EXPLORATION OF 2–AMINOPHENOL AND 1,2–PHENYLENEDIAMINE LIGANDS IN HYPERVALENT PHOSPHORUS(V) CHEMISTRY

by

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The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, a thesis entitled:

Exploration of 2-Aminophenol and 1,2-Phenylenediamine Ligands in Hypervalent Phosphorus(V) Chemistry

submitted by Chuantian Zhan in partial fulfillment of the requirements for the degree of Master of Science in Chemistry

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Abstract

Phosphoranes $\text{P(OC}_6\text{H}_4\text{NR)}_2(\text{OC}_6\text{H}_4\text{NHR}) \ [R = \text{Me (2.2a), Ph (2.2b), C}_6\text{F}_5 (2.2c)]$ were synthesized by treating PCl$_5$ with the respective 2–aminophenol derivative (2.1a–c, 3.1 equiv). In one instance, an intermediate species, $\text{P(OC}_6\text{H}_4\text{NR)}_2\text{Cl} \ [R = \text{Me (2.3a)}]$, was isolated and structurally characterized. Deprotonation of the amine moieties (–$\text{NH}_R$) in phosphoranes 2.2a and 2.2b with a strong alkali–metal base (e.g. $n$–BuLi) in the presence of a strong–donor solvent (e.g. THF) afforded salts composed of the hexacoordinate P(V)–anions [P(OC$_6$H$_4$NR)$_3$]$^-$ (R = Me, [2.4a]$^-$; Ph, [2.4b]$^-$). Employing precursor 2.2a, the salt Li(THF)$_3$fac–[2.4a] was isolated. The X–ray crystal of each enantiomer was determined and, to our knowledge, represents the first structurally characterized example of a salt containing a hexacoordinate P(V)N$_3$O$_3$ anion featuring P(V)–N bonds.

Efforts have also been made to synthesize analogous hypervalent P(V)–derivatives with 1,2–phenylenediamine ligands. Following the synthetic methodology to prepare phosphoranes 2.2a, 2.2b and 2.2c, preliminary investigations with three symmetrical 1,2–phenylenediamine derivatives (3.1a–c) were conducted. No evidence for the formation of five– or six–coordinate product was observed. Instead, an interesting phosphonium cation featuring a four–coordinate phosphorus(V) moiety was isolated as a chloride salt, $\text{P(RNC}_6\text{H}_4\text{NR)}_2\text{Cl} \ [R = \text{Me (3.2b)}]$, which was characterized spectroscopically.
Lay Summary

The development and investigation of unprecedented compounds could lead to significant advancement in both fundamental and applied chemistry. In particular, six–coordinate organophosphorus(V) anions are of widespread fundamental interest, since they are often found as interesting intermediates and exhibit unique reactivities/properties that are potentially useful in catalysis and in some chemical transformations.

Since the 1960s, this field has been remained limited to similar examples that utilize carbon and oxygen donors to stabilize the anionic phosphorus(V) centre. Thus, the possibility to incorporate novel donor ligands featuring other elements (e.g. nitrogen) into this type of compounds represents a largely unexplored area with considerable potential. The central focus of this thesis is to further expand the knowledge in the current field with the aim of synthesizing novel P(V)–anions containing nitrogen donors.
Preface

A version of chapter 2 will be submitted for publication. I performed all the synthesis and prepared the manuscript jointly with Prof. Derek P. Gates. X-ray crystallographic data were collected, refined and solved by Dr. Spencer C. Serin (phosphorane 2.2a), Dr. Brian Patrick (phosphorane 2.2b) and Zeyu Han (phosphoranes 2.2c, 2.3a and the lithium salt of anion [2.4a]−, Li(THF)3fac–[2.4a]).
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<tr>
<td>Å</td>
<td>angstrom (length unit)</td>
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<tr>
<td>Anal.</td>
<td>analysis</td>
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<td>Ar</td>
<td>aryl</td>
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<tr>
<td>avg.</td>
<td>average</td>
</tr>
<tr>
<td>br</td>
<td>broad (NMR spectrum)</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
</tr>
<tr>
<td>°C</td>
<td>degree Celsius (temperature unit)</td>
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<tr>
<td>ca.</td>
<td>circa (approximately)</td>
</tr>
<tr>
<td>Calcd</td>
<td>calculated</td>
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<tr>
<td>CCDC</td>
<td>Cambridge Crystallographic Data Centre</td>
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<tr>
<td>cf.</td>
<td>confer/conferatur (compare)</td>
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<tr>
<td>cod</td>
<td>1,5-cyclooctadiene</td>
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<tr>
<td>δ</td>
<td>NMR chemical shift in parts per million (ppm)</td>
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<tr>
<td>Δδ</td>
<td>difference in chemical shift (NMR spectroscopy)</td>
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<td>deuterium</td>
</tr>
<tr>
<td>d</td>
<td>doublet (NMR spectrum)</td>
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<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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</tr>
<tr>
<td>dppe</td>
<td>1,2–bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>dppp</td>
<td>1,3–bis(diphenylphosphino)propane</td>
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<tr>
<td>e.g.</td>
<td>exempli gratia (for example)</td>
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<tr>
<td>EI</td>
<td>electron impact ionization (mass spectrometry)</td>
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<tr>
<td>ESI</td>
<td>electrospray ionization (mass spectrometry)</td>
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<td>Et</td>
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<td>etc.</td>
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<tr>
<td>equiv</td>
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<tr>
<td>Hz, MHz</td>
<td>hertz, megahertz (frequency units)</td>
</tr>
<tr>
<td>{^1H}</td>
<td>proton decoupled (NMR spectroscopy)</td>
</tr>
<tr>
<td>HMBC</td>
<td>heteronuclear multiple bond correlation (NMR spectroscopy)</td>
</tr>
<tr>
<td>HMPA</td>
<td>hexamethylphosphoramide</td>
</tr>
<tr>
<td>HRMS</td>
<td>high–resolution mass–spectrometry</td>
</tr>
<tr>
<td>HSQC</td>
<td>heteronuclear single quantum coherence (NMR spectroscopy)</td>
</tr>
<tr>
<td>i.e.</td>
<td>id est (that is/in other words)</td>
</tr>
<tr>
<td>in situ</td>
<td>in place or in the reaction</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
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$J$    coupling constant (NMR spectrum)

$K$    kelvin (temperature unit)

Da, kDa  dalton, kilodalton (unified atomic mass units for polymer)

KHMDS  potassium bis(trimethylsilyl)amide

$\Lambda$ lambda (chiral configuration)

LRMS  low–resolution mass–spectrometry

$m$    multiplet (NMR spectrum)

$M$    generic metal

molarity concentration (mol per litre)

Me    methyl

$mer$  meridional (configuration)

min  minute (time unit)

$mL$    millilitre (volume unit)

mol, mmol  mole, millimole (amount units)

$m/z$ mass–to–charge ratio (mass spectrometry)

$n$    normal (structure)

NMR, 2D NMR  nuclear magnetic resonance, two–dimensional NMR

$\%$    percentage

$p$    type of orbital

$\{^{31}\text{P}\}$ phosphorus decoupled (NMR spectroscopy)

PDI  polydispersity index (polymer)

$\text{pH}$ negative logarithm of hydrogen ion concentration

Ph  phenyl
pK$_a$  negative logarithm of acid dissociation constant

ppm  parts per million (NMR chemical shift unit)

R  generic organic substituent

rac  racemic

rt  room temperature

s  singlet (NMR spectrum)

T  temperature (X-ray crystallographic data)

THF  tetrahydrofuran

TMEDA  $N,N',N,N'$-tetramethylethylenediamine

V  volume of a unit cell (X-ray crystallographic data)

vol.  volume

WCA  weakly coordinating anion

wt  weight

Z  number of molecules per unit cell (X-ray crystallographic data)
Acknowledgements

I offer my enduring gratitude to my supervisor, Prof. Derek, P. Gates, for his trust, encouragement and patience over the years. It has been an amazing experience working in Gates group and a great honor to be a UBC graduate.

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To my parents:

who awake the beast inside of me
Foreword

This thesis discusses the development and coordination chemistry of 2-aminophenol and 1,2-phenylenediamine ligands for phosphorus(V). In particular, the synthesis and characterization of the first example of hexacoordinate anionic phosphates that contain a $\sigma^6, \lambda^6$ phosphorus(V) centre with P(V)–N bonds are highlighted. Concurrently, a versatile methodology to synthesize P(V)–derivatives of various coordination numbers (four, five and six) with these N–donor ligands has been developed. This truly reflects their potential as ligand scaffolds in the coordination chemistry of phosphorus(V).

The numbering of compounds in this work is explained as follows: Two integers (separated by a period) are used to name compounds of importance: the first integer denotes the chapter where the compound is first mentioned and the second refers to the order where it appears within that chapter. Small letters (a, b, c, etc.) after the second integer indicates a relation (e.g. similar chemical structures) between the compounds in question. For example, compound 2.1a is the first compound discussed or synthesized within Chapter 2 and does not change throughout this thesis. Within each chapter, generic or known compounds are referred to with capital letters (A, B, C, etc.). Mechanistic details or reaction intermediates are numbered using roman numerals (i, ii, iii, etc.). Simple organic and inorganic compounds are referred by their common names or structural formulas.

Chapter 2 is written in manuscript style, and the stylistic and formatting requirements follow The Royal Society of Chemistry Style Guide. Chapter 1 contains a more general introduction to provide historical aspects that put this work in perspective. However, each chapter is self-contained and includes a brief introduction to refamiliarize the reader with the relevant background.
Chapter 1: Introduction: Hexacoordinate Phosphorus(V) Anions

1.1 Introduction

There is no denying that phosphorus, an element capable of diverse oxidation states, geometries, and bonding environments, has long played a significant and versatile role in coordination chemistry. As a coordinating centre, hexacoordinate phosphorus(V) compounds are of widespread fundamental interest\(^1\)–\(^4\) since they are often found as interesting intermediates\(^5\)–\(^9\) and/or exhibit unique properties (e.g. weakly coordinating, chiral resolving, chemical inertness etc.). Despite the fact that both cationic\(^10\)–\(^13\) and neutral\(^14\)–\(^29\) derivatives are possible for such species, by far the most prevalent are the anionic derivatives of the form \([\text{PX}_6^-]\) (anion \([\text{A}^-]\), Figure 1.1). Over the last two decades, the development and investigation of novel hexacoordinate anionic organophosphates have brought the advancement and innovation that stretch across numerous fields,\(^2\) including lithium batteries,\(^30\)–\(^34\) catalysis/chemical transformations,\(^30,35,36\) bio–inorganic chemistry,\(^20,37,38\) stereochemistry\(^39\)–\(^42\) and polymer chemistry.\(^43\)–\(^46\)

The ligand environment (e.g. electronic and steric influences) around phosphorus(V) largely dictates its reactivity and capabilities. For this reason, fundamental research into ligand design and incorporation of novel ligands remains a valuable pursuit in modern hypervalent phosphorus(V) chemistry. However, the development of hexacoordinate \(\text{P(V)}\)–anions has largely remained limited to similar ligand–designs that utilize bidentate \(\text{O,O}^-\),\(^31\)–\(^34,39,41,42,44,45,47-59\) \(\text{C,O}^-\)\(^7,8,60-62\) or \(\text{C,C}–\)donor ligands\(^63\) as the building blocks (anions of type \([\text{B}^-], [\text{C}^-] \text{ and } [\text{D}^-]\)).\(^2\)\(^,\)\(^3\) Thus, the possibility to incorporate novel donor ligands featuring elements other than oxygen and carbon into hexacoordinate anionic phosphates represents a largely unexplored area with considerable potential. Anionic phosphates containing amino–donors (e.g. type \([\text{E}^-]\) anion) are attractive
synthetic targets that may possess unique properties that are not found for their oxygen and carbon analogues. Therefore, the focus of this thesis is the development of hexacoordinate P(V)–anions featuring bidentate N,O–donor ligands. This introduction will provide a brief historical background and a short outline of the unique molecular design of this class of compounds.

![Selected examples of hexacoordinate P(V)–anions.](image)

**Figure 1.1** Selected examples of hexacoordinate P(V)–anions.

### 1.1.1 Historical Background

The long–standing history of hexacoordinate P(V)–anions can be dated back to the late 1920s, when the flagship of future anionic derivatives of phosphorus(V), [PF₆]⁻, was synthesized. Compounds containing [PF₆]⁻ anions were first prepared from the reactions of PCl₅ with alkali–metal/ammonium fluorides. Additional studies revealed that the hypervalent anionic P(V)–centre in [PF₆]⁻ exhibits a remarkable weak–coordinating nature towards cations. Since then, [PF₆]⁻ was widely touted as a “non–coordinating” anion and has been primarily used within the scope of this concept. However, limitations of [PF₆]⁻ as a WCA such as moderate coordinating ability, toxicity and structural liability were soon realized. This pushed researchers to seek other organic ligands to replace the relatively small and labile fluorine atoms. It was not until 1963 when “modern” hexacoordinate phosphorus chemistry started. Specifically, Allcock discovered the first organic analogue of [PF₆]⁻, [1.1a]⁻, as an ammonium (Et₃NH⁺) salt. Compound [Et₃NH][1.1a] was isolated serendipitously from the degradation of hexachlorophosphazene [(NPCl₂)₃] in the
presence of catechol and Et₃N (Scheme 1.1). The IR spectroscopic analysis of an analogous compound, \((C_8H_{17})_3NH[1.1a]\), showed an identical N–H stretching frequency to that observed for \((C_8H_{17})_3NH[BF_4]\), suggesting a similar basicity for anion \([1.1a]^-\) in comparison to the classical WCA, tetrafluoroborate.

![Scheme 1.1 Discovery of the first hexacoordinate organophosphate anion.](image)

**1.1.2 Modern Molecular Design**

It follows that the development and investigation of novel hexacoordinate anionic phosphates have become a subject of considerable interest. Over the past two decades, \([PF_6]^–\), has formally evolved towards larger and more stable organic derivatives. Modern molecular design for hexacoordinate P(V)–anions favours bulky aromatic ligands, as they could provide multiple benefits. For instance, bulky organic ligands may improve the stability of the resultant complex and, concomitantly its WCA properties. Moreover, ligands with aromatic backbones (e.g. catechol) might exhibit a stronger binding tendency towards phosphorus(V) due to the increased nucleophilicity on the heteroatom (e.g. oxygen, the binding site) through π–donation and resonance effects. The major rationale behind such an approach is in line with the aim to achieve anions of a weakly coordinating nature, an important feature associated with various types of applications (see Section 1.2.2). Small anions tend to bind stronger to the cation, whilst larger anions are more charge–delocalized and thus, results in a weaker ion–pair interaction. Chelating dianionic ligands
are particularly more prevalent than monodentate and tridentate ligands.\textsuperscript{2,3} Although the simultaneous incorporation of two different types of bidentate ligands is possible\textsuperscript{2,3,7,8,49,51,54-57,60,61}, the work discussed hereafter deals exclusively with anionic phosphates containing three identical bidentate ligands. Thus, only this class of molecules will be examined in detail.

1.2 Well–Known P(V)–Anions

The family of anionic phosphates containing three identical dioxo–ligands are highlights within this field. Figure 1.2 depicts some selected examples from anion \([1.1b]^-\) to \([1.5]^-\).\textsuperscript{2,31-33,50,53,66} A more exhaustive list can be found in this review.\textsuperscript{2} While the detailed discussion of every example is beyond the scope of this thesis, an in–depth overview on the well–known P(V)–anions (phosphate \([1.1a]^-\), \([1.1b]^-\) and \([1.2]^-\)) will be provided to highlight the synthesis and various attractive applications for this type of compounds. For a more comprehensive overview on diverse synthetic methodologies and applications of hexacoordinate anionic phosphates, the reader is referred to the following references.\textsuperscript{2,67}

![Figure 1.2 Selected examples of dioxo–ligands for hexacoordinate P(V)–anions of type [B]–.](image-url)
The modular preparation of phosphates [1.1a], [1.1b] and [1.2] employs a facile synthetic protocol developed by Koenig et al. Elaboration of these P(V)–anions is accomplished by reacting the corresponding catecholate derivative or oxalic acid (3 equiv) with PCl₅ (Scheme 1.2). The self–initiated substitution reaction is driven by the evolution of HCl gas and first affords a five–coordinate P(V)–intermediate, phosphorane F. The solely unbound phenol group (–OH) in such species is slightly acidic and can be readily deprotonated. Subsequent addition of a harsh (e.g. n–BuLi, KH, NaH, Et₃N) or a donor solvent (e.g. DMF, DMSO, THF, Et₂O) gives the corresponding hexacooordinate P(V)–anion. Depending on the Lewis base being used, anions [1.1a], [1.1b] and [1.2] can be isolated as either Brønsted acids (H⁺), alkali–metal (Li⁺, Na⁺ and K⁺) salts or ammonium (e.g. Et₃NH⁺) salts. These salts generally exhibit limited solubility in most organic solvents and therefore can be readily collected in high yield and purity.

\[
\begin{align*}
\text{OH} & \quad \text{catechol, tetrachlorocatechol, oxalic acid} \\
\text{OH} & \quad \text{PCl}_5 \\
\text{OH} & \quad \Delta \quad -5\text{HCl} \\
\text{OH} & \quad \text{Lewis base} \quad -\text{H}^+ \\
\end{align*}
\]

**Scheme 1.2** Modular synthesis of phosphates containing three identical dioxo–ligands.

The prospect of utilizing hexacooordinate phosphates as WCAs opens the door to numerous exciting possibilities in catalysis and in some chemical transformations. Historically, the WCA field was dominated by p–block elements and started with “classical anions” such as: [BF₄]⁻, [PF₆]⁻, [AsF₆]⁻, [SbF₆]⁻, [SO₃F]⁻ and [SO₃CF₃]⁻. In comparison to these analogues, it is
expected that hexacoordinate organophosphorus(V) anions are more charge diffused and therefore less coordinating to cations. Anions such as $[1.1a]^-$, $[1.1b]^- 50$ and $[1.2]^- 30$ are highly symmetrical, bulky and charge–diffused, which are great properties for WCAs. In many ways, these phosphates closely resemble the well known “BArF” systems (e.g. $[B(C_6F_5)_4]$ and $[B(3,5–C_6H_2(CF_3)_2)_4]$). Hereinafter, utilities of Bronsted acids and alkali–metal salts containing anions $[1.1a]^-$, $[1.1b]^-$ and $[1.2]^-$ will be discussed. Emphasis will be given to the recent development of their application in cationic polymerization.

### 1.2.1 Initiators for Cationic Polymerization

The extraordinary acidity accompanied with low nucleophilicity of the counter anion qualifies WCA–Based Bronsted acids as well–suited single–component initiators for the cationic polymerization of olefins. In 2009, our group first forayed into the field of P(V)–based cationic initiators with the synthesis of two Bronsted acids bearing phosphate $[1.1a]^-$, namely H(DMF)$_2[1.1a]$ and H(DMSO)$_2[1.1a]$.36 Detailed X–ray diffraction analysis showed that the sole proton in these compounds is coordinated to two donor ligands through asymmetric hydrogen bonding in the solid state (see Figure 1.3). The unusual acidity for H(DMF)$_2[1.1a]$ and H(DMSO)$_2[1.1a]$ was further revealed by the broad downfield–signal (δ = 15.3 and 13.3, respectively) in the $^1$H NMR spectra (CD$_3$CN, 298 K).

H(DMF)$_2[1.1a]$ was shown to be an active cationic initiator for the polymerization of $n$–butyl vinyl ether at 19 °C.71 Polymers of moderate molecular weight and broad PDI ($M_n \approx 10 \text{ kDa}$, PDI = 2.80) were obtained. However, attempts to polymerize styrene and isoprene with H(DMF)$_2[1.1a]$ were unsuccessful, indicating its insufficient acidity towards less reactive vinyl monomers. This is attributed to the presence of basic DMF ligands combined with the labile P–O
bond in anion [1.1a]− at ambient temperature. Anion [1.1a]− was also deemed to be too nucleophilic which may have inhibited propagation by terminating polymerization.

![Molecular structures of H(DMF)$_2$[1.1a] (left) and H(DMSO)$_2$[1.1a] (right).](image)

**Figure 1.3** Molecular structures of H(DMF)$_2$[1.1a] (left) and H(DMSO)$_2$[1.1a] (right). Adapted with permission from *Organometallics, 2009, 28, 4491.* © 2009 American Chemical Society.

As a consequence, our attention shifted to the fully chlorinated derivative of anion [1.1a]−, anion [1.1b]−. It was understood that the presence of increasing number of electron withdrawing groups on the aromatic backbone of ligands can lead to better charge delocalization and decreased nucleophilicity for the resultant WCA. In 2010, Chen et al. described the use of trityl salts (Ph$_3$C$^+$) bearing phosphate [1.1b]$^-$, in conjunction with silyl ketene acetal, as an effective initiator system for the polymerizations of butyrolactone and methacrylate. 44,45 We subsequently reported the isolable H(OEt)$_2$[1.1b], the first example of a strong Bronsted acid containing anion [1.1b]$^-$, which can be readily isolated on gram scale by treating the reaction mixture of PCl$_5$ and tetrachlorocatechol with excess Et$_2$O. 43 More recently, H(DMF)$_2$[1.1b] and H(THF)$_2$[1.1b] were prepared by our group in an analogous fashion. 46 X–ray crystallographic analysis of these compounds revealed a similar molecular structure in the solid state (see Figure 1.4 and Figure 1.5).
Employing less basic Et₂O donor instead of DMF was expected to greatly increase the acidity of the loosely coordinated proton from $pK_a = -1.2 \pm 0.5$ ($[H(DMF)_2]^+$)\textsuperscript{72} to $pK_a = -3.59 \pm 0.10$ ($[H(OEt)_2]^+$).\textsuperscript{73} Detailed polymerization studies of H(OEt)\textsubscript{2}[1.1b] confirmed it to be a
competent single–component initiator in carbocationic polymerization. In particular, moderate
(Mₙ ≈ 10 – 100 kDa) to high (Mₙ ≈ >100 kDa) molecular–weight polymers of n–butyl vinyl ether,
α–methylstyrene, styrene and isoprene were obtained (PDIs = 1.11 – 3.28 ) in moderate to high
yield. The efficacy of H(OEt₂)₂[1.1b] at various temperatures (–84 °C to 19 °C) are similar to the
well–established “BArF” initiators (e.g. H(OEt₂)₂[B(C₆F₅)₄]⁷⁴ and H(OEt₂)₂[B(3,5–
C₆H₂(CF₃)₂)₄]⁷⁵). Of note, a “living” mechanism was revealed for the polymerization of n–butyl
vinyl ether at −78 °C. H(THF)₂[1.1b] and H(DMF)₂[1.1b] showed similar properties in the
polymerization of n–butyl vinyl ether.⁴⁶ Polymers of moderate molecular weight and narrower
PDIs (Mₙ ≈ 9 – 41 kDa, PDI = 1.05 – 2.07) were collected at various temperatures (–84 °C to 18
°C). Further investigation of H(DMF)₂[1.1b] with p–methoxystyrene afforded polymers in almost
quantitative yield, whereas H(THF)₂[1.1b] produced poly(p–methoxystyrene) of much higher
molecular weight (up to Mₙ = 649 kDa).

These P(V)–based initiators {HL₂⁺[1.1b]⁺, L = DMF, THF or Et₂O} are attractive for their
ease and low cost of preparation. Particularly striking is that they tend to work better at higher
temperatures (above −50 °C). This is in stark contrast to the general impression that lower
temperatures are always preferred for cationic polymerization. Thus, HL₂⁺[1.1b]⁺ (L = DMF, THF
or Et₂O) represent a unique initiator system. This interesting behavior makes these P(V)–based
Bronsted acids particularly attractive for industrial applications, since maintaining the low
temperatures (e.g. −100 °C) required for the production of long–chain cationic polymers may
become unnecessary.
1.2.2 Chemical Transformations

WCA–based Bronsted acids also hold promise in acid–induced chemical transformations. One example reported by our group involves the protonolysis of Pd–Me bonds in (dppe)PdMe2. The reaction of H(DMF)2[1.1a] with (dppe)PdMe2 in equal molar amounts gives [(dppe)Pd(NCMe)Me][1.1a] in high yield (85%). This closely resembles the reactivity of “BARF”–based Bronsted acid H(OEt2)2[B(3,5–(CF3)2C6H3)4] towards (P–P)PdMe2 (P–P = neutral bidentate phosphine ligands such as dppe and dppp) reported by Brookhart et al. Interestingly, H(DMF)2[1.1a] (2 equiv) is able to doubly activate (dppe)PdMe2 (1 equiv) to afford [(dppe)Pd(NCMe)2][1.1a]2 (Scheme 1.3). It represents an efficient synthetic methodology to access (dppe)Pd(II)–based dications, which have been noted for numerous catalytic transformations. Despite the fact that many conventional Brønsted acids, such as: H(OEt2)2[BF4], HF–SbF5, HOSO2F and HOSO2CF3, are also active catalysts towards the metal–alkyl bond activation, they are available only in solution or liquid form. Hence, the weighable and solid H(DMF)2[1.1a] could be greatly advantageous to precisely control the stoichiometry.

![Scheme 1.3 Protonolysis of (dppe)PdMe2 with H(DMF)2[1.1a].](image)

The use of H(Et2O)4[1.2] in the production of Vitamin E represents an example of the industrial applications for P(V)–based Brønsted acids. Specifically, H(Et2O)4[1.2] was found to be a remarkably effective catalyst for the Friedel–Crafts alkylation reaction of
trimethylhydroquinone and rac–isophytol to give α–tocopherol, known as Vitamin E (Scheme 1.4). This process is highly promising, as the product can be isolated in excellent yields (≥ 90%) with a relatively low catalyst loading (0.5 mol% or less). Other notable advantages include its ease of synthesis from low–cost starting materials and the absence of heavy metals, sulfur– and fluorine–containing compounds. This is especially important when one takes into account environmental aspects and the worldwide trend in greener chemistry.

Scheme 1.4 Synthesis of Vitamin E catalyzed by H(OEt)₄[1.2].

Advances in P(V)–based WCAs could also facilitate the synthesis and isolation of novel cations. To this end, our group uncovered the facile use of two heavy alkali–metal salts containing [1.1a]⁻, namely Na[1.1a] and K[1.1a], in halide abstraction of transition–metal chlorides. Similar to the sodium salt of “BArF” anion, Na[B(3,5–C₆H₂(CF₃)₂)₄], reactions of K[1.1a] with (dppp)PdCl₂ and [(cod)RhCl]₂ has led to the isolation of two novel cationic species. In particular, a zwitterionic Rh(I) complex [(cod)Rh][1.1a] and an interesting salt [(dppp)Pd(μ–Cl)]₂[1.1a]₂ containing a dimeric Pd(II) dication were confirmed by X–ray crystallography (Scheme 1.5). Both compounds may be of future interest for catalytic applications.

Scheme 1.5 Halide abstraction of (dppe)PdCl₂ and [(cod)RhCl]₂ with K[1.1a].
1.2.3 Other Applications

Other utilities for P(V)–based anions are associated with their point chirality at phosphorus or with their chemical inertness. Hexacoordinate anionic phosphates containing three bidentate ligands are chiral helical molecules that exist in Λ or Δ configuration (see Figure 1.6). However, only few examples\textsuperscript{50,63,78} that can retain their configuration are known due to the \textit{in situ} epimerization in solution.\textsuperscript{49,79} Of these, anion \textbf{[1.1b]}\textsuperscript{−}\textsuperscript{50} and its derivatives\textsuperscript{51,52,54-57,80} have received considerable attention for chiral anion–mediated asymmetric applications.\textsuperscript{2,39-42} Lacour \textit{et al.} first prepared and resolved anion \textbf{[1.1b]}\textsuperscript{−} into stable Δ–configuration by associating it with a chiral acinchonidinium cation.\textsuperscript{50} Motivated by the outstanding configurational stability of the resultant salt, enantiopure Δ or Λ–\textbf{[1.1b]}\textsuperscript{−} was identified as effective NMR chiral solvating, resolving, asymmetry–inducing, and solubilizing reagents. To date, it is widely used as a stable chiral anion to access various enantiopure complexes containing chiral metal/radical cations.\textsuperscript{81-85}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure16.png}
\caption{Λ and Δ enantiomers of a hexacoordinate phosphate anion with three bidentate ligands.}
\end{figure}

Additionally, lithium salts of hexacoordinate phosphorus(V) anions are of special interest as electrolytes due to their extraordinary conducting capability. Lithium batteries containing the \textbf{[PF₆]}\textsuperscript{−} anion were originally commercialized in the late 1960s, yet the chemical and thermal instabilities of \textbf{[PF₆]}\textsuperscript{−} were soon realized and became an issue.\textsuperscript{86} In this regard, anionic phosphates
containing organic ligands are attractive alternatives to \([\text{PF}_6]^-\) due to their great chemical inertness and thermal stability. Detailed electrochemical studies showed that the lithium salts of anions \([1.1a]^-, [1.1c]^-, [1.1d]^-, [1.1e]^-,\) and \([1.1f]^-\) exhibit substantially better thermal and electrochemical stability than \([\text{PF}_6]^-.\) Moreover, enhanced cycling efficiency and discharge characteristics were observed in some cases,\(^{31,32,34}\) indicating their potential to be superior electrolyte–solutions.

### 1.3 2–Aminophenol in Hypervalent Phosphorus(V) Chemistry

Although the chemistry of P(V)–anions continues to thrive and expand, the development of the novel derivatives bearing other types of donor ligands is still at a primitive stage. Our group has been interested in the development of novel hexacoordinate anions of phosphorus(V) that can serve as WCAs,\(^{69,70}\) particularly in the area of cationic polymerization.\(^{36,43,46}\) In an effort to expand upon our discovery of \(\text{HL}_2^+[1.1a]^-(L = \text{DMF and DMSO})\) and \(\text{HL}_2^+[1.1b]^-(L = \text{Et}_2\text{O, THF and DMF})\), we have embarked upon an investigation of unprecedented P(V)–anions containing an N–containing ligand.

Despite the fact that hexacoordinate anionic phosphates with bidentate C,O– and C,C–donor ligands are known (e.g. \([\text{C}]^-\) and \([\text{D}]^-\)),\(^{7,8,60,61,63}\) examples featuring N–donors have remained largely unexplored. The recently reported P(V)–anion \([1.9]^-,\) featuring the chiral tridentate N,N,O–ligand, has been employed in asymmetric catalysis and represents the only fully characterized P(V)–anion with N–donor substituents.\(^{87}\) This is most likely a consequence of a formidable synthetic barrier stemming from the labile P–N linkages in this type of compounds. Previously, a number of sophisticated chelating ligands have been designed to incorporate the P–N linkage into neutral hexacoordinate compounds of phosphorus(V) (see Figure 1.7).\(^{14,22-24,29}\) A more exhaustive list of examples for this class of compounds can be found in these reviews.\(^{1-3,15,18,20}\) In this thesis,
we hypothesized that amido–donors, such as those derived from 2–aminophenol, may provide access to P(V)–based anions of type \([E]^-\).

\[
\begin{align*}
\text{1.6} & \quad \text{t-Bu} & \quad \text{Ph} & \quad t-\text{Bu} & \quad \text{EtO}_2\text{C} & \quad \text{N} & \quad \text{N} & \quad \text{O} & \quad \text{N} & \quad \text{OEt} & \quad \text{t-Bu} \\
\text{1.7} & \quad \text{R} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{1.8} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} \\
\text{1.9} & \quad \text{RO}_2\text{S} & \quad \text{N} & \quad \text{N} & \quad \text{SO}_2\text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} \\
\end{align*}
\]

\[\text{R} = \text{H}, \text{Et}; \text{R}_1 = \text{H}, \text{Ph}, \text{C}_6\text{H}_5 \\
\text{R}_2 = \text{H}, \text{Me}, \text{Ph}, \text{OMe}, \text{OSiMe}_3, \text{OSiPh}_3\]

\[\text{[1.9]}^- \]

\[\text{R} = \text{Me}; \text{R}_1 = \text{H}, \text{CF}_3\]

**Figure 1.7** Selected examples of neutral (upper) and anionic (lower) hexacoordinate P(V)–derivatives containing N–donors.

We note that the 2–aminophenol ligand has been employed as a ligand for P(V) to access transition–metalled phosphoranes (e.g. **1.10a–c**\textsuperscript{88-91} and organophosphoranes (e.g. **1.11a–g**, see Figure 1.8).\textsuperscript{92-101} The goal of this project is to incorporate 2–aminophenol into hexacoordinate anionic organophosphates. Hereinafter, the synthetic context of organophosphoranes **1.11a–g** will be provided to highlight the reactivity of 2–aminophenol towards a wide variety of phosphorus (III or V) precursors.
Historically, Allcock and Kugel first examined 2-aminophenol as a N–donor ligand for P(V) and serendipitously discovered the ring–degradation of halogenophosphazenes.\textsuperscript{47,48} In particular, 2-aminophenol (9 equiv) was treated with a series of halogenophosphazenes [(NPCl\textsubscript{2})\textsubscript{3}, (NPF\textsubscript{2})\textsubscript{2}, (NPBr\textsubscript{2}), (NPCl\textsubscript{2})\textsubscript{4}, (NPCl\textsubscript{2})\textsubscript{n}, etc.], respectively. Nevertheless, the same major product, phosphorane \textbf{1.11a}, was isolated in all cases.\textsuperscript{92,93} Spectroscopic characterization of \textbf{1.11a} revealed it to be a novel phosphorane system in solution. However, the evidence from IR spectroscopy indicated that pseudo–hexacoordinate zwitterionic adduct \textit{iii} might exist in the solid state.\textsuperscript{92}

\textbf{Figure 1.8} Selected examples of transition–metallated phosphoranes (upper) and organophosphoranes (lower) bearing 2-aminophenol.
Detailed mechanistic studies suggested an ionic mechanism for the formation of phosphorane 1.11a.\textsuperscript{94} It was proposed that the condensation reaction of (NPCl\textsubscript{2})\textsubscript{3} with 2–aminophenol in its zwitterionic form (\(\text{o–N}^+\text{H}_2\text{C}_6\text{H}_4\text{O}^-\)) proceeds immediately to afford a highly unstable intermediate \(i\). The exocyclic ring–strain drives the decomposition of \(i\) and produces an amine–bridged (\(-\text{P–NH–P–}\)) diphosphorane \(ii\). Subsequent cleavage of \(ii\) at high temperatures (e.g. reflux in xylene) eventually gives the thermodynamic product 1.11a (Scheme 1.6).\textsuperscript{93} Noteworthy is that the presence of five–membered endocyclic rings in intermediate \(ii\) and phosphorane 1.11a were found to be particularly favoured. This was speculated to be a consequence of the ideal endocyclic \(\angle\text{O–P–N}\) bond angle (90°) in five–membered rings that allows the least ring–strain.\textsuperscript{92-94}

![Scheme 1.6 Ring–degradation of hexachlorophosphazene with 2–aminophenol.](image)

Allcock and Kugel’s pioneering work provoked the research into aminophenol–based bicyclic spirophosphoranes. Shortly after, a broad diversity of phosphorus(III or V) precursors
have been investigated under this concept (see Figure 1.9). Reddy and Koizumi conducted a series of reactions of 2–aminophenol with various aryl–substituted phosphorodichloridates $H$ in the presence of Et$_3$N.$^{95,96}$ However, a disubstituted product $1.11b$ was readily isolated with only an insignificant amount of phosphorane $1.11a$ being formed. Similarly, the reaction of alkylphosphonic dichloride $H'$ with 2–aminophenol also resulted in formation of an analogous disubstituted product $1.11c$ in 1:1 molar ratio to the monosubstituted product.$^{99}$ In another report by Liu et al., treatment of various phosphorodichloridothioates $I$ with 2–aminophenol and Et$_3$N afforded $1.11a$ in a surprisingly straightforward manner.$^{97}$ More recently, Anand et al. reported the isolation of stable amine–bridged diphosphorane $1.12$ from the reaction of 2–aminophenol with PCl$_5$ (Scheme 1.7).$^{102}$ The disubstituted intermediate $i$ was first isolated at 85 °C and underwent dimerization through intra– and/or inter–molecular dehydrohalogenation to give $1.12$ at higher temperature (reflux in toluene).

**Figure 1.9** Reported P(III) (lower) and P(V) (upper) precursors for the synthesis of organophosphoranes bearing 2–aminophenol.
In addition to these P(V)–precursors, some P(III)–derivatives such as benzoxazaphospholidines and phosphorus(III) amides are also shown to be active phosphorane–precursors with 2–aminophenol. Pudovik et al. reported that the reaction of benzoxazaphospholidine J with 2–aminophenol eventually affords phosphorane 1.11d via multiple intermediates.99 Konovalov et al. revealed the similar reactivity for unsubstituted analogue J′ that leads to the formation of phosphorane 1.11e.98 Moreover, Malavaud and Barrans demonstrated that phosphorus(III) amide K can readily react with 2–aminophenol upon heating or treatment of a mild oxidant (I₂, S or Hg²⁺) to afford bicyclic spirophosphoranes 1.11f.103 Analogous reaction of the less bulky phosphorus(III) amide K′ with 2–aminophenol affords a similar product, phosphorane 1.11g.101

1.4 Outline of Thesis

The development and investigation of novel hexacoordinate anionic organophosphates has permitted significant advancement in both fundamental and applied hypervalent phosphorus(V) chemistry. Since the 1960s, this field has been dominated by examples containing P–C and/or P–O linkages with no species incorporating other heteroatoms into this type of compounds. The
central focus of this thesis is to further expand the knowledge in the current field with the aim of synthesizing novel P(V)–anions that are embedded with covalent P–N linkages in their frames.

As a starting point, 2–aminophenol was chosen as the ligand scaffold for our preliminary investigations. Chapter 2 contains two lines of investigation: the first describes the substitution reactions of PCl$_5$ with 2–aminophenol ligands and leads to the isolation of a novel class of phosphoranes; the second details the synthetic use of these phosphoranes as precursors to prepare hexacoordinate anionic phosphates that contain P–N linkages in their backbones. Chapter 3 switches the focus to 1,2–phenylenediamine ligands and discusses their reactions with PCl$_5$. These studies were initially attempted to assess the feasibility of the preparation of analogous hypervalent P(V)–derivatives and unexpectedly gave rise to the synthesis of a novel phosphonium salt. Finally, summary of the results presented in this thesis and future work are provided in Chapter 4.
Chapter 2: Hypervalent Phosphorus(V) Derivatives with 2–Aminophenol Ligands

2.1 Introduction

One conceivable starting point towards the synthesis of P(V)–anions containing bidentate N,O–donor ligands involves the careful design and efficient preparation of the corresponding phosphorane precursors such as compound A. We hypothesized that deprotonation of the last potential binding site (e.g. –NHR) in such species may lead to the formation of the unprecedented hexacoordinate N₃O₃–ligated anionic phosphate [B]⁻ (Scheme 2.1). However, the procedures to phosphoranes of type A with 2–aminophenol were low–yielding (20–40%) and employed unconventional precursors such as: [(N≡PCl₂)₃], [O=P(Cl₂)R, O=P(Cl₂)OR], [S=P(Cl₂)R], [P(NMe₂)₃, PhP(NMe₂)₂] and [(α–RNC₆H₄O)PR].⁸⁸-¹⁰⁰

![Scheme 2.1](image)

Scheme 2.1 Proposed synthetic route to P(V)–anions containing three bidentate N,O–donor ligands.

In this chapter, the convenient and high–yielding synthesis of neutral phosphoranes and hexacoordinate P(V)–anions featuring 2–aminophenol ligands (51–67% yield) will be discussed. Conveniently, our procedure employs PCl₅ as the precursor and the method is analogous to that employed for the preparation of catechol–based P(V)–anions [1.1a]⁻ and [1.1b]⁻. To our knowledge, this represents the first fully characterized example of a salt featuring a type [B]⁻ anion.
2.2 Results and Discussion

2.2.1 Five–coordinate P(V)N$_2$O$_3$ Phosphoranes

Due to their ease of synthesis and purification, three known amino–substituted 2–aminophenol derivatives (2.1a–c)$^{104-107}$ were selected as ligands for this study. In particular, methyl (N–Me, 2.1a), phenyl (N–Ph, 2.1b) and perfluorophenyl (N–C$_6$F$_5$, 2.1c) substituents were employed in an effort to shed light on the steric and electronic factors influencing the stability of the resultant five– and six–coordinate phosphorus(V) derivatives. It has been shown by König and co–workers$^{68}$ and our group$^{35,36,43}$ that catechol reacts directly with PCl$_5$ to quantitatively afford penta–substituted O,O–containing phosphoranes. Although phosphoranes containing N,O–ligands are known, the procedures employed involved P(V)–oxide or P(V)–sulfide precursors and resulted in low yields.$^{92-100}$ We successfully synthesized the desired phosphoranes (2.2a–c) by treating PCl$_5$ with the prepared 2–aminophenol ligands (2.1a–c, 3 equiv) in toluene solution (Scheme 2.2). In each case, the evolution of HCl gas was observed immediately upon mixing and was accompanied by a gradual colour change of the solution from colourless to pale yellow. Analysis of the reaction mixtures by $^{31}$P NMR spectroscopy revealed that the signal assigned to PCl$_5$ was not present ($\delta = -80.1$).

![Scheme 2.2 Synthesis of phosphoranes 2.2a–c from the reaction of PCl$_5$ with the 2–aminophenol derivatives 2.1a–c.](image-url)
In its place were two new upfield shifted resonances (see Figure 2.1). For each pair of signals, the higher-field resonance was assigned to the pentacoordinated compound [$\delta = -48.4$ (2.2a), $-53.9$ (2.2b), $-55.1$ (2.2c)] by comparison to known phosphorane 1.11a ($\delta = -46.3 \pm 1.0$).92 Interestingly, each of the lower-field resonances showed an almost identical difference to the corresponding phosphorane (2.2a–c, $\Delta\delta = 14.0$). In one case, the slow evaporation of the reaction solution derived from 2.1a (2 equiv) and PCl$_5$ in toluene permitted the isolation of a crystalline solid which was analyzed by X-ray diffraction. The molecular structure of intermediate chlorophosphorane 2.3a is shown in Figure 2.2. The $^{31}$P NMR spectrum of a toluene solution of the crystals of 2.3a showed a singlet resonance at $-34.2$ ppm. By extension, the signals at $-39.9$ ppm and $-40.7$ ppm were assigned to chlorophosphoranes 2.3b and 2.3c, respectively.

Figure 2.1 $^{31}$P{$^{1}$H} NMR spectra (121.5 MHz, toluene, 298 K) of the crude reaction mixtures of PCl$_5$ with: (a) 2.1a; (b) 2.1b; (c) 2.1c before (crude) and after the optimization (optimized). Note: The scale corresponds to the crude spectra in each case with the optimized spectra being offset slightly for clarity.
Figure 2.2 Molecular structure of intermediate 2.3a (thermal ellipsoids are displayed at 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–O(1) = 1.6878(16), P(1)–O(2) = 1.6841(15), P(1)–N(1) = 1.6806(18), P(1)–N(2) = 1.6808(19), P(1)–Cl(1) = 2.1101(8), O(1)–P(1)–N(1) = 89.70(8), O(1)–P(1)–O(2) = 178.60(9), O(2)–P(1)–N(2) = 90.42(8), N(1)–P(1)–N(2) = 131.26(10), N(1)–P(1)–Cl(1) = 115.73(7), N(2)–P(1)–Cl(1) = 113.01(7).

The conditions were varied in an effort to optimize the procedure towards phosphoranes 2.2a–c and minimize the formation of 2.3a–c. Specifically, the solvent (toluene, CH₂Cl₂, EtOAc and MeCN), temperature (25 °C to 130 °C), and stoichiometric ratio (i.e. the molar ratio of 2–aminophenol derivatives 2.1a–c to PCl₅ from 1:1 to 4:1) were varied. In addition, the order of addition was reversed (i.e. dropwise addition of solutions of 2.1a–c into a solution of PCl₅ and vice versa). Each reaction mixture was analyzed by ³¹P NMR spectroscopy. Although there were always unassigned signals present, the signal assigned to 2.3a–c could be eliminated in favour of signals assigned to the desired phosphoranes 2.2a–c. (see Figure 2.3 and Figure 2.4). These optimized conditions involved refluxing a toluene solution of 2–aminophenol derivatives 2.1a–c with PCl₅ for ca. 12 h under a nitrogen atmosphere (2.1a : PCl₅ mole ratio = 3.14 : 1).
phosphoranes 2.2b, a higher stoichiometric amount of ligand 2.1b or 2.1c (4:1) afforded the optimal isolated yield (67%). For phosphorane 2.2c, the optimized conditions involved refluxing a toluene solution of 2.1c and PCl5 (4:1 ratio) followed by the addition of Et3N (13.6 equiv) to give the product in 51% isolated yield. Phosphoranes 2.2a–c were isolated after passing the reaction mixtures through a silica plug under a nitrogen atmosphere. Subsequently, colorless crystals suitable for X-ray diffraction analysis were isolated in each case by slow diffusion of dry n-pentane into a concentrated CH2Cl2 solution.

Phosphoranes 2.2a–c and intermediate 2.3a were characterized using multinuclear NMR spectroscopy (1H, 13C, 19F and 31P), mass spectrometry, elemental micro–analysis and X–ray crystallography. The molecular structures of 2.2a–c and 2.3a are shown in Figure 2.3 and Figure 2.4. The selected metrical parameters and related X–ray crystallographic data are given in Tables 2.1 and 2.2, respectively. In the solid state, phosphoranes 2.2a–c and intermediate 2.3a displayed a similar trigonal bipyramidal geometry (see Figure 2.3 and Figure 2.4). In each case, an identical apicophilicity was observed with the oxygen atoms occupying the apical positions and all endocyclic ∠O–P–N angles being nearly 90°. Notably, the bond angle of two axial P–O bonds (∠Oap–P–Oap) showed only minor deviation from the linearity [0.60(6)° (2.2a), 3.39(6)° (2.2b), 2.56(10)° (2.2c), 1.40(9)° (2.3a)]. The central phosphorus atom and the three equatorial substituents are effectively co–planar in all cases with the calculated sum of the angles about phosphorus being close to 360° [∑(∠X–P–Y) = 359.93(7)° (2.2a), 359.95(7)° (2.2b), 359.94(11)° (2.2c), 360.00(10)° (2.3a)]. Within the equatorial plane, the ∠N–P–N bond angles were measured to be 125.75(7)° (2.2a), 129.10(7)° (2.2b), 127.50(11)° (2.2c) and 131.26(10)° (2.3a), while the ∠N–P–O and ∠N–P–Cl bond angles are more acute [range: 112.71(6)° to 118.64(6)°]. These observations are in accord with Bent’s rule108 which would predict a higher degree of p–character
for the more electronegative P–OR or P–Cl bonds compared to the P–NR₂ bond (therefore, the average bond angle $\angle N$–P–Cl $< \angle N$–P–OR $< \angle N$–P–NR₂, see table 2.1). The bond lengths within the aforementioned molecules are as expected and will not be discussed further.

**Figure 2.3** Molecular structures of phosphoranes 2.2a (a) and 2.2b (b) (thermal ellipsoids are displayed at 50% probability level). Hydrogen atoms and the solvent of recrystallization (CH₂Cl₂) are omitted for clarity. Selected bond lengths (Å) and angles (°): 2.2a: P(1)–O(1) = 1.6897(12), P(1)–O(2) = 1.6161(12), P(1)–O(3) = 1.6899(12), P(1)–N(1) = 1.6863(14), P(1)–N(3) = 1.6851(13), O(1)–P(1)–N(1) = 89.67(6), O(3)–P(1)–N(3) = 89.41(6), N(1)–P(1)–N(3) = 125.75(7), N(1)–P(1)–O(2) = 118.64(6), N(3)–P(1)–O(2) = 115.54(6), O(1)–P(1)–O(3) = 179.60(6); 2.2b: P(1)–O(1) = 1.6947(11), P(1)–O(2) = 1.6164(11), P(1)–O(3) = 1.7022(11), P(1)–N(1) = 1.6895(13), P(1)–N(3) = 1.6845(13), O(1)–P(1)–N(1) = 88.81(6), O(3)–P(1)–N(3) = 89.13(6), N(1)–P(1)–N(3) = 129.10(7), N(1)–P(1)–O(2) = 112.71(6), N(3)–P(1)–O(2) = 118.14(6), O(1)–P(1)–O(3) = 176.61(6).
Figure 2.4 Molecular structure of phosphorane 2.2c (thermal ellipsoids are displayed at 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–O(1) = 1.6821(17), P(1)–O(2) = 1.6176(18), P(1)–O(3) = 1.6856(17), P(1)–N(1) = 1.6932(19), P(1)–N(3) = 1.7009(19), O(1)–P(1)–N(1) = 89.51(9), O(3)–P(1)–N(3) = 89.19(9), N(1)–P(1)–N(3) = 127.50(11), N(1)–P(1)–O(2) = 116.49(10), N(3)–P(1)–O(2) = 115.95(10), O(1)–P(1)–O(3) = 177.44(10).

The $^1$H NMR spectra of phosphoranes 2.2a–c and 2.3a in CDCl$_3$ are consistent with their structures in the solid state. Of particular interest is the chemical shift of the amine proton (–NH$_R$), as it offers a rough indication of the acidity of 2.2a–c in solution and its ease of deprotonation to afford hexacoordinate anionic phosphates. In particular, the amine –NH$_R$ signal in phosphoranes 2.2b (δ = 5.99) and 2.2c (δ = 5.59), bearing aromatic substituents, were substantially deshielded when compared to that of 2.2a (δ = 3.79) (see Figure 2.5).
Figure 2.5 $^1$H NMR spectra (300 MHz, CDCl$_3$, 298 K) of: (a) 2.2a; (b) 2.2b; (c) 2.2c; (d) 2.3a recrystallized from CH$_2$Cl$_2$ (* indicates the residual CHCl$_3$ and † indicates the residual CH$_2$Cl$_2$ solvent).

The $^{31}$P{$^1$H} NMR spectra of 2.2a–c and 2.3a in CDCl$_3$ revealed similarly that the aryl substituted phosphoranes 2.2b ($\delta = -53.8$) and 2.2c ($\delta = -55.5$) have similar chemical environments whilst the methyl–substituted 2.2a ($\delta = -48.4$) and 2.3a ($\delta = -34.2$) are significantly different. We note that these N$_2$O$_3$–substituted phosphoranes display significantly higher–field $^{31}$P shifts than the O$_5$–substituted (C, $\delta = -9.6^{68}$ D, $\delta = -29.6^{68}$ E, $\delta = -27.3^{43}$; Figure 2.6). It is plausible that these higher–field shifts are a consequence of the more strongly donating N–donor ligands thereby reducing the electrophilicity at phosphorus. Further support for this hypothesis may be
gleaned from the molecular structure of 2.3a which has a longer P–Cl bond [2.110(1) Å] in comparison to the one found in its catechol analogue C (2.031 Å) (Figure 2.6).\(^{109}\)

![Chemical structures](image)

**Figure 2.6** Catechol–based analogues of 2.2a–c and 2.3a that have been reported in the literature.

Examination of the \(^1\)H NMR spectra of 2.2a and 2.3a in CDCl\(_3\), along with the \(^1\)H\(_{\{31\}P}\) NMR spectra, permitted the determination of the \(^1\)H–\(^{31}\)P coupling constant between the phosphorus and the six adjacent methyl protons (\(P–\text{NCH}_3\); \(^3\)J\(_{HP} = 10\) Hz for 2.2a and 2.3a). Interestingly, there are 10 theoretical isomers for a phosphorane bearing asymmetric bidentate ligands. Therefore, variable temperature NMR experiments on solutions of 2.2a and 2.2c in either C\(_7\)D\(_8\) or CD\(_2\)Cl\(_2\) were performed (–66 to 89 °C, actual temperatures) in an effort to identify a fluxional process such as isomerization. No significant change in either the \(^{31}\)P, \(^{31}\)P\(_{\{1\}H}\), \(^1\)H or \(^1\)H\(_{\{31\}P}\) NMR spectra was observed suggesting that isomerization was not prevalent under these conditions. A similar observation was made for phosphorane 1.11a (Figure 1.9) where only a single isomer was observed.\(^{93}\)

### 2.2.2 Six–coordinate P(V)N\(_3\)O\(_3\) Anions

The O\(_5\)–substituted phosphoranes N and O can be readily deprotonated by bases to afford anions \([1.1a]^–\) and \([1.1b]^–\).\(^{33-36,43,46,50,68}\) Therefore, we postulated that deprotonation of the neutral...
phosphoranes 2.2a–c would afford the corresponding hexacoordinate N₃O₃–ligated phosphorus(V) anion. In initial efforts, we observed that treating 2.2a–c with either a basic donor solvent (Et₂O, DMSO, DMF) or a mild base (NEt₃) resulted in unchanged ³¹P or ¹H NMR spectra. Our strategy then shifted towards employing stronger bases that might deprotonate the unbound Ar–NHR moiety (Scheme 2.3).

![Scheme 2.3 Synthesis of hexacoordinate P(V)N₃O₃ anions [2.4a]⁻ and [2.4b]⁻ with phosphoranes 2.2a and 2.2b.](image)

Treating phosphorane 2.2a with n–BuLi (1 equiv) in a mixture of toluene and THF (ca. 4:1 vol./vol.) resulted in an immediate color change from colorless to pale yellow. ³¹P{¹H} NMR spectroscopic analysis of an aliquot removed from the reaction mixture revealed that the signal attributed to phosphorane 2.2a (δ = −48.4) had been consumed and replaced by a new resonance at −97.6 ppm [see Figure 2.7(a)]. The observation of such a high–field chemical shift is characteristic of a hexacoordinate phosphorus(V) center (cf. Li[1.1a], δ_P = −81.7; Li[1.1c] δ_P = −71.3; etc.).³⁰⁻³⁴ After removing the volatiles in vacuo, the crude reaction product was dissolved in a minimum of THF. The slow evaporation of the solvent afforded colorless crystals of Li(THF)₃fac–[2.4a] that were analyzed by X–ray diffraction (see Figure 2.9)
Figure 2.7 $^{31}$P($^1$H) NMR spectra (121.5 MHz, 298 K): (a) the reaction mixture from treating phosphorane 2.2a in toluene with n–BuLi (1 equiv) in n–hexane in the presence of THF; (b) the reaction mixture from treating phosphorane 2.2a in toluene with KH (2.5 equiv) in MeCN.

The analogous reaction of the phenyl–derivative, 2.2b, with n–BuLi (1 equiv) afforded several products as suggested by $^{31}$P($^1$H) NMR spectroscopy (range: −20 to −60 ppm). Thus, reactions with different bases (e.g. KH, LiNH$_2$) were attempted in a variety of solvents (e.g. Et$_2$O, THF, DMSO and MeCN) in the absence or presence of typical ligands for Li$^+$ ion (e.g. 12–crown–4, Et$_3$N and TMEDA). The treatment of an acetonitrile solution of 2.2b with KH (ca. 2.5 equiv) afforded the best results. In this case, the $^{31}$P($^1$H) NMR spectrum of an aliquot removed from the reaction mixture showed signals at −105.4 and −107.3 ppm [see Figure 2.8(a)].
Figure 2.8 $^{31}$P{1H} NMR spectra (121.5 MHz, 298 K): (a) the isolated precipitate in THF from the reaction of 2.2b with KH (2.5 equiv); (b) the crude reaction mixture of 2.2b in toluene first treated with DMSO–d$_6$ and then LiNH$_2$ (2.5 equiv).

For comparison, the reaction of 2.2a with KH under similar conditions also showed two signals in its $^{31}$P{1H} NMR spectrum [$\delta = -97.6, -103.3$, see Figure 2.7(b)]. Alternatively, treatment of a toluene solution of 2.2b with a solution of LiNH$_2$ (2.5 equiv) in DMSO–d$_6$ resulted in a single product as suggested by the presence of a single resonance in the $^{31}$P{1H} NMR spectrum [$\delta = -111.6$, see Figure 2.8(b)]. Based on the high-field chemical shifts observed, we speculated that the potassium and lithium salts of [2.4b]$^+$ were formed successfully. Despite multiple efforts to obtain crystals suitable for X–ray diffraction, the products, M[2.4b] (M = Li, K), could only be isolated as powders.
As mentioned above, single crystals suitable X–ray crystallographic analysis were obtained for \(\text{Li(THF)}_{3}\text{fac–}[4a]\). The molecular structure of \(\text{Li(THF)}_{3}\text{fac–}[2.4a]\) is shown in Figure 2.9 and reveals the presence of the desired hexacoordinate phosphorus(V) anionic centre that is countered by a hexacoordinate lithium cation (\(\text{Li}^+\)). This compound crystallizes in the chiral space group \(P2_12_12_1\) and the assignment of the \(\Lambda\)–isomer was supported by a Flack parameter of 0.06(4). Analysis of three additional crystals finally afforded the structure of the \(\Delta\)–isomer, whose assignment was supported by the Flack parameter of 0.07(4). Selected metrical parameters and related X–ray crystallographic data are tabulated in Table 2.1 and Table 2.2, respectively.

Of note, anions of both \(\Lambda\)– and \(\Delta\text{–fac–}[2.4a]^-\) bind to \(\text{Li}^+\) through the octahedral face containing the three phenoxy oxygens (\(\text{P–O–Ar}\)). Anion \(\text{fac–}[2.4a]^-\) shows significant deviations from regular octahedral symmetry with angles at phosphorus ranging from 83.38(7)° to 95.45(11)° (see Table 2.1). In addition, the P–O bond lengths [avg. 1.764(2) Å] are significantly longer than a typical P(V)–O single bond (range: 1.571 Å to 1.689 Å)\(^{110}\) and to those in phosphoranes \(2.2\text{a–c}\). For comparison, the P–O bonds in \(\text{fac–}[2.4a]^-\) are also longer than those found in salts of anions \([1.1a]^-\) and \([1.1b]^-\), namely Et\(_3\)NH\([1.1a]\) [avg. 1.716(6) Å],\(^{111,112}\) H(DMSO)\(_2\)[1.1a] [avg. 1.716(1) Å],\(^{36}\) H(DMF)\(_2\)[1.1a] [avg. 1.711(1) Å],\(^{36}\) K[1.1a] [avg. 1.715(1) Å],\(^{35}\) cinchonidinium–[1.1b] [avg. 1.714(6) Å],\(^{50}\) H(OEt)\(_2\)[1.1b] [avg. 1.717(1) Å],\(^{43}\) H(THF)\(_2\)[1.1b] [avg. 1.716(4) Å]\(^{46}\) and H(DMF)\(_2\)[1.1b] [avg. 1.715(5) Å].\(^{46}\)

Of particular interest are the P(V)–N bonds in the \(\text{fac–}[2.4a]^-\) anion [avg. 1.7701(21) Å]. These bonds are considerably longer than the P(V)–N single bonds found in tetracoordinate phosphorus(V) compounds of the type X\(_2\)P(=X)–NR\(_2\) (1.662 Å).\(^{110}\) The P(V)–N bonds of only structurally characterized hexacoordinate phosphorus(V) anion, \([1.9]^-\), has recently been reported and displays quite similar bond lengths \{[HNEt\(_3\)]\([1.9]\), avg. 1.787(3) Å\} to those of \(\text{fac–}[2.4a]^-\)\(^{87}\).
Figure 2.9 Molecular structures of: (a) Li(THF)$_3$Δ-fac–[2.4a] and (b) Li(THF)$_3$Λ-fac–[2.4a] (thermal ellipsoids are displayed at 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°):

Li(THF)$_3$Δ-fac–[2.4a]:
- Li(1)–O(1) = 2.164(5), Li(1)–O(2) = 2.232(6), Li(1)–O(3) = 2.297(5), Li(1)–O(4) = 1.990(6),
- Li(1)–O(5) = 2.015(6), Li(1)–O(6) = 2.036(5), P(1)–Li(1)–O(4) = 119.8(2), P(1)–Li(1)–O(5) = 118.9(2), P(1)–Li(1)–O(6) = 122.1(2), O(4)–Li(1)–O(5) = 98.6(2), O(4)–Li(1)–O(6) = 95.8(2), O(5)–Li(1)–O(6) = 96.1(2), O(1)–P(1)–N(2) = 171.07(11), O(1)–P(1)–O(2) = 83.39(9), O(1)–P(1)–O(3) = 83.97(10), O(1)–P(1)–N(3) = 93.09(10), O(2)–P(1)–N(3) = 171.40(11), O(2)–P(1)–O(3) = 84.33(10), O(2)–P(1)–N(1) = 94.43(10), O(3)–P(1)–N(1) = 171.31(11), O(3)–P(1)–N(2) = 93.79(11), N(1)–P(1)–N(2) = 94.51(11), N(3)–P(1)–N(2) = 94.45(11), N(3)–P(1)–N(1) = 94.25(11);

Li(THF)$_3$Λ-fac–[2.4a]:
- Li(1)–O(1) = 2.167(4), Li(1)–O(2) = 2.237(4), Li(1)–O(3) = 2.298(4), Li(1)–O(4) = 1.989(4),
- Li(1)–O(5) = 2.017(5), Li(1)–O(6) = 2.042(4), P(1)–Li(1)–O(4) = 119.06(18), P(1)–Li(1)–O(5) = 122.04(18), P(1)–Li(1)–O(6) = 119.74(17), O(4)–Li(1)–O(5) = 96.08(17), O(4)–Li(1)–O(6) = 98.71(19), O(5)–Li(1)–O(6) = 95.69(18), O(1)–P(1)–N(2) = 171.24(8), O(1)–P(1)–O(2) = 83.38(7), O(1)–P(1)–O(3) = 84.01(7), O(1)–P(1)–N(3) = 93.11(8), O(2)–P(1)–N(3) = 171.41(9), O(2)–P(1)–N(1) = 93.42(8), O(2)–P(1)–O(3) = 84.31(8), O(3)–P(1)–N(1) = 171.40(9), O(3)–P(1)–N(2) = 93.90(9), N(1)–P(1)–N(2) = 94.31(9), N(1)–P(1)–N(3) = 94.26(9), N(2)–P(1)–N(3) = 95.30(8).
Despite being six-coordinate, the lithium cation of Li(THF)$_3$fac–[2.4a] is highly distorted from octahedral and may be alternatively be envisaged a distorted tetrahedral geometry with the vertices being comprised of the three THF molecules and the average O–position of the anion [2.4a]$^-$. The Li–O distances involving donor solvent molecules (THF) [avg. 2.015(5) Å] are shorter than those involving fac–[2.4a]$^- [avg. 2.233(5) \text{ Å}]$ in Li(THF)$_3$fac–[2.4a]. A survey of the Cambridge Structural Database (CSD) revealed that the typical coordination number for Li$^+$ and O–donors is four such as in [Li(THF)$_4$]$^+$. The Li–O bond lengths generally fall in the range from 1.890 Å to 1.950 Å. With an increasing coordination number, an elongation of the Li–O bond is expected due to the reduced electrophilicity at the cationic lithium centre. The Li–O bond lengths in the limited examples of complexes containing six-coordinate lithium cations are substantially longer. Examples include Li[Monensin]·MeCN [Li–O$_\text{avg}$ = 2.245(5) Å],$^{113}$ [Li(THF)$_6$]$^+$ (Li–O$_\text{avg}$ = 2.169 Å),$^{114,115}$ [Li(THF)$_3$S$_3$]$^+$ (Li–O$_\text{avg}$ = 2.105 Å),$^{116}$ [Li(O–O–O)$_2$]$^+$ [O–O–O = trispirotetrahydrofuran, Li–O$_\text{avg}$ = 2.0785(18) Å],$^{117}$ O–O–O = trispiro ether, Li–O$_\text{avg}$ = 2.079(2) Å],$^{118}$ [Li(THF)$_3$RuH$_3$]$^+$ (Li–O$_\text{avg}$ = 2.032 Å),$^{119}$ [Li(THF)$_3$FCl$_2$]$^+$ [Li–O$_\text{avg}$ = 1.989(4) Å],$^{120}$ [Li(THF)$_3$BH$_3$]$^+$ [Li–O$_\text{avg}$ = 2.051 Å],$^{121}$ 1.979(6) Å,$^{122}$ 1.963 Å,$^{123,124}$ 1.956 Å,$^{125}$ 1.942(10) Å,$^{126}$ [Li(THF)$_3$C$_3$]$^+$ (Li–O$_\text{avg}$ = 1.978 Å).$^{127}$ Therefore, the Li–O bonds in Li(THF)$_3$fac–[2.4a] are at the long end of the range for other six-coordinate Li$^+$ ions suggestive of the weakly coordinating nature of the fac–[2.4a]$^-$ anion.

The new salt, Li(THF)$_3$fac–[2.4a] was also characterized by $^{31}$P, $^1$H and $^{13}$C{${^1}$H} NMR spectroscopy in DMSO–$d_6$ solution. The assignments were made with the aid of $^1$H–$^{13}$C HSQC, HMBC, $^{31}$P{${^1}$H} and $^1$H{$^{31}$P} NMR experiments. The $^{31}$P NMR spectrum shows a decet resonance ($\delta = -99.6, ^3J_{PH} = 11 \text{ Hz}$), resulting from coupling to three N–CH$_3$ moieties. Consistent with this observation, the $^1$H NMR spectrum shows one doublet resonance assigned to the N–CH$_3$ moieties.
(δ = 2.65, \(3J_{HP} = 11\) Hz, 9 H, see Figure 2.10). The equivalence of the N–CH₃ moieties is consistent with the retention of the fac–configuration for \([2.4a]\)^− in DMSO–\(d_6\) solution. Consistent with this hypothesis, the \(^{13}\)C\{\(^{1}\)H\} NMR spectrum shows a doublet resonance assigned to the equivalent N–CH₃ moieties of fac–[2.4a]^− (δ = 32.3, \(2J_{CP} = 2\) Hz, see Figure 2.11). In addition, six resonances with the appropriate \(^{13}\)C–\(^{31}\)P couplings were assigned to the aromatic carbon atoms of the equivalent 2–(methylamino)phenoxy ligands of fac–[2.4a]^−. Signals were also observed in the \(^{1}\)H and \(^{13}\)C\{\(^{1}\)H\} NMR spectra that were assigned to the THF moieties in the solution of Li(THF)\(_3\)fac–[2.4a] (δ\(_H\) = 3.62 and 1.78; δ\(_C\) = 67.5 and 25.6). These signals integrate to two THF molecules per lithium and are similar to those of free THF in DMSO–\(d_6\) (δ\(_H\) = 3.58 and 1.72; δ\(_C\) = 67.21 and 25.31). A THF spiking experiment suggest that these THF moieties are not bound to Li\(^+\) in solution.

Figure 2.10 \(^1\)H NMR spectrum (400 MHz, DMSO–\(d_6\), 298 K) of Li(THF)\(_3\)fac–[2.4a] (* indicates the residue DMSO).
Although the NMR data were fully consistent with the proposed structure, we were unable to obtain satisfactory elemental analysis for Li(THF)$_3$fac–[2.4a]. The C and H analysis were consistently low, perhaps resulting from incomplete combustion of the salt, variability in the THF content, and impurities (e.g. LiOH) in the LiH reagent used. To evaluate the stability of the new P(V)N$_3$O$_3$ anion, [2.4a]$^-$, crystals of Li(THF)$_3$fac–[2.4a] were dissolved in several organic solvents under a nitrogen atmosphere (THF, Et$_2$O, DMSO–$d_6$, CDCl$_3$, C$_7$D$_8$) and their $^{31}$P NMR spectra were recorded. The spectra are shown in Figure 2.12. Analysis of each solution by $^{31}$P NMR spectroscopy revealed that the fac–[4a] anion was most stable in DMSO–$d_6$ [Figure 2.12(c)] with traces of phosphorane 2.2a ($\delta = -47.2$) being present in Et$_2$O and THF [Figure 2.12(a) and (b)]. The spectra in poorly donating solvents (CDCl$_3$, C$_7$D$_8$) are indicative of considerable degradation of the P(V)–based anion [Figure 2.12(e) and (f)]. In DMSO, no degradation was observed with one dominant signal being observed in the $^{31}$P NMR spectrum ($\delta = -99.6$, dectet, $^3J_{PH} = 11$ Hz).
assigned to \( \text{fac-}[\underline{2.4}a] \). Presumably, the Li\(^+\) ion is bound by DMSO and/or THF. Interestingly, a second signal at \(-105.4\) ppm [Figure 2.12(d)], barely visible in the initial spectrum, becomes dominant after six months (78\% based on integration of the \(^{31}\text{P}\) NMR spectrum).

![Figure 2.12 \(^{31}\text{P}\{\,^1\text{H}\}\) NMR spectra (121.5 MHz, 298 K) of Li(THF)\(_3\)fac–[\underline{2.4}a] in: (a) Et\(_2\)O; (b) THF; (c) DMSO–\(d_6\) after 10 min; (d) DMSO–\(d_6\) after six months; (e) CDCl\(_3\); (f) C\(_7\)D\(_8\).]

The \(^1\text{H}\) NMR of this new species shows three doublet resonances are (\(\delta = 2.78, 2.74\) and 2.69; 3H, 3H and 3H, respectively; see Figure 2.13) in addition to the doublet resonance previously assigned to the N–CH\(_3\) moieties of \(\text{fac-}[\underline{2.4}a]^−\) (\(\delta = 2.65, \sim 2.6\)H). Based on the integration and the fact that there are three distinct H–environments, we conclude that this new species is the \(\text{mer-}[\underline{2.4}a]^−\) isomer (ca. 78\%) from the slow isomerization of \(\text{fac-}[\underline{2.4}a]^−\) in DMSO solution (Scheme
2.4). Efforts to selectively crystallize Li(mer–[2.4a]) or to separate it in pure form have not yet been successful.

![Figure 2.13](image)

**Figure 2.13** $^1$H NMR spectra (400 MHz, DMSO–d$_6$, 298 K) of Li(THF)\textsubscript{3}fac–[2.4a] (\* indicates the solvent).

![Scheme 2.4](image)

**Scheme 2.4** Slow isomerization between fac–[2.4a]$^-$ and mer–[2.4a]$^-$ in DMSO solution.

### 2.3 Summary

A new methodology has been developed to synthesize neutral phosphoranes and anionic phosphates featuring penta– and hexacoordinate phosphorus(V) moieties with 2–aminophenol...
ligands. In particular, substitution reactions of PCl₅ with ligands 2.1a–c (3.1 equiv) have enabled the facile synthesis and structural characterization of a novel class of phosphoranes (2.2a–c and 2.3a). Subsequent activation of the last potential binding site (−NRH) in phosphorane 2.2a using n–BuLi (1 equiv) afforded the isolable lithium salt, Li(THF)₃fac–[2.4a], which contains the chiral P(V)–anion, fac–[2.4a]⁻. This compound was characterized spectroscopically and structurally. Of note, X–ray diffraction analysis of Li(THF)₃[2.4a] revealed a fac–configuration for anion [2.4a]⁻ and the structures of both the Λ– and Δ–enantiomers were determined by random selection of single crystals. Additionally, lithium cation (Li⁺) adopts a six–coordinate geometry being bound the three phenoxy oxygens of anion fac–[2.4a]⁻ and by three THF molecules. Examination of the long–term stability of solutions of Li(THF)₃fac–[2.4a] in various organic solvents has led to the observation of the spontaneous yet slow isomerization of fac–[2.4a]⁻ into mer–[2.4a]⁻. To our knowledge, this is the first anionic example that contains a σ₆, λ₆ phosphorus(V) centre with P(V)–N bonds. Future work is underway to further investigate the chemical characteristics of Li(THF)₃[2.4a] and its potential use as a weakly coordinating chiral anion.

2.4 Experimental Section

2.4.1 Materials and Methods

All manipulations were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. n–hexane was deoxygenated with dry nitrogen and dried over a column containing activated alumina. Acetonitrile (MeCN), dichloromethane (CH₂Cl₂), diethyl ether (Et₂O), ethyl acetate (EtOAc), n–pentane, toluene, and triethylamine (Et₃N) were distilled over calcium hydride (CaH₂) and stored over molecular sieves (3 Å). Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were dried over molecular sieves (3 Å) and distilled prior to use. THF
was dried over sodium/ benzophenone ketyl and distilled prior to use. Water (H₂O) was triple distilled and deoxygenated with nitrogen prior to use. Methanol (MeOH) was purchased from Sigma–Aldrich and used as received. CDCl₃ was purchased from Cambridge Isotope Laboratories Inc. and used as received. Other deuterated solvents (CD₂Cl₂, CD₃CN, DMSO–d₆ and C₇D₈) were purchased from Sigma–Aldrich and used as received. Phosphorus(v) pentachloride (PCl₅) was purchased from Sigma–Aldrich and sublimed twice prior to use. Potassium hydride (KH) (30 wt% dispersion in mineral oil) was purchased from Sigma–Aldrich, washed with hot n–hexane and dried prior to use. 2–Anisidine (≥99.0%), boron tribromide (BBr₃, Reagent–Plus®, ≥99.0%), n–BuLi (1.6 M in n–hexane), 12–crown–4 ether (98.0%), hexafluorobenzene (C₆F₆, 99.0%), lithium amide (LiNH₂, 95.0%) and potassium bis(trimethylsilyl)amide (KHMDS, 95.0%) were purchased from Sigma–Aldrich and used as received. 2–(methylamino)phenol (2.1a)¹⁰⁷ and 2–(phenylamino)phenol (2.1b)¹⁰⁵,¹⁰⁶ were synthesized following literature procedures. Compound 2.1a was further purified by recrystallization from Et₂O or sublimation in vacuo prior to use. Similarly, compound 2.1b was sublimed in vacuo prior to use.

Unless specified, ¹H, ¹³C{¹H}, ¹⁹F{¹H} and ³¹P{¹H} NMR spectra were recorded at room temperature (ca. 24 °C) on Bruker Avance 300 or 400 MHz spectrometers. ¹H NMR spectra were referenced to the residual protonated solvent signal and ¹³C{¹H} NMR spectra were referenced to the deuterated solvent signal. Phosphoric acid (H₃PO₄, 85%) and trichlorofluoromethane (CFCl₃) were used as external standards (δ = 0.0) for ³¹P and ¹⁹F, respectively. Elemental micro–analyses were performed in the University of British Columbia Chemistry Micro–analysis Facility. Mass spectra were acquired on a Waters Micromass ZQ™ Mass Spectrometer in ESI mode (LRMS), Kratos MS 50 instrument in EI mode (70 eV, HRMS) or Waters Micromass LCT Premier TOF Mass Spectrometer in ESI mode (HRMS).
2.4.2 Syntheses

2.4.2.1 Synthesis of ligand 2.1c

Compound 2.1c has been reported previously\textsuperscript{104} but was prepared here in two steps from 2–anisidine following a different procedure.

*Step (a)* This method was adopted from a general method used to convert Ar–NH\textsubscript{2} to Ar–NH(C\textsubscript{6}F\textsubscript{5})\textsuperscript{129} To a stirred solution of 2–anisidine (2.46 g, 20.0 mmol) in THF (7.5 mL) at –78 °C was added dropwise KHMDS (6.70 g, 40.0 mmol) in THF (20.5 mL). The reaction mixture slowly turned to deep red after 10 min. Subsequently, C\textsubscript{6}F\textsubscript{6} (1.80 g, 10.0 mmol) was rapidly added and the reaction mixture was slowly warmed to ambient temperature (*ca. 1 h*) with vigorous stirring. After 3 d, H\textsubscript{2}O (50 mL) was added and this aqueous–organic mixture was extracted with Et\textsubscript{2}O (3 x 25 mL). The combined organic layers were dried with Na\textsubscript{2}SO\textsubscript{4}, filtered and the solvent was removed *in vacuo*. The isolated yellow–brown solid was further purified by column chromatography on silica gel (230–400 mesh) with *n*–hexane to afford 2,3,4,5,6–pentafluoro–N–(2–methoxyphenyl)aniline (2.1c′) as a colorless solid (2.02 g, 70%). δ\textsubscript{H} (300 MHz, CDCl\textsubscript{3}) 7.0–6.9 (3H, m, Ar–H), 6.7–6.6 (1H, m, Ar–H), 5.9 (1H, br s, –NH), 4.0 (3H, s, –CH\textsubscript{3}); δ\textsubscript{F} (282 MHz, CDCl\textsubscript{3}) –149.1 (2F, dd, \textsuperscript{1}J\textsubscript{FF} = 19 Hz, \textsuperscript{2}J\textsubscript{FF} = 4 Hz, Ar–F), –163.6 (3F, m, Ar–F). HRMS (EI, 70 eV): m/z 289.0526; Calcd for C\textsubscript{13}H\textsubscript{8}F\textsubscript{5}NO: 289.0526. Anal. found (%): C, 54.30; H, 3.19; N, 4.72; Calcd for C\textsubscript{13}H\textsubscript{8}F\textsubscript{5}NO: C, 53.99; H, 2.79; N, 4.84.

*Step (b)* This method was adopted from a general method for the demethylation of Ar–OMe compounds.\textsuperscript{130} To a stirred solution of 2,3,4,5,6–pentafluoro–N–(2–methoxyphenyl)aniline (2.1c′, 1.01 g, 3.5 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (20 mL) at –78 °C was added dropwise BBr\textsubscript{3} (6.6 mL, 70.0 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (70 mL). The reaction mixture was then slowly warmed to ambient temperature (*ca. 1 h*) with vigorous stirring. After 60 h, MeOH was added (50 mL) to the reaction mixture at
0 °C followed by the addition of H$_2$O (50 mL). The mixture was further stirred for another 2 h at ambient temperature. Subsequently, the pH of the aqueous layer was adjusted to 6 with 5% aqueous NaOH solution. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered and the solvent was removed in vacuo. The isolated beige solid was recrystallized from n–hexane to give 2.1c as a white solid (0.72 g, 75%).

δ$_H$ (300 MHz, CDCl$_3$) 7.03–6.76 (4H, m, Ar–H), 5.42 (1H, br s, –NH), 5.30 (1H, s, –OH); δ$_F$ (282 MHz, CDCl$_3$) –152.8 (2F, d, $J_{FF} = 19$ Hz, Ar–F), –164.1 (2F, t, $J_{FF} = 22$ Hz, Ar–F).

### 2.4.2.2 Synthesis of Phosphorane 2.2a

A mixture of 2–(methylamino)phenol (2.1a) (0.38 g, 3.1 mmol) and PCl$_5$ (0.21 g, 1.0 mmol) was dissolved in toluene (10 mL). Evolution of gas was observed immediately. The resultant solution was stirred at reflux temperature for 12 h, during which time the solution changed from colorless to pale yellow. The $^{31}$P{$^1$H} NMR spectrum of an aliquot removed from the solution suggested the almost quantitative conversion of PCl$_5$ (δ = –80.1) to 2.2a (δ = –47.6). The reaction mixture was then cooled to room temperature and passed through a silica plug (230–400 mesh) under a nitrogen atmosphere. Removal of the solvent afforded 2.2a as a white solid (0.29 g, 73%). Colorless crystals of 2.2a suitable for X–ray diffraction were obtained from slow diffusion of n–pentane into a concentrated CH$_2$Cl$_2$ solution of 2.2a at –30 °C over several days. δ$_P$ (121.5 MHz, CDCl$_3$) –48.4; δ$_P$ (162 MHz, CD$_2$Cl$_2$) –47.5; δ$_H$ (300 MHz, CDCl$_3$) 6.97–6.37 (12H, m, Ar–H), 3.79 (1H, s, –NH), 3.36 (6H, d, $^3J_{HP} = 10$ Hz, N–CH$_3$), 2.66 (3H, s, NH–CH$_3$); δ$_H$ (400 MHz, CD$_2$Cl$_2$) 7.15–6.54 (12H, m, Ar–H), 4.02 (1H, s, –NH), 3.49 (6H, d, $^3J_{HP} = 10$ Hz, N–CH$_3$), 2.79 (3H, br s, NH–CH$_3$); δ$_C$ (100.5 MHz, CD$_2$Cl$_2$) 144.9 (d, $J_{CP} = 2$ Hz, Ar–C), 141.8 (d, $J_{CP} = 5$ Hz,
2.4.2.3  **Synthesis of Phosphorane 2.2b**

A mixture of 2–(phenylamino)phenol (2.1b) (0.74 g, 4.0 mmol) and PCl₅ (0.21 g, 1.0 mmol) was dissolved in toluene (10 mL). The resultant solution was stirred under reflux for 12 h, during which time the solution turned from colorless to pale yellow. Analysis of an aliquot removed from the solution by ³¹P NMR spectroscopy showed the complete consumption of the starring material (PCl₅, δ = –80.1) and the presence of a dominant high-field signal (2.2b, δ = –53.9). The reaction mixture was then cooled to room temperature and passed through a silica plug (230–400 mesh) under a nitrogen atmosphere. Removal of the solvent afforded 2.2b as a white solid (0.39 g, 67%). Colorless X–ray quality crystals of 2.2b were obtained from slow diffusion of n–pentane into a concentrated CH₂Cl₂ solution at –30 °C over several days. δₓ (121.5 MHz, CDCl₃) –53.8; δₓ (300 MHz, CDCl₃) 7.44–6.18 (27H, m, Ar–H), 6.00 (1H, s, –NH). LRMS (ESI⁺): m/z (%) 580.5, 581.5 (100, 28, M – H⁺).

2.4.2.4  **Synthesis of Phosphorane 2.2c**

A mixture of 2–[(perfluorophenyl)amino] phenol (2.1c) (1.11 g, 4.0 mmol) and PCl₅ (0.21 g, 1.0 mmol) was dissolved in toluene (10 mL). Evolution of gas was observed immediately. The
resultant solution was stirred at reflux temperature for 12 h, during which time the solution turned from colorless to pale yellow. An aliquot was removed, and the analysis by $^{31}$P NMR spectroscopy indicated the complete consumption of the starting material (PCl$_5$, $\delta = -80.1$) and the appearance of a new dominant high-field resonance ($\delta = -40.7$). Subsequently, the solution was cooled to room temperature, and Et$_3$N (1 mL) was added. $^{31}$P{$^1$H} spectrum of the resultant solution showed the complete conversion of the signal ($\delta = -40.7$) to two new higher-field resonances ($\delta = -54.6$ and $-56.5$). The reaction solution was then passed through a silica plug (230–400 mesh) under a nitrogen atmosphere. Removal of the solvent afforded 2.2c as a white solid (0.43 g, 51%).

Colorless crystals of 2.2c suitable for X-ray diffraction were obtained from slow diffusion of n-pentane into a concentrated CH$_2$Cl$_2$ solution at $-30 \, ^\circ$C over several days. $\delta$$_P$(121.5 MHz, CDCl$_3$) $-55.5$; $\delta$$_H$(300 MHz, CDCl$_3$) 7.06–6.27 (12H, m, Ar–H), 5.59 (1H, s, –NH); $\delta$$_F$(282 MHz, CDCl$_3$) $-145.5$ (4F, d, $J_{FF} = 17$ Hz, Ar–F), $-149.5$ (2F, d, $J_{FF} = 19$ Hz, Ar–F), $-153.9$ (2F, t, $J_{FF} = 21$ Hz, Ar–F), $-161.3$ (2F, s, Ar–F), $-162.2$ (2F, t, $J_{FF} = 21$ Hz, Ar–F), $-163.5$ (3F, m, Ar–F).

### 2.4.2.5 Synthesis of Phosphorane 2.3a

A mixture of 2–(methylamino)phenol (2.1a) (0.26 g, 2.1 mmol) and PCl$_5$ (0.21 g, 1.0 mmol) was dissolved in toluene (10 mL). Evolution of gas was observed immediately. The resultant solution was stirred at room temperature for 12 h, during which time the solution slowly turned from colorless to deep green and then settled with a pale–yellow color. Analysis of an aliquot removed from the solution by $^{31}$P NMR spectroscopy showed the almost quantitative conversion of the starting material (PCl$_5$, $\delta = -80.1$) to chlorophosphorane 2.3a ($\delta = -34.2$). Slow evaporation of the solvent afforded 2.3a as colorless crystals over a week (0.26 g, 85%). $\delta$$_P$ NMR (121.5 MHz, toluene) $-34.2$; $\delta$$_H$(300 MHz, CDCl$_3$) 7.08–6.72 (8H, m, Ar–H), 3.40 (6H, d, $^3J_{HP} = 10$ Hz, –CH$_3$).
2.4.2.6 Synthesis of Li(THF)$_3$fac–[2.4a]

To a stirred solution of phosphorane 2.2a (1.58 g, 4.0 mmol) in toluene (40 mL) at ambient temperature was added THF (ca. 10 mL) followed by the addition of n–BuLi in n–hexane (4.2 mmol, 1.6 M, 2.6 mL). The solution immediately turned pale yellow. After 10 h, the $^{31}$P{$_1$H} spectrum of an aliquot removed from the reaction solution revealed the quantitative conversion of the starting material (2.2a, $\delta = -47.6$) to the product (fac–[2.4a], $\delta = -97.6$). The solvent was removed in vacuo, and the resultant yellow residue was re–dissolved in minimum amount of THF. Recrystallization over several days gave colorless crystals of Li(THF)$_3$fac–[2.4a] suitable for X–ray analysis (2.24g, 91%). $\delta$P (162 MHz, DMSO–d$_6$) –99.6; $\delta$H (400 MHz, DMSO–d$_6$) 6.50–6.07 (12H, m, Ar–H), 3.62 (10H, m, THF, OCH$_2$CH$_2$), 2.65 (9H, d, $^3$J$_{HP}$ = 11 Hz, –CH$_3$), 1.78 (10H, m, THF, OCH$_2$CH$_2$); $\delta$C (100.5 MHz, DMSO–d$_6$) 147.6 (s, Ar–C), 139.2 (d, $^2$J$_{CP}$ = 21 Hz, Ar–C), 118.1 (s, Ar–C), 114.2 (s, Ar–C), 118.1 (s, Ar–C), 106.3 (d, $^3$J$_{CP}$ = 13 Hz, Ar–C), 103.8 (d, $^3$J$_{CP}$ = 13 Hz, Ar–C), 67.5 (s, THF, OCH$_2$CH$_2$), 32.3 (d, $^2$J$_{CP}$ = 2 Hz, –CH$_3$), 25.6 (s, THF, OCH$_2$CH$_2$).

2.4.2.7 Synthesis of Li(THF)$_3$mer–[2.4a]

Crystals of Li(THF)$_3$fac–[2.4a] (50 mg) were dissolved in DMSO–d$_6$ (ca. 0.5 mL) in an NMR tube under a nitrogen atmosphere. After six months at room temperature (ca. 24 °C), the $^{31}$P{$_1$H} NMR spectrum showed that the resonance assigned to fac–[4a] ($\delta = -99.6$) was no longer dominant with a second singlet resonance at –105.4 ppm being dominant. The new higher–field signal was assigned to Li(THF)$_3$mer–[2.4a]. However, attempts to separate Li(THF)$_3$mer–[2.4a] were unsuccessful. $\delta$P (162 MHz, DMSO–d$_6$) –105.4; $\delta$H (400 MHz, DMSO–d$_6$) 6.60–6.00 (12H, m, Ar–H), 3.62 (m, THF, OCH$_2$CH$_2$), 2.78 (3H, d, $^3$J$_{HP}$ = 11 Hz, –CH$_3$), 2.74 (3H, d, $^3$J$_{HP}$ = 9 Hz, –CH$_3$), 2.69 (3H, d, $^3$J$_{HP}$ = 12 Hz, –CH$_3$), 1.78 (m, THF, OCH$_2$CH$_2$); $\delta$C (100.5 MHz, DMSO–d$_6$)
147.1 (s, Ar–C), 146.8 (s, Ar–C), 146.4 (s, Ar–C), 141.2 (d, $^2J_{CP} = 19$ Hz, Ar–C), 140.0 (d, $^2J_{CP} = 10$ Hz, Ar–C), 139.9 (d, $^2J_{CP} = 12$ Hz, Ar–C), 119.2 (s, Ar–C), 119.1 (s, Ar–C), 118.3 (s, Ar–C), 113.9 (s, Ar–C), 113.1 (s, Ar–C), 112.9 (s, Ar–C), 107.1 (d, $^3J_{CP} = 12$ Hz, Ar–C), 106.8 (d, $^3J_{CP} = 2$ Hz, Ar–C), 106.7 (d, $^3J_{CP} = 4$ Hz, Ar–C), 104.0 (d, $^3J_{CP} = 12$ Hz, Ar–C), 103.4 (d, $^3J_{CP} = 12$ Hz, Ar–C), 103.0 (d, $^3J_{CP} = 14$ Hz, Ar–C), 67.5 (s, THF, OCH$_2$CH$_2$), 33.5 (d, $^2J_{CP} = 1$ Hz, –CH$_3$), 33.0 (d, $^2J_{CP} = 3$ Hz, –CH$_3$), 25.6 (s, THF, OCH$_2$CH$_2$).

### 2.4.2.8 Synthesis of K[2.4a]

To a MeCN (ca. 0.5 mL) solution of phosphorane 2.2a (50 mg) in an NMR tube at room temperature was added KH (ca. 40 mg). Evolution of gas was observed immediately. $^{31}$P NMR spectroscopic analysis indicated the complete consumption of 2.2a ($\delta = -47.6$) and the formation of two new higher-field resonances ([2.4a]$^-$, $\delta = -97.6$ and –103.3) upon standing for 12 h. The solution was filtered, and the solvent was removed in vacuo to afford K[2.4a] as a white solid. Yield not determined. $\delta_P$ (121.5 MHz, CD$_3$CN) –97.6 (20%), –103.3 (80%).

### 2.4.2.9 Synthesis of Li[2.4b]

To a stirred solution of phosphorane 2.2b (2.32 g, 4.0 mmol) in toluene (40 mL) at ambient temperature was added DMSO–d$_6$ (ca. 8 mL) followed by the addition of LiNH$_2$ (0.23 g, 10.0 mmol). The solution slowly turned from orange to deep brown along with the formation of an orange precipitate over a period of 12 h. Analysis of an aliquot removed from the reaction solution by $^{31}$P NMR spectroscopy revealed the quantitative conversion of the starting material (2.2b, $\delta = -53.8$) to a new higher-field resonance ([2.4b]$^-$, $\delta = -111.6$). Removed of the solvent in vacuo afforded Li[2.4b] as an orange powder. Yield not determined. $\delta_P$ (121.5 MHz, DMSO–d$_6$) –111.6.
2.4.2.10 **Synthesis of K[2.4b]**

To a stirred solution of phosphorane 2.2b (2.32 g, 4.0 mmol) in MeCN (40 mL) at room temperature was added KH (0.40 g, 10.0 mmol). The solution slowly turned to deep brown along with the formation of a beige precipitate over a period of 12 h. $^{31}$P NMR spectroscopic analysis of the reaction solution suggested the complete disappearance of the starting material (2.2b, δ = −53.8) and the presence of a dominant signal attributable to chlorophosphorane 2.3b (δ = −42.1). The solution was filtered, and the collected precipitate was dried *in vacuo* to afford K[2.4b] as a beige powder. Yield not determined. δ$_P$ (121.5 MHz, THF) −105.4 (85%), −107.3 (15%).

2.4.3 **X–ray Crystallography**

All single crystals were immersed in oil and mounted on a glass fibre. All measurements were made on a Bruker X8 APEX II diffractometer with a TRIUMPH curved–crystal monochromator with Mo$_{Kα}$ radiation. Data were collected and integrated using the Bruker SAINT$^{131}$ software package and corrected for absorption effects using the multi–scan technique (SADABS).$^{132,133}$ All structures were solved by direct methods$^{134}$ and subsequent Fourier difference techniques. Unless noted, all nonhydrogen atoms were refined anisotropically, whereas all hydrogen atoms were included in calculated positions but not refined. All data sets were corrected for Lorentz and polarization effects. All refinements were performed using SHELXL–2014$^{135,136}$ via the OLEX2 interface.$^{137,138}$ Crystal data and refinement parameters for the structures reported in this chapter are listed in Table 3.1. Except for the Δ–isomer of Li(THF)$_3$fac–[2.4a], all crystallographic data has been deposited with the Cambridge Structural Database (CCDC 1563688–1563692).
Table 2.1 Selected metrical parameters for phosphoranes 2.2a–c, 2.3a and P(V)–anion fac–[2.4a]⁻.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>2.2a</th>
<th>2.2b</th>
<th>2.2c</th>
<th>2.3a</th>
<th>Δ–fac–[2.4a]⁻</th>
<th>Δ–fac–[2.4a]⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>P–O(1)</td>
<td>1.6897(12)</td>
<td>1.6947(11)</td>
<td>1.6821(17)</td>
<td>1.6878(16)</td>
<td>1.7713(15)</td>
<td>1.766(2)</td>
</tr>
<tr>
<td>P–O(2)</td>
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<td>1.6176(18)</td>
<td>1.6841(15)</td>
<td>1.7595(15)</td>
<td>1.762(2)</td>
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<td>P–O(3)</td>
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<td>1.6856(17)</td>
<td>1.7631(16)</td>
<td>1.762(2)</td>
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<tr>
<td>P–N(1)</td>
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<td>1.6895(13)</td>
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<td>1.6806(18)</td>
<td>1.7709(19)</td>
<td>1.772(2)</td>
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<tr>
<td>P–N(2)</td>
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<tr>
<td>P–N(3)</td>
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<td>1.6845(13)</td>
<td>1.7009(19)</td>
<td></td>
<td>1.7710(19)</td>
<td>1.770(3)</td>
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</tbody>
</table>

| Bond Angles (°)                                |             |             |             |             |               |               |
| θO(1)–P–N(1)                                   | 89.67(6)    | 88.81(6)    | 89.51(9)    | 89.70(8)    | 87.49(8)      | 87.44(10)     |
| θO(2)–P–N(2)                                   |             |             |             |             | 90.42(8)     | 87.95(8)      | 87.79(11)     |
| θO(3)–P–N(3)                                   | 89.41(6)    | 89.13(6)    | 89.19(9)    |             | 87.54(8)     | 87.50(11)     |
| θap–P–Oap a                                    | 179.60(6)   |             |             |             |               |               |
| θeq–P–Neq b                                    | 125.75(7)   | 129.10(7)   | 127.50(11)  | 131.26(10)  |               |               |
| θeq–P–Oeq or θeq–P–Cl eq c                    | 111.09(6)   | 115.43(6)   | 116.22(10)  | 114.37(7)   |               |               |
| Σ(θX–P–Y)eq                                   | 359.93(7)   | 359.95(7)   | 359.94(11)  | 360.00(10)  |               |               |

a ap = apical. b eq = equatorial. c average angle.
Table 2.2 X–ray crystallographic data for phosphoranes 2.2a–c, 2.3a and Li(THF)\textsubscript{3}fac–[2.4a] (Λ– and Δ–isomers).

<table>
<thead>
<tr>
<th></th>
<th>2.2a</th>
<th>2.2b</th>
<th>2.2c-CH\textsubscript{2}Cl\textsubscript{2}</th>
<th>2.3a</th>
<th>Λ–isomer</th>
<th>Δ–isomer</th>
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</thead>
<tbody>
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<td>C\textsubscript{36}H\textsubscript{28}N\textsubscript{3}O\textsubscript{3}P</td>
<td>C\textsubscript{36}H\textsubscript{33}F\textsubscript{15}N\textsubscript{3}O\textsubscript{3}P·CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>C\textsubscript{14}H\textsubscript{14}ClN\textsubscript{2}O\textsubscript{2}P</td>
<td>C\textsubscript{21}H\textsubscript{21}LiN\textsubscript{3}O\textsubscript{3}P·(C\textsubscript{4}H\textsubscript{8}O)\textsubscript{3}</td>
<td>C\textsubscript{21}H\textsubscript{21}LiN\textsubscript{3}O\textsubscript{3}P·(C\textsubscript{4}H\textsubscript{8}O)\textsubscript{3}</td>
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<td>Space group</td>
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<td>P–1</td>
<td>P2\textsubscript{1}/n</td>
<td>P2\textsubscript{1}/c</td>
<td>P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}</td>
<td>P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}</td>
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<td>β [°]</td>
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<td>18414</td>
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<td>Goodness of fit on F\textsuperscript{2}</td>
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<td>1.040</td>
<td>1.077</td>
<td>1.025</td>
<td>1.030</td>
</tr>
<tr>
<td>R\textsubscript{1}[I &gt; 2σ(I)]</td>
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<td>0.0501</td>
<td>0.0391</td>
<td>0.0545</td>
<td>0.0414</td>
<td>0.0537</td>
</tr>
<tr>
<td>wR\textsubscript{2}(all data)</td>
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<td>0.1348</td>
<td>0.0896</td>
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</tr>
<tr>
<td>CCDC</td>
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<td>1563691</td>
<td>1563692</td>
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<td>1563690</td>
</tr>
</tbody>
</table>

\[ a R_1 = \sum |F_0| - |F_c| / \sum |F_0|. \quad b wR_2 = \frac{\sum w(F_0^2 - F_c^2)^2}{\sum w(F_0^2)^2} \]
2.5 Supplementary Section

Figure 2.14 $^{31}$P$[^1]$H NMR spectra (121 MHz, CDCl$_3$, 298 K) of phosphoranes 2.2a–c and intermediate 2.3a.

Figure 2.15 $^{13}$C$[^1]$H NMR spectrum (100.5 MHz, CD$_2$Cl$_2$, 298 K) of phosphorane 2.2a (* indicates the solvent).
Figure 2.16 $^{19}$F($^1$H) NMR spectrum (282 MHz, CDCl$_3$, 298 K) of phosphorane 2.2c.

Figure 2.17 $^1$H–$^{13}$C($^1$H) HSQC NMR spectrum (400 MHz for $^1$H, 100.5 MHz for $^{13}$C, DMSO–$d_6$, 298 K) of Li(THF)$_3$fac–[2.4a] (The ordinate axis shows the $^{13}$C($^1$H) NMR spectrum and the abscissa axis shows the $^1$H NMR spectrum; * indicates the solvent).
**Figure 2.18** \(^1\text{H}-^{13}\text{C}[^1\text{H}]\) HMBC NMR spectrum (400 MHz for \(^1\text{H}\), 100.5 MHz for \(^{13}\text{C}\), DMSO–d6, 298 K) of Li(THF)\(_2\)\textit{fac}–[2.4a] (The ordinate axis shows the \(^{13}\text{C}[^1\text{H}]\) NMR spectrum and the abscissa axis shows the \(^1\text{H}\) NMR spectrum; * indicates the solvent).
Figure 2.19 $^1H(^{31}P)$ NMR spectra (400 MHz, DMSO–$d_6$, 298 K) of Li(THF)$_3$fac–[2.4a].
Figure 2.20 $^{13}\text{C}{ }^1\text{H}$ NMR spectra (100.5 MHz, DMSO-$d_6$, 298 K) of Li(THF)$_3$fac–[2.4a].
Figure 2.21 $^1$H–$^{31}$P($^1$H) HMBC NMR spectrum (400 MHz for $^1$H, 162 MHz for $^{31}$P, 298 K) of Li(THF)$_3$fac–[2.4a] in DMSO–$d_6$ after 6 months (The ordinate axis shows the $^{31}$P($^1$H) NMR spectrum and the abscissa axis shows the $^1$H NMR spectrum).
**Figure 2.22** Partial $^1$H–$^{31}$P($^1$H) HMBC NMR spectrum (400 MHz for $^1$H, 162 MHz for $^{31}$P, 298 K) of Li(THF)$_3$fac–[2.4a] in DMSO–$d_6$ after 6 months (The ordinate axis shows the $^{31}$P($^1$H) NMR spectrum and the abscissa axis shows the $^1$H NMR spectrum).
Figure 2.23 Partial $^1$H–$^{31}$P{$^1$H} HMBC NMR spectrum (400 MHz for $^1$H, 162 MHz for $^{31}$P, 298 K) of Li(THF)$_3$fac–[2.4a] in DMSO–$d_6$ after 6 months (The ordinate axis shows the $^{31}$P{$^1$H} NMR spectrum and the abscissa axis shows the $^1$H NMR spectrum).
Chapter 3: Attempts to Synthesize P(V)N\textsubscript{6} Anions with 1,2–Phenylenediamine Ligands

3.1 Introduction

It has been demonstrated in Chapter 2 that 2–aminophenol derivatives are a class of promising ligands for P(V) permitting the synthesis of novel five–coordinate P(V)N\textsubscript{2}O\textsubscript{3} phosphoranes and six–coordinate P(V)N\textsubscript{3}O\textsubscript{3} anions. In view of this success, we were motivated to further explore the feasibility of preparing analogous hypervalent P(V)–compounds with 1,2–phenylenediamine derivatives. Specifically, 1,2–phenylenediamine (3.1\text{a}), N,N’–dimethyl–1,2–phenylenediamine (3.1\text{b}) and 3,4,5,6–tetrafluoro–N,N’–diphenyl–1,2–phenylenediamine (3.1\text{c}) were selected for our preliminary investigations (Figure 3.1).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3_1}
\caption{Three 1,2–phenylenediamine derivatives investigated in this chapter}
\end{figure}

In this chapter, following the similar synthetic protocol developed previously with 2–aminophenol ligands, attempts to prepare penta– and hexacoordinate P(V)–derivatives with 3.1\text{a}–\text{c} will be described. An interesting N\textsubscript{4}–substituted phosphonium salt was isolated upon the reaction of 3.1\text{b} with PCl\textsubscript{5} and was characterized spectroscopically. The exact formulation has yet to be assigned to the products isolated from the reaction mixtures of 3.1\text{a} and 3.1\text{c} with PCl\textsubscript{5} due to the lack of conclusive spectroscopic data.
3.2 Results and Discussion

3.2.1 Reaction of 3.1a with PCl₅

Few reports have been found in the literature regarding the reaction of 1,2-phenylenediamine with PCl₅. It has been shown by Anand et al.¹³⁹ that reaction of 3.1a (2 equiv) and PCl₅ results in isolation of a stable N₄-substituted phosphorane 3.2a (Scheme 3.1), which is similar to the intermediate 2.3a isolated from the reaction of 2-aminophenol (2 equiv) with PCl₅. As a starting point, we investigated the reaction of PCl₅ with a higher equivalence of 3.1a (3.1 equiv) in an effort to prepare the corresponding N₅-substituted phosphorane.

![Scheme 3.1 Reaction of 3.1a (2 equiv) with PCl₅ reported by Anand et al.](image)

In particular, a mixture of 3.1a (3.1 equiv) and PCl₅ was refluxed in toluene under a nitrogen atmosphere. An off-white precipitate was formed after 12 h and isolated from the pale-yellow solution by filtration. Analysis of an aliquot removed from the filtrate by ³¹P NMR spectroscopy revealed the drastically broadened base-line with no presence of any significant resonances. The ¹H NMR (in CD₃OD) and mass spectra (in MeOH) of the precipitate [LRMS (ESI⁺): m/z (%) 109.0 (100, 3.1a + H⁺); LRMS (ESI⁻): m/z (%) 34.6, 36.6 (100, 37, Cl⁻)] are consistent with the unreacted 3.1a as hydrochloride salts [see Figure 3.1(a)]. However, the ³¹P NMR spectra showed sharp singlet resonances [δ = 10.0 in CD₃OD, δ = −0.9 in DMSO–d₆; see Figure 3.2(a) and Figure 3.2(b), respectively]. These results are consistent with a mixture of the
(mono- and/or di-) hydrochlorides of 3.1a and partially substituted PCl₅ [e.g. P(HNC₆H₄NH)Cl₃]. Additional evidence for the presence of species containing partially substituted phosphorus can be gleaned from the ¹H and ¹H{³¹P} NMR spectra of the product in DMSO–d₆, in which an interesting ¹H–³¹P coupling ($J_{HP} = 17$ Hz) was revealed [see Figure 3.1(b)]. Noteworthy, dissolution of the product in DMSO–d₆ afforded a reddish cloudy solution and gave a different ¹H NMR spectrum after ca. 12 h [Figure 3.1(c)]. Nevertheless, we could not obtain conclusive spectroscopic data to gain insight into the chemical structural of the product due to its limited solubility in other organic solvents (e.g. $n$–hexane, toluene, Et₂O, CH₂Cl₂, CDCl₃, MeCN, etc.). Efforts to separate or to recrystallize the phosphorus–containing product were not successful.

![Figure 3.1](image.png)

**Figure 3.1** ¹H NMR spectra (400 MHz, 298 K) of the off–white precipitate isolated from the reaction of 3.1a (3.1 equiv) with PCl₅ in: (a) CD₃OD; (b) DMSO–d₆ after 10 min; (c) DMSO–d₆ after 12 h (* indicates the residual CD₃HOD and DMSO; † indicates the residual toluene solvent).
Figure 3.2 $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectra (162 MHz, 298 K) of the off–white precipitate isolated from the reaction of 3.1a (3.1 equiv) with PCl$_5$ in: (a) CD$_3$OD; (b) DMSO–$d_6$.

3.2.2 Reaction of 3.1b with PCl$_5$

We hypothesized that introduction of alkyl substituents onto the amino groups of 3.1a may improve the solubility of the prospective products from the reaction with PCl$_5$. To this end, ligand 3.1b with methyl substituents was investigated under the same condition (i.e. 3.1 equiv of ligand, reflux in toluene under a nitrogen atmosphere; Scheme 3.2). Over a period of 12 h, the reaction mixture turned to a clear light green solution and a purple precipitate was readily isolated via filtration.

Scheme 3.2 Substitution reaction of PCl$_5$ with 3.1b.
$^{31}$P spectroscopic analysis of the filtrate revealed that multiple lower–field resonances ($\delta = 148.3, 37.2, 22.9$ and 13.2) were present and that the signal assigned to PCl$_5$ ($\delta = -80.1$) was absent [see Figure 3.3(a)]. The $^{31}$P NMR spectrum of the purple precipitate in CDCl$_3$ showed one singlet resonance at 36.8 ppm assigned to compound 3.2b [Figure 3.3(b)]. Sublimation in vacuo afforded pure 3.2b as a dark blue solid. Although multiple attempts to obtain the single crystal of 3.2b were unsuccessful, the proposed structure for 3.2b was unequivocally confirmed by multinuclear NMR spectroscopies ($^1$H and $^{13}$C), LRMS and elemental microanalysis. The ionic nature of 3.2b in solution was preliminarily revealed by its low–field $^{31}$P shift ($\delta = 36.8$) which is characteristic of a phosphonium cation. By comparison, the analogous compound, phosphorane 2.3a, showed a dramatically up–field shifted signal ($\delta = -34.2$) in the same solvent (CDCl$_3$) [see Figure 3.3(c)].

![Figure 3.3 $^{31}$P NMR spectra (162 MHz, 298 K) of (a) the crude reaction mixture of 3.1b (3.1 equiv) and PCl$_5$ after reflux in toluene for 12 h; (b) 3.2b in CDCl$_3$; (c) 2.3a in CDCl$_3$.](image-url)
Examination of the $^{31}\text{P}$ and $^1\text{H}$ (Figure 3.4) NMR spectra of 3.2b in CDCl₃, along with the $^1\text{H}\{^{31}\text{P}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, permitted the determination of the $^1\text{H}–^{31}\text{P}$ coupling constant between the phosphorus and the twelve adjacent methyl protons ($P–\text{NCH}_3$, $^3J_{HP} = 11$ Hz). The $^{31}\text{P}$ NMR spectrum showed a sept splitting pattern, suggesting that the phosphonium cation of 3.2b adopts a tetrahedral geometry in solution [see Figure 3.3(b)]. Similarly, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed a doublet resonance ($\delta = 28.1$, $^2J_{\text{CP}} = 5$ Hz) assigned to the equivalent N–CH₃ moieties of 3.2b. Three resonances with the appropriate $^{13}\text{C}–^{31}\text{P}$ couplings were assigned to the carbon atoms of the equivalent dimethyl–1,2–phenylenediamino ligands in 3.2b (see Figure 3.5).
3.2.3 Reaction of 3.1c with PCl₅

Known compound 3.1c is prepared according to a literature procedure. The amine protons (–NH) of 3.1c were expected to be relatively more acidic than those of 3.1a and 3.1b due to the presence of fluorine atoms and the phenyl substituents on the amino–group. Reflux of a mixture of 3.1c (3.1 equiv) and PCl₅ in toluene over a period of 12 h resulted in the formation of a dark purple gel that is barely soluble in any organic solvents (e.g. CDCl₃, CD₃CN, DMSO–d₆, CD₃OD etc.). ${^31}$P NMR spectroscopic analysis of an aliquot removed from the reaction mixture suggested the existence of multiple species [δ = 0 to 15, see Figure 3.6(a)]. Equally revealing is the drastically broadened base–line, indicating that the insoluble purple gel should chemically contain phosphorus.

Figure 3.5 ${^{13}}$C[¹H] NMR spectrum (400 MHz, CDCl₃, 298 K) of 3.2b (* indicates the solvent).
Figure 3.6 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (121.5 MHz, 298 K) of (a) the crude reaction mixture of 3.1c (3.1 equiv) and PCl$_5$ after reflux in toluene for 12 h; (b) the CD$_3$CN solution of the insoluble purple gel after stirring for 12 h at 50 °C; (c) the CD$_3$OD solution of the insoluble purple gel after stirring for 12 h at 50 °C.

Efforts were made to dissolve the purple gel by stirring it in CD$_3$CN and CD$_3$OD for ca. 12 h with moderate heat (50 °C). However, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these solutions showed similar signals [$\delta = 0$ to 7, see Figure 3.6(b) and (c)] with majority of the gel still undissolved. No characteristic resonance attributable to the penta– ($\delta = -30$ to $-60$) or hexacoordinate ($\delta = -80$ ppm to $-120$ ppm) derivatives of phosphorus(V) was observed. As a consequence of the limited solubility and the unexpected $^{31}\text{P}$ shifts, further investigation was not conducted.

### 3.3 Summary

Reactions of 1,2–phenylenediamine derivatives 3.1a and 3.1c (3.1 equiv) with PCl$_5$ in toluene at reflux temperature afforded products with limited solubility in most organic solvents.
Preliminary $^{31}$P NMR spectroscopic analysis of these compounds revealed similar resonances that fall in the region of 0 ppm to 20 ppm. No plausible chemical structures nor formulas were proposed in accordance with the data obtained thus far. In contrast, formation of a phosphonium salt (3.2b) was confirmed upon the reaction of 3.2a (3.1 equiv) with PCl$_5$ under the same condition. Compound 3.2b was spectroscopically characterized.

### 3.4 Experimental Section

#### 3.4.1 Materials and Methods

All manipulations were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. Diethyl ether (Et$_2$O) and toluene were distilled over calcium hydride (CaH$_2$) and stored over molecular sieves (3 Å). THF was dried over sodium/benzophenone ketyl and distilled prior to use. Petroleum ether (ACS grade, 35 °C to 60 °C) was dispensed from the University of British Columbia Chemistry Stores and used as received. Water (H$_2$O) was triple distilled and deoxygenated with nitrogen prior to use. Methanol (MeOH) was purchased from Sigma–Aldrich and used as received. CDCl$_3$ was purchased from Cambridge Isotope Laboratories Inc. and used as received. Other deuterated solvents (CD$_3$CN, DMSO–d$_6$ and CD$_3$OD) were purchased from Sigma–Aldrich and used as received. Aniline (ACS reagent, ≥99.5%) was distilled over CaH$_2$ and stored over molecular sieves (3 Å). 1,2–Phenylenediamine (3.1a, aflaked, 99.5%), hexafluorobenzene (C$_6$F$_6$, 99.0%), hexamethylphosphoramide (HMPA, 99.0%), lithium amide (LiNH$_2$, 95.0%), N,N′–dimethyl–1,2–phenylenediamine (3.1b, 97.0%) were purchased from Sigma–Aldrich and used as received. 3,4,5,6–tetrafluoro–N,N′–diphenyl–1,2–phenylene–diamine (3.1c) was synthesized following literature procedures.$^{140}$
Unless specified, $^1\text{H}$, $^{13}\text{C}$$^1\text{H}$, $^{19}\text{F}$$^1\text{H}$ and $^{31}\text{P}$$^1\text{H}$ NMR spectra were recorded at room temperature (ca. 24 °C) on Bruker Avance 300 or 400 MHz spectrometers. $^1\text{H}$ NMR spectra were referenced to the residual protonated solvent signal and $^{13}\text{C}$$^1\text{H}$ NMR spectra were referenced to the deuterated solvent signal. Phosphoric acid (H$_3$PO$_4$, 85%) and trichlorofluoromethane (CFCl$_3$) were used as external standards ($\delta = 0.0$ ppm) for $^{31}\text{P}$ and $^{19}\text{F}$, respectively. Elemental micro–analyses were performed in the University of British Columbia Chemistry Micro–analysis Facility. Mass spectra were acquired on a Waters Micromass ZQ™ Mass Spectrometer in ESI mode (LRMS).

3.4.2 Syntheses

3.4.2.1 Reaction of 3.1a with PCl$_5$

A mixture of 3.1a (0.34 g, 3.1 mmol) and PCl$_5$ (0.21 g, 1.0 mmol) was dissolved in toluene (10 mL). The resultant solution was stirred at reflux temperature for 12 h, at which time the reaction mixture changed to pale yellow and the formation of an off–white precipitate was observed. Analysis of the clear solution by $^{31}\text{P}$ NMR spectroscopy revealed a drastically broadened base line and that the signal assigned to the starting material (PCl$_5$, $\delta = –80.1$) was not present. The reaction mixture was then cooled down to ambient temperature and filtered under a nitrogen atmosphere. Subsequently, the isolated precipitate was washed with toluene and dried in vacuo.

3.4.2.2 Synthesis of Phosphonium Salt 3.2b

A mixture of 3.1b (1.00 g, 7.3 mmol) and PCl$_5$ (0.48 g, 2.3 mmol) was dissolved in toluene (25 mL). The resultant solution was stirred at reflux temperature for 12 h, during which time the reaction mixture turned from dark purple to pale green along with the formation of a purple
precipitate. The $^{31}$P NMR spectrum of an aliquot removed from the reaction solution showed multiple resonances (δ = 148.3, 36.8, 22.9 and 13.2) and that the PCl$_5$ resonance (δ = −80.1) was absent. The reaction solution was then cooled to ambient temperature and filtered under a nitrogen atmosphere. Subsequently, the isolated purple precipitate was washed with toluene, dried in vacuo and sublimed to afford 3.2b as a dark purple solid (0.25 g, 33%). δ$_P$ (162 MHz, CDCl$_3$) 35.6; δ$_H$ (400 MHz, CDCl$_3$) 7.10–7.00 (8H, m, Ar–H), 3.21 (12H, d, $^3$J$_{HP}$=11 Hz, –CH$_3$); δ$_C$ (100.5 MHz, CDCl$_3$) 129.2 (d, $^2$J$_{CP}$ =20 Hz, Ar–H), 123.4 (s, Ar–H), 110.2 (d, $^3$J$_{CP}$ =10 Hz, Ar–H), 28.1 (d, $^2$J$_{CP}$ =5 Hz, –CH$_3$). LRMS (ESI$^+$) m/z (%) 299.3, 300.3, 301.3 (100, 28, 2, M$^+$); LRMS (ESI$^-$) m/z (%) 34.8, 36.7 (100, 37, Cl$^-$). Anal. Found (%): C, 57.67; H, 6.37; N, 16.33; Calcd for C$_{16}$H$_{20}$ClN$_4$P: C, 57.40; H, 6.02; N, 16.74.

3.4.2.3 Reaction of 3.1c with PCl$_5$

A mixture of 3.1c (1.03 g, 3.1 mmol) and PCl$_5$ (0.15 g, 0.7 mmol) was dissolved in toluene (10 mL). The resultant deep purple solution was stirred at reflux temperature for 12 h, during which time the reaction solution turned pale green along with the formation of a purple gel. $^{31}$P NMR spectroscopic analysis of an aliquot removed from the clear solution suggested the disappearance of the signal assigned to PCl$_5$ (δ = −80.1) and the emergence of multiple signals in the region from 0 ppm to 14 ppm. The reaction mixture was then cooled to room temperature, and the solution was decanted. Subsequently, the isolated purple gel was washed with toluene and dried in vacuo.
Chapter 4: Summary and Future Work

4.1 Summary of Thesis

In view of our previous success with the Brønsted acids featuring the P(V)O₆ anion \([1.1b]^{-}\) \(\{\text{HL}_2\text{[1.1b]}\}^{-}\) \((L = \text{Et}_2\text{O}, \text{THF} \text{ and } \text{DMF})\) in cationic polymerization, we have embarked on the development of novel hexacoordinate anionic phosphates that contain N–donors. Although P(V)–anions with bidentate O,O–, C,O– and C,C–donor ligands are known, examples containing bidentate N,O–donor or N,N–donor ligands have remained largely unexplored.

As a starting point, 2–aminophenol ligands were chosen for our preliminary investigations. In Chapter 2, a facile synthetic methodology to access neutral phosphoranes \((2.2a–c)\) and anionic phosphates \((\text{2.4a}^{-} \text{ and } \text{2.4b}^{-})\) with 2–aminophenol ligands \((2.1a–c)\) was presented (Scheme 4.1). Of note, deprotonation of phosphorane \(2.2a\) with \(n\–\text{BuLi}\) (1 equiv) afforded chiral P(V)–anion \([2.4a]^{-}\) as a stable lithium salt, \(\text{Li(THF)}_3\text{fac–2.4a}\). This compound was characterized spectroscopically and structurally, representing the first anionic example that contains a \(\sigma^6, \lambda^6\) phosphorus(V) centre with P(V)–N bonds.

![Scheme 4.1 Synthesis of hexacoordinate P(V)–anions \([2.4a]^{-}\) and \([2.4b]^{-}\) bearing bidentate N,O–donor ligands.](image-url)

\[\begin{align*}
2.1a & \quad R = \text{Me} \\
2.1b & \quad R = \text{Ph} \\
2.1c & \quad R = \text{C}_6\text{F}_5 \\
2.2a & \quad R = \text{Me} \\
2.2b & \quad R = \text{Ph} \\
2.2c & \quad R = \text{C}_6\text{F}_5 \\
\end{align*}\]
We further examined the possibility of incorporating bidentate N,N–donor ligands into anionic derivatives of phosphorus(V). Chapter 3 discusses the reactions of three amino–substituted 1,2–phenylenediamine derivatives (3.1a–c) with PCl₅. Refluxing of a stoichiometric amount (3.1 equiv) of 3.1a and 3.1c in toluene affords products with limited solubility that hinders their structural characterization. In contrast, a readily soluble P(V)N₄ phosphonium salt, 3.2b, was isolated from the reaction mixture of 3.1b and PCl₅ under the same condition (Scheme 4.2) and was spectroscopically characterized.

![Scheme 4.2 Synthesis of P(V)N₄ phosphonium salt 3.2b.](image)

### 4.2 Future Work

Our attention in the future will focus on the isolation and detailed characterization of anion [2.4b]⁻. Concurrently, attempts to synthesize the analogous P(V)–anions with phosphorane 2.2c will be undertaken. The application of P(V)O₆ anionic phosphates³⁰,³⁵,³⁶,⁴³–⁴⁵ and P(V)N₄ phosphonium salts in some chemical transformations and in organocatalysis has been well documented.¹⁴¹,¹⁴² Thus, further examination of Li(THF)₃fac–[2.4a] and 3.2b in the quest for potential specialty applications, particularly in cationic polymerization, is also of future interest.

Another logical expansion of this thesis work involves the investigation of the mechanistic/kinetic aspects of the substitution reactions between aromatic dinucleophiles (2–aminophenol and 1,2–phenylenediamine) and PCl₅. In addition, efforts will be made to introduce
electron–withdrawing substituents into ligands 2.1a–c and 3.1a–c and investigate the reactions of the resultant derivatives with PCl₅.

4.3 Concluding Remarks

The development of synthetic procedures to incorporate novel ligands into hypervalent derivatives of phosphorus(V) could pave the road to fascinating molecules with to date unassessed potential for application. In this regard, we examined 2–aminophenol derivatives and first demonstrated their capability as viable N,O–ligands for P(V). To conclude, a new methodology has been developed to synthesize neutral phosphoranes and anionic phosphates featuring five– and six–coordinate phosphorus(V) moieties with 2–aminophenol ligands. The first known example of a salt that contains a σ⁶, λ⁶ phosphorus(V) centre with P(V)–N bonds was reported and fully characterized. The established synthetic routine with 2–aminophenol ligands may serve as a spark and potentially enables the incorporation of other heteroatoms into this type of compounds. If successful, intriguing possibilities will be opened for chemists to explore, further expanding the frontiers of this exciting field.
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