0, 1.64%), ^tBuPd-Cl (δ_P 35.2, 8.94%), unknown intermediate (δ_P 33.5, 35.81%), zwitterion **36** (δ_P 32.1, 3.38%), starting complex **42** (δ_P 31.6, 47.09%), and Ph₃PO (δ_P 28.2, 0.82%). The orthopalladated species **44** formed in insignificant amount. After 72 hours, ³¹P NMR spectra established that decomposition of **42** proceeded further, revealing a mixture that contains **44** (δ_P 47.0, 7.64%), ^tBuPd-Cl (δ_P 35.2, 9.52%), unknown intermediate (δ_P 33.5, 26.69%), zwitterion **36** (δ_P 32.1, 4.45%), starting complex **42** in overlapping with an unknown (δ_P 31.7 and 31.6, 48.78%), and Ph₃PO (δ_P 27.1, 2.92%). After 120 hours, ³¹P NMR spectra established that decomposition of **42** had not completed, revealing a mixture that contains **44** (δ_P 47.0, 10.0%), ^tBuPd-Cl (δ_P 35.2, 7.43%), unknown intermediate (δ_P 33.5, 11.74%), starting complex **42** in overlapping

with an unknown (δ_P 31.7 and 31.6, 51.24%), and Ph_3PO (δ_P 27.1, 12.05%). Zwitterion was not observed. ^1H NMR spectrum of the 120 hour experiment was too complicated to be interpreted. Due to serious overlapped peaks, it had been difficult to assign integration numbers to each peak. Only chemical shifts of some observable proton peaks are listed here. ^1H NMR (CDCl_3): δ 10.33d, 8.80d, 8.66d, 8.60d, 6.82d, 6.44d, 2.24s, 2.15s, 1.37s, 1.31s, 1.25s, 0.85s, 0.17s. ^{31}P NMR (CDCl_3): δ_P 47.0 (**44**, 10.0%), 35.2 ($^{\text{tBu}}\text{Pd-Cl}$, 7.43%), 33.5 (11.74%), 31.7 and 31.6 (51.24%), and δ_P 27.1 (Ph_3PO , 12.05%). In C_6D_6 at 68 °C. A valved NMR tube was loaded with **42** (15.0 mg, 21 μmol) and C_6D_6 (0.5 mL) was added via vacuum transfer at -196 °C. After flushed with N_2 gas, the tube was sealed and warmed to 25 °C and shaken to result in a greenish solution. ^1H and ^{31}P NMR spectra established that **44** had not formed. The solution was heated to 68 °C for 2 and 24 hours. ^1H and ^{31}P NMR spectra were obtained for each time interval. After 2 hours, ^{31}P NMR spectra established that decomposition of **42** had proceeded to an insignificant degree and revealed a mixture containing multiple phosphorous compounds, **44** (δ_P 45.4, 2.97%), unknown intermediate (δ_P 34.6, 0.74%), and **42** (δ_P 30.8, 96.30%). After 24 hours, ^{31}P NMR spectra established that decomposition of **42** had proceeded to a significant degree and revealed a mixture containing a mixture containing multiple phosphorous compounds, **44** (δ_P 45.4, 28.61%), unknown intermediate (δ_P 34.6, 1.38%), **42** (δ_P 30.8, 69.42%) and Ph_3PO (δ_P 24.7, 0.58%). ^1H and ^{31}P NMR data from the 24 hour experiment are as follows: ^1H NMR (CDCl_3): 8.63 (d, J = 6.8, 0.93H), 8.56(d, J = 4.0, 1.35H), 8.40(s, 1.15H), 8.29 (m, 5.84H), 8.18 (d, J = 6.8, H = 2.37), 7.91 (m, 2H), 6.70-7.20 (m, 14.96H), 6.83 (d, J = 6.4, 1.23H), 6.78 (m, 1.49H), 6.64 (d, J = 8.0, 1.1H), 6.55 (d, 0.60 H), 6.47(d, J = 6.4, 1.40H), 6.36 (d, J = 6.8, 2H), 1.87 (s, 2.93H), 1.85(s, 1.61H), 1.00 (s, 4.19H),

0.79s and 0.78s (3.95H), 0.58(s, 3H), 0.15(s, 0.61H, CH₄). ³¹P NMR (C₆D₆): δ_P 45.4 (**44**, 28.61%), 34.6 (unknown, 1.38%), 30.8 (53, 69.42%), and 24.7 (Ph₃PO, 0.58%).

In C₆D₆CD₃ at 70 °C. A valved NMR tube was loaded with **42** (5 mg, 7.5 μmol) and toluene-d₈ (0.5 mL) was added via vacuum transfer at -196 °C. After flushed with N₂ gas, the tube was sealed and warmed to 25 °C and shaken to result in a solution. ¹H and ³¹P NMR spectra established that **44** had not formed. After 2 hours, ³¹P NMR spectra established that decomposition of **42** had proceeded to an insignificant degree and revealed a mixture containing multiple phosphorous compounds, **44** (δ_P 50.4, 7.80%), unknown intermediate (δ_P 39.6, 2.96%), and **42** (δ_P 35.8, 87.9%). After 24 hours, ³¹P NMR spectra established that decomposition of **42** had proceeded further, revealing a mixture containing multiple phosphorous compounds, **44** (δ_P 50.4, 35.72%), unknown intermediate (δ_P 39.6, 3.25%), and **42** (δ_P 35.8, 57.92%). ¹H and ³¹P NMR data from the 24 hour experiment are as follows: ¹H NMR (C₆D₅CD₃): 8.84 (d, *J* = 5.6, 0.15H), 8.58 (d, *J* = 4.8, 0.55H), 8.49 (d, *J* = 4.0, 0.48H), 8.39 (s, 0.49H), 8.23 (m, 3.26H), 8.15 (d, *J* = 5.2, *H* = 1.14), 7.90 (m, 1.22H), 6.90-7.30 (m, 12.68H), 6.72-6.85 (m, 2.03H), 6.55-6.65 (m, 1.39), 6.35-6.52 (m, 2.48H), 1.92s and 1.89s (2.78H), 1.01(s, 3H), 0.62-0.92 (m, 10.65H), 0.46 (s, 1.65H), 0.17(s, 0.41H, CH₄). ³¹P NMR (C₆D₆): δ_P 50.4 (**44**, 35.42%), 39.6 (unknown, 3.25%), 35.8 (53, 57.99%). *In C₆D₆CD₃ at 25 °C.*

A valved NMR tube was loaded with **42** (10.0 mg, 14 μmol) and C₆D₅CD₃ (0.5 mL) was added via vacuum transfer at -196 °C. After flushed with N₂ gas, the tube was sealed and warmed to 25 °C and shaken to result in a greenish solution. ¹H and ³¹P NMR spectra established that **44** had not formed. The solution sat at room temperature for 6 and 48 hours, ¹H and ³¹P NMR spectra established that **44** had not formed. *In C₆D₆CD₃ at 80 °C*

A valved NMR tube was loaded with **42** (5 mg, 7.5 μmol) and toluene- d_8 (0.5 mL) was added via vacuum transfer at -196°C . After flushed with N_2 gas, the tube was sealed and warmed to 25°C and shaken to result in a solution. ^1H and ^{31}P NMR spectra established that **44** had not formed. The solution was heated to 80°C for 2, 6, and 24 hours. ^1H and ^{31}P NMR spectra were obtained for each time interval. The integration of ^{31}P NMR spectra established that after 2 hours at 80°C , **42** and **44** coexisted in the solution and 37.08% of the starting **42** had been converted to **44**; after 6 hours, **42** was almost completely consumed and **44** was present in the solution only and 98.5.0% of the starting **42** had been converted to **44**; after 6 hours, **42** was completely consumed and it showed 100% **44** on the ^{31}P NMR. ^1H and ^{31}P NMR data from the 24 hour experiment are as follows: ^1H NMR (toluene- d_8): δ 8.55 (d, $J = 6.8$, 2 H, 2,6- CH of 4- $^t\text{BuPy}$), 8.41 (s, 1H, 6- CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 7.89 (m, 4H, 2,6- CH of $-\text{Ph}_2\text{P}=\text{N}-$), 7.60-7.78 (m, 20H), 6.95-7.22 (m, 45H), 6.70-6.85 (m, 3H), 6.55 (d, $J = 6.8$, 2H, 3,5- CH of 4- $^t\text{BuPy}$), 6.50 (d, $J = 6.0$, 6.38 (s, 2H), 1.89 (s, 3H, 5-Me), 0.84 (s, 9H, ^tBu), 0.18 (s, 0.83H, CH_4). ^{31}P NMR (toluene- d_8): δ 50.2 (**44**). *In $\text{C}_6\text{D}_6\text{CD}_3$ at 80°C in 8 hours without Internal Standard.* A valved NMR tube was loaded with **42** (3.0 mg, 4.2 μmol) and toluene- d_8 (0.5 mL) was added via vacuum transfer at -196°C . After flushed with N_2 gas, the tube was sealed and warmed to 25°C and shaken to result in a solution. ^1H and ^{31}P NMR spectra established that **44** had not formed. The solution was heated to 80°C for 8 hours. ^1H and ^{31}P NMR spectra were obtained. The integration of ^{31}P NMR spectra established that after 8 hours at 80°C , after 6 hours, **42** was completely consumed up and it showed 100% **44** on the ^{31}P NMR. ^1H and ^{31}P NMR data from the 24 hour experiment are as follows: ^1H NMR (toluene- d_8): δ 8.54 (d, $J = 6.8$, 2 H, 2,6- CH of 4- $^t\text{BuPy}$), 8.44 (s, 1H, 6- CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$

), 7.90 (m, 4H, 2,6-CH of $-\text{Ph}_2\text{P}=\text{N}-$), 7.60-7.78 (m, 20H), 6.95-7.22 (m, 45H), 6.70-6.85 (m, 3H), 6.55 (d, $J = 6.8$, 2H, 3,5-CH of 4- $^t\text{BuPy}$), 6.50 (d, $J = 6.0$, 6.38 (s, 2H), 1.89 (s, 3H, 5-Me), 0.84 (s, 9H, ^tBu), 0.18 (s, 0.83H, CH_4). ^{31}P NMR (toluene- d_8): δ 50.2 (**44**). In $\text{C}_6\text{D}_6\text{CD}_3$ at 80 °C in 16 hours with Ph_3PO as Internal Standard. A valved NMR tube was loaded with **42** (3.0 mg, 4.2 μmol) and Ph_3PO (3.0 mg, 10.8 μmol) and toluene- d_8 (0.5 mL) was added via vacuum transfer at -196 °C. After flushed with N_2 gas, the tube was sealed and warmed to 25 °C and shaken to result in a solution. ^1H and ^{31}P NMR spectra established that **44** had not formed. The solution was heated to 80 °C for 16 hours. ^1H and ^{31}P NMR spectra were obtained. ^{31}P NMR spectra established that **42** was completely converted to **44**. ^1H NMR (toluene- d_8): δ 8.56 (d, $J = 6.8$, 2 H, 2,6-CH of 4- $^t\text{BuPy}$), 8.41(s, 1H, 6-CH of $-\text{C}_6\text{H}_3\text{SO}_3-$), 7.89 (m, 4H, 2,6-CH of $-\text{Ph}_2\text{P}=\text{N}-$), 7.60-7.78 (m, 14H), 6.95-7.22 (m, 40H), 6.70-6.80 (m, 3H), 6.53 (d, $J = 6.8$, 3H), 6.37 (s, 2H), 1.90 (s, 3H, 5-Me), 0.85 (s, 9H, ^tBu), 0.18 (s, 0.58H, CH_4). ^{31}P NMR (toluene- d_8): δ 50.2 (**44**, 44.2%), 28.7 (Ph_3PO , 100%).

[2-((C₆H₄)Ph₂P=N)-5-MeC₆H₃SO₃]Pd(4- $^t\text{BuPy}$) (44**)** A solution of [2-($\text{Ph}_3\text{P}=\text{N}$)-5-MeC₆H₃SO₃]Pd(4- $^t\text{BuPy}$)Me (**42**) (0.28 mmol, 0.20 g) in toluene (20 mL) was heated to 80 °C for 15 hours, resulting a solution with black solid.

The reaction mixture was filtered through Celite to give a yellow solution. Evaporation of the solution yielded **44** as a yellow powder (47 mg, 24%). ^1H NMR (toluene- d_8): δ 8.56 (d, $J = 6.8$, 2 H, 2,6-CH of 4- $^t\text{BuPy}$), 8.40 (s, 1H, 6-CH of $-\text{C}_6\text{H}_3\text{SO}_3-$), 7.90 (m, 4H, 2,6-CH of $-\text{Ph}_2\text{P}=\text{N}-$), 6.70-6.85 (m, 3H), 6.55 (d, $J = 6.8$, 2H, 3,5-CH of 4- $^t\text{BuPy}$), 6.50 (d, J

= 6.0, 2H), 6.37 (s, 2H), 1.89 (s, 3H, 5-Me), 0.84 (s, 9H, ^tBu). ³¹P NMR (toluene-d₈): δ 50.2.

Crystal data and structure refinement for 44

Empirical formula	C ₄₃ H ₂₃ N ₂ O ₃ P Pd S	
Formula weight	785.06	
Temperature	99.9(1) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.3572(6) Å	α = 87.010(6)°
	b = 11.8341(8) Å	β = 87.005(6)°
	c = 18.5228(14) Å	γ = 69.223(6)°
Volume	1913.9(2) Å ³	
Z	2	
Density (calculated)	1.362 Mg/m ³	
Absorption coefficient	0.622 mm ⁻¹	
F(000)	792	
Crystal color, habit	colorless plate	
Crystal size	0.21 x 0.05 x 0.01 mm ³	
Theta range for data collection	3.26 to 27.56°	
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -24 ≤ l ≤ 24	
Reflections collected	30705	
Independent reflections	8824 [R(int) = 0.0622]	
Completeness to theta = 27.56°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.888	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8824 / 6 / 410	
Goodness-of-fit on F ²	1.084	
Final R indices [I > 2σ(I)]	R1 = 0.0502, wR2 = 0.1071	
R indices (all data)	R1 = 0.0694, wR2 = 0.1151	
Largest diff. peak and hole	1.507 and -1.183 e.Å ⁻³	

Ethylene Reactivity of 42. At room temperature. To a high-pressure glass reactor, 42

(10.3 mg, 0.015 mmol) was loaded in a glovebox. Under positive N₂ gas, toluene (20 mL) was added. After a brief evacuation, ethylene gas (5 atm) was introduced. The mixture was stirred for 6 hours at room temperature to result in a turbid suspension. MeOH was

added and the mixture turned clear with some black residues. The mixture was filtered through Celite. The obtained filtrate was pumped down to afford a white powder (32 mg). ^1H and ^{31}P NMR spectra were obtained for the white powder. ^1H NMR (CDCl_3): δ 10.59 (d, 0.62H, **36**), 7.6-8.0 (m, 10.7), 6.80 (m, 1.01 H, **36**), 6.38 (m, 0.89H, **36**), 2.23 (s, 3H, **36**), 1.25-1.35 (m, 5.85H, alkanes), 0.88 (m, 2.26H, alkanes). ^{31}P NMR (CDCl_3): δ 31.0 (**36**). At 80 °C. To a high-pressure glass reactor, **42** (10.3 mg, 0.015 mmol) was loaded in a glovebox. Under positive N_2 gas, toluene (20 mL) was added. After a brief evacuation, ethylene gas (5 atm) was introduced. The mixture was heated to 80 °C and stirred for 6 hours to result in a turbid suspension. MeOH was added and the mixture turned clear with some black residues. The mixture was filtered through Celite. The obtained filtrate was pumped down. ^1H and ^{31}P NMR spectra were obtained for the residues. ^1H NMR (CDCl_3): δ 10.14 (d, 0.89H, **36**), 8.68 (d, 0.73H, tBuPy), 8.09 (s, 1.11H), 7.6-8.0 (m, 15.8H), 6.80 (dd, 1.00 H, **36**), 6.38 (d, 1.00H, **36**), 2.23 (s, 3H, **36**), 1.36 (s, 3.69H, tBuPy), 1.29 (s, 2.76H, alkanes), 1.25 (bs, 4.29H, alkanes), 0.85 (t, 1.77H, alkanes), 0.06 (s, 0.46H, **44**), ^{31}P NMR (CDCl_3): δ 43.9 (**44**), 31.3 (**36**).

CHAPTER FOUR

SYNTHESIS AND REACTIVITY OF
ALKYL-BASED PHOSPHINIMINE-SULFONATE PALLADIUM
METHYL PYRIDINE COMPLEXES

4.1 Introduction

In chapter three, our initial work indicates triphenylphosphinimine sulfonate palladium methyl pyridine complex can catalyze oligomerization of ethylene to form alkanes. Our study of the thermal behavior shows that orthopalladation occurs when the complex is heated to 80 °C. Our study also shows that the orthopalladated product itself does not catalyze the oligomerization process. Therefore, orthopalladation can be regarded as a pathway of deactivation of the catalyst. Orthopalladation occurs on the 2 position of a phosphininobenzene ring. To avoid orthopalladation, we have synthesized alkyl analogues such as methyldiphenyl, dibutylphenyl, and tributylphosphinimine sulfonate palladium methyl pyridine complexes. Their thermal behavior and catalytic properties are investigated.

4.2 Results and Discussion

Synthesis of Methyldiphenyl, Di-n-butylphenyl, and Tri-n-butylphosphinimine-sulfonate Palladium Methyl 4-tert-Butylpyridine Complexes

The synthesis of alkyl-based phosphinimine-sulfonate palladium complexes methyldiphenylphosphinimine-sulfonate palladium methyl 4-tert-butylpyridine (**45**), di-n-butylphenylphosphinimine-sulfonate palladium methyl 4-tert-butylpyridine (**46**), and tri-n-butylphosphinimine-sulfonate palladium methyl 4-tert-butylpyridine (**47**) started with the corresponding zwitterions methyldiphenylphosphiniminium-sulfonate (**37**), di-n-butylphenylphosphinimine-sulfonate (**48**) and tri-n-butylphosphinimine-sulfonate (**49**) (**48** and **49** were synthesized by following the procedure described in chapter two). The zwitterions were deprotonated with NaH to generate their sodium salts (**50**, **51**, and **52**), which reacted with bis(4-tert-butylpyridine)palladium methyl chloride at room temperature to form the desired complexes **45**, **46**, and **47** (Scheme 4.1).

Scheme 4.1 Synthesis of **45-47**

Methyldiphenylphosphinimine-sulfonate palladium methyl 4-tert-butylpyridine (**45**) was characterized by interpretation of ^1H , ^{31}P , and ^{13}C NMR spectra and 2D NMR spectra including HMQC and HMBC. On the ^1H NMR spectrum of **45**, a high intensity sharp

singlet $\delta_{\text{H}} = -6.0$ ppm in the upfield region demonstrates the presence of a methyl on palladium. Palladium 4-tert-butylpyridine gave a set of AB signals including a doublet at $\delta_{\text{H}} = 8.20$ ppm and a doublet at $\delta_{\text{H}} = 7.13$ ppm with a coupling constant $J_{\text{AB}} = 6.8$ Hz. Compared to free pyridine, an obvious change is that the 2 and 6

Table 4.1 1D and 2 D NMR Spectral Data of **45** (δ_{C} and δ_{H} in ppm; J in Hz)

Carbon	δ_{C} (J)	δ_{H} (J)	HMQC	HMBC	NOSEY
1	142.5d (9.1)		C	H-3	
2	132.7		C	H-3	
3	126.3d (5.3)	6.78dd (8.0, 2.0)	CH		
4	131.0d (2.3)	6.88dd (8.0, 2.0)	CH	H-6	H-8
5	143.6		C	H-4 H-6	
6	128.8	7.75s	CH		
7	20.4	2.26s	CH ₃	H-4 H-6	
8	14.2d (68.3)	2.35d (13.2)	CH ₃		H-4 H-10' H-18
9	131.7d (109.3)		C	H-11	
9'	129.6d (91.8)		C	H-11'	
10	133.4d (10.6)	8.24m	CH		H-18
10'	133.0 d (9.9)	7.95m	CH		H-18'
11	128.8d (11.4)	7.60m	CH		
11'	128.5d (12.9)	7.60m	CH		
12	132.6	7.67m	CH	H-10	
12'	132.6	7.67m	CH	H-10'	
13	151.2	8.21d (5.2)	CH	H-14	
14	122.0	7.23d (5.2)	CH	H-13	H-17

15	162.0		C	H-13	
16	34.8		C	H-14	
17	29.9	1.26s	CH ₃		H-14
18	-6.0	0.27s	CH ₃		H-8 H-10 H-10'

position protons are shifted to upfield by 0.30 ppm, 3 and 5 position protons are shifted upfield by 0.13 ppm. The combination of 3 groups of multiplets at 8.27, 7.85-7.95, and 7.50-7.70 ppm, 2 doublets of doublets at 6.84 and 6.73 ppm, a doublet at 2.33 ppm and a singlet at 2.25 ppm showed the presence of methyldiphenylphosphinimine-sulfonate ligand. The ³¹P NMR showed a singlet at 34.7 ppm, downfield shifted for 33.3 ppm compared to its sodium salt. All peaks are sharp and well split. This is in contrast to its precursor, sodium triphenylphosphinimine-sulfonate, which had a set of broadened peaks in CD₂Cl₂. ¹³C NMR chemical shifts have been completely assigned by aid of some 2D NMR including HMQC and HMBC (Table 4.1).

Figure 4.1 NOESY correlations in cis-**45**

In complex **45**, the relative positions between the methyl group and pyridine can form two types of isomers, *cis*- or *trans*- isomers (Figure 4.1). Based on the convention used for differentiation of the geometric isomers of phosphine-sulfonate palladium complexes,

the *cis*-isomer defines that the labile ligand pyridine orients itself on the side of the sulfonate group, whereas the *trans*-isomer defines that the labile ligand pyridine orients itself opposite to the side of the sulfonate group. The differentiation of *cis*-**45** from *trans*-**45** was realized using NOESY. In the NOESY spectrum of *cis*-**45**, the methyl group is expected to have 3 correlations, one with methyl group of PPh₂Me, one with the 2,6-protons of PPh₂Me, and the other with the 2,6-protons of pyridine. In the NOESY spectrum of *trans*-**45**, only one correlation between the methyl and the 2,6-protons of pyridine can be seen. Our experiment showed the scenario of the *cis*-**45**. The NOESY correlations are listed in Table 4.1.

Di-*n*-butylphenylphosphinimine-sulfonate palladium methyl 4-*tert*-butylpyridine (**46**) was characterized by interpretation of ¹H, ³¹P, and ¹³C NMR spectra. On the ¹H NMR spectrum of **46**, a high intensity sharp singlet $\delta_{\text{H}} = 0.47$ ppm in the very upfield region demonstrates the presence of a methyl on palladium. Palladium 4-*tert*-butylpyridine gave a set of AB signals including a doublet at $\delta_{\text{H}} = 8.34$ ppm and a doublet at $\delta_{\text{H}} = 7.17$ ppm with a coupling constant $J_{\text{AB}} = 6.4$ Hz. Compared to free pyridine, an obvious change is that the 2 and 6 position protons are shifted upfield by 0.16 ppm, while the 3 and 5 position protons are shifted upfield by 0.08 ppm. The combination of a multiplet at 7.97, a multiplet at 7.55, a singlet at 7.89, 2 doublets of doublets at 6.89 and 6.72 ppm, a doublet at 2.33 ppm and a singlet at 2.26 ppm showed the presence of the backbone of the di-*n*-butylphenylphosphinimine-sulfonate ligand. The two *n*-butyl groups are magnetically inequivalent, showing a complex pattern of multiplets in the upfield region from 1.00 to 2.75 ppm. The ³¹P NMR showed a singlet at 39.9 ppm, downfield shifted for 19.4 ppm compared to its sodium salt. All peaks are sharp and well split. This

is in contrast to its precursor, sodium di-*n*-butylphenylphosphinimine-sulfonate, which had a set of broadened peaks.

Tri-*n*-butylphosphinimine-sulfonate palladium methyl 4-*tert*-butylpyridine (**47**) was characterized by interpretation of ^1H , ^{31}P , and ^{13}C NMR spectra. On the ^1H NMR spectrum of **47**, a high intensity sharp singlet $\delta_{\text{H}} = 0.62$ ppm in the upfield region demonstrates the presence of a methyl on palladium. Palladium 4-*tert*-butylpyridine gave a set of AB signals including a doublet at $\delta_{\text{H}} = 8.39$ ppm and a doublet at $\delta_{\text{H}} = 7.29$ ppm with a coupling constant $J_{\text{AB}} = 4.8$ Hz. Compared to free pyridine, an obvious change is that the 2 and 6 position protons are shifted upfield by 0.11 ppm, 3 and 5 position protons are shifted downfield by 0.04 ppm. The combination of 2 doublets of doublets at 7.29 and 7.04 ppm, a singlet at 2.26 ppm and a series of multiplets in the aliphatic region showed the presence of the backbone of the tri-*n*-butylphosphinimine-sulfonate ligand. Three *n*-butyl groups are magnetically inequivalent, showing a complex pattern of multiplets in the upfield from 1.00 to 2.75 ppm. The ^{31}P NMR showed a singlet at 44.8 ppm, downfield shifted for 18.3 ppm compared to its sodium salt. All peaks are sharp and well split. This is in contrast to its precursor, sodium tri-*n*-butylphosphinimine-sulfonate, which had a set of broadened peaks.

Thermal Behavior of Methyldiphenyl, Di-*n*-butylphenyl, and Tri-*n*-butylphosphinimine-sulfonate Palladium Methyl 4-*tert*-Butylpyridine Complexes

Orthopalladation is a known reaction of palladium complexes containing a phosphinimine donor.⁶⁰ In a phosphinimine supported palladium complex, palladium abstracts an *ortho* hydrogen from either a P attached arene ring to form a 5-membered

exo orthopalladated species or a N-C linked arene ring to form a 5-membered *endo* orthopalladated species.^{60g} To understand how orthopalladation occurs in phosphinimine-sulfonate palladium complexes, we studied the thermal behavior of complexes **45**, and **46**. The experiment was carried out under different conditions including NMR solvents, temperatures, and time. NMR solvents included halogenated solvents CDCl₃/CD₂Cl₂ and non-halogenated solvents benzene-d₆/toluene-d₈. Complex **45** was heated in toluene-d₈ and **46** in benzene-d₆. As shown in scheme 4.2, endo-orthopalladated

Scheme 4.2 Thermal behavior of **45** and **46**

Table 4.2 Percentages of Orthopalladation

Complex	Solvent	Temperature(°C)	Time (h)	Orthorpalladation(%)
45	C ₆ D ₅ CD ₃	25	2	0
			6	0
			24	0
			48	0
			72	0
		80	2	6.0
			6	13.7
			10	16.2
			26	59.0
46	C ₆ D ₆	80	2	2.1
			24	0
			48	0

species **53** and **54** are formed from the corresponding palladium complexes **45** and **46**. Table 4.2 summarizes experimental results of integration percentages of peaks on ^{31}P NMR spectra. Complex **45**, when standing up to 72 hours at room temperature, did not undergo orthopalladation; but when heated to 80 °C, generated 6.0% , 13.7%, 16.2%, and 59% orthopalladated products in 2, 6, 10, and 26 hours respectively. Complex **46**, when heated to 80 °C for 48 hours, did not undergo orthopalladation despite 2.1% orthopalladation being observed for the 2 hour timepoint. Apparently, increasing the content of alkyl groups in the phosphine motif can sharply shut down the process of orthopalladation.

Ethylene Reactivity of Methyldiphenyl, Di-*n*-butylphenyl, and Tri-*n*-butylphosphinimine-sulfonate Palladium Methyl 4-*tert*-Butylpyridine Complexes

For understanding of catalytic properties, **45- 47** were reacted with ethylene at the catalytic amount. In the experiments, toluene was the solvent, ethylene pressure was 5 atm, and temperature was 80 °C. After 6 hours, the reactions resulted a solution with black materials, which indicated generation of Pd^0 . The reactions were quenched with methanol. The ^1H NMR spectra of the obtained residues did not show apparent formation of polyethylene or alkenes or alkanes. Instead, zwitterions **37**, **48**, and **49** and free 4-*tert*-butylpyridine were observed on ^1H NMR spectra. ^{31}P NMR demonstrated also the formation of corresponding zwitterions.

These palladium complexes have shown interesting reactivities. Under nitrogen atmosphere, they are converted to orthopalladated products. Orthopalladation occurs at the 2- or 6-position of a phosphiniminobenzene ring. Thus, it shows a trend that the presence of benzene rings in the PN^+SO ligand leads to greater orthopalladated product,

as is observed by ^{31}P NMR. According to the 24-hour profiling, percentages of orthopalladation can be arranged in a decreasing order: **42**>**45**>**46** (**47** does not undergo orthopalladation). Under ethylene atmosphere, complexes **42** and **45-47** appear to have different reactivities. In the 4 reactions, black materials have been observed, suggesting formation of Pd^0 and $\text{PN}^{\wedge}\text{SO}$ ligand for the 4 complexes. After quenching with methanol, ^1H and ^{31}P NMR spectral data were acquired for understanding the reactivities, which is discussed below. Orthopalladated products were not observed in the 4 reactions. But the reactivities toward ethylene are different. Based on the ^1H NMR spectra, only the all-aryl-based ligand $\text{Ph}_3\text{-PN}^{\wedge}\text{SO}$ supported complex **42** has promoted formation of alkanes (δ_{H} 1.24, 1.20, 0.86 ppm).

These facts can be rationalized by aid of schemes. Scheme 4.3a summarizes the differentiated reactivities of complexes **42**, **45-47** in N_2 and C_2H_4 atmospheres at the same temperature, $80\text{ }^{\circ}\text{C}$. Under N_2 atmosphere, orthopalladation dominates the reactivity. Under C_2H_4 atmosphere, however, orthopalladation does not occur and ligand regeneration dominates the reactivity. Scheme 4.3b can explain how the orthopalladation pathway is prohibited and ligand regeneration along with ethylene oligomerization is preferred under C_2H_4 atmosphere. According to this mechanism, the reactions involve two routes, orthopalladation (A) and ethylene association (B). Under high pressure, A is slow process and B is a fast one. Therefore route B dominates the whole reactivity. Along with route B, association of C_2H_4 can be via two paths, either B1 or B2. Via path B1, a C_2H_4 molecule replaces a pyridine molecule to give an intermediate, $[\text{PN}^{\wedge}\text{SO}]\text{Pd}(\text{C}_2\text{H}_4)\text{Me}$. The intermediate complex takes route C, in the case of starting

complex **42**, to allow ethylene insertion to Pd-Me bond to form complex [PN[^]SO]Pd-ⁿPr.

Following cycles of ethylene association and insertion to complex [PN[^]SO]Pd-ⁿPr result

Scheme 4.3 Complexes **42**, **45-46**: Reactivities and mechanism

a. Reactivities of complexes **43**, **45-46**

b. Proposed mechanism

in ethylene oligomerization (route D), giving alkane products. The intermediate complex

can also take route E1, where another C₂H₄ molecule replaces the sulfonate donor

forming the non-chelate bisethylenepalladium complex, OS[^]PN-Pd(C₂H₄)₂Me.

Bisethylenepalladium complex can undergo ligand regeneration step (F) giving PN[^]SO ligand and Pd⁰. Via path B2, a molecule replaces sulfonate donor forming non-chelate palladium methyl ethylene pyridine complex, OS[^]PN-Pd(C₂H₄)(Py)Me. This complex takes route E2 accepting association by another C₂H₄ molecule to form the above mentioned bisethylenepalladium complex, OS[^]PN-Pd(C₂H₄)₂Me. This merges into route F to regenerate PN[^]SO ligand and form Pd⁰. Route F is available for all starting complexes, **42**, **45-47**.

Routes A, C, and F are ethylene independent, whereas routes B1, B2, E1, and E2 are ethylene dependent. Too much C₂H₄ yields Pd⁰ via B1-E1-F or B2-E2-F path. Absence of C₂H₄ yields orthopalladation products via A path. It suggests that an intermediate C₂H₄ atmosphere is needed to promote the ethylene polymerization reactivity. Path B-C-D is available for starting complex **42**. Compared with the other three complexes **45-47**, **42** has a maximum number of phenyl groups on the P atom. This suggests that steric factor plays an important role in ethylene oligomer/polymer chain growth. This reflects the importance of steric factor recognized in ethylene polymerization by the α -diimine palladium complexes.^{47a}

4.3 Conclusions

Phosphinimine-sulfonate palladium methyl complexes are thermally instable and subject to orthopalladation. Structural elucidation shows that phosphinimine-sulfonate palladium methyl complexes form *endo*-orthopalladated bicyclo compounds, in which the palladium-carbon bond lies on the P side, not the N side of the phosphazene functionality. Orthopalladation can be affected by factors including structure, temperature, solvent, and

time. Mechanistically, orthopalladation requires the presence of ortho aryl protons on the P side. Alkyl protons are not involved in orthopalladation. Decreased number of benzene rings on the P side can sharply alleviate the orthopalladation process. While the replacement of phenyl groups with alkyl groups alleviates orthopalladation, ethylene reactivity is not improved.

4.4 Experimental Section

General Procedures. All manipulations were performed under N₂ or vacuum using standard Schlenk or high vacuum techniques or in N₂-filled drybox unless otherwise specified. N₂ was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger. Pentane, hexanes, toluene, benzene, and dichloromethane were purified by passage through columns of activated 4 Å molecular sieves. Diethyl ether and tetrahydrofuran were distilled from Na/benzophenone ketyl. CDCl₃ and CD₂Cl₂ were dried over CaH₂ for 24 hours, degassed by freeze-pump-thaw cycles, and vacuum transferred to a storage vessel. Piperidine was obtained from Aldrich and distilled before using. All other solvents were purchased from Aldrich and used without further purification. ¹H, ¹³C, ³¹P, and 2D NMR spectra were recorded in Teflon valve sealed tubes on Varian 400 and 500 spectrometers at ambient probe temperature unless otherwise indicated. ¹H and ¹³C chemical shifts are reported versus SiMe₄ and were determined by reference to the residual ¹H and ¹³C solvent peaks. ³¹P chemical shifts were referenced to external 85% aqueous H₃PO₄. All the ligands and their precursors bear a sulfonated toluidine parental structure which has an atom-labeling scheme as follows:

[(2-MePh₂P=N)-5-MeC₆H₃SO₃]Pd(4-^tBuPy)Me (45). A flask containing sodium 2-(methyldiphenylphosphiniminino)-5-methylbenzenesulfonate (**50**) (0.20 g, 0.5 mmol) and bis(4-tert-butylpyridine)palladium (II) methyl chloride (4-

^tBuPy₂PdMeCl) (0.21 g, 0.5 mmol) was charged with benzene (30 mL) while stirring. Shortly, an initially observed clear greenish solution turned to a clear yellowish solution. The reaction proceeded for 2 hours, resulting in a clear yellow solution. The yellow solution was filtered through Celite along with 2x10 mL benzene rinsing. Evaporation of the filtrate afforded a yellowish solid residue, which was further treated with pentane (30 mL) to give a yellowish precipitate. The precipitate was filtered onto a Buchner funnel top and washed with pentane (3x10 mL) yielding **45** (0.26 g, 95%) as a greenish solid. ¹H NMR (CD₂Cl₂): 8.24 (m, 2H, 2,6-CH of the front benzene ring in -(C₆H₅)₂P=N-), 8.21 (d, *J* = 5.2, 2H, 2,6-CH of (4-(CH₃)₃CC₅H₄N)Pd), 7.95 (m, 2H, 2,6-CH of the back benzene ring in -(C₆H₅)₂P=N-), 7.75 (s, 1H, 6-CH of -C₆H₃SO₃-), 7.67 (m, 2H, 4-CH of -(C₆H₅)₂P=N-), 7.60 (m, 4H, 3,5-CH -(C₆H₅)₂P=N-), 7.23 (d, *J* = 5.2, 2H, 3,5-CH of (4-(CH₃)₃C(C₅H₄N))Pd), 6.88 (dd, *J* = 8.0, 2.0, 1H, 4-CH of -C₆H₃SO₃-), 6.78 (dd, *J* = 8.0, 2.0, 1H, 3-CH of -C₆H₃SO₃-), 2.35 (d, *J*_{PH} = 13.2, 3H, -CH₃P=N-), 2.26 (s, 3H, 5-CH₃ of -C₆H₃SO₃-), 1.26 (s, 9H, 4-(CH₃)₃C(C₅H₄N))Pd), 0.27 (s, 3H, PdCH₃). ³¹P NMR (CD₂Cl₂): δ 34.5. ¹³C NMR (CD₂Cl₂): 162.0, 151.2, 143.6, 142.5 (d, *J*_{PC} = 9.1), 133.4 (d, *J*_{PC} = 10.6), 133.0 (d, *J*_{PC} = 9.9), 132.7, 132.6, 131.7 (d, *J*_{PC} = 109.3), 131.0 (d, *J*_{PC} = 2.3),

129.6 (d, $J_{\text{PC}} = 91.8$), 128.8, 128.8 (d, $J_{\text{PC}} = 11.4$), 128.5 (d, $J_{\text{PC}} = 12.9$), 126.3 (d, $J_{\text{PC}} = 5.3$), 122.0, 34.8, 29.9, 20.4, 14.2 (d, $J_{\text{PC}} = 68.3$), -6.0. The assignments of ^{13}C NMR and 2D NMR data are as shown in Table 4.1.

[(2- ^tBu PhP=N-5-MeC $_6$ H $_3$ SO $_3$)]Pd(4- ^tBu Py)Me (46**). A**

flask containing sodium toluene-4-di-n-butylphenylphosphinimine-3-sulfonate (**51**) (0.75 g, 1.75 mmol) and bis(4-tert-butylpyridine)palladium (II) methyl chloride (4- ^tBu Py $_2$ PdMeCl) (0.21 g, 0.43 mmol) was

charged with benzene (30 mL) while stirring. Shortly, an initially observed clear greenish solution turned to a clear yellowish solution. The reaction proceeded for 2 hours, resulting in a clear yellow solution. The yellow solution was filtered through Celite along with 2x10 mL benzene rinsing. Evaporation of the filtrate afforded a yellowish solid residue, which was further treated with pentane (30 mL) to give a yellowish precipitate. The precipitate was filtered onto a Buchner funnel top and washed with pentane (3x10 mL) yielding **46** (0.54 g, 47%) as a greenish solid. ^1H NMR (CDCl_3): 8.34 (d, $J = 6.4$, 2H, 2,6-CH of 4- ^tBu Py), 7.97 (m, 2H, 2,6-CH of PhPN), 7.88 (s, 1H, 6-CH of -C $_6$ H $_3$ SO $_3$ -), 7.45-7.62 (m, 3H, 3,4,5-CH of -PhPN-), 7.18 (d, $J = 6.4$, 2H, 3,5-CH of 4- ^tBu Py), 6.89 (dd, $J = 8.0$, 2.0, 1H, 4-CH of -C $_6$ H $_3$ SO $_3$ -), 6.72 (dd, $J = 8.0$, 2.0, 1H, 3-CH of -C $_6$ H $_3$ SO $_3$ -), 2.60 (m, 2H, α -CH $_2$ of front ^tBu), 2.46 (m, 2H, α -CH $_2$ of back ^tBu), 2.26 (s, 3H, 5-CH $_3$ of -C $_6$ H $_3$ SO $_3$ -), 2.06 (m, 2H, β -CH $_2$ of front ^tBu), 1.70 (m, 2H, β -CH $_2$ of back ^tBu), 1.45-1.60 (m, 4H, γ -CH $_2$ of front and back ^tBu), 1.26 (s, 9H, 4-(CH $_3$) $_3$ C(C $_5$ H $_4$ N))Pd), 0.94 (3H, Me of front ^tBu), 0.78 (3H, Me of back ^tBu), 0.47 (s, 3H, PdCH $_3$). ^{31}P NMR (CDCl_3): δ 39.9. ^{13}C NMR (CDCl_3): 161.8, 151.2, 143.1, 142.8 (d, $J_{\text{PC}} = 8.3$), 132.4,

132.1 (d, $J_{\text{PC}} = 9.6$), 130.9, 130.2, 129.5, 128.7 (d, $J_{\text{PC}} = 11.4$), 126.7 (d, $J_{\text{PC}} = 3.0$), 122.0, 34.8, 30.1, 26.9 (d, $J_{\text{PC}} = 69.0$), 26.08 (d, $J_{\text{PC}} = 60.0$), 24.8, 23.9, 20.6, 13.4 (d, $J_{\text{PC}} = 18.2$), -6.8.

[(2-^tBu₃P=N)-5-MeC₆H₃SO₃]Pd(4-^tBuPy)(CH₃) (47**). A flask containing sodium 2-(methyldiphenylphosphiniminino)-5-methylbenzenesulfonate (**52**) (0.32 g, 0.75 mmol) and bis(4-tert-butylpyridine)palladium (II) methyl chloride (4-^tBuPy₂PdMeCl) (0.43 g, 0.75 mmol) was charged with benzene (30 mL) while stirring. Shortly, an initially observed clear greenish solution turned to a clear yellowish solution. The reaction proceeded for 2 hours, resulting in a clear yellow solution. The yellow solution was filtered through Celite along with 2x10 mL benzene rinsing. Evaporation of the filtrate afforded a yellowish solid residue, which was further treated with pentane (30 mL) to give a yellowish precipitate. The precipitate was filtered onto a Buchner funnel top and washed with pentane (3x10 mL) yielding **47** (0.36 g, 74%) as a greenish solid. ¹H NMR (CD₂Cl₂): 8.39 (dd, $J = 4.8, 1.6$, 2H, 2,6-CH of (4-(CH₃)₃CC₅H₄N)Pd), 7.71 (s, 1H, 6-CH of -C₆H₃SO₃-), 7.29 (d, $J = 4.8, 1.6$, 2H, 3,5-CH of (4-(CH₃)₃C(C₅H₄N))Pd), 7.04 (dd, $J = 8.0, 2.0$, 1H, 4-CH of -C₆H₃SO₃-), 2.31 (s, 3H, 5-CH₃ of -C₆H₃SO₃-), 2.21 (m, 3H, Ha of α-methylene of ⁿBu), 2.02 (m, 3H, Hb of α-methylene of ⁿBu), 1.83 (m, 3H, Ha of β-methylene of ⁿBu), 1.67 (m, 3H, Hb of β-methylene of ⁿBu), 1.44 (m, 3H, Hb of β-methylene of ⁿBu), 0.95 (t, $J = 7.6, 9$, 9H, Me of ⁿBu), 0.62 (s, 3H, PdMe). ³¹P NMR (CD₂Cl₂): δ 44.8. ¹³C NMR (CD₂Cl₂): 162.2, 151.0, 131.0, 128.6, 127.6, 122.1, 34.8, 29.9, 12.9 (d, $J_{\text{PC}} = 60.7$), 24.5 (d, $J_{\text{PC}} = 56.4$), 24.1, 20.4, 13.3, -8.0.**

(**2-^tBu₂PhP=NH**)-5-MeC₆H₃SO₃ (**48**). To a clear brown solution of n-propyl 2-azido-5-methylbenzenesulfonate (3.87 g, 15.2 mmol) in toluene (40 mL) in a 200 mL Kjeldahl flask P(^tBu)₂Ph (4.1 mL, 16.7 mmol) was added dropwise at 25 °C. Effervescence was observed immediately after addition of P(^tBu)₂Ph. The solution was

stirred for 2 hours and a clear yellow solution resulted. Removal of the solvent under vacuum afforded a yellow viscous material which was redissolved with CH₂Cl₂ (40 mL). The resulting clear yellow solution was transferred via cannula over to a suspension of pyridinium tetrafluoroborate ([PyrH][BF₄]) (2.39 g, 14.3 mmol) in CH₂Cl₂ (40 mL). The Kjeldahl flask was rinsed with CH₂Cl₂ (40 mL) and the rinsing solution was transferred to the reaction flask via cannula. Pyridine (1.8 mL, 21.5 mmol) was added to the white suspension in CH₂Cl₂ and the reaction mixture was refluxed for 12 hours. After cooling the reaction to 25 °C, a clear pale green solution was observed and the volatiles were removed under vacuum. The resulting viscous residue was treated with CH₂Cl₂ (20 mL) and diethyl ether (100 mL) followed by filtration to give a white solid. The solid was separated by column chromatography using silica gel (160 g) and CH₂Cl₂. The column was eluted with CH₂Cl₂-MeOH 95:5 (2000 mL). The fractions (100 mL) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum, affording a white foam. The foam was treated with CH₂Cl₂ (40 mL) and diethyl ether (80 mL) to afford a white precipitate. Filtration of the precipitate followed by diethyl ether washes (3 x 20 mL) afforded **37** (1.54g, 22%) as a white powder. ¹H NMR (CDCl₃): δ 9.51 (d, J = 9.6, 1H, NH), 7.95 (m, 2H, 2,6-CH of ^tBu₂C₆H₅P), 7.81 (s, 1H, 6-CH of -C₆H₃SO-), 7.72 (m, 1H, 4-CH of ^tBu₂C₆H₅P), 6.86 6.86(dd, J = 8.0, 1.2, 1H, 4-CH of -

$\text{C}_6\text{H}_3\text{SO}_3^-$), 6.36 (d, $J = 8.0$, 1H, 3-CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 2.69 (m, 2H, α -methylene of front ^nBu), 2.59 (m, 2H, α -methylene of back ^nBu), 2.20 (s, 3H, 5- CH_3 of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 1.59 (m, 4H, β -methylene of ^nBu), 1.39 (m, 4H, γ -methylene of ^nBu), 0.82 (t, $J = 7.2$, 6H, Me of ^nBu), ^{31}P NMR (CDCl_3): δ 46.0. ^{13}C NMR (CDCl_3): δ 136.3 (d, $J_{\text{PC}} = 7.6$), 135.0 (d, $J_{\text{PC}} = 3.1$, *para*-CH of $^n\text{Bu}_2\text{C}_6\text{H}_5\text{P}$), 133.4, 132.1, 132.0 (d, $J_{\text{PC}} = 10.6$, *ortho*-CH of $^n\text{Bu}_2\text{C}_6\text{H}_5\text{P}$), 130.8, 130.2 (d, $J_{\text{PC}} = 12.2$, *meta*-CH of $^n\text{Bu}_2\text{C}_6\text{H}_5\text{P}$), 129.5, 120.6 (d, $J_{\text{PC}} = 91.9$, ipso C of $\text{C}_6\text{H}_5\text{P}$), 117.8 (d, $J = 3.0$), 23.7, 23.5 (d, $J_{\text{PC}} = 14.0$), 23.14, 22.9 (d, $J_{\text{PC}} = 4.6$), 20.5, 13.2.

(2- $^n\text{Bu}_3\text{P}=\text{NH}$)-5-Me $\text{C}_6\text{H}_3\text{SO}_3$ (49). To a 200 mL pear-

shaped flask containing a clear brown solution of n-propyl 2-azido-5-methylbenzenesulfonate, **20** (2.95 g, 11.4 mmol) in

toluene (10 mL) chilled to 0 °C for 15 minutes, a solution of

$\text{P}(\text{n-C}_4\text{H}_9)_3$ (2.42 g, 12.0 mmol) in toluene (30 mL) was added

via cannula transfer by aid of rinsing with toluene (10 mL), resulting in a yellow solution.

The mixture was allowed to return to 25 °C and stirred for 15 minutes. Effervescence

was observed gradually after addition of the $\text{P}(\text{n-C}_4\text{H}_9)_3$ solution. The reaction mixture

was stirred for 4 hours until no effervescence was observed. A yellow solution was

obtained and the solvent was removed under vacuum to afford a yellow frothy solid. The

solid was dissolved in CH_2Cl_2 (20 mL). The resulting yellow solution was transferred via

cannula to a 300 mL Kjeldahl flask containing a suspension of $[\text{PyH}][\text{BF}_4]$ (1.92 g, 11.4

mmol) in CH_2Cl_2 (20 mL). The 200 mL pear-shaped flask was rinsed with CH_2Cl_2 (3 x

20 mL) and the rinsing solutions were transferred to the reaction flask via cannula.

Gradually, the yellow reaction mixture turned red with white precipitate present. The

reaction mixture was stirred for 1 hour and the white solid almost disappeared. Pyridine (1.7 mL, 17.1 mmol) was added to the resulting reaction solution. The reaction was stirred at 25 °C for 36 hours. The resulting brown solution was pumped down under vacuum giving a glutinous residue, which was treated with CH₂Cl₂ (15 mL) and Et₂O (75 mL). A brown oily insoluble precipitate was observed. Decantation of the liquid layer afforded a gelatinous solid. Treatment with Et₂O (75 mL) and decantation of the ether layer were performed. The resulting viscous solid was pumped down to a brown foam. The frothy solid was separated by column chromatography using silica gel (150g) and CHCl₃. The column was eluted with CHCl₃ (100 mL), CHCl₃-MeOH 98:2 (1500 mL), CHCl₃-MeOH 95:5 (500 mL), and CHCl₃-MeOH 90:10 (500 mL). The fractions (100 mL) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum, affording a brown oil. The brown oil was treated consequentially with CHCl₃ /Et₂O (20 mL/80 mL), hexane (30 mL), and benzene (3x30 mL) to give an off-white precipitate (4.00 g). The resulting solid was washed with Et₂O (2 x 50 mL) yielding **49** as a white powder (2.50 g, 57%). ¹H NMR (dms_o-d₆): δ 8.63(d, *J* = 6.4, 1H, *NH*), 7.53 (s, 1H, 6-*CH* of -C₆H₃SO₃-), 7.16 (d, *J* = 7.8, 1H, 4-*CH* of -C₆H₃SO₃-), 7.09 (d, *J* = 7.8, 1H, 3-*CH* of -C₆H₃SO₃-), 2.51 (m, 6H, (CH₃CH₂CH₂CH₂)₃P=NH-), 2.30 (s, 3H, 5-CH₃ of -C₆H₃SO₃-), 1.53 (m, 6H, (CH₃CH₂CH₂CH₂)₃P=NH-), 1.42 (m, 6H, (CH₃CH₂CH₂CH₂)₃P=NH-), 0.90 (m, 9H, (CH₃CH₂CH₂CH₂)₃P=NH-). ³¹P NMR (dms_o-d₆): δ 56.7. ¹³C NMR (dms_o-d₆): δ 140.8 (d, *J*_{PC} = 5.4), 136.1, 131.0 (d, *J*_{PC} = 4.7), 130.8, (d, *J*_{PC} = 6), 130.6, (d, *J*_{PC} = 5.4), 129.6 (d, *J*_{PC} = 3.1), 128.7, 128.6 (d, *J*_{PC} = 3.9), 127.2 (d, *J*_{PC} = 7.0), 123.5 (d, *J*_{PC} = 2.3), 29.9 (d, *J*_{PC} = 54.2), 20.4.

(2-MePh₂P=N)-5-MeC₆H₃SO₃Na (50). To a flask loaded with **37** (1.00 g, 2.60 mmol) and NaH (94 mg, 3.90 mmol), THF (50 mL) was added while stirring. The turbid mixture was stirred for 4 hours to give a clear slightly yellow solution, which was filtered through Celite. Removal of THF afforded a yellow solid, which was stirred in pentane (40 mL) for 30 minutes. The resulting suspension was filtered off and the collected solid was washed with pentane (2x10 mL) yielding **50** (0.97 g, 91%) as a pale yellow powder. ¹H NMR (THF-d₈): δ 7.85 (m, 4H, 2, 6-CH of Ph₂PN), 7.67 (s, 1H, 6-CH of -C₆H₃SO₃-), 7.20-7.41 (m, 6H, 3,4,5-CH of Ph₂PN), 6.44 (d, *J* = 8.0, 1H, 4-CH of -C₆H₃SO₃-), 6.20 (d, *J* = 8.0, 1H, 4-CH of -C₆H₃SO₃-), 2.19 (d, *J* = 13.2, 3H, MePN), 2.00 (s, 3H, 5-CH₃ of -C₆H₃SO₃-). ³¹P NMR (THF-d₈): δ 10.2. ¹³C NMR (THF-d₈): 147.0, 137.8, 132.3 (d, *J*_{PC} = 9.1), 131.3, 130.7, 129.5, 128.8 (d, *J*_{PC} = 166.2), 128.3 (d, *J*_{PC} = 11.2), 124.4, 123.1 (d, *J*_{PC} = 12.2), 19.5, 15.4 (d, *J*_{PC} = 82.7).

(2-nBu₂PhP=N)-5-MeC₆H₃SO₃Na (51). To a flask loaded with **48** (1.54 g, 3.42 mmol) and NaH (0.12 g, 5.14 mmol), THF (50 mL) was added while stirring. The turbid mixture was stirred for 4 hours to give a clear slightly yellow solution, which was filtered through Celite. Removal of THF afforded a yellow solid, which was stirred in pentane (40 mL) for 30 minutes. The resulting suspension was filtered off and the collected solid was washed with pentane (2x10 mL) yielding **51** (1.47 g, 95%) as a pale yellow powder. ¹H NMR (THF/benzene-d₆): δ 7.71 (s, 1H, 6-CH of -C₆H₃SO₃-), 7.71 (broad, 2H, 2,6-CH of PhPN), 7.59 (m, 4-CH of PhPN), 7.07 (broad, 2H, 3,5-CH of PhPN), 6.52 (bd, *J* = 8.0, 1H, 4-CH of -C₆H₃SO₃-), 6.29 (bd, *J* = 8.0, 1H, 4-

CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 2.20-2.50 (m, α -methylene of ^nBu), 1.94(s, 3H, 5- CH_3 of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 1.45(m, 6H, β -methylene of ^nBu), 1.32(m, 3H, γ -methylene of ^nBu), 0.63 (t, $J = 7.6$, 9H, Me of ^nBu). ^{31}P NMR (THF- d_8): δ 20.1. ^{13}C NMR (THF- d_8): 161.8, 151.7, 146.6(d, $J_{\text{PC}} = 7.6$), 143.8, 122.1, 30.2, 26.3 (d, $J_{\text{PC}} = 61.5$), 24.5(d, $J_{\text{PC}} = 41.5$), 15.3.

(2- $^n\text{Bu}_3\text{P}=\text{N}$)-5-Me $\text{C}_6\text{H}_3\text{SO}_3\text{Na}$ (52**).** A flask loaded with **49**

(1.58 g, 3.68 mmol) and NaH (0.32 g, 5.52 mmol), THF (50 mL)

was added while stirring. The turbid mixture was stirred for 4

hours to give a clear slightly yellow solution, which was filtered

through Celite. Removal of THF afforded a yellow solid, which

was stirred in pentane (40 mL) for 30 minutes. The resulting suspension was filtered off

and the collected solid was washed with pentane (2x10 mL) yielding **52** (1.33 g, 89%) as

a pale yellow powder. ^1H NMR (THF- d_8): δ 7.71 (s, 1H, 6- CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 6.80 (dd, J

= 8.0, 2.0, 1H, 4- CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 6.56 (dd, $J = 8.0$, 2.0, 1H, 4- CH of $-\text{C}_6\text{H}_3\text{SO}_3^-$),

2.17(s, 3H, 5- CH_3 of $-\text{C}_6\text{H}_3\text{SO}_3^-$), 2.00 (m, 6H, α -methylene of ^nBu), 1.45(m, 6H, β -

methylene of ^nBu), 1.32(m, 3H, γ -methylene of ^nBu), 0.83 (t, $J = 7.6$, 9H, Me of ^nBu). ^{31}P

NMR (THF- d_8): δ 26.5. ^{13}C NMR (THF- d_8): 161.8, 151.7, 146.6(d, $J_{\text{PC}} = 7.6$), 143.8,

122.1, 30.2, 26.3 (d, $J_{\text{PC}} = 61.5$), 24.5(d, $J_{\text{PC}} = 41.5$), 15.3.

Thermal Behavior of [2-(MePh $_2\text{P}=\text{N}$)-5-Me $\text{C}_6\text{H}_3\text{SO}_3$]Pd(4- $^t\text{BuPy}$)Me (45**).** Formation

of [2-((C_6H_4)PhMeP= N)-5-Me $\text{C}_6\text{H}_3\text{SO}_3$]Pd(4- $^t\text{BuPy}$) (**53**). In $\text{C}_6\text{D}_5\text{CD}_3$ at 25 $^\circ\text{C}$. A

valved NMR tube was loaded with **45** (5.0 mg, 7.1 μmol) and $\text{C}_6\text{D}_5\text{CD}_3$ (0.5 mL) was

added via vacuum transfer at -196 $^\circ\text{C}$. After flushed with N_2 gas, the tube was sealed and

warmed to 25 $^\circ\text{C}$ and shaken to result in a greenish solution. ^1H and ^{31}P NMR spectra

established that **53** had not formed. The solution sat at room temperature for 2, 6, 24, 48,

and 72 hours, ^1H and ^{31}P NMR spectra established that **53** had not formed. *In $\text{C}_6\text{D}_5\text{CD}_3$ at 80 °C.* A valved NMR tube was loaded with **45** (5 mg, 7.1 μmol) and toluene- d_8 (0.5 mL) was added via vacuum transfer at -196 °C. After flushed with N_2 gas, the tube was sealed and warmed to 25 °C and shaken to result in a solution. ^1H and ^{31}P NMR spectra established that **53** had not formed. The solution was heated to 80 °C for 2, 6, 10, and 24 hours. ^1H and ^{31}P NMR spectra were obtained for each time interval. The integration of ^{31}P NMR spectra established that after 2 hours at 80 °C, **45** and **53** coexisted in the solution and 5.98% of the starting **45** had been converted to **53**; after 6 hours, **45** and **53** coexisted in the solution and 13.68% of the starting **45** had been converted to **53**; after 10 hours, **45** and **53** coexisted in the solution and 16.20% of the starting **45** had been converted to **53**; after 24 hours, **45** and **53** coexisted in the solution and 58.96% of the starting **45** had been converted to **53**. ^1H and ^{31}P NMR data from the 24 hour experiment are as follows: ^1H NMR (toluene- d_8): δ 8.67 (d, $J = 8.0$, 2.3H, 2,6- CH of 4- $t\text{BuPy}$), 8.50 (d, $J = 4.0$, 1.12H), 8.35-8.50(m, 3.25H), 8.08 (d, $J = 8.0$, 1.74H), 7.78 (m, 2.34H), 6.83 (m, 2.32H), 6.77 (m, 2.36H), 6.45-6.65 (m, 7.03H), 6.39 (d, $J = 8.0$, 1.71H), 6.33 (d, $J = 8.0$, 1.81), 2.21s and 2.18s (2.45H), 2.00 (s, 2.58H), 1.94 (s, 4.51H), 0.88 (s, 9H), 0.82 (s, 4.61H), 0.53 (s, 1.91H), 0.18 (s, 0.96H).

Thermal Behavior of $[2-(^n\text{Bu}_2\text{PhP=N})\text{-5-MeC}_6\text{H}_3\text{SO}_3]\text{Pd}(4\text{-}^t\text{BuPy})\text{Me}$ (46**):** Formation of $[2-((\text{C}_6\text{H}_4)^n\text{Bu}_2\text{P=N})\text{-5-MeC}_6\text{H}_3\text{SO}_3]\text{Pd}(4\text{-}^t\text{BuPy})$ (**54**). *In C_6D_6 at 80 °C.* A valved NMR tube was loaded with **46** (5 mg, 7.5 μmol) and toluene- d_8 (0.5 mL) was added via vacuum transfer at -196 °C. After flushed with N_2 gas, the tube was sealed and warmed to 25 °C and shaken to result in a solution. ^1H and ^{31}P NMR spectra established that **54** had not formed. The solution was heated to 80 °C for 2, 24, and 48 hours. ^1H and ^{31}P NMR

spectra were obtained for each time interval. The integration of ^{31}P NMR spectra established that after 2 hours at 80 °C, 2.1% **54** existed in the solution; after 24 and 48 hours, no **54** existed in the solution. ^1H NMR (benzene- d_8): δ 8.50 (s, 0.9 H, 6-*CH*), 8.24 (d, J = 8.0, 1.89 H, 2,6-*CH* of 4-*t*BuPy), 7.20 (m, 3.0 H), 6.91 (m, 1.2 H), 6.76 (m, 1.1 H), 6.36 (d, J = 8.0, 1.99 H, 2,6-*CH* of 4-*t*BuPy), 2.76 (m, 1.1 H), 2.54 (m, 2.9 H), 2.21 (m, 1.1 H), 2.05 (m, 1.1H), 1.95 (s, 3H), 1.35 (m, 3.3 H), 1.10 (m, 1.6 H), 1.01 (m, 2.1 H), 0.83 (t, 2.6 H), 0.76 (s, 8.6 H), 0.61 (t, 3.7 H). ^{31}P NMR (benzene- d_8): δ 39.9.

Ethylene Reactivity of 45. To a high-pressure glass reactor, **45** (10.3 mg, 0.018 mmol) was loaded in a glovebox. Under positive N_2 gas, toluene (20 mL) was added. After a brief evacuation, ethylene gas (5 atm) was introduced. The mixture was heated to 80 °C and stirred for 6 hours to result in a turbid suspension. MeOH was added and the mixture turned clear with some black residues. The mixture was filtered through Celite. The filtrate was evaporated on rotavapor. ^1H and ^{31}P NMR spectra were obtained for the residues. ^1H NMR (CDCl_3): δ 9.17 (bs, 0.48H, **37**), 8.75 (d, J = 6.8, 0.66H, *t*BuPy), 8.09 (m, 4.25 H) 7.60-7.80 (m, 1.8H), 7.40-7.60 (m, 1.89 H), 7.56 (m, 1.66 H), 7.45 (m, 1.36 H), 7.13 (m, 1.78H, 7.05 (m, 2.70 H), 6.91 (d, J = 8.4, 1.26 H, **36**), 6.42 (d, 1.00H, **36**), 3.51 (s, 12H), 2.51 (s, 3.44H), 2.49 (d, J = 12.8, 1.22H, **36**), 2.25 (s, 3H, **36**), 1.46 (bs, 2.62H), 1.37 (s, 1.88 H), 1.31 (s, 8.90H, *t*BuPy), 1.27 (s, 2.76H), 1.07 (bs, 4.22 H), 0.92 (t, 2.11H). ^{31}P NMR (CDCl_3): δ 39.1 (**36**).

Ethylene Reactivity of 46. To a high-pressure glass reactor, **46** (10.5 mg, 0.015 mmol) was loaded in a glovebox. Under positive N_2 gas, toluene (20 mL) was added. After a brief evacuation, ethylene gas (5 atm) was introduced. The mixture was heated to 80 °C and stirred for 6 hours to result in a turbid suspension. MeOH was added and the mixture

turned clear with some black residues. The mixture was filtered through Celite. The filtrate was evaporated on rotavapor. ^1H and ^{31}P NMR spectra were obtained for the residues. ^1H NMR (CDCl_3): δ 9.57 (d, 0.86 H, **48**), 7.95 (t, 2.74 H), 7.79 (m, 1.06 H), 7.68 (m, 1.99 H), 7.38 (s, 2.49 H), 7.14 (d, 2.44 H), 6.85 (d, 0.99 H), 6.67 (d, $J = 8.0$, 2.34 H), 6.48 (d, 1.0H), 3.48 (s, 2.88 H), 3.31 (s, 4.72H), 2.82 (s, 7.04 H), 2.60 (m, 3.99 H), 2.25 (s, 9.58 H), 2.17 (s, 3.71 H), 1.92 (bs, 1.45H), 1.65 (m, 4.41H), 1.42 (m, 4.14 H), 0.89 (t, $J = 6.80$). ^{31}P NMR (CDCl_3): δ 45.5 (**48**).

Ethylene Reactivity of 47. To a high-pressure glass reactor, **47** (10.5 mg, 0.017 mmol) was loaded in a glovebox. Under positive N_2 gas, toluene (20 mL) was added. After a brief evacuation, ethylene gas (5 atm) was introduced. The mixture was heated to $80\text{ }^\circ\text{C}$ and stirred for 6 hours to result in a turbid suspension. MeOH was added and the mixture turned clear with some black residues. The mixture was filtered through Celite. The filtrate was evaporated on rotavapor. ^1H and ^{31}P NMR spectra were obtained for the residues. ^1H NMR (CDCl_3): δ 8.61 (d, $J = 7.2$, 0.52 H, NH), 8.50 (d, $J = 5.6$, 0.92 H, $^t\text{BuPy}$), 7.85 (s, 0.98 H, 6-CH), 7.02 (d, $J = 6.4$, 1.19 H), 6.62 (d, $J = 8.4$, 1H), 2.15-2.35 (m, 9.11H), 1.45-1.55 (9.14H), 1.31-1.44 (m, 9.25H), 1.10-1.25 (m, 10.15H), 0.70-0.92 (m, 14.09H). ^{31}P NMR (CDCl_3): δ 56.6.

CHAPTER FIVE

CONCLUSIONS

In this dissertation research, we have successfully designed and developed new bidentate sulfonate ligands, specifically phosphinimine-sulfonates (PN^{SO}). We have successfully streamlined the synthesis of the corresponding palladium methyl pyridine complexes ([PN^{SO}]PdPyMe). We have also successfully studied the thermal behavior and ethylene reactivity of these palladium complexes.

Phosphinimine-sulfonate ligands are designed on the basis of a sulfonate donor and a phosphinimine co-donor. Presumably, PN^{SO} ligands have an enhanced donor strength from the sp² nitrogen donor, the phosphinimine unit while keep the unique catalytic properties of the sulfonate donor. The ligands we synthesized are in zwitterionic forms that are air-stable and have a long shelf expectancy. The ligands can be easily generated for coordination chemistry and can coordinate with palladium precursors (cod)PdMeCl and py₂PdMeCl with ease forming stable palladium methyl pyridine complexes.

The synthetic route for PN^{SO} ligands includes 7 reactions, chlorination, esterification, diazotization, azidation, Staudinger reaction, protonation, and deprotonation. In addition to the success of synthesizing new bidentate sulfonate ligands, several improvements and innovations in synthetic chemistry have been achieved and deserve a highlight.

In the chlorination step, the conditions reported in a 1933 patent did not work to achieve the desired product. In our research, we have updated these conditions by applying a new reaction time, 2 hours, to this step. This is a critical update. Following the patent, when the reaction was heated for 8 hours, the desired pale-yellow solid never came out as a product. We screened reaction times and found that the 2-hour reaction time is the best condition to get the desired yellow solid. We have also successfully developed a new workup. In the patent, it is reported to harvest the product by extracting the product from diethyl ether. Our independent experiments showed that extraction was unworkable because the target sulfonate chloride decomposed on rotavapor. My independent work has proven that oven-drying at 40 °C is by no means the best way for isolation of a water-free product.

We have innovated the diazotization/azidation reaction for introduction of an azido group ortho to a sulfonate group. In literature, diazotization and azidation reactions are manipulated in a one-pot method. In our experiments, we have found that this method is rather dangerous. In the presence of a strong acid like H_2SO_4 or HCl , NaN_3 can be acidified to hydrazoic acid, HN_3 . This weak acid is a toxic volatile liquid that causes severe safety issues to operators. We have designed a new method for handling the diazotization and azidation reactions. In our method, diazotization employs HBF_4 as an acid. The diazonium tetrafluoroborate is relatively stable in air based on Schieman reaction conditions. This allowed a quick filtration in air for complete removal of the unreacted acid. The isolated diazonium salt can react with NaN_3 at a neutral condition to avoid formation of the toxic liquid HN_3 . In addition, our method gives a much higher yield of azides than the one-pot method.

We have created a new methodology of protection and deprotection of the sulfonic acid group. In literature, sulfonic acids are usually protected by neopentyl or isobutyl sulfonate. The deprotecting reagents are Bu_4NI or piperidine. In our research, we have updated this chemistry by using for the first time the more labile n-propyl sulfonate esters for protection of the sulfonic acid. We have also developed a brand new deprotecting reagent, pyridinium tetrafluoroborate. Employment of pyridinium tetrafluoroborate to deblock a protecting group makes the cleavage of n-propyl sulfonate rather neat and efficient. In our case, an additional benefit has been obvious in that a tandem reaction of protonation and deprotection provides us with a facile access to air-stable zwitterion ligand library. To look into the protection and deprotection chemistry, we have proposed mechanisms for the protonation and deprotonation reactions.

We have successfully synthesized $\text{PN}^{\wedge}\text{SO}$ Pd complexes **42**, **45-47**. We have tested their reactivities under N_2 and C_2H_4 atmospheres. These complexes have different reactivities. Under the N_2 atmosphere, **42**, **45**, and **46** were orthopalladated. Under the C_2H_4 atmosphere, orthopalladation was prohibited and the corresponding $\text{PN}^{\wedge}\text{SO}$ ligands and Pd^0 were regenerated. We also observed that **42** catalyzed the formation of alkanes. A mechanism has been proposed for the reactivities. $\text{PN}^{\wedge}\text{SO}$ Pd complexes are promising catalyst candidates that may promote insertion polymerization.

In summary, this dissertation research has developed a new type of phosphinimine-sulfonate ligand. The new ligand sets provide bidentate chelating ligand environments for coordination to form palladium methyl complexes. Reactivity study has allowed us to examine $[\text{PN}^{\wedge}\text{SO}]\text{Pd}$ complexes for their catalytic potential such as in ethylene oligomerization and polymerization. An in-depth understanding of these newly

synthesized palladium complexes derives from our proposed mechanism. For ethylene polymerization, future studies should be directed toward changing ethylene pressures and tuning ligand steric factors. To a wide view, other transition metals such as Ru(II), Ru(IV), Cu(I), Cu(II), Rh(I) should be chosen to form new PN[^]SO complexes for catalytic studies.

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APPENDICES
NMR SPECTRA

4 (Ch. 2)

5 (Ch. 2)

10 (Ch. 2)

13 (Ch. 2)

17 (Ch. 2)

17 (Ch. 2)

18 (Ch. 2)

20 (Ch. 2)

20 (Ch. 2)

21 (Ch. 2)

21 (Ch. 2)

22 (Ch. 2)

22 (Ch. 2)

24 (Ch. 2)

24 (Ch. 2)

Ar = p-Tolyl

25 (Ch. 2)

Ar = p-Tolyl

25 (Ch. 2)

26 (Ch. 2)

26 (Ch. 2)

26 (Ch. 2)

35 (Ch. 2)

35 (Ch. 2)

35 (Ch. 2)

-1.065

35 (Ch. 2)

-152.771

36 (Ch. 2)

36 (Ch. 2)

36 (Ch. 2)

37 (Ch. 2)

37 (Ch. 2)

37 (Ch. 2)

39.002

ppm

-20

0

20

40

60

80

100

120

140

160

38 (Ch. 2)

38 (Ch. 2)

38 (Ch. 2)

43.622

39 (Ch. 2)

39 (Ch. 2)

39 (Ch. 2)

35.889

40 (Ch. 2)

48.949

160 140 120 100 80 60 40 20 0 -20 ppm

41 (Ch. 3)

41 (Ch. 3)

31.589

¹H NMR, CDCl₃, 68 °C, 24 h)

Thermal Behavior of **41**
 ^{31}P NMR, CDCl_3 , 68 °C, 24 h)

42 (Ch. 3)

42 (10 °C, Ch. 3)

42 (-10 °C, Ch. 3)

42 (-30 °C, Ch. 3)

42 (-60 °C, Ch. 3)

42 (-70 °C, Ch. 3)

42 (-90 °C, Ch. 3)

Thermal Behavior of **42**
¹H NMR, CDCl₃, 70 °C, 24 h)

Thermal Behavior of **42**
¹H NMR, CD₂Cl₂, 46 °C, 24 h)

Thermal Behavior of **42**
 ^{31}P NMR, CD_2Cl_2 , 46 °C, 24 h)

Thermal Behavior of **42**
 ^1H NMR, C_6D_6 , 68 °C, 24 h)

Thermal Behavior of **42**
 ^{31}P NMR, $\text{C}_6\text{D}_5\text{CD}_3$, 70 °C, 24 h)

Thermal Behavior of **42**
¹H NMR, C₆D₅CD₃, 80 °C, 24 h)

Emylene reactivity of **4a**
 ^1H NMR, CDCl_3 , 80 °C, 6 h

Ethylene Reactivity of **42**
 ^{31}P NMR, CDCl_3 , 80 °C, 6 h)

44 (Ch. 3)

47.051

PHOSPHORUS_001
³¹P NMR, C₆D₅CD₃, 80°C, 24 h)

¹H NMR, CDCl₃

48 (Ch. 4)

ABBREVIATIONS

1D NMR	One-dimensional nuclear magnetic resonance
2D NMR	Two-dimensional nuclear magnetic resonance
benzene-d ₆	Deuterated benzene
C ₆ D ₆	Deuterated benzene
C ₆ D ₅ CD ₃	Deuterated toluene
CDCl ₃	Deuterated chloroform
CD ₂ Cl ₂	Deuterated dichloromethane
COD	E,E-1,5-cyclooctadiene
Py	Pyridine
DABCO	1,4-Diazobicyclo[2.2.2]octane
DMSO	Dimethyl sulfoxide
HMBC	Heteronuclear multiple bond correlation
HMQC	Heteronuclear multiple quantum correlation
HSQC	Heteronuclear single quantum correlation
M _n	Number average molecular weight
NHC	N-heterocyclic carbene
NHC ^{SO}	NHC-sulfonate ligand
NMR	Nuclear magnetic resonance
NOESY	Nuclear Overhauser effect spectroscopy
O ^{SO}	Phenolate-sulfonate ligand
P ^{SO}	Phosphine-sulfonate ligand
PN ^{SO}	Phosphinimine-sulfonate ligand
TMS	Tetramethylsilyl
thf-d ₈	Deuterated tetrahydrofuran
toluene-d ₈	Deuterated toluene

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