March 18th-20th, 2026 – Dresden, Germany

22nd European Workshop on Pnictogen Chemistry

TECHNISCHE UNIVERSITÄT DRESDEN

FREIE UNIVERSITÄT BERLIN

Dear Participants,

Welcome to the 22nd European Workshop on Pnictogen Chemistry at TU Dresden, Germany!

The long-standing tradition of workshops previously centered around the element phosphorus began in Kaiserslautern (2004), followed by Bonn (2005), Leipzig (2006), Zandvoort (2007), Regensburg (2008), Florence (2009), Budapest (2010), Münster (2011), Rennes (2012), Regensburg (2013), Sofia (2014), Kassel (2015), Berlin (2016), Cluj-Napoca (2017), Uppsala (2018), Bristol (2019), Rennes (2020), Rostock (2022), San Sebastián (2023), Würzburg (2024), and Innsbruck (2025). This tradition will be continued with the 22nd EWPC – European Workshop on Pnictogen Chemistry 2026 in Dresden, Germany.

This workshop series has earned a strong reputation for the fruitful exchange of ideas and opinions, as well as for excellent discussions. The aspects of pnictogen chemistry covered by this workshop span organic, inorganic, polymer, materials, and biological chemistry.

The program will include talks, "how-to-do" lectures, and poster presentations by PhD students and young postdoctoral researchers, as well as an invited Pioneers Lecture given by Prof. Dr. Evamarie Hey-Hawkins.

We would like to thank the sponsors for their generous financial support, which has helped us create this program.

Beyond the fascination of pnictogen chemistry, we hope you will find time to explore the beautiful city of Dresden, which offers a wealth of cultural opportunities and sights.

We wish you a pleasant and enjoyable stay in Dresden!

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Program

Wednesday, March 18, 2026

Time		
8.30 am	Registration	
9.15 am	Welcome	J. J. Weigand/ C. Müller
Session 1		Chair: Clara Roller
09.20 am	O1/ Luis-Antonio Coelho-Figueredo	
09.40 am	O2/ Sotirios Pavlidis	
10.00 am	O3/ Gal Dama	
10.20 am	Coffee Break / Put Up Posters	
Session 2		Chair: Simon Muhm
11.00 am	O4/ Moritz Ernst	
11.20 am	O5/ Leon Kessner	
11.40 am	O6/ Pascal Schmidt	
12.00 pm	O7/ Katharina Eichhorn	
12.20 pm	Lunch Break	
Session 3		Chair: Erik Kertesz
01.50 pm	O8/ Christina Papke	
02.10 pm	O9/ Dan Dean	
02.30 pm	O10/ Eetu Hakkarainen	
02.50 pm	Coffee Break / Put Up Posters	
Session 4		Chair: Matthew Mundy
03.30 pm	O11/ Xiangrong Liu	
03.50 pm	O12/ Toma Bhowmick	
04.10 pm	O13/ Julian Glock	
04.30 pm	Magritek	
04.45 pm to 05.30 pm	group leaders meeting	
Poster Session 1		
05.00 pm to 7.00 pm		

Program

Thursday, March 19, 2026

Time		
Session 5		Chair: Katharina Eichhorn
9.20 am	O14/ Daniel Meleschko	
9.40 am	O15/ Eugen Khitro	
10.00 am	O16/ Batoul Karim	
10.20 am	O17/ Kobe Tickner	
10.40 am	Coffee Break	
Session 6		Chair: Christina Papke
11.10 am	O18/ Matthew Mundy	
11.30 am	O19/ Owen Jones	
11.50 am	O20/ Clara Roller	
12.10 pm	Lunch Break	
Session 7		Chair: Mengsi Lu
1.40 pm	O21/ Simon Edin	
1.50 pm	O22/ Erik Kertész	
2.10 pm	O23/ Arran Embleton	
2.30 pm	Coffee Break	
Pioneers Lecture		Chair J.J. Weigand/ C. Müller
2.50 pm	Prof. Evamarie Hey-Hawkins	
Group Photo		
Conference Dinner – Lohrmanns 6.30 pm to 09.00 pm		

Program

Friday, March 20, 2026

Time		
Session 8		Chair: Toma Bhowmick
9.20 am	O24/ Simon Muhm	
9.40 am	O25/ Mengsi Lu	
10.00 am	O26/ Joel Nitzsche	
10.20 am	O27/ Philipp Royla	
10.40 am	Short break	
Closing and Prizes		Jan J. Weigand/ C. Müller
11.00 am to 11.20 am		

Afterwards, the general meeting of the
GDCh Working Group Phosphorus Chemistry will take place.

Conference @ Chemistry Building TU Dresden
Bergstrasse 66
01069 Dresden

Lecture Session CHE089
Poster Session CHE 183-184
Coffee Break CHE 183-184

Conference Dinner @ Lohrmanns
Kraftwerk Mitte 6
01067 Dresden

Four Decades of Multifaceted Chemistry with Phosphorus Compounds – in a Nutshell

Evamarie Hey-Hawkins

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The chemistry of phosphorus is, without a doubt, one of the most intriguing fields of inorganic and organic chemistry. When I started my academic career, my main interest was in metal complexes with reactive M–P and P–substituent bonds, which proved to be very interesting starting materials for the synthesis of functionalised phosphines, also phosphorus-rich ligands, in the coordination sphere of organometallic zirconium(IV) and tantalum(V) complexes. While oligophosphines and oligophosphanide anions were known at that time, in most cases rational high-yielding syntheses were rare. We succeeded in developing a targeted synthesis for several cyclic and catenated oligophosphanide anions, which show a very rich main group and transition metal chemistry, leading to phosphorus-rich metal complexes, some of which proved to be suitable precursors for phosphorus-rich metal phosphides, but also giving access to neutral oligophosphines via oxidative coupling.

We have also been interested in phosphine ligands with non-innocent backbones. For example, the ferrocene moiety in dendritic ferrocenyl phosphines can be reversibly oxidised and reduced thus allowing switching the catalytic activity of a metal complex. We have also prepared the little siblings of these large dendritic molecules, namely tris-ferrocenylphosphine ligands with benzene, trifluorobenzene or triazine as core and could show that the corresponding complexes with gold(I) chloride exhibit four well-defined switching states for the three ferrocene moieties allowing to tune the catalytic properties stepwise.

Boron clusters, specifically *closo*-dicarbadodecaboranes (carboranes), are very interesting non-innocent scaffolds for bis-phosphines, which have a very rich chemistry, e.g. the formation of a 1,2-diphosphetane via reductive P–P bond formation. The P–P bond in strained diphosphetanes is highly reactive and for example can be cleaved oxidatively or reductively yielding interesting new phosphorus-based heterocycles.

Another class of heterocycles that we have been interested in are phospholes. We have developed facile synthetic routes to phosphole-based materials with outstanding optical properties, which have already demonstrated potential applications as biomarkers.

These examples are just a few of the contributions that we have made to the chemistry of phosphorus – four decades in a nutshell.

Acknowledgements

I would like to thank all those who have contributed to this work, enthusiastic and creative co-workers, collaborators and students, over more than four decades and those who have funded the work.

References

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Electrochemical functionalization of white phosphorus mediated by main-group compounds

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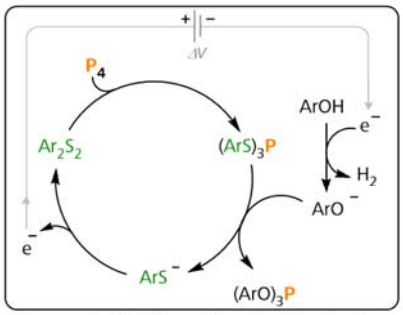
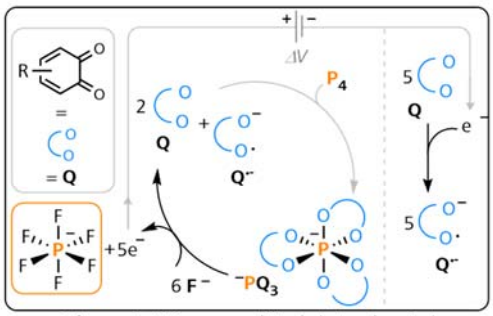
White phosphorus (P_4) serves as the primary starting material for the preparation of nearly all commercially significant monophosphorus compounds. Currently, the most widely used methods to synthesize P_1 products depend on the oxidation of P_4 with chlorine gas (Cl_2) or on its acid/base-mediated disproportionation, which produce intermediates such as phosphorus trichloride (PCl_3) and phosphine (PH_3).[1] However, the dependence on multiple reaction steps and the generation of copious amounts of chemical waste have long raised concerns and highlighted the need for the development of safer and more environmentally friendly alternatives.[2]

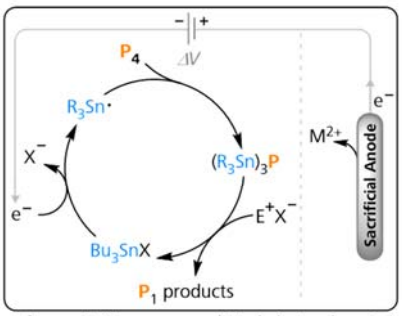
We are developing straightforward strategies for preparing monophosphorus products directly from P_4. Our methods involve oxidative and reductive electrochemical systems mediated by abundant and recyclable main-group compounds. Using diaryl disulfides as redox mediators in the presence of nucleophiles, we have been able to catalytically synthesize P(+III) products, such as aromatic phosphites (Scheme 1).[3] When *ortho*-quinone/catechol motifs provide the redox framework instead, PF_6^- can be obtained as the main P(+V) product in the presence of fluoride (Scheme 2). Meanwhile, tin-based mediators allow access to P(-III) synthons (Scheme 3). With acyl chlorides as electrophiles and substoichiometric amounts of tributyltin chloride, triacylphosphines can be generated in a *one-pot* manner. By electrochemically regenerating the mediators, we are developing new catalytic/closed-loop systems that produce only benign byproducts.



Scheme 1. Disulfide-catalyzed electrochemical oxidative functionalization of P_4



Scheme 2. Quinone-mediated electrochemical oxidative functionalization of P_4



Scheme 3. Stannane-mediated electrochemical reductive functionalization of P_4

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Heavy T-Shaped Group 15 Trisamides planarized by a rigid, redox-active NNN pincer ligand

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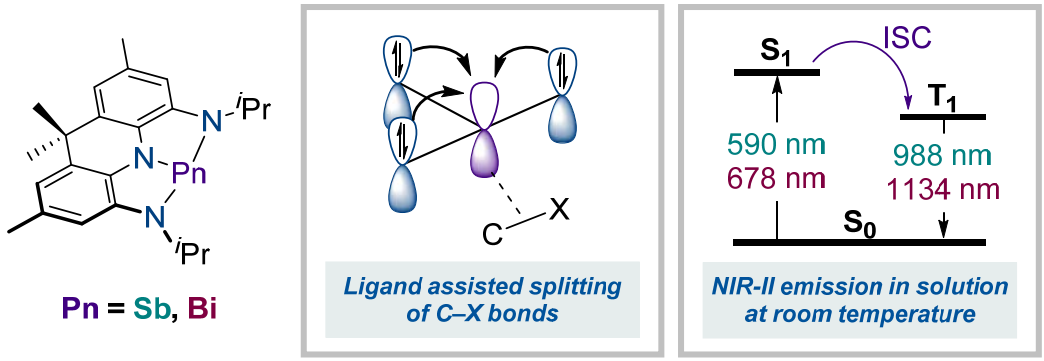
Geometric constraint of group 15 elements has emerged as a powerful strategy to unlock metallomimetic reactivity patterns, including C–element bond forming and splitting reactions, which have enabled catalytic applications.[1] These transformations typically involve changes in the pnictogen oxidation state, such as Pn(I/III) and Pn(III/V) redox cycles, whose fine-tuning remains challenging.



Here, we report the unique reactivities and electronic structures of heavy T-shaped pnictogen(III) centers,[2] planarized by a rigid, redox-active acridane-derived NNN pincer ligand. The coupling between a low-lying vacant Pn(p) orbital and the NNN ligand's π-system facilitates C–X bond scission at Bi(III), leveraging redox equivalents stored on the pincer ligand, reminiscent of transition metal–ligand cooperativity paradigms.[3] The exotic electronic structure of these intensely colored pnictogen pincer compounds further results in unique photophysical properties. Bi(NNN) and Sb(NNN) are the first examples of Pn(III) compounds exhibiting phosphorescence in the NIR-II region at room temperature in solution, associated with excited state lifetimes of up to the microsecond region.

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Unveiling the True Identity of Carborane-Fused Phosphorus Heterocycles

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Over the last decade, researchers have examined whether 2D and 3D aromatic systems – particularly carborane-fused rings – can exhibit aromatic conjugation. Although early studies suggested that such interactions might exist, more recent evidence shows that this type of aromatic conjugation does not exist.[1,2] Very recently, carboranes fused with phosphorus heterocycles have been reported. While phospholes typically show weak aromaticity, they can possess significant aromatic character in presence of bulky substituents on the phosphorus atom. Recent syntheses of *o*-carborane-fused phosphorus heterocycles suggest that they may display greater aromatic character than analogous benzophospholes, contradicting trends observed for other five-membered heterocycles.[3] This discrepancy raises the question of whether phosphorus-containing rings might uniquely enable 2D-3D aromaticity in carborane-fused systems.

Our work demonstrates that phosphorus heterocycles fused with *o*-carborane do not show any 2D-3D aromatic conjugation between the planar ring and the three-dimensional carborane cluster.[4]

Figure: Carborane-fused phosphorus heterocycles

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Cyclo-P_5^- Revisited: The Surprisingly Stable Uncoordinated Pentaphospholide Anion

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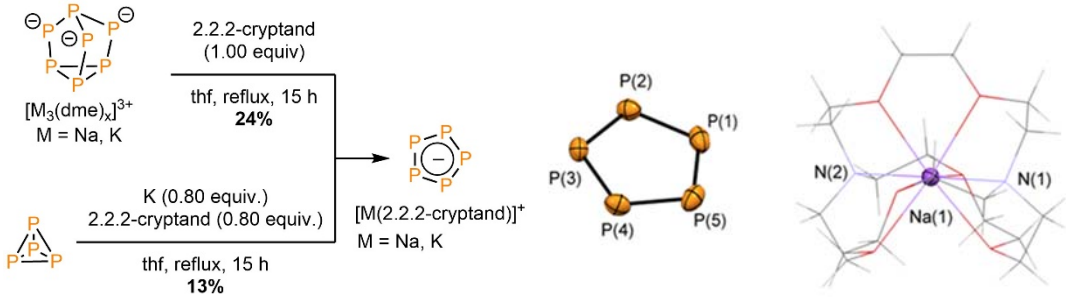
The pentaphospholide anion (*cyclo*-P_5^-), which is isolobal to the well-known cyclopentadienide anion and spectroscopically known since the 1980s.[1] However, due to its inherent instability, it has only been prepared and handled in solution so far.[2,3] We have developed a novel synthetic pathway towards the *cyclo*-P_5^- starting from the respective alkali metal heptaphosphides M_3P_7 (M = Na, K) and [2.2.2]cryptand. The [M([2.2.2]cryptand)][*cyclo*-P_5] salts were found to be surprisingly stable in the solid state, allowing the *cyclo*-P_5^- to be characterized crystallographically for the first time in its uncoordinated form. This structural elucidation proves its planar D_{5h} symmetry, not only as a ligand in different sandwich complexes, but also in its uncoordinated form. Furthermore, c*yclo*-P_5^- was characterized in solution by UV/Vis spectroscopy, as well as in the solid state by Raman and ^{31}P MAS NMR spectroscopy. The reaction of [Na([2.2.2]cryptand)][*cyclo*-P_5] with LiCp* and $FeCl_2$ yields the ferrocene derivative [Cp*Fe(*cyclo*-P_5)], demonstrating the application of uncoordinated [*cyclo*-P_5] as a ligand.



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P-Heterocyclic Tetrylenes

Leon Kressner,[a] Christopher Golz,[b] Regine Herbst-Irmer[a] Oliver P. E. Townrow,[c] Malte Fischer*[a]

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Since the synthesis of the first monomeric crystalline *N*-heterocyclic carbene (NHC) by Arduengo *et. al*. in 1991, these compounds have developed a rich chemistry in various fields over the last decades.[1] Their facile synthesis and tuneable steric and electronic properties have made them indispensable to modern synthetic chemistry. The heavier tetrel substituted analogues also displayed a versatile chemistry in small molecule activation and as ligand platforms.[2] Substitution of the nitrogen for a heavier pnictogen however has been far less explored, with only a few examples from Bertrand *et. al*.[3] The challenge to stabilize these compounds lies in the creation of effective pπ-pπ overlap, which could be achieved by the incorporation of sterically demanding substituents, forcing the phosphorus atoms into a trigonal planar geometry. This work shows the synthesis and reactivity of the first heavier *P*-heterocyclic tetrylenes.[4]

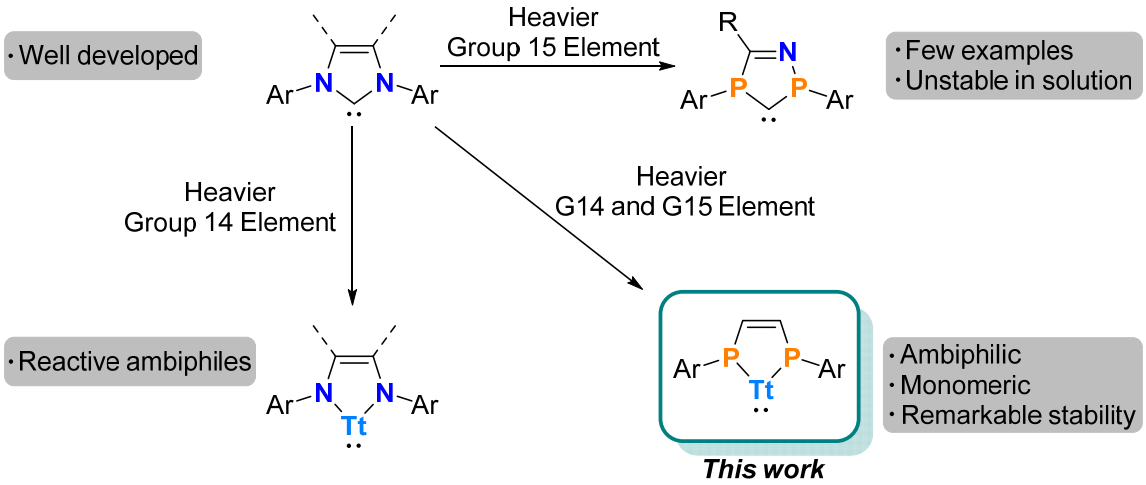

Figure 1: Development route from NHCs to heavier analogues and the first PHTts.

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Heavy Group 15 Element Pacman Complexes

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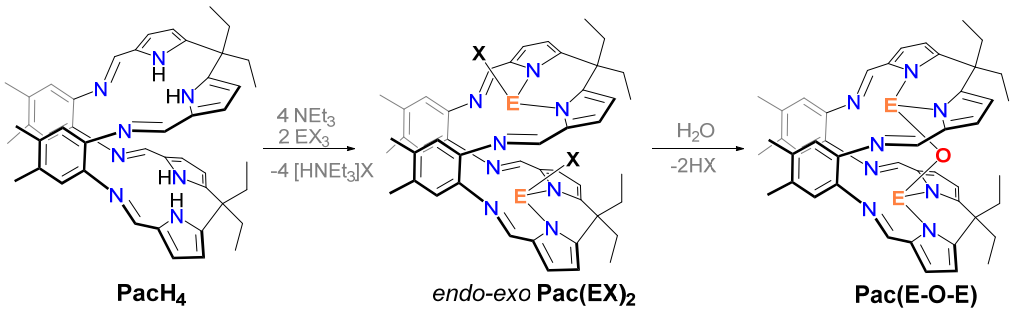
Recent advances have expanded Pacman chemistry beyond transition metals, with our group demonstrating the successful incorporation of phosphorus(III) centers into calix[4]pyrrole macrocycles (Pacman ligands), yielding Pacman chlorophosphanes (**Pac(PR)$_2$**).[1,2] In this study Pacman ligands were used to incorporate heavy pnictogens (As, Sb, and Bi), yielding halo complexes (**Pac(EX)$_2$**, E = As, Sb, Bi; X = Cl, I). Arsenic(III) chloro complex **Pac(AsCl)$_2$** and antimony(III) chloro complex **Pac(SbCl$_2$)$_2$** were synthesized in solution and isolated, while arsenic(III), antimony(III) and bismuth (III) complexes (**Pac(AsI)$_2$**, **Pac(SbCl)$_2$**, **Pac(BiCl)$_2$**, **Pac(BiI)$_2$**) were formed in solution but could not be isolated. Controlled hydrolysis of transient iodoarsane and chlorostibane produced oxygen-bridged complexes of the type **Pac(E-O-E)**.



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β-Carboxyphospholes via carboxylative desilylation: luminophores with a versatile connectivity attached

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Phospholes are highly versatile building blocks with interesting and tunable optical and electronic properties.[1-4] With our synthetic approach it is possible to introduce a silyl functionality in the phosphole's *β*-position, which can be modified postsynthetically and thus be used, e.g. as anchor group.[5-8] Until now, incorporation of reactive functional groups at the phosphole ring allowing facile modification or bioconjugation is rather limited. Therefore, we developed a synthetic route towards *β*-carboxyphospholes via carboxylative desilylation of their *β*-TMS-substituted analogues in a CO_2 atmosphere. The title carboxylic acids allow facile transformation into the respective acyl chloride, carboxamide, ester and anhydride, which are compatible with bioconjugation, while the integrity of the phosphole unit is maintained.[9]

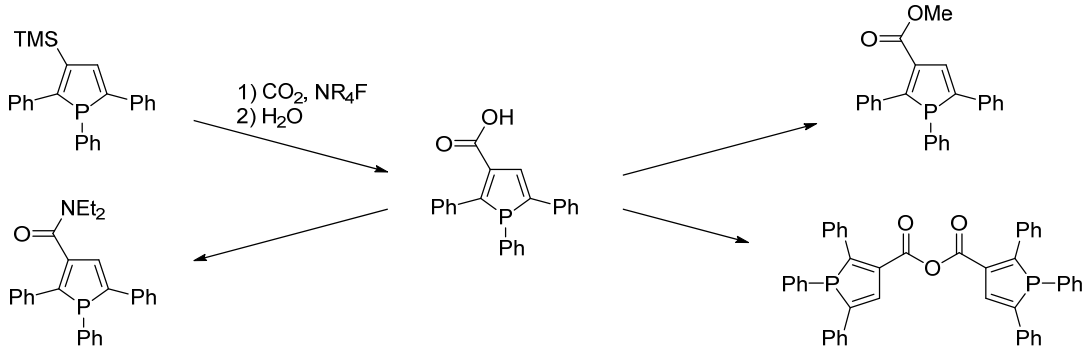

Figure 1: Synthesis of a *β*-Carboxyphosphole and conversion into ester, amide and anhydride.

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2-(Diphenylphosphino)benzoic Acid: A Versatile Hybrid Ligand for Heterobimetallic Coordination Compounds

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Hetero-donating hybrid ligands are powerful molecules for the controlled synthesis of heterobimetallic coordination compounds.[1] By incorporating multiple, distinct donor sites, these ligands can exploit the Hard and Soft Acid-Base (HSAB) principle to direct selective metal binding: hard donors, such as oxygen or nitrogen, preferentially coordinate hard Lewis acids (e.g., rare-earth metals, RE), whereas softer donors, such as phosphorus, target softer transition metals (TM).[2] This strategic placement of metals in one molecule enables cooperative interactions, that yield unique photophysical, magnetic, and catalytic properties, often surpassing those of homometallic analogues (1 + 1 > 2).[3]

While O,N- and P,N-based ligands have been widely explored, P,O-based ligands remain comparatively scarce. To address this gap, we investigated the versatile coordination chemistry of 2-(diphenylphosphino)benzoic acid (2-DPPBA). Initial studies afforded homometallic trinuclear rare-earth clusters, with the hard rare-earth metal ions being coordinated by carboxylate oxygens in diverse coordination modes. Subsequent reactions with [Au(tht)Cl] (tht = tetrahydrothiophene) yielded heterobimetallic complexes, in which gold selectively binds the soft phosphorus site. Photophysical studies revealed that, whereas monometallic rare-earth complexes luminesce only at –196 °C, heterobimetallic complexes exhibit luminescence already at room temperature.[4] Replacing gold with rhodium carbonyl chloride as precursor generates RE/Rh complexes with distinct structural motifs and promising hydroformylation activity.[5] Furthermore, reversing the order of metal addition, for example by introducing Cu before RE, also affords different architectures and highlights the versatile and tunable coordination chemistry of this ligand.[6]

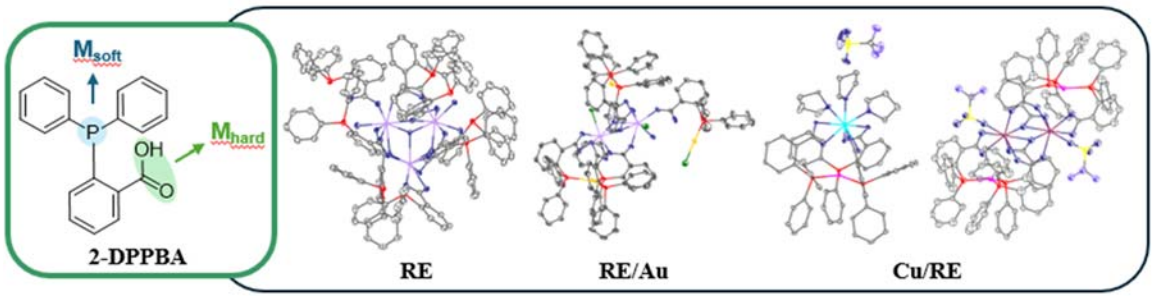

Figure 1 | 2-DPPBA as hetero-donating hybrid ligand for the formation of RE, RE/Au, RE/Rh and Cu/RE complexes.

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Synthesis and Reactivity of a Unique Bicyclic Diphosphane

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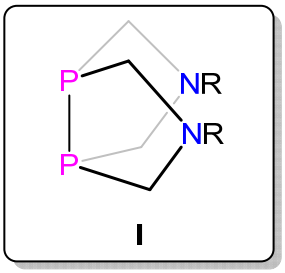
Trivalent phosphorus compounds, such as tertiary phosphines (PR_3), are an excellent class of ligand that continue to play a pivotal role in coordination/organometallic chemistry. In contrast, diphosphanes ($R_2P–PR_2$) bearing a P–P single bond have received considerable less attention which is somewhat surprising. We recently described[1,2] the bicyclic diphosphanes **I** (Figure 1) building on previous work reported, by Frank and Drake, some 50 years ago.[3] In this oral presentation, I will present some of our findings on the synthesis and reactivity studies of this unusual class of diphosphane.



I

Figure 1

Acknowledgements

The Authors would like to thank Syensqo for their kind donation of tetrahydroxymethylphosphonium chloride (THPC) and the UK National Crystallography Service for X-ray data collections.

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Pnictogenium Pairs for Generating Efficient Phosphorescence

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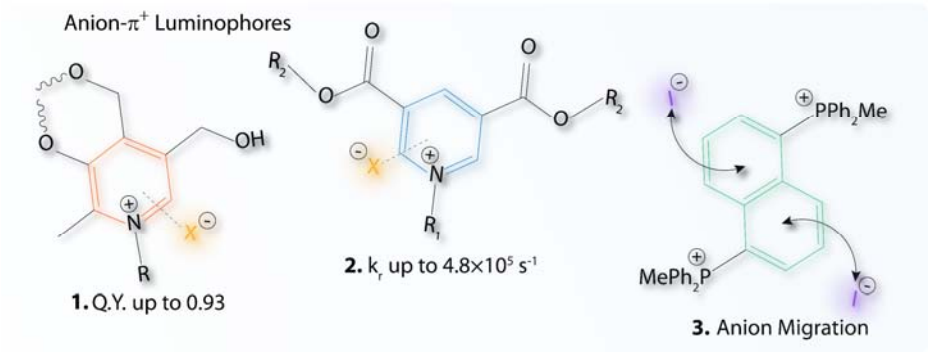
Luminescent organic ionic materials are a promising alternative to more extensively studied metal-based species (*e.g.*, Ir or Pt), but achieving competitive emissive properties is a current challenge. In this perspective, the ability to manipulate these ionic materials through non-covalent interactions between ions enables tunable photoluminescent properties, where complex charge transfer processes depend on the strength of anion–π^+ interactions and the intrinsic mobility of anion-cation pairs. Controlling the resulting optoelectronic characteristics via atomic-level modifications, such as pnictogen variation, and molecular-level adjustments shows great potential for developing next-generation materials for organic light-emitting diodes (OLEDs), anticounterfeiting, medical X-ray imaging, data storage, and solar cells.[1,2]



In response to the demand for high-performance functional materials, we have designed and developed three families of pnictogenium-based contact-ion pairs (CIPs). The first group (**1**, see Figure above) consists of provitamin B6-derived pyridinium salts, which exhibit exceptional quantum yields up to 93% of phosphorescence, and, notably, the top candidate was successfully used in the preparation of X-ray scintillating films.[3] Incorporation of electron-withdrawing methoxycarbonyl groups to the pyridinium core (**2**) further enables the improvement of phosphorescence rate, setting a record for metal-free phosphors with a k_r up to 4.8×10^5 s^{-1}. Last but not least, using the heavier pnictogen homolog phosphorus (**3**), a series of diphosphonium salts was synthesized, where the solid-state solvent-dependent controllable relocation of counter anions results in unforeseen vapochromic properties for the top CIP.

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Unified Synthesis of Alkylbismuth Reagents with Broad Utility

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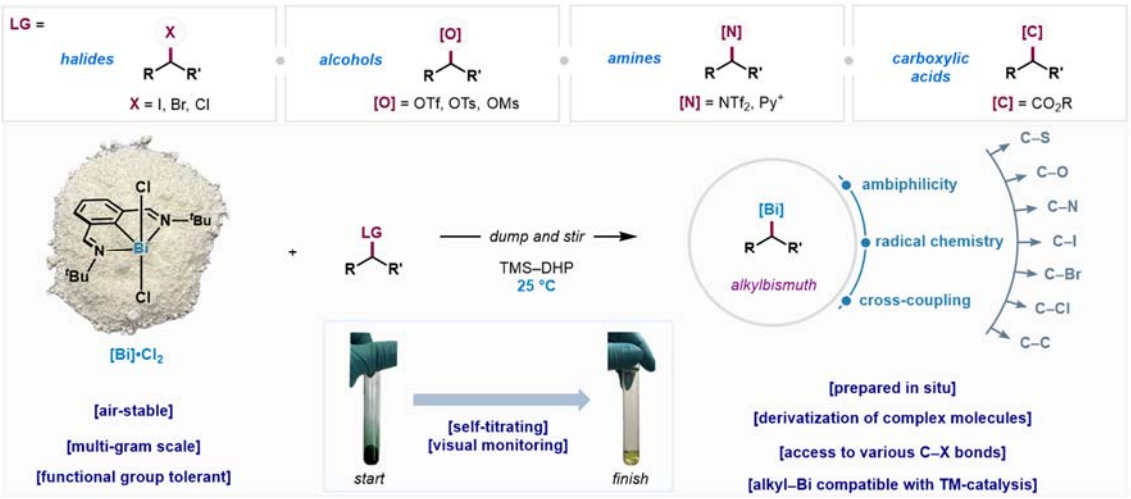
Alkyl-metal nucleophiles (alkyl–M) represent valuable reagents in organic synthesis, widely employed for the construction of a myriad of C–X bonds.[1] Despite of high reactivity, their preparation compromises functional-group compatibility, typically restricted to a narrow range of electrophiles precursors with tailor-made protocols.[2] Hence, a unified, practical and efficient strategy to access alkyl nucleophiles from a wide variety of precursors is highly coveted.

Herein, we present a unified approach towards C–Bi based alkyl nucleophiles as well as its downstream applications in organic synthesis. Alkylbismuth reagents are easily accessed from readily available compounds—alkyl halides, alcohols, carboxylic acids or amines—in excellent yields and high efficiency, starting from an air-stable Bi complex.[3] The platform exhibits broad functional-group compatibility including unprotected alcohols and carboxylic acids, and features a qualitative internal visual indicator. Notably, these alkylbismuth reagents can be easily transformed into the corresponding C–Cl, C–I, C–Br, C–C, C–N, C–O or C–S bond products in one-pot. They also engage effectively in Ni- or Pd-catalyzed C(sp^3)–C(sp^2) cross-couplings with aryl-, vinyl-, or acyl halides, highlighting the versality and robustness of the platform.



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Designing phosphaalkene-based intramolecular donor-acceptor systems

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Extended π-conjugated systems like truxene have been widely explored in organic optoelectronics and solar cells.[1] Introducing a π-accepting phosphinidine fragment in a polyaromatic core is an interesting way of tuning the acceptor properties by stabilizing the LUMO level and reducing the HOMO-LUMO gap.[2-3] Keeping all these in mind, our group has previously reported the 3,8,13-tribromotruxenetruxene-based triphosphaalkene, **Br$_3$P3**, which showed enticing π-acceptor properties, i.e., very mild redox features compared to those of the unsubstituted truxene-triphosphaalkene, **P3**.[4.] In the present work, we further functionalize the **Br$_3$P3** to design intramolecular donor-acceptor systems. Two sets of secondary amines, phenothiazine (PTZ) and 3,6-di-*tert*-butylcarbazole ($^{t\text{Bu}}$Cbz), are selected as the donor species. Buchwald-Hartwig amination is performed using a common procedure in both coupling reactions, which results in a satisfactory yield of the final products. Going forward, we plan to investigate the intramolecular charge transfer processes in these novel donor-acceptor systems, using spectroelectrochemistry, cyclic voltammetry, UV-Vis spectroscopy, fluorescence, and transient absorption spectroscopy.

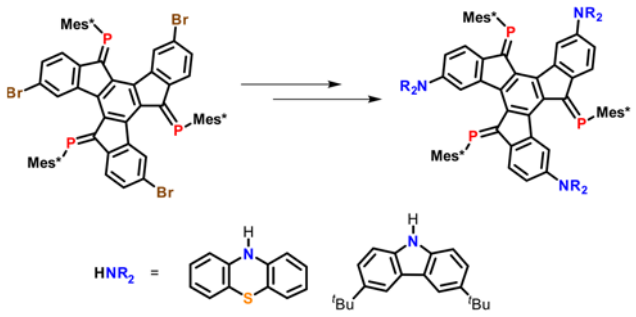

Figure: Synthesis of amine-substituted phosphaalkenes

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Poly(*p*-phenylene phosphaborene): A Modified Poly(*p*-phenylene vinylene) with π-Conjugated B═P Linkages

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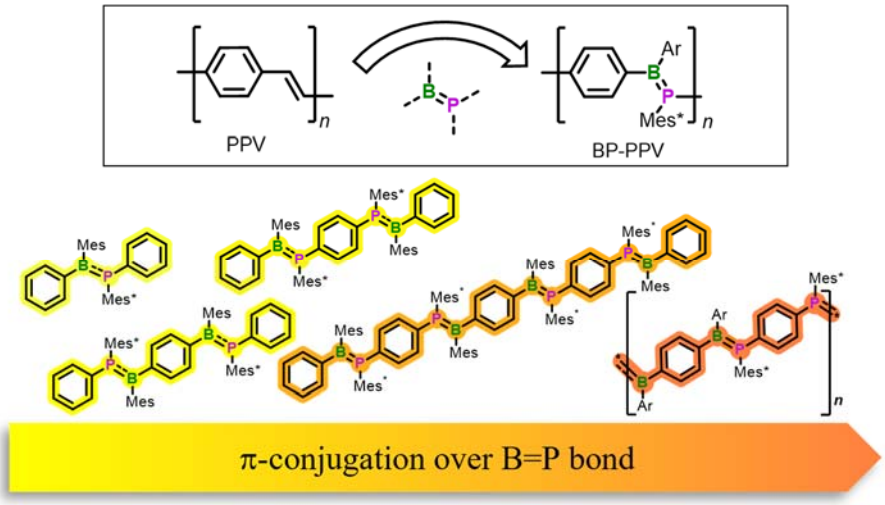
The replacement of selected C=C units in well-established π-conjugated organic materials by isosteric and isoelectronic heteroatomic units, e.g., B=N,[1] has led to various novel hybrid materials, many of which show intriguing properties and functions. Our group recently presented an unprecedented BN-modified poly(*p*-phenylene vinylene) (PPV).[2]

We now aimed at introducing valence isoelectronic B=P units into such PPVs. We prepared the first poly(*p*-phenylene phosphaborene) (BP-PPV) as well as BP-PPV-type oligomers, which exhibit a planar backbone with extended π-conjugation. Our novel BCP compounds show distinct fluorescence emission in solution and the solid state, aggregation-induced emission enhancement (AIEE), and low temperature phosphorescence.[3]



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Exploring the Reactivity of Heavy Dipnictenes with Metal Complexes

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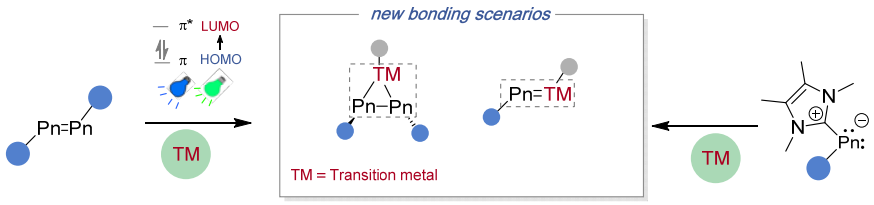
The chemistry of multiple bonds has fascinated chemists for decades, particularly in the case of dipnictenes. Azobenzene, the lightest representative of this class, is well known for its reversible interaction with light and has therefore found widespread application in both academic research and industrial processes.[1] Extending this chemistry to heavier group 15 analogues, however, presents significant synthetic challenges, as the corresponding double bonds are highly reactive and prone to cyclization or decomposition. To address these issues, sterically demanding ligands (e.g. Tbb (2,6-$[CH(SiMe_3)_2]_2$-4-(^{t}Bu)C_6H_2) have been employed to provide kinetic stabilization. While this strategy has enabled the isolation of heavier dipnictenes, it has also significantly reduced their chemical reactivity. In particular, for distibenes and dibismuthenes, excessive steric protection restricts further functionalization and limits progress in exploring their fundamental reactivity and potential applications.[2, 3]

Recently, we reported the synthesis and investigation of novel multimetallic systems derived from dipnictenes, examining their chemical behavior and interactions with reactive small molecules, which revealed new opportunities for reactivity in heavy dipnictene chemistry.[4, 5]



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Phosphorus-based electrolyte additives for Ni-rich cathode materials

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State-of-the-art lithium-ion batteries (LIBs) can reach specific energies above 250 Wh/kg at cell level, which makes them one of the most important energy storage technologies. However, cell voltages above 4.2 V have an adverse effect on structural stability of nickel-rich cathodes, resulting in degradation of the active material. The degradation of materials can be attributed to five main mechanisms: particle cracking, phase change & oxygen release, metal dissolution, cation mixing and parasitic reactions. This results in thermal instability, capacity fade and reduction of the cycle life.[1]

Phosphorous-based additives have been shown to be effective in generating a robust cathode-electrolyte interphase (CEI), which mitigates the degradation of the cathode materials to improve both the lifespan and safety of LIBs.[2-3] In this work, functionalized neutral pentafluoroethylphosphorus compounds and pentafluoroethylphosphinates were synthesized and analyzed by nuclear magnetic resonance spectroscopy (NMR), single-crystal X-ray diffraction, thermal analysis and other characterization methods. The additives were added to standard lithium-ion battery electrolytes and tested with Ni-rich cathodes electrochemically. When testing the additives as part of electrolyte formulations without an additional film-forming additive for the graphite, the cell performance is slightly lower than the reference electrolyte. Additionally, the neutral pentafluoroethyl-functionalized phosphates react with the $Li[PF_6]$ conductive salt in the electrolyte during formulation. Therefore, the resulting additive decomposition products were identified by NMR spectroscopy to enable further investigation of the additive function in the resulting electrolyte.

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Iminophosphorane-Based Ligands for New NPN Co^{II} Complexes in Hydrosilylation reactions

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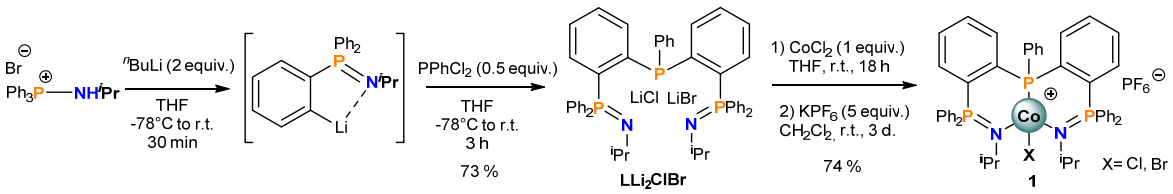
The development of novel phosphorus ligands remains a central theme in pnictogen chemistry, offering access to metal complexes with attractive electronic properties and reactivity. Iminophosphorane ligands are characterized by polarized P=N bonds providing strong electron rich N based ligands. When associated to other coordinating groups, they can coordinate to a large variety of metals.[1,2] As the replacement of -noble metals by more abundant ones with affordable price and lower environmental impact has become a necessity, we have investigated the reactivity of earth-abundant metal complexes supported by unprecedented mixed iminophosphorane ligands.[3] We will therefore present the synthesis of new bis(iminophosphorane)phosphine (NPN) ligand that combines a central phosphine donor with two iminophosphorane units, as well as the synthesis and characterization of its Co^{II} complexes. Their catalytic ability for hydrosilylation reactions will also be discussed.[4]



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Asymmetric and Non-Asymmetric Hydrogenation of Phosphaalkenes Using Rhodium Complexes

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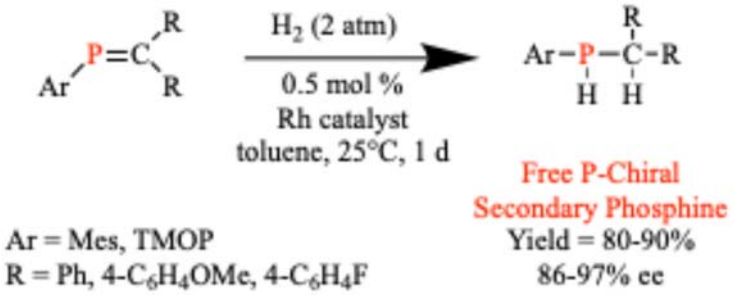
The development of transition-metal-catalyzed hydrogenation of unsaturated bonds such as C=C, C=O, or C=N has become a critical transformation of a wide variety of organic syntheses.[1,2] Despite the close analogy between the P=C bond in phosphaalkenes and the C=C bond in alkenes, phosphaalkenes possess a lone pair that can bind the metal center and inhibit the catalytic turnover which is typically not an issue for olefin hydrogenation.[3] As a result, metal catalyzed hydrogenation of phosphaalkenes has not been extensively studied to the degree of olefins. In this presentation, the rhodium-catalyzed hydrogenation (including asymmetric hydrogenation) of P=C containing compounds will be discussed. This new methodology permits the isolation of the first examples of enantio-pure P-chiral secondary phosphines. Specifically, the hydrogenation of $ArP=CR_2$ (Ar = Mes, TMOP; R = Ph, 4-C_6H_4OMe, 4-C_6H_4F) affords three unprecedented P-stereogenic secondary phosphines in 80%-90% isolated yields with 86%-97% enantiomeric excess (ee). These isolable P-chiral secondary phosphines can provide a building block for further modifications of the P-chiral center for use as ligands in catalysis.



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Photo(redox)-Promoted Reductive Elimination at T-shaped Phosphines

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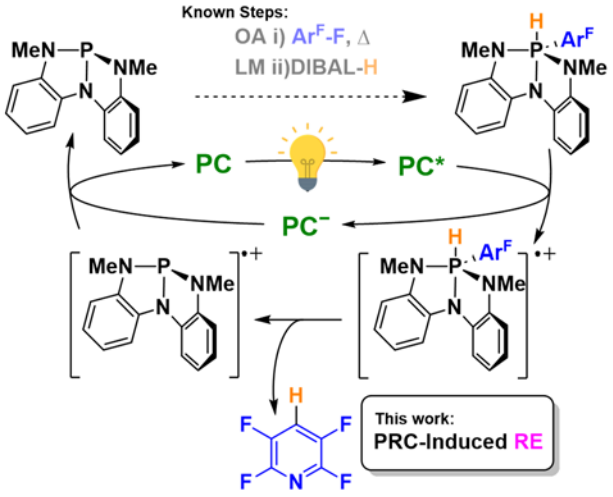
Precious metal (PM) catalysis, while vital to the modern chemical industry, is fraught with sustainability issues, and, in many contexts, currently has no viable alternative. Replacement with main group catalysis is an attractive prospect for reasons of both sustainability and cost. However, there are still major challenges in replicating the elementary steps of the prototypical PM catalytic cycle. This is particularly true of reductive elimination, which typically provides the key bond forming step in such cycles.[1] We suggest photoredox catalysis (PRC) as a solution to driving facile reductive elimination at main group centres. Herein, we describe the first investigation into the use of PRC for this purpose. In this concept, transient oxidation of a redox active supporting ligand bound to a main group element is used to induce reductive elimination. The electron is then "returned" to the complex by the photocatalyst to close the cycle. A successful proof of concept demonstration has been achieved using a constrained phosphorus pincer complex as a model (see Figure). This system has previously been shown to carry out RE only upon extended, major heating to 160 °C over a period of 7 days.[2] In contrast, we are able to achieve the same reaction at room temperature in under 6 hours via irradiation using a Kessel lamp in the presence of the photocatalyst 4CzIPN.



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An Alkali Amide Approach to 1,3,5-triphosphabenzenes

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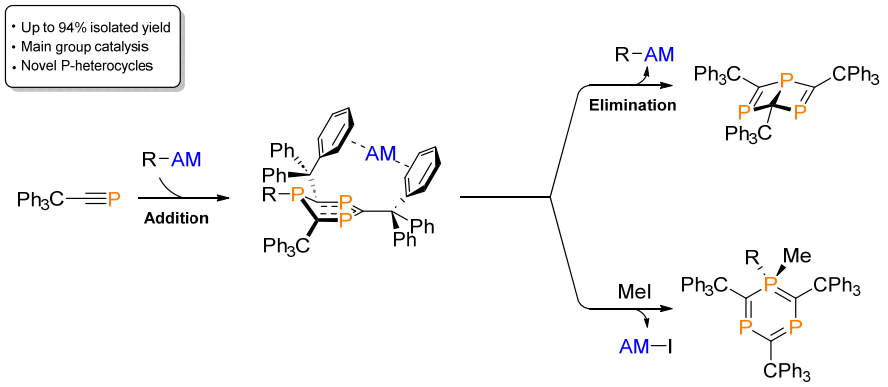
The discovery of kinetically stabilised phosphaalkynes has paved the way for synthesising 1,3,5-triphosphabenzenes *via* cyclotrimerisations.[1] Previous approaches require transition metal complexes, which often draw inspiration from analogous alkyne-based systems.[2-4] In contrast, synthesising the lighter congener, 1,3,5-triazine, is easily achieved by reacting benzonitrile with alkyl lithium or amide reagents.[5-6] These reactions are highly solvent dependent, with non-polar solvents favouring an addition-elimination of R–Li and forming 1,3,5-triazine catalytically. We hypothesize that, if extendable to phosphaalkynes, this reactivity could provide an elegant route to 1,3,5-triphosphabenzenes using simple organometallic reagents. Herein, we report a lithium amide catalysed route to Dewar 1,3,5-triphosphabenzene, a non-aromatic valence isomer. Furthermore, $KN(SiMe_3)_2$ is shown to mediate the cyclotrimerisation of Ph_3CCP *via* a $C(sp^3)$–H activation of benzyl derivatives, allowing the synthesis and characterisation of functionalised λ^4-triphosphabenzene anions and λ^5-triphosphabenzenes.



Scheme 1. Synthesis of 1,3,5-triphosphabenzenes using simple alkali metal reagents

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Controlling Aggregation in Phosphanyl-Supported Tetrylenes *via* NHC-Coordination and Ligand Sterics

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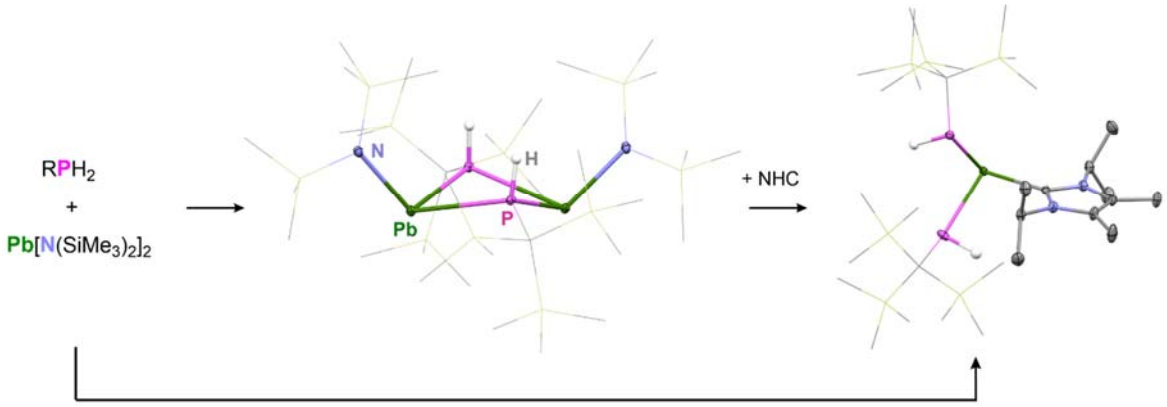
Phosphane donors are established, versatile ligands for transition metal chemistry, where tunable steric and electronic profiles enable diverse reactivity and coordination modes.[1,2] In contrast, phosphanyl-supported, low-valent p-block species – particularly heavier tetrylenes – remain comparatively underdeveloped[3-6] relative to their amide-based counterparts that surged after Arduengo's landmark synthesis of the first N-heterocyclic carbene (NHC).[7] Building on our recent identification of an amidophosphaplumbylene dimer $[(\mu2\text{-}R(H)P)Pb(N(SiMe_3)_2)]_2$ (R = $C(SiMe_3)_3$) and isolation of heteronuclear cluster motifs such as cubanes $[(RP)E]_4$ and [1.1.1]propellanes $[(RP)_3E_2]$ (E = Sn, Pb), we now expand the chemistry with a focus on controllable disruption of dimeric/oligomeric arrangements *via* NHC-coordination. We established a direct route to NHC-stabilized stannylenes and plumbylenes that bypasses dimer formation, yielding species with enhanced solution-state stability. This, in turn, enabled more detailed spectroscopic characterization and more controllable follow-up chemistry.



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Unleashing Phosporus Mononitride

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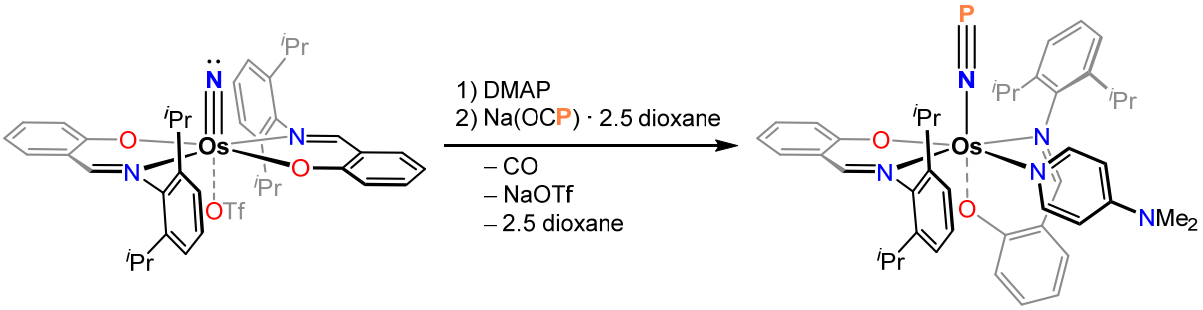
The interstellar diatomic molecule, phosphorus mononitride (P≡N), is highly unstable under conditions typical on Earth, and its utility for constructing elusive P–N multiple-bonded archetypes is essentially uncharted. Herein, we show how Na(OCP) transfers a P atom to an electrophilic osmium nitride complex to form a terminally bound P≡N functionality. Quantum chemical calculations and X-ray absorption spectroscopy unveil a cumulenic [Os^{IV}=N=P] electronic structure comprising orthogonal Os=N and N=P bonding. The highly reduced P≡N ligand, formally $[PN]^{2-}$, undergoes two-fold oxidation with elemental sulfur to form a trigonal planar $[NPS2]^{2-}$ group. On reaction with Ph_3CCl, the P≡N ligand forms a bent [NPCl]– motif coordinated to OsIII (S = ½). [3+2] cycloaddition of this radical species with Me_3SiN_3 forms an aromatic heterocyclic interpnictide, $[PN_4]$–, that cannot be accessed from the parent P≡N system.



Structure-Property Relationships and Chiroptical Tuning in Phosphetene-based Polyaromatics

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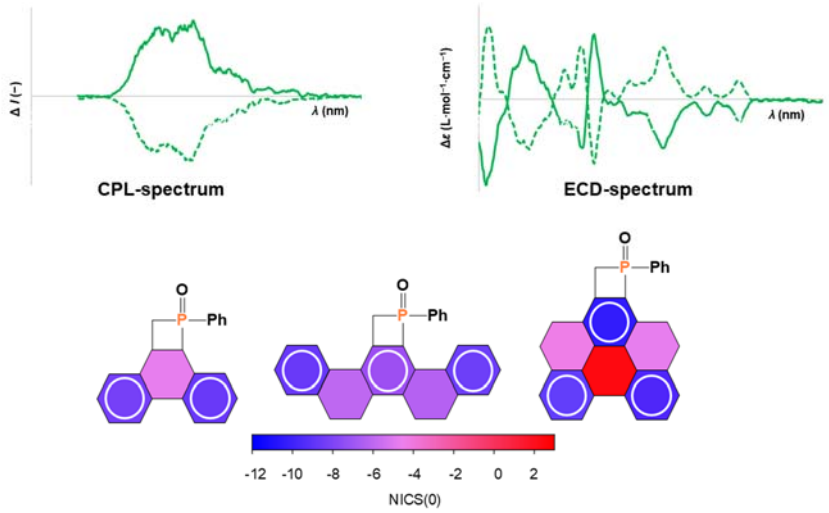
PAHs (polycyclic aromatic hydrocarbons) have many applications in the field of optoelectronics; however, their symmetry typically hampers the chiral tuning of properties. Due to the chiral phosphorus center, phosphetene-fused PAHs may become perturbed chromophores exhibiting chiroptical features such as electronic circular dichroism and circularly polarized luminescence (ECD and CPL). Although neither the phosphorus atom nor the four-membered phosphetene ring is part of either the HOMO or LUMO, the structural changes have a significant effect on the distortion of the molecular orbitals, which ultimately leads to the appearance of chiroptical properties. We have investigated the effect of the chiral phosphorus center on the inherently achiral PAH molecule, and we have found clear relationships between chirality, (a)symmetry of molecular orbitals, and geometrical modifications, which observations may facilitate the design of further promising compounds.[1]



Acknowledgements

Supported by K-147095 of NKFIH and the Doctoral Excellence Fellowship Programme (DCEP).

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Dynamics of a phosphine-tris-ether ligand with Cu(I) halides

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Copper(I) complexes play important roles across a wide range of fields, including luminescent materials, biomimetic chemistry, catalysis, electron-transfer processes, and small-molecule activation.[1] Carefully tailored ligands and structural features around the copper centre often determine not only stability, but also the functional properties that make these complexes so versatile. Recently, we reported several coordination compounds and polymers derived from a flexidentate tri(o-methylthiomethylphenyl)phosphine ligand (PS_3).[2] Due to its accordion-like flexibility, this ligand can modulate phosphorus-metal distances in the resulting complexes. Inspired by this ligand system, here we report our first investigation with the oxygen analogue of PS_3, a phosphine ligand with three *o*-ether arms: tri[(2-methoxymethyl)phenyl]phosphine (PO_3).[3] PO_3 has been investigated for its coordination behaviour toward Cu(I) halides, revealing a structural versatility unique to Cu(I) chemistry. The combination of a soft phosphine donor with multiple hard and hemilabile ether groups enables a dynamic range of binding modes, from simple mononuclear complexes to dimeric architectures. Several complexes of the type $[Cu(PO_3)]X$ have been isolated in good yield and high purity. In the solid state, the complexes are dimeric in nature. However, ^{31}P, ^{1}H, and ^{1}H DOSY solution NMR spectroscopy reveals that in solution the complexes exist in their monomeric form, with a symmetric coordination of the three ether arms.

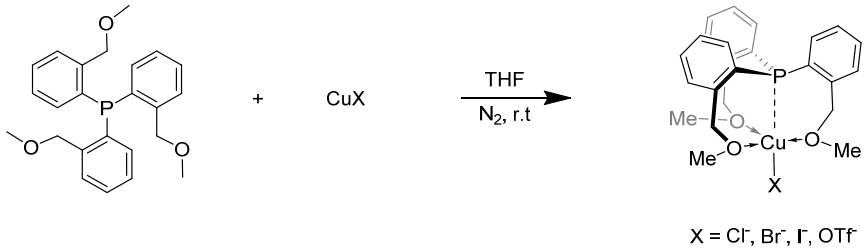

Figure 1. Synthesis of copper(I) complexes bearing the hemilabile flexible ligand PO_3.

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On the Reactivity of the Hexaphenyl-1,2-Diphosphonium $[Ph_3P–PPh_3]^{2+}$ Dication

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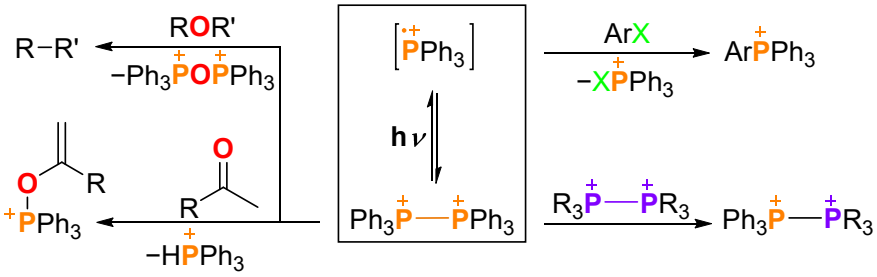
Contrasting the persistency of the trityl radical, valence isoelectronic triphenylphosphine cation radicals require steric protection to allow for their isolation.[1] The corresponding dimers, 1,2-diphosphonium dications, had been isolated in 2007 in the form of all-aliphatic hexaalkyl-1,2-diphosphonium triflate salts,[2] and we recently introduced the corresponding hexaphenyl-1,2-diphosphonium dication.[3] In this presentation I will present on its reactivity with organic substrates such as alkynes, ketones, aryl halides, cyclic ethers as well as the metathetical reaction with other hexaaryl-1,2-diphosphonium dications.[4]



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4. In preparation.

Scalable and Cost-effective Synthesis of Inositol Pyrophosphates

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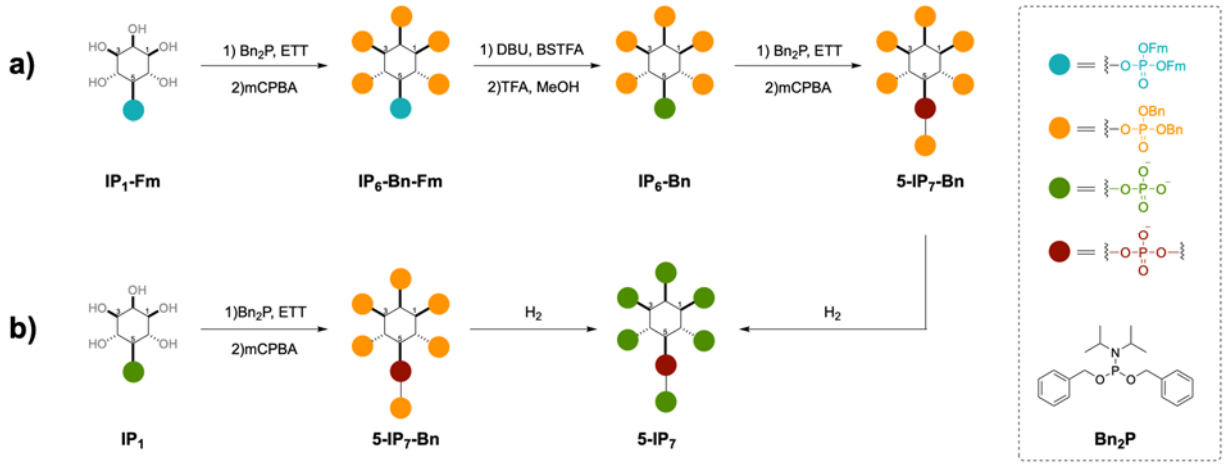
Inositol phosphates (IP) are key molecules in cellular signaling, phosphate storage and metabolism. [1-4] The synthetic feasibility enables the external mimicry of bioactivities and serve as a powerful probe for tracing. However, the conventional synthesis of highly phosphorylated inositol derivatives, such as IP_7, is insufficient. The stepwise synthetic route starts from IP_1 to IP_6, followed by deprotection, phosphorylation and final hydrogenation (scheme 1a).

During the process, two challenges arise:

1) Laborious steps due to the protection/deprotection process
2) Dependence on moisture-sensitive reagent (BSTFA) for deprotection, which increases the risk of reaction failure



Scheme 1, synthetic routes of 5-IP_7.

To address these issues, a new, one-pot global phosphorylation strategy was developed, enabling a direct phosphorylation from IP1 to IP7 precursors followed by final hydrogenation (scheme 1b). By closely monitoring the reaction and controlling the parameters, the reaction was successfully optimized:

1) The product overall yield increased threefold with decreased workflow time by 50%
2) Excellent reproducibility was achieved without the need for moisture-sensitive reagents

This approach not only improves the synthesis of 5-IP_7 but also provides a scalable, cost-effective method for obtaining phosphorylated inositol derivatives ($IP_{7\text{-}9}$), reducing redundancy while increasing efficiency.

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Formation of *Lewis* Pairs between the 1-Bismolane Cation and Group 15 Bases

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Alkyl-substituted bismuth cations are significantly less represented in the literature than their aryl-substituted counterparts.[1–4] Therefore, we aim to develop new alkyl-substituted bismuth cations and to investigate their ability to form *Lewis* pairs with group 15 bases. In this study, we synthesized the five-membered ring compounds $Bi(CH_2)_4X$ (X = Br, SbF_6) and successfully formed and characterized novel *Lewis* pairs. This study also aims to compare the stability of the Lewis pairs of group 15 bases. Notably, we were able to isolate acid–base pairs featuring bismuth–bismuth and bismuth–antimony interactions, which remain rare in the literature.[5,6]

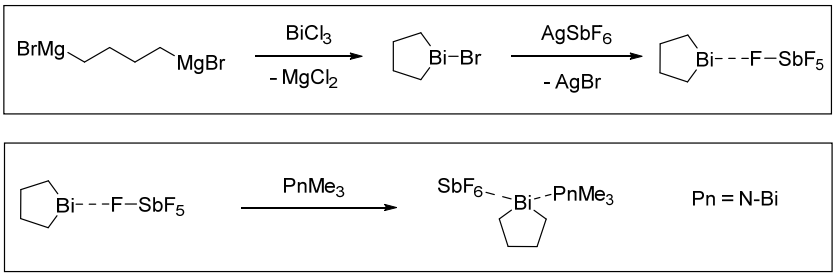

Figure 1: general synthesis of compounds of the type $(CH_2)BiBr$ and $(CH_2)BiSbF_6$ and follow up reactions to form *Lewis* pairs.

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Chemoselectivity in the Cationic Phospha-Wittig Reaction

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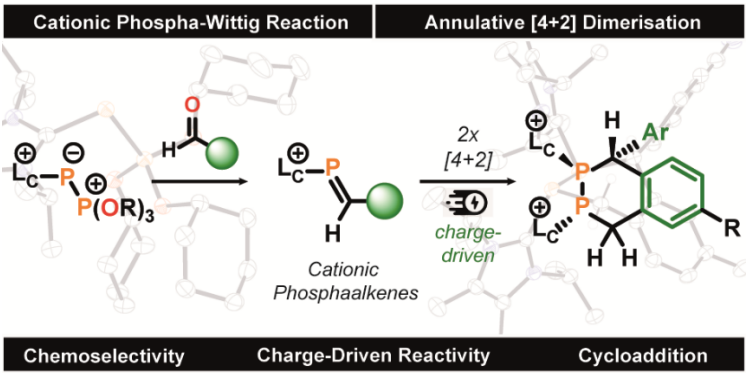
Phosphaalkenes have emerged as versatile building blocks in main-group chemistry, finding applications in π-conjugated molecules, inorganic polymers, and as ligands in transition-metal catalysis. However, the lack of reliable and modular synthetic procedures that allow systematic tuning of their electronic and steric properties limits the broader use of phosphaalkenes. In this context, cationic *P*-imidazoliumyl-substituted phosphaalkenes offer a promising solution, as the P–L_C bond enables a) derivatization routes that are otherwise inaccessible and b) a straightforward post-synthetic modification with a broad range of nucleophiles.[1]



We now report the synthesis of isolable phosphito-phosphanides that enable a cationic phospha-Wittig reaction with a broad range of aldehydes for the first time. The chemoselectivity of this transformation is systematically investigated, allowing controlled access to phosphaalkenes and related phosphorus heterocycles. Importantly, this chemistry reveals distinct reactivity differences between charged and neutral phosphaalkenes, such as an unprecedented, charge-driven [4+2] annulative dimerisation of *C*-aryl-substituted phosphaalkenes.[2]

Acknowledgements: We gratefully acknowledge financial support from the German Research Foundation (DFG, WE4621/6-1 and WE4621/6-2) and the Fonds der Chemischen Industrie (Kekulé Fellowship for P.R.).

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Investigations Phospha- and Arsaalkyne Platinum Complexes: Synthetic Pathways to Cyaphido and Cyarsido Complexes

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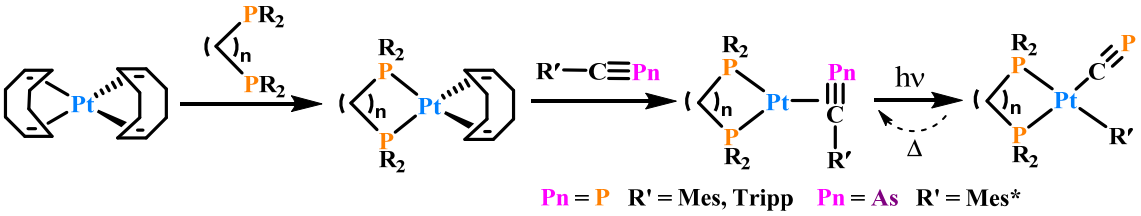
Terminal cyaphido (C≡P⁻) complexes rank among the most challenging main-group systems containing C≡P multiple bonds[1] as their synthesis has traditionally depended on desilylation-rearrangement or reductive cleavage strategies that often produce thermally and kinetically stable species with limited reactivity at the C≡P moiety.[2] Although the coordination of the cyaphido ligand to transition-metal and actinide centers has been reported, systematic exploration of this ligand class remains comparatively underdeveloped.[3] Recently, our group reported the first example of a photochemical C(sp)–C(sp²) bond activation in η^2-coordinated aryl phosphaalkynes, selectively generating reactive Pt(II)–cyaphido complexes via a reversible oxidative addition pathway.[3c]



We now started to investigate this photochemical approach for structurally diverse phosphaalkynes and, for the first time, also to arsaalkynes. We could successfully prepare and structurally characterize aPt(0) complex that contains an η^2-coordinated aryl arsaalkyne. Furthermore, a variety of di-phosphine co-ligands have been used to modulate the steric and electronic properties of the co-ligands. We also currently investigate the possibility to prepare silyl-substituted phosphaalkynes that coordinate in an η^2-fashion to Pt(II), with the idea to photochemically selectively the C–Si bond to access cyaphido complexes.

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Enhancing biocompatibility of anticancer metal-complexes through amino-acid derived PNP-ligands

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With the discovery of cisplatin and its antiproliferative effect on bacteria and cancer cells,[1] metal-based anticancer agents have received broad attention. However to this day, their medical application is connected to severe limitations such as side effects and resistances.[2] In this instance, phosphine ligand systems remain rather scarce in the development of platinum anticancer complexes, despite their promising characteristics, such as their steric and electronic tunability. Combined with the versatile, readily available and biocompatible amino acids, (S)-*N*,*N'*-bis(diphenylphosphine)amino acid methyl esters (aaPNP) serve as an interesting scaffold to enhance antiproliferative effects. In preliminary studies against HeLa (cervical cancer), *cis*-dichloroplatinum PNP-based complexes (Figure 1), have shown promising *in vitro* feasibility, while maintaining remarkable stability in solution.[4] To enhance the solubility of the complexes in aqueous media, platinum(IV)-prodrugs bearing water-soluble axial ligands, such as L-cysteine, are of key interests. Moreover, the applicability of the ligand system in *cis*-dichlororuthenium(II)-complexes is investigated (Figure 1).

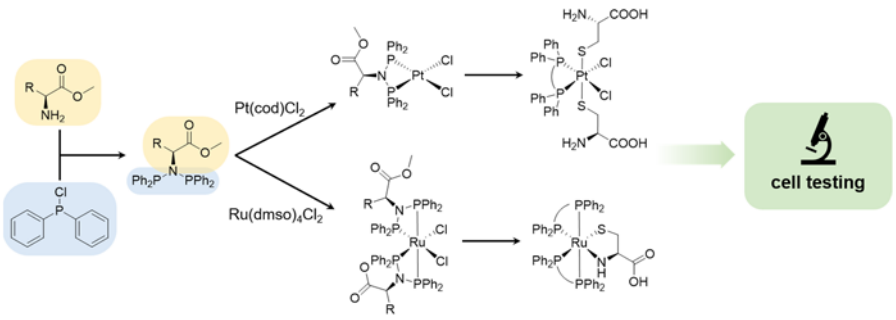

Figure 2: Synthesis and design of aaPNP-ligands for application in metal-based anticancer agents.

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Controlling triplet emission in diphosphonium salts

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Anion–π^+ (including π^+= pnictogenium organic cation) emitters represent an emerging class of ionic luminophores whose charge-transfer (^{3}CT) relaxation pathways enable them to emulate key aspects of triplet-state photophysics typical of conventional phosphorescent systems, while offering distinct advantages arising from their simplified, modular ionic architecture.[1] Unlike traditional rigid luminophores, anion–π^+ systems inherently possess a degree of anion mobility. Even in solid matrices, electric fields generated in the excited state and free volume within the lattice can permit limited ion motion. Rather than treating this mobility as a drawback, we posit that it can be deliberately harnessed to activate nontraditional excited-state relaxation and transition channels that are otherwise inaccessible in static chromophoric systems.

External perturbations – including heating, shearing, grinding, pressure, and solvent exposure—are expected to drive controlled translocation of anion–π^+ pairs within the material, thereby modulating emission, and our results support this concept. In 1,5-diphosphonium naphthalene diiodide, emission is initially suppressed due to large iodide–cation separation. However, solvent-triggered anion relocation switches emission "on," generating a sequence of stable pairs, and emissive states: $^{1/3}\pi\pi^*$ (420 nm), mixed $^3\pi\pi^*$/CT (520 nm), and pure ^{3}CT (620 nm), spanning a broad spectral range. This system demonstrates that an intrinsic structural "disadvantage" – long anion–π^+ separation – can be converted into a functional asset under controlled environmental conditions, yielding a highly responsive, solvent-sensing luminescent material based on a single molecular module.

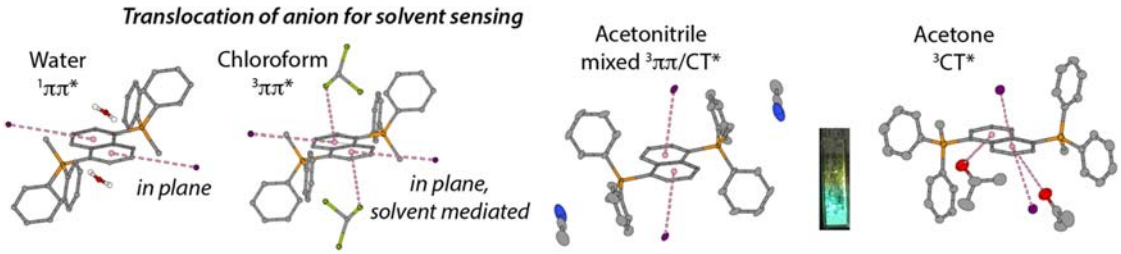

Figure 1. Tunable anion-π+ interaction for functional ^{3}CT states (experimental scXRD data).

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Synthesis of Defined *myo*-Inositol Phosphates and their Metabolic Fate in an In Vitro Human Intestinal Model

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Myo-inositol phosphates (InsPs) serve essential functions in eukaryotic cells, such as phosphate storage, and are key molecules in second-messenger systems. Their most prominent representative – 1,4,5-$InsP_3$ – is, for example, the main factor controlling the cellular calcium signaling.[1] However, to study the role of these InsPs further, they need to be synthetically prepared first, which remains quite challenging, requiring several regio- and enantioselective transformations. Here we present the current synthesis towards 1,4,5-IP_3.[2] The final step represents a divergent synthesis, so that both the target $InsP_3$ and a precursor for subsequent phosphorylations are obtained, which explore the concept of the directing-neighboring-group effect. Biotransformations of InsPs are investigated utilizing the Caco-2 cell line, which in vitro reflects the morphological and functional conditions present in the human intestine.[3]

The novel synthetic strategies presented here have the potential to significantly accelerate the access to various defined inositol phosphates, while the in vitro studies contribute to a better understanding of their metabolism.

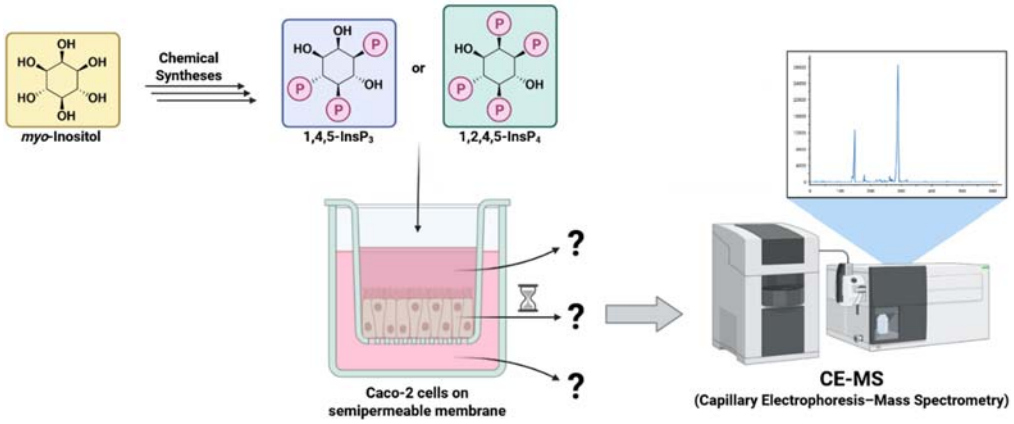

Figure 1: Defined InsPs are chemically synthesized. After in vitro metabolism studies, cell-extracts are analyzed by CE-MS for their metabolized $InsP_n$ contents. Figure created with BioRender.com.

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Design and Synthesis of π-Extended Azaphosphole-Derivatives

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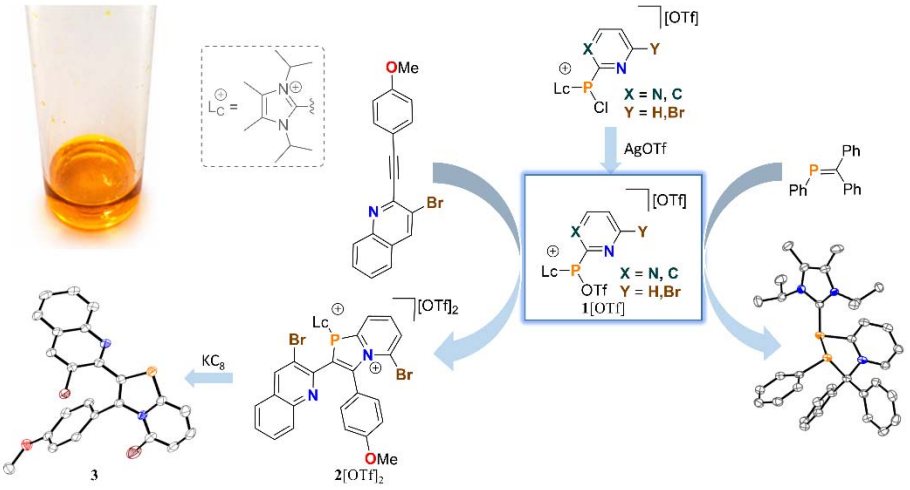
The advent of 1,3-dipolar cycloadditions in organic chemistry has introduced a powerful tool for constructing novel ring systems.[1] However, methods for synthesizing inorganic phosphorus-containing rings *via* 1,3-dipolar cycloadditions have remained largely limited. Recently, we described the synthesis of 1,3-dipolar triflatophosphanes (**1**[OTf]) and demonstrated their ability to engage in (3 + 2) cycloaddition reactions with a variety of dipolarophiles such as alkynes[2,3] and nitriles,[1] yielding a wide range of heteroatom-functionalized aza- and diazaphospholium compounds, e.g. **2**$[OTf]_2$. Subsequent reduction releases the NHC and affords neutral aza- and diazaphospholes, e.g., **3**, which exhibit interesting optoelectronic properties.

This versatile methodology allows for straightforward derivatization and functionalization, for example by varying the dipolarophile (e.g., phosphaalkenes),[4] extending the π-system or introducing heavier heteroatoms, thereby tuning optoelectronic properties of these azaphospholes.



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Functionalized Cyclotriphosphazene-Based Cobalt Coordination Polymer: Synthesis, Characterization, And Catalytic Efficiency Evaluation

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Among phosphorus–nitrogen based frameworks, metal-containing cyclic phosphazenes stand out for their remarkable structural versatility, catalytic potential, and electronic tunability. These hybrid materials merge the intrinsic stability of the P–N backbone with the functional diversity provided by coordinated metal centers, offering opportunities for applications in catalysis, sensing, and environmental remediation. Despite these advantages, the development of metal-based phosphazenes has progressed more slowly compared to other classes of metal-containing materials [1].

In this work, a flexible hexapod-shaped molecular building block, hexakis(methyl-2-(4-phenoxyphenyl)acetatebenzene) cyclotriphosphazene (H6L1), was employed as an organic linker to construct a Co(II)-based coordination polymer (CP). The incorporation of Co(II) ions into the phosphazene framework imparts enhanced redox and catalytic functionality to the resulting material.

Utilizing the catalytic activity of coordination polymers has recently emerged as an efficient approach for the degradation and removal of organic pollutants from wastewater [2]. Accordingly, the synthesized CP, designated as GTU-4, was systematically investigated for its catalytic performance in the decomposition of representative dye contaminants, including Rhodamine B, Methylene Blue, Acid Red-17, and Rifampicin. The results highlight the potential of this phosphazene-based coordination polymer as a multifunctional catalyst for environmental applications.

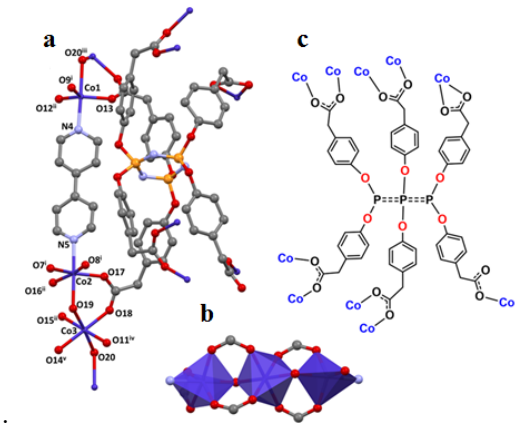

Figure-1: Synthesis of Ligand

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We would like to thank TÜBİTAK TEŞVİK-2024 for their support.

A Stable Diphosphaquinoid Platform for Structural and Electronic Insights into a Phospha-*p*-Semiquinoid Radical Anion

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Quinoidal molecules play essential roles in both biological electron-transfer pathways and the design of functional molecular materials. Unlike classical quinoids, whose electronic structures are governed by compact 2p–2p π-interactions, heavier main-group analogues introduce fundamentally different orbital interactions, redox energetics, and electron delocalization pathways. However, incorporating main-group fragments often increases molecular reactivity, and progress has been limited by the scarcity of synthetically robust quinoidal scaffolds capable of ensuring sufficient stability.

In this contribution, we report a series of diphosphaquinoids built on an anthraquinodimethane (AQD) scaffold (Figure 1A). The AQD framework, which features two Clar's sextets and adopts an intrinsically contorted geometry, offers both aromatic stabilization and structural flexibility, enabling the isolation of an air-stable, non-planar diphosphaquinoid. The corresponding dinuclear gold(I) complex (Figure 1B) was examined for comparison, providing insight into structure–electronic relationships. Most importantly, we achieve the first comprehensive characterization of a phospha-*p*-semiquinoid radical anion in both solution and the solid state (Figure 1C). Together, these findings provide detailed insight into main-group quinoid/semiquinoid and expand the landscape of redox-active, main-group-functionalized polycyclic aromatic hydrocarbons.

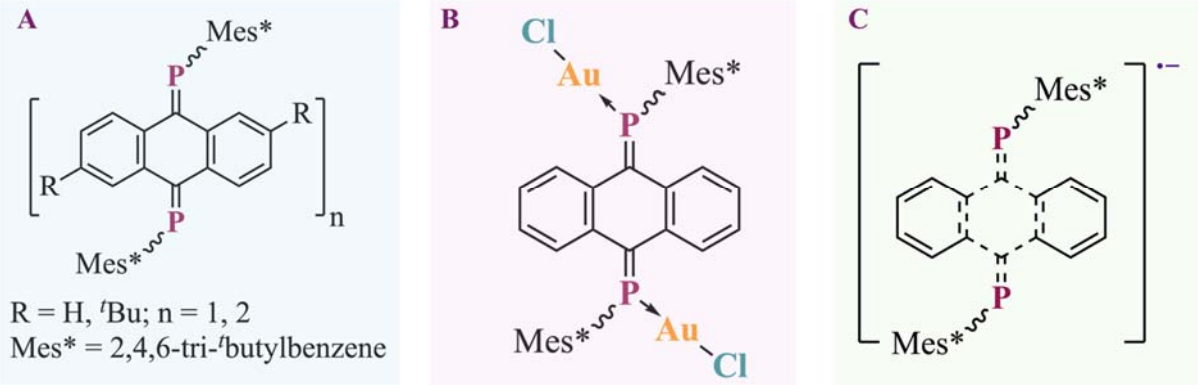

Figure 1. (A) AQD-based diphosphaquinoid; (B) its corresponding dinuclear gold(I) complex; and (C) the associated phospha-*p*-semiquinoid radical anion.

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First *P,C,P*-pincer organobismuth compounds

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Organobismuth compounds have attracted a lot of attention during last 20 years. Thanks to that, there are many known species described in the literature belonging to the organobismuth family, including compounds coordinated by oxygen or nitrogen atoms.[1-3] Regarding organobismuth compounds stabilized by intramolecular coordination of phosphorus atoms, only a few species are known to this date.[4] The univalent bismuthinidenes stabilized by *N,C,N*-pincers represent a special class of bismuth compounds, the Cornella´s group transformed to unprecedented main group redox catalysts.[5] First examples of analogous *P,C,P*-organobismuth chlorides stabilized containing either L^{CH2} or L^{O} ligand will be reported. Their reactivity, including oxidation at P atoms, ionization of bismuth center and the possibility to synthesize *P,C,P*-bismuthinidenes will be delivered as well.

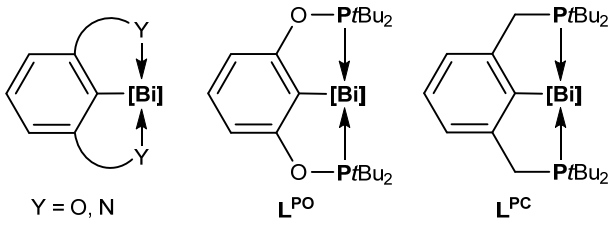

Figure 1. Discussed pincer organobismuth compounds.

Acknowledgements

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Investigation of the Lewis acid-base properties of the cyanate anion and its heavier homologues

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Historically, salts of the cyanate anion (NCO^-) and its heavier chalcogen homologues, thiocyanate (NCS^-) and selenocyanate ($NCSe^-$), have long been known compounds. The first targeted syntheses of cyanate salts were carried out by Gay-Lussac in 1816 and, building on this, by Wöhler in 1822.[1-2] Further work also focused on the synthesis of the heavier pnictogen homologues of these compounds.[3-5] In our work, we focus on the Lewis base properties of these anions in relation to various triel-based Lewis acids with different steric requirements.[6] The compounds shown were mainly investigated using X-ray structural analysis on single crystals, NMR and IR spectroscopy, and elemental analysis. A wide variety of coordination patterns could be observed, and the concept of the HSAB principle was impressively demonstrated.

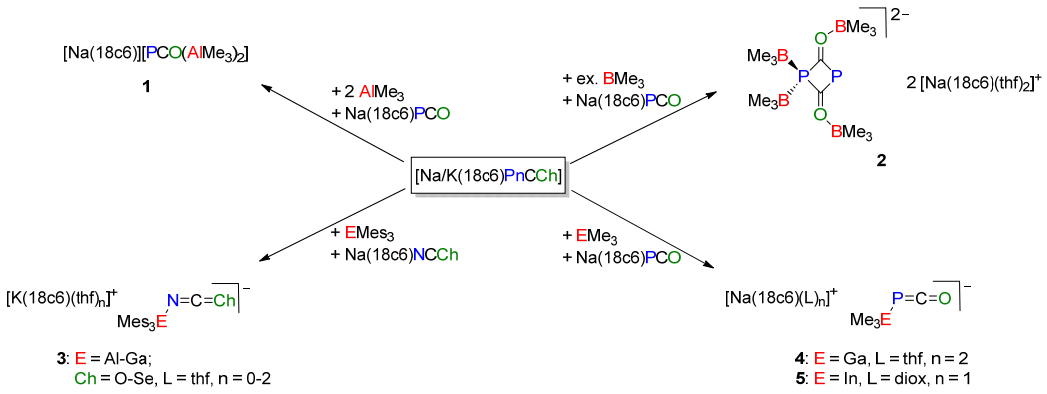

Figure 1: Overview diagram of the synthesized Lewis acid-base adducts of cyanate anions and their heavy homologues towards triel-based Lewis acids.

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Automated 5‘-Triphosphorylation of Synthetic DNA and RNA Oligonucleotides using cPyPA

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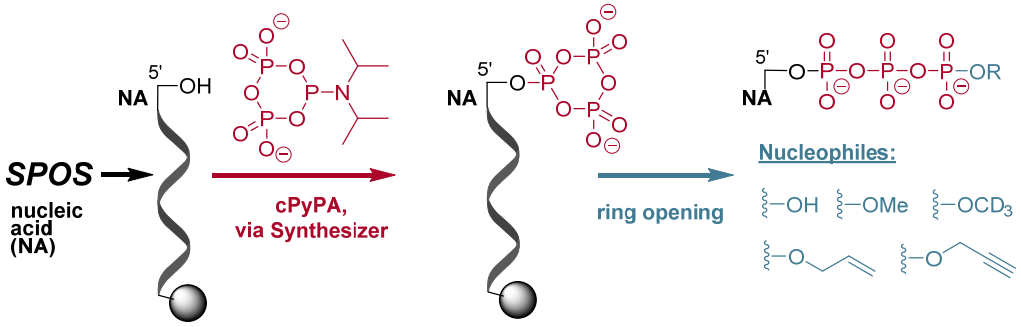
Nucleic acids have a fundamental role in living organisms as they are responsible for gene expression and protein production. Studying and influencing these processes asks for precisely modified synthetic nucleic acids. The terminal 5’-OH group of oligonucleotides can be modified after the solid phase oligonucleotide synthesis (SPOS) and is of interest because 5’-phosphate modifications can be recognized by proteins[1,2] and used for bioconjugation reactions.[3]

We developed an automated 5’-triphosphorylation method for synthetic DNA and RNA compatible with SPOS: The phosphorus(III)-amidite reagent cPyPA is used to phosphorylate the 5’-OH group to obtain a solid phase-bound 5’-cyclotriphosphate. Subsequently, the solid-phase-bound cyclotriphosphate is linearized by a ring opening with different nucleophiles. This enables the synthesis of oligomers with several natural and unnatural 5’-triphosphate modifications.

The new 5’-triphosphorylation approach with cPyPA is complementary compared to the before-known phosphorus(III)-amidite-based[4] or phosphorus(V)-amidate-based[5] protocols. To expand this promising technique, the scopes of 5’-phosphate modifications and oligomer sequences will be broadened.



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Cyclotriphosphazene Derivatives as a New Class of Circadian Rhythm-Safe Bioactive Compounds

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In this study, a new series of biocompatible cyclotriphosphazene derivatives were designed, synthesized, and evaluated for their *in vitro* biological activities and effects on circadian rhythm. Based on these observations, it is worth investigating how the incorporation of heterocyclic morpholine or thiomorpholine groups, with or without triazole moieties, onto a regio- and stereo-specific cyclotriphosphazene scaffold may confer novel biological properties. The resulting molecules were further designed to possess amphiphilic tripodal architectures to enhance their interaction with biological systems.[1]

Comprehensive biological assays, including cytotoxicity tests (IC_{50} determination, population doubling time, and colony formation) and flow cytometric analysis of cell cycle distribution, were conducted. Because the circadian clock regulates most metabolic and physiological processes, the effects of these cyclotriphosphazene derivatives on circadian rhythm were also examined using a real-time bioluminescence method. Some compounds exhibited notable antiproliferative activity, inducing G_2/M phase arrest, while most derivatives showed no detrimental influence on circadian rhythm. Overall, these findings identify cyclotriphosphazene-based derivatives as a promising new class of circadian rhythm-safe bioactive molecules.[2]

Acknowledgement

This study was supported by Scientific and Technological Research Council of Türkiye (TÜBİTAK). Project No: 121Z228. We thank Central Research Laboratory Application and Research Center (GTU-MAR) for allowing us to use their infrastructure facilities.

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From Boron to Bismuth: Trapping the Pre-transmetalation Complex

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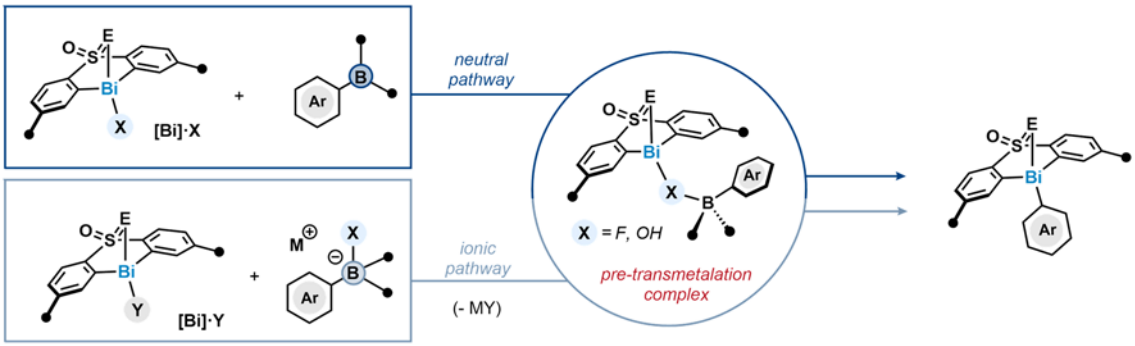
Arylboron reagents are indispensable building blocks in a wide range of catalytically relevant transformations. Their reactivity is largely governed by the transmetalation step involving the aryl transfer from boron to a metal center. Two general pathways for this process have been identified: *neutral* and *ionic* routes, both of which proceed through a B–X–M pre-transmetalation intermediate (X = OH, F), a key yet rarely observed species.[1] While several studies have provided spectroscopic evidence or isolated oxygen-bridged examples in transition-metal chemistry,[2] analogous intermediates in main-group systems remain largely unexplored.

In recent years, B-to-Bi transmetalation has attracted increasing attention, either as a central elementary step in high-valent bismuth catalysis [3] or as a reaction to access triaryl bismuth compounds that serve as stoichiometric aryl donors.[4] In this study, we provided detailed mechanistic insight into the transmetalation of aryl boron nucleophiles to Bi(III). Importantly, we report the isolation and structural characterization of two unprecedented pre-transmetalation intermediates linking B and Bi through a F– or an OH– bridge. Furthermore, we establish that B-to-Bi transmetalation can proceed either via a *neutral pathway* involving [Bi]·X species (X = OH, F) and neutral boranes, or via an *ionic pathway* involving cationic [Bi]·Y intermediates (Y = OTf, BF_4, Cl, I, SO_2Ph) and pre-formed ionic boronates.



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Substitution reactions of the weak Lewis pair H_3P-$AlCl_3$: mechanistic insights

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Phosphine (PH_3) is a highly toxic and poorly functionalizable molecule, which severely limits its direct use in chemistry. We have recently described a Lewis-acid-assisted strategy that enables efficient monosubstitution of PH_3 under mild conditions.[1] In the presence of aluminum chloride, PH_3 forms a labile $H_3P{\rightarrow}AlCl_3$ Lewis pair that readily reacts with alkyl halides in organic solvents, affording primary phosphines within minutes at room temperature. Experimental observations demonstrate the broad applicability of this approach, including the synthesis of sterically demanding phosphines such as adamantyl- and *tert*-butylphosphine, as well as the scalability to kilogram quantities for selected substrates.

Our density functional theory (DFT) calculations reveal that the weak P–Al interaction facilitates dissociation upon contact with alkyl chlorides, enabling a Lewis-acid-assisted nucleophilic attack that proceeds via formation of the phosphonium salt $[R{-}PH_3]^+[AlCl_4]^-$. According to our mechanistic analysis, while *tert*-butyl chloride reacts via an S_N1 pathway due to the stability of the *tert*-butyl carbocation, adamantyl chloride undergoes a unique S_N2-type substitution with a so-called frontside attack, reflecting the inability of the adamantyl framework to invert at its C center. Further comparative studies on methyl chloride and endo-norbornyl bromide provide additional insight into reaction pathways.

Acknowledgements

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Phosphonium-substituted Diphosphacyclobutadienyl complexes of Mn(I): From Activation to Catalysis

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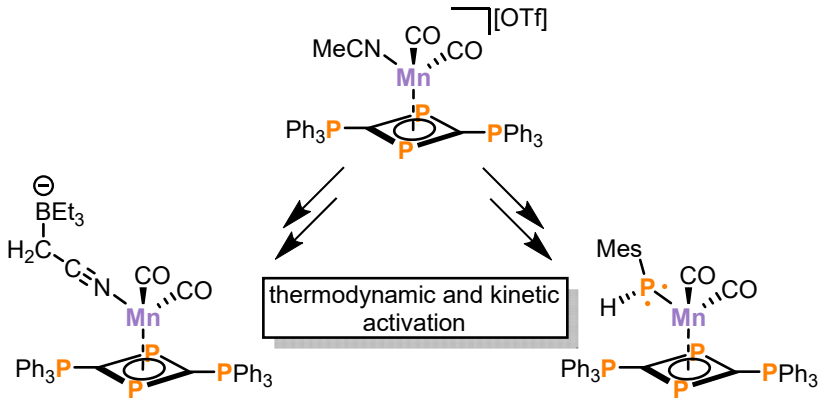
In recent years, phosphorus centered biradicaloids gained significant attention due to their interesting ligand properties such as such as their strong binding to metal centers, their redox non-innocent behavior and the presence of Lewis-basic sites. However, the synthetic accessibility of these biradicaloids often relies on kinetic stabilization through bulky substituents (e. g. IPr), which potentially limits the applications of the resulting complexes.[1-3] Previously, we reported a synthetic strategy to utilize tricarbonyl manganese (I) complexes with sterically less demanding biradicaloid-ligands, e. g. triphenylphosonium substituents. For this manganese complex, we demonstrated an endergonic, light-driven carbonyl exchange with acetonitrile, resulting in an activated complex.[4]

This activated complex serves as a valuable synthon for further manipulation. We are able to show that upon coordination, the acetonitrile is kinetically and thermodynamically activated. First, this activation allows the selective deprotonation of the coordinated acetonitrile with superhydride solution which is in sharp contrast to conventional reduction of nitriles with borohydrides.

Second, the acetonitrile ligand can be exchanged with a variety of primary and secondary phosphines, giving access to a library of manganese phosphine complexes. In the case of mesitylphosphine, subsequent deprotonation allows the isolation of a rare example of a terminal phosphanido complex. According to our calculations and preliminary experiments, this complex is classified as a superbase, showing high activity in hydrophosphination experiments.



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Valence Tautomerism and Element Ligand Cooperativity in Structurally Constrained Phosphorus Cations

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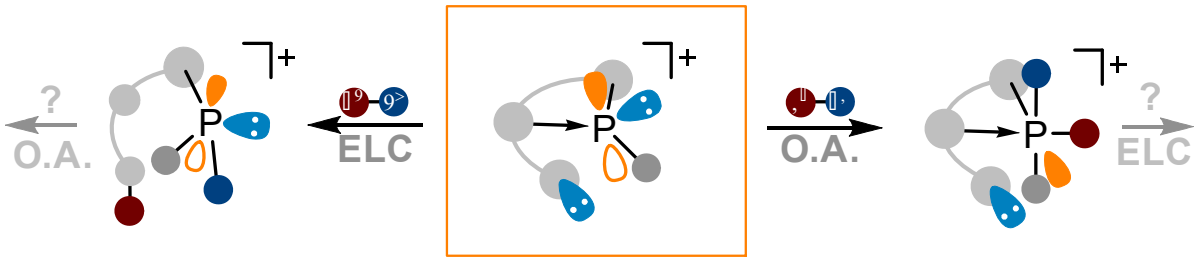
Metal–ligand cooperativity (MLC) has emerged as an effective strategy for transition-metal-mediated bond activation and catalysis, enabling substrate transformation without changes in the oxidation state of the metal center. An analogous concept has recently gained attention in p-block chemistry, where synergistic interactions between an element and its ligand facilitate substrate activation or catalytic processes, a phenomenon referred to as element–ligand cooperativity (ELC). Phosphenium cations, $[PR_2]^+$, are highly reactive main-group species that are isoelectronic with singlet carbenes, silylenes, and nitrenium ions, and exhibit pronounced ambiphilic character. This dual reactivity renders them attractive reagents and ligands in modern main-group chemistry. In this work, we seek to integrate element–ligand cooperativity with phosphenium chemistry within a single molecular framework, enabling the development of systems that feature two orthogonal reactivity channels and expanded potential for bond activation and catalysis.



This dual-reactivity platform opens the door to **substrate-specific reaction pathways**, as well as **sequential or concerted multi-site transformations** involving distinct substrates.

Acknowledgements
The authors would like to thank Prof. Dr. Robert Wolf and his group (University of Regensburg) for constant guidance and help.

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Combining Distibine, Diazoolefins, and Visible-light: Synthesis and Reactivity of Inorganic Rings

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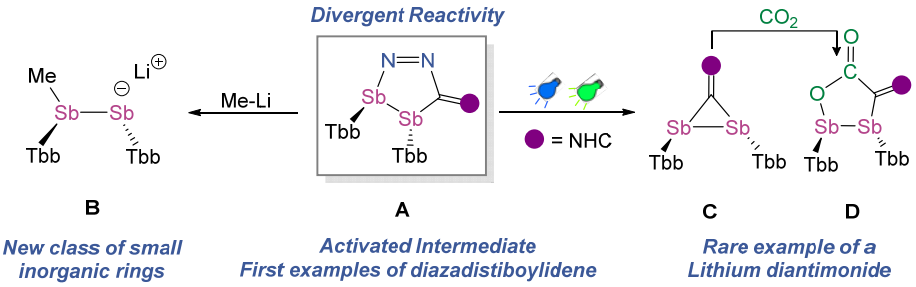
The chemistry of heterocycles containing "diaza" units has been extensively explored owing to their broad applications ranging from pharmaceuticals to advanced materials.[1-2] However, antimony (Sb) and bismuth (Bi) containing heterocycles remain exceptionally rare and lack general synthetic methodologies.[3] Herein, we present a comprehensive experimental and theoretical study of the first diazadistiboylidenes (**A**), synthesized *via* a [3+2]−cycloaddition between a distibene and diazoolefins.[4] We show that these diazadistiboylidenes act as key intermediates for selective nucleophilic substitution reactions, leading to the formation of a rare diantimonyl anion (**B**). Furthermore, exposure to visible light allows the isolation of the first methylenedistibiranes (**C**), representing heavier analogues of methylenediaziridine ($C_2H_4N_2$). Together, these findings establish a new framework for heavy dipnictogen chemistry. This approach highlights the potential of diazoolefins and photochemical activation to access previously unknown heterocycles and to enable the activation of carbon dioxide (**D**).



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Persubstituted anilino-derivatives of cyclophosphazenes: exploring substituent effects and supramolecular assembly

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While persubstituted oxy-derivatives of cyclophosphazenes have been extensively documented in literature for their applications as flame retardants, their amino-substituted counterparts have not been thoroughly studied. This study is broadening the family of persubstituted anilino-derivatives, specifically expanding the chemical space of cyclic tetramers where only a few examples previously existed.[1,2]

We report the successful preparation and characterization of these compounds (Figure 1) using multi-nuclear NMR, mass spectrometry, and X-ray crystallography. Single-crystal analysis revealed a diverse range of packing behaviors, most notably a specific derivative that self-assembles into complex supramolecular architectures featuring distinct internal cavities (occupying 25 % of the crystal volume). We studied a correlation between the electronic nature of the functional groups (electron-donating vs. electron-withdrawing) and the resulting absorption and emission profiles. These findings broaden the library of available anilino cyclophosphazene derivatives but also provide a framework for the rational design of functional supramolecular materials.

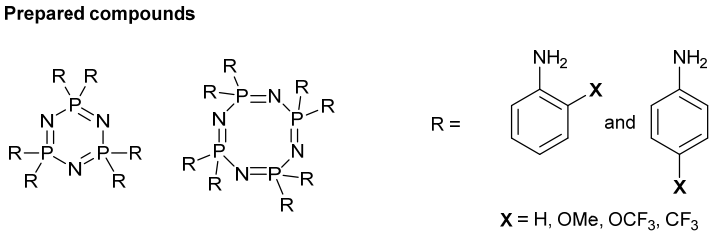

Figure 1: Prepared anilino-derivatives of cyclophosphazenes.

Acknowledgements

This work was supported by the Ministry of Education of the Czech Republic (LUC24043).

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Computational Investigations on the Group-transfer Reactivity of Heavier Pnictaketenes toward Carbenes

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Starting from 2011, the chemistry of the $[PCO]^-$ anion emerged from laboratory curiosity to synthetic building block.[1] Its main reactivity modes span across various cycloadditions, nucleophilic substitutions and P^--transfer reactions. Similar reactivity was also demonstrated for phosphaketenes (R-PCO, obtained from the anion *via* P-functionalisation),[2] and recently for arsaketenes (R-AsCO) as well.[3] These milestones serve as an early example for transition metal-like behavior on a main group centre.[2]

As the ligand-exchange/group-transfer reaction have gained significant interest,[4] and the reactivity of heavier R-ECX (E: P, As; X: O, S, Se) ketene analogues is largely unexplored, in this work, we computationally investigated the the addition reaction of Me_3Ge-E=C=X phospha- and arsaketenes with carbenes. We apply N,N'-dimethyl imidazol-2-ildene as a model NHC and investigate the CO-to-carbene ligand-exchange reactions for all possible E: P, As; X: O, S, Se combinations. According to our results, the heavier X=S, Se ketene analogues clearly prefer the addition pathway over the ligand-exchange, which can be traced back to the difference in thermodynamic stability between the CO *versus* CS/CSe species.

Acknowledgements

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Phosphorylation of Amino Acids and Dipeptides with a PO_2 Synthon and their Interaction with *f*-Elements

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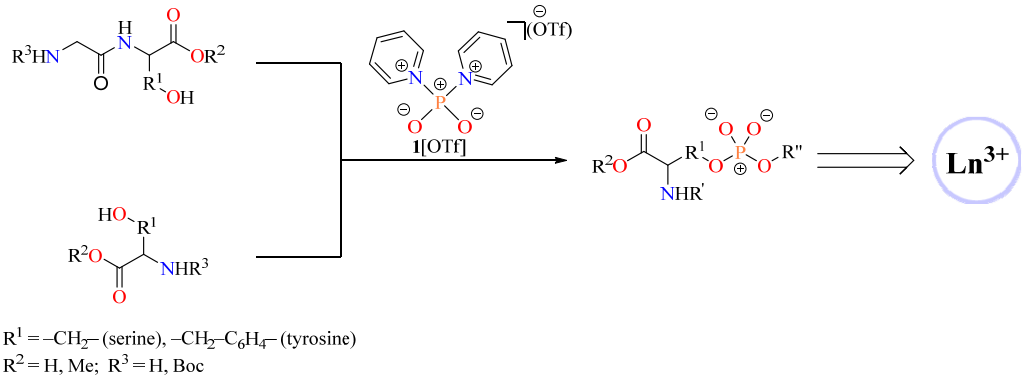
The phosphoryl group is known to exhibit a strong affinity for certain metals due to its hard Lewis basic character. Metalloproteins and biomimetic protein systems have been studied for their coordination with *f*-elements,[1–4] and these studies suggest that phosphoryl groups, often present as phosphoserine residues, can lead to an increased affinity for these ions. Thus, phosphorylated amino acids and dipeptides are envisioned as model compounds for the deeper understanding of the coordination behaviour of *f*-elements by phosphoproteins.

To obtain these model compounds, the phosphorylation reagent $(py)_2PO_2[OTf]$ (**1**[OTf]; py = pyridine)[5] was reacted with various protected amino acids and dipeptides (Scheme 1). The coordination properties of these model compounds toward lanthanides were investigated using La(III), Sm(III), and Lu(III) as early, middle, and late lanthanide representatives. The binding behaviour of these phosphorylated biomolecules will be presented.



Scheme 1. *Representation of the synthesis of the amino acid model compound using **1**[OTf].*

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A Zwitterionic Imidazoliumyl-Diphosphetide: A Building Block for Pentafluorophenyl-Phosphaalkyne-Derived Frameworks

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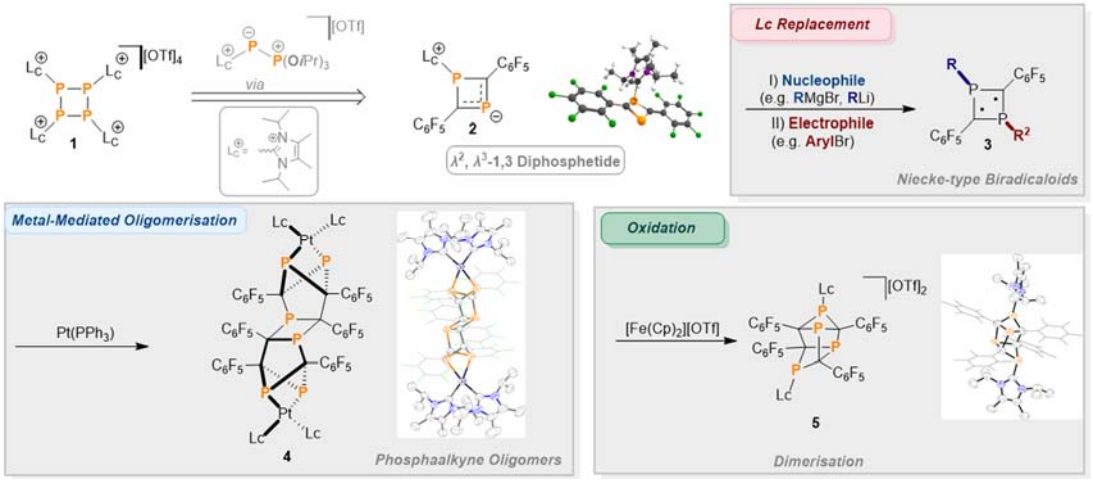
The targeted incorporation of phosphorus atoms into heterocyclic structures has proven to be a valuable strategy for developing efficient functional materials, spanning areas from optoelectronics[1-2] to small molecule activation[3]. Phosphaalkynes are valuable building blocks in this regard, as they enable the construction of diverse oligomers[4] and heterocycles.[5] However, the isolation and storage of non-stabilised derivatives remain particularly challenging. With these limitations in mind, we designed an imidazoliumyl-stabilised electron-deficient diphosphetide (**2**) that possesses reactivity complementary to that of known phosphaalkyne frameworks.[6] The diphosphetide (**2**) can be formally understood as a dimer of the pentafluorophenyl-phosphaalkyne which is stabilised by an imidazoliumyl-moiety to enable isolation, structural analysis and subsequent functionalisation.



Thise building block allows access to related diphosphetideanions and NIECKE-type biradicaloids (**3**) through suitable imidazoliumyl-replacement reactions. The formation of novel oligomeric structures (e.g. **4**) is further accessible through metal-mediated processes, in which the selection of suitable metals enables targeted modification during the oligomerisation process.

Acknowledgements

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Exploring Stabilization Effects in Phosphinyl Radicals: The scope of the captodative functionalization

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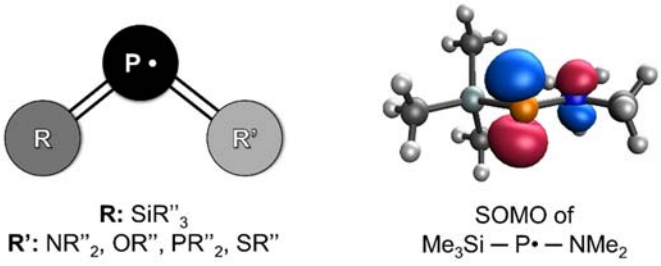
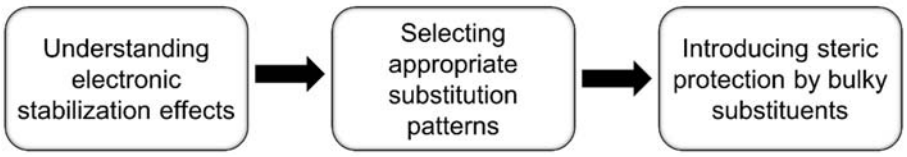
Accessing stable phosphinyl radicals continues to pose a major synthetic challenge. Our computational study systematically explores the possibilities and limitations of electronic and steric effects governing the stability of phosphinyl radicals, with a particular focus on captodative substitutions.[1] The electronic structures of various radicals have been scrutinized using natural bonding orbital analyses. The best stabilizing effects are primarily provided by π-donor groups; however, the most efficient π-donors suffer from a so-called saturation effect. To compensate for this disadvantageous phenomenon, various captodative substitutions have been assessed, and several combinations have been found to benefit from additional stabilization. Moreover, to prevent the dimerization of the radicals, spherical groups (such as *tert*-butyl or trimethyl silyl) placed at the donor and acceptor sites provide better steric protection than planar groups (such as phenyl and its substituted analogues). Integrating the results of our systematic investigations, we propose several potential candidates for synthetic purposes.





Acknowledgement

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A Rainbow of Low-Valent Phosphorus Compounds

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Phosphines are indispensable as ligands for transition-metal complexes, employed across the broad fields of organometallic chemistry. Lower oxidation states P-compounds, *i.e.* phosphinidenes and their dimers, diphosphenes, demonstrate a more electron-rich coordination environment. Such P-compounds, in this regard, are unique ligands with diverse coordination chemistry. This becomes especially apparent when we look towards diphosphine metal carbonyl complexes, which show an array of binding modes,[1] and can even undergo photoinduced *cis-/trans*-isomerizations[2] akin to azobenzenes.

In our work, we have developed a new family of carbene-stabilized bis-phosphinidene systems, which may also be regarded as inversely polarized phosphaalkenes. Chelating derivatives of these ligands undergo Ni-induced P-P homocoupling reactions forming an unprecedented class of bis-diphosphene macrocycles. In addition to multiple coordination modes of nickel, heterotetrametallic Cu/Ni assemblies could be realized.[3]

Beyond their coordination chemistry, the low-valent phosphorus units exhibit strong electronic communication with conjugated organic π-systems.[4] This interaction enables systematic modulation of optical properties through molecular design, providing access to P-containing chromophores with tunable absorption characteristics.[5] Our work towards combining these modern facets of low-valent P-chemistry, underlining multifunctionality at the interface of coordination chemistry and photoresponsive materials, will be presented.

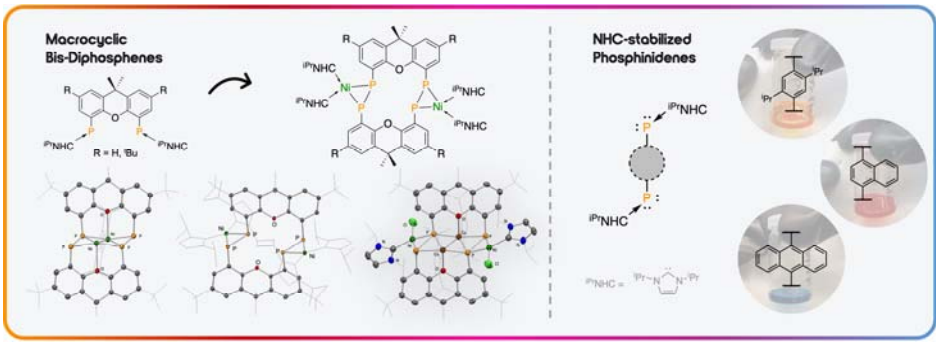

Fig 3. Exemplary representation of Macrocyclic Bis-Diphosphenes and colourful NHC-stabilized Phosphinidenes

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The bisphosphanylphosphanido-ligand as adaptive donor towards heavy tetrylenes

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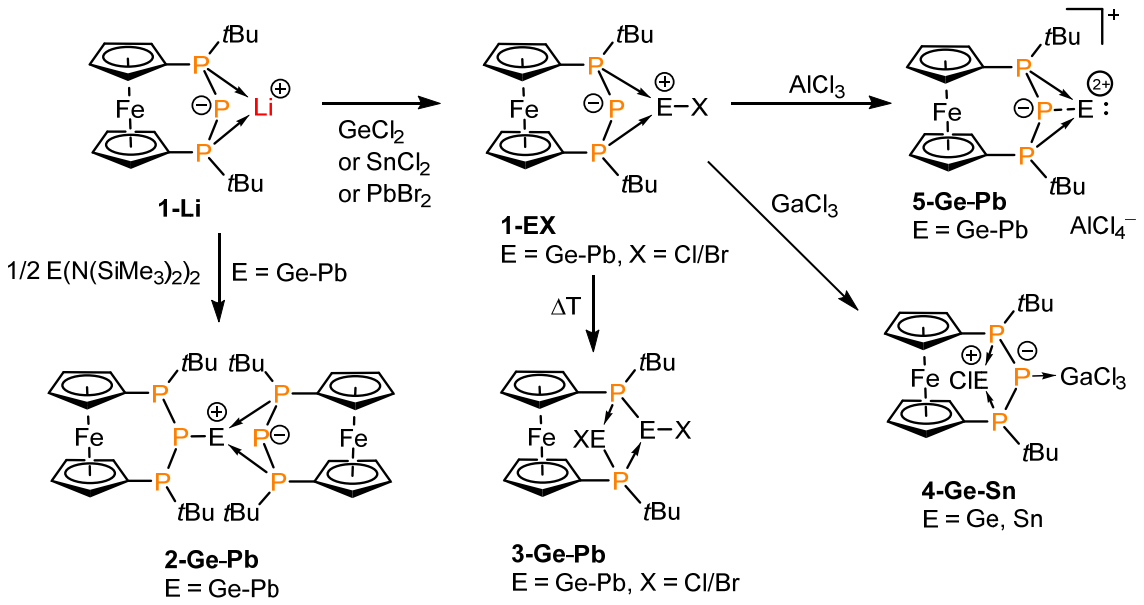
Our group developed a stereochemically confined triphospha-[3]ferrocenophane, which entails a P_3-chain capable of coordinating to electrophilic metal atoms in an adaptive manner with each P-atom.[1–3] Using this scaffold, we recently synthesized a tetraphosphenium ion capable of P^+ transfer and featuring the longest P(III)–P(III) bond observed so far.[4] Based on this, we investigated the coordination behavior of the model scaffold towards the isoelectronic heavier tetrylenes. To this end, donor-stabilized halogenotetrylenes (**1-EX**) were prepared, their decomposition products identified (**3-Ge-Pb**), and the halide was exchanged by a second [3]ferrocenophane unit (**2-Ge-Pb**). The attempted abstraction of the halides by scavengers uncovered an unexpected difference in reactivity between $GaCl_3$, which instead was coordinated by the central P-atom of the P_3-chain (**4-Ge-Sn**), and $AlCl_3$, which accomplished the envisaged halide abstraction (**5-Ge-Pb**), giving rise to highly electrophilic, dicationic tetrel species.



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On the Facile Synthesis of Triazaarsoles Using Acyclic Precursors

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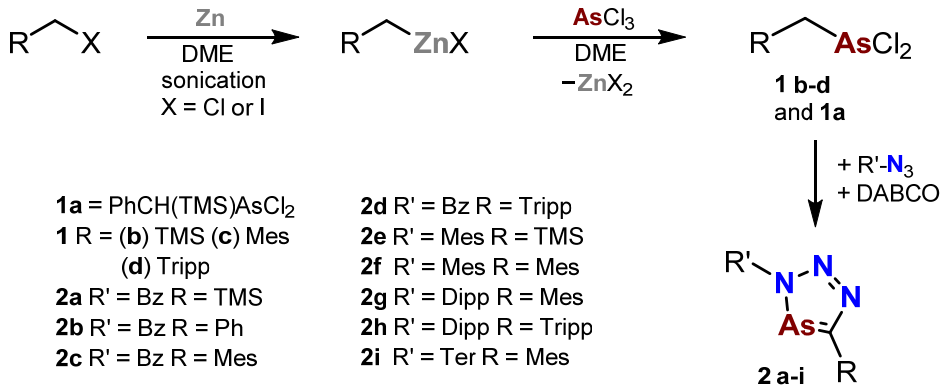
Triazapnictoles are low coordinated, ($\lambda^3\sigma^2$) Hückel-aromatic five-membered planar heterocycles, exhibiting one pnictogen (phosphorus or arsenic, respectively), one carbon and three nitrogen atoms. First reported by REGITZ and RÖSCH *et al.* in 1984, 3,5-disubstituted triazaphospholes can be synthesized *via* the conversion of widely available phosphaalkynes of the type R–C≡P with organic azides R–N_3 in [3+2] cycloaddition reactions.[1,2] Whilst triazaphospholes have been extensively investigated over the past years,[3,4] their heavier analogues, triazaarsoles, have rarely been reported. In contrast to phosphaalkynes and cyaphido complexes, the heavier arsaalkynes and cyarsido complexes are significantly more labile. Until today, the Mes*-substituted derivative Mes*C≡As remains the only reported stable arsaalkyne which can be synthesized, isolated on a larger scale and converted in cycloaddition reactions with azides to yield triazaarsoles.[5] However, this synthetic method limits the substitution pattern to the Mes*-substituent in the 5-position of triazarsole ring systems. We found that the conversion of easily accessible alkyl dichloroarsoles of the type R–CH_2AsCl_2 (**1a-d**) with organic azides R'–N_3 in the presence of the base DABCO selectively yields triazaarsoles (**2a-i**).[6] Thereby, a reactive species is generated *in situ* from the dichloroarsane by reaction with the base, which then undergoes a cycloaddition reaction with the respective azide. A variety of differently substituted triazaarsoles was synthesized *via* this novel route and could be isolated and characterized.



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Bz= benzyl $PhCH_2$-; TMS = trimethylsilyl; Mes = mesitylene, Mes* = 1,3,5-tri(*tert*butyl)phenyl; Tripp = 1,3,5-tri(*iso*propyl)phenyl

Synthesis and Reactivity of NHC-substituted Diphosphaindenylids

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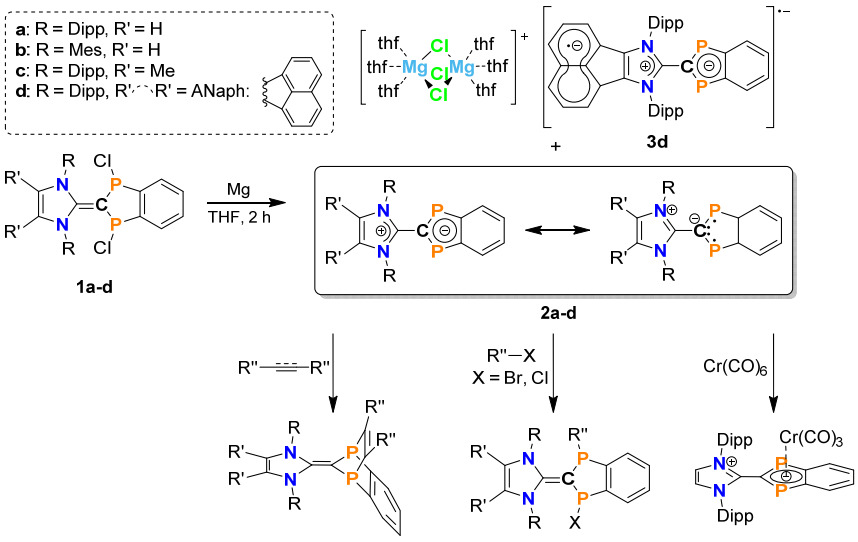
In previous work, our group synthesized five-membered, resonance-stabilized bi- and tetraradicals in the form of azadiphosphaindane-1,3-diyls and 2,6-diaza-1,3,5,7-tetraphospha-s-hydrindacene-1,3,5,6-tetrayls.[1,2] More recently, linking imidazole-based *N*-heterocyclic olefins (NHOs) with terminal CH_2 donor groups to a bisphosphane fragment yielded open-shell singlet diphosphaindenylide systems – a new class of *P*-heterocycles that can be interpreted both as phosphorus-centered diradicaloids and as zwitterions with a permanent, overall charge separation between the *N*- and *P*-heterocyclic ring systems.



The reduction of the dichlorodiphosphaheteroindanes **1a-d** with magnesium yields **2a-d**. Notably, in the case of derivative **d**, a partial overreduction occurs, leading to the formation of a radical anion. CASSCF calculations of the four derivatives **2a-d** suggest a low biradical character of 14%. Nevertheless, **2a-d** exhibit open-shell singlet biradical-type reactivity towards molecules bearing triple and double bonds upon heating. Furthermore, the radical reactivity of **2a–d**, as demonstrated by haloalkane activation, and their coordination properties as heteroindenylid ligands are currently being investigated.

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Synergistic P···Mg Reactivity in Phosphine-Stabilized [Mg-H] species

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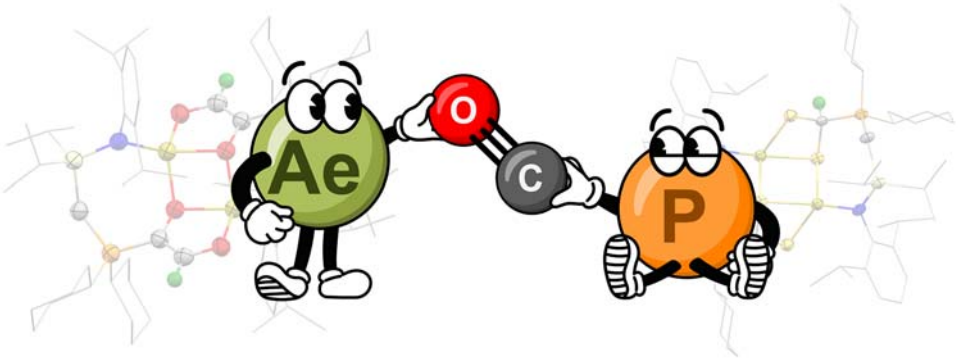
Phosphines are versatile ligands in transition metal (TM) complexes, driven by their tuneable donor properties, easy access, and low cost. Due to the soft nature of P-donors, they are typically not suited to *s*-block coordination chemistry, with the majority of examples utilising chelation-driven binding. In this light, the Hadlington group has focused on utilising chelating phosphine arms in reactive tetrylene and triylene TM complexes.[1,2] In the effort to move towards more sustainable and environmentally benign chemistry, we aimed to expand this approach to alkaline-earth (Ae) metal systems.

Ae metals, *e.g.* like Mg and Ca, have been employed extensively in driving chemical transformations and catalysis over the past two decades, especially in the heterofunctionalisation of alkenes and alkynes.[3,4] Building on these advances, we took these two concepts towards multi-component coupling reactions, through targeted design of new P-functionalised Ae metal systems.

In this contribution we describe the reactivity of bespoke P-stabilized [Mg-H] complexes towards the carbon oxides and their congeners, including carbon monoxide. In all cases non-innocent behaviour of the chelating phosphine arm is observed, *e.g.* allowing for cooperative P···Mg CO-Coupling.[5] Efforts towards making this catalytic are also described.



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Computational exploration of the Selective Scrambling of Phenyl-Stannanes: Main Group Catalysis with Aromatic Phosphorus Heterocycles

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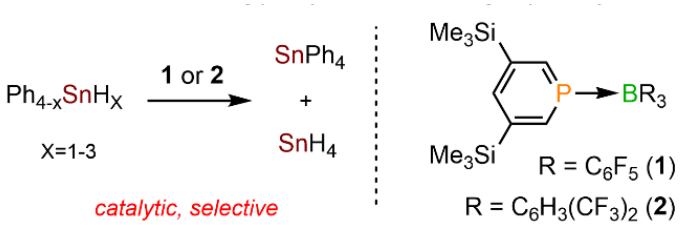
Metal-free catalysis has emerged as a sustainable alternative to traditional transition-metal-mediated processes. Herein, we report a novel catalytic paradigm using aromatic phosphorus heterocycles to mediate mutual hydride–phenyl substituent transfers between tin centers. Utilizing a labile phosphinine–borane adduct as the catalyst, phenylstannanes (Ph_nSnH_{4-n}) can be selectively and quantitatively converted into $SnPh_4$, H_2, and elemental Sn via a transient SnH_4 intermediate.



Comprehensive experimental and computational studies (at the ωB97XD /def2-TZVP and LNO-CCSD(T) levels) reveal a mechanism comprising three interconnected catalytic cycles. This process is initiated by the intrinsically weak and dynamic P→B interaction, where the borane acts as a hydride abstractor while the phosphinine facilitates stannyl transfer—a step reminiscent of electrophilic aromatic substitution. Unlike classical phosphane-based Lewis pairs which are either inert or prone to decomposition, the phosphinine–borane adduct enables controlled substituent redistribution by balancing the energetics of the reaction network. This work establishes a new frontier in main-group catalysis, highlighting the unique reactivity of low-coordinate phosphorus species in unlocking unconventional transformation modes for organometallic reagents.

Acknowledgements

The authors would like to thanks for the support of NKFIH (grant K-147095), the Stipendium Hungaricum program, the China Scholarship Council, and KIFÜ for resources at Komondor.

Synthesis of dipyrromethene-stabilized group 14-dihydrogenpnictogenides

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The formation and stabilization of bonds between heavier main-group elements have attracted considerable interest in recent years. For instance, earlier works of our group demonstrated the formation of heavy group 14-15 bonds, using a series of (^{Dipp}NacNac)E_{14} halide compounds and metal-bistrimethylsilyl pnictogenides, thus filling the gap left in this field of compounds featuring covalent single bonds. Employing this ligand system, even some terminal metal phosphanes and -arsanes of germanium as well as selected 3d transition metals have been synthesized. These studies demonstrate the indispensable role of a sterically encumbering ligand system in the stabilization of otherwise elusive bonding motifs. The use of the even bulkier, mesityl substituted 2,2'-dipyrromethene-ligand (^{Mes}DPM), which is typically known as an optically active ligand in biosynthesis, enabled us to obtain the desired dihydrogen pnictogenides of the heavier group 14 congeners. This advance paves the way for systematic reactivity studies regarding the construction of main-group multiple bonds and strained heterocyclic frameworks in the future.[1-3]

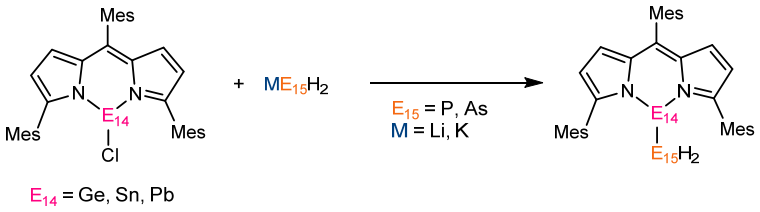

Figure 1: General synthetic approach to the targeted compounds of the type (^{Mes}DPM)$E_{14}E_{15}H_2$.

Applying the synthetic route shown in figure 1, compounds of the type (^{Mes}DPM)$E_{14}E_{15}H_2$ could be isolated for E_{14} = Ge, Sn, Pb and E_{15} = P, As. All compounds were characterized via x-ray structure analysis. Additionally, NMR and infrared spectroscopy as well as elemental analysis and mass spectrometry was performed.

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Conversion of Ubiquitous Phosphate Sources to Thiophosphates ($OP(SAr)_3$, Ar = aryl) and Subsequent Functionalization Reactions

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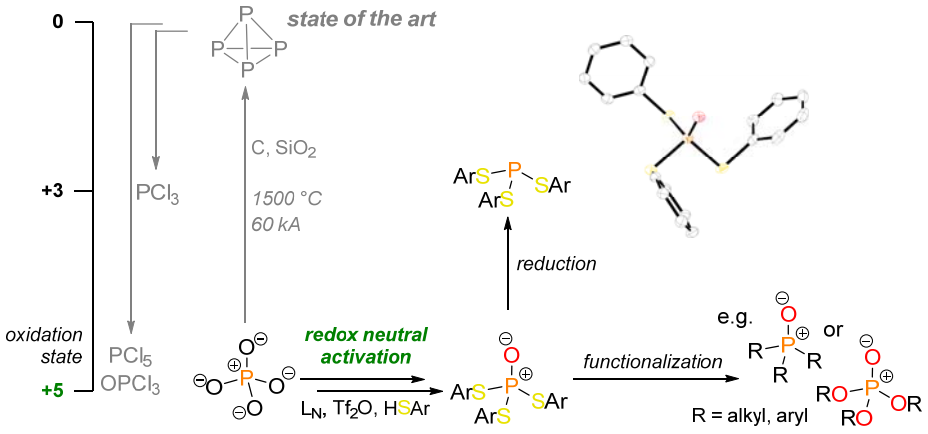
Phosphorus and its compounds are cornerstones of biological life and have extensive applications in industry, academia and everyday products. However, a common feature of synthetic strategies for the formation of value-added phosphorus chemicals is their dependence on intermediates downstream of white phosphorus (P_4), which poses significant drawbacks.

By adopting the ambitious idea of avoiding P_4 altogether,[1,2] recent work – including contributions from our group – has elucidated pathways that directly convert abundant phosphate sources into value-added organophosphorus compounds.[3] In this regard, we developed the redox-neutral conversion of ubiquitous P(V) sources into the versatile PO_2^+ phosphorylation reagent $(L_N)_2PO_2[OTf]$ (L_N = pyridine, DMAP), from which a variety of phosphorus compounds of type $R_2P(O)OH$ are accessible through P–O, P–N and P–C bond forming reactions.[3]



By replacing the substituent L_N with thiophenolates, $(ArS)^-$ (Ar = aryl), the removal of a third oxygen atom from phosphate (PO_4^{3-}) becomes feasible. The leaving-group ability of the thiophenolate substituents in thiophosphates ($OP(SAr)_3$) is showcased in subsequent functionalization reactions with alcohols and Grignard reagents, as well as their reduction to the P(III) derivative $P(SAr)_3$.

Acknowledgements: We thank the TU Dresden and the German Research Foundation (DFG, Reinhart Koselleck Grant WE 4621/10-1) for financial support.

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Pnictogen dihydrides of the alkaline earth metals Mg, Ca, and Sr

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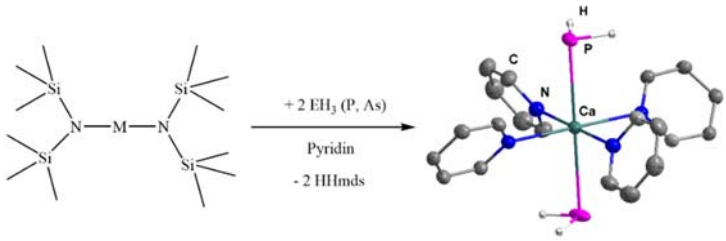
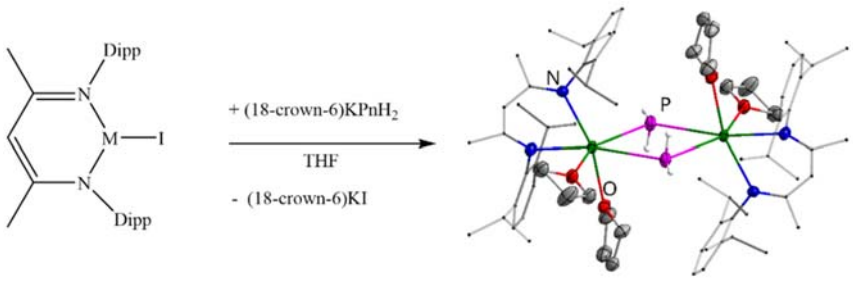
Compounds with PnH_2 (Pn = P-As) provides access to a wide range of chemicals ranging from primary silyl pnictogenides to transition metal pnictides.[1,2] The commonly used starting compounds are almost exclusively alkali metal dihydrogenpnictogenides while the alkaline earth metal analogues have hardly been investigated at all.

Here we show two different synthetic routes to obtain pniktogendihydrides of the earth alkaline metals. The first synthesis route is based on the production of alkali metal compounds by reacting $M(hmds)_2$ (M = Mg, Ca; hmds = hexamethyldisilazanide) with PhH_3 (Pn = P, As) in pyridine to obtain compounds of the form $[M(Py)_4(PnH_2)_2]$.[3] Furthermore, it is possible to obtain compounds of the form $[^{Dipp}NacNacSrPnH_2]_2$ ($^{Dipp}NacNac$ = HC{C-(Me)N(Dipp)}$_2$; Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$)) via a salt metathesis reaction with $^{Dipp}NacNacSrI$ and (18-crown-6)$KPnH_2$.



Scheme 1: Synthesis of $[M(Py)_4(PnH_2)_2]$ (M = Mg, Ca, Pn = P, As) via deprotonation of PnH_3 with $M(hmds)_2$.



Scheme 2: Synthesis of $[DipNacNacMPnH_2]_2$ (Pn = P, As) via a salt metathesis reaction.

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Structural and Stereochemical Features of Phenol-Pyrazole Substituted Cyclic Phosphazenes

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The chemical formula for cyclotriphosphazene, a cyclic inorganic molecule, is N_3P_3. This special molecule is made up of a six-membered ring with two chlorine atoms connected to alternating nitrogen and phosphorus atoms.[1] The pentavalent and tetra-coordinated phosphorus atoms in cyclophosphazene derivatives may also be stereocenters, similar to tetrahedral carbon atoms.[2]

In this study, the reactions between 2-(1*H*-Pyrazol-3-yl)phenol, a pyrazole reagent that is an asymmetric and tautomeric molecule, and cyclotriphosphazene were carefully examined. As a result of these reactions, products containing spiro bonded (**3**, **5**, and **8a-b**) and both *N*-substituted and spiro bonded (**4a-b**, **6**, and **7**) were obtained.[3] The isolated compounds (**3-8**) were characterized by elemental analysis, FT-IR, MALDI-TOF mass spectrometry, 1D (^{1}H, ^{31}P) and 2D (^{13}C APT-Attached Proton Test, HETCOR-Heteronuclear correlation) NMR spectroscopies. The molecular and crystal structures of **3** and **5-7** were illuminated by single crystal X-Ray crystallography for the first time. At the same time, the chiral properties of all obtained compounds were evaluated, considering stereochemical terms.[3]

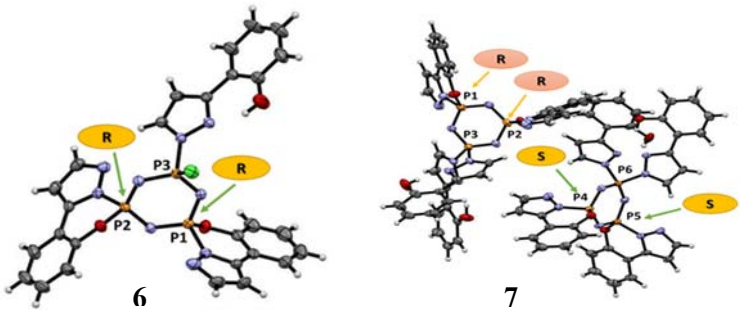

Figure: The structures of compounds **6** and **7**, which contain two tautomers of pyrazole scaffold, determined by single-crystal X-Ray diffraction technique.

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Reactivity of Transferable NHC-Stabilized Phosphaborenes Towards Aliphatic and Aromatic Acid Chlorides

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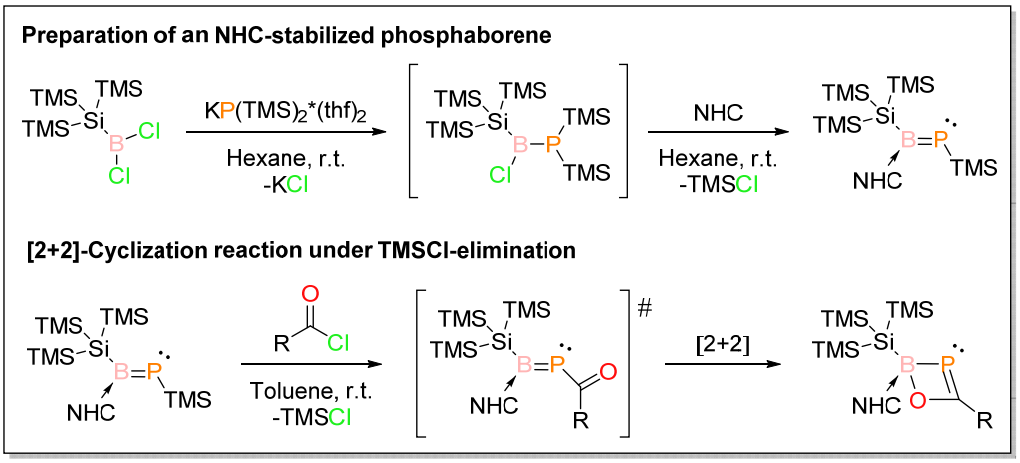
The synthesis and isolation of multiply bonded compounds containing heavy main group 13 and 15 elements has drawn high attention over the past years.[1] Although the chemistry and the bonding situation of carbon-based compounds have been thoroughly investigated,[2] this is not the case for the isoelectronic heavier group 13/15 compounds. This is mainly a consequence of their low stability resulting from big atomic radii and reduced orbital overlap.[3] Nevertheless, the usage of sterically demanding substituents, as well as the incorporation of external Lewis acids and bases, have enabled the isolation of fascinating examples featuring exotic unsaturated units.[1, 4-6]

Phosphaborene species represent an excellent case where the intriguing reactivity can be use in metathesis reactions, cycloadditions and Wittig-type reactions.[7, 8] In 2022, our group reported the synthesis and isolation of a Lewis base-stabilized phosphaborene bearing a terminal P-TMS group.[8] The reactivity of this P=B-bonded compound was tested with various halide-containing substrates, leading under TMSCl-elimination to the desired products. In this work, we will give an overview of the reactivity of Lewis base-stabilized phosphaborenes, previously synthesized and reported by our working group, with a variety of alkyl and aryl substituted acid chlorides. The experimental results display a high tendency toward [2+2]-cycloaddition reaction, resulting to the formation of the corresponding central BPCO-four membered rings. We will discuss different outcomes of the reactions according to the nature of the substituents used.



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Structural Diversity in Amine-Alcohol Substituted Cyclotetraphosphazenes

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Cyclophosphazenes constitute an important class of inorganic heterocyclic compounds owing to their high solubility in organic solvents, chemically robust skeletal frameworks, and the presence of multiple reactive P-Cl bonds[1]. Among this family, hexachlorocyclotriphosphazene (trimer) and octachlorocyclotetraphosphazene (tetramer) are the most widely studied members[1]. In particular, the tetramer offers an increased number of P-Cl bonds available for nucleophilic substitution, which significantly enhances structural diversity, especially in reactions involving difunctional nucleophiles[2]. However, compared to the trimer, the reactions of the tetramer have been less investigated due to challenges in isolating products and determining their structures.

In this work, the nucleophilic substitution reactions of cyclotetraphosphazene with 3-amino-1-propanol were systematically investigated, demonstrating that the nature of the base governs product distribution. Triethylamine afforded single-bridged, mono-spiro, and *N*-substituted open-chain derivatives, whereas 3-amino-1-propanol selectively yielded single-bridged and mono-spiro products. In contrast, sodium hydride favored the formation of single-bridged and 1,3-mono-ansa derivatives. All products were characterized by NMR (^{1}H, ^{13}C and ^{31}P) spectroscopy, MALDI-TOF mass, and elemental analysis, and the crystal structure of the single-bridged derivative was determined for the first time by single-crystal X-ray diffraction (Figure 1).

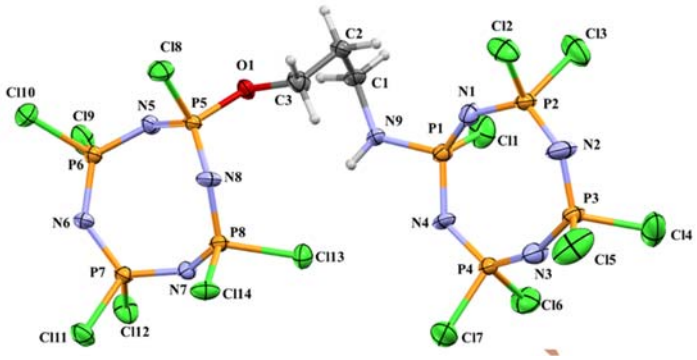

Figure 1. The crystal structure of single-bridged cyclotetraphosphazene compound.

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Phosphine based hard-soft ligands for RE/TM synergy

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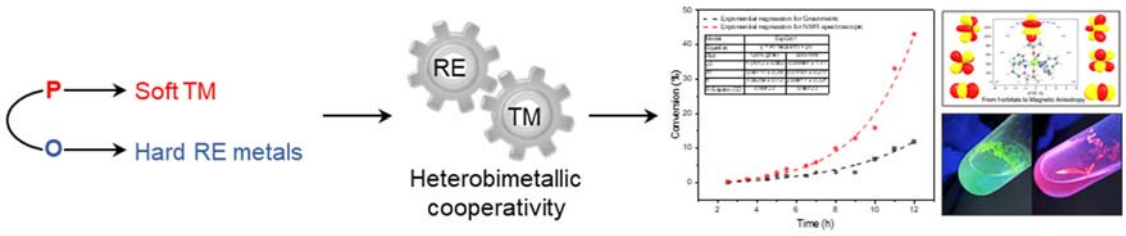
Phosphine ligands play a central role in homogeneous catalysis due to their soft donor character and tunable electronic properties.[1,2] Introducing additional hard donor atoms into phosphine-based frameworks enables the synthesis of heterobimetallic catalysts with cooperative reactivity. Herein, we report ambidentate phosphorus ligands bearing soft phosphine and hard oxygen donors for the controlled assembly of heterobimetallic rare earth (RE)/transition metal (TM) complexes.

The ligand tetraphenyldiphosphine monoxide ($Ph_2PP(O)Ph_2$, PPO) demonstrates effective hard- soft donor differentiation, selectively coordinating soft TMs (Cu(I), Au(I), Mo(0)) at P(II) and oxophilic RE metals (Y(III), Sm(III), Dy(III), Er(III), Lu(III)) at the O site. However, the direct synthesis is impeded by the preferential formation of TM complex and the underlying phosphorotropic tautomerisation.[3] Mo(0) stabilises the PPO tautomer through P coordination, allowing subsequent RE(III) coordination at O leading to heterobimetallic architectures.[4]

Building on this concept, we introduce other P,O-based multidentate ligands, such as phenoxydiphenylphosphane (PPh_2OPh) and others, which retain distinct soft P and hard O donor sites within a compact scaffold. Site-selective metal binding is anticipated to afford tripodal metallaligand-type RE/TM heterobimetallic complexes.



These systems integrate complementary catalytic functions,[5] combining TM mediated bond activation with RE based Lewis acidic substrate activation, for cooperative catalysis.

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Synthesis and characterization of novel cationic Bi(I) complexes

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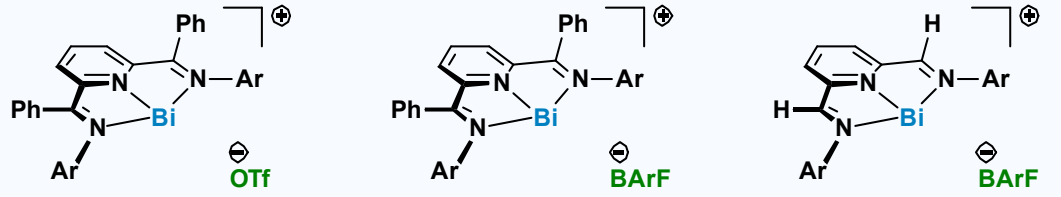
Neutral Bi(I) complexes have received significant focus over the past decade, on account of their unique electronic structure and their applicability as photo-active catalysts.[1,2] Although a handful of cationic Bi(I) complexes have been reported,[3-5] the investigation of such complexes in catalysis has not yet been reported. Here, we present a simplified and improved synthetic route to yield a series of cationic Bi(I) complexes (following previous work from our group)[6] and investigate their applicability as catalysts. The new complexes were isolated and fully characterized, revealing bathochromic shifts when compared to their neutral bismuthinidene analogues in their absorption spectra. Catalytic reactions with these complexes were also successfully performed, though the nature of the catalytically active species and role of the Bi(I) cation remains under investigation.

This Work: Synthesis and characterization of novel cationic Bi(I) complexes



[NMR] [XRD] [UV-Vis] [CV] [initial reactivity] [catalytic investigations]

Acknowledgements

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Synthesis, Characterization, and reactivity of novel bismacyclic azides

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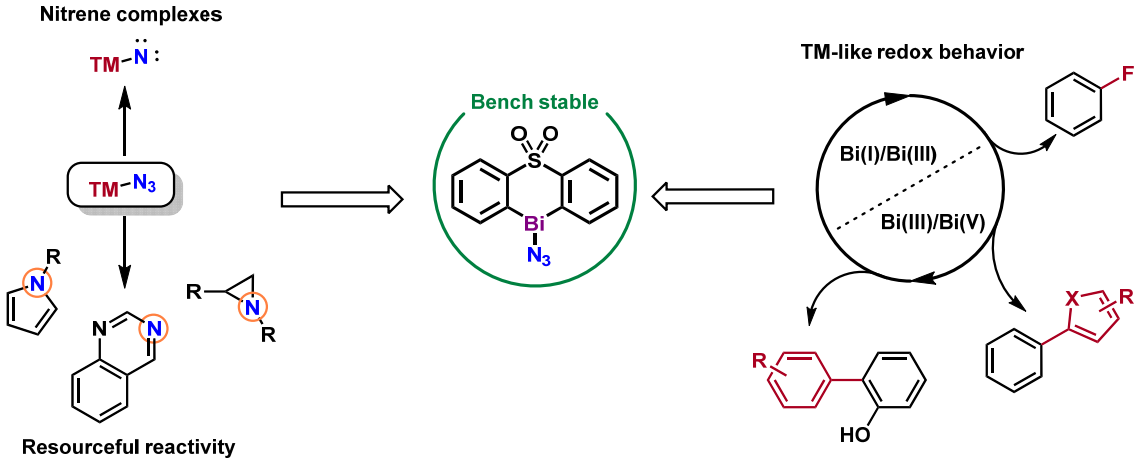
Azido compounds are generally regarded as synthetically useful thanks to their ability to undergo a number of transformations such as the Staudinger reaction, amidation reactions or nitrogen release to form the corresponding intermediate nitrene derivative.[1,2] While transition metal azides have been extensively investigated over the past decades, considerably less attention has been paid their main group element analogs. Among main group elements, bismuth emerges for its similarity with transition metals from a redox perspective, being able to shuttle between its I/III/V oxidation states.[3,4] Despite the potential, bismuth azides remain scarcely understood with very little known about their reactivity. Here we report the synthesis, charachterization and reactivity of a novel class of bismuth azides which showcase remarkable bench stability thanks to the Suzuki-type ligand motif.



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The Novel *tert*-Butyl Substituted Biphosphinine: Synthesis, Coordination Chemistry and Electrochemical investigations

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2,2'-Biphosphinines, the phosphorus analogues of bipyridines, are a unique class of low-coordinate, bidentate phosphorus ligands with strong π-acceptor and weak σ-donor properties.[1] First reported by MATHEY in 1991,[2] we have now synthesized the novel *tert*-butyl-biphosphinine **1** by a modified literature procedure, which allows access to this compound in a rather facile manner.[3] The increased steric bulk around the phosphorus centres further modulates both electronic and steric properties, which is an important aspect for applications.

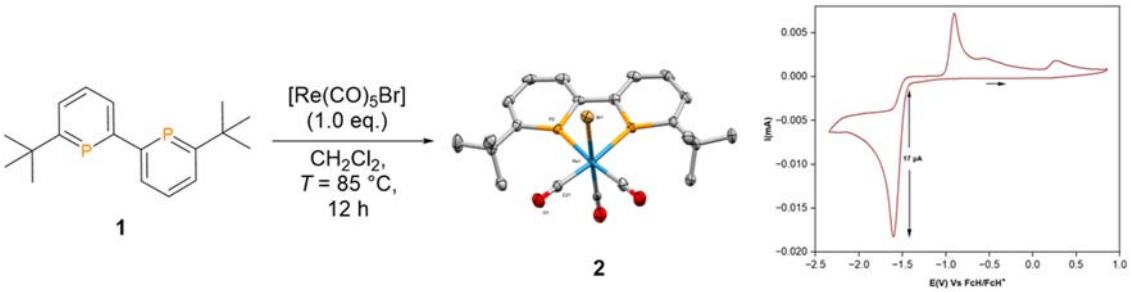

Figure 1: Synthesis of a Re(I) complex of **1** and CV of **2**

Currently, we are focusing on investigating the electrocatalytic activity of the complex **2** towards CO_2 reduction by cyclic voltammetry. Under argon, a quasi-reversible reduction is observed at −1.60V vs FcH/FcH^+ in THF. Upon purging the solution with CO_2, the cathodic current at this wave increases by 17µA, while the peak potential remains essentially unchanged. Such current enhancement in the presence of CO_2 is a characteristic for a molecular electrocatalysts for CO_2 reduction and indicates that **2** is competent for CO_2 activation under these conditions.

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Synthesis of Transition Metal Complexes of the 'Parent' Phosphinine

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Although the 'parent' phosphinine, PC_5H_5 (**1**), was reported as early as 1971,[1,2] synthetic procedures towards this molecule are challenging, involving multiple steps and resulting in low yields.[3,4] As a result, the reactivity of **1** has only been explored to a limited extent.[5–9]

Here, we show that **1** can be synthesized using readily accessible reagents, the pyrylium salt $[OC_5H_5]BF_4$ and $P(SiMe_3)_3$. The novel synthesis of **1** has enabled us to explore its transition metal coordination chemistry. We will present the synthesis and characterization of cobalt(–I) and iron(+I) phosphinine complexes **2** and **3**, in which **1** adopts terminal and bridging coordination modes, respectively. The molecular structures of **2** and **3**, along with their spectroscopic properties, will be discussed.

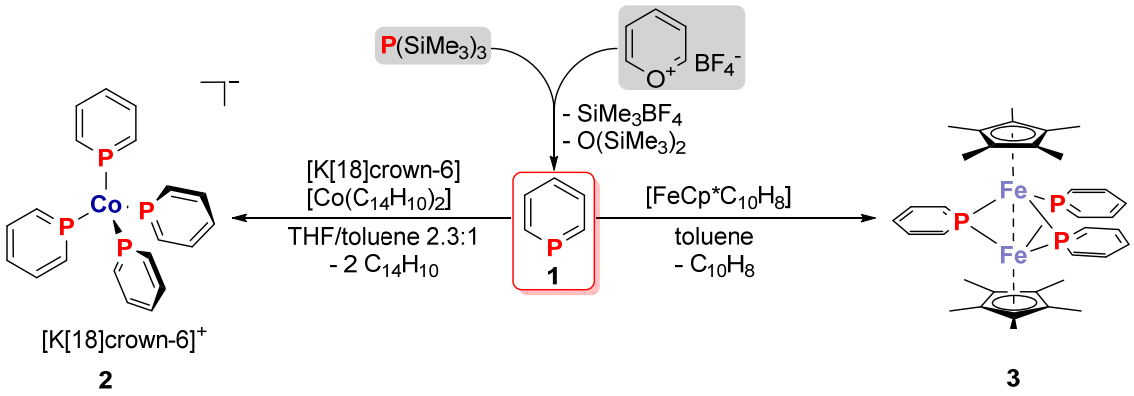

Figure 4. *Synthesis of the 'parent' phosphinine **1** and its cobalt and iron complexes **2** and **3**.*

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Carborane-Fused heterocycles, phosphorus in the focus

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In recent years, the possible conjugation between 2D and 3D aromatic unit has been widely debated. Carboranes are well-known 3D aromatic compounds, and several studies suggest aromatic conjugation in case of carborane fused heterocycles.[1,2] Despite the promising preliminar results, recent studies concluded that such a conjugation does not exist in case of the investigated carborane fused systems.[3] While phosphorus heterocycles fused with carboranes are known, the aromatic character in carborane-fused phospholes was only recently suggested.[4] However, our computational study found that these compounds lack 2D aromaticity.[5] Instead, they should be viewed not as a fusion of an aromatic ring but as a fusion of an unsaturated ring with carboranes.

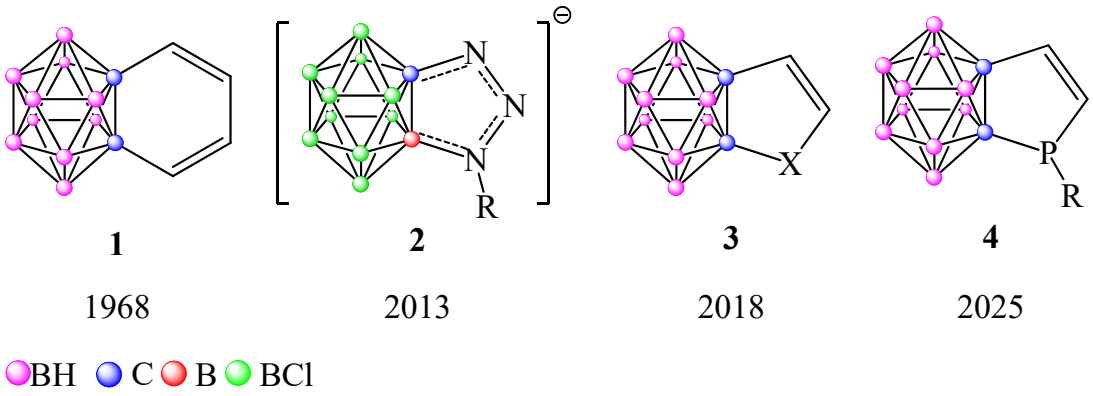

Figure: Structures of synthesised carborane-fused systems[1,2,4,6]

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Phosphanyl-Substituted Siloles: Synthesis and Structural Study

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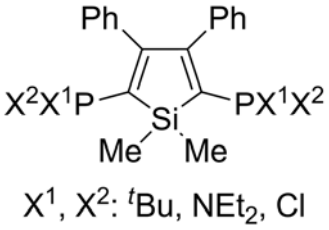
Siloles are five-membered silicon-containing heterocycles with unique electronic properties, including low-lying LUMO levels and favorable charge-transfer characteristics, making them valuable building blocks for optoelectronic materials.[1–2] Incorporation of phosphorus substituents into π-conjugated systems has been shown to modulate optical, electronic, and redox properties, but phosphanyl-substituted siloles remain largely unexplored.[3–4]

In this study, we investigated the synthesis and structural properties of six phosphanyl-substituted siloles with varying steric and electronic substituents at the phosphorus centers. The resulting products were characterized by $^{31}P\{^{1}H\}$ NMR spectroscopy, SC-XRD, and DFT calculations.

Structural analysis revealed that bulky substituents such as ^{t}Bu and NEt_2 reduce pyramidalization at the phosphorus centers, yielding more planar geometries. For the halogen-substituted derivatives, a measurable $^{35}Cl/^{37}Cl$ secondary isotope effect is observed in the $^{31}P\{^{1}H\}$ NMR spectra even at room temperature. DFT calculations confirmed minimal electronic interaction between the phosphanyl substituents and the silole π-system, consistent with the structural data.

These results demonstrate how steric and electronic factors influence the structure and NMR behavior of phosphanyl-substituted siloles, providing insights for the design of functional P-containing silole derivatives for optoelectronic applications.



Scheme: The investigated phosphanyl-substituted siloles.

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Phospohavinyl Formation Through Trapping of Phosphinidene

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The short-lived and elusive phosphinidene (M=P̈) is a highly reactive specie with large potential in phosphorus atom transfer (PAT) chemistry. In recent years, phosphinidene has been of interest due to its high reactivity for its possible way to be functionalized.[1, 2] The phosphinidene has been stabilized by both main-group chemistry[3] and as coordination with metalorganic complexes.[4]

In this work, we demonstrate a multistep synthesis to generate an iridium-phosphinidene for PAT chemistry. By photolytic activation of [(PCP)Ir(PCO)], the short-lived iridium supported triplet phosphinidene intermediate [Ir=P̈:] was generated and trapped using different phosphorus ylides. This resulted in a formation of a room temperature stable phosphavinyl, complex [(PCP)Ir(P=CH_2)]. Notably the structure of the complex was elucidated by single-crystal X-ray diffraction, revealed that the [P=CH_2]$^-$ ligand sits in a plane perpendicular to the square planar pincer complex. Due to rotational restriction about the P=C double bond, the hydrogens on the [P=CH_2]$^-$ fragment are chemically inequivalent. This allowed the hydrogens to be identified by NOESY NMR, which showed which of the hydrogen is in closer proximity to the iridium ^{t}Bu group. Variable temperature NMR studies of the complex indicate an exchange of the hydrogen on [P=CH_2]$^-$ fragment and several scenarios of the exchange were considered in conjunction with DFT studies. Further reactivity of phosphavinyl showed an oxidation with an azide.

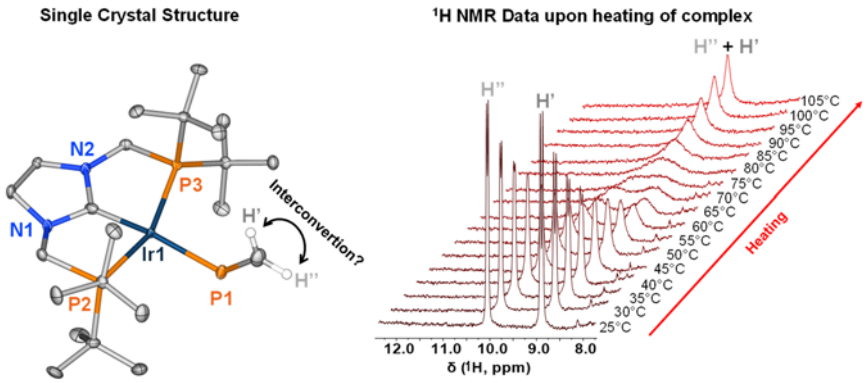

Figure 1, Crystallographic structure of iridium phosphavinyl and temperature variation ^{1}H NMR with the interconvertion of phosphavinyl hydrogens.

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Disbiradicals with flexible and rigid linkers

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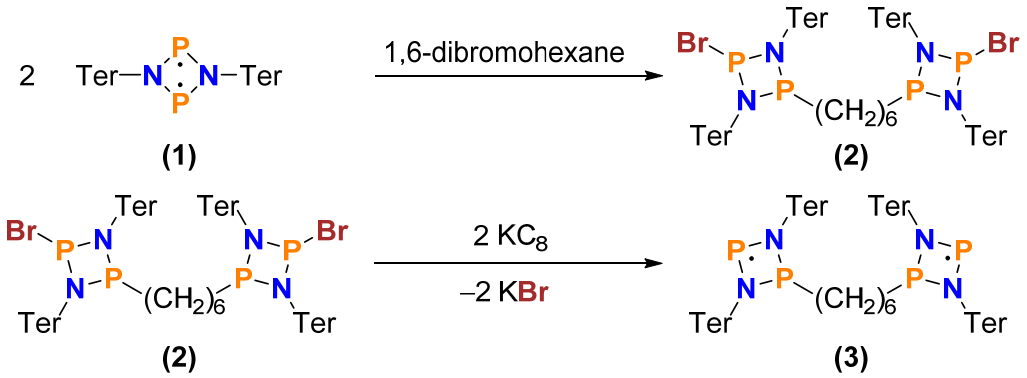
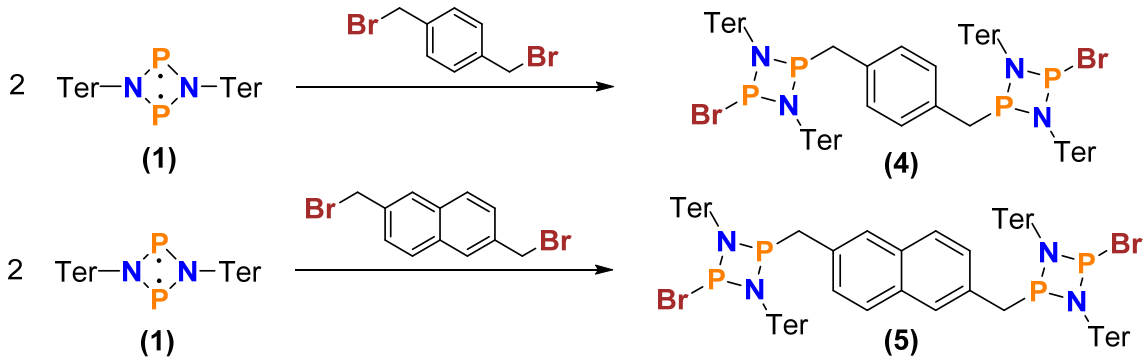
Biradicaloids may display both closed-shell as well as radical reactivity. For example, bromoalkanes add to the biradicaloid [·P(μ-NTer)]$_2$ (**1**) in a radical reaction mechanism.[1] This facile addition was exploited for the reaction of **1** and 1,6-dibromohexane, yielding the addition product **2**, a precursor for the phosphorus-centered disbiradical **3** which was obtained by reduction with KC_8.



Scheme 1: Synthesis of the addition product **2** with further reduction to the disbiradical **3**.[2]

Despite the large distance between the two radical centers in the solid state (~11 Å), the EPR spectrum of **3** shows significant coupling between the unpaired electrons, due to molecular dynamics in solution.[2] To tune the electronic interaction, new alkyl bromide adduct derivatives **(4**, **5)** with more rigid organic linkers were synthesized and characterized.



Scheme 2: Synthesis of the alkylbromide adducts **(4)** and **(5)** with rigid organic linkers.

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Redox-Neutral Phosphate-to-Phosphinate Conversion Enables Vinyl-Functional Building Blocks for Phosphorus-Containing Polymer Networks

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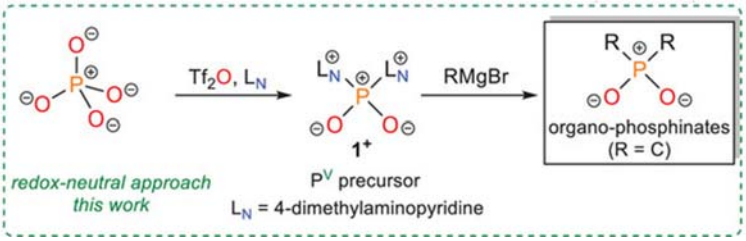
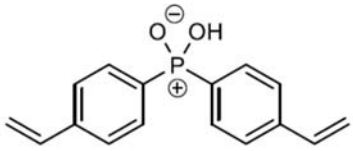
Organophosphinic acids and derivatives, $R_2P(O)(OH)$, are versatile compounds in coordination and materials chemistry and are attractive as functional motifs in ligand design and polymer architectures.[1] Yet, many established synthetic routes to organophosphorus building blocks still rely on white phosphorus (P_4) and downstream chlorination chemistry,[2] despite the well-recognized safety and sustainability drawbacks associated with P_4 production.[3]





Building on redox-neutral phosphate activation with trifluoromethanesulfonic anhydride (Tf_2O) and Lewis bases, we employ an electrophilic PO_2^+ reagent platform in which the leaving group can be tuned to expand reactivity.[4] In particular, substitution of pyridine by 4-dimethylaminopyridine enables reactions with Grignard reagents, providing access to a series of diaryl- and dialkynylphosphinate derivatives directly from ubiquitous P(V) sources.[5] To connect this chemistry to polymer synthesis, a vinyl-functional diarylphosphinic-acid derivative was evaluated as a monomer candidate and subjected to radical curing, affording phosphorus-containing polymer solids and cast films. Spectroscopic monitoring is consistent with monomer-to-polymer conversion; detailed structure assignment and property evaluation are ongoing. Overall, this collaboration between TU Dresden and UM6P links P_4-free P(V) functionalization chemistry with access to phosphorus-containing polymer networks.

Acknowledgment

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Catalytic C–H Amination Enabled by Photoactive Iminobismuthane

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Direct C–H functionalization has received significant attention and achieved widespread application for synthesizing diverse and valuable molecules. For this reason, direct C–H amination strategies have been extensively developed over the years for constructing amine motifs from simple hydrocarbon frameworks.[1] Such transformations are well developed using transition-metal nitrenoid complexes (e.g. TM–NR), which enable efficient and selective C–H bond amination (Figure 1, left). In contrast, despite the numerous reports on nitrenoid complexes of main-group elements, their application in catalytic C–H amination reactions have not yet been realized, largely due to the absence of accessible valence *d*-orbitals that shows reversible coordinative and oxidative reactivity.[2] Here we report how a photoactive iminobismuthane is capable of catalytic C–H amination reactions (Figure 1, right).[3] We realized that transient *N*-centered radicals could be accessible by light irradiation of iminoibismuthanes via charge transfer, showing HAT reactivity and subsequent C–N bond formation.

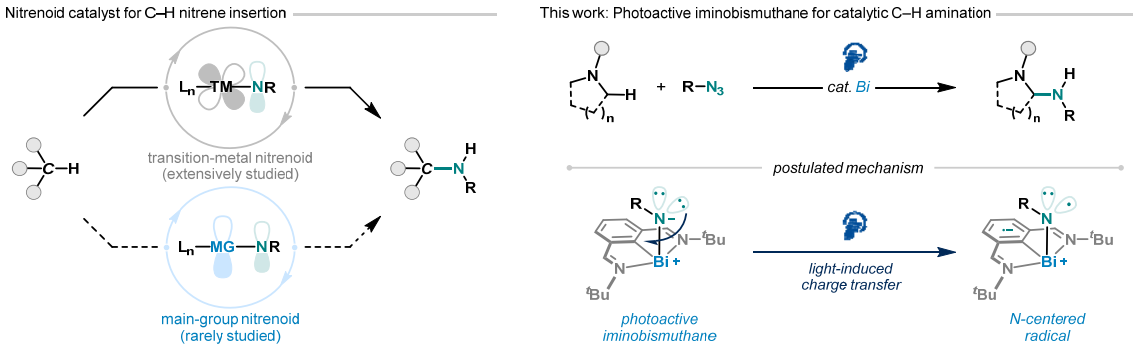

Figure 1. Schematic representation of C–H amination with nitrenoid intermediates.

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Hydrogen-Atom-Transfer Reactivity of a Half-Parent Phosphaborene

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Phosphaborenes, featuring a *bona fide* B=P double bond, have gained revival interest in the recent years.[1] This is due to a significant increase of stability provided donor acceptor interactions with strong Lewis bases, which allow the reduction of steric hindrance and hence reactivity exploration. Intriguingly, the minimal phosphaborene (H–P═B–H), analogue of acetylene, remains elusive and synthetically challenging. Unlike iminoborane with B=NH moiety,[2] phosphaborenes with either B=PH or P=BH entities are hitherto unknown. In this contribution, we show the first isolation of phosphaborenes **3**[1d] and **4** with a PH-functional group, via cleavage of the respective P-TMS bonds using pyridinium chloride at room temperature. Interestingly, mechanistic studies reveal that P-H functionalization of **3** proceeds through a hydrogen-atom-transfer rather than a proton or hydride transfer. We describe the reactivity by reactions with diphenyl dichalogenides, glavinoxyl radical, lead bis[bis(trimethylsilyl)amide] and triphenylmethyl chloride at room temperature as outlined in the Figure below.

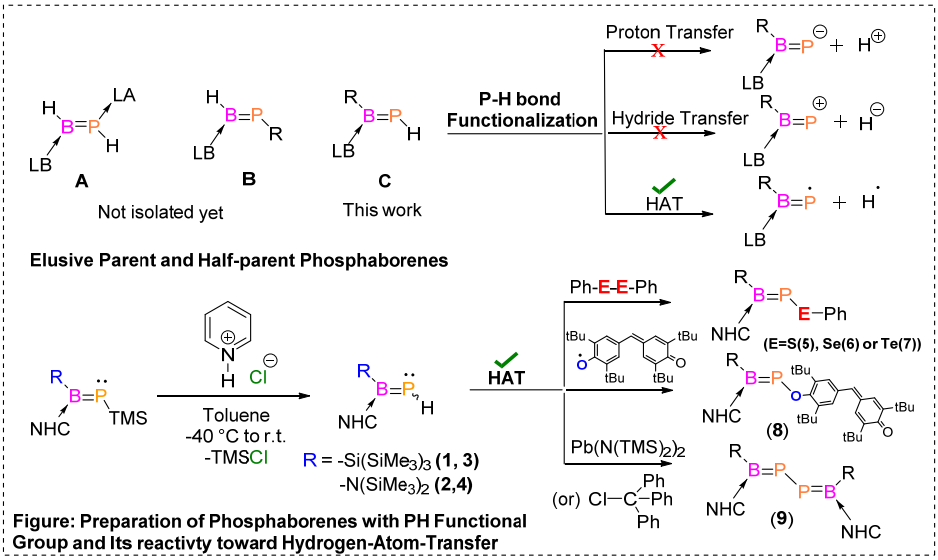

Figure: Preparation of Phosphaborenes with PH Functional Group and Its reactivty toward Hydrogen-Atom-Transfer

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Copper(I)-Mediated Functionalisation of White Phosphorus

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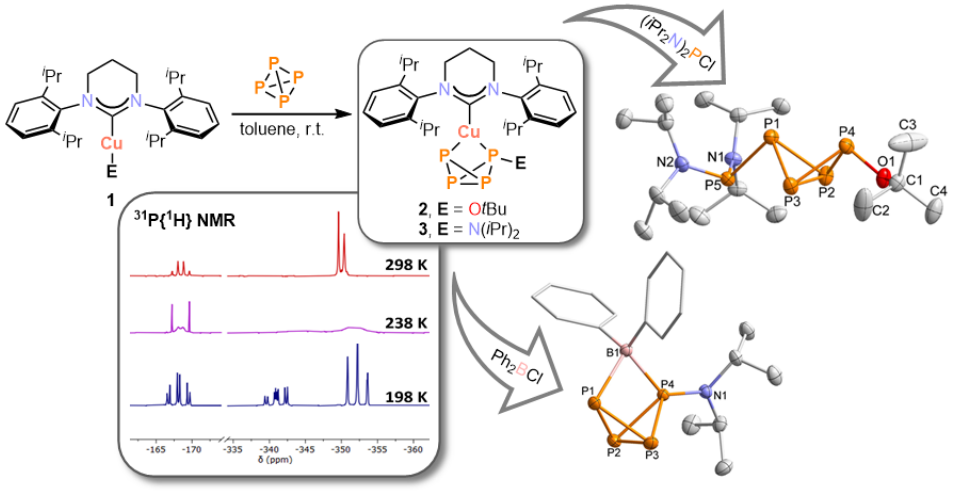
The activation of white phosphorus (P_4) by organometallic complexes has yielded a myriad of polyphosphorus motifs through aggregation and degradation of the phosphorus tetrahedron.[1] While low-valent transition metal complexes can reduce P_4 to form stable polyphosphido ligands, their high stability often precludes further functionalisation to isolable organophosphorus compounds.[2]

Herein, we present the selective functionalisation of P_4 using *N*-heterocyclic carbene-supported copper(I) complexes **1**. Reactions of P_4 with (6Dipp)CuO^{t}Bu and (6Dipp)CuN(^{i}Pr)$_2$ result in the cleavage of a single P–P bond, affording functionalised polyphosphido complexes **2** and **3**. These complexes exhibit dynamic solution behaviour, consistent with the rotation of the polyphosphido ligand around the Cu–P bond. Subsequent treatment with electrophiles displaces the $[P_4E]^-$ ligands, forming asymmetrically substituted, metal-free organophosphorus butterfly compounds with unique substitution patterns. The reactivity of selected products is examined.



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A diazadiphospholenium cation featuring a reactive P=P bond

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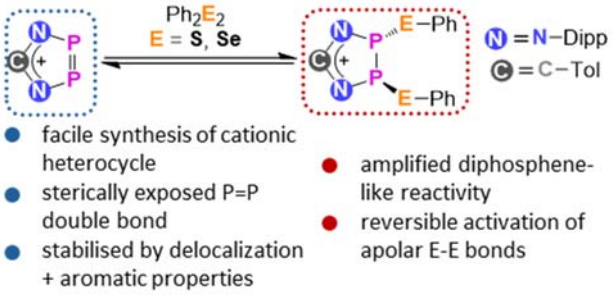
Multiply bonded species of heavier main-group elements are of considerable interest due to their distinctive bonding and high intrinsic reactivity, yet their controlled synthesis and selective reactivity remain challenging. We recently reported the high-yielding synthesis of a novel diazadiphospholenium cation featuring a sterically exposed, formal P=P double bond.[1] The cation is accessed via ligand abstraction from a neutral amidinato-substituted diphosphene or, alternatively, through two-electron oxidation of a P_4 butterfly precursor. Structural, spectroscopic, and computational analyses reveal a planar heterocycle with significant π-delocalisation and aromatic character, which provides sufficient thermodynamic stabilization despite the presence of a highly reactive P=P unit.

Compared to its neutral diphosphene precursor, the diazadiphospholenium cation displays markedly enhanced reactivity and selectivity. It undergoes rapid and selective [4+2] cycloaddition with 2,3-dimethylbutadiene, and subsequent reductive ligand elimination enables access to dihydro-diphosphinine derivates. Furthermore, the cation is capable of activating non-polar E–E bonds, as demonstrated by the selective scission of S–S and Se–Se bonds in diphenyldichalcogenides. Notably, the dichalcogenide activation is reversible, highlighting the role of restored aromatic delocalization as a driving force. These findings establish diazadiphospholenium cations as promising platforms for reversible main-group bond activation and lay the groundwork for future applications in catalytic element–element bond transformations.



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Cryogenic Matrix Isolation Spectroscopy of Phosphorus Radicals in *para*-H_2

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At low temperatures, *p*-H_2 is classified as quantum solid. If used as host-material for cryogenic matrix isolation spectroscopy, the build matrix is softer than usually used noble gases which reduces the so-called cage effect and allows for highly efficient photolysis. The increased spectral resolution for IR and UV/Vis spectroscopy under these conditions was first shown by Lee et al.[1] and is now expanded by matrix isolation ESR spectroscopy. Especially for phosphorus-centered radicals **2** and **4,** we were able to resolve the hyperfine coupling constants of the unpaired electron with the hydrogen atoms.[2,3]

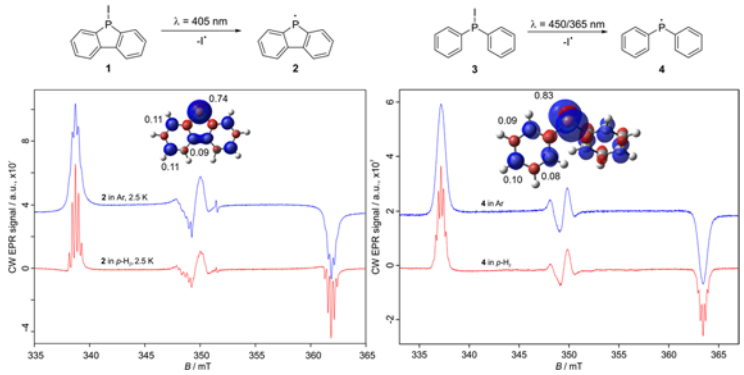

Figure 5. Comparison of matrix isolated ESR spectra of Diphenylphosphinyl radical **4** (right) and P-dibenzophospholyl radical **1** (left) in Ar and *p*-H_2. The calculated LUMO (π-radical) and the calculated spin densities at the UB3LYP/def2-TZVP level of theory are given.

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Addition reactions of phosphorus-centered radicals onto olefins: Computational insights

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Radicals are reactive species with unpaired electrons and play important roles in chemistry, biology and even in physics. In general, radicals are highly reactive and may find applications in industry, e.g., to initiate chemical reactions, including additions and polymerizations. The computational study presented here aims to explore the addition reactions of phosphorus-centered radicals to functionalized C=C double bonds, by systematically varying the substituent at both the radical and the olefin, allowing us to decipher how electronic effects influence reactivity and selectivity.

To begin with, we inspected the simplest P-centered radicals, including phosphinyl, phosphonyl, as well as thiophosphonyl types and studied their reactions with ethylene, as they may serve as fundamental models for understanding intrinsic radical behavior without additional stabilization. In order to capture a wider range of stabilization mechanisms and to identify potentially industrially relevant species, we expanded our study to various functional groups, including organic substituents relevant to industrial photoinitiators such as BAPO-type species, and cyclic substituents, and the effect of electron-donating, electron-withdrawing groups was revealed.

We demonstrate that radical stabilization energy (RSE), a descriptor that can be readily obtained from quantum chemical calculations, is directly linked to reactivity, and can serve as a practical predictor for the addition reactivity of phosphorus-centered radicals, especially for σ-type species commonly used in photopolymerization. After evaluating a wide range of phosphorus-centered radicals with ethylene, the study investigates how substituents on olefins affect radical addition reactions.

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Investigation of the ligand properties of a phosphonium-substituted Diphosphaindenylide (PPI)

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The cyclopentadienide anion, $[C_5H_5]^-$, is an ubiquitous ligand in organometallic chemistry with widespread applications in coordination chemistry and catalysis. Complexes of the indenyl anion $[C_9H_7]^-$, the benzannulated derivative of $[C_5H_5]^-$, often show distinctively different properties and reactivities (Figure 1).[1] This is attributed to the "indenyl effect" which promotes facile $\eta^5 \rightarrow \eta^3$ hapticity changes.[2] An additional conceivable way to further alter the electronic structure and thus the properties of indenyl complexes is the introduction of endo-cyclic heteroatoms into the five-membered ring of $[C_9H_7]^-$. However, although a number of such formal derivatives exist, their coordination chemistry is largely unexplored.

To close this apparent gap, we here introduce the ylide PPI (Figure 1). In the uncoordinated state, this zwitterionic heterocycle displays a nuanced biradical character. Coordinated to a metal, however, it acts as a good 6π-donor and π-acceptor. Here, we present an exploration of the resulting ligand properties on a series of group 6 and 8 metal complexes exhibiting multimetallic bonding, a group 7 manganese redox pair as well as group 9 systems, including both half-sandwich and sandwich rhodium complexes (Figure 1). Notably, the latter unambiguously demonstrate the indenyl effect within this heterocyclic framework.

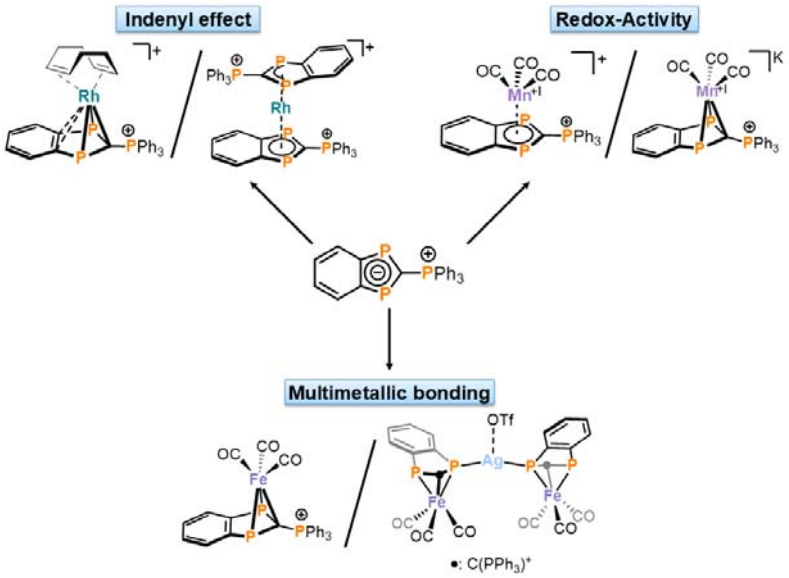

Figure 6: Coordination chemistry of PPI and its key properties: indenyl effect, redox-activity, and multimetallic bonding.

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