New Polyphosphorus Organic Compounds

by

Christopher Massone

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

2003

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Abstract

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The phosphorus to phosphorus bond is an intriguing area of chemistry which became of significant interest back in the 1960's. Our research has explored two new phosphorus to phosphorus bonds. The first is in hexacoordinate phosphorus compounds, compounds which have a negatively charged central phosphorus center. Original work was done in this area by adding mono- and bidentate nitrogen ligands to a pentacoordinated phosphorus center. In our project we have added different mono- and bidentate nitrogen ligands along with mono- and bidentate phosphorus ligands to two phosphorus centered precursors. The second new type of phosphorus to phosphorus bond is in phosphonium amide analogues, amides in which the amide nitrogen and carbonyl carbon are replaced by phosphorus atoms. These compounds were made by adding mono-, bi- and tridentate phosphorus ligands to several phosphoryl compounds. Each compound synthesized in both studies were characterized by proton, carbon, and phosphorus NMR.

Acknowledgements

With so many people to thank I want to first apologize to anybody important who I omit from here. With that said I would like to start at the beginning with my parents Anthony and Eileen, my sister Michele, and my grandparents whose support and encouragement never let me waiver off course. Before you can be successful on the graduate level you need to have a good undergraduate foundation, so I would like to thank the chemistry faculty of Fordham University, in particularly Dr. D. Bray, Father R. Cloney, Dr. J.Ciaccio, Dr. S.Saba, and my undergraduate mentor Dr. M.K. Kaloustian. I worked with so many wonderful people in the lab while doing research but I would especially like to thank Dr. J.I.Cohen for all her help. I would also like to thank the chemistry faculty of Queens College with special mention to Dr. A. Baker and Dr. T. Strekas for all their guidance. I would also like to thank Dr. K. Ramig of Baruch College for serving on my thesis committee. Finally I would like to thank the two most important people who made this possible, my wife Sabrina and my mentor Dr. R.Engel. Sabrina is a true partner, friend, and I owe so much to her. I am eternally grateful and only hope that my future success will continue to make her proud. As far as Dr. Engel goes what can I say. Based on my time with him and learning from him, I am truly convinced that no one could ask for a better mentor than Dr. Engel.

-Chris Massone

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I. Introduction

A. The Phosphorus to Phosphorus Bond

Compounds containing phosphorus to phosphorus bonds became of particular interest starting in the 1960's. In a review by Cowley [1] the distinguishing characteristics of the phosphorus to phosphorus bond were discussed. One interesting characteristic is the existence of 60° angles in the P_4 tetrahedron of white phosphorus and in P_4S_3. This unusual bond angle for a stable system is due to the fact that the phosphorus orbitals used in these systems are predominately 3p in type and the bonds are "bent" so that the lines of maximum charge density do not correspond with the direct internuclear axis of the phosphorus atoms. Another interesting characteristic of the phosphorus to phosphorus bond is the consistency of its length in different compounds (Table 1).

Table 1: P-P Bond Lengths

Compound	Bond Length (angstroms)	Reference
P_2I_4	2.15-2.27	2
P_4S_5	2.185-2.235	3
$P_4S_3I_2$	2.196-2.204	4
P_4	2.19-2.23	5
$(CF_3P)_4$	2.208-2.218	6
$(CF_3P)_5$	2.223	7
P_4S_3	2.230-2.240	8

The P-P bond length seems to be insensitive to the electronic characteristics of the substituents or to changes in its oxidation state.

In terms of bond strength the P-P single bond (51.3 kcal/mol) is about equal in strength to the S-S bond (50.9 kcal/mol) [9].

A third characteristic is the question of how much any lone pairs on phosphorus participate in the bonding between phosphorus atoms. It appears that the two atoms in a phosphorus to phosphorus bond involving trivalent phosphorus atoms (diphosphines) are joined by a sigma bond with a lone pair of electrons remaining on each atom (Figure 1).

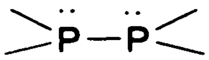


Figure 1: P-P Bond

There is evidence however for the contribution of the following three structures to this type of P-P bond, each of which involve π-type bonding between *p* and *d* orbitals (Figure 2) [1]:

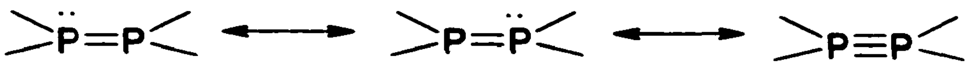


Figure 2: Resonance Forms of the P-P Bond

In general the reactions of compounds with P-P bonds can be grouped into two classes. The first result in cleavage of the P-P bond. Treatment with equimolar amounts of halogens usually causes quantitative P-P bond cleavage of both symmetrical [10-12] and unsymmetrical [13-14] diphosphines. For example when chlorine reacts with phosphobenzene the P-P double bond is broken giving 2 equivalents of phenyldichlorophosphine (Figure 3) [15].

$$C_6H_5P{=}PC_6H_5 \quad + \quad Cl_2 \longrightarrow 2\ C_6H_5PCl_2$$

Figure 3: Reaction of Phosphobenzene and Chlorine

A similar example to the one in Figure 3 involves the reaction of chlorine with the CF_3P tetramer to give a quantitative conversion to CF_3PCl_4 (Figure 4) [16].

$$(CF_3P)_4 \quad + \ 8\ Cl_2 \longrightarrow 4\ CF_3PCl_4$$

Figure 4: Reaction of CF_3P Tetramer and Chlorine

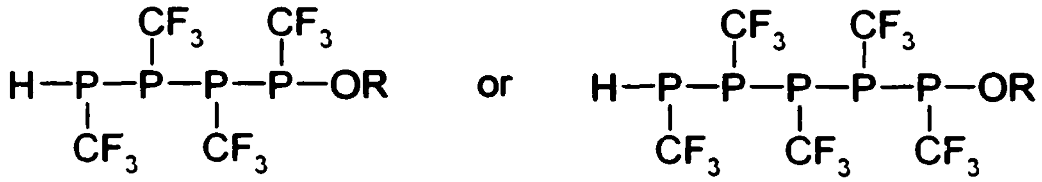
In general substituted diphosphines do not react with water at room temperature, but hydrolytic cleavage of the P-P bond is possible under more forcing conditions. For example $(CF_3)_4P_2$ undergoes alkaline hydrolysis yielding exactly half of the CF_3 groups in the form HCF_3 [16]. This is the expected result if the CF_3P units were equally and quantitatively converted to $(CF_3)_2PH$ and $(CF_3)_2P(OH)$. $(CF_3)_2PH$ yields one mole of HCF_3, while $(CF_3)_2P(OH)$ yields two moles of HCF_3 giving three moles of HCF_3, the desired product in this effort. The unsymmetrical diphosphine $(CH_3)_2P\text{-}P(CF_3)_2$ undergoes hydrolysis according to the following sequence with the first step possibly involving a rapid exchange between $(CF_3)_2PH$ and $(CH_3)_2POH$ (Figure 5) [17].

$$(CF_3)_2P\text{-}P(CH_3)_2 + H_2O \longrightarrow (CF_3)_2PH + (CH_3)_2POH \quad (a)$$

$$2\ (CH_3)_2POH \longrightarrow (CH_3)_2PH + (CH_3)_2POOH \quad (b)$$

Figure 5: Hydrolysis of $(CH_3)_2P\text{-}P(CF_3)_2$

Another way to cleave the P-P bond is through the use of alcohols. Alcohols cleave a P-P bond in $(CF_3P)_4$ or $(CF_3P)_5$ [18] forming first a full-length open chain, as shown in Figure 6.



$$\mathrm{H{-}P(CF_3){-}P(CF_3){-}P(CF_3){-}P(CF_3){-}OR} \quad \text{or} \quad \mathrm{H{-}P(CF_3){-}P(CF_3){-}P(CF_3){-}P(CF_3){-}P(CF_3){-}OR}$$

Figure 6: Open Chain Compounds Formed upon Alcoholysis of $(CF_3P)_4$ and $(CF_3P)_5$

It turns out that a secondary hydrolysis begins during the process of open chain formation and the two major products are the triphosphine $H_2(CF_3P)_3$ and the tetraphosphine $H_2(CF_3P)_4$ One final way in which the P-P bond is cleaved comes from Burg's "pseudo-halogen" concept [19] in which the R_2P- moiety of a diphosphine is compared to a halogen atom. Thus $(CF_3)_4P_2$ or $(CH_3)_4P_2$ will add across a double bond in the same way a halogen molecule does (Figure 7).

$$R_2P\text{-}PR_2 \;+\; H_2C{=}CH_2 \longrightarrow R_2P\text{-}CH_2\text{-}CH_2\text{-}PR_2$$

Figure 7: "Pseudo-Halogen" Reaction of a Diphosphine

The second group of reactions of P-P bonds are those which involve oxidation or coordination of the tricoordinate phosphorus atom without bond rupture. Most of these examples come from the reactions of various transition metal compounds with phosphine ligands. The first indication that this type of reaction was possible was from Burg and Mahlers observation [20] that $(CF_3)_4P_2$ reacts with nickel carbonyl to form the stoichiometric complex $(CF_3)_4P_2 \cdot 2\ Ni(CO)_3$. Another example is from the reaction of $(CH_3)_4P_2$ with $Fe(CO)_2(NO)_2$ [21]. In this case two types of diphosphine carbonyls are formed, both with the P-P bond intact (Figure 8).

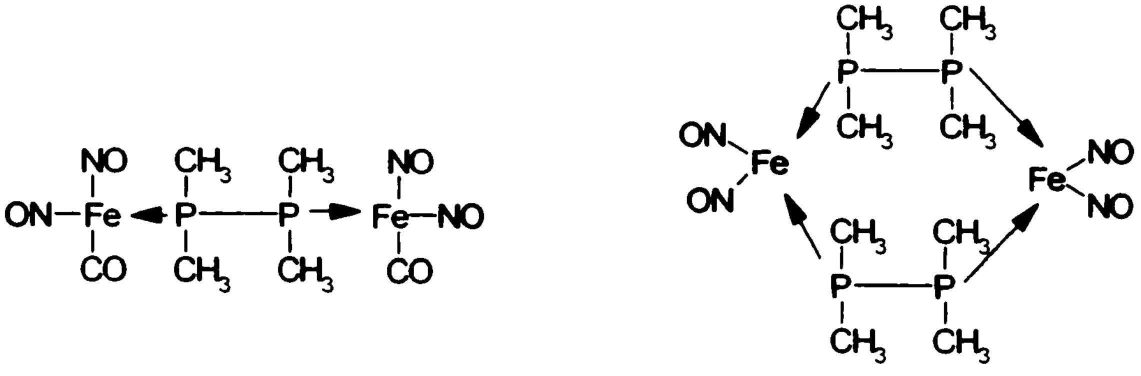
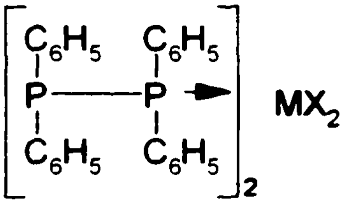


Figure 8: Two Types of Diphosphine Carbonyls

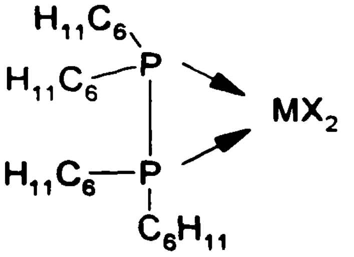
Another example comes from the reactions of $(C_6H_5)_4P_2$ and $(C_6H_{11})_4P_2$ with transition metal halides [22-23]. $(C_6H_5)_4P_2$ behaves as a monodentate ligand to give a 2:1 complex (Figure 9).



$MX_2 = CoBr_2, CoI_2, NiBr_2, PdCl_2$

Figure 9: Complex of $(C_6H_5)_4P_2$ with Transition Metal Halides

Also, $(C_6H_{11})_4P_2$ gives a 1:1 complex whose structure is based on measurements of dipole moment and paramagnetic/diamagnetic character (Figure 10) [24-25].



$MX_2 = CoBr_2, CoI_2, NiBr_2, PdCl_2, NiCl_2$

Figure 10: Complex of $(C_6H_{11})_4P_2$ with Transition Metal Halides

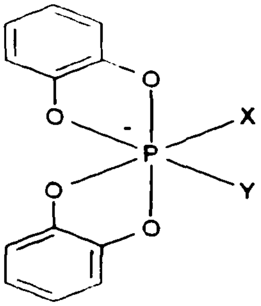
The difference in complexation between the two compounds comes from the increased basicity of $(C_6H_{11})_4P_2$ which enables it to function as a bidentate ligand.

B. ^{31}Phosphorus NMR

^{31}P NMR became an important tool for structure elucidation in 1955 with the first availability of commercial multinuclear NMR spectrometers [26]. These machines required neat samples in large nonrotating tubes. The use of ^{31}P NMR greatly expanded in the 1970s with the introduction of Fourier-transform (FT) and high-field superconducting magnet NMR spectrometers [26]. These machines allowed not only small organic and inorganic compounds to be studied, but large biological phosphorus compounds could be studied as well.

At this time a significant change in notation regarding ^{31}P NMR spectra took place, correlating positive shift values to high frequency (low field) [27]. Prior to this, the chemical shifts for compounds of pentacoordinated phosphorus were said to be in the range of -30 to $+100$ ppm, while the shifts for compounds of hexacoordinated phosphorus were told to be in the range of $+135$ to $+300$ ppm (Table 2) [27-28]. Notations after this data (and currently) use the opposite sign.

Table 2: ^{31}P NMR Data for Hexacoordinated Phosphorus Compounds (early sign convention) [28]



	X	Y	δ^{31} P (ppm)
a	C_6H_4-C_6H_4		106
b	H	CH_3	113.5
c	H	C_6H_5	108.8
d	H	C_6F_5	133.4
e	H	$N(CH_2)_4$	99.1
f	H	$NC_5H_5^+$	96.97
g	H	O-Alkyl	97.1-98.1
h	H	O-Aryl	98.1-99
l	$NC_5H_5^+$	$NC_5H_5^+$	100
j	$NC_5H_4CH_3(4)^+$	$NC_5H_4CH_3(4)^+$	102
k	2,2'-NC_5H_4-NH-$C_5H_4^{2+}$		112
l	2,2'-NC_5H_4-N-$C_5H_4^+$		120
m	2,2'-NC_5H_4-$C_5H_4N^{2+}$		95
n	Cl	$NC_5H_5^+$	84.5
o	Cl	$NC_5H_4CH_3(4)^+$	86.5
p	OCH_3	$NC_5H_5^+$	58
q	OC_6H_4	$NC_5H_5^+$	43.5
r	OCH_2-$C_5H_4N(2)^+$		87
s	8-$OC_9H_6N^+$		78
t	OC_6H_5	OC_6H_5	107
u	$OCCH_3$=CH-CH_3CO^+		104.1
v	2-OC_6H_4-CO_2^-		106
w	2-OC_6H_4O		83
x	OCC_6H_5-C_6H_5CO		86
y	OCR_2-CO_2^-		90-91

Further improvements in FT NMR spectrometers led to more applications of ^{31}P NMR in biological and medical applications during the 1980s.

Today's commercial NMR spectrometers measure ^{31}P resonances using frequencies ranging from 32-243 MHz [26]. Typical acquisition times for ^{31}P free induction decay (FID) following a 90° radio frequency pulse are 1-8 seconds depending on the required resolution [26]. The temperature of the sample can be controlled to within 1°C by commercial spectrometer temperature control units [26]. ^{31}P NMR spectra are usually referenced to an external sample of 85% H_3PO_4 [26]. In a ^{31}P NMR spectrum signal assignment can often be made by comparison of chemical shifts to known compounds. This can be done because of the wide dispersion of chemical shifts (Table 3) [29].

Table 3: ^{31}P NMR Chemical Shifts (new sign convention) [29]

Type	**Shift Ranges**
CPH_2	-150 to -120 ppm
C_2PH	-100 to 80 ppm
C_3P	-60 to -10 ppm
C_2PHal	80 to 150 ppm
$P(NR)_3$	115 to 130 ppm
$P(OR)_3$	125 to 145 ppm
$P(SR)_2$	110 to 120 ppm
$PHal_3$	120 to 225 ppm
$P(OR)_2Hal$	140 to 190 ppm
$CPHal_2$	160 to 200 ppm
$CPHalN$	165 to 185 ppm
$O{=}PHal_3$	-80 to 5 ppm
$O{=}P(OR)Hal_2$	-30 to 15 ppm
$O{=}P(OR)_2Hal$	-20 to 25 ppm
$O{=}P(OR)_3$	-20 to 0 ppm
$S{=}P(OR)_3$	60 to 75 ppm
$CP({=}O)(OR)_2$	-5 to 70 ppm
$CP({=}S)(OR)_2$	80 to 110 ppm
$CP({=}O)(OH)_2$	-5 to 25 ppm
$(RO)_2POH$	0 to 20 ppm
$C_2P({=}O)OR$	0 to 60 ppm
$CP({=}O)Hal_2$	5 to 70 ppm
$CP({=}O)HalN$	25 to 50 ppm
$C_3P{=}OC_3P{=}S$	20 to 60 ppm
$C_2P({=}O)Hal$	40 to 90 ppm
$P(OR)_5$	-75 to -5 ppm
$C_4P^{+}Hal^{-}$	-5 to 30 ppm
$Ar_3P{=}CR_2$	5 to 25 ppm

There are several factors which contribute to the ^{31}P NMR shifts seen for phosphorus compounds. These factors include the effect of neighboring atoms and the effect of the net charge of the compound. With respect to the effect of neighboring atoms, there appears to be no simple general correlation between any of the standard measures of electron-donating or electron-withdrawing power of the substituents. This indicates that in a symmetrical environment the two major factors that contribute to shielding of the phosphorus atom are ionic character of the α-bond [27] and the amount of π-bond feedback which is not a simple function of electronegativity or related parameters [27].

Compounds with new types of phosphorus to phosphorus bonds have become of interest to our research group and we explored two new types of compounds. The first involves a P-P bond between a hexacoordinated phosphorus atom and a phosphonium atom in a new series of hexacoordinated phosphorus compounds. The second is a P-P bond between a phosphoryl phosphorus and a phosphonium atom in phosphonium analogues of amide compounds.

C. Hexacoordinated Phosphorus Compounds

Hexacoordinated phosphorus compounds bear significant potential to serve as models for the investigation of biological supramolecular interactions, catalysts of classical organic and inorganic reactions, ionophores and ion-exchange agents. The foundation for the new hexacoordinated phosphorus compounds synthesized in this effort was work done by Schmidpeter and co-workers [28]. Schmidpeter started his efforts using the compound dicatechylphosphorus monochloride (1), as the precursor to a group of hexacoordinated compounds. (Figure 11).

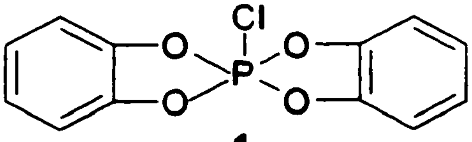


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Figure 11: Dicatechylphosphorus Monochloride

While this is the reported structure in chloroform, based on the fact that we observe two signals in the phosphorus NMR for this compound we believe that this compound exists in equilibrium with its tetracoordinated form, as shown in Figure 12.

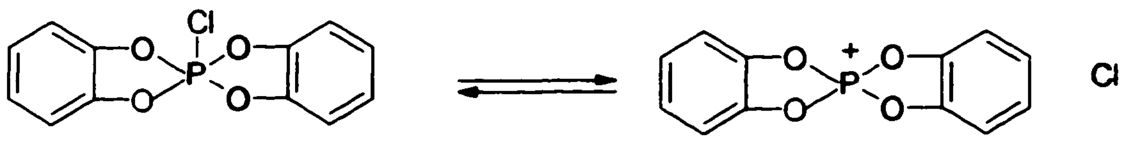


Figure 12: Equilibrium forms of Dicatechylphosphorus Monochloride

The compound's three-dimensional structure for the pentacoordinated form, in accord with one of the ^{31}P NMR signals, is postulated to be rectangular pyramidal (Figure 13) [30].

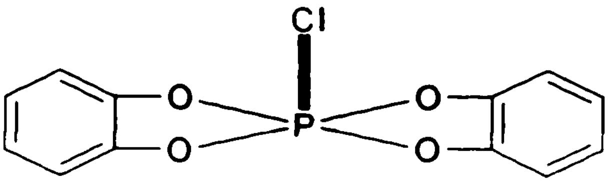


Figure 13: 3-Dimensional Structure for Pentacoordinated Dicatechylphosphorus Monochloride (1)

This compound cannot pseudorotate to a different diastereomer as the strain introduced by such a pseudorotation would be too high for the dioxaphosphorane rings [31-33].

Two nitrogen bearing ligands used by Schmidpeter for related systems were pyridine and 2,2'-bipyridyl. For the addition of pyridine to dicatechylphosphorus monochloride (1) [28], Schmidpeter postulated the mechanism of the reaction to be as follows: initially pyridine is added in a fast first step without dissociation to yield neutral compound 2, followed by another addition of pyridine in a much slower step to yield cationic compound 3 (Figure 14).

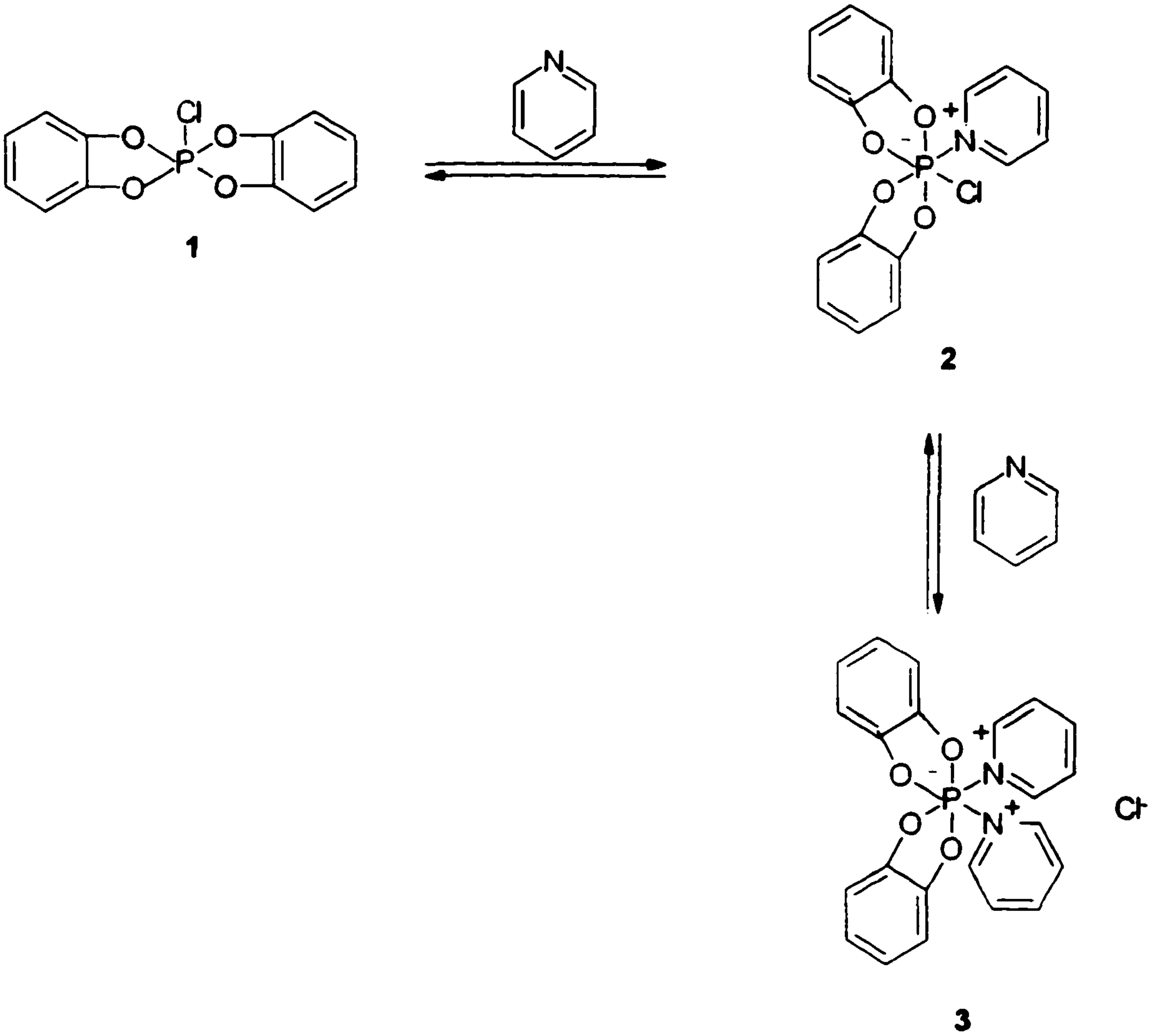


Figure 14: Schmidpeter Mechanism for Formation of Dicatechylphosphorus Dipyridinium Chloride

One intriguing feature of these types of compounds, for example **3**, is the fact that they are considered "cationic" even though the central phosphorus atom is negatively charged. Schmidpeter believed that the pyridines are added *cis* to each other in the hexacoordinated compound.

A second interesting aspect of these structures is that they are chiral and potentially capable of resolution. These compounds are chiral even though they do not contain a classical stereogenic center. An example of a class of compounds that are chiral without a stereogenic center are the allenes. Allenes contain a helical axis resulting from their structure being an "extended tetrahedron", making them capable of being optically active, as shown in Figure 15 [34].

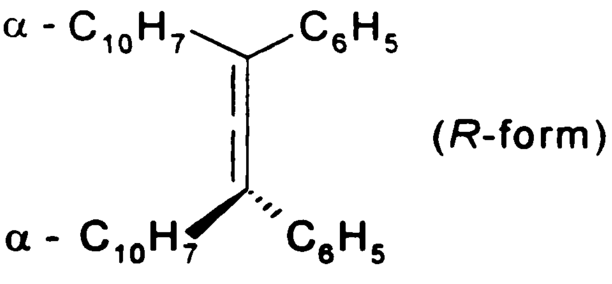


Figure 15: Optically Active Allene

Other compounds which are chiral without a stereogenic center are those whose structures are inherently helical. Watson and Crick [35] formulated the structure of DNA to be a double helix (Figure 16).

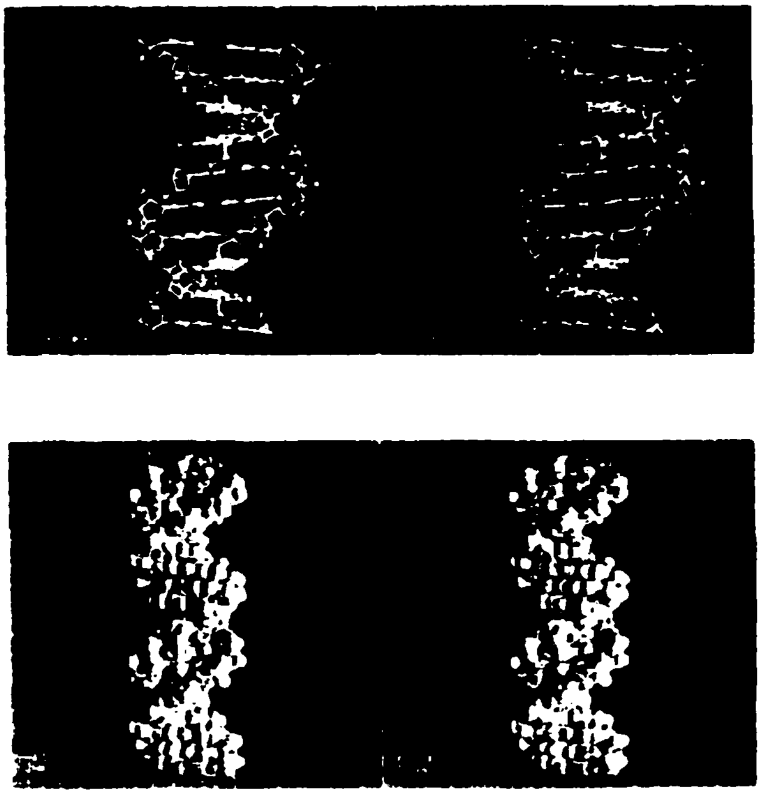


Figure 16: β-DNA Ball and Stick and Space-filling Models

Each of its two strands is coiled about a central axis in the β form as a right-handed helix [36-37]. The two sugar-phosphate backbones wind around the outside of the bases and are exposed to the aqueous solution. The phosphodiester bonds in the two interwoven strands run in opposite directions, making them antiparallel. The aromatic rings of the bases are hydrophobic and are stacked in the interior, almost perpendicular to the long axis of the helix.

The secondary structure of many proteins is one of the α-helix. Such α-helices can be either right-handed or left-handed. In proteins, a right-handed α-helix is more stable than a left handed one because of steric interference between the C=O and the side chains [38-39]. Only the right-handed α-helix has been found in protein structure (Figure 17).

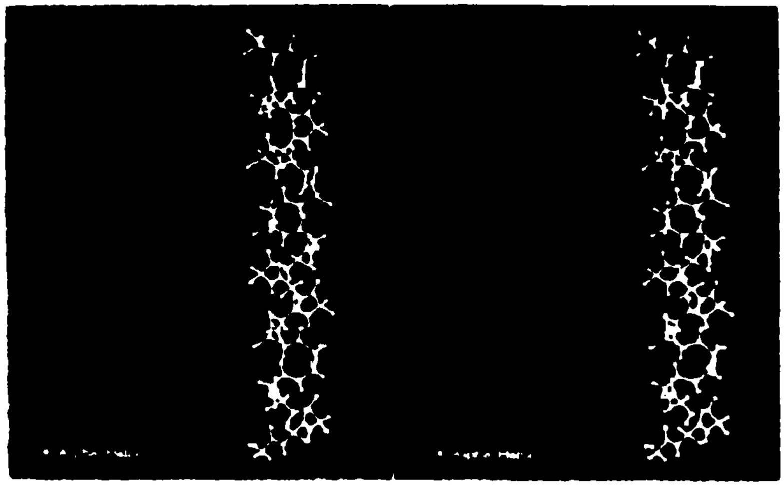


Figure 17: Side View of a Right-Handed α-Helix of a Protein-Ball and Stick Model

Some protein species can exist as a racemic mixture. For example the helical homopolypeptides of γ-methyl-D- and L- glutamate form racemic compounds in solution and the solid state [40]. Upon resolution, the isolated enantiomers showed different optical activities.

D. Phosphonium Amide Analogues

Amides are an interesting group of compounds distinguished by having a carbonyl group directly attached to a nitrogen atom (Figure 18).

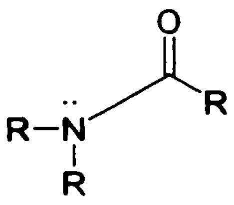


Figure 18: General Structure of an Amide

Amides can be prepared in a variety of ways, starting with carboxylic acids, carboxylic salts, acyl chlorides, acid anhydrides, and esters [41-45]. All of these methods involve nucleophilic substitution reactions by an amine or ammonia at an acyl carbon. Primary, secondary, and tertiary amides can be isolated rather easily, where as quaternary amides are not easily isolated. For example, acyl chlorides react with tertiary amines to form an acylammonium chloride which is not stable in the presence of water or any hydroxylic solvent (Figure 19) [46].

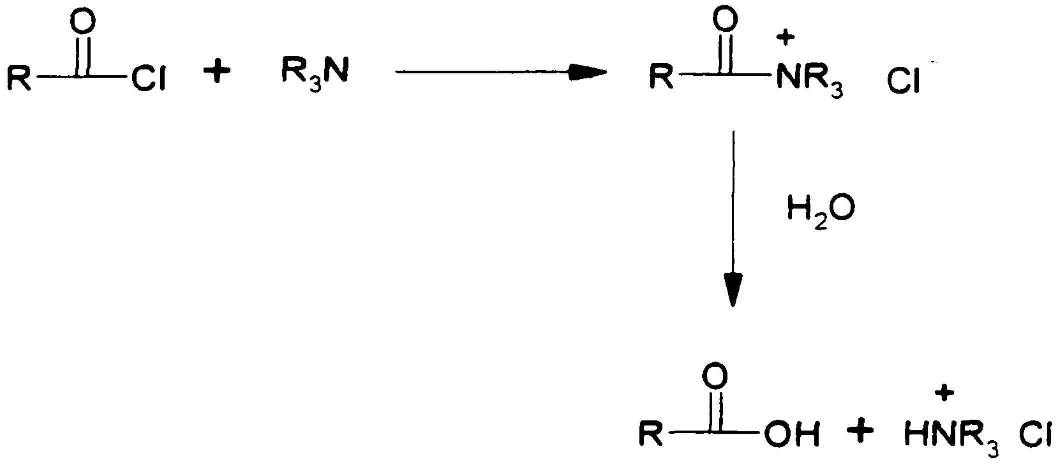


Figure 19: Formation of Acylammonium Chloride

In this study we are looking at a new type of quaternary amide, replacing both the carbonyl carbon and the nitrogen atom with phosphorus atoms.

Previous work in this area was done by Lindner and Beer [47] as they synthesized compounds having the general formula shown in Figure 20.

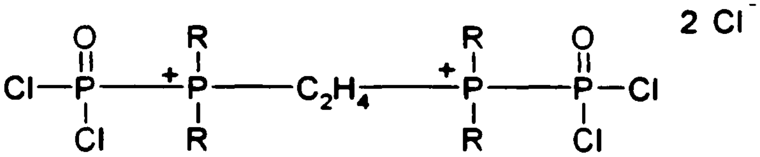


Figure 20: General Structure of Amide Analogues from Linder and Beer

The compounds synthesized by Lindner and Beer were not stable in water and decomposed rather readily (Figure 21) [47].

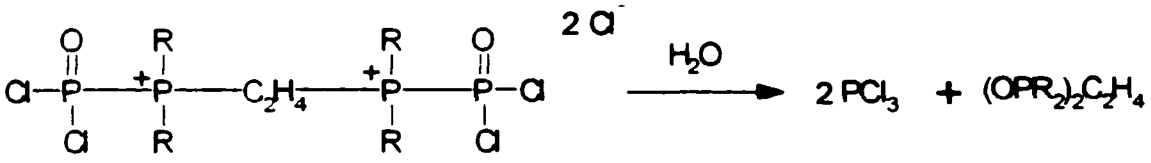


Figure 21: Decomposition of Amide Analogues from Linder and Beer

Other work in this area was done by Fluck and Binder [48] who found that trialkyl phosphites react with diphenylchlorophosphine to give compounds with the general structure shown in Figure 22.

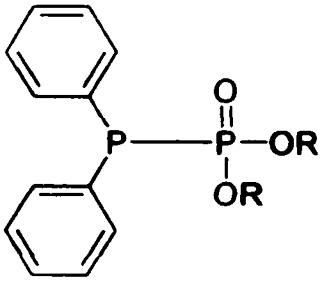


Figure 22: General Structure of Amide Analogues from Fluck and Binder

In this reaction the first step is a Lewis acid-base addition forming the phosphorus to phosphorus bond, followed by an elimination of alkyl halide leading to the indicated product (Figure 23) [48].

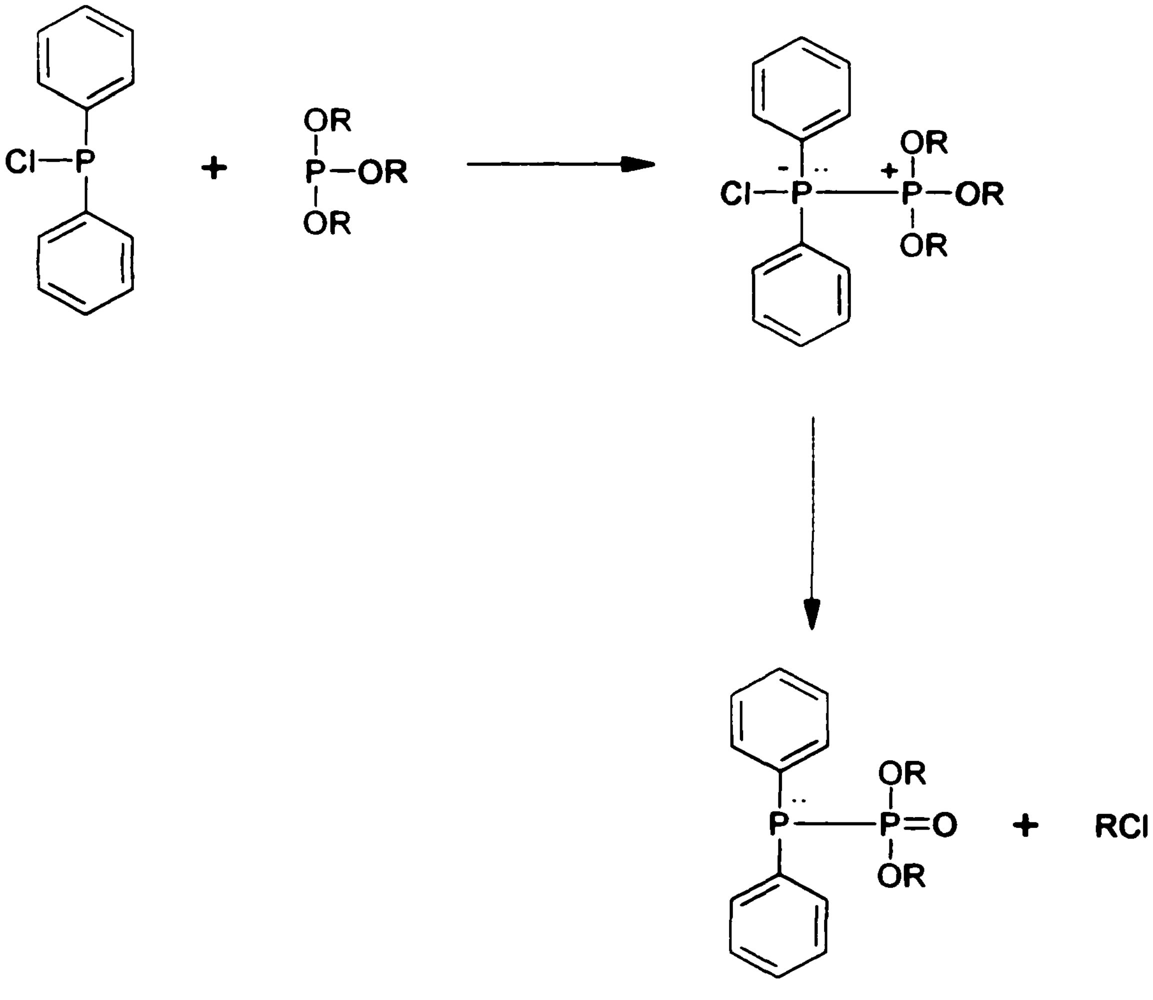
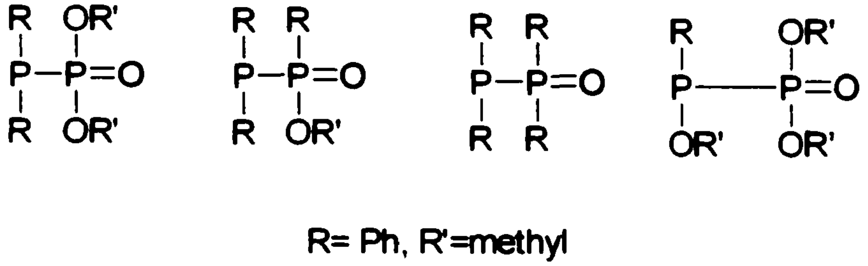


Figure 23: Mechanism for the Formation of Amide Analogues from Fluck and Binder

Fluck and Binder were able to widen the scope of this reaction to include esters of other acids with a lone electron pair on the phosphorus atom as long as the electron-donor power is sufficiently strong, and to include halogen-containing phosphorus(III) compounds that have enough Lewis-acid character, giving rise to several different types of compounds (Figure 24) [48].



R= Ph, R'=methyl

Figure 24: Different Classes of Amide Analogues from Fluck and Binder

Another aspect of the current project was to make a new type of dendrimer. Dendrimeric molecules, also known as cascade molecules, represent a class of molecules whose distinguishing characteristic are regular and repetitive branching within the molecule [49]. One type of dendrimer includes those in which phosphorus is present in the form of quaternary phosphonium ions. These dendrimers were prepared by using tri(*p*-methoxymethyl)phenylphosphine (4) for the construction of both the core and branch points, as shown in Figure 25 [50-53].

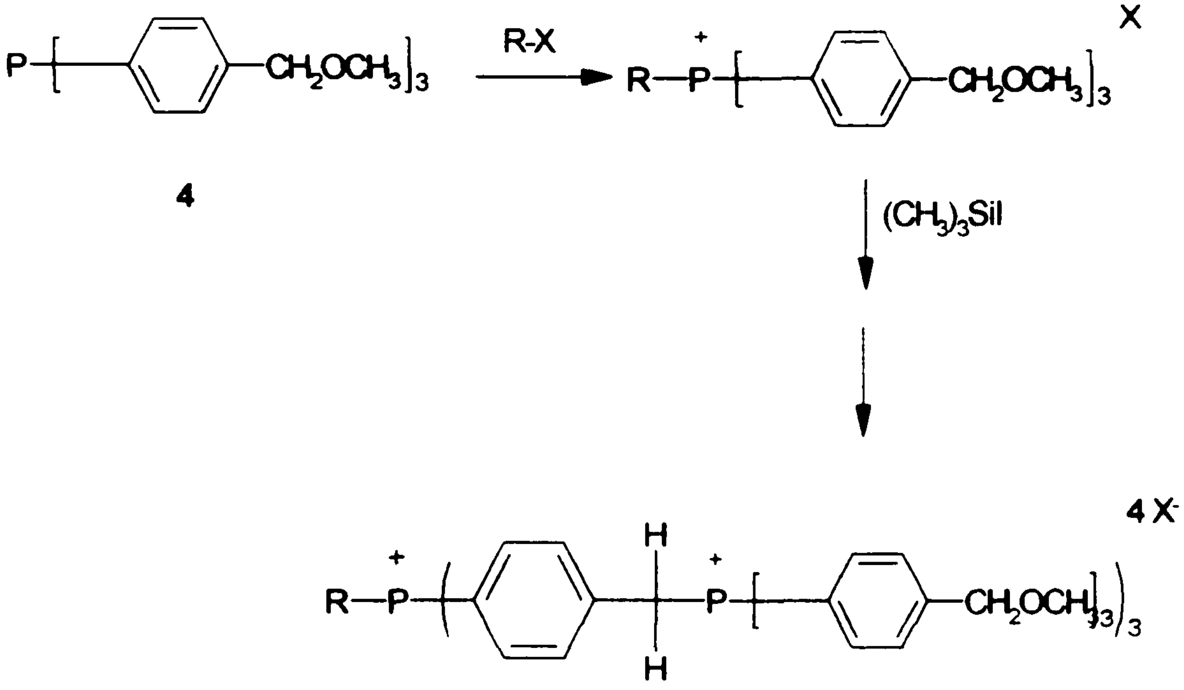
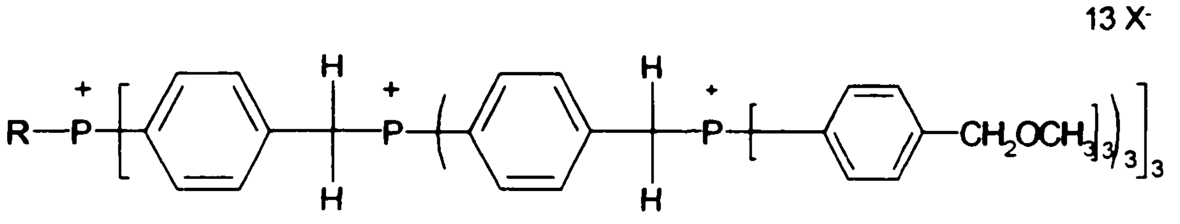


Figure 25: Formation of Phosphonium Ion Dendrimer Core

Subsequent generations were formed by a repetitive sequence of two reactions, the one-step deblocking of the benzylic ether linkages with simultaneous formation of the reactive benzylic iodide, followed by dendrimer elaboration by reaction with 4 [49]. In this manner two different types of dendrimers were generated. The first are "balloon" type dendrimers (5) generated with a variety of different alkyl groups as the "tail", and the second are "star" type dendrimers (6) (Figure 26) [49].



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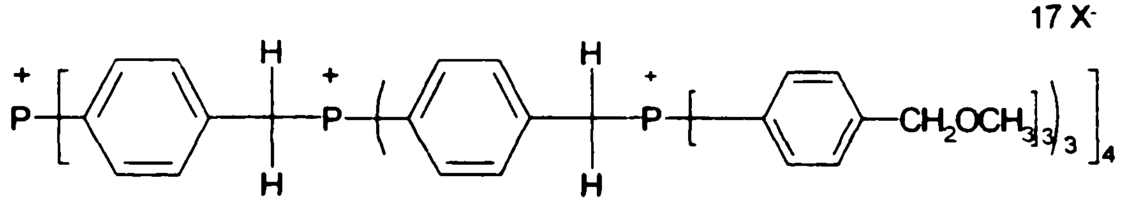

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Figure 26: "Balloon" and "Star" Phosphonium Ion Dendrimers

These compounds exhibit significant solubility in a wide range of organic and aqueous media, and showed distinctive signals in the ^{31}P NMR spectrum for each generation of phosphonium ion site [49]. Further, the phosphonium ion core of the "star" tetraarylphosphonium ion is subject to addition of a fifth aryl group at phosphorus to generate pentaarylphosphorane **7** (Figure 27).

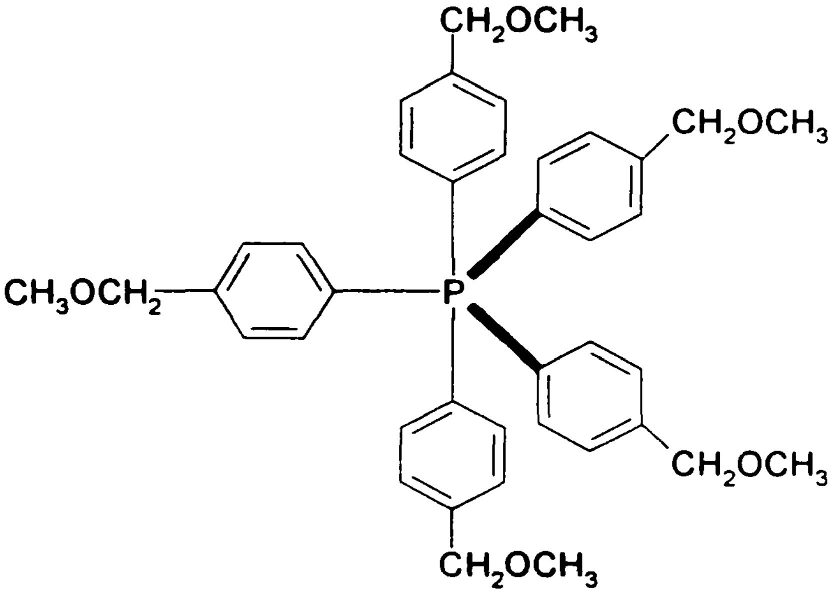

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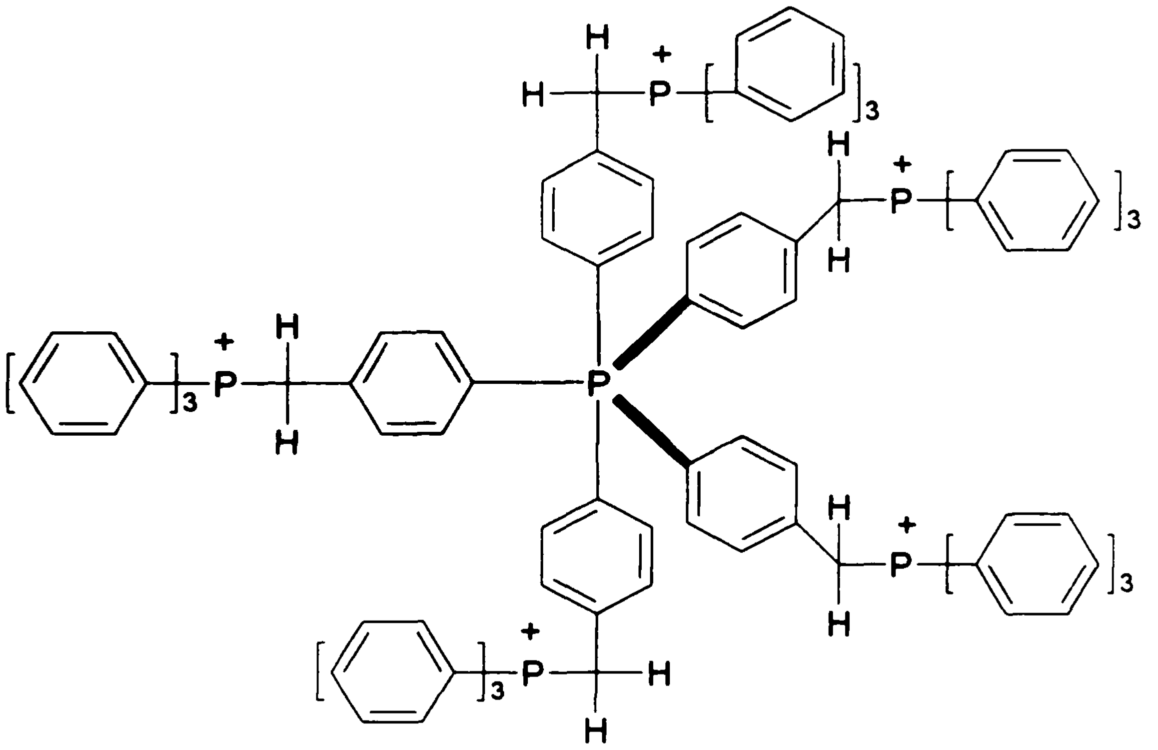
Figure 27: A Pentaarylphosphorane

This material can be elaborated to higher generations of phosphorane/phosphonium ion dendrimers, including **8**, which bears an electrically neutral pentadirectional monatomic core site (Figure 28) [49].



8

Figure 28: Higher Generation Phosphorane/Phosphonium Ion Dendrimer

Dendrimers, bearing cores other than the phosphonium ion type, have been generated from tri(*p*-methoxymethyl)phenylphosphine as well [49]. Oxidation of 4 leads to the corresponding oxide upon which elaboration can be accomplished using the same sequence of reactions as the elaboration to form 5 and 6. The resultant phosphine oxide/phosphonium ion dendrimer 9 is capable of undergoing reduction at the core to generate a phosphine/phosphonium ion dendrimer **10** which exhibits usual phosphine chemistry at the core site (Figure 29) [52-53].

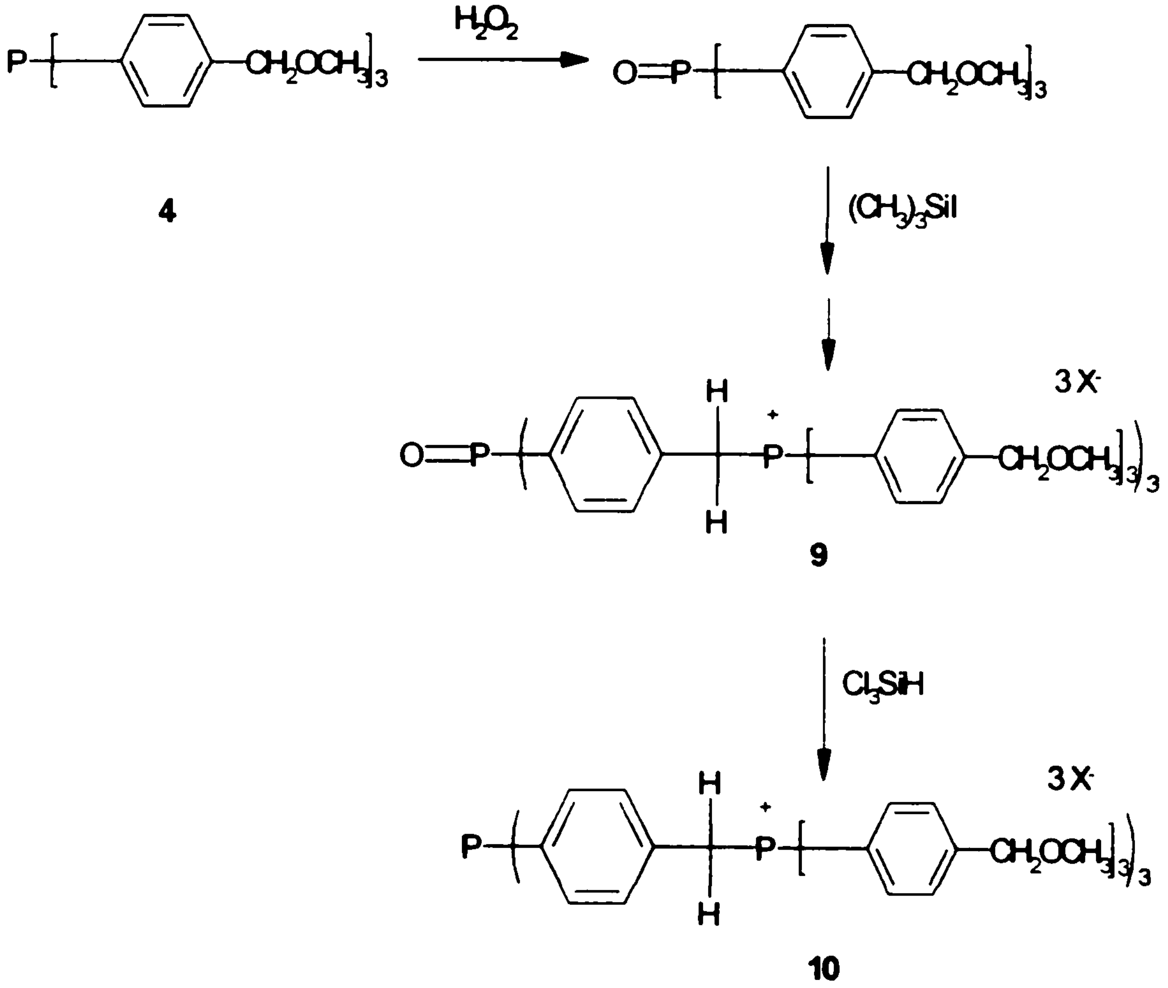
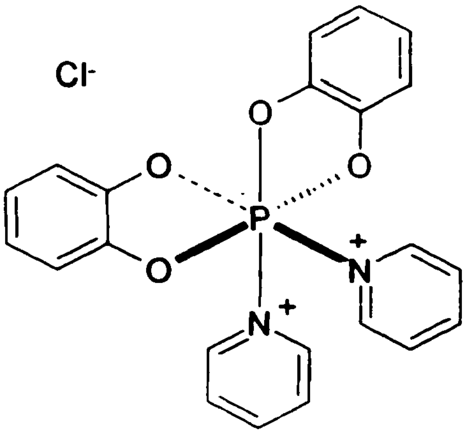


Figure 29: Formation of Phosphine/Phosphonium Ion Dendrimer

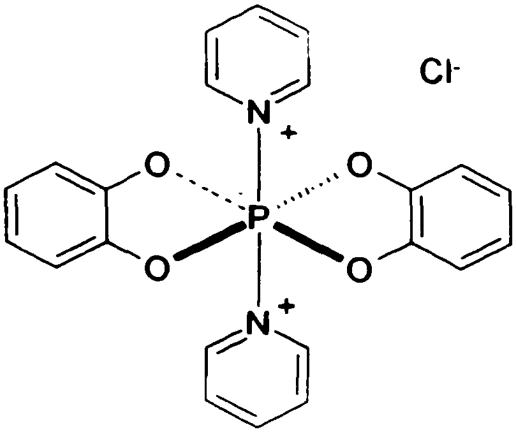
II. Results and Discussion

A. Hexacoordinated Phosphorus Compounds

In some octahedral complexes the central atom has unshared electron pairs. These pairs occupy *trans* positions in the octahedron, in order to minimize the repulsion between the electron pairs [54]. In this same way it would seem reasonable that ligands would add to form an octahedral complex in a way that would minimize repulsion between like charges. Thus, an alternative structure that we might postulate to the *cis* structure given by Schmidpeter for dicatechylphosphorus dipyridinium chloride (**11a**) based on the understanding that the pyridine ligands would add to dicatechylphosphorus monochloride (**1**) in such a way that would keep them as far from each other as possible, as shown in Figure 30. Thus we postulate the hexacoordinated compound derived from this reaction to have a *trans* structure (**11b**).



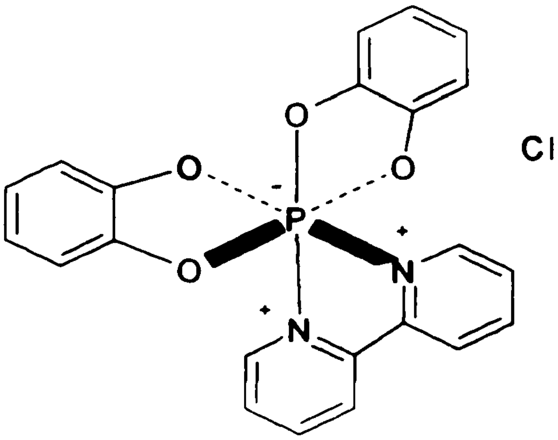
11a



11b

Figure 30: *Cis* and *Trans* Forms of Dicatechylphosphorus Dipyridinium Chloride

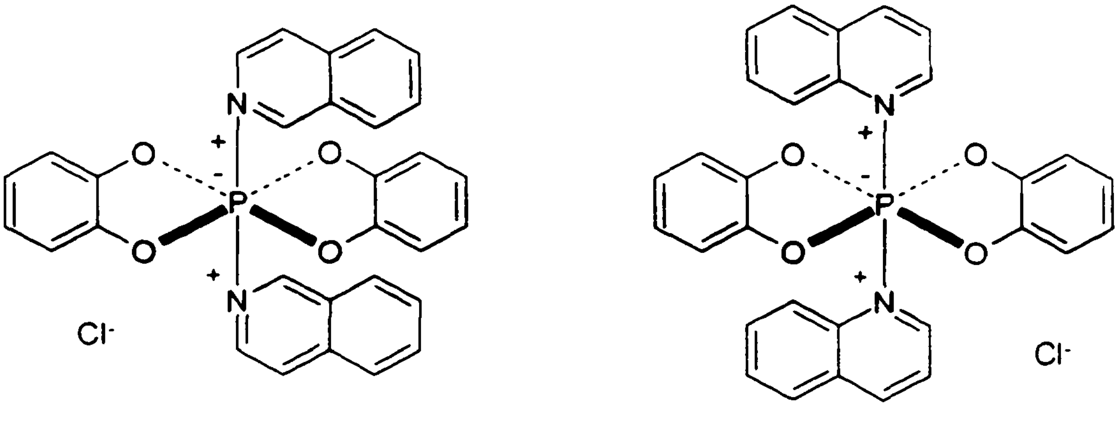
The addition of 2,2'-bipyridyl to dicatechylphosphorus monochloride was found to provide the hexacoordinated compound **12**, for which a *cis* linkage is necessary (Figure 31) (Table 8).



12

Figure 31: 2,2'-Bipyridyl Dicatechylphosphorus Chloride

The first new area of our investigation of hexacoordinated phosphorus compounds was involved with the study of the addition of two new monodentate nitrogen ligands, isoquinoline and quinoline, to **1**. The synthesis of these adducts as single species has been successful as the ^{31}P NMR of these compounds shows only one peak, at approximately −81 ppm, indicative of a hexacoordinated phosphorus atom (Table 4). We understand that these two ligands add to dicatechylphosphorus monochloride in the same way that pyridine does, yielding *trans* compounds **13** and **14** respectively (Figure 32).



13

14

Figure 32: Diisoquinoline and Diquinoline Dicatechylphosphorus Chlorides

Table 4: ^{31}P NMR data for Hexacoordinated Phosphorus Compounds with **1** and Nitrogen Ligands

Material	^{31}P NMR
11	-81.596
12	-81.035
13	-81.615
14	-81.614
15	-81.045

Further, a new bidentate nitrogen ligand was investigated, 1,10-phenanthroline. The reaction of 1,10-phenanthroline and **1** has been successfully characterized using ^{31}P NMR and we found that this ligand adds to dicatechylphosphorus monochloride (**1**) (Table 4). Again, a *cis* structure is required, as shown in Figure 33.

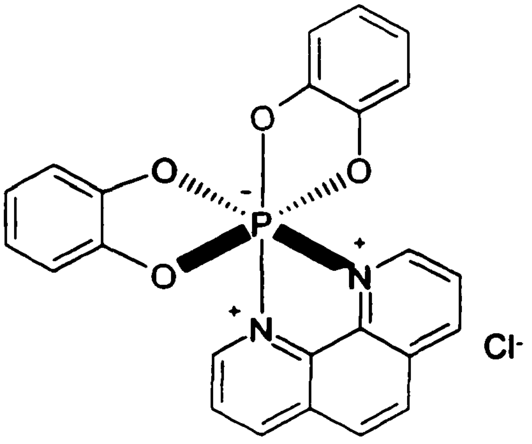


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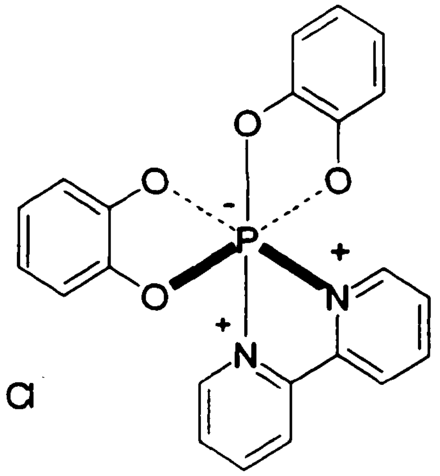
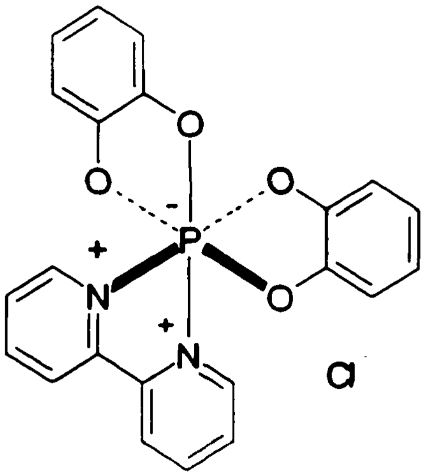
Figure 33: 1,10-Phenanthroline Dicatechylphosphorus Chloride

The synthesis of hexacoordinated phosphorus compounds with bidentate nitrogen ligands necessarily yields racemic mixtures rather than a single enantiomer. That is, in the synthesis with 2,2'-bipyridyl a mixture (**12a**/**12b**) would be generated from the reaction with **1** (Figure 34).



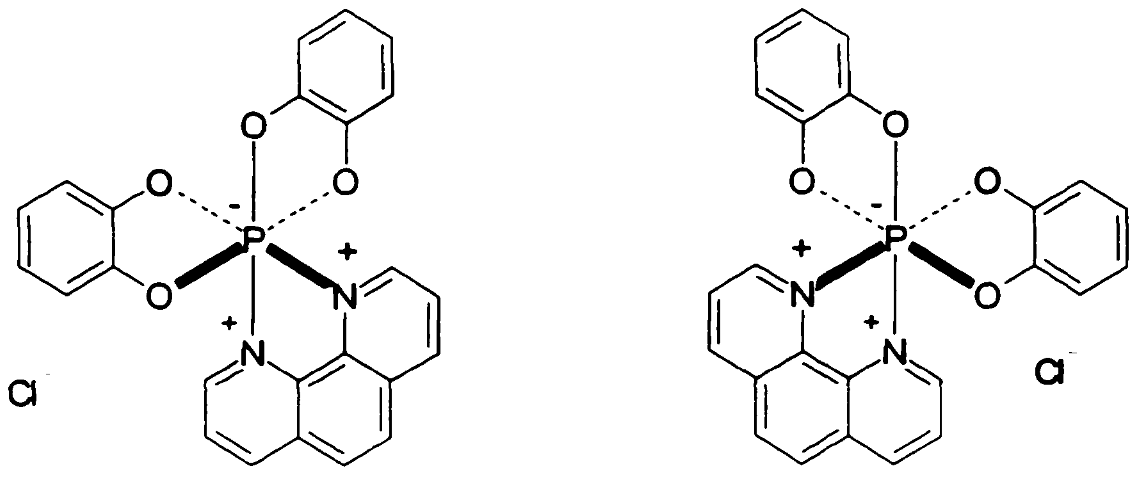
12a



12b

Figure 34: Enantiomers of 2,2'-Bipyridyl Dicatechylphosphorus Monochloride

Further, the reaction of **1** with 1,10-phenanthroline would yield the racemic mixture **15a/15b** (Figure 35).



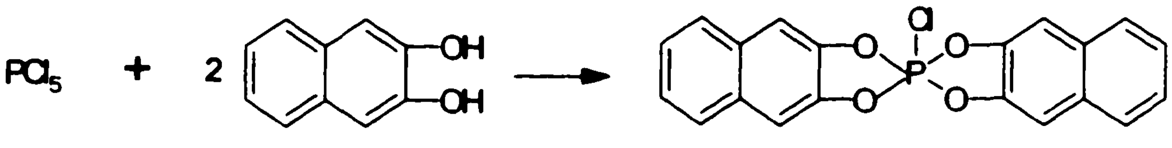
15a **15b**

Figure 35: Enantiomers of 1,10-Phenanthroline Dicatechylphosphorus Chloride

One goal of the current effort was to resolve these enantiomeric mixtures generating optically pure materials. One method of resolution attempted was an approach that was used in the resolution of ruthenium tris(diimine) complexes [55-57]. This method involves the use of a solution of disodium (+)-*O,O'*-dibenzoyl-D-tartrate. For example *cis*-$[Ru(bpy)_2(py)_2]Cl_2$ was taken with disodium (+)-*O,O'*-dibenzoyl-D-tartrate in aqueous media [55]. After evaporation of the solvent red crystals of Δ-$[Ru(bpy)_2(py)_2]$[(+)-*O,O'*-dibenzoyl-D-tartrate]·12 H_2O were collected.

To this end, each of **12a/12b** and **15a/15b** were taken with the disodium salt of *O,O'*-dibenzoyl tartaric acid in an aqueous media. The intent was that on partial evaporation one enantiomer would precipitate out of solution while the other one remained in solution. Upon performance of this effort the precipitate was collected, dried, and an anion exchange was performed on the solid to remove the tartrate anion and change the anion back to chloride. Unfortunately, this approach toward the resolution of these compounds has been unsuccessful, indicated by loss of the hexacoordinated phosphorus peak in the ^{31}P NMR spectra. Apparently the hexacoordinated phosphorus species is disrupted under the reaction conditions.

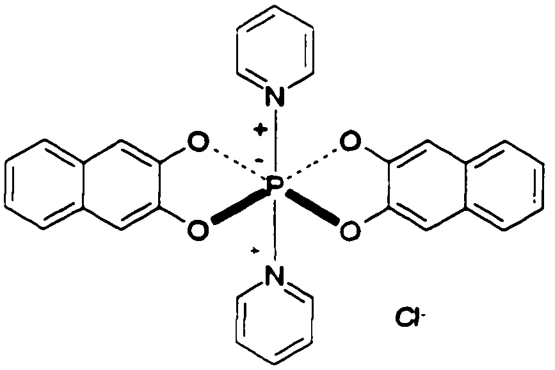
An alternative approach to the preparation of hexacoordinated phosphorus compounds was used with the monodentate and bidentate nitrogen ligands. This approach, using the reaction of phosphorus pentachloride and 2,3-dihydroxynaphthalene, is shown in Figure 36 [58].



16

Figure 36: Formation of Di-2,3-dihydroxynaphthylphosphorus Monochloride

This compound proved not stable enough to be isolated and as such it was used *in situ* in subsequent reactions. With the monodentate nitrogen ligands pyridine, isoquinoline, and quinoline, the synthesis of new hexacoordinated phosphorus compounds was successful as indicated by a peak at −81 ppm in the ^{31}P NMR of each of the compounds (Table 5). It was understood that the ligands are again added in a *trans* manner so that the like charges are as far away from each other as possible, yielding compounds 17-19 (Figure 37) [53].



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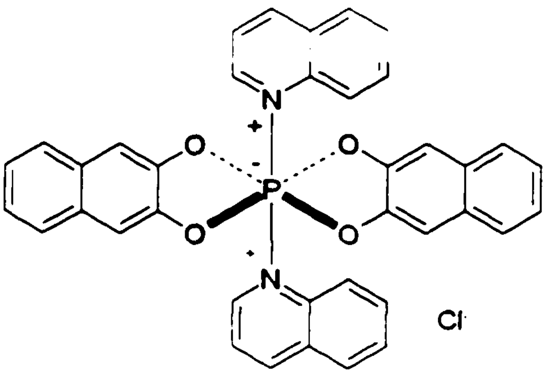

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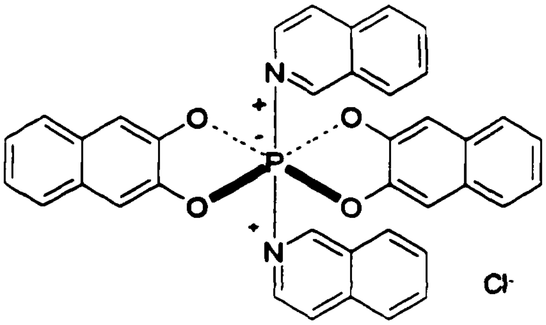

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Figure 37: Dipyrdinium, Diquinoline and Diisoquinoline Di-2,3-dihydoxynaphthylphosphorus Chlorides

Table 5: ^{31}P NMR data for Hexacoordinated Phosphorus Compounds generated from **16** and Nitrogen Ligands

Material	**^{31}P NMR**
17	-81.662
18	-81.659
19	-81.656
20	-81.031
21	-81.037

This approach also worked to generate racemates with the bidentate ligands 2,2'-bipyridyl and 1,10-phenanthroline, that is mixtures **20a/20b** and **21a/21b** respectively (Figure 38) (Table 5).

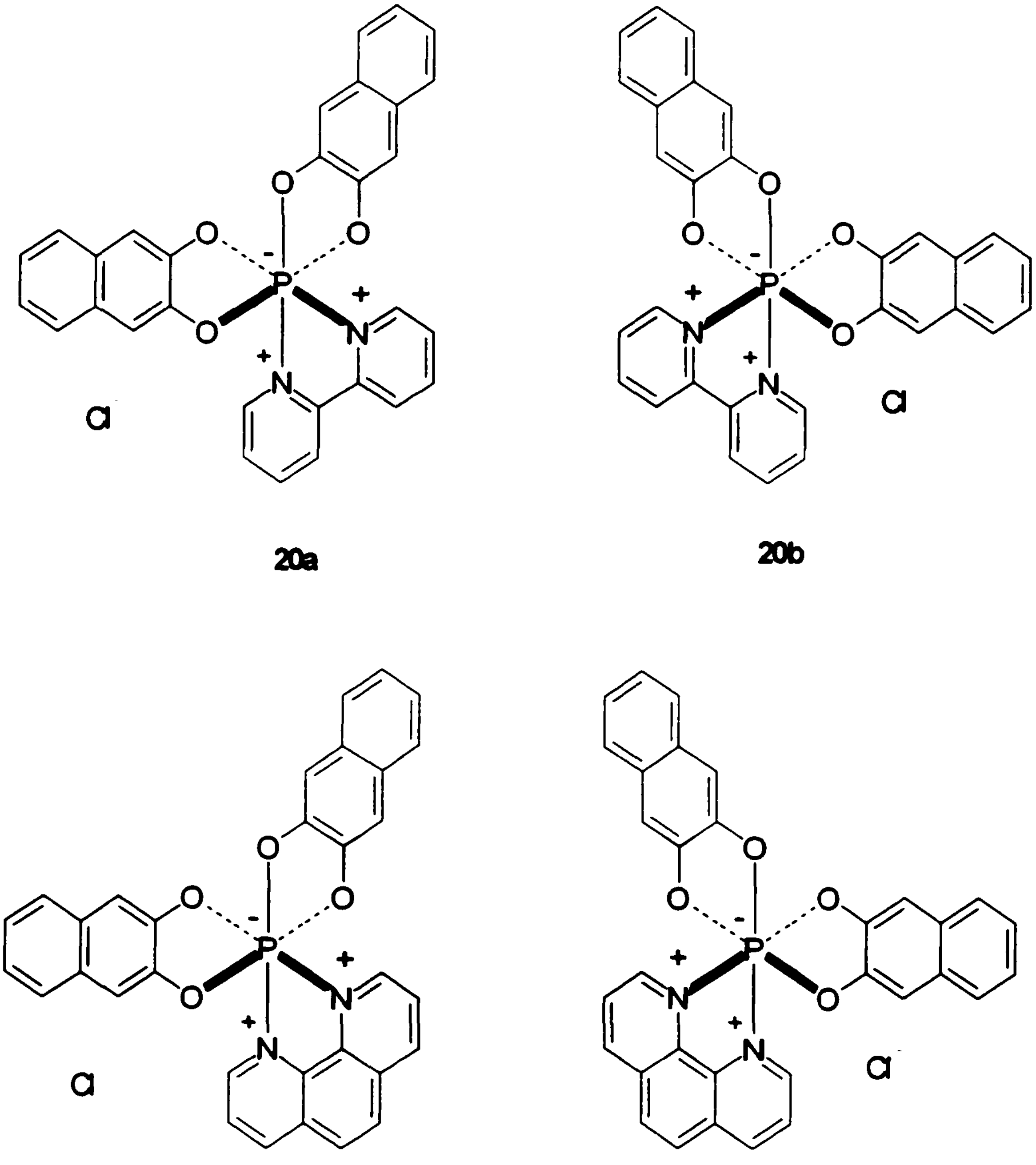


Figure 38: Enantiomers of 2,2'-Bipyridyl and 1,10-Phenanthroline Di-2,3-dihydroxynaphthylphosphorus Chlorides

Again the resolution of these compounds was attempted using the disodium salt of O,O'-dibenzoyl tartaric acid and then a subsequent anion exchange for conversion back to the chloride form. Once again the resolution using this method was unsuccessful as it appeared to destroy the hexacoordinate phosphorus compound.

Another alternative approach involved separating the racemic mixtures *via* column chromatography. With this method diastereomeric complexes are formed on optically active adsorbents by reversible adsorption, and their different stabilities result in different rates of elution of the two enantiomers [59]. The choice of adsorbent for our chromatographic resolution was cellulose. Cellulose has seen use in paper chromatography in the separation of racemic mixtures of catechol complexes [59], epicatechol complexes [59], amino acids [60-62], and alkaloids [63-64]. One drawback to the use of cellulose in column chromatography are the small differences in R_f- values are usually insufficient to obtain preparative amounts of enantiomers [59].

However, this alternative approach was successful as one enantiomer was able to be isolated in the cases of **20a/20b** and **21a/21b**. In this effort **20a/20b** was dissolved in methanol giving a yellow liquid. This liquid was poured through the column packed with cellulose, along with more methanol. A brown liquid was obtained from the column and upon removal of the solvent a brown solid was left. The optical activity of this enantiomer was measured, being 5.7 x 10^2 (deg*cm^2)/g.

This high optical activity is quite reasonable for a compound whose structure is truly helical, rather than bearing simply a stereogenic atom.

In yet another set of experiments, the preparation of a new set of hexacoordinated phosphorus compounds was attempted using monodentate and bidentate phosphorus ligands with the catechyl **(1)** and 2,3-dihydroxynaphthyl **(16)** precursors.

The monodentate ligands used with the catechyl system included trioctylphosphine **(22)**, tributylphosphine **(23)**, tricyclohexylphosphine **(24)**, triisobutylphosphine **(25)**, and tripropylphosphine **(26)** in the attempted preparation of compounds as shown in Figure 39.

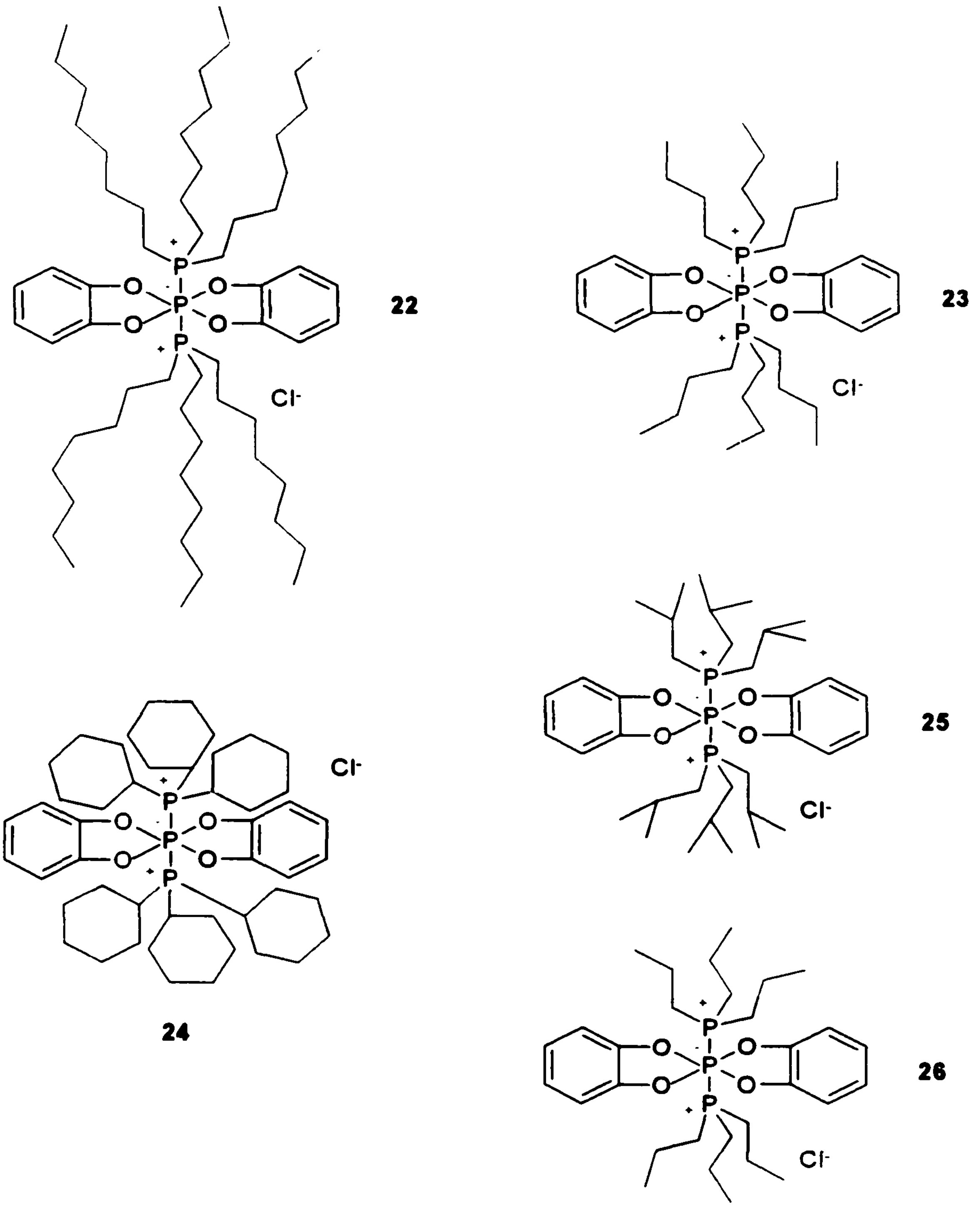


Figure 39: **Formation of Hexacoordinated Phosphorus Compounds from 1 and Monodentate Phosphorus Ligands**

Each of these compounds exhibits several peaks in the phosphorus NMR spectrum, that help to understand the nature of the reaction (Table 6).

Table 6: ^{31}P NMR data for Hexacoordinated Phosphorus Compounds generated From **1** and Monodentate Phosphorus Ligands

Material	**^{31}P NMR**	
22	65.128	62.583
	-4.189	-81.834
23	57.46	48.137
	-4.528	-81.586
24	58.0505	50.1426
	-4.6117	
25	56.0831	45.639
	-4.558	-81.587
26	47.294	34.111
	-4.513	-81.588

Each material (except for **24**) exhibited two peaks in the "phosphonium" range, between 45 and 70 ppm, and one peak between –80 and –83 ppm indicating a hexacoordinated phosphorus. The peak between –5 and 0 ppm represents the penatcoordinated system as an impurity (Figure 40).

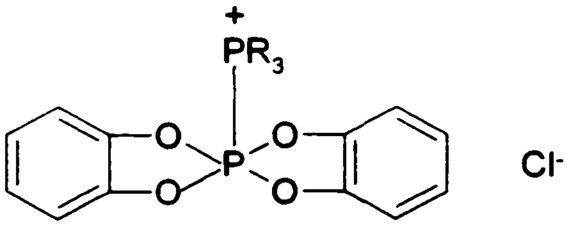


Figure 40: Pentacoordinated By-product Formed from 1 and Monodentate Phosphorus Ligands

as a by-product of the reaction. The peak between −80 and −83 ppm is indicative of a hexacoordinated phosphorus atom with the 2 unequal peaks between 45 and 60 ppm indicating a mixture of *cis* and *trans* isomers (Figure 41).

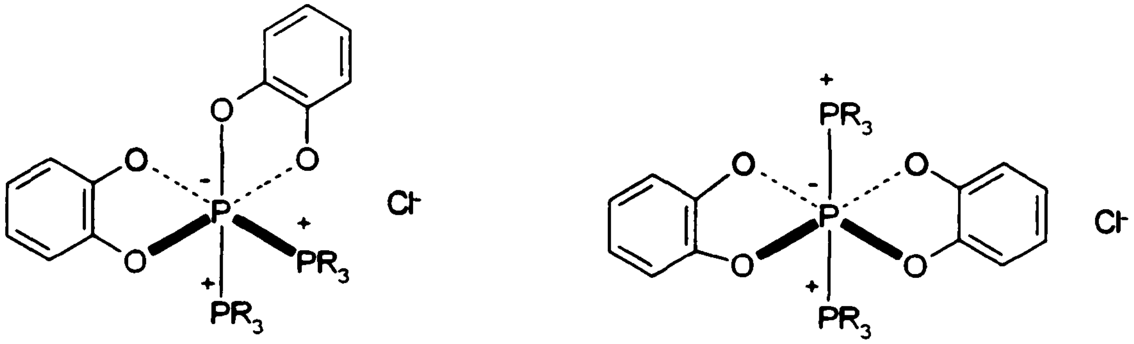
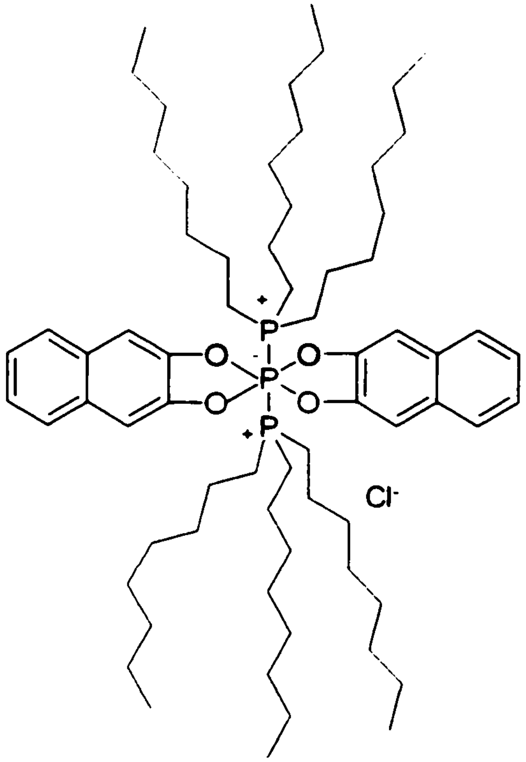


Figure 41: Isomers Formed from 1 and Monodentate Phosphorus Ligands

The larger peak presumably represents the *trans* isomer as in this isomer the like charges are placed furthest apart and would be energetically favored.

The only compound in this series we were not able to prepare was **24**. This reaction showed no peak indicative of a hexacoordinated phosphorus atom in the phosphorus NMR spectrum. This reaction involved a highly hindered tertiary phosphine and presumably was unsuccessful owing to steric interactions.

The 2,3-dihydroxynaphthyl systems derived with monodentate phosphorus ligands include trioctylphosphine **(27)**, tributylphosphine **(28)**, tripropylphosphine **(29)** and triisobutylphosphine **(30)** (Figure 42).



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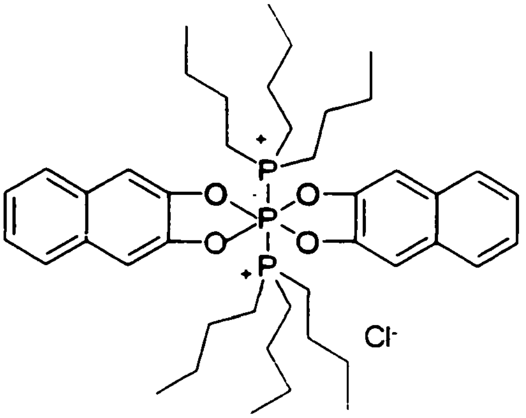

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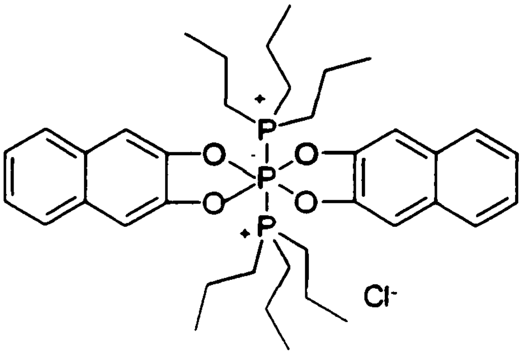

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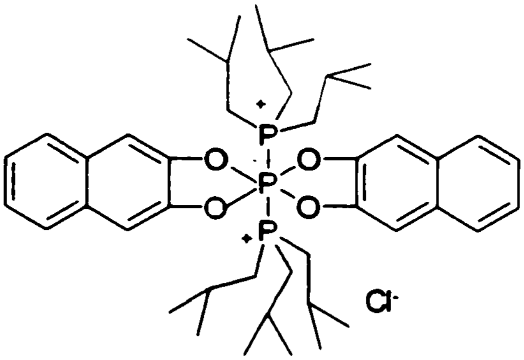

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Figure 42: Compounds Formed from **16** and Monodentate Phosphorus Ligands

The 2,3-dihydroxynaphthyl systems showed some different physical characteristics than the catechyl-based systems. For example, when tributylphosphine was used as the ligand the catechyl system was a liquid, while the 2,3-dihydroxynaphthyl system was a solid. The phosphorus NMR of these compounds showed differences as well (Table 7).

Table 7: ^{31}P NMR data for Hexacoordinated Phosphorus Compounds generated From **16** and Monodentate Phosphorus Ligands

Material	**^{31}P NMR**	
27	13.5977 -82.193	10.6511
28	14.087 -82.113	10.68
29	13.985 -82.177	10.128
30	14.063 -82.158	10.591

The peak between 0 and 5 ppm which was present in the catechyl-based systems is no longer present in 2,3-dihydroxynaphthyl systems. This seems to indicate that the pentacoordinated by-products are no longer present, possibly removed before filtration by washing each product with a portion of methanol. This was not done in the synthesis of the catechyl systems as the desired products here were easily isolated. The two peaks which were found at 48 and 57 ppm have now shifted downfield and are now found at 10 and 14 ppm. This downfield shift presumably results from an increased shielding by the naphthyl ring portions of the 2,3-dihydroxynaphthyl systems. Again, the two positive shifts indicates a mixture of *cis* and *trans* isomers (Figure 43).

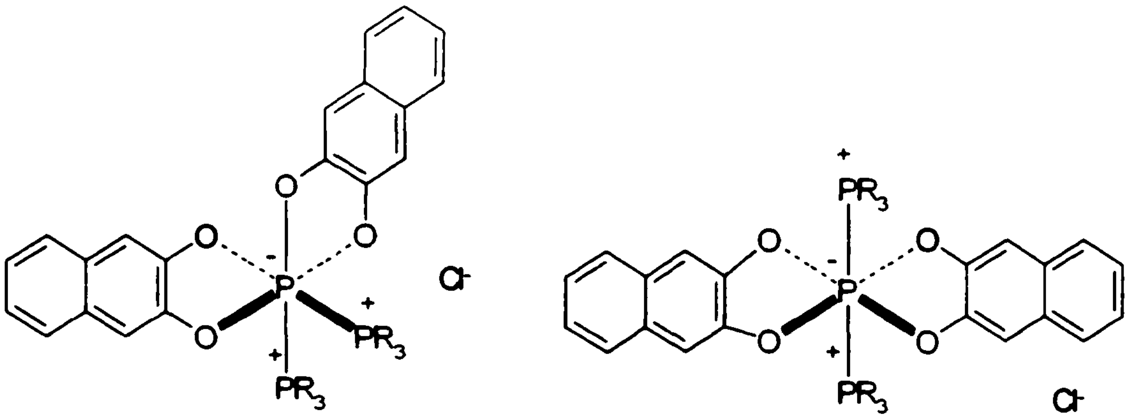


Figure 43: Isomers Formed from 16 and Monodentate Phosphorus Ligands

The larger of the two peaks presumably represents the <u>*trans*</u> isomer, as in this system the like charges are again furthest apart making this system more favorable energetically.

The bidentate phosphorus ligands used to generate hexacoordinated phosphorus compounds were 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane. These catechyl systems (**24-25**) once again showed a series of peaks in the ^{31}P NMR (Table 8).

Table 8: ^{31}P NMR data for Hexacoordinated Phosphorus Compounds generated From **1** and **16** and Bidentate Phosphorus Ligands

Material	^{31}P NMR	
31a/31b	57.842	49.458
	-17.267	
32a/32b	34.706	30.676
	-14.478	
32-resolution product	34.076	-13.736
33a/33b	37.922	23.888
	-14.076	
33-resolution product	34.855	-13.619
34a/34b	2.315	1.24
	-10.368	
34-resolution product	33.878	-13.813

The hexacoordinated phosphorus signals in these systems have shifted significantly upfield to −17 ppm.

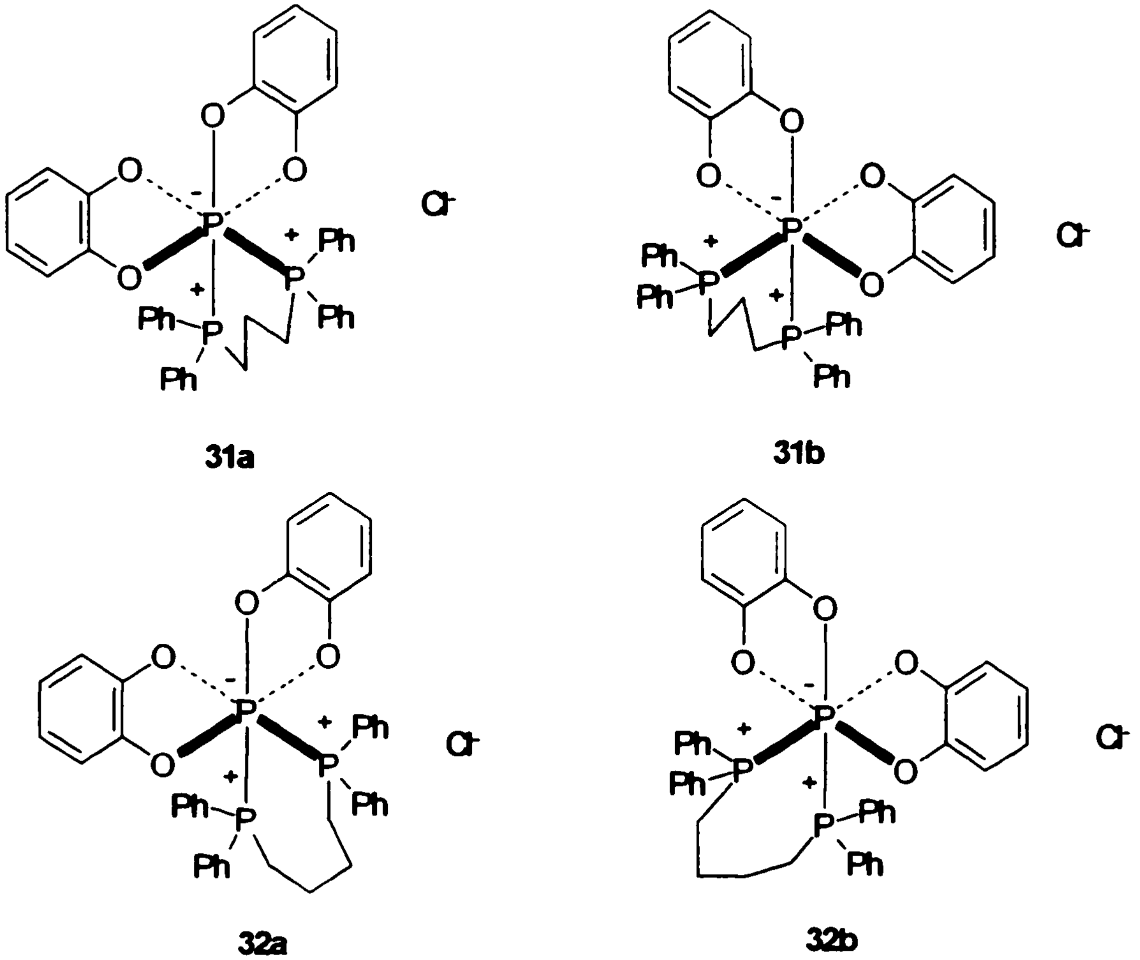
Octahedral complexes containing three bidentate ligands exist as a pair of enantiomers, differing by the rotation of the helix formed by the ligands [65-67]. Right rotation of the helix is designated delta (Δ) and left rotation is designated by lambda (Λ) (Figure 44).

Δ-designation

Λ-designation

Figure 44: Enantiomeric Octahedral Complexes Formed by Three Bidentate Ligands

Therefore we expect the hexacoordinated phosphorus compounds synthesized with bidentate phosphorus ligands to exist as racemic mixtures. The presence of two peaks between 30 and 60 in **31-32** indicates the presence of enantiomers along with a small amount of impurity in the products (Figure 45).

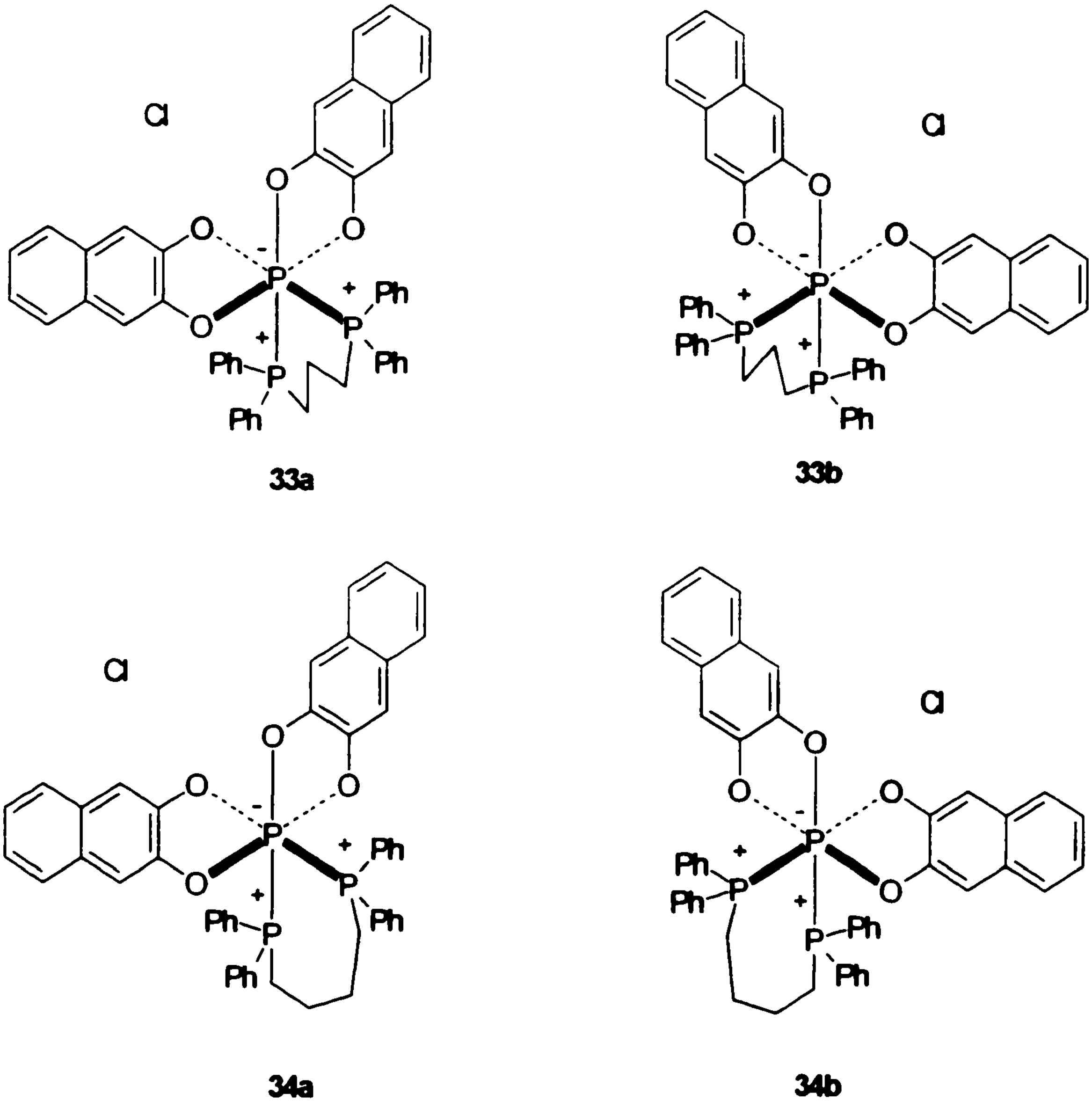


31a **31b**

32a **32b**

Figure 45: Enantiomers Formed from 1 and Bidentate Phosphorus Ligands

The resolution of **32a/32b** was done by dissolving the compound in chloroform and passing it through a column packed with cellulose. We again postulate that one enantiomer will pass through the column while the other one is retained on the cellulose. The phosphorus NMR of the resolution product showed one peak at 40 ppm indicating that passing the product through the column removed the impurity as well as possibly separating the enantiomers (Table 8). The peak at −17 ppm indicating our hexacoordinated phosphorus atom is still present as well. On the other hand the resolution of **31a/31b** using the cellulose packed column has been unsuccessful. It appears that this technique might not be useful for liquids since **31a/32b** is a liquid compound. These two bidentate phosphorus ligands were reacted with **16** as well yielding racemic mixtures (Figure 46).



33a

33b

34a

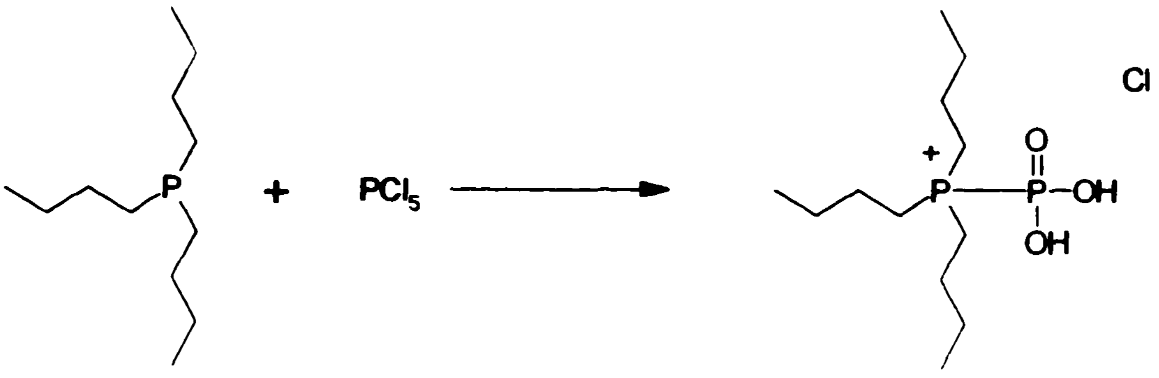
34b

Figure 46: Enantiomers Formed from **16** and Bidentate Phosphorus Ligands

In the 1,3-bis(diphenylphosphino)propane-2,3-dihydroxynaphthyl system **(33a/33b)** the hexacoordinated peak was shifted upfield, falling at −14 ppm. Two peaks were found for this system between 20 and 40 ppm, again indicating a small amount of impurity in the product (Table 8). In the 1,4-bis(diphenylphosphino)butane-2,3-dihydroxynaphthyl system **(34a/34b)** the hexacoordinate phosphorus peak is significantly downfield at −10 ppm. The two peaks representing the enantiomers and an impurity have shifted upfield compared to the rest of the systems, now falling at 2 and 1 ppm (Table 8). Resolution of **33a/33b** and **34a/34b** was done using the cellulose packed column. In the ^{31}P NMR of the resolution products there are two peaks, one at about −13 ppm again representing the hexacoordinate phosphorus atom and another between 33-35 ppm indicating the phosphonium atoms. The presence of only two peaks indicates the removal of impurities from these systems along with possible separation of the enantiomers (Table 8).

B. Phosphonium Amide Analogues

What was evident from the proton NMR of the first "dendrimer" synthesized (compound **35**) was that there appeared to be some OH present most likely in the form of P(O)OH based on a peak around 11.5 ppm. To further determine if OH was present in the compound an IR spectrum of the compound was obtained. A broad peak in the range of 3800-3200 cm^{-1} was found, highly indicative of a hydroxyl group. A band at 1050 cm^{-1}, indicative of a phosphate group, was present in the IR spectrum as well. It was determined that the compound had hydrolyzed and that a phosphate group along with one phosphorus to phosphorus bond was present. The compound formed was tributylphosphino chlorophosphate **35** (Figure 47).

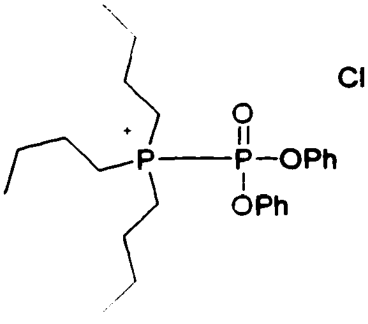


35

Figure 47: Formation of Tributylphosphino Chlorophosphate

The aspect of this reaction most interesting was that this compound seemed to be relatively stable. Based on this finding a new series of compounds with the P(O)-P(+) linkage were created.

The first phosphate compound that was used was diphenyl chlorophosphate. This compound was treated with numerous alkylphosphines including: tributylphosphine **(36)**, trimethylphosphine **(37)**, tricyclohexylphosphine **(38)**, triphenylphosphine **(39)**, trioctylphosphine **(40)**, tripropylphosphine **(41)**, and triisobutylphosphine **(42)**, each forming a liquid product with initially postulated structures shown as follows (Figure 48).



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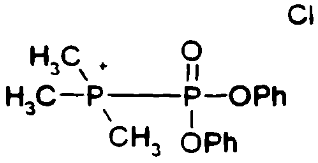

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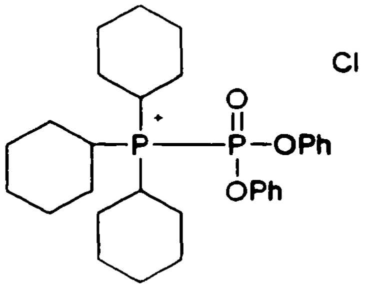

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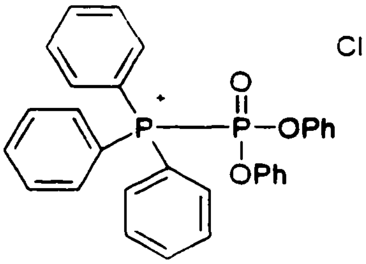

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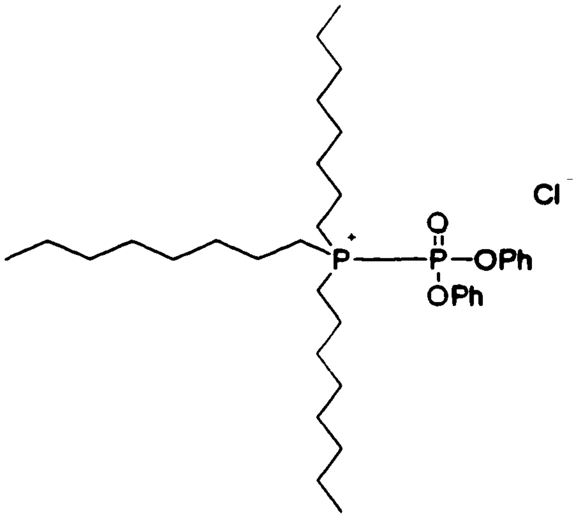

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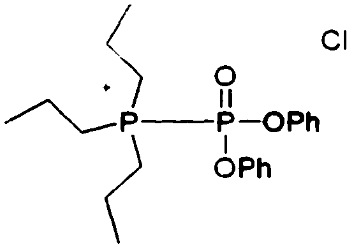

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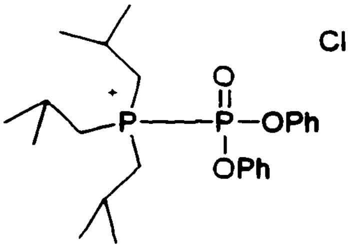
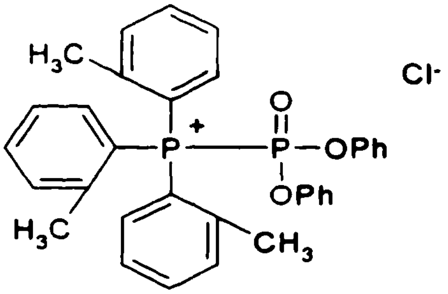


42

Figure 48: Formation of Liquid Compounds from Monodentate Phosphorus Ligands and Diphenyl Chlorophosphate

Each of these compounds were able to be isolated except for **37**. The ^1H NMR of this compound shows that one of the methyl groups is removed during the synthesis, leaving one phosphorus as a phosphine instead of being a phosphonium atom.

The three alkylphosphines which produced solids were tri-*o*-tolyl-phosphine (**43**), tri-*p*-tolyl-phosphine (**44**), and tribenzylphosphine (**45**) (Figure 49).



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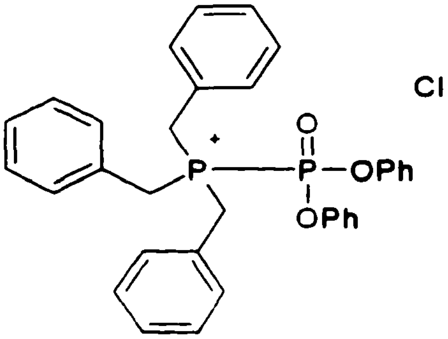

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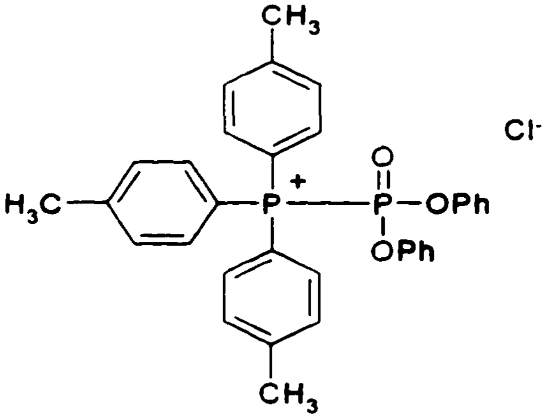


44

Figure 49: Formation of Solid Compounds from Monodentate Phosphorus Ligands and Diphenyl Chlorophosphate

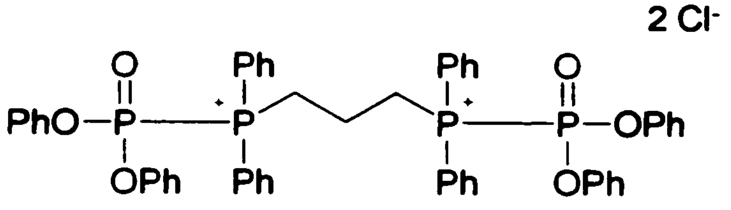
Each compound was characterized by proton, carbon and phosphorus NMR. The ^{31}P NMR for each compound, whether solid or liquid, showed 2 peaks (Table 9).

Table 9: ^{31}P NMR data for Amide Analogues Generated from Monodentate Phosphorus Ligands and Diphenyl Chlorophosphate

Material	**^{31}P NMR**	
36	58.683	-10.932
37	-5.047	-10.842
38	58.478	-10.945
39	26.799	-10.702
40	56.802	-10.923
41	57.999	-11.001
42	50.364	-10.966
43	36.718	-10.621
44	33.486	-6.6013
45	51.816	-10.852

The first peak was found in the range of –10 to -15 ppm. This peak is indicative of a phosphate group. The other peak falls in the range of 30-60 ppm. This indicates the presence of a phosphonium atom. This peak is missing in **37** and is a further indication of its lack of a phosphonium atom. The stability of each of these compounds in water was tested. Based on proton, carbon, and phosphorus NMR the new compounds synthesized seem to be reasonably stable in water for periods of time allowing them to be studied.

Diphenyl chlorophosphate was also allowed to react with two bidentate phosphorus ligand, 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane and one tridentate ligand 1,1,1-tris(diphenylphosphinomethyl)ethane to give compounds **46**, **47**, and **48** respectively (Figure 50).



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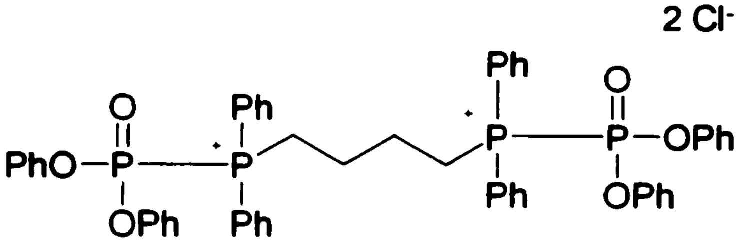

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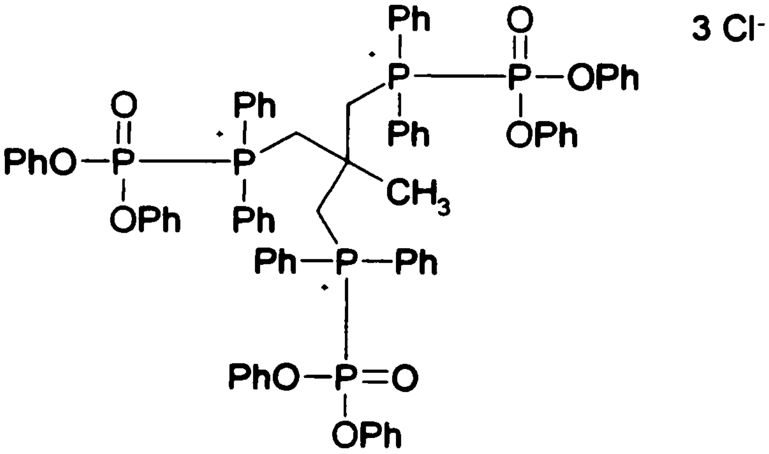


48

Figure 50: Compounds Formed from Bi- and Tridentate Phosphorus Ligands and Diphenyl Chlorophosphate

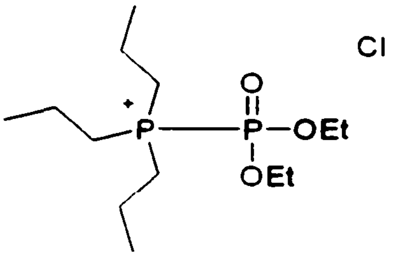
Each of these solid compounds showed two peaks in the ^{31}P NMR spectrum (Table 10).

Table 10: ^{31}P NMR Data for Amide Analogues Generated from Bi- and Tridentate Phosphorus Ligands and Diphenyl Chlorophosphate

Material	**^{31}P NMR**	
46	37.393	-10.354
47	33.759	-14.198
48	32.901	-10.377

The first peak between 30 and 40 ppm represents the positively charged phosphonium atoms. The second peak between −10 and −15 ppm represents the phosphorus atoms of the phosphate groups.

The other phosphate used in this study was diethylchlorophosphate and it was taken in reaction with several alkylphosphines including tripropylphosphine, triisobutylphosphine, tricyclohexylphosphine, tributylphosphine, trioctylphosphine, tribenzylphosphine, and triphenylphosphine, giving liquid compounds **49-55** (Figure 51).



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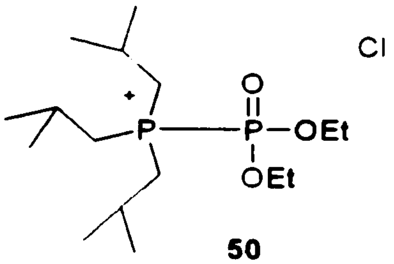

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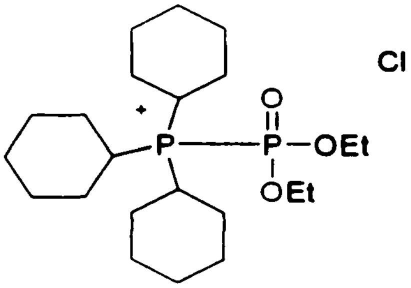

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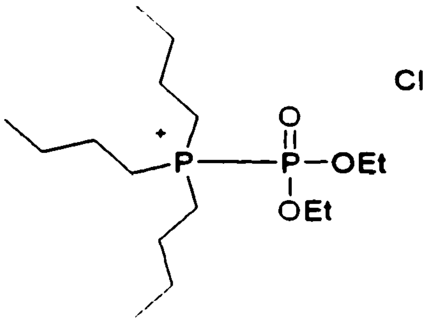

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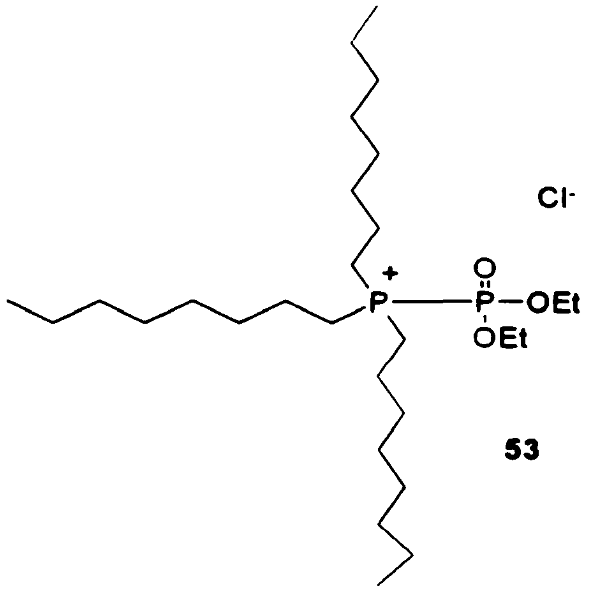

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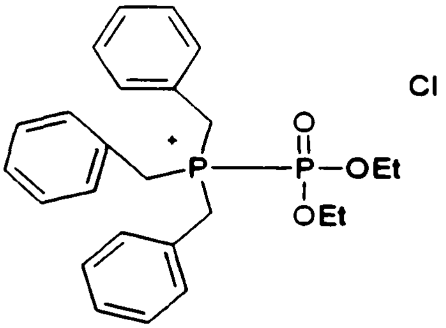

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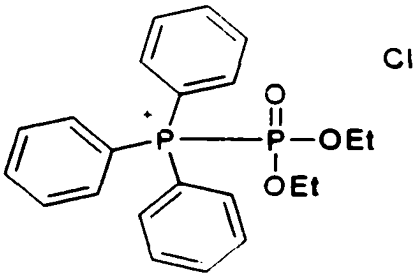


55

Figure 51: Liquid Compounds Formed from Monodentate Phosphorus Ligands and Diethyl Chlorophosphate

The ^{31}P NMR for compounds **49-53** showed a series of peaks (Table 11). These series of peaks seems to indicate that these compounds synthesized are impure, containing a substantial amount of hydrolyzed product (Figure 52).

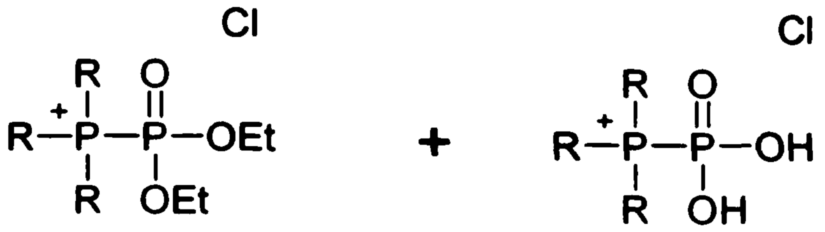
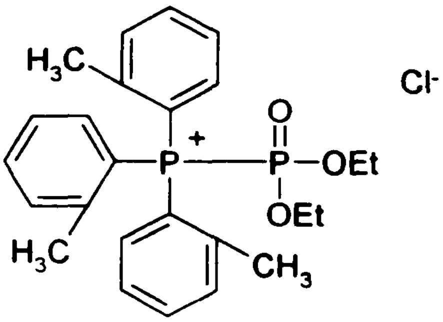


Figure 52: Mixture of Products Formed for Compounds **49-53**

Compounds **54** and **55** showed only 2 peaks and are much purer compounds (Table 11). The peak between 25 and 30 ppm represents the phosphonium atom, and the peak around 0 ppm represents the diethylphosphate phosphorus atom.

Solids were generated when tri-*o*-tolylphosphine **56** and tri-*p*-tolylphosphine **57** were used (Figure 53).



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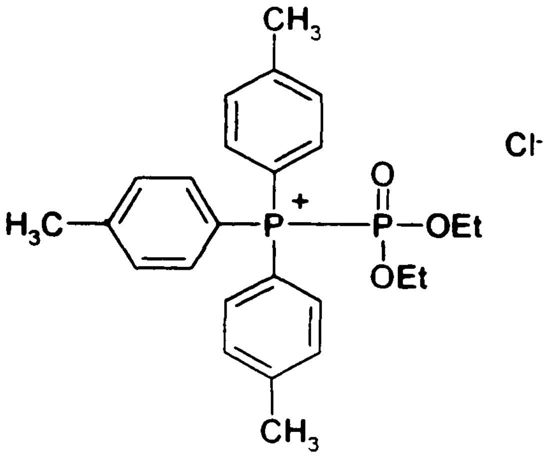


57

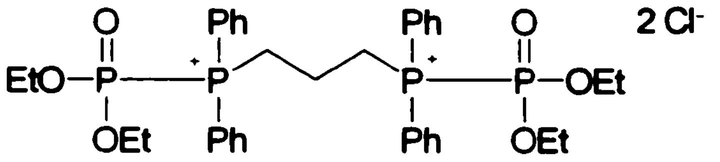
Figure 53: Solid Compounds Generated from Monodentate Phosphorus Ligands and Diethyl Chlorophosphate

The phosphorus NMR for each of these solid compounds again showed 2 peaks indicating relatively pure products (Table 11). The first between 25 and 30 ppm represents the positively charged phosphonium atom and the second peak around 0 ppm represents the phosphorus atom of the diethylphosphate group.

Table 11: ^{31}P NMR data for Amide Analogues Generated from Monodentate Phosphorus Ligands and Diethyl Chlorophosphate

Material	**^{31}P NMR**		
49	57.288	51.206	-0.313
	-12.081	-25.384	
50	55.967	47.034	-0.322
	-12.032	-25.184	
51	58.279	55.722	-0.217
	-11.921	-25.49	
52	56.198	53.816	-0.308
	-12.015	-25.386	
53	51.253	50.083	-0.241
	-11.908	-25.048	
54	28.851	-0.286	
55	26.799	-0.253	
56	40.769	-0.969	
57	31.753	-6.6915	

1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane, and 1,1,1-tris(diphenylphosphinomethyl)ethane were again used as bidentate and tridentate ligands giving rise to compounds **58**, **59**, and **60** (Figure 54).



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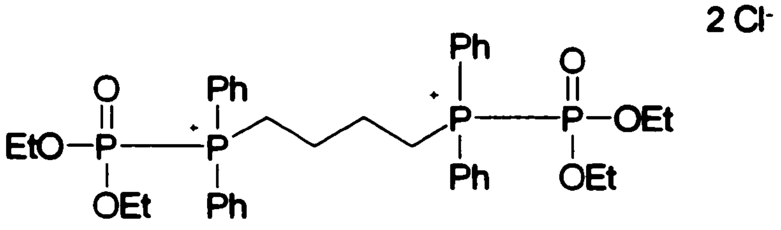

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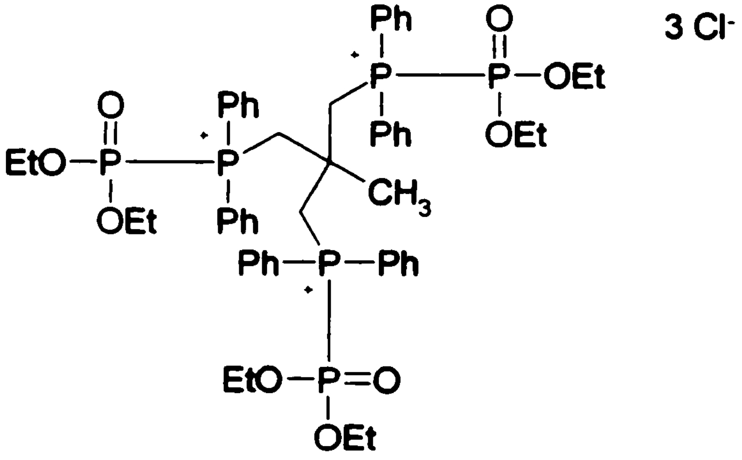


60

Figure 54: Compounds Formed from Bi- and Tridentate Ligands and Diethyl Chlorophosphate

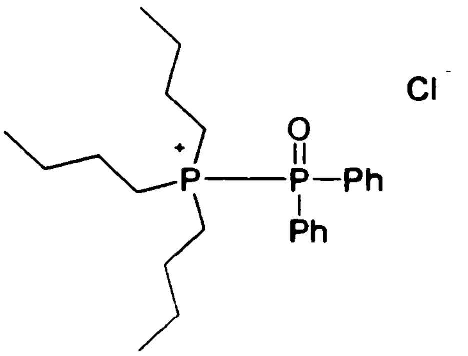
Each of these solid compounds showed up to 3 peaks (Table 12).

Table 12: ^{31}P NMR data for Amide Analogues generated from Bi- and Tridentate Phosphorus Ligands and Diethyl Chlorophosphate

Material	**^{31}P NMR**	
58	37.674 -12.852	1.082
59	33.438	-14.198
60	28.564 -12.278	-0.08

The peak between 25 and 40 ppm represents the positively charged phosphonium atoms. The peak between −10 and −15 ppm represents the phosphorus atoms of the diethylphosphate groups. The small peaks around 0 ppm in **58** and **60** show minor impurities in these compounds.

A third series of compounds of amide analogues were generated by using diphenylphosphinic chloride. The monodentate phosphorus ligands used were tributylphosphine (**61**), triphenylphosphine (**62**), and tricyclohexylphosphine (**63**) (Figure 55).



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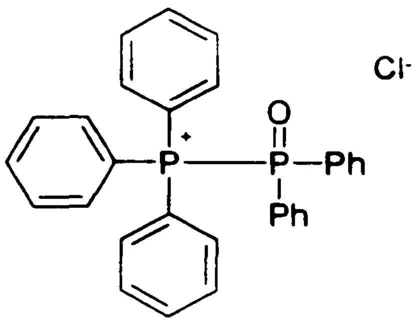

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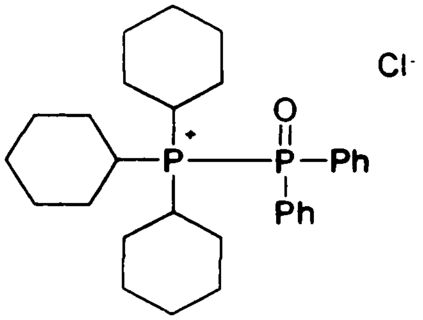


63

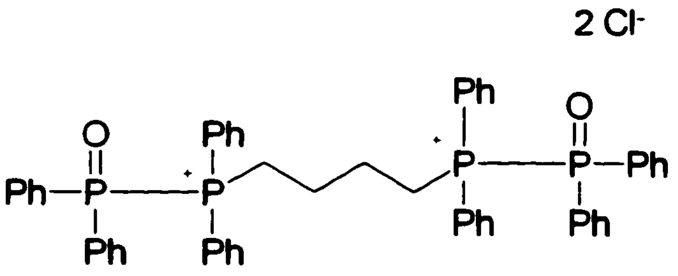
Figure 55: Compounds Formed from Monodentate Phosphorus Ligands and Diphenylphosphinic Chloride

Each of these compounds were solids and the ^{31}P NMR of each compound showed two peaks, both between 15 and 35 ppm (Table 13), in accord with having phosphonium and phosphoryl units within the molecules.

Table 13: ^{31}P NMR data for Amide Analogues Generated from Monodentate Phosphorus ligands and Diphenylphosphinic Chloride

Material	**^{31}P NMR**	
61	29.6903	14.058
62	29.7326	27.3601
63	34.5604	29.728

Reaction of diphenylphosphinic chloride with 1,4-bis(diphenylphosphino)butane and 1,1,1-tris(diphenylphosphinomethyl)ethane generated compounds **64** and **65** respectively (Figure 56).



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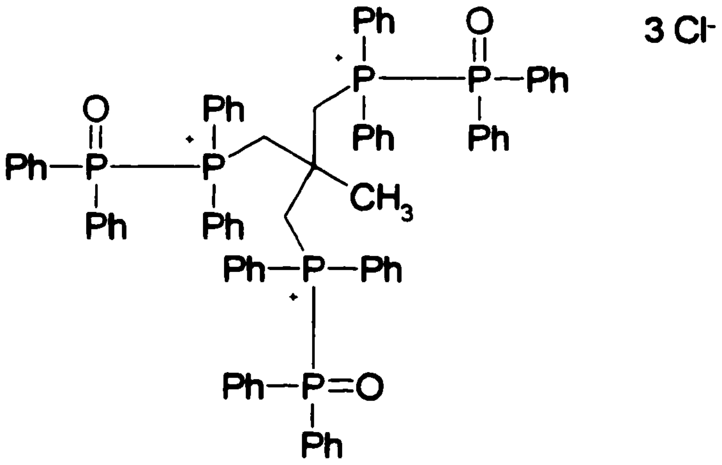


65

Figure 56: Compounds Formed from Bi- and Tridentate Phosphorus Ligands and Diphenylphosphinic Chloride

These two solid compounds each showed two peaks in their ^{31}P NMR spectrum (Table 14).

Table 14: ^{31}P NMR data for Amide Analogues generated from Bi- and Tridentate Phosphorus Ligands and Diphenylphosphinic Chloride

Material	**^{31}P NMR**	
64	33.776	-13.939
65	35.187	-23.785

The peak between 30 and 35 ppm represents the positively charged phosphonium atoms and the peak between –10 and –25 ppm represents the phosphoryl phosphorus atoms.

III. Conclusion

This exploratory research has led us to synthesize compounds with two new types of phosphorus to phosphorus bonds. The first is between a negatively charged hexacoordinated phosphorus atom and phosphonium atoms in compounds classified as hexacoordinated phosphorus compounds. The second new type of bond is between phosphoryl atoms and phosphonium atoms in compounds classified as phosphorus amide analogues. Successful reactions in both cases were characterized by proton, carbon, and phosphorus NMR.

Future work on this project will focus on two areas. The first area will be to complete the separation of the racemic mixtures of the hexacoordinated phosphorus compounds. With the bidentate nitrogen ligands, optical rotations of resolved products will be obtained. With the bidentate phosphorus ligands a first determination will have to be made to see if the resolution using a cellulose packed column worked. Since the yields of these resolution products are small an alternative to measuring optical rotation will be used. This includes the possibilities of taking a CD spectrum of resolved products or obtaining an X-ray structure of the resolved products. These methods can be used with bidentate nitrogen ligands as well, as they will tell us whether we have isolated the delta or lambda enantiomer in all cases.

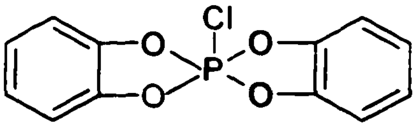
The second area of research will be to expand on both areas of the current project. With the hexacoordinated phosphorus compounds, new precursors to these compounds can be synthesized. The ligands used for these compounds can also be expanded upon to include much bigger and more complex ones. With the phosphorus amide analogues, the groups attached to the phosphoryl atom can be varied to include other alkyl, aromatic, nitrogen, and sulfur groups, making several new classes of analogues. Each one of these compounds, "new" and "old", will be tested to see their utility in the vast growing application of organophosphorus compounds to all aspects of science.

IV. Experimental Section

General

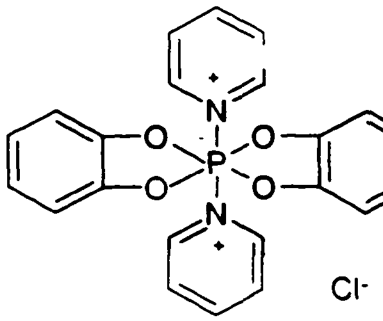
All chemicals used in synthesis, purification, and comparison analyses were of commercial reagent quality and were used without purification. NMR spectra were measured using a Bruker 400 MHz DPX400 instrument. All optical rotations were measured using a Jasco DIP-140 instrument (1 dm cell, aqueous solution with sodium vapor lamp).

Preparations



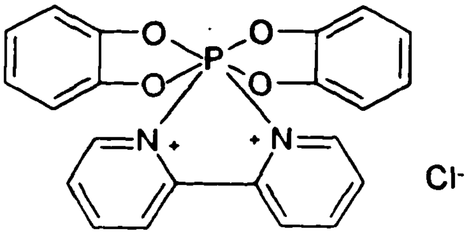
1

Preparation of Dicatechylphosphorus Monochloride. To a 250 mL three-necked round-bottomed flask fitted with a drying tube and a dropping funnel, phosphorus pentachloride (4.96 g; 0.0237 mol) was added and dissolved in dry benzene (75 mL) by stirring. To a separate flask catechol (5.23g; 0.0475 mol) was added and dissolved in anhydrous ether (30 mL). The catechol mixture was then placed into the dropping funnel and added to the PCl_5 mixture dropwise with fast stirring. When the addition was complete the mixture was stirred and heated at low temperature for 24 hours. The solid that forms was collected *via* vacuum filtration, washed with anhydrous ether (2x30 mL), and dried giving **1** as a white solid (5.68 g; 85% yield). NMR (δ, $CDCl_3$)- ^1H: 6.73, d, 4H; 6.85, t, 4H. ^{13}C: 111.35, 117.62, 140.86. ^{31}P: 17.963, -26.317.



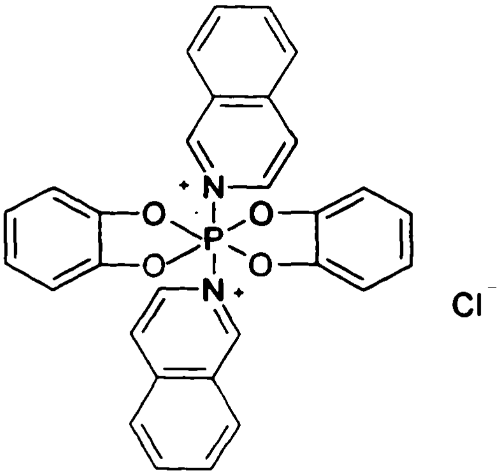
11

Preparation of Dicatechylphosphorus Dipyridinium Chloride. To a 250 mL round-bottomed flask dicatechylphosphorus monochloride (**1**) (2.08 g; 0.0093 mol) was added and dissolved in chloroform (25 mL) by stirring. To a separate flask pyridine (1.83 g; 0.0233 mol) was added and dissolved in chloroform (15 mL). The two mixtures were then combined *via* and heated at low temperature for 24 hours. The solid that formed was collected *via* vacuum filtration, washed with anhydrous ether (2x30 mL), and dried giving **11** as a white solid (3.35 g; 82% yield). NMR (δ, DMSO) ^1H: 6.71, d, 4H; 6.86, t, 4H; 7.83, d, 4H; 8.38, t, 2H; 8.76, t, 4H. ^{13}C: 110.95, 120.47, 128.82, 145.46, 147.93. ^{31}P: –81.032.



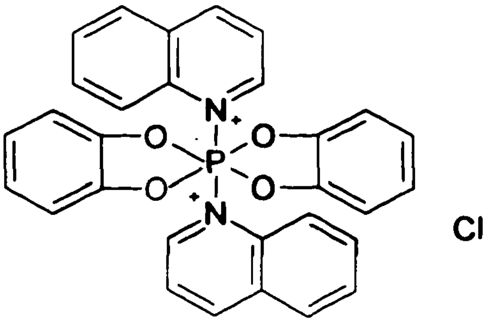
12

Preparation of Dicatechylphosphorus 2,2'-Bipyridyl Chloride. To a round-bottomed flask dicatechylphosphorus monochloride (**1**) (2.58 g; 0.00914 mol) was added and dissolved by stirring in chloroform (50 mL). To a separate flask 2,2' bipyridyl (1.43 g; 0.00914 mol) was added and dissolved in chloroform (15 mL). The two mixtures were then combined and heated at low temperature for 24 hours. The solid that formed was collected *via* vacuum filtration, washed with anhydrous ether (2x30 mL), and dried giving **12** as a yellow solid (3.52 g; 88% yield). NMR (δ, DMSO)- ^{1}H: 6.75, d, 4H; 6.82, t, 4H; 7.87, t, 2H; 8.33, d, 2H; 8.64, t, 2H; 9.06, d, 2H. ^{13}C: 108.62, 109.59, 118.44, 122.37, 126.84, 140.17, 145.67, 148.52. ^{31}P: -81.035.



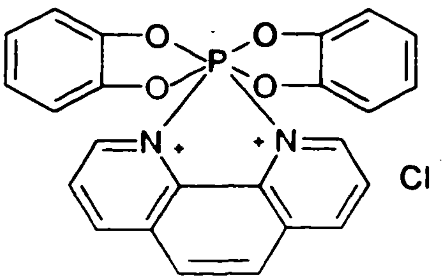
13

Preparation of Dicatechylphosphorus Diisoquinoline Chloride. To a round-bottomed flask dicatechylphosphorus monochloride (**1**) (1.25 g; 0.00443 mol) was added and dissolved by stirring in chloroform (50 mL). To a separate flask isoquinoline (1.16 g; 0.00887 mol) was added and dissolved in chloroform (20 mL). The two mixtures were then combined and heated at low temperature for 24 hours. The solid that formed was collected *via* vacuum filtration, washed with anhydrous ether (2x30 mL), and dried giving **13** as a yellow solid (2.08 g; 87% yield). NMR (δ, DMSO)- ^{1}H: 6.53, d, 4H; 6.65, t, 4H; 8.01, d, 2H; 8.10, t, 2H; 8.36, t, 2H; 8.45, d, 2H; 8.53, d, 2H; 8.79, d, 2H; 9.82, s, 2H. ^{13}C: 107.83, 117.16, 122.54, 125.62, 127.77, 128.48, 131.62, 134.55, 137.61, 142.85, 143.36, 146.90. ^{31}P: -81.037.



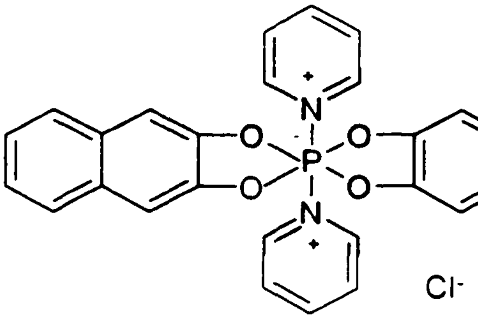
14

Preparation of Dicatechylphosphorus Diquinoline Chloride. To a round-bottomed flask dicatechylphosphorus monochloride (**1**) (1.64 g; 0.00582 mol) was added and dissolved by stirring in chloroform (50 mL). To a separate flask quinoline (1.52 g; 0.0116 mol) was added and dissolved in chloroform (20 mL). The two mixtures were then combined and heated at low temperature for 24 hours. The solid that formed was collected *via* vacuum filtration, washed with anhydrous ether (2x30 mL), and dried giving **14** as a yellow solid (2.70 g; 86% yield). NMR (δ, DMSO)- ^{1}H: 6.54, d, 4H; 6.76, t, 4H; 7.91, t, 2H; 8.03, t, 2H; 8.18, d, 2H; 8.25, t, 2H; 8.30, d, 2H; 9.09, d, 2H; 9.24, d, 2H. ^{13}C: 108.71, 118.48, 121.32, 122.85, 128.37, 129.93, 130.46, 133.72, 143.33, 144.59, 145.62, 146.48. ^{31}P: -81.041.



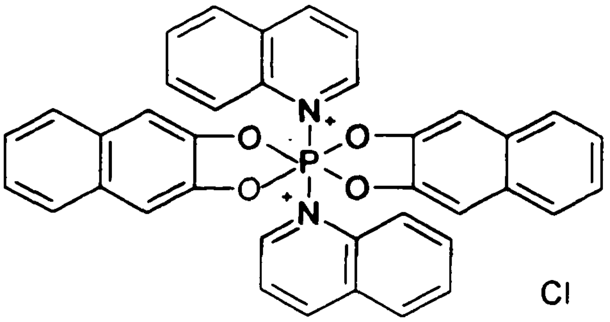
15

Preparation of Dicatechylphosphorus 1,10-Phenanthroline Chloride. To a round-bottomed flask dicatechylphosphorus monochloride (**1**) (2.20 g; 0.0078 mol) was added and dissolved by stirring in chloroform (50 mL). To a separate flask 1,10-phenanthroline (1.51 g; 0.0078 mol) was added and dissolved in chloroform (20 mL). The two mixtures were then combined and heated at low temperature for 24 hours. The solid that formed was collected *via* vacuum filtration, washed with anhydrous ether (2x30 mL), and dried giving **15** as a yellow solid (2.63 g; 73% yield). NMR (δ, $CDCl_3$) ^{1}H: 6.57, d, 4H; 6.78, t, 4H; 7.72, d, 2H; 7.95, t, 2H; 8.58, d, 2H; 9.11, d, 2H. ^{13}C: 115.57, 119.31, 122.67, 125.43, 127.82, 136.47, 137.55, 143.58, 148.94. ^{31}P: -81.045.



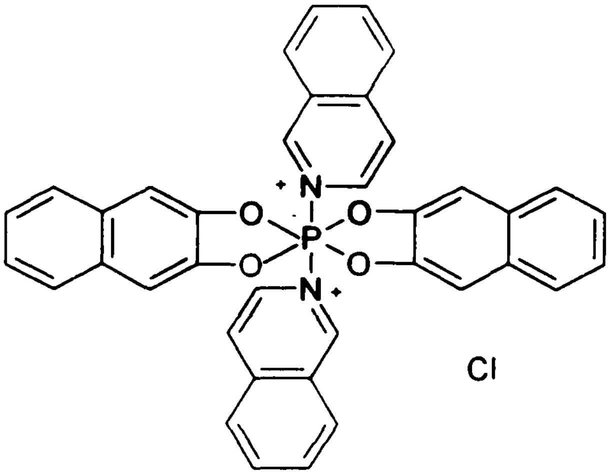
17

Preparation of Di-2,3-dihydroxynaphthylphosphorus Dipyridinium Chloride. To a 250 mL three-necked round bottomed flask fitted with a drying tube and dropping funnel phosphorus pentachloride (3.07 g; 0.0147 mol) was added and dissolved by stirring in dry benzene (50 mL). To a separate flask 2,3-dihydroxynaphthalene (4.70 g; 0.0294 mol) was added and dissolved in anhydrous ether (30 mL). This mixture was then added to the PCl_5 mixture *via* dropping funnel and the reaction was stirred and heated for 24 hours. To a separate flask pyridine (2.32 g; 0.0294 mol) was added and dissolved in chloroform (40 mL). This mixture was then added to the reaction and the entire mixture was heated and stirred for another 24 hours. The solid that formed in the flask was washed with methanol (50 mL) and then collected *via* vacuum filtration giving **17** as a white solid (5.87 g; 79% yield). NMR (δ, DMSO)- ^{1}H: 6.86, s, 4H; 7.04, t, 4H; 7.41, d, 4H; 7.89, d, 4H; 8.35, t, 2H; 8.73, t, 4H. ^{13}C: 103.86, 104.54, 123.37, 126.89, 127.82, 129.76, 143.41, 146.35. ^{31}P: -81.043.



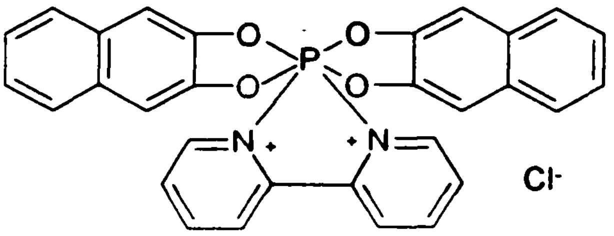
18

Preparation of Di-2,3-dihydroxynaphthylphosphorus Diquinoline Chloride. To a 250 mL three-necked round bottomed flask fitted with a drying tube and dropping funnel phosphorus pentachloride (1.83 g; 0.00876 mol) was added and dissolved by stirring in dry benzene (50 mL). To a separate flask 2,3-dihydroxynaphthalene (2.81 g; 0.0175 mol) was added and dissolved in anhydrous ether (30 mL). This mixture was then added to the PCl_5 mixture *via* dropping funnel and the reaction was stirred and heated for 24 hours. To a separate flask quinoline (2.29 g; 0.0175 mol) was added and dissolved in chloroform (30 mL). This mixture was then added to the reaction and the entire mixture was heated and stirred for another 24 hours. The solid that formed in the flask was washed with methanol and then collected *via* vacuum filtration giving **18** a yellow solid (3.64 g; 65% yield). NMR (δ, DMSO)-^{1}H: 7.36, s, 4H; 7.52, t, 4H; 7.72, d, 4H; 7.98, t, 2H; 8.10, t, 2H; 8.24, t, 2H; 8.36, d, 2H; 8.42, d, 2H; 9.10, d, 2H; 9.47, d, 2H. ^{13}C: 103.73, 104.51, 118.36, 123.39, 125.68, 126.72, 127.36, 128.52, 129.20, 130.63, 131.38, 137.44, 139.83, 146.57. ^{31}P: -81.036.



19

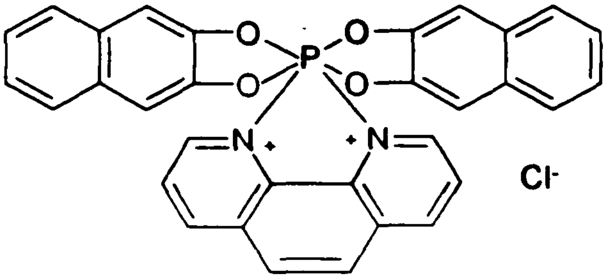
Preparation of Di-2,3-dihydroxynaphthylphosphorus Diisoquinoline Chloride. To a 250 mL three-necked round bottomed flask fitted with a drying tube and dropping funnel phosphorus pentachloride (4.53 g; 0.0217 mol) was added and dissolved by stirring in dry benzene (50 mL). To a separate flask 2,3-dihydroxynaphthalene (6.94 g; 0.0433 mol) was added and dissolved in anhydrous ether (30 mL). This mixture was then added to the PCl_5 mixture *via* dropping funnel and the reaction was stirred and heated for 24 hours. To a separate flask isoquinoline (5.66 g; 0.0433 mol) was added and dissolved in chloroform (50 mL). This mixture was then added to the reaction and the entire mixture was heated and stirred for another 24 hours. The solid that formed in the flask was washed with methanol and then collected *via* vacuum filtration giving **19** a brownish solid (8.19 g; 59% yield). NMR (δ, $CDCl_3$)- ^1H: 7.03, s, 4H; 7.21, t, 4H; 7.56, d, 4H; 8.08, d, 2H; 8.19, t, 2H; 8.35, t, 2H; 8.43, d, 2H; 8.57, d, 2H; 8.70, d, 2H; 9.72, s, 2H. ^{13}C: 103.97, 104.21, 118.95, 123.36, 125.71, 126.32, 127.74, 128.86, 129.24, 130.64, 131.82, 137.95, 139.58, 146.17. ^{31}P: -81.035.



20

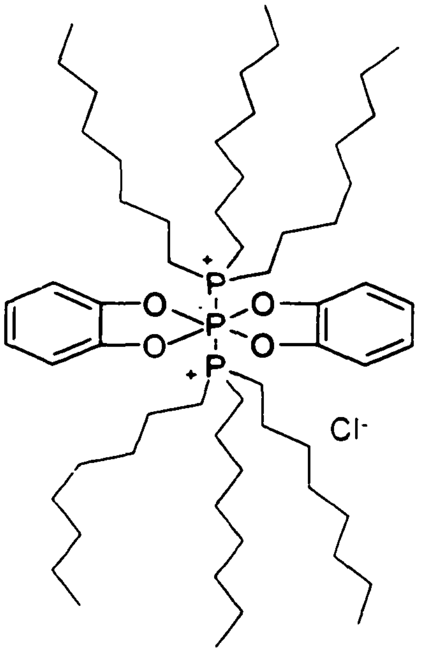
<u>Preparation of Di-2,3-dihydroxynaphthylphosphorus 2,2'-Bipyridyl Chloride</u>. To a 250 mL three-necked round bottomed flask fitted with a drying tube and dropping funnel phosphorus pentachloride (4.27 g; 0.0204 mol) was added and dissolved by stirring in dry benzene (60 mL). To a separate flask 2,3-dihydroxynaphthalene (6.54 g; 0.0409 mol) was added and dissolved in anhydrous ether (30 mL). This mixture was then added to the PCl_5 mixture and the entire mixture was stirred and heated for 24 hours. To a separate flask 2,2'-bipyridyl (3.18 g; 0.0204 mol) was added and dissolved in chloroform (40 mL). This mixture was then added to the reaction and the entire mixture was heated and stirred for another 24 hours. The solid that formed in the flask was washed with methanol (50 mL) and then

collected *via* vacuum filtration giving **20** as a yellow solid (6.91 g; 63% yield). NMR (δ, DMSO)- ^{1}H: 7.06-7.32, br, 12H; 7.69-8.34, br, 6H; 8.83, d, 2H. ^{13}C: 103.64, 109.27, 122.85, 123.26, 126.90, 128.25, 129.61, 140.37, 146.84, 147.27. ^{31}P NMR: -81.031. A portion of solid **20** (2.02g) was then dissolved in methanol (100 mL) by stirring and passed through a column packed with cellulose. Methanol (100 mL) was then poured through the column and a 50 mL fraction was collected. The solvent was removed from the fraction leaving a brownish solid, **20-resolution product** (1.23g). A portion of solid **20-resolution product** (0.28g) was dissolved in methanol (100 mL) by stirring and this solution was diluted to a concentration of 2.8×10^{-5} g/mL. The optical rotation of **20-resolution product** was then measured ($[\alpha] = 5.7 \times 10^2$ (deg*cm^2)/g) at 25°C).



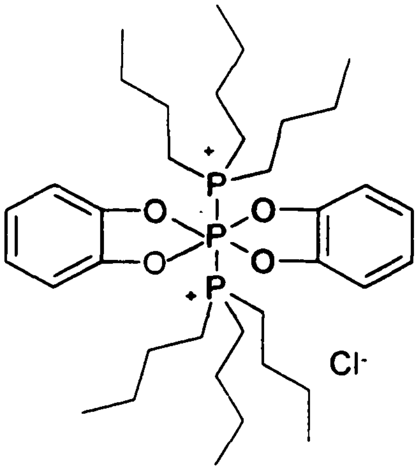
21

Preparation of Di-2,3-dihydroxynaphthylphosphorus 1,10-Phenanthroline Chloride. To a 250 mL three-necked round bottomed flask fitted with a drying tube and dropping funnel phosphorus pentachloride (2.53 g; 0.0121 mol) was added and dissolved by stirring in dry benzene (50 mL). To a separate flask 2,3-dihydroxynaphthalene (3.87 g; 0.0242 mol) was added and dissolved in anhydrous ether (30 mL). This mixture was then added to the PCl_5 mixture *via* dropping funnel and the entire mixture was stirred and heated for 24 hours. To a separate flask 1,10-phenanthroline (2.60 g; 0.0121 mol) was added and dissolved in chloroform (50 mL). This mixture was added to the reaction and the entire mixture was heated and stirred for another 24 hours. The solid that formed in the flask was washed with methanol (50 mL) and then collected *via* vacuum filtration giving **21** as a yellow solid (4.62 g; 68% yield). NMR (δ, DMSO)- ^1H: 7.14, s, 4H; 7.36, t, 4H; 7.52, d, 4H; 8.18, d, 2H; 8.33, t, 2H; 8.95, d, 2H; 9.23, d, 2H. ^{13}C: 105.84, 111.27, 124.62, 126.89, 127.72, 128.43, 130.57, 140.78, 142.25, 147.85. ^{31}P: -81.037.



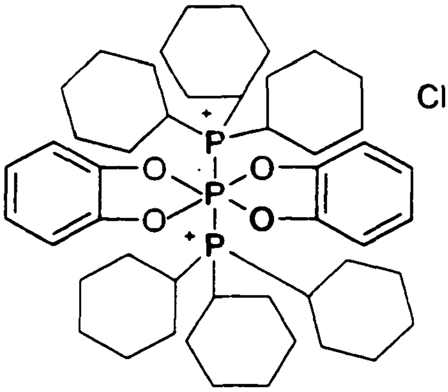
22

Preparation of Dicatechylphosphorus Ditrioctylphosphine Chloride. To a round-bottomed flask trioctylphosphine (3 mL; 0.00673 mol) was added and dissolved by stirring in chloroform (25 mL). To a separate flask dicatechylphosphorus monochloride (**1**) (0.95 g; 0.00337 mol) was added and dissolved in chloroform (25 mL). This mixture was then added to the trioctylphosphine mixture and the entire mixture was heated and stirred for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator and the product was dried *via* vacuum leaving **22** a cloudy liquid (2.72 g; 79% yield). NMR (δ, $CDCl_3$)- ^{1}H: 0.75, t, 18H; 1.01, m, 12H; 1.09-1.22, br, 36H; 1.46, t, 12H; 1.64, quintet, 12H; 1.87, quintet, 12H; 6.74, d, 4H; 6.88, t, 4H. ^{13}C: 13.79, 20.48, 21.62, 27.53, 28.81, 29.47, 30.92, 48.37, 121.26, 126.95, 145.38. ^{31}P: 65.128, 62.583, -4.189, -81.834.



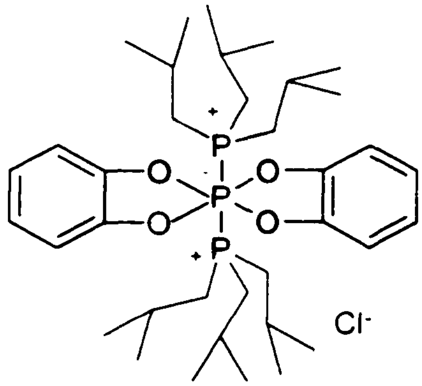
23

Preparation of Dicatechylphosphorus Ditributylphosphine chloride. To a round-bottomed flask tributylphosphine (4 mL; 0.01604 mol) was added and dissolved by stirring in chloroform (25 mL). To a separate flask dicatechylphosphorus monochloride (**1**) (2.26 g; 0.00802 mol) was added and dissolved in chloroform (25 mL). This mixture was then added to the Bu_3P mixture and the entire mixture was heated and stirred for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator and the product was dried *via* vacuum leaving **23** as a liquid (4.53 g; 83% yield). NMR (δ, $CDCl_3$)- ^{1}H: 0.84, q, 18H; 1.47, t, 12H; 1.65, m, 24H; 6.76, d, 4H; 6.89, s, 4H. ^{13}C: 13.33, 17.85, 24.92, 30.37, 120.04, 126.16, 145.63. ^{31}P: 57.460, 48.137, -4.528, -81.586.



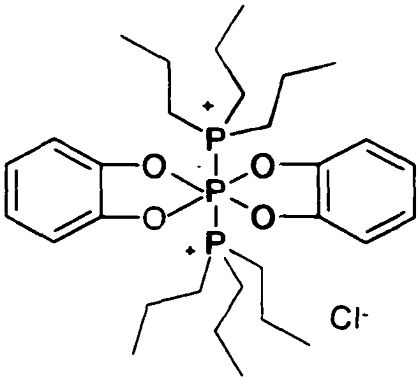
24

Preparation of Dicatechylphosphorus Ditricyclohexylphosphine Chloride. To a round-bottomed flask tricyclohexylphosphine (0.86 g; 0.00307 mol) was added and dissolved by stirring in chloroform (25 mL). To a separate flask dicatechylphosphorus monochloride (**1**) (0.43 g; 0.00153 mol) was added and dissolved in chloroform (15 mL). This mixture was then added to the tricyclohexylphosphine mixture and the entire mixture was heated and stirred for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator and the product was dried *via* vacuum leaving **24** as a yellow liquid (0.94 g; 73% yield). NMR (δ, $CDCl_3$)- ^1H: 1.30-1.56, br, 60H; 1.72, quintet, 6H; 6.58, d, 4H; 6.72, t, 4H. ^{13}C: 16.21, 26.53, 34.43, 64.27, 115.97, 119.30, 145.56. ^{31}P: 58.051, 50.1426, -4.6117.



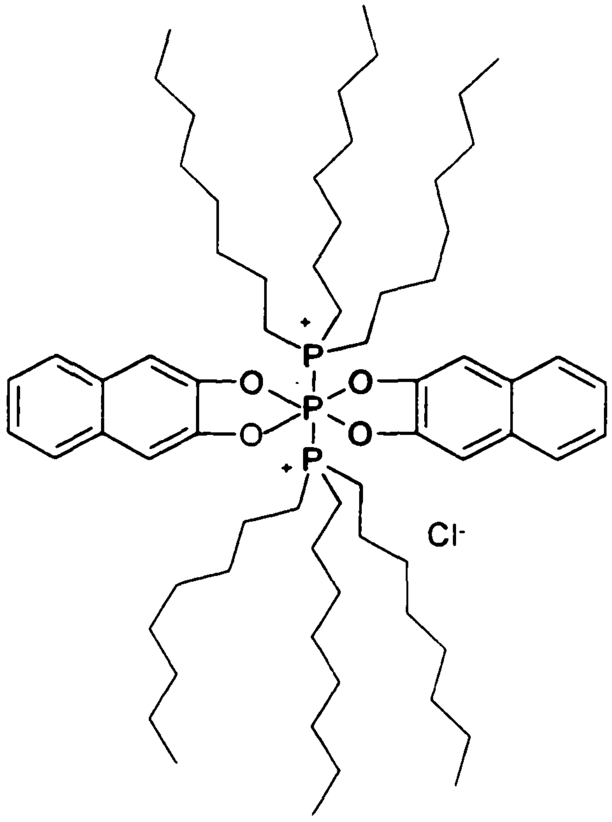
25

Preparation of Dicatechylphosphorus Ditrisopbutylphosphine Chloride. To a round-bottomed flask triisobutylphosphine (0.96 g; 0.00474 mol) was added and dissolved by stirring in chloroform (25 mL). To a separate flask dicatechylphosphorus monochloride (**1**) (0.67 g; 0.00237 mol) was added and dissolved in chloroform (15 mL). This mixture was then added to the triisobutylphosphine mixture and the entire mixture was heated and stirred for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator and the product was dried *via* vacuum leaving a crude solid in the flask. The product was dissolved in methanol (25 mL) and cooled precipitating **25** as a white solid (1.33 g; 82% yield). NMR (δ, DMSO)- ^{1}H: 0.86, d, 36H; 1.22, d, 12H; 1.80, m, 6H; 6.75, d, 4H; 6.91, t, 4H. ^{13}C: 14.90, 22.36, 62.67, 119.41, 123.38, 146.86. ^{31}P: 56.083, 45.639, -4.558, -81.587.



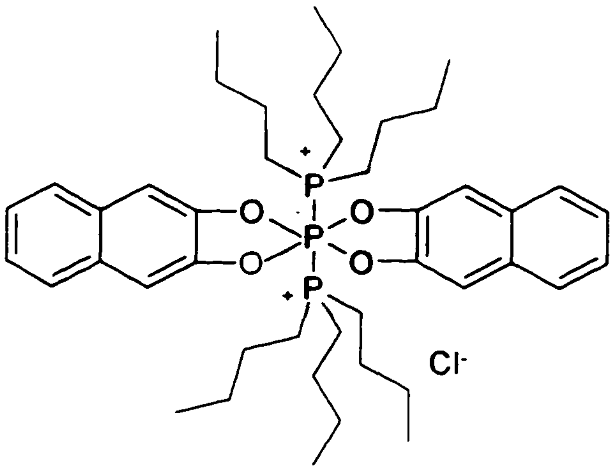
26

Preparation of Dicatechylphosphorus Ditripropylphosphine Chloride. To a round-bottomed flask tripropylphosphine (0.54 g; 0.00337 mol) was added and dissolved by stirring in chloroform (25 mL). To a separate flask dicatechylphosphorus monochloride (**1**) (0.50 g; 0.00168 mol) was added and dissolved in chloroform (15 mL). This mixture was then added to the tripropylphosphine mixture and the entire mixture was heated and stirred for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator and the product was dried *via* vacuum leaving **26** as a brown liquid (0.78 g; 77% yield). NMR (δ, DMSO) ^{1}H: 0.95, q, 18H; 1.34, t, 12H; 1.58, quintet, 12H; 6.79, d, 4H; 6.95, t, 4H. ^{13}C: 15.08, 18.48, 30.12, 118.64, 121.72, 145.56. ^{31}P: 47.294, 34.111, -4.513, -81.586.



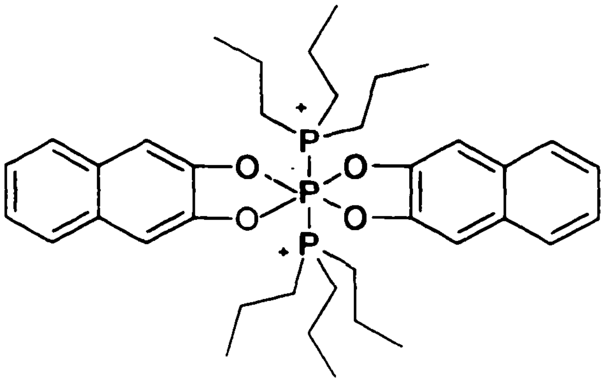
27

Preparation of Di-2,3-Dihydroxynaphthylphosphorus Ditrioctyllphosphine Chloride. To a 250 mL three-necked round bottomed flask fitted with a drying tube and dropping funnel phosphorus pentachloride (2.00 g; 0.00957 mol) was added and dissolved in dry benzene (50 mL). To a separate flask 2,3-dihydroxynaphthalene (3.09 g; 0.0191 mol) was added and dissolved in anhydrous ether (25 mL). This mixture was then added to the PCl_5 mixture slowly *via* addition funnel and the reaction was then stirred and heated for 24 hours. To a separate flask trioctylphosphine (6 mL; 0.0191 mol) was added and dissolved in dry benzene (30 mL). This mixture was then added to the previous mixture and the entire mixture was stirred and heated for 24 hours. The solid that formed in the flask was removed from the mixture *via* vacuum filtration. The solid was washed with anhydrous ether (2x20 mL) and collected. To further purify the solid it was washed with methanol (30 mL) and again collected *via* vacuum filtration giving **27** as a light yellow solid (6.43 g; 85% yield). NMR (δ, $CDCl_3$)- ^{1}H: 0.73, t, 18H; 0.99, m, 12H; 1.12-1.23, br, 36H; 1.42, t, 12H; 1.67, quintet, 12H; 1.91, quintet, 12H; 7.12, s, 4H; 7.20, t, 4H; 7.45, d, 4H. ^{13}C: 13.51, 20.62, 21.47, 27.92, 28.31, 29.44, 30.77, 48.14, 109.09, 122.95, 125.18, 127.11, 146.40. ^{31}P: 13.5977, 10.6511, -82.193.



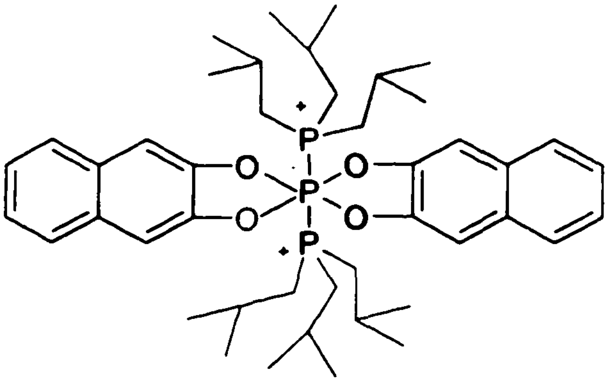
28

Preparation of Di-2,3-dihydroxynaphthylphosphorus Ditributylphosphine Chloride. To a 250 mL three-necked round bottomed flask fitted with a drying tube and dropping funnel phosphorus pentachloride (2.00 g; 0.00957 mol) was added and dissolved in dry benzene (50 mL). To a separate flask 2,3-dihydroxynaphthalene (3.09 g; 0.0191 mol) was added and dissolved in anhydrous ether (25 mL). This mixture was then added to the PCl_5 mixture slowly *via* addition funnel and the entire mixture was stirred and heated for 24 hours. To a separate flask tributylphosphine (6 mL; 0.0191 mol) was added and dissolved in dry benzene (30 mL). This mixture was then added to the reaction and the entire mixture was stirred and heated for 24 hours. The solid that formed in the flask was removed from the mixture *via* vacuum filtration. The solid was washed with anhydrous ether (2x20 mL) and collected. To further purify the solid it was washed with methanol (30 mL) and again collected *via* vacuum filtration giving **28** as a light yellow solid (6.43 g; 85% yield). NMR (δ, $CDCl_3$)- 0.77, q, 18H; 0.93, t, 12H; 1.20, m, 24H; 6.94, s, 4H; 7.06, t, 4H; 7.28, d, 4H. ^{13}C: 13.93, 16.48, 24.22, 39.04, 104.02, 110.14, 124.73, 129.97, 146.54. ^{31}P: 14.087, 10.680, -82.113.



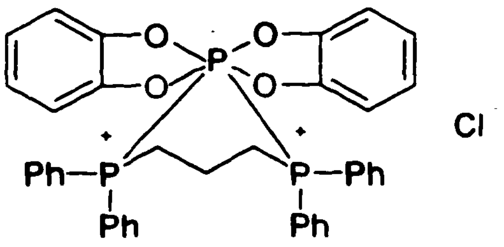
29

Preparation of Di-2,3-dihydroxynaphthylphosphorus Ditripropylphosphine Chloride. To a 250 mL three-necked round bottomed flask fitted with a drying tube and dropping funnel phosphorus pentachloride (2.00 g; 0.00957 mol) was added and dissolved in dry benzene (50 mL). To a separate flask 2,3-dihydroxynaphthalene (3.09 g; 0.0191 mol) was added and dissolved in anhydrous ether (25 mL). This mixture was then added to the PCl_5 mixture slowly *via* addition funnel and the entire mixture was stirred and heated for 24 hours. To a separate flask tripropylphosphine (6 mL; 0.0191 mol) was added and dissolved in dry benzene (30 mL). This mixture was then added to the reaction and the entire mixture was stirred and heated for 24 hours. The solid that formed in the flask was removed from the mixture *via* vacuum filtration. The solid was washed with anhydrous ether (2x20 mL) and collected. To further purify the solid it was washed with methanol (30 mL) and again collected *via* vacuum filtration giving 29 as a light yellow solid (6.43 g; 85% yield). NMR (δ, $CDCl_3$)- 0.84, q, 18H; 1.26, t, 12H; 1.64, m, 12H; 6.99, s, 4H; 7.15, t, 4H; 7.21, d, 4H. ^{13}C: 14.57, 19.34, 28.61, 108.84, 110.16, 124.82, 129.93, 146.12. ^{31}P: 13.985, 10.128, -82.177.



30

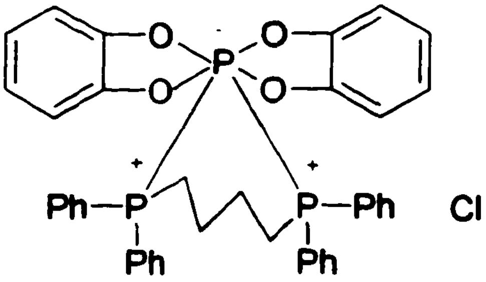
Preparation of Di-2,3-dihydroxynaphthylphosphorus Ditributylphosphine Chloride. To a 250 mL three-necked round bottomed flask fitted with a drying tube and dropping funnel phosphorus pentachloride (2.00 g; 0.00957 mol) was added and dissolved in dry benzene (50 mL). To a separate flask 2,3-dihydroxynaphthalene (3.09 g; 0.0191 mol) was added and dissolved in anhydrous ether (25 mL). This mixture was then added to the PCl_5 mixture slowly *via* addition funnel and the entire mixture was stirred and heated for 24 hours. To a separate flask tributylphosphine (6 mL; 0.0191 mol) was added and dissolved in dry benzene (30 mL). This mixture was then added to the reaction and the entire mixture was stirred and heated for 24 hours. The solid that formed in the flask was removed from the mixture *via* vacuum filtration. The solid was washed with anhydrous ether (2x20 mL) and collected. To further purify the solid it was washed with methanol (30 mL) and again collected *via* vacuum filtration giving **30** as a light yellow solid (6.43 g; 85% yield). NMR (δ, $CDCl_3$)- ^1H: 0.78, d, 36H; 1.13, d, 12H; 1.95, m, 6H; 6.80, s, 4H; 7.03, t, 4H; 7.26, d, 4H. ^{13}C: 15.06, 21.37, 60.72, 109.81, 112.28, 125.66, 130.59, 145. ^{31}P: 14.063, 10.591, -82.158.



31

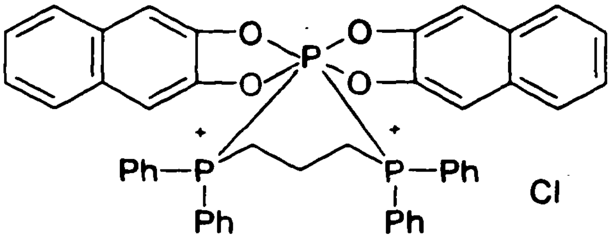
<u>Preparation of Dicatechylphosphorus 1,3-Bis(diphenylphosphino)propane Chloride</u>. To a 250 mL three-necked round bottomed dicatechylphosphorus monochloride (0.50 g; 0.00239 mol) was added and dissolved in chloroform (30 mL). To a separate flask 1,3-Bis(diphenylphosphino)propane (1.06 g; 0.00239 mol) was added and dissolved in chloroform (25 mL). The two mixtures were

then combined and the entire mixture was heated and stirred for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator. This left a yellow liquid in the flask which was washed with methanol (25 mL). Upon cooling a white solid precipitated from the mixture and was collected *via* vacuum filtration giving **31** (1.24 g; 75% yield). NMR (δ, DMSO)- ^{1}H: 0.86, t, 4H; 1.31, quintet, 2H; 6.74, d, 4H; 6.85, t, 4H; 7.09, t, 4H; 7.13, t, 8H; 7.37, d, 8H. ^{13}C: 14.95, 24.32, 116.48, 121.76, 125.19, 129.37, 132.45, 138.64, 145.71. ^{31}P: 57.842, 49.458, -17.267.



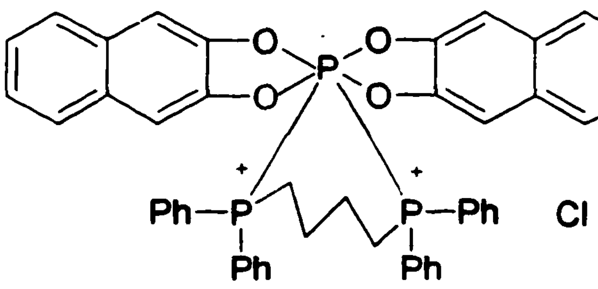
32

Preparation of Dicatechylphosphorus 1,4-Bis(diphenylphosphino)butane Chloride. To a 250 mL three-necked round bottomed flask dicatechylphosphorus monochloride (**1**) (0.54 g; 0.00191 mol) was added and dissolved in chloroform (30 mL). To a separate flask 1,4-Bis(diphenylphosphino)butane (0.82 g; 0.00191 mol) was added and dissolved in chloroform (25 mL). This mixture was then added to the reaction and the entire mixture was heated and stirred for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator. This left a yellow liquid in the flask which was washed with methanol (25 mL). Upon cooling a solid precipitated from the mixture and was collected *via* vacuum filtration giving **32** as a white solid (0.96 g; 71% yield). NMR (δ, $CDCl_3$)- ^{1}H: 1.40, t, 4H; 1.92, quintet, 4H; 6.76, d, 4H; 6.88, t, 4H; 7.04, d, 4H; 7.16, t, 8H; 7.32, d, 8H. ^{13}C: 29.89, 42.74, 118.03, 122.07, 130.14, 132.28, 134.52 140.46, 142.11. ^{31}P: 34.706, 30.676, −14.478. The solid was then dissolved in chloroform (20 mL) by stirring and passed through a column packed with cellulose. Chloroform (100 mL) was then poured through the column and a 50 mL fraction was collected. The solvent was removed from the fraction leaving a reddish solid. **32-resolution product** (0.14 g). NMR (δ, $CDCl_3$)- ^{31}P: 34.076, -13.736.



33

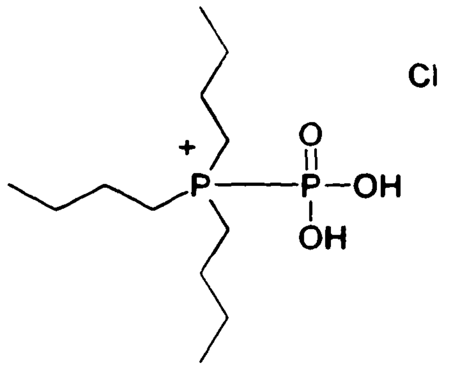
Preparation of 2,3-Dihydroxynaphthylphosphorus 1,3-bis(diphenylphosphino)propane Chloride. To a 250 mL three-necked round bottomed flask fitted with a drying tube and dropping funnel phosphorus pentachloride (0.50 g; 0.00239 mol) was added and dissolved in dry benzene (50 mL). To a separate flask 2,3-dihydroxynaphthalene (0.77 g; 0.0478 mol) was added and dissolved in anhydrous ether (25 mL). This mixture was then added to the PCl_5 mixture slowly *via* addition funnel and the reaction was stirred and heated for 24 hours. To a separate flask 1,3-bis(diphenylphosphino)propane (0.99 g; 0.0239 mol) was added and dissolved in chloroform (30 mL). This mixture was then added to the reaction and the entire mixture was stirred and heated for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator. This left a yellow liquid in the flask, which was purified by dissolving it in methanol (20 mL). Upon cooling a yellowish solid precipitated from the mixture and was collected *via* vacuum filtration giving **33** (1.51 g; 84% yield). NMR (δ, $CDCl_3$)- 1.25, t, 2H; 2.17, quintet, 4H; 6.94, s, 4H; 7.08, t, 8H; 7.22, d, 8H; 7.34, t, 4H; 7.56, d, 4H; 7.70, s, 4H. ^{13}C: 16.62, 28.85, 110.04, 118.25, 123.76, 124.92, 126.53, 129.66, 132.84, 138.51, 147.68. ^{31}P: 37.922, 23.888, −14.076. The solid was then dissolved in chloroform (20 mL) by stirring and passed through a column packed with cellulose. Chloroform (100 mL) was then poured through the column and a 50 mL fraction was collected. The solvent was removed from the fraction leaving a white solid, **33-resolution product** (0.11g). NMR (δ, $CDCl_3$)- ^{31}P: 34.855, -13.619.



34

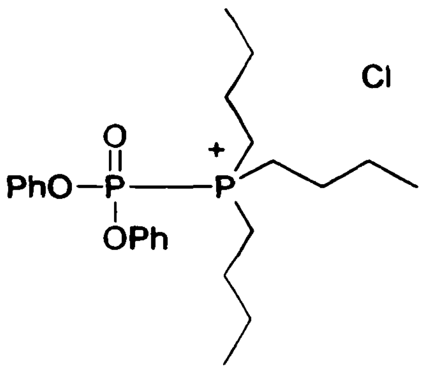
Preparation of 2,3-Dihydroxynaphthylphosphorus 1,4-bis(diphenylphosphino)butane Chloride. To a 250 mL three-necked round bottomed flask fitted with a drying tube and dropping funnel phosphorus pentachloride (0.51 g; 0.00244 mol) was added and dissolved in dry benzene (50 mL). To a separate flask 2,3-dihydroxynaphthalene (0.78 g; 0.0488 mol) was added and dissolved in anhydrous ether (25 mL). This mixture was then added to the PCl_5 mixture slowly *via* addition funnel and the entire mixture was stirred and heated for 24 hours. To a separate flask 1,4-bis(diphenylphosphino)butane (1.04

g; 0.0244 mol) was added and dissolved in chloroform (30 mL). This mixture was then added to the reaction and the entire mixture was stirred and heated for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator. This left a yellow liquid in the flask which was purified by dissolving it in methanol (20 mL). Upon cooling a solid precipitated from the mixture and was collected *via* vacuum filtration giving **34** as a dark brown solid (1.34 g; 68% yield). ^{1}H NMR (δ, MeOH)- 1.77, quintet, 4H; 2.73, t, 4H; 7.02, t, 4H; 7.18, t, 8H; 7.24, d, 8H; 7.43, t, 4H; 7.58, d, 4H; 7.71, s, 4H. ^{13}C NMR (δ, MeOH)- 26.26, 38.75, 110.81, 112.48, 124.50, 125.96, 126.73, 128.52, 131.38, 134.72, 148.06. ^{31}P NMR (δ, $CDCl_3$)- 2.315, 1.240, −10.368. The solid was then dissolved in chloroform (20 mL) by stirring and passed through a column packed with cellulose. Chloroform (100 mL) was then poured through the column and a 50 mL fraction was collected. The solvent was removed from the fraction leaving a light brown solid, **34-resolution product** (0.16 g). NMR (δ, $CDCl_3$)- ^{31}P: 33.878, -13.813.



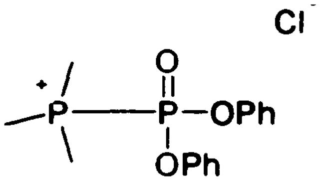
35

Preparation of Tributylphosphino Chlorophosphate. To a 250 mL three-necked round bottomed flask tributylphosphine (6 mL; 0.0241 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask phosphorus pentachloride (5.03 g; 0.0241 mol) was added and dissolved in acetonitrile (50 mL) by heating and stirring. When dissolved the phosphorus pentachloride mixture was added to the tributylphosphine mixture, slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at reflux until a clear liquid was obtained. The solvent was then removed from the liquid *via* rotary evaporator, giving the desired liquid product **35** (7.28 g; 66% yield). NMR (δ, $CDCl_3$)- ^{1}H: 0.84, q, 9H; 1.13, t, 6H; 1.47, m, 12H; 9.56, br, 2H. ^{13}C: 12.13, 22.14, 24.30, 26.49. ^{31}P: 58.74, 0.33, -11.81, -24.17.



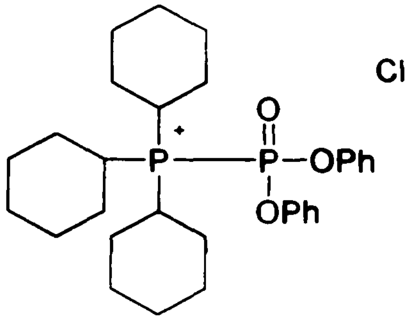
36

<u>Preparation of Tributylphosphino Diphenyl Chlorophosphate</u>. To a 250 mL three-necked round-bottomed flask tributylphosphine (8 mL; 0.0321 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask diphenyl chlorophosphate (8.66 g; 0.0321 mol) was added and dissolved in acetonitrile (45 mL). The diphenyl chlorophosphate mixture was then added to the tributylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving the desired liquid product **36** (11.8 g; 78% yield). NMR (δ, $CDCl_3$)- ^1H: 0.96, q, 9H; 1.26, t, 6H; 1.40, m, 12H; 7.18, d, 4H; 7.34, t, 2H; 7.51, t, 4H. ^{13}C: 13.07, 18.46, 19.28, 25.63, 116.47, 123.52, 126.95, 148.38. ^{31}P: 58.683, -10.932.



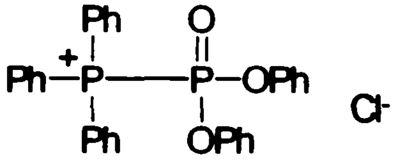
37

Preparation of Trimethylphosphino Diphenyl Chlorophosphate. To a 250 mL three-necked round-bottomed flask trimethylphosphine (4 mL; 0.0450 mol) was added and dissolved in dry benzene (25 mL) by stirring and heating at low temperature. To a separate flask diphenyl chlorophosphate (12.07 g; 0.0450 mol) was added and dissolved in dry benzene (25 mL). The diphenyl chlorophosphate mixture was then added to the trimethylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving the desired liquid product **37** (11.8 g; 78% yield). NMR (δ, $CDCl_3$)- ^{1}H: 1.47, s, 3H; 2.28, s, 6H, 6.93, d, 4H, 7.08, t, 2H, 7.23, t, 4H. ^{13}C: 13.36, 19.84, 115.70, 122.46, 128.33, 150.25. ^{31}P: -5.047, -10.842. Proton and phosphorus NMR are not in accord with proposed structure.



38

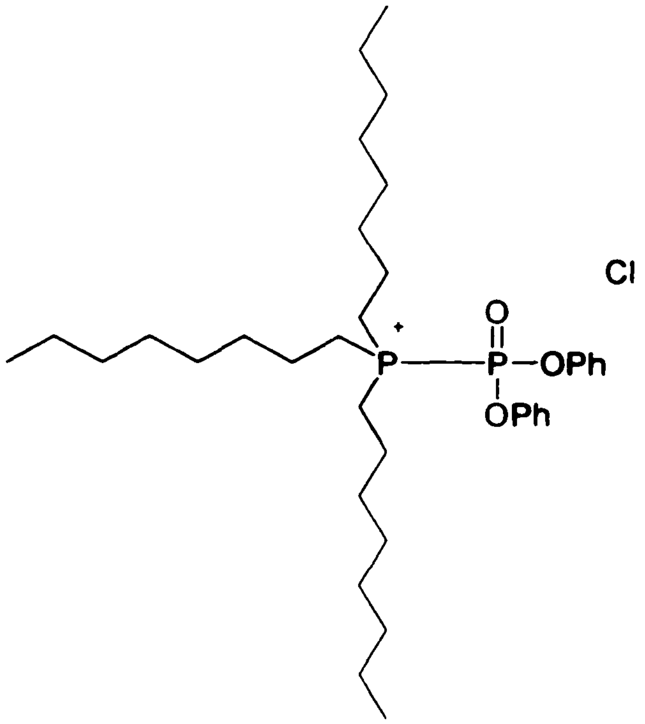
Preparation of Tricyclohexylphosphino Diphenyl Chlorophosphate. To a 250 mL three-necked round-bottomed flask tricyclohexylphosphine (1.07 g; 0.00382 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask diphenyl chlorophosphate (1.02 g; 0.00382 mol) was added and dissolved in acetonitrile (45 mL). The diphenyl chlorophosphate mixture was then added to the tricyclohexylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then stirred and heated at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a light orange liquid product **38** (1.63 g; 78% yield). NMR (δ, DMSO)- ^{1}H: 1.35, br, 30H; 1.68, br, 3H; 7.27, d, 4H; 7.44, t, 2H; 7.58, t, 4H. ^{13}C: 23.83, 24.23, 32.06, 37.57, 117.62, 122.78, 127.36, 149.15. ^{31}P: 58.478, -10.945.



$\mathrm{Ph_3P^{+}{-}P(=O)(OPh)_2\ Cl^{-}}$

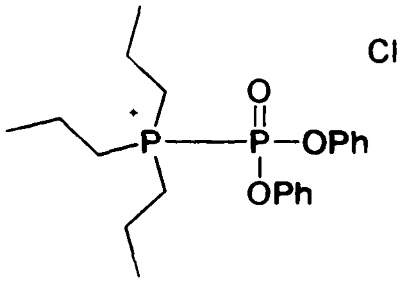
39

Preparation of Triphenylphosphino Diphenyl Chlorophosphate. To a 250-mL three-necked round-bottomed flask triphenylphosphine (3.45 g; 0.0132 mol) was added and dissolved in ethyl acetate (40 mL) by stirring and heating at low temperature. To a separate flask diphenyl chlorophosphate (3.51 g; 0.0132 mol) was added and dissolved in ethyl acetate (45 mL). The diphenyl chlorophosphate mixture was then added to the triphenylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 48 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a liquid which was further dried under reduced pressure yielding a light yellow liquid product **39** (5.73 g; 82% yield). NMR (δ, DMSO)- ^{1}H: 7.03-7.36, br, 10H; 7.44-7.67, br, 15H. ^{13}C: 120.53, 124.27, 128.02, 129.61, 130.46, 132.88, 151.65, 170.09. ^{31}P: 26.799, -10.702.



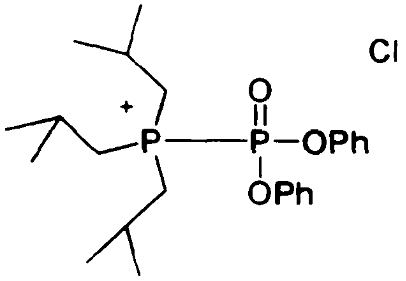
40

Preparation of Trioctylphosphino Diphenyl Chlorophosphate. To a 250 mL three-necked round-bottomed flask trioctylphosphine (4 mL; 0.00897 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask diphenyl chlorophosphate (2.41 g; 0.00897 mol) was added and dissolved in acetonitrile (45 mL). The diphenyl chlorophosphate mixture was then added to the trioctylphosphine mixture, slowly *via* pasteur pipette, and the entire mixture was then heated at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a yellow liquid product **40** (4.69 g; 82% yield). NMR (δ, DMSO)- ^{1}H: 0.72, t, 9H; 1.08, m, 6H; 1.14-1.25, br, 18H; 1.43, t, 6H; 1.62, quintet, 6H; 1.86, quintet, 6H; 7.25, d, 4H; 7.40, t, 2H; 7.59, t, 4H. ^{13}C: 13.64, 20.62, 21.34, 27.81, 28.36, 29.44, 30.78, 48.32, 115.23, 125.63, 127.28, 149.55. ^{31}P: 56.802, -10.923.



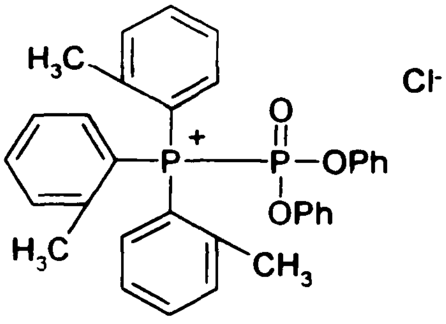
41

Preparation of Tripropylphosphino Diphenyl Chlorophosphate. To a 250 mL three-necked round-bottomed flask tripropylphosphine (1.10 g; 0.00686 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask diphenyl chlorophosphate (1.84 g; 0.00686 mol) was added and dissolved in acetonitrile (45 mL). The diphenyl chlorophosphate mixture was then added to the tripropylphosphine mixture, slowly *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a yellow liquid product **41** (2.11 g; 72% yield). NMR (δ, DMSO)- ^{1}H: 0.96, t, 9H; 1.52, t, 6H; 2.14, m, 6H; 7.08, d, 4H; 7.11, t, 2H; 7.36, t, 4H. ^{13}C: 13.71, 16.45, 26.02, 118.26, 122.73, 128.59, 149.82. ^{31}P: 57.999, -11.001.



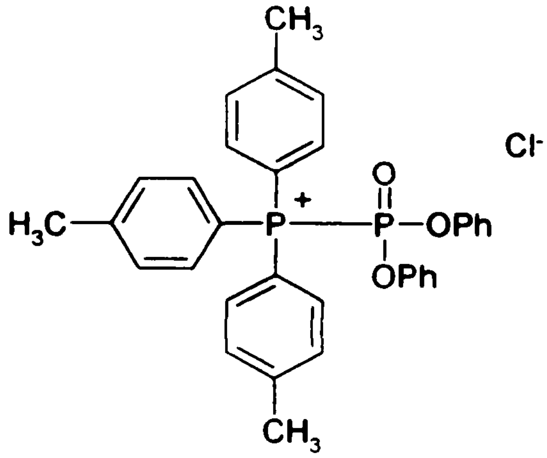
42

Preparation of Triisobutylphosphino Diphenyl Chlorophosphate. To a 250 mL three-necked round-bottomed flask triisobutylphosphine (1.36 g; 0.00677 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask diphenylchlorophosphate (1.82 g; 0.00677 mol) was added and dissolved in acetonitrile (45 mL). The diphenyl chlorophosphate mixture was then added to the triisobutylphosphine mixture, slowly *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving the desired liquid product **42** (2.55 g; 80% yield). NMR (δ, DMSO)- ^{1}H: 1.07, d, 18H; 1.62, d, 6H; 2.08, m, 3H; 7.13, d, 4H; 7.29, t, 2H; 7.42, t, 4H. ^{13}C: 23.84, 26.28, 38.06, 120.53, 124.92, 130.53, 151.69. ^{31}P: 50.364, -10.966.



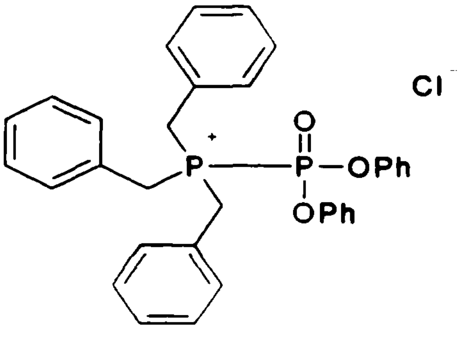
43

Preparation of Tri-o-tolyl-phosphino Diphenyl Chlorophosphate. To a 250-mL three-necked round-bottomed flask tri-*o*-tolyl-phosphine (1.86 g; 0.00612 mol) was added and dissolved in ethyl acetate (40 mL) by stirring and heating at low temperature. To a separate flask diphenyl chlorophosphate (1.64 g; 0.00612 mol) was added and dissolved in ethyl acetate (45 mL). The diphenyl chlorophosphate mixture was then added to the tri-*o*-tolyl-phosphine mixture, slowly *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 48 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a liquid which was further dried under reduced pressure yielding a yellow solid product **43** (2.87 g; 82% yield). NMR (δ, DMSO)- ^{1}H: 2.46, s, 9H; 7.02-7.26, br, 10H; 7.35-7.59, br, 12H ^{13}C: 21.85, 120.34, 124.09, 126.78, 130.72, 131.14, 132.28, 133.94, 139.58, 142.46, 151.63. ^{31}P: 36.718, -10.621.



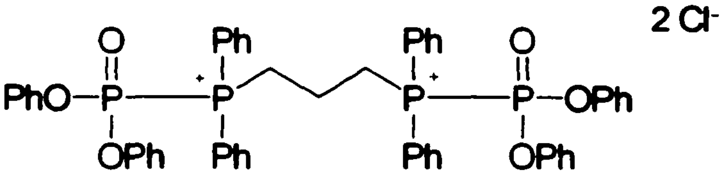
44

Preparation of Tri-p-tolyl-phosphino Diphenyl Chlorophosphate. To a 250 mL three-necked round-bottomed flask tri-*p*-tolyl-phosphine (1.19 g; 0.00391 mol) was added and dissolved in ethyl acetate (40 mL) by stirring and heating at low temperature. To a separate flask diphenyl chlorophosphate (1.05 g; 0.00391 mol) was added and dissolved in ethyl acetate (45 mL). The diphenyl chlorophosphate mixture was then added to the tri-*p*-tolyl-phosphine mixture, slowly *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 48 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a liquid which was further dried under reduced pressure yielding a brown solid product **44** (1.84 g; 82% yield). NMR (δ, $CDCl_3$)- ^{1}H: 2.2, s, 9H; 7.00-7.24, br, 12H; 7.31-7.56, br, 10H. ^{13}C: 42.74, 122.21, 131.96, 132.46, 134.24, 136.85, 145.04, 152.16. ^{31}P: 33.486, -6.6013.



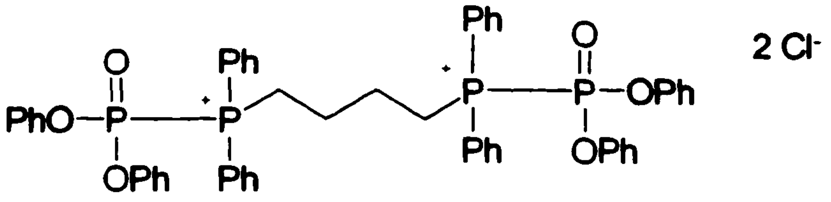
45

Preparation of Tribenzylphosphino Diphenyl Chlorophosphate. To a 250 mL three-necked round-bottomed flask tribenzylphosphine (0.98 g; 0.00322 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask diphenyl chlorophosphate (0.86 g; 0.00322 mol) was added and dissolved in acetonitrile (45 mL). The diphenyl chlorophosphate mixture was then added to the tribenzylphosphine mixture, slowly *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving an orange liquid product **45** (1.31 g; 71% yield). NMR (δ, $CDCl_3$)- ^1H: 3.12, s, 6H; 7.24-7.56, br, 25H. ^{13}C: 60.16, 118.32, 122.65, 126.72, 127.48, 128.63, 129.09, 141.16, 149.37. ^{31}P: 51.816, -10.852.



46

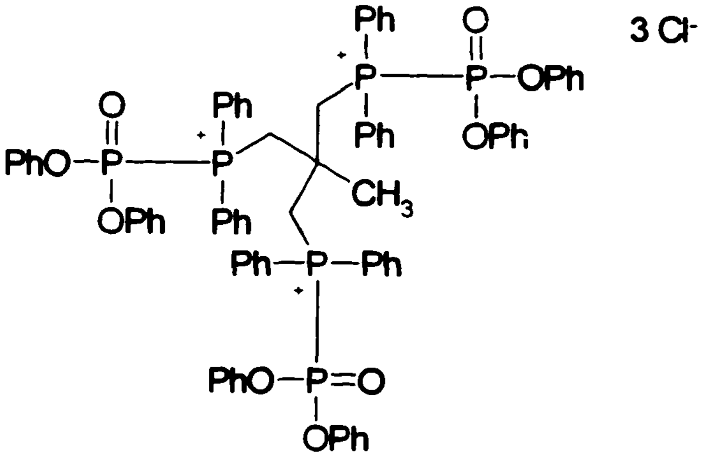
<u>Preparation of 1,3-Bis(diphenyl phosphate diphenyl phosphino) propane dichloride</u>. To a 250 mL three-necked round bottomed flask 1,3-Bis(diphenyl phosphino) propane (0.89 g; 0.00216 mol) was added and dissolved by stirring in chloroform (30 mL). To a separate flask diphenyl chlorophosphate (1.16 g; 0.00432 mol) was added and dissolved in chloroform (20 mL). This mixture was then added to the 1,3-Bis(diphenyl phosphino) propane mixture and the reaction was stirred and heated for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator. This gave the desired product **46** as a liquid (1.17 g; 57% yield). NMR (δ, MeOH)- ^{1}H: 1.73, t, 4H; 2.87, quintet, 2H; 7.28-7.91, br, 40H. ^{13}C NMR (MeOH) 19.64, 78.02, 119.16, 125.72, 129.45, 130.69, 132.31, 140.52, 150.08, 151.68. ^{31}P: 37.393, -10.354.



47

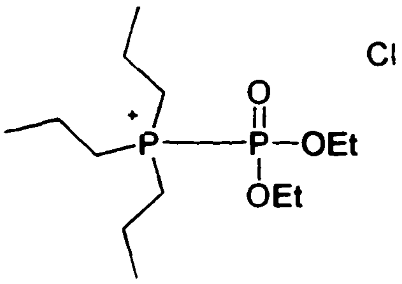
Preparation of 1,4-Bis(diphenyl phosphate diphenyl phosphino) butane dichloride.

To a 250 mL three-necked round bottomed flask 1,4-Bis(diphenyl phosphino) butane (0.97 g; 0.00228 mol) was added and dissolved by stirring in chloroform (30 mL). To a separate flask diphenyl chlorophosphate (1.22 g; 0.00455 mol) was added and dissolved in chloroform (20 mL). This mixture was then added to the 1,4-Bis(diphenyl phosphino) butane mixture and the reaction was stirred and heated for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator. This gave the desired product 47 as a white solid (1.93 g; 88% yield). NMR (δ, $CDCl_3$)- ^{1}H: 1.54, t, 4H; 2.03, quintet, 4H; 7.18-7.45, br, 40H. ^{13}C: 21.88, 29.73, 130.12, 131.63, 134.37, 135.06, 139.59, 141.41. ^{31}P: 33.759, -14.198.



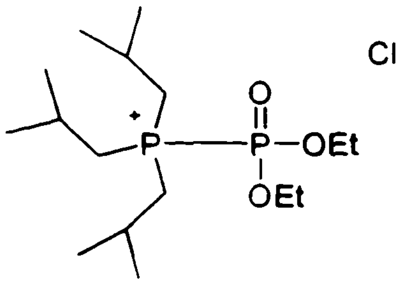
48

Preparation of 1,1,1-Tris(diphenyl phosphate diphenyl phosphino methyl) ethane trichloride. To a 250 mL three-necked round bottomed flask 1,1,1-Tris(diphenyl phosphino methyl) ethane (1.29 g; 0.00207 mol) was added and dissolved by stirring in chloroform (30 mL). To a separate flask diphenyl chlorophosphate (1.66 g; 0.00620 mol) was added and dissolved in chloroform (25 mL). This mixture was then added to the 1,1,1-Tris(diphenyl phosphino methyl) ethane mixture and the reaction was stirred and heated for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator. This gave the desired product **48** as a liquid (0.59 g; 53% yield). NMR (δ, MeOH)- ^{1}H: 1.16, s, 3H, 2.87, s, 6H; 7.21-7.48, br, 60H. ^{13}C: 27.09, 38.61, 77.25, 119.83, 124.48, 128.03, 129.11, 130.36, 132.97, 149.47, 150.82. ^{31}P: 32.901, -10.377



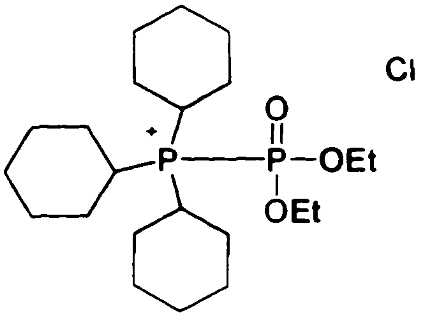
49

Preparation of Tripropylphosphino Diethyl Chlorophosphate. To a 250-mL three-necked round-bottomed flask tripropylphosphine (1.25 g; 0.0078 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask diethyl chlorophosphate (1.35 g; 0.0078 mol) was added and dissolved in acetonitrile (45 mL). The diethyl chlorophosphate mixture was then added to the tripropylphosphine mixture, slowly *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving the desired liquid product **49** (2.22g g; 86% yield). NMR (δ, DMSO)- ^{1}H: 0.98, t, 9H; 1.22, t, 6H; 1.56, t, 6H; 1.73, m, 6H; 3.99, q, 4H. ^{13}C: 13.46, 14.86, 26.93, 27.05, 62.24. ^{31}P: 57.288, 51.206, -0.313, -12.081, -25.384. 5 phosphorus NMR peaks indicates presence of hydrolyzed by-product in the reaction.



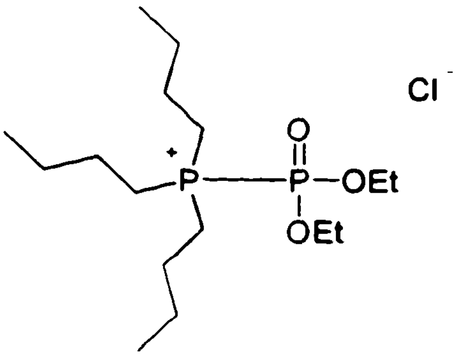
50

Preparation of Triisobutylphosphino Diethyl chlorophosphate. To a 250-mL three-necked round-bottomed flask triisobutylphosphine (4 mL; 0.01604 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask diethyl chlorophosphate (2.77 g; 0.01604 mol) was added and dissolved in acetonitrile (45 mL). The diethyl chlorophosphate mixture was then added to the tributylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving the desired liquid product **50** (5.32 g; 89% yield). NMR (δ, $CDCl_3$)- ^{1}H: 1.16, d, 9H; 1.32, t, 6H; 1.57, d, 6H; 1.85, m, 3H; 3.90, q, 4H. ^{13}C: 16.14, 19.97, 24.52, 38.68, 60.73. ^{31}P: 55.967, 47.034, -0.322, -12.032, -25.184. 5 phosphorus NMR peaks indicates presence of hydrolyzed by-product in the reaction.



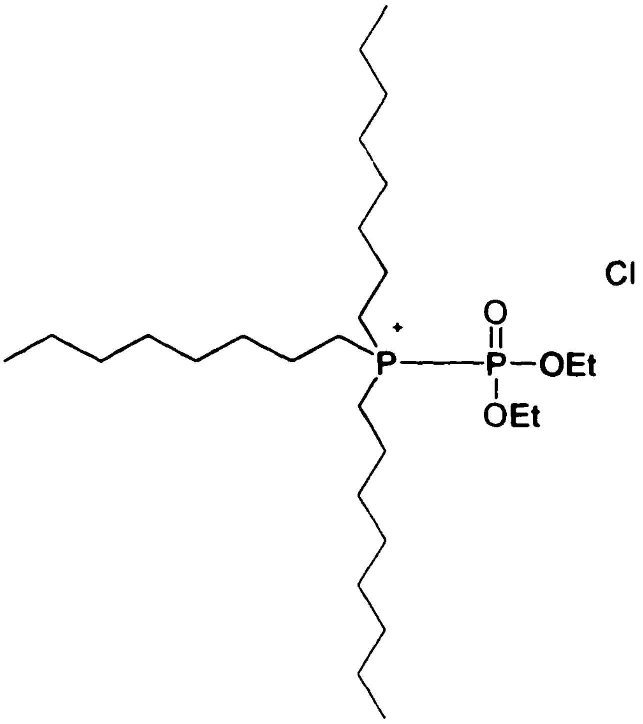
51

Preparation of Tricyclohexylphosphino Diethyl Chlorophosphate. To a 250 mL three-necked round-bottomed flask tricyclohexylphosphine (1.04 g; 0.00871 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask diethyl chlorophosphate (0.64 g; 0.00871 mol) was added and dissolved in acetonitrile (45 mL). The diethyl chlorophosphate mixture was then added to the tricyclohexylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving the desired liquid product **51** (1.39 g; 35% yield). NMR (δ, DMSO)- ^{1}H: 1.26, t, 6H; 1.53, br, 30H; 1.78, quintet, 3H; 3.97, q, 4H. ^{13}C: 16.29, 23.04, 25.33, 26.62, 34.97, 62.31. ^{31}P: 58.279, 55.722, -0.217, -11.921, -25.490. 5 phosphorus NMR peaks indicates presence of hydrolyzed by-product in the reaction.



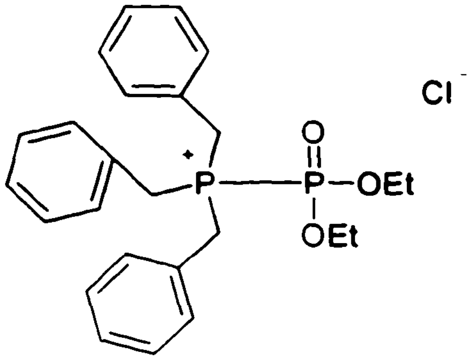
52

Preparation of Tributylphosphino Diethyl Chlorophosphate. To a 250 mL three-necked round-bottomed flask tributylphosphine (4 mL; 0.01604 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask diethyl chlorophosphate (2.77 g; 0.01604 mol) was added and dissolved in acetonitrile (45 mL). The diethyl chlorophosphate mixture was then added to the tributylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving the desired liquid product **52** (5.32 g; 89% yield). NMR (δ, $CDCl_3$)- ^1H: 0.98, t, 9H; 1.42, t, 6H; 1.66, t, 6H; 1.84, m, 12H; 3.81, q, 6H. ^{13}C: 13.07, 15.58, 17.41, 20.32, 26.48, 62.93. ^{31}P: 56.198, 53.816, -0.308, -12.015, -25.386. 5 phosphorus NMR peaks indicates presence of hydrolyzed by-product in the reaction.



53

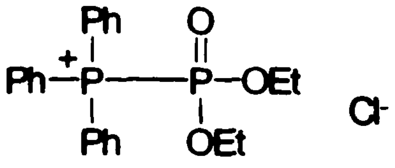
Preparation of Trioctylphosphino Diethyl Chlorophosphate. To a 250 mL three-necked round-bottomed flask trioctylphosphine (0.95 g; 0.00312 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask diethyl chlorophosphate (0.54 g; 0.00312 mol) was added and dissolved in acetonitrile (45 mL). The diethyl chlorophosphate mixture was then added to the trioctylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a yellow liquid product **53** (1.25 g; 84% yield). NMR (δ, $CDCl_3$)- ^1H: 0.85, t, 9H; 1.19-1.42, br, 50H; 3.88, q, 4H. ^{13}C: 14.26, 16.41, 22.42, 26.60, 28.55, 29.04, 30.68, 31.56, 48.74, 62.27. ^{31}P: 51.253, 50.083, -0.241, -11.908, -25.048. 5 phosphorus NMR peaks indicates presence of hydrolyzed by-product in the reaction.



54

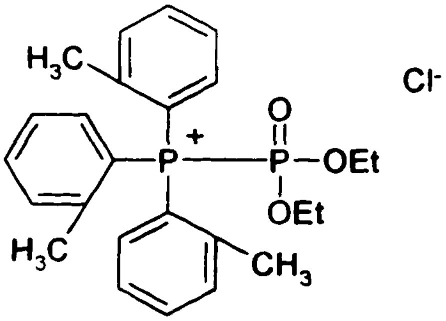
<u>Preparation of Tribenzylphosphino Diethyl Chlorophosphate</u>. To a 250 mL three-necked round-bottomed flask tribenzylphosphine (0.95 g; 0.00312 mol) was added and dissolved in acetonitrile (40 mL) by stirring and heating at low temperature. To a separate flask diethyl chlorophosphate (0.54 g; 0.00312 mol) was added and dissolved in acetonitrile (45 mL). The diethyl chlorophosphate mixture was then added to the tribenzylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 24 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a yellow liquid product **54** (1.25 g; 84% yield). NMR (δ, $CDCl_3$)- ^{1}H: 1.28, t, 6H; 3.06, s, 6H;

3.81, q, 4H; 7.28-7.41, br, 15H. ^{13}C: 17.65, 60.07, 64.83, 126.89, 127.38, 128.34, 140.72. ^{31}P: 28.851, -0.286.



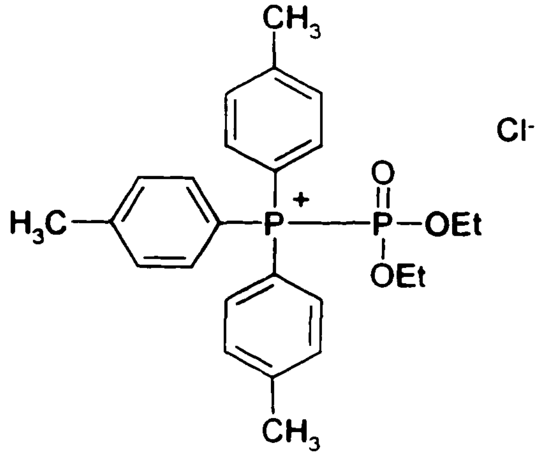
55

Preparation of Triphenylphosphino Diethyl Chlorophosphate. To a 250mL three-necked round-bottomed flask triphenylphosphine (3.77 g; 0.0144 mol) was added and dissolved in ethyl acetate (40 mL) by stirring and heating at low temperature. To a separate flask diethyl chlorophosphate (2.48 g; 0.0144 mol) was added and dissolved in ethyl acetate (45 mL). The diethyl chlorophosphate mixture was then added to the triphenylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 48 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a liquid which was further dried under reduced pressure yielding a yellow liquid product **55** (4.19 g; 67% yield). NMR (δ, DMSO)- ^{1}H: 1.26, t, 6H; 3.92, q, 4H; 7.44-7.68, br, 15H. ^{13}C: 16.60, 61.42, 129.36, 131.77, 133.80, 170.44. ^{31}P: 26.799, -0.253.



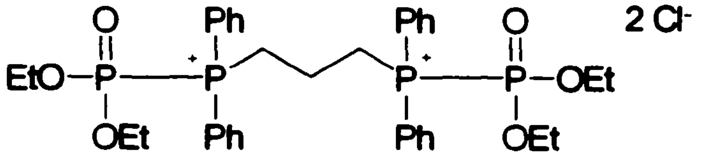
56

Preparation of Tri-o-tolyl-phosphino Diethyl Chlorophosphate. To a 250 mL three-necked round-bottomed flask tri-*o*-tolyl-phosphine (2.28 g; 0.00750 mol) was added and dissolved in ethyl acetate (40 mL) by stirring and heating at low temperature. To a separate flask diethyl chlorophosphate (1.29 g; 0.00750 mol) was added and dissolved in ethyl acetate (45 mL). The diethyl chlorophosphate mixture was then added to the tri-*o*-tolyl-phosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 48 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a liquid which was further dried under reduced pressure yielding a yellow solid product **56** (2.71 g; 76% yield). NMR (δ, MeOH)- ^{1}H: 1.25, t, 6H; 2.37, s, 12H; 3.91, q, 4H; 7.10-7.36, br, 12H. ^{13}C: 18.75, 23.31, 62.03, 126.48 128.99, 130.64, 131.36, 132.54, 142.68. ^{31}P: 40.769, -0.969.



57

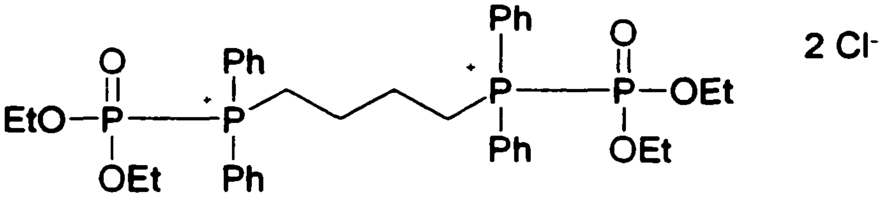
Preparation of Tri-p-tolyl-phosphino Diethyl Chlorophosphate. To a 250 mL three-necked round-bottomed flask tri-*p*-tolyl-phosphine (1.53 g; 0.00503 mol) was added and dissolved in ethyl acetate (40 mL) by stirring and heating at low temperature. To a separate flask diethyl chlorophosphate (0.87 g; 0.00503 mol) was added and dissolved in ethyl acetate (45 mL). The diethyl chlorophosphate mixture was then added to the tri-*p*-tolyl-phosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 48 hours. The solvent was then removed from the liquid *via* rotary evaporator, giving a liquid which was further dried under reduced pressure yielding a white solid product **57** (1.80 g; 75% yield). NMR (δ, $CDCl_3$)- ^{1}H: 1.33, t, 6H; 2.21, s, 9H; 3.46, q, 4H; 7.04, d, 6H, 7.29, d, 6H. ^{13}C: 21.18, 40.02, 89.72, 129.58, 132.61, 139.45. ^{31}P: 31.753, -6.6915.



58

Preparation of 1,3-Bis(diethyl phosphate diphenyl phosphino) propane Dichloride.

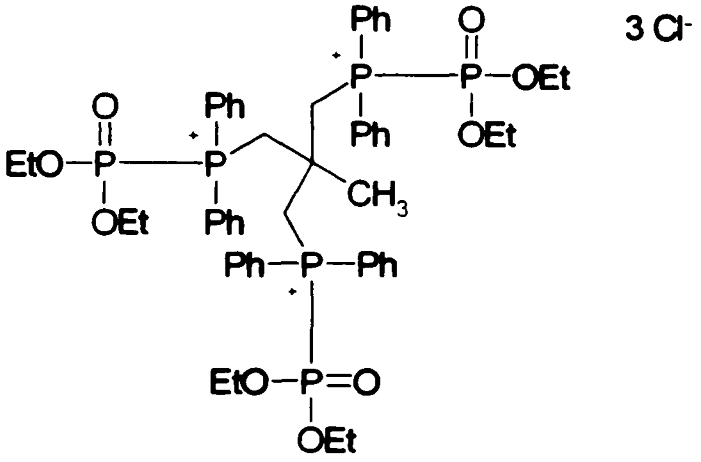
To a 250 mL three-necked round bottomed flask 1,3-Bis(diphenyl phosphino) propane (0.60 g; 0.00146 mol) was added and dissolved in chloroform (30 mL) by stirring. To a separate flask diethyl chlorophosphate (0.50 g; 0.00291 mol) was added and dissolved in chloroform (20 mL). This mixture was then added to the 1,3-Bis(diphenyl phosphino) propane mixture and the reaction was stirred and heated for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator. This gave the desired product **58** as a liquid (1.53 g; 52%) NMR (δ, MeOH)- ^{1}H: 1.05, t, 12H; 1.32, quintet, 2H; 2.67, triplet, 4H; 3.92, q, 8H; 7.21-7.58, br, 20H. ^{13}C: 16.57, 21.04, 26.48, 79.77, 120.34, 131.72, 132.86, 137.49. ^{31}P: 37.674, 1.082, -12.852.



59

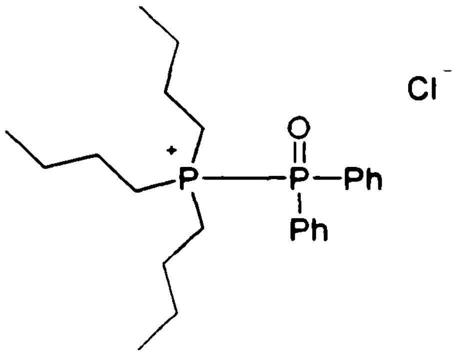
Preparation of 1,4-Bis(diethyl phosphate diphenyl phosphino) butane Dichloride.

To a 250 mL three-necked round bottomed flask 1,4-Bis(diphenyl phosphino) butane (1.08 g; 0.00254 mol) was added and dissolved in chloroform (30 mL) by stirring. To a separate flask diethyl chlorophosphate (0.87 g; 0.00507 mol) was added and dissolved in chloroform (20 mL). This mixture was then added to the 1,4-Bis(diphenyl phosphino) butane mixture and the reaction was stirred and heated for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator. This gave the desired product **59** as a white solid (1.69 g; 86% yield). NMR (δ, MeOH)- ^{1}H: 0.94, t, 12H; 1.56, quintet, 4H; 2.51, t, 4H; 3.87, q, 8H; 7.22-7.53, br, 20H. ^{13}C: 17.83, 22.18, 25.02, 77.41, 122.85, 131.89, 132.24, 135.51. ^{31}P: 33.438, -14.198.



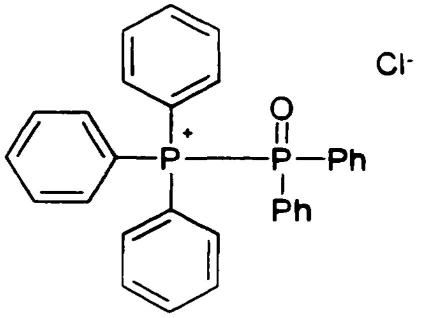
60

Preparation of 1,1,1-Tris(diphenyl phosphate diethyl phosphino methyl) ethane trichloride. To a 250 mL three-necked round bottomed flask 1,1,1-Tris(diphenyl phosphino methyl) ethane (0.53 g; 0.000849 mol) was added and dissolved in chloroform (30 mL) by stirring. To a separate flask diethyl chlorophosphate (0.44 g; 0.00255 mol) was added and dissolved in chloroform (20 mL). This mixture was then added to the 1,1,1-Tris(diphenyl phosphino methyl) ethane mixture and the reaction was stirred and heated for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator. This gave a liquid which was washed with methanol (10 mL). Upon cooling a solid precipitated and was collected giving **60** as a white solid (0.57 g; 59% yield). NMR (δ, DMSO)- ^{1}H: 0.91, s, 3H; 1.24, t, 18H; 3.15, s, 6H; 4.03, q, 12H; 7.23-7.56, br, 30H. ^{13}C: 16.39, 28.56, 40.08, 63.45, 79.21, 128.87, 129.50, 131.23, 136.64. ^{31}P: 28.564, -0.08, -12.278.



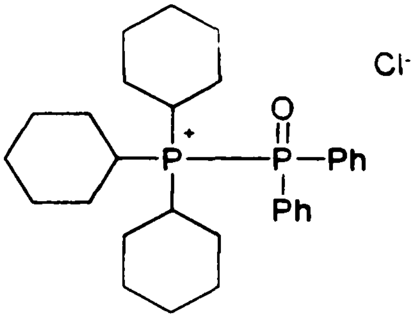
61

Preparation of Tributylphosphine Diphenylphosphinic Chloride. To a 250-mL three-necked round-bottomed flask tributylphosphine (1.05 g; 0.00519 mol) was added and dissolved in chloroform (40 mL) by stirring. To a separate flask diphenylphosphinic chloride (1.22 g; 0.00519 mol) was added and dissolved in chloroform (45 mL). The diethyl chlorophosphate mixture was then added to the tributylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 48 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a liquid which was further dried under reduced pressure yielding a white solid **61** (1.79 g; 79% yield). NMR (δ, MeOH)- ^{1}H: 0.92, t, 9H; 1.36, t, 6H; 1.67, m, 12H; 7.31, t, 4H; 7.45, t, 2H; 7.68, d, 2H. ^{13}C: 13.01, 22.23, 23.64, 24.72, 128.92, 131.36, 135.74, 139.52. ^{31}P: 29.6903, 14.058.



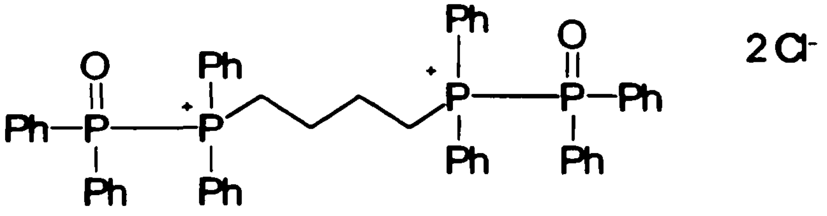
62

Preparation of Triphenylphosphino Diphenylphosphinic Chloride. To a 250-mL three-necked round-bottomed flask triphenylphosphine (1.57 g; 0.00557 mol) was added and dissolved in ethyl acetate (40 mL) by stirring. To a separate flask diphenylphosphinic chloride (1.31 g; 0.00557 mol) was added and dissolved in ethyl acetate (45 mL). The diphenylphosphinic chloride mixture was then added to the triphenylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 48 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a liquid which was further dried under reduced pressure yielding a pink solid **62** (2.40 g; 83% yield). NMR (δ, MeOH)- ^{1}H: 7.32-7.54, br, 15H; 7.67-7.91, br, 10H. ^{13}C (δ, DMSO): 128.02, 129.35, 130.72, 131.94, 132.65, 133.38, 135.62, 136.17. ^{31}P (δ, MeOH): 29.7326, 27.3601.



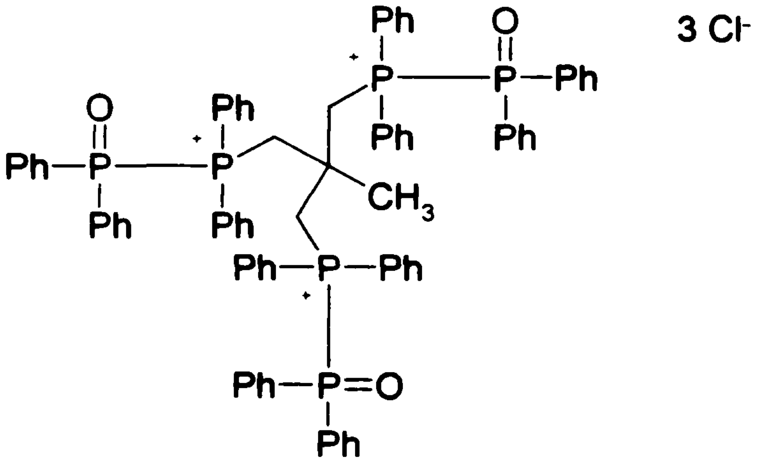
63

Preparation of Tricyclohexylphosphino Diphenylphosphinic Chloride. To a 250 mL three-necked round-bottomed flask tricyclohexylphosphine (0.18 g; 0.000643 mol) was added and dissolved in chloroform (40 mL) by stirring and heating at low temperature. To a separate flask diphenylphosphinic chloride (0.15 g; 0.000643 mol) was added and dissolved in chloroform (45 mL). The diphenylphosphinic chloride mixture was then added to the tricyclohexylphosphine mixture slowly, *via* pasteur pipette, and the entire mixture was then heated and stirred at low temperature for 48 hours. The solvent was then removed from the liquid *via* rotary evaporator giving a liquid which was further dried under reduced pressure yielding an orange solid **63** (0.24 g; 76% yield). NMR (δ, MeOH)- ^{1}H: 1.14, br, 30H; 1.86, quintet, 3H; 7.33, t, 4H; 7.51, t, 2H; 7.65, d, 4H. ^{13}C: 26.09, 27.14, 29.12, 30.37, 130.61, 132.57, 133.83, 135.26. ^{31}P: 34.5604, 29.728.



64

Preparation of 1,4-Bis(diphenyl phosphinic diphenyl phosphino) butane Dichloride. To a 250 mL three-necked round bottomed flask 1,4-Bis(diphenyl phosphino) butane (0.97 g; 0.00228 mol) was added and dissolved in chloroform (30 mL) by stirring. To a separate flask diphenylphosphinic chloride (1.07 g; 0.00455 mol) was added and dissolved in chloroform (20 mL). This mixture was then added to the 1,4-Bis(diphenylphosphino) butane mixture and the reaction was stirred and heated for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator. This gave the desired product **64** as a white solid (1.74 g; 85% yield). NMR (δ, $CDCl_3$)- ^1H: 1.62, quintet, 4H; 2.48, t, 4H; 7.10-7.39, br, 40H. ^{13}C: 27.83, 28.25, 128.75, 129.41, 130.34, 131.06, 132.23, 133.47, 134.82, 137.93. ^{31}P: 33.776, -13.939.



65

Preparation of 1,1,1-Tris(diphenyl phosphinic diphenyl phosphino methyl) ethane Trichloride. To a 250 mL three-necked round bottomed flask 1,1,1-Tris(diphenyl phosphino methyl) ethane (1.51 g; 0.00242 mol) was added and dissolved in chloroform (30 mL) by stirring. To a separate flask diphenylphosphinic chloride (1.71 g; 0.00726 mol) was added and dissolved in chloroform (25 mL). This mixture was then added to the 1,1,1-Tris(diphenylphosphino methyl) ethane mixture and the reaction was stirred and heated for 24 hours. The solvent was then removed from the mixture *via* rotary evaporator. This gave the desired product **65** as a white solid (2.38 g; 74% yield). NMR (δ, $CDCl_3$)- ^{1}H: 0.88, s, 3H; 2.39, s, 6H; 7.13-7.21, br, 30H, 7.25-7.35, br, 30H. ^{13}C: 23.13, 26.64, 38.87, 120.59, 124.31, 130.94, 151.26. ^{31}P: 35.187, -23,785.

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