Low-Coordinate Organophosphorus Compounds

Synthesis and Optoelectronic Properties

MUHAMMAD ANWAR SHAMEEM
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Abstract

This thesis work is based on the development of novel organopnictogen compounds and the exploration of their potential applications in organic electronics. In particular, incorporation of phosphorus and arsenic into π-conjugated systems is known to modify the optoelectronic properties.

The first chapter of this thesis is fully devoted to the development of a metal-free synthetic route that allows direct, sequential and stereoselective alkynylation of C,C-dibromophosphaalkenes. The subsequent unusual reactivity of thus synthesized C-monodiacetylenicphosphaalkenes with terminal acetylenes afforded highly substituted 1-phosphpha-1,3-butadienes heavier analogue of all carbon 1,3-butadiene motifs. Optimization of the reaction condition favored exclusively the formation of 1-phospha-1,3-butadienes. Unveiling the unique cyclization of the 3-ynyl-1-phospha-1,3-butadiene gave highly substituted phosphole derivatives. Further, it has been experimentally shown that the P=C unit is essential for this rare cyclization and rearrangement to give π-conjugated phosphole derivatives.

The second chapter of this thesis work deals with incorporation of P/As in the form of phosphinidene and or arsinidene units as an exocyclic substituent at the bridge of the fused rigid cyclpentadithiophenes (p-CPDT) core. Furthermore, it demonstrates how this chemical modification at the bridgehead position selectively lowers the LUMO level. At a later stage, substitutions at α and α’ positions of the central CPDT core was used to modify the HOMO level without further affecting the LUMO level. We also performed DFT calculations on these phosphinidene/arsinidene p-CPDT derivatives to theoretical evaluate the impact of P and or As incorporation. The phosphinidene/arsinidene p-CPDT derivatives were fully characterized using electrochemical and optical spectroscopic techniques including transient absorption spectroscopy. Additionally, the arsinidene-p-CPDT were electrochemically polymerized, and the resultant polymer film was characterized by means of SEM and EDX.

The last chapter of this research work is dealing with the exploration and functionalization of open-ended small fragments of fullerene-C60 such as sumanene and truxene. Functionalisation of these motifs was achieved via the introduction of pnictogens (P/As), either in the form of phosphinidene/arsinidene or as heteroles. The optoelectronic spectra of the unprecedented pnictindenotruxene exhibited significantly redshift absorption and three fully reversible reduction events upon electrochemical reduction.

Keywords: Pnictogen, phosphorus, arsenic, phosphaalkenes, arsaalkenes, phospholes, arsoles, alkynes, π-conjugation, PAHs, Fullerene-C60, sumanene, truxene, organic electronics

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To my beloved Mom and Dad
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


II  Shameem M.A, Orthaber A. Highly branched 2,3-diyne-1-phospha-1,3-butadiene motifs via Pd/Cu mediated alkynyl additions. In manuscript.


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<td>I</td>
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<td>II</td>
<td>Performed all the synthetic work and characterization except X-ray. Contributed to the writing of the manuscript.</td>
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<tr>
<td>III</td>
<td>Performed all the synthetic work and characterization except X-ray and transient absorption spectroscopy. Contributed to the writing of the manuscript.</td>
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<tr>
<td>Chapter-5</td>
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## Abbreviations

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<th>Full Form</th>
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<tbody>
<tr>
<td>CAN</td>
<td>Ceric ammonium nitrate</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DBU</td>
<td>1,8-Diazabicyclo[5.4.0]undec-7-ene</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DEE</td>
<td>Diethynylethene</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>Dmp</td>
<td>2,5-Dimesitylphenyl</td>
</tr>
<tr>
<td>E-Chem</td>
<td>Electrochemistry</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Bandgap</td>
</tr>
<tr>
<td>eq.</td>
<td>Equivalent</td>
</tr>
<tr>
<td>FBW</td>
<td>Fritsch-Buttenberg-Wiechell</td>
</tr>
<tr>
<td>LDA</td>
<td>Lithium diisopropylamide</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>Mes*</td>
<td>Supermesityl = 2,4,6-tri-$t$-butylphenyl</td>
</tr>
<tr>
<td>m-CPBA</td>
<td>meta-Chloroperoxybenzoic acid</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>TBAPF$_6$</td>
<td>Tetrabutylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>TEE</td>
<td>Tertraethynylethene</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TMEDA</td>
<td>$N,N,N',N$-Tetramethylethylenediamine</td>
</tr>
<tr>
<td>Spec-Echem.</td>
<td>Spectroelectrochemistry</td>
</tr>
<tr>
<td>Tol</td>
<td>Tolyl</td>
</tr>
<tr>
<td>Ts</td>
<td>Tosyl</td>
</tr>
<tr>
<td>VT</td>
<td>Variable temperature</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
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</table>
1 Introduction

With the discovery that small organic molecules can act as conductor/semiconductor, since then this field of organic conductors, attracted much of interest due to their potential application as components in electronics and optoelectronics devices. Moreover, the organic electronic offer great flexibility and low-cost manufacturing much reduce size and high efficiency compare to solid-state electronics. The advantage with organic electronic are huge, as they can be easily print on flat surface i.e. electronic paper completely change the look of foreseen future life. As example large area, organic photovoltaic cells (OPVs) painted on the walls and roofs of buildings and industries, transparent display windows, organic field transistors (OFETs), and organic light emitting diodes (OLEDs) etc. The progressive understanding within the fundamentals of electronics properties and the synthetic molecular designing is essential to fabricate the future organic electronics materials. Huge advancement have been already reported such as polycrystalline pentancene films exhibit high charge carrier motilities relative to amorphous silicon.\cite{1} Organic molecular semiconductor usually exhibit high photoluminescence quantum yield with the capability of flexible color ranges. However the common problem associated with such systems are their long-term structural instability.\cite{2} One way to overcome this problem is to use organic conjugated polymers that maintain good charge transport, enhance photoluminescence, structure rigidity as well as metal like semiconducting properties. In this regards polyphenylene vinylene exhibit rigid structure with excellent mechanical properties have been used as active layer in OLEDs. Similarly, it has been demonstrated that oligothiophenes possess good field effect mobilities \cite{3} indeed the most crucial factor to be consider in these organic polymers to adjust the energy positons of HOMO-LUMO energy levels that in turn modify the optoelectronics properties. Fine-tuning of HOMO-LUMO energy levels can be achieve via the combination donor (n-type) and acceptor (p-type) systems. In other way to adjust the HOMO-LUMO levels is to incorporate the pnictogen center such as phosphorus in its low coordinate state significantly lower the LUMO levels.\cite{4} Phosphorus based organic polymers such as copolymer of phosphafluorenes have been reported and exhibit blue and white electroluminescence depending on the modification at the
phosphorus center. \cite{5} This thesis work is concerned with incorporation of pnictogen into small π-conjugated molecules, characterization and studies of the associated optoelectronic properties.
2 Background

2.1 Multiple bonding in heavier main group elements

Early bonding concepts suggested that elements with principle quantum numbers greater than 2, i.e., heavier elements, would not usually be capable of undergoing homonuclear or heteronuclear multiple bond formation involving (p-p) π-bonds.\[^6\] The proposed explanation for this was that these elements possess more diffused frontier orbitals, leading to poor orbital overlap. The resulting π-bonds would therefore be weaker, and tend to oxidize and/or oligomerize; hence, it was assumed that multiple-bonded systems involving heavier main group elements could exist, but were usually short-lived or highly reactive. It was further argued that π-contributions in multiple bonds between lighter elements (C, N, O) are about equal to or larger than the σ-contributions seen in the cases of C-C and O-O double bonds respectively (Table 1). Additionally lighter elements are relatively small in size hence; valence s- and p-orbitals can roughly be in the same region of space and approximately equivalent in size allowing efficient hybridization. When comparing multiple bonding in lighter elements to heavier elements (generally 2\(^{\text{nd}}\) and 3\(^{\text{rd}}\) row elements) based on arbitrary σ- and π- contributions, the π-contribution for homonuclear multiple bonded compounds of 2\(^{\text{nd}}\) row elements are almost double when compared to those seen for 3\(^{\text{rd}}\) row (Si, P). On the other hand, only slight differences in π-contributions were observed when comparing multiple bonds in 3\(^{\text{rd}}\) and subsequent higher row elements (Table 1). Most surprisingly, in the case of 3\(^{\text{rd}}\) and higher row elements, the σ-contributions are significantly higher (with the exception of CS\(_2\) and SO\(_2\), for which σ and π-contributions are almost comparable) than the respective π-contribution. This reduced π-contribution possibly caused by an inefficient overlap of higher order diffuse valence orbitals available for bonding in the case of heavier elements. Hence, generally in the case of heavy element combinations such as Si-Si, P-P or As-As, the σ-bond is much more stable when compared to 2\(^{\text{nd}}\) row lighter elements in particular to O-O and N-N σ-bonds (Table 1). The latter possess relatively weaker σ-bonds possibly due to interatomic electronic repulsion of lone pairs in these lighter elements.\[^7\] [^8] [^9]\ In practice the relative π-bond strength can also be estimated from the hydrogenation energies of the multiple bonded systems (Table 1). Heats of hydrogenation involving 2\(^{\text{nd}}\) row elements such as C=C, C=N, and N=N are approximately of the same strength however, proceeding down the group a significant decrease in π-bond strength
can be noticed. This is well exemplified by the P=P double bond which is approximately half of the strength of the C=C double bond and hence more reactive. Based on the heats of hydrogenations, the Si=Si double bond is the weakest thus most reactive double bond followed by the Si=P double bond.\[10\]

Table 1. $\pi$-bond strengths (kcal/mol) of lighter 2nd row elements (C, N and O) vs heavier (Si, P, or As and S) main group elements.

<table>
<thead>
<tr>
<th>X= X/Y (π-bond)</th>
<th>Heat of Hydrogenation (kcal/mol)</th>
<th>Bond increments (kcal/mol) for σ/π-bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C</td>
<td>62</td>
<td>80/70</td>
</tr>
<tr>
<td>N=N</td>
<td>69</td>
<td>38/70</td>
</tr>
<tr>
<td>O=O</td>
<td>-</td>
<td>35/83</td>
</tr>
<tr>
<td>C=N</td>
<td>65</td>
<td>70/65</td>
</tr>
<tr>
<td>Si=Si</td>
<td>23</td>
<td>46/28</td>
</tr>
<tr>
<td>C=Si</td>
<td>37</td>
<td>72/33</td>
</tr>
<tr>
<td>C=P</td>
<td>45</td>
<td>64/48</td>
</tr>
<tr>
<td>P=P</td>
<td>35</td>
<td>48/34</td>
</tr>
<tr>
<td>As=As</td>
<td>-</td>
<td>42/29</td>
</tr>
<tr>
<td>Si=P</td>
<td>35</td>
<td>-</td>
</tr>
</tbody>
</table>

Despite this, curiosity regarding the possibility of stable heavier multiple bonded compounds persisted within the main group chemistry community. This was encouraged by examples of compounds involving the previously mentioned multiple bonds between lighter carbon/oxygen atoms and the heavier element sulfur, which give rise to the long-known materials SO$_2$ (from the global sulfur cycle) and CS$_2$ (from the degradation of fossils).\[12\] \[13\] The potential synthetic applications of heavier multiple bonded compounds, which could act as possible substitutes for unsaturated carbonaceous materials in various chemical reactions such as hydrogenations, olefinations, and cycloadditions, also excited researchers.\[14\] \[15\] \[16\] \[9\] Meanwhile, the ability to influence the electronic properties of conventional carbon-rich polymers\[17\] \[17\] attracted further attention to attempt to stabilize multiple bonds involving heavier elements. The quest to engage heavier elements in multiple bonds continued until
experiments and theoretical calculations revealed that heavier elements could form homo- and heteronuclear multiple bonds when provided with proper steric or electronic stabilization by means of delocalization or metal coordination.\textsuperscript{[9]}\textsuperscript{[18]}\textsuperscript{[19]} Indeed thermodynamic stabilization greatly stabilizes the ground states of the reactive heavier multiple bonds by (cyclic) delocalization of the $\pi$-electrons over the whole $\pi$-system. Hence, significant changes in the nature of heavier multiple bonds are also introduced. On the other hand, kinetic stabilization is now widely accepted as one of the most effective synthetic tools when aiming to stabilize localized multiple bonds between heavier elements. Sterically demanding aromatic as well as alkyl ligands such as 1,3,5 trimethylphenyl (Mes, \textbf{Fig. 1, 1}) 2,4,6-tri-\textit{tert}-butylphenyl (Mes*, \textbf{Fig. 1, 2}), 2,6-dimesityl phenyl (Dmp, \textbf{Fig. 1, 3}), 2,4,6-tris[\textit{bis}(trimethylsilyl)methyl]phenyl (Tbt, \textbf{Fig. 1, 4}), \textit{tris}(trimethylsilyl)methyl (R’’, \textbf{Fig. 1, 5}), \textit{bis}(trimethylsilyl)methyl (R’’/Dis, \textbf{Fig. 1, 6}), adamantyl (Ad, \textbf{Fig. 1, 7}), and tri-\textit{tert}-butylsilyle (ttbs, \textbf{Fig. 1, 8}) groups were successfully used to encumber undesirable cyclodeaddition reactions and hydrogenation reactions, and thus kinetically stabilize multiple bonds involving heavier elements.\textsuperscript{[20]}

![Figure 1. Some common protecting groups used in stabilizing heavier main group elements, 1-8.](image-url)

However, depending on the steric demand of these ligands, they either completely or partially impede the highly reactive natures of the element-element bond in homo- or heteronuclear double bonded main group compounds. One of the early breakthroughs to synthesize a heavier group 14 based double
bonded compound was achieved by Lappert and co-workers. In 1976 they reported the first crystallographically characterized Sn-Sn double bond (Fig. 2, 9), using the [CH(SiMe3)2] as protecting group. The distannene however existed as the stannylene in solution due to its small dissociation energy ($\Delta H = 12.8$ Kcal mol$^{-1}$). Hence, the bond was characterized as a double dative bond due to the very weak interaction in which the two coupling monomers donate lone pairs into the empty pz orbitals of each other. In the solid state, 9 exhibits a trans bent geometry, as the Sn atoms being observed to be highly pyramidal with a Sn-Sn bond distance of 2.768(1) Å, slightly shorter than the Sn-Sn single bond seen in elemental tin (2.80 Å) [21] [22]. In 1981, Robert West and co-workers reported the first compound containing a Si-Si double bond using Mes substituents as protecting groups (Fig. 2, 10). The compound 10 was stable at room temperature but reacts with O$_2$ to give 1,2-disila-3,4-dioxetane (Fig. 2, 10a). Additionally the compound also readily undergoes addition reaction when exposed to HCl to give monochlorodisilane (Fig. 2, 10b), while EtOH adds slowly to the Si-Si double bond producing ethoxydisilane (Fig. 2, 10c).[23] Hence, compound 10 undergoes addition reaction across double bond just like olefins. In 1982, soon after this seminal finding, Brook reported the first silaethylene (Fig. 2, 11), a heteronuclear version of ethylene having a Si-C double bond (instead of a C-C double bond). The Si-C double bond length was found to be 1.764 Å, significantly shorter than a typical Si-C single bond (1.87-1.91 Å). The molecule adopts a slightly twisted geometry due to the bulky groups.[24] The Si-C bond distance for the parent H$_2$Si=CH$_2$ system was calculated to be 1.70 Å, and due to electronegativity differences the Si-C double bond is considerably polar, in which most of the positive charge (+) residing on the Si atom. However depending on natures of the substituents on either end of Si-C bond, the polarity of the bond can be tuned as desired. The Si-C $\pi$-bond strength of is markedly lower (33 Kcal/mol) than the $\pi$-bond in analogous ethylenes, with this weak $\pi$-contribution explaining the high reactivity observed in these species (Table 1).[25]
Figure 2: Selected examples of the early group 14 homo- and heteronuclear multiple bonded systems and their reactivity towards small molecules.
3 Phosphaalkene: A heavier multiple bonded system (Paper I and II)

Phosphorus belongs to group 15 of the periodic table, known as the pnictogen family (N, P, As, Sb, and Bi). Its diagonal relationship to carbon, the “element of richest chemistry”, makes it especially prominent within the main group elements. In σ-bonded compounds with other elements, phosphorus adopts sp^3-hybridization with nearly tetrahedral geometry in a similar manner to carbon, and forms covalent bonds with most other elements. Some of the common low valence modes of phosphorus are depicted in Fig. 3. In the low valent \( \lambda^3-\sigma^2 \) (trivalent-two coordinate) and \( \lambda^3-\sigma^1 \) (trivalent-singly coordinate) modes, phosphorus exhibits a similar chemical bonding nature to unsaturated carbon analogues. Of these, the \( \lambda^3-\sigma^2 \) coordination mode is of particular interest for this research. This coordination mode results from a formal replacement of carbene fragments (:CR₂) in alkenes with phosphinidene fragments (:PR), resulting in P=C species, isolobal relatives of C=C.

Moreover, the HOMO in parent phosphaethene HP=CH₂ (-10.3 eV) is the π-bond, which is slightly higher in energy than the lone pair (HOMO-1) (-10.7 eV), (Fig. 4-1). This means that most of the reactions of phosphaalkene take place through the π-bond, similar to ethylene. Importantly, Mulliken population analysis has shown that low coordinate phosphorus exhibits a very similar effective π-electronegativity to carbon.
Figure 4-1. HOMO-LUMO of ethylene vs phosphaethylene, calculated orbital energies in parentheses.

Due to the close similarities between C and P in low coordination states, phosphorus is often regarded as a carbon copy. However, there are several striking differences between conventional alkenes (C=C) and phosphaalkenes (P=C). The first is that carbon and phosphorus have slightly different Pauling electronegativity values (χ = 2.5 and χ = 2.1, respectively). Moreover, the overall charge density (σ+π) is appreciably localized on the carbon center in P=C systems, hence imparting a slight polarization. In P=C bonds, this localization can easily be tuned as desired with the help of electron donating or withdrawing substituents for example in phosphaalkene 12a (Fig. 4-2) the P^{III} center exhibits a partial negative charge due the electron donating nature of the amino group towards the P=C π-bond. The second significant difference is that the lone pair on the phosphorus center hosts a coordination site for Lewis acids. Finally, the most pronounced effect of the phosphorus center in phosphaalkenes is to lower the LUMO energy level and at the same time slightly destabilize (i.e. raise) the HOMO energy level, causing a reduction in the HOMO-LUMO gap when compared to related alkenes (C=C) (Fig. 4-1). This imparts exciting chemical and opto-electronic properties to phosphaalkenes.
3.1 Synthetic accessibility of phosphaalkenes

There are two main synthetic approaches used to stabilize multiple bonds involving trivalent two-coordinate ($\lambda^3$-$\sigma^2$) phosphorus atoms. The first is thermodynamic stabilization via delocalization, as used in phosphinines/phosphabenzenes\cite{19} \cite{34} and phosphole derivatives.\cite{35} \cite{36} \cite{37} The second is kinetic stabilization using sterically demanding groups, which is in general applied to localized double bonded systems.\cite{38} \cite{20} In this work, we mostly utilize kinetic stabilization of P=C bonds. The first stable phosphaalkenes were reported in 1976, and were synthesized via condensation reactions of bis(trimethylsilyl)phosphine with acyl chloride followed by fast, irreversible 1,3-silyl shifts (I Fig. 5). These reactions have since been named Becker rearrangements. The main driving force for these reactions is the inherent oxophilicity of silicon atoms, which shifts the double bond toward phosphorus. Bulky substituents such as $t$-butyl and trimethylsilyl groups provide the necessary kinetic support.\cite{39} A similar synthetic protocol can also be used to condense phosgene or isocyanide dichlorides with aryl-bis(trimethylsilyl)phosphanes via elimination of silyl chlorides followed by silyl migration, resulting in P=C double bond formation (II Fig. 5).\cite{40} \cite{41} Moreover, compounds that exhibit cumulative double bonds such as carbodiimides, carbon disulfide, and dioxides can also be inserted into P-Si bonds, which then energetically favor 1,3 silyl shifts to produce phosphaalkenes (III Fig. 5).\cite{42} \cite{43} Another well-established approach used to synthesize kinetically stable phosphaalkenes is the addition of diarylmethylolithium compounds to aryldichlorophosphines and a subsequent non-nucleophilic-base-induced 1,2-elimination reaction. The mesitylene group (1,3,5-trimethylphenyl) was used as a kinetically stabilizing group (IV Fig. 5).\cite{44} In another approach, trihalomethanes (HCX$_3$) were used to generate dihalocarbenes in situ, which subsequently add to arylyphosphenes or aryldichlorophosphines and eliminate hydro-halides (HX) upon addition of non-nucleophilic bases. This synthetic route is used for the efficient synthesis of $C$-halogen-substituted phosphaalkenes (V Fig. 5). Typically non-nucleophilic bases are used to avoid undesirable addition reactions to the P=C double bond once it has been formed.\cite{45} \cite{46}
One of the most important olefination reactions in organic chemistry is the Peterson olefination, which is based on the condensation of silyl carbanions with aldehydes or ketones. This approach has been successfully mimicked to generate acyclic P=C double bonds by replacing the silyl carbanion with lithium silylarylphosphides and is known as the phospha-Peterson reaction (VI Fig. 5). However, depending upon the nature of the substrate, there is also the possibility of use mild base KOH as catalyst to assist this type of condensation. Secondary vinyl phosphines can also undergo thermal rearrangements to the corresponding phosphaalkene (VII Fig. 5). Furthermore, it is also possible to synthesize stable phosphavinyl Grignard reagents by reacting phosphalkynes with RMgX. Importantly, the addition of these Grignard reagents is regiospecific, with the metal center adding to the carbon terminus of the phosphaalkyne (VIII Fig. 5). Extending the carbon-phosphorus analogy, in 1988 Mathey et al. unveiled a modification of the Wittig reaction to provide phosphaalkenes, which after a few modifications has been extended to two different versions, known as the phospha-Wittig and phospha-Wittig-Horner reactions. These differ with respect to the nature of the ligands on the pentavalent P\textsuperscript{V} center. Phosphanyliden-\(\sigma^4\)-phosphorane analogues of phosphor ylides synthesized from aryl dichlorophosphines or aryl phosphines are usually unstable due to their embedded two coordinate phosphorus centers. However, the necessary stabilization can be provided by sterically demanding groups or by coordination to early transition metal centers. These intermediates can then be reacted with aldehydes or ketones to afford the corresponding phosphaalkenes in a similar manner to the Wittig olefination (IX and X Fig. 5). Similarly, terminal phosphinidene complexes of zirconium and arylphosphines react with aldehydes or ketones to form the corresponding phosphaalkene.
Figure 5. Synthetic routes to phosphaalkenes.

3.2 Conjugated and Cross-conjugated systems

In an organic chemistry context, conjugated systems are usually molecules or complex molecular systems that exhibit an extended series of \( \pi \)-orbitals (Fig. 6, 6a). These \( \pi \)-orbitals serve as channels for electronic communication between different parts of these molecular systems. Thus, in its most prominent form conjugation refers to the interaction of neighboring \( \pi \)-orbitals across a sigma bridge, allowing the delocalization of \( \pi \)-electrons via alternating single and multiple bonds\(^{52}\). In unsaturated organic compounds, \( \pi \)-conjugation is fundamentally responsible for imparting interesting chemical and electro-optical properties to the molecules including their ability to act as semiconductors upon chemical and/or electrochemical doping\(^{53}\). Most of these properties are functions of conjugation length (Fig. 6, 6b), connectivity, pattern of repeating units, and the nature of the groups involved, for example the presence of donor or acceptor systems\(^{52,54}\).
Depending on the type of connectivity, π-conjugated systems can be divided into through-conjugated systems such as polyacetylene 6a (Fig. 6) and cross-conjugated systems such as diethynylethenes (DEE) 14 and tetraethynylethenes (TEE) 15 (Fig. 7). Cross-conjugated systems are comprised of a minimum of three unsaturated fragments, in which two unsaturated fragments are lacking direct conjugation to each other, but are connected via a third unsaturated fragment. This gives a cross-linked systems e.g. the cross conjugated motifs 13, 14 and 15 (Fig. 7). Theoretical studies also show that variations in the π-backbone, such as introducing a terminal alkyne
into a π-conjugated system, can enhance the total delocalization energy at the expense of conjugation efficiency,\(^{[58]}\) while at the same time terminal alkyne units are potential synthons for metal-catalyzed cross-coupling reactions.\(^{[59]}\)

Compared to linearly conjugated systems, cross-conjugated systems possess additional channels for π-communication (Fig. 7, 14) due to the possibility of the conjugation extending over the cross-linked atom (bifurcation point, Fig. 7, 13) within the same molecule. Determining which channel will dominate the electronic communication in a molecule is therefore critical for predicting the molecular and opto-electronic properties of such systems. As an example in gem-DEE (Fig. 7, 14) the A1, A2 channels represent a linear conjugation path while channel B represents a cross conjugated path within the same molecular architectures. However, in π-conjugated systems like TEE 15 the nature of the pendent groups define the direction of effective π-conjugation of the system\(^{[52]} [54] [60] [57] [61]\)

The chemical and physical nature of the π-conjugated systems strongly depend on their molecular and electronic structures. Cross-conjugated systems generally display poor electronic delocalization along the π-backbone, and thus possess a HOMO-LUMO energy gap that is less dependent on chain length.\(^{[52]}\) For this reason, replacing C atoms in conventional C-C conjugated systems with heavier main group elements not only changes the molecular structure, but may also induce changes in the electronic structure of the π-conjugated system.\(^{[62]}\) As mentioned earlier, main group elements such as phosphorus in its low valent \(\lambda^3-\sigma^2\) state are isolobal to carbon. It is therefore an attractive challenge to replace carbon atoms in π-conjugated oligoacetylenes with phosphorus to produce acetylenic phosphaalkenes. Cross-conjugated oligoacetylenes e.g. gem-DEE are suitable candidates for the replacement of an ethylenic carbon with a phosphorus atom. The phosphaalkenes derived from gem-DEE can be classified into C-acetylenic and P-acetylenenic phosphaalkene (Fig. 8)
where compounds 16-18 represent C-acetylenic phosphaalkenes and compounds 19-21 represent P-acetylenic phosphaalkenes. In all of these compounds, phosphorus adopts the low valent $\lambda^3\sigma^2$ state; moreover, the low valent phosphorus centers in these acetylenic phosphaalkenes contain lone pairs that can act as coordination sites for suitable metals or Lewis acids. The C-acetylenic phosphaalkenes can also be used as molecular building blocks for the construction of larger cross-conjugated systems. Parts of this thesis work will discuss the synthesis and characterization of C-acetylenic phosphaalkenes.

![Figure 8: Cross-conjugated C-acetylenic phosphaalkenes 16-18 and P-acetylenic phosphaalkenes 19-21.](image)

### 3.3 Synthetic accessibility of cross-conjugated phosphaalkenes

There are only a handful of synthetic procedures describing the synthesis of C-acetylenic phosphaalkenes. Bickelhaupt (and co-workers) reported the first C-mono acetylenic phosphaalkenes of type 16 and 17 (Fig. 8), where the introduction of the acetylenic functionality on the C-terminus was performed via a two-step process. First, a silyl or methyl functionality was introduced on the C-terminus of a dihalophosphaalkene to eliminate one halogen group. The resultant trans-C-monohalophosphaethenes were then reacted with arylacetylenic Grignard reagents in the presence of tetrakis(triphenylphosphine)palladium(0) as a catalyst to afford the C-mono acetylenic phosphaethenes 24 (Scheme 1). The only other contribution comes from Ott et al., in which the direct synthesis of C,C-diacylenic phosphaethenes 26 (Scheme 1) was
achieved via the reaction of relatively unstable chloroallenes with Mes*PCl₂ below -78 °C in the presence of a non-nucleophilic base (LDA).[65]

Scheme 1. Synthetic routes towards cross-conjugated C-mono and C,C-diacylenic phosphaalkene.[64] [65]
3.4 Development of new synthetic routes towards C-mono and C,C-diacetylenic phosphaalkenes

This section deals with the development of metal-free synthetic routes that facilitate the sequential coupling of alkynyl moieties to dibromophosphaalkenes. C-mono- and C,C-diacetylenic phosphaalkenes underwent unusual addition reactions when exposed to terminal acetylenes in the presence of Pd[0].

In order to construct cross-conjugated oligomers featuring P=C bonds, it is essential to couple unsaturated units such as alkynes to the P=C bond. Our research mainly focused on functionalizing P=C bonds through the C-terminus while at the same time integrating a sterically demanding group at the P-terminus to provide the necessary stabilization (Fig. 9, 29-31). In practice, without proper stabilization P=C bonds are vulnerable to cycloaddition, and polymerization reactions. A large variety of bulky ligands have been synthesized for this purpose as discussed in Chapter-2 (Fig. 1).\textsuperscript{[20]} Mes* in particular is an excellent protecting ligand because the two tert-butyl groups at the 2- and 6-positions provide good shielding for the reactive localized P=C bond at the ipso position, preventing side reactions. Replacing the tert-butyl groups in Mes* with smaller substituents such as methyl groups (Fig. 1, 1) or hydrogen atoms leads to an abrupt decrease in stability (Fig. 9, 32).\textsuperscript{[67]} Similarly in case the of diphosphenes 33 (Fig. 9), having a less bulky group on the P\textsuperscript{III} atoms leads to slow decomposition and dimerization at room temperature, clearly emphasizing the crucial role of steric protecting groups for the stabilization of multiple bonding in heavier main group elements. However, in rare cases using bulkier groups (in particular Mes*) can lead to C-H activation; as an example in the attempted synthesis of Mes*-SbCl\textsubscript{2} (Fig. 9, 34a), a C-H activation from one of the tert-butyl groups occurs to yield the cyclic compound 34b (Fig. 9).\textsuperscript{[68]} [69] [70] [71]

Concluding from the above discussion, it is clear that accessing C-mono- and C,C-diacetylenic phosphaalkenes 29-31 (Fig. 9) would pose a significant synthetic challenge and that using an appropriate protecting group will greatly stabilize the P=C bond.
Figure 9. Cis and trans C-monoacetylenic phosphaalkene 29-30. C,C-acetylenic phosphaalkene 31. Phosphaalkene dimerization 32. Slow dimerization of diphosphenes using Dis as protecting group 33. Insertion of Sb into C-H bond 34a-34b.

Retrosynthetic analysis indicated that C-mono- and C,C-diacetylenic phosphaalkenes might be accessible from Mes*dihalophosphaalkenes, which are stable, readily available synthons used for synthesizing functionalized phosphaalkenes (Fig. 10, a). Under palladium-catalyzed cross coupling conditions with terminal acetylenes, carbon analogues of Mes*dibromophosphaethene (vinylidihalides) yield gem-DEE, (Fig. 10, b). Unfortunately, dibromophosphaethene does not afford C-mono or C,C-diacetylenic phosphaalkenes when exposed to typical palladium-mediated cross coupling conditions. Instead, they lead to the formation of phosphaalkynes via the Fritsch-Buttenberg-Wiechell (FBW) rearrangements with the elimination of palladium dibromide, (Fig. 10, c). However, Mes*monobromophosphaethene can be coupled with ethynylmagnesiumbromide under Pd-catalyzed cross
coupling conditions to smoothly afford the C-monoacetylenicphosphaethene 24 as discussed earlier (Scheme 1).[72] Ito and co-workers have also recently re-investigated the metal mediated pathway, and found that it is possible to effectively suppress phosphaalkyne formation and thereby selectively introduce terminal alkynyl moieties onto phosphaalkenes by using suitable ligands with large bite angles and optimized reaction conditions. Their study showed that when 1,1-bis(diphenylphosphino)ferrocene was used as ligand in the Pd mediated coupling, afforded C-mono- as well as C,C-diacytylenicphosphaalkenes in high yields at 0 °C using diethyl ether as a solvent. However, they still observed some phosphaalkyne formation.[74]

Another very different approach to access C,C-diacytylenic phosphaalkenes is based on the condensation of propargyl chlorides or chloroallenes with Mes*PCl₂ in the presence of base such as n-BuLi or LDA. Usually, the relatively unstable chloroallenes result in the formation of the corresponding C,C-diacytylenicphosphaethenes 26 (Scheme 1). While, depending on the substituents, propargyl chlorides can also undergo rearrangements to form butadiene-substituted phosphaalkenes 28 (Scheme 1). However, this method does not allow the introduction of chosen acetylenic moieties in a sequential manner due to the lack of regio- and stereo-control.

A study of the literature suggested that arylsulfonylacetylenes (α-β-acetylenic sulfones) can be used as nucleophilic coupling reagents for the construction of C<sub>sp</sub>-C<sub>sp³</sub> and C<sub>sp</sub>-C<sub>sp₂</sub> bonds. In these coupling reactions, lithium carbenoids are generated at low temperature from the corresponding halogenated alkenyl or aryl species. Which then reacted with arylsulfonyl acetylenes. This results in <i>ipso</i>-substitution rather than addition to the triple bond (Fig. 10, d). The mechanistic explanation for this is based on the pre-complexation of the lithium carbenoid species with the sulfonyl oxygen atoms facilitating attack at the α-position rather than the relatively remote β-position, leading to the unexpected formation of the α-substituted product.[75] Garcia Ruano et al. explored the reaction further, and found that it can facilitate C<sub>sp²</sub>-C<sub>sp</sub> and C<sub>sp³</sub>-C<sub>sp</sub> couplings with full stereo- and regio-control, regardless of the electronic nature of the systems.[76] Most importantly, this coupling reaction employs milder conditions and totally excludes the use of transition metals, which have previously been shown to halt coupling reactions between dihalophosphaalkenes and terminal acetyl groups.[72] Inspired by this metal-free C<sub>sp²</sub>-C<sub>sp</sub> coupling, we were interested in the use of arylsulfonyl acetylenes (C<sub>sp</sub> centers) as coupling reagents for the alkynylation of Mes*di bromophosphaethene (C<sub>sp²</sub> center).
Figure 10: a) Retrosynthetic analysis of C,C-diacetylenicphosphaalkene. b) Sonogashira coupling of vinylhalides with terminal acetylene. c) Conversion of dihalophosphaethenes to phosphaalkyne under Sonogashira coupling conditions. d) Reaction of sulfonylacetylene with alkenes.

3.5 Synthesis of arylsulfonylacetylenes

Arylsulfonylacetylenes were synthesized according to a literature procedure\(^7\), in which a mixture of the acetylene, sodium \(p\)-toluene sulfinate, and sodium iodide was reacted with ceric ammonium nitrate (CAN) in dry acetonitrile. After stirring for one hour at room temperature, the arylvinylsulfone intermediate was formed in a 60% yield. This was subsequently
treated with one equivalent of tert-BuOK at room temperature, resulting in the formation of the corresponding acetylenic sulfone in an 80% yield.\cite{78}

3.6 Synthesis of acetylenic phosphaalkenes

Mes* dibromophosphaethene (Mes*P=CBr₂) \textbf{35 (Scheme 2)} is a useful starting synthon, as it can be selectively lithiated at temperatures < -100 °C to access the kinetically stable cis-Li phosphacarbenoid \textbf{36a (Scheme 2)}. As such, Mes*P=CBr₂ \textbf{35} was first treated with 1 eq of \textit{n}-BuLi at temperatures below -100 °C to generate the Li-carbenoid \textbf{36a}. This was subsequently treated with three different arylsulfonylacetylenes precursors i.e. \textbf{a}, \textbf{b} and \textbf{c} (Scheme 2) in separate reactions. Reaction with arylsulfonylacetylene \textbf{a} or \textbf{b} resulted in the formation of C-monoacetylenic phosphaethenes \textbf{37a} and \textbf{37b} in acceptable yields with the side product \textbf{39}. These compounds were characterized by downfield shifts in the $^{31}$P NMR resonance from 271.0 ppm for \textbf{35} to 291.0 ppm for \textbf{37a}, and 294.2 ppm for \textbf{37b}. Additionally when treated with arylsulfonyl \textbf{c} the reaction afforded compound \textbf{38}, which had smaller downfield shift to 280 ppm, mainly owing to nature of pendent group. In contrast, lithiation of Mes*P=CBr₂ \textbf{35} at -78 °C afforded the isomeric mixture \textbf{36b} which subsequently reacted with arylsulfonylacetylene \textbf{a} or \textbf{b} to gave cis- and trans-C-monoacetylenic phosphaethenes \textbf{37a-b} and \textbf{41a (Scheme 2)}. Temperature control is crucial, as lithiation at -78 °C gives a mixture of cis- and trans-lithium phosphacarbenoids \textbf{36b}, while at temperatures above -65 °C the lithium phosphacarbenoids \textbf{36b} tend to decompose.

The trans-\textbf{41a} $^{31}$P-NMR with a resonance at 284 ppm still showed a downfield shift $^{31}$P NMR spectrum relative to \textbf{35}. However, this represents a 7 ppm upfield shift compared to the cis-\textbf{37a}. The cis and trans isomers can also be distinguished based on their $^1$H NMR spectra. In the trans-\textbf{41a}, the two ortho protons of the phenylacetylene group experience a shielding effect due to the aromatic ring current from the Mes* aromatic cavity, causing an upfield shift to 6.89 ppm. This was further confirmed by single crystal X-ray diffraction (XRD) analysis (Fig. 11). It can clearly be seen that the two ortho protons in the trans-\textbf{41a} sit directly in front of the Mes* pocket, resulting in a shielding effect and a consequent upfield shift in the $^1$H NMR spectrum. The cis-\textbf{37a} and the trans-\textbf{41a} show similar P=C bond distances of 1.682(4) and 1.684(4) Å, respectively. The angle between the Mes* and P=C unit was found to be 101.9(2)° and 101.6(2)° for the cis-\textbf{37a} and the trans-\textbf{41a} respectively. On the other hand, the Br-C-P angle was found to greatly depend on the stereochemistry. This can be observed in the single XRD structure (Fig. 11) that in the cis-\textbf{37a} the Br atom experiences a repulsive interaction from Mes* tert-buty1 groups therefore exhibits a wider angle of 126.0(2)° while in the case of the trans-\textbf{41a} the angle is reduced to 115.1(2)°.
Scheme 2: (i) n-BuLi, diethyl ether (dry), \(-100 \, ^\circ C\). (ii) \(-100 \, ^\circ C\) to r.t. (iii), \(-100 \, ^\circ C\), to r.t.(iv) n-BuLi, diethyl ether (dry), \(-78 \, ^\circ C\). (v) \(-78 \, ^\circ C\) to r.t.

The successful formation of \(37b\) indicates that it is also possible to couple arylacetylenes with halogen-functionalized aromatics, which could be utilize in the future to synthesize larger oligomeric and cyclic structures. In this series, the ferrocenyl derivative \(38\) was found to be unstable on silica gel and could only be characterized as a crude product by \(^1\)H and \(^{31}\)P NMR spectroscopy after extraction with \(n\)-pentane. A notable exception observed during this study was the attempted coupling of trimethysilylsulfonylacetylene \(g\) to the \(35\), which did not show the expected alkynylation product. After a thorough
analysis of the crude mixture, we identified the TMS transfer product 40 based on X-ray crystallography and NMR data reported by Bickelhaupt et al.\textsuperscript{[79]} The single crystal structure of 40 (Fig. 11) showed no significant changes in the P=C bond distance compared to the C-monoacetylenic phosphaethenes cis-37a and trans-41a. This suggest that in the case of trimethylsilylsulfonylacetylene, the carbenoid nucleophile attacked at the silicon atom rather than the α-carbon.

![Figure 11: Solid-state structure of cis-37a, trans-41a and 40. The Mes* group carbons atoms except C1, C6 and C8 are depicted as wireframe. All the hydrogen atoms are omitted for clarity. Selected bond lengths and angles, cis-37a P1-C7 1.682(5) Å, C7-P1-C8 101.9(2)°, P1-C7-Br1 125.9(3)°. trans-41a, P1-C7 1.684(4) Å, C7-P1-C6 101.6(2)°, P1-C7-Br1 115.1(2)°. 40 P1-C19 1.685(5), C19-P1-C1, 103.9(2)°, P1-C19-Br1, 125.1(3)°.](image-url)
Another unexpected result was observed when 35 was treated with 2.1 equivalents of n-BuLi at -78 °C in dry diethyl ether, and was followed by addition of sulfonyleacetylene a or b, which resulted in the formation of the expected C-monoacetylenic phosphaalkene and the unexpected generation of the symmetrically disubstituted C,C-diacetylenic phosphaalkene 26d-e (Scheme 2 and Fig 12, A-B).[65] The direct formation of the dilithiated carbenoid was thought to be unlikely, with a four step successive mechanism being more feasible: Li-halogen exchange producing the Li-carbenoid, which then reacted with the sulfonyleacetylene, followed by a second Li-halogen exchange and subsequent reaction with another sulfonyleacetylene. Unfortunately, this explanation can also be easily discounted, as sulfonyleacetylene would immediately react with the unreacted n-BuLi in the reaction vessel awaiting the second lithiation step.[76] This was confirmed by a test reaction, in which one equivalent of phenylsulfonylacetylene was added to an equimolar mixture of n-BuLi and Ph-Li, where it was deduced from the crude reaction mixture that the phenylsulfonylacetylene reacted immediately with n-BuLi and Ph-Li. So far, we have been unable to confirm the exact mechanism of the formation of the disubstituted derivative in this one pot reaction.
To further explore the scope of the reaction, we replaced the Mes* group with Dmp (2,6-bis-(2,4,6-trimethylphenyl)phenyl), a meta-terphenyl ligand often used to provide kinetic stabilization to P=C bonds and related heavy-atom-containing unsaturated analogues. To examine the reactivity of our freshly developed protocol, a Dmp-based cis-Li-phosphacarbenoid was reacted with phenylsulfonylacetylene at a temperature below -100 °C. This attempt resulted in the formation of the hydrolysis product of the lithiumcarbenoid 45 detected as a major peak in the 31P NMR spectrum, while the C-monoacetylenic phosphaethene 44 was present as a minor peak with a 31P-NMR resonance at 290.7 ppm (Scheme 3). However, substituting tolyl for phenyl in the sulfonylacetylene improved the reactivity, and the resulting C-monoacetylenic phosphaethene was observed as the major product (30% isolated yield).
The reason for the low isolated yield was the slow decomposition of the product on silica gel during purification. Variation of the aromatic substituent on the sulfonylacetyleylene seemed to affect the solubility and subsequently the reactivity of the sulfonylacetyleylene.

Scheme 3: Reactivity of Dmp protected dibromophosphaethen with arylsulfonylacetylene. (i) n-BuLi, <-100 °C. (ii) <-100 °C to r.t.

3.7 Sonogashira cross coupling of C-monoacetylenic phosphaalkene

Our newly developed transition metal-free coupling reaction bypasses common problems associated with the metal-mediated coupling of dibromophosphaalkene. The resulting C-monoacetylenic phosphaalkenes have additional C-Br functionality that retains the possibility of formation of larger, more complex structures. For example, it has been demonstrated that C-monobromophosphaethenes usually undergo inversion of stereochemistry via cationic three-membered palladacyclic intermediates 46 (Fig. 13) when subjected to Sonogashira coupling conditions. [82] [83]
To test this reactivity, we attempted to couple the C-monoacetylenic phosphaethenes 37a with ferrocenylacetylene, and obtained the expected C,C-di-acetylenic phosphaethenes 47 (Scheme 4). Based on aromatic ring current analogy, this also exhibited characteristic upfield aromatic protons and a distinctive $^{31}$P-NMR resonance at 324.4 ppm. The other stereoisomer 49 (Scheme 4) was obtained from C-monoferrocenylacetylenic phosphaethenes 38 (Scheme 2). As mentioned, earlier the reactive nature of 38 leads to decomposition on silica during column chromatography. The collected fractions were analyzed by NMR spectroscopy. An unexpected characteristic shift was observed at 181.2 ppm in the $^{13}$C-NMR spectrum, indicating the presence of a carbonyl group. This was confirmed by IR spectroscopy, which showed a strong absorption band at 1618 cm$^{-1}$, indicating the presence of a carbonyl functionality. Additionally, an absorption band with medium intensity at 2184 cm$^{-1}$, suggesting a -C≡C-functional group. Based on this experimental evidence, it was determined that during silica column chromatography the phosphorus center of compound 38 was selectively substituted with oxygen, followed by rearrangement to ketone 48. However, we have yet to study this elimination rearrangement reaction in detail.

Due to the instability of 38 towards purification by column chromatography, it was reacted with phenylacetylene under in situ Sonogashira coupling conditions, which yielded the C,C-diacylenic phosphaethene 49 (Scheme 4). This exhibited a $^{31}$P NMR resonance at 322.5 ppm, with an overall yield of 32%. We also observed an unexpected side product 50 with a characteristic $^{31}$P NMR resonance at 300.0 ppm, (Scheme 4) which will be discuss in detail in section-3.8.
Scheme 4: Reaction conditions (i), [Pd(PPh₃)₂Cl₂], CuI, Et₃N, THF, 70-75 °C, o.n (ii), [Pd(PPh₃)₂Cl₂], CuI, Et₃N, THF, 70-75 °C o.n, over all yield 32%.
3.8 Formation and reactivity of 1-phospha-1,3-butadienes

This section will deal with the optimization of reaction conditions towards selective formation of the unexpected 1-phospha-1,3-butadiene 50, and the substrate scope of this unprecedented reactivity, as well as the key mechanistic steps involved in the formation of 50 and its unique way of cyclization towards highly substituted and extended π-conjugated phosphole derivatives. Phospholes, or phosphacyclopentadienes, found wide application as components in organic electronics materials, e.g. for OLEDs, due to their fascinating electronic properties such as electroluminescence, lower aromaticity and the ease with which these electronic properties can be tuned via the reactive PIII center.[84] [85].

Unveiling the formation of 50, a thorough investigation of the in situ cross coupling Sonogashira reaction of 38 with excess of phenylacetylene, CuI and PdII was carried out. While 50 was afforded under these conditions, 49 was found to be the major product. As mentioned in the previous section, the side product 50 exhibits an up field shifted $^{31}\text{P}$ resonance at 300 ppm, indicative of extended π-conjugation. Single crystals of compound 50 suitable for single crystal XRD studies were obtained from slow evaporation of mixed pentane/acetonitrile solutions of 50 as orange crystals. From the solid-state structure (Fig. 14), 50 was characterized as 1-phospha-1,3-butadiene-2,3-diyne. The single X-ray structure revealed the P1-C1 distance to be 1.7018(2) Å well in the range of P=C bonds found in π-extended conjugated systems.[33]. As discussed (previously in this chapter) inversion of stereochemistry during the Sonogashira coupling reaction caused the ferrocenylacetylenic moiety to be in cis position with respect to the Mes* group. The 1-phospha-1,3-butadiene fragment (comprised of P1, C19, C32, and C41) is almost planar. However, the two substituents (ferrocenylacetylene at C19 and phenylacetylene at C32) are slightly twisted out from the 1,3-butadiene plane. The C1, P1, and C19 angle was measured to be 99.35(9) Å indicating a high degree s-character of the lone pair. A similar compound containing such a 1-phospha-1,3-butadiene core was also reported by Öberg et.al. [86] [87] In their report Mes*-P=C(Me)Br was reacted with vinylmagnesium bromide in the presence of [Pd(dba)$_2$],PPh$_3$ as a catalyst in THF and afforded Mes*-P=C(Me)-CH=CH$_2$. 
After confirming of the molecular structure of 50, we were interested to investigate the mechanism of this unexpected alkynyl addition product. Moreover, we also wanted to optimize the reaction conditions to direct the synthesis (exclusively) towards this unexpected side product.

To investigate the reaction mechanism, we designed an NMR-scale experiment to follow the reaction progress in a stepwise manner. The C,C-diacetylenic phosphaethene 49 was dissolved in THF-d8 in an NMR tube. As soon as 1.0 eq of [Pd(PPh3)4] was added to this reaction mixture, an immediate color change from red to dark brown was observed. After 30 min, 31P-NMR spectra (Fig. 15) display a triplet at 306 ppm (3Jpp = 228 Hz) and a doublet at 23.6 ppm (3Jpp = 228 Hz), clearly indicating the formation of complex 51 via coordination of phosphaethene 49 to a Pd(PPh3)2 unit.
Scheme 5: Formation of complex 51 and subsequent conversion to alkylnyl addition product 50. (i) Pd(PPh3)4, THF-d8, 24 h r.t. (ii), phenylacetylene, Et3N r.t (iii), CuI.

Figure 15: Stepwise coordination of 49 followed by alkylnyl addition reaction, and the stepwise progress was monitored by 31P-NMR spectroscopy. The peak at 271 ppm was assigned as unknown.

The 31P-NMR resonance at 320.5ppm corresponds to unconsumed starting material 49 (Fig. 15, A). Moreover, the peak at 24.1 ppm in the 31P-NMR
spectrum supports the release of triphenylphosphine ligands from the Pd center. While the broad signal at 17.2 ppm corresponds to the chemically equivalent triphenylphosphine ligands of [Pd(PPh₃)₄]. The line broadening of this signal indicates restricted rotation within the coordination environment of complex 51. Thus, a pseudo square planar coordination environment due to partial coordination of the triple bond with the Pd(0) center was hypothesized on the basis of ³¹P-NMR analysis (Scheme 5). However, we were unable to obtain a single crystal of this proposed intermediate.

After 24 h, when full conversion to the complex 51 had been observed, (Fig. 15, B). Phenylacetylene and Et₃N was added to this reaction mixture and the progress was followed by ³¹P-NMR spectroscopy. To our surprise, the resonance at 320.5 ppm (assigned to 49) was observed again while the resonance at 306 ppm disappeared, indicating breakup of the complexation between 49 and the Pd(0) center (Fig. 15, C). In the next step, CuI was added to this reaction mixture and after 2 h, observed moderate conversion to the previously observed addition product 50. Hence, based on these results it was inferred that formation of 50 requires CuI as co-catalyst. The role of Et₃N is to facilitate the formation of copper acetylides followed by the transmetallation step and the subsequent stepwise addition of acetylides to the triple bond and protonation, resulting in the addition product 50.

The next task was to demonstrate the role of the heteroatom in this reactivity. Compound 52 (Scheme 6) was reacted with excess phenylacetylene under similar reaction conditions to those used for the formation of 50. However, did not observe any alkynyl addition products even when the reaction mixture was heated at 70-75 °C for 48 h, with only starting material 52 being identified and isolated in this case. This suggests that heteroatoms such as phosphorus are essential for alkynyl addition. Indeed, recently Yao et.al reported that all carbon ene-yne systems could only undergo alkynyl addition in the presence of electron-withdrawing group such as CHO, CN and COOEt (Scheme 6, 55), which would also be able to coordinate to their Pd catalyst.

Despite the lack of mechanistic explanations in their work, the choice of co-catalyst and regio- and stereo selectivities of the reaction outcomes indicate that both reactions might occur via similar mechanistic steps.
Scheme 6: (i) $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$, CuI, Et$_3$N, arylacetylene, THF, 70-80 °C. (ii), $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$, CuI, Et$_3$N, arylacetylene, MeCN, 50 °C.

After determining the key elements and reagents required for this reactivity, we wanted to explore the substrate scope of this reaction. Initial studies focused on monoacetylenic phosphaethene Mes*P=C(Me)CCPh 57 (Scheme 7) in order to explore the role of the substituents at the C-terminus of the phosphaethene. Compound 57 was reacted with 1 eq. of phenylacetylene in the presence of 5 mol% $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$, 10 mol% of CuI, and 1 ml of Et$_3$N in degassed THF. The reaction mixture was heated at 75 °C in a sealed Schlenk flask for 12 h, and the reaction progress was monitored by $^{31}$P-NMR spectroscopy.
Scheme 7: Synthesis of alkynyl addition product 58. (i) n-BuLi, MeI, THF (dry), < -100 °C. (ii), Pd(PPh₃)₂Cl₂, CuI, Et₃N, phenylacetylene, THF, 70-80 °C. (iii) Pd(PPh₃)₂Cl₂, CuI, Et₃N, phenylacetylene, THF, 70-80 °C

A resonance was observed at 264.2 ppm (in addition to the resonance at 283.4 ppm corresponding to unconsumed 57), which represented almost 36% conversion to the alkynyl addition product 58, as estimated from ³¹P NMR spectroscopy (Fig. 16, A). To increase conversion, this reaction mixture was loaded with an additional 5 mol% of [Pd(PPh₃)₂Cl₂] and 1 eq of phenylacetylene, and heated at 75 °C for additional 5 h. At this point, ³¹P-NMR measurements showed 60% conversion (Fig. 16, B). Quantitative conversion to 58 could be achieved under the same conditions by increasing the catalyst loading to 20% (Fig. 16, D). From these experimental observations, it is clear that relatively high loadings of catalyst and a CuI co-catalyst are needed to achieve quantitative conversion.
Figure 16:- Gradual conversion of 57 to 58, monitored by $^{31}\text{P}$-NMR spectroscopy.

The crude product obtained was purified by flash column chromatography on silica gel using n-pentane as an eluent. The purified fraction showed a single $^{31}\text{P}$-NMR resonance at 264.2 ppm in deuterated benzene (C$_6$D$_6$) (Fig. 17, A). Notably, it was observed that 58 undergoes isomerization and/or rearrangements to secondary products when exposed to light and/or silica for extended periods (Fig. 17, B).

One of the secondary products 59 showed a $^{31}\text{P}$-NMR resonance at 266.5 ppm. This product was isolated and further spectroscopic analysis revealed minor structural changes such as isomerization of a double bond. Moreover, during variable temperature (VT-)NMR analysis, we did not observe any interconversion between the $^{31}\text{P}$-NMR resonance for the 58 and the 59, except for slight signal broadening at higher temperature (Fig. 18, A-B) We also performed selective 1D-NOE (Nuclear Overhauser effect) experiments during which compound 58 showed a clear NOE effect between the P=C methyl protons with vinylic proton and the ortho protons of the olefinic phenyl substituent (Fig. 19). Hence, it was confirmed to be the alkynyl addition product 58. However, for 59 irradiation of the P=C methyl proton did not show any through space correlation (Fig. 20). Notably, irradiation of the vinylic proton in this case is not very selective, because it also affects the ortho protons on the olefinic phenyl substituent, due to almost overlapping signals. Hence, based on these 1D-NOE results, it can be conclude that 58 undergoes a restricted C=C or P=C isomerization to yield 59, the identity of which could be 59a or 59b (Fig. 20).
Figure 17: $^{31}$P-NMR spectra representing isomerization of 58 on silica gel (and/or chlorinated solvents).
Figure 18: VT $^{31}$P-NMR spectra of 58 (A) $^{31}$P-NMR spectrum recorded at r.t. (B) $^{31}$P-NMR spectrum recorded at 50 °C, showing broadening of signals at higher temperature, but no changes in relative signal intensities.
Figure 19: 1D-NOE experiment of compound 58. The arrows indicate the expected NOE correlation in the 58.

Figure 20: The possible stereoisomers of P=C 59a and C=C 59b isomerization. The arrows indicate the expected NOE correlation in these isomers. The restricted rotation around the C-C single bond indicated in bold (59b) make difficult to observe any appreciable NOE between the P=C methyl protons and vinylc proton.
3.9 Cyclization of unsymmetrical 1-phospha-1,3-butadienes towards highly substituted and/or extended π-conjugated phosphole derivatives.

The steric and electronic natures of the substituents on 1-phosha-1,3-butadienes are crucial in defining whether the resultant 1-phospha-1,3-butadiene can be isolated or can only be detected as an intermediate by $^{31}$P-NMR spectroscopy. For example when starting from C,C-diacetylenic phosphaaethene 49 (Scheme 4 or 5) the resultant alkynyl addition product, i.e. the 1-phosha-1,3-butadiene 50 was easily isolated by column chromatography. However, when C-monoacetylenicphosphaethene 57 was used the resultant alkynyl addition product 58 underwent slow re-arrangement to other species in halogenated solvents (or on silica gel), which exhibited $^{31}$P-NMR resonances in the range of +1.5 ppm to +3.5 ppm (Fig. 21).

One of the products 61, with a $^{31}$P-NMR resonance at 2.98 ppm (Fig. 22, A-B) was isolated by silica gel column chromatography and the subsequently 2D-NMR analysis suggested the highly substituted phosphole derivative 61, suggesting a nucleophile-induce 1,5 endo-dig cyclization (Scheme 8).
Figure 22:-(A) $^{31}$P-NMR spectrum of 58 representing three new resonances around +1.5 to +3.5ppm. (B) $^{31}$P-NMR spectrum representing the isolation of compound 61 $^{31}$P-NMR resonance at 2.9 ppm.

Scheme 8:- Nucleophile-induced 1,5-endo-dig cyclization of 58 towards highly substituted phospholes 61.

Upon oxidation under ambient conditions this highly substituted phosphole could be recrystallized as single crystals by slow evaporation from a chloroform solution of 61 and was characterized as the corresponding phosphole oxide 62 (Fig. 23) by means of X-ray crystallography.
In the next attempted synthesis in which C-monoacetylenic phosphaalkene 57 was reacted with ethynyl naphthalene 63, and the reaction progress was followed by $^{31}$P-NMR spectroscopy (Fig. 24, A-E).

After heating for 24 h at 70 °C in a sealed Schlenk flask, we observed the gradual formation of the 64. This species shows a $^{31}$P-NMR resonance at 265.9 ppm and was tentatively assigned to the alknynl addition product (Fig. 24, A). The reaction mixture was then loaded with additional catalyst and ethynyl naphthalene 63 and refluxed for 48 h with reaction progress being monitored by $^{31}$P-NMR spectroscopy. This time a slight increase in the intensity of the resonance at 265.9 ppm was noticed, along with a small peak appearing at 4.2 ppm (Fig. 24, B). The reaction mixture was again supplied with additional catalyst, loaded with further ethynyl naphthalene 63 and refluxed for an additional 72 h.

Surprisingly, when the reaction progress was monitored by $^{31}$P-NMR spectroscopy we observed almost complete disappearance of the starting material 57 with only traces of alkylnyl addition intermediate 64 and a substantial increase in the final product with a resonance at 4.2 ppm (Fig. 24, C). Initially, it was assumed that the resultant highly substituted alkylnyl addition product slowly cyclized to the corresponding phosphole. In order to obtain a more stable product we subjected the mixture to oxidation with the tert-BuOOH, and observed two new $^{31}$P-NMR resonances at 29.9 ppm and 42.7 ppm.
Scheme 9: Alkynyl addition reaction of 57 with ethynyl napthalene 63. (i) Pd(PPh3)2Cl2, CuI, Et3N, THF, reflux 70-80 °C.

After purification the peak at 29.9 ppm was identified as triphenylphosphine oxide (PPh3=O)\(^{[88]}\) and the second product 67 (Scheme 10) at 42.7 ppm was subjected to further spectroscopic characterization. It showed two strongly coupled doublets in its \(^1\)H-NMR spectrum at 3.88 ppm and 3.95 ppm (\(J_{HH} = 28 \text{ Hz}\)) with difference in chemical shifts being equal to the coupling constant (\(\Delta\delta = 28 \text{ Hz}\)) resulting in characteristic roof effect (Fig. 25). After detailed spectroscopic analysis 67 (\(^{31}\)P-NMR, 42.7 ppm) was characterized as a P-phenylbenzophosphole (Scheme 10) which suggests that C-monoacetylenic phosphaethene 57 could undergone an unusual elimination and cyclization reaction in the presence of Pd(0) to afford compound 67.
Figure 24: A-C $^{31}$P-NMR spectra representing progress of reaction between ethynyl naphthalene 63 and 57. D-E $^{31}$P-NMR spectra after tert-BuOOH addition and purification.

Figure 25: Expansion of $^1$H-NMR spectrum of compound 67.

Scheme 10: Possible elimination and cyclization mechanism of 57.
To explore substrate scope further we reacted C-monoacetylenic phosphaethene 68 with phenylacetylene using similar coupling conditions (Scheme 11). After refluxing for 48 h, the reaction mixture showed a major $^{31}$P-NMR peak at 22.78 ppm (Fig. 26, A). This reaction mixture was then oxidized in situ with meta-chloroperoxybenzoic acid (m-CPBA) and no observable change was identified by $^{31}$P-NMR spectroscopy (Fig. 26, B). However after working up, in the crude mixture we observed a $^{31}$P-NMR resonance corresponding to PPh$_3$=O at 29.57 ppm and a second resonance at 43.3 ppm (Fig. 26, C). We attempted to purify the crude mixture by silica gel column chromatography and were able to partially isolate the product with $^{31}$P shift of 42.3 ppm peak along with a new product with a $^{31}$P-NMR resonance at 65.0 ppm (Fig. 26, D). This fraction slowly recrystallized to single crystals from ethyl acetate solutions and molecular structure was obtained and were characterized as extended π-conjugated phosphole oxide 72 (Fig. 27). The P1-C1B distance was found to be 1.789(9) Å, while P1-C2 distance was 1.795(9) Å. A small impurity from this mixture also crystallized along with 72, which revealed cleavage of the phosphorus center (Fig. 28). Either this likely occurred during the oxidation step or during silica gel chromatographic separation. The C2-O2 and C8-O1 bond distances were measured to be 1.221(3) Å while C1-C4 distance was found to be 1.346(3) Å.

From this result, it can be inferred that the corresponding alkynyl addition intermediate cyclized first to phosphole 71 and subsequently oxidized to phosphole oxide 72 when reacted with m-CPBA and/or during silica column chromatography. We are also not sure which peak in $^{31}$P-NMR spectrum belongs to the corresponding phosphole 72. However, from the molecular structure it seems that the phosphole oxide 72 underwent ring opening and elimination reaction to afford diketone 73 (Fig. 28).
Scheme 11: (i) Pd(PPh3)2Cl2, CuI, Et3N, Phenylacetylene, THF, reflux 70-80 °C. (ii), Cyclization and rearrangement of the intermediate 69 to phosphole 71 followed by oxidation to the corresponding phosphole oxide 72.

Figure 26: 31P-NMR spectra showing the stepwise progress of the reaction between 68 and phenyacetylene.
Figure 27: Solid-state structure of the 72. The Mes* carbons atoms except C1B, are depicted as wireframe. All the hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P1-C2 1.795(9), P1-C5 1.837(8), P1-O1 1.478(7), P1-C1B 1.789(9).

Figure 28: Solid-state structure of the 73. All the hydrogen atoms are omitted for clarity. Selected bond lengths (Å): O1-C8 1.212(3), O2-C2 1.221(3), C1-C4 1.346(3).
4 Fused $\pi$-conjugated ring systems (Paper III)

In linearly $\pi$-conjugated chains such as polyacetylene, it might be expected that the carbon atoms would be spaced equally with each carbon atom possessing one half-filled p orbital; hence, it would exhibit metallic character due to the mutual degeneracy of the valence band and the conduction band. However, such one-dimensional equally spaced chains are fundamentally unstable. Consequently, atoms in chains (or one-dimensional lattices) tend to rearrange into pairs or dimerize causing lattice deformation. This lowers the total energy of the system and introduces an energy bandgap ($E_g$) between the top of the valence band (HOMO) and bottom of the conduction band (LUMO), and consequently, the two bands become non-degenerate. This in turn leads to localization of $\pi$-electrons in the form of single and double bonds, and is known as the Peierls distortion (Fig 29). Additionally, this leads to bond length alternation (BLA); for example, the greater the splitting between the HOMO and LUMO levels becomes, the larger the difference in C-C single and double bond lengths becomes (i.e., BLA increases).\[89\] [90] [91]
Linear conjugated chains also tend to adopt rigid conformations in order to retain efficient π-conjugation along their backbones. This structural rigidity usually leads to solubility problems, limiting the use of such polymers as solution-processable materials.\cite{92} \cite{93} The use of conjugated rings as monomer units instead of (-CH\textsubscript{x}-), such as poly(paraphenylene) (PPP), poly(paraphenylene vinylene) (PPV), and polythiophene (PTs), (Fig 30, a-c) not only stabilizes the polymer chain but also enhances co-planarity, structural rigidity, and at the same time improves the ease of chemical modification, which are all greatly desirable.\cite{94} \cite{95} However, the degree of aromaticity of the conjugated rings is also crucial, as strongly aromatic rings such as benzene tend to localize electrons within individual rings. As an example, in the case of PPP, the aromatic benzene rings are unable to planarize with respect to each other due to mutual steric repulsion. This significantly limits the effective π-conjugation length, and results in a relatively high $E_g$. The introduction of heterocycles with a lower degree of aromaticity as monomer units, for example thiophenes, usually limits the localization of electrons inside the heterocyclic ring, and instead the electrons are relatively free to delocalize over longer distances, as they have a higher propensity towards quinoidal structures.

For this reason, polythiophenes (Fig 30, c) have been widely used as π-conjugated backbones in low bandgap materials due to their stability, intrinsic
band gap of around 2.0 eV, and versatile chemical structure. Unlike trans-polyacetylene (Fig 30, b), which has two degenerate ground states, polythiophene (PTs) and related aromatic systems exhibit two non-degenerate states: the benzenoidal state (Fig 30, c1), which shows aromatic character, and the quinonoidal state (Fig 30, c2), which is higher in energy. The latter has a lower ionization energy and higher electron affinity, and so polythiophene possesses a smaller bandgap due to the significant reduction in aromaticity and loss in resonance energy, and is therefore more suitable for p-doping. The energy required interconverting between the aromatic (and / or benzenoidal) and quinonoidal structures greatly depends on the resonance energy of the aromatic units. Bredas and coworkers tried to establish theoretically a correlation between band gap and BLA and predicted that in case of polythiophene when in quinonoid structures the BLA become equal to $\delta r = +0.06$ Å the energy of the bandgap approaches to almost zero hence, these materials will exhibit more metallic like conductive nature. Therefore, the synthesis of small bandgap polymers requires structural modifications so that the resultant polymer backbone exhibits more stabilization of the quinoidal (resonance) structure.$^{[96]}$ $^{[97]}$ $^{[98]}$

![Diagram showing different types of polyaromatic polymers and their bandgaps.](image)

**Figure 30:** a-c) Different types of polyaromatic polymers. d) Two degenerate ground states of polyacetylene. c1-c2) non-degenerate benzenoidal and quinoidal structures of polythiophene.
In polythiophenes, the individual thiophene units are most often linked to each other at the alpha position via single bonds, and the mutual co-planarity of these thiophenes rings affects the effective conjugation length. Therefore, to maximize the conjugation length it is highly desirable to synthesize regio-regular polythiophenes of a fixed chain length, via either chemical or electrochemical processes. Mechanistically, the electrochemical polymerization of thiophenes involves the initial oxidation of a monomer 74, resulting in the formation of a cationic radical 74a (Scheme 12). This then captures another adjacent radical cation 74a to produce a di-cation or a doubly charged σ-dimer 74b. Alternatively, a mono-cationic radical 74a can attack a neutral monomer 74 to produce a radical cation dimer 74c, which undergoes further oxidation to produce the similar di-cation 74b as mentioned earlier. A neutral dimer 75 then forms via the loss of two protons from the di-cationic species 74b. This neutral dimer can then undergo similar electrochemical steps (i.e., oxidation, coupling, and deprotonation), resulting in the formation of trimers, tetramers, and so on. Importantly, dimers and subsequent oligomers usually oxidize at lower potentials than the corresponding monomers, which is a characteristic feature of PTs.\textsuperscript{99} [100]

Scheme 12: 74, neutral monomer; 74a radical cation, 74b di-cation or a doubly charged σ-dimer, 74c radical cation dimer, 75 neutral dimer.
PTs usually exhibit a high degree of thiophene-thiophene inter-ring rotation. However, the introduction of an ethylene bridge between two thiophene units in an oligomeric framework (Fig 31, a) can significantly reduce the degree of rotational freedom, enhancing planarity and increasing the effective conjugation length. Additionally, this significantly reduces the overall aromaticity of the system, which leads to a reduction in the bandgap ($E_g$) from 2.00 eV (polyythiophene PTs) to 1.70 eV (polythienylvinylene PTVs). Insertion of additional ethylenic spacers will further reduce the degree of aromaticity; however, at the same time, it enhances the vibrational degrees of freedom and therefore affects the BLA, thus limiting the further decrease in band gap. However, as mentioned earlier, improvements can be made by enhancing the quinoidal ground states of thiophenes, which intrinsically exhibit a higher degree of electron delocalization along the backbone. This could be achieve by stabilizing the quinoidal state via aromatic ring fusion, which eventually leads to further decreases in bandgap. In this context, a thiophenes is fused with a conjugated ring structure that possess a higher resonance energy ($E_{res}$), such as benzene ($E_{res} = 1.56$ eV), such that only one ring (the ring with higher resonance energy) can retain aromaticity, giving structures such as isothianaphthene (ITN, Fig 31, b). Due to its lower resonance energy ($E_{res} = 1.26$ eV), the thiophenes rings adopts a quinoidal structure, increasing the double bond character of the C–C bonds between the thiophenes rings and suppressing inter-ring rotation. This leads to more efficient electronic delocalization along the chain, generating lower bandgap polymers (1.0 eV) and enhancing photo-physical properties.[92]

Figure 31:- a) Polythiophenes and polythienylvinlenes. b), benzenoidal vs quinoidal structure of isothianaphthene (ITN).
Another particularly important method of reducing the bandgap is covalent rigidification, such as in cyclopentadithiophene (CPDT), where a cyclopentenyl ring is annulated between two thiophene rings (Fig 32). This results in a highly planar and rigid structure with efficient conjugation and a smaller $E_g$. Additionally, the presence of such fused rings within a molecule greatly reduces the reorganization energy, which in turn modifies the rate of intramolecular charge hopping as the rate of charge hopping and the charge carrier mobilities are directly proportional. Thus, rigidification and planarization in the form of ring fusion can greatly enhance the electrical conductivities of organic semiconductors.\[102]\[103]

Cyclopentadithiophene has three isomers ortho-76, meta-77, and para-78 depending on the positions of the sulfur atoms within the thiophene rings relative to the bridgehead carbon atom (Fig 32).\[104\] The focus of this work is to synthesize, functionalize, and characterize the para-78 (or $p$)-CPDT unit, as this isomer shows the longest red shift of absorption relative to bithiophene ($\lambda_{\text{max}} = 302$ nm for bithiophene, $\lambda_{\text{max}} = 312$ nm for $p$-CPDT). Most previous efforts in this regard have been devoted to the synthesis of solution-processable polymers incorporating solubilizing groups at the bridgehead carbon atom.$^{105}$

Unsubstituted and mono-alkylated $p$-CPDTs 79 (Fig 32) exhibit smaller HOMO-LUMO bandgaps when polymerized compared to polybithiophene, at a cost of lower solubility. On the other hand, di-alkylated $p$-CPDTs 80 (Fig 32) with alkyl chains of longer than four carbon atoms show good solubility in chloroform. Unfortunately, mono-alkylated $p$-CPDTs 79 show higher conductivity than di-alkylated $p$-CPDT 80 derivatives.$^{106}$

Another suitable approach to lowering the $E_g$ is based on intramolecular charge transfer via the introduction of electron donor and acceptor units such as a ketones or dicyanomethylenes. In the case of $p$-CPDT, a suitable acceptor unit can be integrated at the bridgehead position to selectively stabilize the LUMO level. Importantly, substituents at the bridgehead are relatively remote to the reactive $\alpha/\alpha'$-positions of the thiophene rings, which are involved in oxidative coupling during electrochemical and/or chemical polymerization. This means that bridgehead substitution has minimal impact on the oxidation potential. After electrochemical polymerization, cyclopentadithiophen-4-one 81b (Fig 32) showed an energy bandgap of 1.2 eV, which was attributed to the electron withdrawing ability of the carbonyl group stabilizing the quinonoid structure. For this reason, such electron withdrawing groups are believed to be useful for low bandgap $p$-CPDT-based materials. It is also possible to utilize a wide range of donor/acceptor co-monomers that will tune the HOMO and LUMO level of the final polymer while retaining the rigidity and planarity of the $p$-CPDT unit.$^{106}$ $^{102}$

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Figure 32: Examples of annulated thiophene rings. Different regio-isomers of CPDT 76-78. Alkylation of CPDT at bridgehead position 79-80. Incorporation of acceptor unit (C=O) at bridgehead position of CPDT 81a-b.

4.1 Synthetic accessibility of Cyclopentadithiophenes

In an attempt to mimic diazafluorenes, Kraak et al. synthesized $p$-CPDT in four steps. In the first step, 3,3'-dithienylcarbinol 83 was reacted with an equimolar mixture of lithium aluminium hydride (LiAlH₄) and AlCl₃ in dry ether, which afforded 3,3'-dithienylmethane 84. In the next step, an aqueous bromine solution was added to a mixture of 3,3'-dithienylmethane 84 and carbon tetrachloride at 15 °C, forming 2,2'-dibromodithienylmethane 85 in moderate yield. This compound was then converted to the target molecule 78 via metal-halogen exchange followed by intramolecular oxidative coupling using CuIICl₂ (Route-I, Scheme 13). Another relatively efficient approach was based on the condensation of one equivalent of 3-bromothiophene 82 and 0.2 equivalents of ethyl formate in the presence of n-BuLi, resulting in the formation of compound 83. This step was followed by in situ dilithiation of 86 at the 2- and 2'-positions and reaction with diiodoethane. This gave bis(2-iodo-3-thienyl)methanol 87, which was oxidized in the presence of pyridinium chlorochromate to yield bis(2-iodo-3-ethienyl)ketone 88. A pentenyl ring was then annulated via Ullman coupling to form the cyclopentylketone 89. This step was followed by Wolff-Kishner reduction, leading to the final compound cyclopentadithiophene 78 (Route-II, Scheme 13). A slightly different pro-
procedure involved the condensation of 3-bromothiophene 82 and 3-thiophene-carboxaldehyde 90 in the presence of $n$-BuLi, followed by successive dilithiation and diiodonation as a single two-step procedure (Route-III, Scheme 13). The final three steps (oxidation, cyclization, and reduction) were performed as mentioned in the procedure above.\[^{[109]}\]

Scheme 13: Synthetic routes towards cyclpentadithiophenes.
4.2 Results and discussion of Cyclopenta[2,1-b:3,4-\(b\)']dithiophene (CPDT):

In this section, we discuss novel arsa/phosphaalkene systems comprised of planar rigid fused ring cores in the form of cyclopentadithiophenes. The electron accepting properties of arsa/phosphaalkenes have been studied with the help of UV/Vis and transient absorption spectroscopy, as well as electrochemically and computationally.

4.3 Synthetic strategy

Cyclopentadithiophenes (CPDTs) have become attractive building blocks for \(\pi\)-conjugated materials due to their enhanced charge carrier mobility and rich redox chemistry.\[^{110}\] The \(p\)-CPDT core has two principle locations at which appropriate substitutions may impart novel optoelectronic properties. The first is the alpha (\(\alpha, \alpha'\)) positions of the thiophene rings, where the donor and acceptor moieties of choice can be introduced in a sequential manner. Alternatively, the bridgehead position can be used for incorporation of suitable substituents that can greatly alter the frontier orbital energy levels, (Fig 33).[^{111}\][^92]

![Bridgehead position](image)

**Figure 33.** Cyclopentadithiophene (\(p\)-CPDT) core

The fabrication of novel oligomers with highly defined structures and tunable frontier orbitals/energy levels is challenging. In this work, we are interested in introducing pnictogen elements such as phosphorus and arsenic to the bridgehead position in the form of phospha/arsaalkenes. The unsaturated phospha/arsaalkene units are expected to induce strong electron accepting character in the rigid cyclic CPDT core consequently will modify the LUMO level. Moreover, it also introduces an extra coordination site for post-synthetic modification.\[^{112}\] At a later stage, chemical modifications in the form of electron donating moieties at peripheral positions (\(\alpha, \alpha'\)) can be used to modify the HOMO levels without further affecting the LOMO level.

Thus the combination of an acceptor moiety in the form of an unsaturated pnictogen atom at the bridgehead and donor moieties at the alpha positions (\(\alpha, \alpha'\)) will be explored to fine-tune the HOMO-LIMO levels and the associated optoelectronic properties.
4.4 Synthesis of phospha/arsaalkene-containing Cyclopentadithiophenes (PA/AsA-CPDT):

The \( p \)-CPDT core 78 was bridged with pnictogen centers (P and As) via exocyclic double bonds. To achieve this novel synthesis, we started from Mes*-ECl\(_2\) (where E = P, As) and condensed this with the deprotonated/lithiated \( p \)-CPDT core (\( p \)-CPDT was synthesized according the literature procedure reported by Drozdov et al.\[113\]) In situ treatment of the resulting intermediate species (91a or 91b) with the non-nucleophilic base diazobicyclo-undecane (DBU) directly afforded our designed phospha/arsaalkene systems 92 and 93, respectively in good overall yields (Scheme 14). Thereafter, 92 and 93 were characterized using NMR (\(^{31}\)P, \(^{13}\)C, and \(^1\)H) and UV-Visible spectroscopy, as well as X-ray diffraction (XRD) techniques. Interestingly, \(^1\)H NMR revealed that after the introduction of the pnictogen center, the two \( \beta \)-protons on the \( p \)-CPDT core were no longer identical due to the symmetry-breaking effect of the Mes* group. The proton positioned directly below the Mes* aromatic cavity experienced an aromatic shielding effect and therefore shifted upfield, being observed as doublets at 4.46 ppm and 4.45 ppm in the proton NMR spectra of 92 and 93, respectively. Furthermore, the \(^{13}\)C spectra also clearly showed the differences between the P=C and As=C motifs. Due to the decrease in electronic density on the E=C carbon atom in 93, the carbon resonance shifted from 164.1 ppm (92, \( d, J_{P=C} = 40 \) Hz) to 177.5 ppm (93) (Fig 34).\[114\]

**Scheme 14:** (i) \( n \)-BuLi, Mes*P/As-Cl\(_2\), THF, \(-78 \) °C. (ii) DBU, THF, \(-78 \) °C to r.t.(iii) AuCl-tht, THF, r.t.

![Scheme 14](image)
Unambiguous single X-ray crystal structure analysis revealed the structure of 92 (Fig 35) and confirmed the closeness of H25 to the Mes* group (centroid Mes*- H25 = 3.64 Å), with this interaction being responsible for the above-mentioned upfield shift observed in the ¹H NMR spectrum. The X-ray diffraction analysis also showed that the P1-C7 bond length was typical for an isolated P=C bond, at 1.667(5) Å. The observed C6-P1-C7 bond angle of 102.6(2)° suggested highly s-character of lone pair. The co-planarity of the P=C bond and the CPDT core provides evidence of the extension of the π-conjugated system.

Importantly, the pnictogen lone pair acted as a coordination site for Lewis acids. In this regard, the phosphaalkene system smoothly underwent coordination with gold (I) chloride (AuCl) to afford complex 94, with a characteristic upfield shift in ³¹P-NMR from 256.6 ppm (92) to 175.6 ppm (94). Surprisingly, the complexation of gold to the arsaalkene system was not possible, even after long reaction times and prolonged heating.
4.5 UV-Vis spectroscopic analysis:

The electronic absorption spectra of compounds 92 and 93 were recorded in DCM (Fig 36). The unsubstituted PA-CPDT 92 showed an absorption maxima (λ_max) at 517 nm, which was associated with the π (HOMO) to π* (LUMO) electronic transition. The substitution of the heavier pnictogen As, (93) shifted λ_max towards longer wavelengths by 32 nm. This trend in UV-Vis absorption reflects the degree of non-hybridization in the valence orbitals, which consequently leads to smaller energy gaps between the HOMO and LUMO levels.[10]
Cyclic voltammetry:  
Cyclic voltammetry was performed in order to investigate the redox properties of the synthesized monomers 92, 93, and 94, with irreversible oxidation peaks being observed at 0.94 V and 0.87 V verses Fc/Fc⁺ for 92 and 93, respectively (Fig 37, A). Surprisingly, two additional features were observed on the reductive scan following the oxidative scan, at +0.5 and +0.25 V in the case of 92, and +0.45 and +0.23 V for 93, with these new features exhibiting quasi-reversibility. Moreover, upon repetitive cycling, a gradual decrease in oxidation potentials was witnessed, indicative of the formation of polymer films on the electrode surface.

On the other hand, we observed fully reversible behavior for the reduction peaks at -1.62 and -1.50 V in 92 and 93, respectively. The difference between the reduction potentials of the monomers gives an indication of the impact of the coplanar pnictogen centers, which significantly alter the LUMO energy levels of CPDT.

The Au'Cl complex of 94 showed an irreversible oxidation peak at 0.68 V and an irreversible reduction at -1.56 V versus Fc/Fc⁺. However, it was noted that the reductive current increased at higher scan rates (ν = 1 V/s) and exhibited quasi reversibility (E1/2 = -1.56, Fig 37, B), which indicates slow decomposition of the reduced species.
Figure 37:- Cyclic voltammograms of 92(1.0mM), 93(0.5mM), and 94(1.0mM). TBAPF$_6$ = 0.1M, WE = glassy carbon (GC), RE = Ag/AgNO$_3$, CE = Pt, $\nu =$ 100mVs$^{-1}$ (solid) and $\nu =$ 1Vs$^{-1}$ (dotted).
4.7 Electropolymerization:

Electrochemical polymerization of 93 was carried out on fluorine-doped tin oxide (FTO) electrodes, which allowed us to study the optical properties and composition of the resulting films. During the deposition of polymer films from solutions of 93, we observed that the characteristic oxidation potential peak shifted towards milder oxidation potentials as the number of scans was increased (Fig 38). This shift in oxidation potential was attributed to the formation of longer polymer chains on the FTO electrode surface. Additionally, the increase in current showed a linear dependence on the number of scans, which indicates diffusion control in combination with the electro-activity of the polymer thin film deposited on the FTO surface.

Thus, an adherent film was deposited on the FTO electrode surface during electropolymerization. Polymer film formation was fully reproducible, and the material showed no change in electro-activity under repeated scans. It could be stored for extended times under ambient conditions, and was insoluble in DCM and acetonitrile (Fig 39).
4.8 Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis of thin film

SEM is used to obtain information about the surface topologies and compositions of materials. After electropolymerization, the FTO electrode showed a more granular and globular morphology than the blank reference FTO electrode (Fig 40). The polymer thin film had a thickness of 1 μm and was mostly homogenous; however, aggregation could also be observed in some places. EDX analysis clarified the relative composition of As with respect to sulfur atoms, which provided good evidence that the intact arsaalkene monomer 93 was incorporated in the film (Fig 41).
Figure 40: SEM pictures of 93 polymer film deposited on FTO electrode surface.

Figure 41: Overlay of the EDX spectra of the 93-polymer film (red line) and an FTO substrate (blue line). The green star represents the arsenic peak, while the yellow star represents the sulfur peak in this EDX spectrum.
4.9 Calculations:

Frontier molecular orbital (FMO) energy levels play a crucial role in defining the optoelectronic properties of most organic molecules. We performed ground state and time-dependent density functional theory (TD-DFT) calculations in order to help understand the optical properties of the novel compounds 92, 93, and 94. Our key interest was to unveil the electronic impact of the P/As centers integrated as phosphinidene/arsinidene unit at the bridgehead position on the FMOs, the nature of the coordinating centers at the pnictogen atoms, and their influence on the optoelectronic properties of the systems.

During our first calculations, we also studied analogous systems to those containing the P/As=C fragment, replacing it with a C=C fragment to represent the carbon-containing parent system (96), and an O=C fragment to investigate the effect of the strongly electron withdrawing oxygen atom (89). By comparing the calculated HOMO and LUMO energy levels of 92, 93, and 96 (Fig 42, A), we observed that incorporation of pnictogen centers significantly stabilized the LUMO level (ΔE_{LUMO(C=C vs P=C)} = 0.68 eV and ΔE_{LUMO(C=C vs As=C)} = 0.81 eV) while maintaining the HOMO at the same level. The greater LUMO stabilization in 93 compared to 92 (ΔE_{LUMO(As=C vs P=C)} = 0.13 eV) can be attributed to the As atom possessing much more diffused orbitals, making hybridization difficult and causing poor orbital overlap. On the other hand, the strongly electron withdrawing nature of the oxygen atom in 89 also induced LUMO stabilization at a similar magnitude to that seen for the pnictogen materials (ΔE_{LUMO(As=C vs O=C)} = 0.04 eV), but at the same time caused a significant stabilization in the HOMO level (ΔE_{HOMO(As=C vs O=C)} = 0.51 eV). Consequently, these calculations suggested a relatively lower ΔE for 93, which is in agreement with our cyclic voltammetry findings.

In the electron density plots of the HOMOs and LUMOs of 92 and 93 (Fig 42, B), the LUMOs can be seen to be mostly delocalized over the central cyclopentadiene (fulvenoid) rings, with a significant contributions from the exocyclic hetero P/As=C fragments. However, a slight contribution from the two sulfur atoms of the planar fused aromatic ring core can also be observed. The HOMOs of all four materials are entirely comprised of the planar p-CPDT π-orbitals. In the pnictogen-containing materials, the HOMO-1 plots show major contributions from the P/As=C π-bonds, along with diminishing contributions from the p-CPDT cores. The HOMO-2 plots show the lone pairs of the pnictogens, along with some contributions from the Mes* aromatic rings.
Figure 42: Theoretical study of 89, 92, 93, and 96 at the DFT [B3LYP/6-311++G**] level. A) Electron density plots of selected molecular orbitals of model compounds 89, 92, 93, and 96. B) Energy level diagram of model compounds 89, 92, 93, and 96.
4.10 Calculation of spin densities:
We also calculated the formation of radical cations in 92 and 93, which governs the electro-polymerization behavior, using open-shell DFT calculations. The spin density plots (Fig 43), predict that the spin densities mostly reside at the alpha positions, although some degree of spin densities are also present at the quaternary carbon atoms of the central five-membered rings of the CPDT cores. Importantly, no traces of spin densities were found on the β-carbon atoms of the thiophene rings, nor on the pnictogen centers or the P/As=C carbon atom. These results clearly indicate that polymerization should predominantly occur via the alpha positions, leaving the phospha- and arsaalkene motif unaltered.

![Figure 43: Calculated spin density plots of 92 and 93.](image)

4.11 UV-Visible spectroscopy:
The UV-Visible spectra of 92, 93, and 94 showed strong absorptions in the UV region and weak absorptions in the visible region, at 517, 550, and 579 nm for compounds 92, 93, and 94 respectively (Fig 44-46). The weak absorptions (λmax) were characterized as π-π* transitions from the CPDT core to the heterofulvenoid section based on our TD-DFT calculations. This charge transfer band showed a red shift of 34 nm upon substitution of P with the next heavier pnictogen atom, As, as this substitution results in lower LUMO levels. Upon coordination of gold chloride to the P center, there was an even further red shift of 64 nm owing to the stretching of the accepter orbitals over to the metal center, increasing the accepter character of the fulvenoid section. The calculated UV-Vis spectra of model compounds 92, 93, and 94 showed similar trends (Fig 44-46), except that the UV-Vis spectrum of model compound 94 predicted an additional band at around 340 nm, which was observed as a shoulder in the experimental spectrum. The intense bands below 400 nm can be attributed to the π(fulvene)-π*(fulvene) and π(CPDT)-π*(CPDT+P=C) transitions.

Moreover, calculations using a functional including the Coulomb attenuating method (CAM B3LYP) revealed that the lowest energy transition is associated with a charge transfer band, making exact energy predictions difficult.
However, comparison of different DFT functionals show the same general trends and natures of the various transitions of these conjugated systems.

Figure 44: Calculated TD-DFT absorption spectrum of 92. Inserted plots represent electron difference density maps (EDDMs) of the indicated transitions.

Figure 45: Calculated TD-DFT absorption spectrum of 93. Inserted plots represent electron difference density maps (EDDMs) of the indicated transitions.
4.12 Time-resolved optical spectroscopy:

Light-induced processes were followed using time-resolved femtosecond absorption spectroscopy in collaboration with A. El-Nahhas, P. Chabrera, and J. Uhlig from Lund University. In order to shed light on the dynamics of the lowest energy absorption band (attributed to charge transfer), and to identify the key steps for light-harvesting applications, transient absorption experiments were performed on solutions of 92, 93, and 94 in dichloromethane. These compounds were excited with a laser pulse (λ = 550 nm) and probed with a broad-band white light pulse. The kinetic traces recorded for 92 and 93 at different probe wavelengths showed two sets of exponential decay in each case after fitting. For 92, \( t_1 = 0.6 \) ps (intersystem crossing) and \( t_2 = 7.8 \) ps (internal conversion and finally decay to the ground state), while for 93, \( t_1 = 0.6 \) ps (intersystem crossing) and \( t_2 = 9.7 \) ps (internal conversion and finally decay to the ground state, (Fig 47, A). The similar decay times indicate that the pnictogen centers seem to have little effect on the relaxation process, despite the fact that they greatly influence the transition energies. For the Au1Cl complex of 94, three distinctive dynamic ranges were observed, with three fast decays in the sub-picosecond range (sub 10 ps), an intermediate decay of 460 ps, and a slower decay with a lifetime of >18 ns (Fig 47, B). Fitting the data yielded lifetimes of \( t_1 = 2.5 \) ps (intersystem crossing), \( t_2 = 2.6 \) ps, \( t_3 = 9.6 \) ps (a comparatively long decay time), \( t_4 = 460 \) ps (representing internal conversion within the triplet state), and finally \( t_5 = >18 \) ns, with this final, even longer lifetime being a result of a long-lived state before decay to ground state. Future measurements with transient X-ray spectroscopy will give further insights into these photo-induced processes.
4.13 Synthesis of phospha/arsaalkenes-CPDT derivatives:

92 was treated with N-bromosuccinimide in order to introduce halogen functionalities at the α-positions to facilitate coupling reactions with several electron donating (or accepting) moieties. Treatment with one equivalent of N-bromosuccinimide gave mono halogenated cis-96 (31P-NMR chemical shift 262.9 ppm) and trans-96 (31P-NMR chemical shift 263.1 ppm) as a mixture of cis and trans isomers (Scheme 15, a). Upon chromatographic workup, it was possible to separate cis-96 and trans-96. However, in solution the material underwent rapid isomerization, thus making it impossible to work with the different isomers. In a different approach, we used a protocol in which the alpha substituent was introduced prior to the bridgehead functionalization. The p-CPDT-ketone 89 was halogenated using N-bromo-/iodosuccinimide (Scheme 15, b), and then coupled with carbazole under Suzuki-Miyaura coupling conditions. This gave a single product, the carbazole-p-CPDT-ketone 99, which on reduction with hydrazine hydrate followed by condensation with Mes*ECl₂ (as described earlier in this work) afforded carbazole substituted derivative 101. Similarly, this approach also gives an isomeric mixture cis-101 and trans-101 with two distinct chemical shifts observable in the 31P NMR spectroscopy (Fig 48). Recrystallization from a toluene/acetonitrile mixture afforded crystals that were suitable for X-ray diffraction analysis. Note that two types of crystals (blue and greenish) were manually sorted under a microscope and both were measured (Fig 49).
Scheme 15: Halogenation and synthesis of 92 derivatives. (i) 1 eq NBS, DCM 1 h. (ii) 2 eq NBS, DCM 1 h. (iii) NIS/NBS, DCM 1 h, yield 60%. (iv) Pd(PPh3)2Cl2, 9-ethylcarbazole boronic acid, K2CO3, THF reflux overnight, yield 40-55%. (v) N2H4, ethylene glycol, KOH, glass pressure vessel, 180 °C, 24 h, yield 70%. (vi) n-BuLi, Mes*PCL2, DBU, THF.
Figure 48. $^{31}$P-NMR spectrum of mixture of cis-101 and trans-101.

Figure 49. Solid-state structure of cis-101 and trans-101. Mes* carbon atoms except C24 are depicted as wireframes, and all hydrogen atoms are omitted for clarity. (a) cis-101. Selected bond lengths [Å]: P1-C1 = 1.683(3), P1-C24 = 1.848(3), C9-C10 = 1.474(4). Selected bond angles [°]: C1-P1-C24 = 103.7(1), S2-C9-C10 = 120.4(2). (b) trans-101. Selected bond lengths [Å]: P1-C1 = 1.684(2), P1-C24 = 1.843(2), C9-C10 = 1.468(3). Selected bond angles [°]: C1-P1-C24 = 102.6(1), S1-C9-C10 = 120.9(2), C11-C10-C9 = 119.6(3).
The P1-C1 distances were 1.683(3) and 1.684(2) Å for cis-101 and trans-101, respectively, in agreement with the typical lengths for isolated P=C double bonds.\[116\] Furthermore, the C24-P1-C1 bond angles were found to be 103.70(14)° and 102.65(14)° for cis-101 and trans-101, respectively, which correspond to Mes*P=C systems. Additionally, the carbazole unit in cis-101 is slightly twisted with respect to the p-CPDT plane with an angle of approx. 20°, whereas in trans-101 it exhibits a smaller twist angle of approx. 9.0° indicating significant delocalization within both π-systems. In an alternative approach to the functionalization of the p-CPDT core motif, we first treated 92 with 1 eq LDA followed by reaction with chlorotriphenylsilane at -78 °C, forming the corresponding PA-p-CPDT triphenylsilane (Scheme 16). This also led to a mixture of the cis-102 and trans-102 isomers of the product. This is evident from the chemical shifts observed at 257.2 ppm and 258.0 ppm in the $^{31}$P NMR spectrum (Fig 50). We were only able to crystallize the cis-102 (Fig 51), which showed a typical P=C bond distance of 1.678(2) Å while the Si-C bond was measured to be 1.852(2) Å, slightly shorter than a normal Si-C single bond (1.87-1.91 Å).\[24\] The Mes* protecting group is almost perpendicular to the P=C plane, with a C1-P1-C10 bond angle of 103.2(1)° typical for these compounds.

![Scheme 16](image)

Scheme 16:- Synthesis of triphenylsilyl-substituted cis-102 and trans-102. (i) LDA, ClSi(Ph)$_3$, THF, < -78 °C.

![Figure 50](image)

Figure 50:- $^{31}$P-NMR spectrum of triphenylsilyl-substituted derivatives cis-102 and trans-102.
Figure 51: Solid-state structure of triphenylsilyl-substituted cis-102. The Mes* carbon atoms except C10 and the triphenyl carbon atoms are depicted as wireframes and all the hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: P1-C1 = 1.678(2), Si1-C9 = 1.852(2). C1-P1-C10 = 103.2(1)°.

4.14 UV/Vis spectroscopy of PA-CPDT derivatives:

The impacts of substitutions at α and/or α’ positions on the optoelectronic properties of 92 were substantial. This is evident from the Fig 52, where it can be seen that the absorption maximum of 92 was λ_{max} = 517 nm, associated with a π-π* transition and attributed to a charge transfer band based on the results of the TD-DFT calculations. This charge transfer band was red-shifted by 32 nm upon substitution with Br at α and α’ positions (97).

Coordination of the pnictogen center with gold chloride (AuCl, complex 94) increased the acceptor character of the fulvene core, resulting in a 62 nm red shift. Replacing [Cl] with a non-coordinating [PF_6] counter anion (95) caused a 100 nm redshift of the charge transfer band. Incorporation of the electron-donating carbazole unit cis-101 and trans-101 not only shifted the absorption maxima to a longer wavelength (λ_{max} = 573 nm), but also enhanced the molar absorptivity up to 3-fold compared to the 92.
Figure 52: Steady state absorption spectra of 92, 94, 95, 97, cis-101 and trans-101.
5 Heterobuckybowls:

5.1 Linear, angular, and cluster polyaromatic hydrocarbons

As discussed earlier, fused π-conjugated systems such as π-extended aromatics, usually called polyaromatic hydrocarbons (PAHs, Fig. 53),[117] possess rigid planar structures with high stabilities and exhibit unique electronic and photophysical properties. PAHs are mainly comprised of sp² carbon atoms and relatively few hydrogen atoms. Depending on their shape and size, PAHs can be constructed from the fusion of two or more aromatic rings in a linear, angular or cluster arrangement. As an example, anthracene 103 comprised of three aromatic rings fused in a linear fashion, while benzo[a]anthracene 104 is angular, and pyrene 105 represents cluster PAHs. Interestingly, the optical and chemical properties strongly depend on the size and geometry of the corresponding PAHs. Angular PAHs usually exhibit larger HOMO-LUMO gaps and are relatively stable compared to their respective linear isomers. This is because in linear PAHs the frontier orbitals (i.e., the HOMO and LUMO levels) are localized on the zigzag edges, while in angular and cluster PAHs the frontier orbitals are distributed over the entire molecular structure.[118] This means that anthracene (ΔE = 3.5 eV)[119] can undergo photodimerization by the action of UV light to generate paranthracene, a dianthracene. Meanwhile, pentacene 108 possesses a significantly lower ΔE ≈ 2.21 eV, and is therefore found in organic electronic applications such as OLEDs and OFETs; however, this also makes it highly unstable and it readily oxidizes when expose to air and light.[120]

Triphenylene 107 is extremely stable against oxidation, possessing a higher ΔE (4.84 eV) and a higher resonance energy, while benzoanthracene 104 has a lower ΔE (3.72 eV) and absorbs at longer wavelengths.[119] Most PAHs display fluorescence and can emit light upon excitation. For example, perylene 109 exhibits blue fluorescence and is used as a blue emitting dopant in OLEDs, and its derivatives are widely used as dyes.[121] Larger PAHs can be construct from smaller PAHs via further annulation of aromatic rings. As an example, the dibenzopyrene 106 can be constructed from the fusion of two aromatic rings to a pyrene core 105, while fusing three aromatic rings to the perylene core 109 will generate a tribenzo[b,n,pqr]perylene 110 PAHs are usually fully conjugated aromatic systems, and in the absence of any steric repulsion exhibit planar structures. However, the planar arrangement can be
force into a non-planar (or curved) structure (Fig. 54) by the introduction of: a) steric strain in the form of atom crowding, or b) five-membered rings that may contain sp$^3$ carbon atoms or heteroatom bridges. As consequences of these structural modifications, the planar structure is forced to curve by the imposed angular strain. This structural distortion will result in an inefficient overlap of p-orbitals, hence lower resonance energies, reductions in $\Delta E$, and higher tendencies towards cycloaddition reactions compared to planar $\pi$-conjugated aromatic systems.\textsuperscript{[122] [123] [124] [125]}

![Figure 53: Polyaromatic hydrocarbons (PAHs)](image1)

![Figure 54: Representation of planar vs curved $\pi$-systems.](image2)

Buckminsterfullerene, often referred to as fullerene-C$_{60}$, was discovered in 1985 (Fig. 55, A).\textsuperscript{[126]} This system consists of sixty carbon atoms arranged in 12 pentagons and 20 hexagons, and adopts a non-planar structure similar to a soccer ball.\textsuperscript{[127]} Fullerene-C$_{60}$ and its derivatives exhibit excellent electron acceptor properties and have attracted much interest in polymer electronics and within the field of photovoltaics.\textsuperscript{[128] [129]}
Fig 55: Structure of Buckminsterfullerene (C₆₀)

Smaller, open-ended fragments or units are perceivable on the surface of C₆₀, for example C₂₁H₁₂ and C₂₀H₁₀ (referring to the polar caps and end caps of the C₆₀ structural motif, respectively) (Fig. 55, A). These fragments usually exhibit bent bowl-shaped structures and therefore called buckybowls or simply π-bowls. The bending in the structure is due to the five-membered rings embedded inside the fused aromatic systems, forcing the adoption of curved structures such as those seen in sumanene and corannulene. Corannulene displays C₅ᵥ symmetry due to its 5-membered central ring, while sumanene has C₃ᵥ symmetry and a 6-membered central aromatic ring (Fig. 55, A).[130] [131] Interestingly, these open-ended π-bowls possess concave and convex surfaces, (Fig. 55, B), leading to rare out-of-plane anisotropy that is not observed in most planar functionalized π-conjugated systems, which possess in-plane electronic anisotropy.[132] [133] Consequently, their ability to distinguish curvilinear surfaces via concave-convex π-π interactions makes them fascinating for supramolecular chemistry as well as transition metal complexes.[134] [135] [136] Owing to their anisotropic surfaces, these π-bowls usually prefer to stack in well-ordered columnar arrays, imparting characteristic properties such as unidirectional charge mobility.[137] Properties such as the surface curvature and rigidity of these π-bowls are characteristic, and usually depend on bowl depth and bowl-to-bowl inversion barrier (ΔG*ₗⁱⁿv). In this context, the parent sumanene exhibits a deeper bowl depth of 1.1 Å relative to the parent corannulene depth of 0.87 Å.[133] [138] The bowl-to-bowl inversion barrier of sumanene takes place via a flat transition state in solution, and is approximately 87 kJ mol⁻¹ (Fig. 56). However, the parent corannulene exhibits ΔG*ₗⁱⁿv = 48 kJ mol⁻¹ due to its shallower bowl depth.[139] [140] Transition metal-coordinated π-bowl complexes also exhibit bowl-to-bowl dynamics in solution.[141]
The parent corannulene core was first reported in 1966 via a long and tedious synthetic route, and since then the material has been extensively investigated for its photophysical properties. In 1991, Scott et al. synthesized corannulene via flash vacuum pyrolysis (FVP). In contrast, sumanene remained elusive despite the fact that it comprised of peripheral sp\(^3\) carbon centers that are amenable to structural and chemical functionalization. The FVP synthesis of the parent sumanene core starting from the more planar triphenylene was ineffective, likely due to the increase in strain energy upon annulation (Scheme 17, A). Finally, in 2003 Sakuari et al. reported the first solution processable synthesis of the parent sumanene core based on condensation, ring opening, and ring closing metathesis reactions followed by oxidative aromatization (Scheme 17, B).

The parent sumanene core is comprised of three annulated fluorene moieties that in turn contain three peripheral sp\(^3\) hybridized carbon atoms (Fig. 57). Fluorene possesses unique optoelectronics properties, and its derivatives usually exhibit blue fluorescence. Hence, fluorene is extensively applied in optoelectronic devices and is also widely used as \(\pi\)-spacer in electron donor-acceptor systems.
Figure 57: Sumanene core can be perceived as a fusion of three fluorene moieties.

Another planar rigid PAH, truxene, can also be traced out on the fullerene-C\textsubscript{60} surface (Fig 58). Structurally it can be constructed from mutual fusion of three fluorene units that share a central aromatic ring, such that it results in a heptacyclic structure with three-fold symmetry. Truxene also serves as a building block for the construction of larger π-architectures such as cages, fused spiro-compounds, and dendrimers. Moreover, due to fusion of five membered rings with six membered aromatic rings, truxene is used as a precursor for synthesizing π-bowls. However, the problem with the truxene core is its insolubility in most organic solvents due to its rigid, planar structure. Truxene and its derivatives are considered to be promising scaffolds for organic electronic materials, and usually exhibit blue fluorescence, meaning that they have found broad application as blue light-emitting materials for OLEDs. Due to their excellent affinity towards fullerene-C\textsubscript{60}, they are also used in OPVs. Truxene and its derivatives usually exhibit enhanced photoluminescence properties relative to triphenylene, which has a very low quantum yield (6.6%) due to efficient intersystem system crossing\textsuperscript{[117]}\textsuperscript{[117]} An increase in arm lengths in the truxene core via further annulation or fusion of aromatic rings shifts the absorption and emission towards longer wavelengths\textsuperscript{[149]}\textsuperscript{[149]}

Figure 58: Truxene, smaller fragment of fullerene-C\textsubscript{60}.

Truxene has two isomeric forms, truxene 119 and iso-truxene 120 (Fig. 59). In the latter isomer, the three methylene (-CH\textsubscript{2}-) bridges are arranged differently (constitutional isomerism), resulting in breaking of symmetry. In truxene 119, the -CH\textsubscript{2}- units arranged such that the molecule as whole adopts a C\textsubscript{3} symmetric arrangement. The first synthesis of truxene was reported in 1894 via acid-catalyzed cyclization of 3-propanoic acid 117, facilitating the in situ formation of 1-indanone 118 that undergoes self-condensation to afford a mixture of truxene 119 and iso-truxene 120 and/or the dimerization product of 1-
However, the first selective synthesis of truxene 119 was carried out from (3-methylthio)indene 121. Later on, Bergman reported the acid-catalyzed cyclotrimerization of 1-indanone 118. Oded et al. also reduced the truxenetrione/truxenone 122 to 119 using hydrazine hydrate and ethylene glycol.

Figure 59: Synthetic routes to the truxene core.
5.2 Heterosumanene:

It has been observed that the replacement of sp³ carbon atoms in PAHs with heteroatoms can impart high electron conductivity, enabling the resulting materials to be used as organic dyes for solar cells (Fig 60). In this regard, incorporation of heteroatoms in the parent sumanene core would be expected to greatly influence the bowl depth and bowl-to-bowl inversion barrier, thus altering the physicochemical properties of the molecule. The size of the heteroatom is crucial, as the curvature of the sumanene core will decrease with increasing heteroatom size (or covalent radius), as a consequence also facilitating ring closure during synthesis. Consequently, insertion of S trithiasumanene and Se triselenasumanene in to the sumanene core exhibit bowl depths of 0.65 and 0.47 Å, respectively, while insertion of Si trisilasumanene and Te tritellurasumanene were found to be almost planar (Fig 60, 125). Moreover, triphosphasumanene trisulfide insertion of P, exhibited two isomeric products in syn- and anti-conformations; the latter was characterized as a planar molecule, while the former exhibited a bowl depth of 0.46 Å. Consequently, the syn-isomer demonstrated high out-of-plane anisotropy and a large dipole moment (12.0 D) due to the electron-rich sulfur atoms.

![Figure 60: Insertion of heteroatoms into PAHs.](image)

5.3 Synthesis of heterosumanenes:

Two principal synthetic routes are used for the synthesis of heterobuckybowls: the trindene route (Scheme 18) and the triphenylene (or non-pyrolytic) route (Scheme 19-21). In the latter, each successive ring closure step is endothermic, and the resulting increase in strain energy for each successive step makes the final ring closure step almost impossible. In this regard, Klemm et al. concluded that in the synthesis of trithiasumanene starting from the highly aromatic triphenylene, the final ring closure step would require an energy of 40 kcal mol⁻¹. In the case of the trindene route, calculations predict
negative reaction energies for each successive ring closure step. In fact, the high strain energies for the triphenylene route are due to its highly aromatic nature compared to the trindene route, which involves the cyclization of less aromatic heterocyclic rings.\[^{160}\]

For this reason, the trindene route was used by Imamura to prepare the first heterobuckybowl, trithiasumanene, in 1999 (Scheme 18), starting by brominating trithiophene 126 followed by Sonogashira coupling and desilylation to afford the triacetylenic derivative 127. Addition of an acid resulted in the tris(chlorovinyl) compound 128, which was exposed to FVP conditions to afford the desired trithiasumanene 129 in an overall yield of 6%.\[^{156}\] However, this route utilizes an expensive starting material, benzotrithiophene 126, and also suffers from low yield and involves harsh reaction conditions.

Scheme 18: Trindene route for trithiasumanene synthesis.

To avoid these difficulties, the triphenylene or non-pyrolytic route started to attract attention. Initially, an intramolecular sila-Friedel-Crafts reaction was used to silylate electron-rich aromatic rings. However, non-activated aromatic rings are less favored for this reaction, resulting in low yields. An alternative strategy was based on the formation of a dibenzosilole-type framework starting from triphenylene 130 (Scheme 19), which was first halogenated in the bay region. In the next step, the halogenated compound 131 was reacted with \(n\)-BuLi and dichloro-diphenyl silane then reduced with LiAlH\(_4\) to afford hydrosilane 132. This was then reacted with a trityl cation to produce an intermediate silicenium ion that rearranged to a silicenium aren complex that was further reacted with mild base to afford triphenylenedisilole 133. Repeating the same procedure once more resulted in the trisilasuamene 134.\[^{158}\]
X. Li et al. modified the triphenylene route, and designed a two-step synthetic protocol (Scheme 20) involving non-pyrolytic 1,2-dithiin ring formation in the bay region of the triphenylene core 136, followed by copper-mediated desulfurization at 200 °C to provide the trithiasumanene product 137. Later on, stepwise introduction of silicon in the bay region of triphenylene was shown to facilitate the synthesis of trisilasumanene 139, though in a low yield. In this procedure, a mixture of \( n \)-BuLi and TMEDA (N,N,N,N-tetramethylenediamine) in \( n \)-hexane was reacted with triphenylene 130 to afford the 1,2-dilithiotriphenylene intermediate 135. Treating this intermediate species with dichlorodimethylsilane and copper cyanide as a catalyst afforded triphenylenesilole 138. During the second step, the use of chlorodimethylsilane instead of dichlorodimethylsilane under the same reaction conditions greatly improved the yield. In the final step, 138 was treated with \( n \)-BuLi and TMEDA and then reacted with dichlorodimethylsilane to afford the trisilasumanene 139. However, treating the triphenylenesilole moiety with excess \( n \)-BuLi resulted in the substitution of the butyl group from the butyllithium onto the silicon atom.
The above method of sequential lithiation can also be used to introduce different main group elements. Li et al. reported the first triselenasumanene via this non-pyrolytic triphenylene route. Treating triphenylene 130 (Scheme 21) with 10 eq of the n-BuLi/TMEDA complex in n-hexane facilitated the immediate formation of the hexalithiated triphenylene 140. This lithiated intermediate was treated with selenium powder to afford compound 141, which contains two selenophene rings and one diselenin ring. In the following step, compound 141 was deselenated in the presence of copper powder at 200 °C to smoothly afford the first triselenasumane 142 on a gram scale. Soon after, Wang et al. reported tritellurasumanene, starting from hexaalkoxytriphenylene 130, which was first converted to the hexalithiated intermediate 140 in the presence of the n-BuLi/TMEDA complex. This was reacted with tellurium powder at -78 °C and stirred under sonication for 12 h to afford tellurasumanene 143 (Scheme 21). Within the same year, Furukawa et al. reported the first pnictogen-containing heterosoumanene, triphosphasumanene trisulfide; (Scheme 21). Applying the same one-pot synthetic strategy, the resultant hexalithiotriphenylene 140 was first treated with PhPCl₂ followed by oxidation with elemental sulfur. The resulting crude mixture was then separated by silica gel chromatography into the syn-145 and anti-145 isomers of the product.
Scheme 21: Synthetic route towards sumanene derivatives of trichalocgens and trispnicotogens.
5.4 Heterotruxene:

Replacement of the -CH2- groups in α-truxene cores with heteroatoms such as N or P can significantly modify the opto-electronic properties and enhance the solubility. As an example, the replacement of all three methylene groups with N results in triazatruxene 146 (Fig 61), three carbazole units fused together via 6-membered central aromatic ring, an excellent electron donor system with an extended π-conjugated structure that has found broad application as a dye and hole transport material in organic electronics. Additionally, Kojima et al. successfully replaced the sp3 bridging carbon atoms with RP units to generate phosphatruxene 147.[168] [169]

Truxenetrione 122 is a precursor for making truxene with integrated acceptor units in the form of C=O. The acceptor strength of this planar molecule can easily be modify. Nilesen et al. replaced the C=O functional group with strong electron withdrawing dicyanovinylene to create 148, which significantly modified the acceptor properties. Thus, 148 has found broad application as an electron acceptor layer in organic photovoltaics.[170] To date, no one has attempted to introduce phosphaalkene units as exocyclic substituents of truxene.

Figure 61: Heterotruxene derivatives.
5.5 Synthesis of heterotruxenes:

As mentioned before, truxene has three -CH$_2$- bridges with weakly acidic protons that are accessible for further functionalization using suitable reagents. As an example, Echavarren et al. introduced alkyl chains through these -CH$_2$- bridges. The use of strong bases such as KH/n-BuLi generates trianions 149-K/149-Li (Scheme 22) that in subsequent steps react with alkylhalides to afford the anti-150 and syn-150 trialkylated truxenes respectively. When NaH was used as a base, the reaction afforded only anti-150, which can then be easily isomerized to syn-150 using the base tert-BuOK.[171]

To make extended polyaromatic systems, the trianion 149 of truxene 119 was generated using a suitable base and treated with 2-bromobenzyl bromide to give the tribromo derivative 151, which affords π-bowl shaped molecule 152 in the subsequent palladium-catalyzed intramolecular arylation reaction. Alternatively, triazatruxene 146 was synthesized from indole 153, which was first reacted with Br$_2$ to obtained hexabromotriindole 154 then debrominated in the presence of triethylammonium formate and Pd/C to yield the desired triazatruxene, 146. The phosphorus center was introduced into the truxene core in the form of phosphole 147 via a sextuple aromatic nucleophilic substitution reaction. The hexa-fluorinated compound 155 was refluxed with phenylphosphine in the presence of K$_2$CO$_3$ as a base to afford the triphosphatruxene, 147. However, due to the pyramidal nature of the P$_{III}$ center the compound existed as syn and anti-isomers. Compound 147 was oxidized with tert-BuOOH at room temperature to afford the trioxide, 156.[151] [152] [169] Truxenetrione 122, which possesses exocyclic C=O bridges, can be easily synthesized in good yields by cyclotrimerization of indan-1,3-dione 157 in the presence of protic acids.[172] The subsequent condensation of 122 with malononitrile produces the dicyanomethylene exocyclic bridges 148.[170]
Scheme 22: Synthetic routes towards heterotruxenes.
5.6 Results and discussion: pnicta-truxenes and pnicta-sumanenes

This section deals with functionalization of truxene 119 and sumanene 116 with pnictogens. The resultant compounds have been evaluated using different spectroscopic techniques. However, the outlook of this chapter will mostly discuss the synthesis of pnicta-sumanenes and their characterization.

5.7 Synthetic strategy:

The sp$^3$ carbon center in truxene 119 will be modified to an sp$^2$ carbon center via sequential introduction of P/As centers in form of phosphinidene or arsinidene fragments (Fig 62, A). This modification will result in P=C or As=C exocyclic double bonds acting as acceptor units, and will therefore selectively lower the LUMO levels. Importantly, the model compound A (Fig 62) contains up to three fulveniod subunits in a single molecule. In addition, this will result in a further extension of π-conjugation compared to the parent truxene 119. Due to the lone pair on P$^{III}$ and the 2,4,6-tris-tert-butylphenyl protecting group (Mes*) the solubility of the compound in common organic solvents will be greatly improved. Moreover, the three lone pairs will provide coordination sites for Lewis acids and the π-π interactions between the extended π-conjugated aromatic core and other PAHs will be explored.[173]

Phosphorus-based radicals are involved in many organic and biological reactions, and therefore efforts have been made to stabilize these radicals. For example, phosphorus-based mono- and biradicals anions 158 and 159, respectively, (Fig 62) have been generated from fluorene/indenofluorene-bridging phosphaalkenes and were isolated and spectroscopically fully characterized.[174] [175]

Similarly, tris-pnicta-truxenes can potentially undergo up to three-electron reduction upon electrochemical and/or chemical reduction. These reduced species/radicals will be further characterized using spectroelectrochemistry in order to understand their radical natures and consequently their electronic properties.
5.8 Synthesis of 10,15-dihydro-5H-diindeno[1,2-α;1′,2′-c]fluorene precursor (truxene-119):

Compound 119 was synthesized according to literature procedure, in which 1-indanone 118 was refluxed in acetic acid (Scheme 23). Thus, 118 undergoes cyclotrimerization with elimination of H2O to produce 119. The resultant mixture was first neutralized with an ice-cold saturated solution of Na2CO3, followed by extensive sequential washing with H2O, acetone, and DCM to afford pure 119 in 50-60% yield. Compound 119 as dried under vacuum for 30 min and served as a precursor for further functionalization with P/As centers.
5.9 Synthesis of phosphatruxene:

To access phosphatruxene, Mes*-Br was lithiated using 1 eq of n-BuLi at \( \leq -78 \, ^\circ\text{C} \) in dry THF and then reacted with an excess of PCl\(_3\) according to the literature procedure.\[^{177}\] This reaction mixture was first dried under vacuum to remove the excess PCl\(_3\), then re-dissolved in dry THF and reacted with trianion 149-Li, generated from the reaction of 119 with 3 eq of n-BuLi at \( \leq -78 \, ^\circ\text{C} \) in dry THF (Scheme 24). The reaction mixture of this salt metathesis was analyzed by \(^{31}\)P NMR, and three major resonances at 87.8, 84.7, and -22 ppm were observed, along with one at 153 ppm corresponding to unconsumed Mes*-PCl\(_2\) (Fig 63). The resonances at 84.7 and -22.0 ppm were characterized as butyl-substituted Mes*-P(C\(_4\)H\(_9\))Cl and Mes*-P(C\(_4\)H\(_9\))\(_2\), respectively. Without any purification, this reaction mixture was subsequently reacted with excess of non-nucleophilic base (1,8-diazabicyclo[5.4.0]undec-7-ene, DBU), and the resulting reaction mixture was analyzed by means of \(^{31}\)P NMR spectroscopy. The only changes observed was the disappearance of the \(^{31}\)P peak at 87.8 ppm and the appearance of three new resonances at 267.5, 263.8, and 258.5 ppm (Fig 64, A-B). One possible interpretation of this \(^{31}\)P NMR result is that the three resonances represent the syn- and anti-isomers of either di- or tri-phosphinidenotruxene along with the mono-phosphinidenotruxene; alternatively, they could simply be a mixture of mono, di, and tri-phosphinidenotrxene.

![Figure 63: \(^{31}\)P NMR spectrum of reaction mixture after Mes*-PCl\(_2\) addition.](image-url)
However, two type of compounds were isolated after purification: monophosphinidenotruxene 160, with a $^{31}$P-NMR resonance at 269.8 ppm, and diphenolphinidene truxene 161, with two equally intensities $^{31}$P-NMR resonances at 265.4 and 259.5 ppm (Fig 65, Scheme 24). This demonstrates that the two phosphorus atoms in 161 are no longer chemically equivalent. Interestingly, 160 showed a characteristic pseudo-triplet at 9.8 ppm with a rare example of through-space P-H coupling ($J \approx 8.0$ Hz, Fig 66, A), which in $^1$H($^{31}$P)-NMR was resolved into a doublet ($^3J_{HH} \approx 8.0$ Hz, Fig 66, B). The peaks were assigned to aromatic protons close in space to the P III center. Furthermore, the two pairs of methylene-bridge (-CH$_2$-) protons were observed at 4.30 and 4.20 ppm as broad singlets. The $^1$H-NMR of 161 shows two broad singlets of equal intensities at 7.55 and 7.54 ppm, identified as the CH (meta) aromatic protons of the Mes* group. In addition, a broad singlet identified as the methylene (-CH$_2$-) protons was observed at 4.24 ppm. Interestingly, two downfield-shifted doublets were observed at 9.57 ppm ($^3J_{HH} \approx 8.0$ Hz) and 9.33 ppm ($^3J_{HH} \approx 8.0$ Hz) in 161 (Fig 66, C). The appearance of these two doublets indicates more distortion in the planar truxene 119 core, leading to longer distances between the arene CH protons and the P III centers. Compound 161 was recrystallized from n-pentane to afford single crystals suitable for X-ray analysis. From the X-ray structure (Fig 67), it is clear that the two P III centers are in different chemical environments. Additionally, the two substituted indenofluorene units of the truxene core are slightly twisted, while the unsubstituted
indenofluorene unit remains planar with respect to the central 6-membered aromatic ring. The P1-C1 distance was found to be 1.696(2) Å, while the P2-C17 distance was 1.694(2) Å, which agreed with literature data for isolated P=C double bond distances.\cite{178} The C28-P1 and C46-P2 distances were measured to be 1.841(2) and 1.837(2) Å, respectively. Moreover, the C28-P1-C1 angle was found to be 104.0(1)°, slightly wider than the C46-P2-C17 bond angle of 103.7(1)°.

Scheme 24:- Synthesis of mono- and di-phosphinidene-truxene 160 and 161. (i) 3 eq of n-BuLi at ≤-78 °C, Mes*-PCl₂, DBU.

Figure 65:- Expansion of the ³¹P-NMR spectra of 160 and 161 after purification.
Figure 66:- Expansions of the most downfield shifted resonances of 160 and 161.

Figure 67:- Solid-state structure of 161. The Mes* carbon atoms except C28 and C46 are depicted as wireframes and all the hydrogen atoms are omitted for clarity. Selected bond lengths [$\AA$]: P1-C1 1.696(2), P2-C17 1.694(2), C28-P1 1.841(2), C46-P1 1.837(2). Selected bond angle [$^\circ$]: C28-P1-C17 104.0(1), C46-P2-C17 103.781)
It was inferred from the above experiments that the lithiation of 119 suffered due to hydrolysis. Therefore, the experiment was repeated, but this time 119 was thoroughly dried under vacuum for 3 days before performing the lithiation. By repeating the same synthetic steps (Scheme 25), this time with large excess of n-BuLi (i.e., 4-6 eq), the resultant crude reaction mixture after addition of DBU showed a single $^{31}$P-NMR resonance at 259.6 ppm (compound 162 Scheme 25, Fig. 68, A-C). After aqueous work up, acetonitrile wash and repeated silica gel chromatographic purification (7% isolated yield), a broad doublet ($^{3}J_{HH}$ ≈ 8 Hz) was observed at 9.1 ppm in the $^{1}$H-NMR spectrum (Fig. 69). Interestingly, only a broad singlet (integration ≈ 6H) was observed at 7.50 ppm for the CH (meta) aromatic protons of the Mes* group. Moreover, only a single broad resonance at 1.43 ppm was observed for the t-butyls groups (integration ≈ 81H), indicating similar chemical environments for all these protons. Hence, NMR analysis suggested that the tri-phosphinidennotruxene 162 is fully symmetric, with all the Mes* groups pointing in the same direction. The attempted sequential introduction of P/As as phosphinidene or arsinidene units using 1 or 2 eq of n-BuLi suffered from formation of mono-, di-, and tri-substituted product. One potential reason for this could be the insolubility of 119 in common organic solvents, which could subsequently limit the formation of the trianion of 149-Li and result in a mixture of mono-, di-, and trianions. From the earlier experimental results (Scheme 24) where mono-160 and di-161 were obtained, the sequential introduction reaction can be optimized by taking advantage of the beneficial role of H$_{2}$O during this synthesis.

Scheme 25: A) Vacuum drying of truxene 119, excess (4-6 eq) of n-BuLi at ≤-78 °C, Mes*-PCl$_{2}$, DBU. B) 1 or 2 eq of n-BuLi at ≤-78°C, Mes*-PCl$_{2}$, DBU.
Figure 68: Synthesis of 162. Stepwise progress followed by $^{31}$P-NMR spectroscopy.

Figure 69: Expansion of $^1$H-NMR spectrum of 162 showing the most downfield resonance at 9.1 ppm.
5.10 Photophysical properties:

The electronic absorption spectra of the synthesized compounds 160 161, and 162 were measured in DCM (Fig 70). The photophysical data of 160 161, and 162 as well as the precursor 119 are listed in Table 2. Notably, 162 exhibited a substantially redshifted absorption maxima ($\pi-\pi^*$ electronic transition), with $\lambda_{\text{max}}$ increasing from 298 nm (119) to 452 nm (162). This red shift of 154 nm can be explained on the basis that 119 exhibits a planar and rigid conformation, and absorbs at the lower limit of the visible region. However, when integrated with an acceptor unit as in 160, there is an abrupt shift toward longer wavelengths, with $\lambda_{\text{max}} \approx 428$ nm. This indicates that the integration of acceptor units in the form of phosphinidene fragments considerably lowers the LUMO level. This chemical modification also introduced structural changes in the planar core of 119, and was consequently responsible for this substantial 130 nm red shift. On the addition of subsequent phosphinidene fragments, there was a gradual decrease in LUMO level, observed as a red shift of 7 nm and 24 nm for compounds 161 and 162, respectively.

![Figure 70: UV-Vis spectra of 160, 161, and 162 in DCM at r.t.](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>428, 317</td>
</tr>
<tr>
<td>161</td>
<td>435, 325</td>
</tr>
<tr>
<td>162</td>
<td>452, 390, 330</td>
</tr>
</tbody>
</table>

Figure 70:- UV-Vis spectra of 160, 161, and 162 in DCM at r.t.
Table 2. Comparison of $\lambda_{\text{max}}$ of 119, 160, 161, and 162.

<table>
<thead>
<tr>
<th>Entry</th>
<th>$\lambda_{\text{max}}$ nm</th>
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<tbody>
<tr>
<td>119</td>
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<td>160</td>
<td>428, 317</td>
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<tr>
<td>161</td>
<td>435, 325</td>
</tr>
<tr>
<td>162</td>
<td>452, 390, 330</td>
</tr>
</tbody>
</table>

5.11 Electrochemistry:

Cyclic voltammetry was performed for compounds 161 and 162 to uncover the redox properties of these interesting new molecules. A DCM solution of compound 161 exhibited two reversible reduction peaks at -1.92 and -2.20 V (Table 3), while an irreversible oxidation peak was seen at 0.80 V versus Fe/Fe$^+$ (Fig 71). The first reduction is fully reversible even at slower scan rates, while the proximity to the solvent window makes analysis of the second reduction peak more difficult. The similar chemical systems 159 (Fig 62) exhibited a phosphorus centered radical anion and diradical dianion character upon electrochemical reduction in THF versus Ag/AgNO$_3$, observed as one fully reversible reduction peak at -1.72 V and a quasi-reversible reduction peak at -2.35 V (Table 3).

The electrochemical analysis of 162 was carried out in THF instead of DCM. The cyclic voltammogram of 162 exhibited three fully reversible reduction peaks at -1.89, -2.23, and -2.67 V versus Fe/Fe$^+$. These were due to the three phosphinidene acceptor units in 162, which allow it to exhibit one-, two-, and three-electron reduction in the same molecule (Fig 72).[175]
Table 3. Redox data of 161, 162 vs 119 and 159.

<table>
<thead>
<tr>
<th>Entry</th>
<th>$E_{1/2}^{(\text{Red})}$ (V)</th>
<th>$E_{1/2}^{(\text{Ox})}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>119</td>
<td>-2.59 (irr) mV (DMF)</td>
<td></td>
</tr>
<tr>
<td>159</td>
<td>-1.72 (rev), -2.35 (quasi) (THF)</td>
<td></td>
</tr>
<tr>
<td>161</td>
<td>-1.92 (rev), -2.20 (rev) (DCM)</td>
<td>$E_{pa}$ 0.80 (irr)</td>
</tr>
<tr>
<td>162</td>
<td>-1.89 (rev), -2.23 (rev), -2.67 (rev) (THF)</td>
<td>$E_{pa}$ 0.78, $E_{pc}$ 0.68 (DCM)</td>
</tr>
</tbody>
</table>

Figure 71: Cyclic voltammogram of 161, 1.0 mM in DCM, TBAPF = 0.1 M, scan rate 100 mV/s, working electrode (WE) = glassy carbon (GC), reference electrode (RE) = Ag/AgNO₃, counter electrode (CE) = Platinum
Figure 72: Cyclic voltammogram of 162, 1.0 mM in THF, TBAPF = 0.1M, scan rate 100 mV/s, working electrode (WE) = glassy carbon (GC), reference electrode (RE) = Ag wire, counter electrode (CE) = Platinum. Asterisk sign (*) represent Fc/Fc+ peak.

5.12 Spectroelectrochemistry:-

UV-Vis spectroelectrochemistry was used to monitor the spectral changes of tri-phosphinidenotruxene 162 upon reduction to the corresponding mono-, di- and trianion. Steady-state UV-Vis spectra of 162 (as discussed earlier Fig. 70) exhibit characteristic π-π* absorption bands at 452 and 390 nm. At an applied potential of -1.8 V (versus Ag/AgNO3; sufficient to create the monoanion) these absorption band gradually start to decrease in intensity and shift to slightly longer and shorter wavelengths, respectively. Another broad absorption feature started appearing as a shoulder at 620 nm and a further shoulder around 760 nm. The isosbestic point at 491 nm indicates a clean reduction process. Full reduction to the monoanion 162^- was achieved after approx. 500 s (Fig. 73, A) and the potential was changed to -2.2 V in order to obtain the dianion. We observed a gradual decrease in the absorption intensity λ_{max} at 455 nm (band) and the appearance of new absorptions at 515 nm (shoulder) and 620 nm (band) and an increased intensity of the 780 nm band. This new species was assigned to the formation of 162^{2-}, which could be diradical in nature (Fig. 73, B). This transition from 162^- to 162^{2-} is associated with an isosbestic point at 493 nm. Further reduction at -2.7 V provides the trianion. We observed the opposite trends i.e. the absorption at 600 nm diminishes gradually, while at the same time a new feature at 448 nm started to gradually
increase with concomitant re-emergence of a band at 390 nm. This was assigned to the formation of the trianion $^{162}\text{I}^{3}$ (Fig. 73, C). Although an isosbestic-like point at 480 nm indicates a clean transformation, minor decomposition or solvent interferences might partially obscure the full stability and reversibility, observed in the CV-experiments.

Figure 73: - UV-Vis Spectroelectrochemistry of tri-phosphinidenotruxene $^{162}$, 1.7 mM in THF, working electrode (WE) = platinum mesh, reference electrode (RE) = Ag/AgNO$_3$, counter electrode (CE) = Platinum. The potential was held at A) -1.8 V, B) -2.2 V each for 500 s and C) -2.7 V for 400 s. The red circle indicate isosbestic points in each spectra.
5.13 Outlook

The functionalization of mixed five- and six-membered ring PAHs such as the sumanene core with isoelectronic pnictogen substituents in particular As, will be explored for its unique reactivity. This replacement of benzylic sp³ carbon atoms with Arsenic centers will be anticipated to induce significant changes in the π-bowls curvature due to the larger covalent radius of As compared to C. On the other hand it would provide the possibility to isolate the triarsasumane with trivalent As centers. As the triphenylene route offers an advantage to sequentially introduce heteroatoms, therefore it is also worthwhile to introduce two (or even three) different types of heteroatoms into the sumanene core. Thus, this mixed metal combination of pnictogen centers can have different binding preferences. Additionally, this mixed metal substitution will also greatly modify the LUMO level. The two (or three) pnictogen centers are expected to be reduce at different potentials making it an interesting acceptor material.

These π-bowls possess convex and concave surfaces and therefore they have the capability to encapsulate metal centers. It has been shown that sumanenyl monoanion reacts with Cs⁺ to afford the organometallic sandwich complex [Cs(C₂₁H₁₁⁻)₂]. Notably the Cs⁺ displays interaction with the entire concave surface of the sumanenyl monoanion.\(^{179}\) Similarly, incorporation of pnictogens P/As in the form of heteroles can have the ability to produce pnictogen based radical anions that can be further explored toward cation interactions. Interestingly, these buckybowls exhibit multiple coordinating sites due to their concave and convex surfaces and thus depending on the nature of transition metal centers can undergo either exo-coordination at the convex surface or endo-coordination at the concave surface.\(^{180}\) Apart from this, extension of π-conjugation in the sumanene core would also be possible as exocyclic pnictinidene substituents at the benzylic carbon atom.\(^{181}\)

We reported the novel synthesis of a phosphinidenotruxene in this thesis work. It can be expect that the introduction of arsinidene units in the truxene core will further modify the LUMO level. The sequential introduction of pnictinidene units in the truxene core will provide the opportunity to have mixed pnictogen truxene derivatives. The study of these mixed truxene systems will help to understand the chemical nature, the impact on the electrochemical as well as optoelectronic properties of the systems. Furthermore, these systems could be advanced toward the application in supramolecular chemistry and material science.
Summary and Concluding Remarks

In this research work, we explored different kinds of π-systems incorporating low coordinated pnictogens in particular P and or As. In the first part of this thesis work, we focused on the development of a synthetic route to selectively alkynylate Mes*-P=C(Br)₂ (dibromophosphaethene, a stable synthon for an isolated P=C double bond) at the C-terminus of the P=C double bond. A direct, sequential and stereo-selective method of alkynylation was successfully developed, in which arylsulfonylacetylene was used as coupling partner with dibromophosphaethene. In the later stage, a second acetylenic moiety was introduced via Sonogashira coupling reaction on the C-terminus of the P=C double bond. The synthesis started with selective lithiation Mes*-P=C(Br)₂ at temperature below -100 °C. The resultant Li-carbenoid was kept at <-100 °C for the subsequent reaction with the arylsulfonylacetylene to afford C-monoacetylenicphosphaethenes. Temperature control is crucial, as elevated temperatures will result in cis/trans isomers and the diacetylenicphosphaethene all at once. The C-monoacetylenicphosphaethene after successful isolation was reacted with terminal alkynes to afford the desired C,C-diacetylenicphosphaethenes. Notably, it was observed that with access of terminal alkynes and slightly higher catalyst loadings, the C,C-diacetylenicphosphaethene potentially undergoes further alkynyl addition to afford highly branched 1-phospha-1,3-butadienes a heavier analogue of 1,3-butadiene. The stepwise formation of these 1-phospha-1,3-butadienes was thoroughly investigated. It was inferred based on NMR spectroscopic studies that the formation of 1-phospha-1,3-butadienes requires relatively highly load of Pd[0] catalyst and a co-catalyst (CuI). Further, reactivity of these 1-phospha-1,3-butadienes was explored. It was found that 1-phospha-1,3-butadienes cyclizes in the presence of light, silica gel and/or chlorinated solvents to highly substituted phospholes.

In the second part, we integrated pnictogen (P/As), as exocyclic substituents in from of phosphinidene or arsinidene fragments into the cyclpentadithiophenes (p-CPDT) core. The optoelectronic properties of these novel compounds were investigated by means of UV-Vis (steady state and transient absorption) spectroscopy and electrochemical techniques. Indeed, the pnictogen centers greatly modify the LUMO level. The corresponding HOMO level was later addressed by incorporation of donor moieties at the peripheral position (α) of the p-CPDT core. The electrochemical studies in combination with theoretical calculations show that the heavier pnictogen (As) possessed the lowest HOMO-LUMO gap. Further facile complexation of the pnictogen center...
in PA-\textit{p}-CPDT with Au\textsuperscript{I}Cl shifts $\lambda_{\text{max}}$ further toward longer wavelengths. Importantly, the Au\textsuperscript{I}Cl complex of PA- \textit{p}-CPDT shows an extended lifetime of the excited states possibly due to additional triplet states.

In the third part, synthesis of unprecedented tri-phosphinidenotruxene was attempted. This smaller fragment of fullerene-C\textsubscript{60}, i.e. truxene, was first lithiated to generate the respective trianion, which was then reacted with Mes*PCl\textsubscript{2} and a non-nucleophilic base to establish exocyclic P=C bonds. We synthesized for the first time a series of mono, di and tri-phosphinidenotruxene derivatives, which were fully characterized by NMR spectroscopy, XRD, UV-Vis spectroscopy and electrochemistry. The UV-Vis measurement showed a significant red shift of the longest wavelength upon pnictogen incorporation as exocyclic substituents. Importantly the most interesting electrochemical outcome was observed in the case of the tri-phosphinidenotruxene. This compound exhibits three one-electron reduction processes. The synthesis of arsinidenophosphotruxene are currently under investigation in our lab. The future aim of this project is to establish a mixed pnictogen truxene derivatives and to explore their optoelectronic properties based on different pnictene centers within the same molecule.

Furthermore, the attempted synthesis of arsa-sumanene resulted in mixtures of syn and anti-isomers. This isomeric mixture without further purification has been oxidized in situ to afford the corresponding arsole oxides. Further studies on these systems will be performed.

In summary, a) A highly efficient synthetic route was developed starting from stable synthon Mes*-P=C(Br)\textsubscript{2}, that converts to cross conjugated C,C di-acetylenicphosphaethen and finally via intermediate 1-phospha-1,3-butadienes to the highly conjugated phosphole.

b) Functionalization of the \textit{p}-CPDT core with pnictogen allowed fine-tuning of LUMO levels, while the HOMO levels could be adjusted by incorporating electron donor moieties; additionally, coordination to a metal center (Au\textsuperscript{I}Cl) enhanced the acceptor character of the phosphinidene unit.

c) Phosphaalkenes were successfully incorporated in the truxene core. In the resultant tri-phosphinidenotruxene, the absorption maximum was substantially shifted towards longer wavelengths and up to three reversible electrochemical reduction process are observed.
Svensk sammanfattning

I detta forskningsarbete har vi undersökt olika typer av π-system med lågkoordinerade pnictogen, i synnerhet P och As. I den första delen av denna avhandling fokuserade vi på utvecklingen av en syntetisk rut för att selektivt alkynylera Mes*-P=C(Br)₂ (dibromfosfaeten, en stabil synton med integrerad P=C dubbelbindning) vid C-terminal av P=C dubbelbindningen. En direkt, sekventiell och stereoselektiv metod för alkynylering har framgångsfullt utvecklats, i vilken arylsulfonylacetylen användes som kopplingspartner med dibromfosfaeten. Senare introducerades en andra alkynylgrupp via en Sono-gashira-kopplingsreaktion på C-terminal av P=C dubbelbindningen. Syntesen började med selektiv litiering av Mes*-P=C(Br)₂ vid en temperatur under -100 °C. Den resulterande Li-karboniden, fortfarande vid <-100 °C, reagerades sedan med tidigare förberedd arylsulfonylacetylen för att bilda C-monoacetylenicfosfaeten. Temperaturen visades vara avgörande, då högre temperaturer resulterar i både cis-, trans- och diacetylenicfosfaeten samtidigt. C-monoacetylenicfosfaeten, efter lyckad isolering, reagerades med terminala alkyner för att skapa önskad C,C-diacetylenicfosfaeten. I synnerhet observerades att C,C-diacetylenicfosfaeten, med överskott av terminala alkyner och något hög katalysatorladdning, potentiellt undergår alkynyladdition för att skapa höggradigt förgrenade 1-fosfa-1,3-butadiener, tyngre analoger av 1,3-butadien. Den stegvisa formationen av 1-fosfa-1,3-butadiener undersöktes grundligt. Det drogs slutsatsen, från NMR-spektroskopiska mätningar, att formationen av 1-fosfa-1,3-butadiener behöver relativt hög laddning av Pd[0] katalysator och CuI co-katalysator. Vidare undersöktes reaktiviteten av 1-fosfa-1,3-butadiener. Det upptäcktes att 1-fosfa-1,3-butadiener cykliserar i närvaro av ljus, silikagel och/eller klorerade lösningsmedel, för att bilda de korresponderande π-konjugerade fosfolerna.

I den andra delen integrerade vi pnictogenerna P och As, som exocykliska substituenter, i form av fosfiniden eller arsiniden, till en cyklopentaditiofen-(p-CPDT) kärna. De optoelektroniska egenskaperna av dessa nya föreningar undersöktes med hjälp av UV-Vis, transient absorptionsspektroskop och elektrokemiska metoder. Sannerligen modifierar pnictogencentra starkt LUMO-nivåerna. De korresponderande HOMO-nivåerna justerades senare via elektrongivande grupper vid den perifera positionen av p-CPDT-kärnan. Genom de elektrokemiska undersökningarna, tillsammans med teoretiska beräkningar, visades, för tyngre pnictogen, att AsA-p-CPDT hade den minsta
energiskillnaden mellan HOMO- och LUMO-nivåerna. Vidare enkel komplexering av pnictogencentrumet i PA-p-CPDT med AuICl förskjuter absorptionsmaximum till längre våglängder. Huvudsakligen visade det exciterade tillståndet av AuICl-komplexet av PA-p-CPDT en längre livstid i analysen genom transient absorptionsspektroskopi, möjlig på grund av ytterligare tillgänglighet till triplettilstånd på grund av Au-centrets närvaro.


Vidare resulterade den försökta syntesen av arsa-sumanen i en blandning av syn- och anti-isomerer. Denna isomeriska blandning oxideras in situ, utan vidare rening, för att skapa korresponderande arsoloxid.

Sammanfattningsvis:

a) En högeffektiv syntetisk ruttskapades, med början från stabila summnen Mes*-P=C(Br)_2, som konverteras till korskonjugerad C,C-diacetylenicfosfaeten och till slut via intermediären 1-fosfa-1,3-butadien till högkonjugerad fosfol.

b) Funktionalisering av en p-CPDT-kärna med pnictogen tillåt finjustering av LUMO-nivån, medan HOMO-nivån kunde justeras genom att inkorporera elektrongivande grupper vid perifera positionen av p-CPDT-kärnan. Dessutom förstärkte koordinering till ett metallercentrum (AuI) acceptorkarakteren av fosfinidenenheten.

c) P-centra har framgångsfullt integrerats i den plana stela truxenkärnan. I den resulterande tri-fosfinidenotruxen hade absorptionsmaximum förskjutits till längre våglängder och tre-eletronreduktion kunde genomföras.

Översatt av Robin.Tyburski
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