New frontiers: 1,4-diphosphinines and P-bridged bis(NHCs)

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This review describes synthetic concepts and breakthroughs in 1,4-diphosphinine and related P-bridged bis(NHCs) chemistry, covering the last four decades, starting from monocyclic 1,4-dihydro-1,4-diphosphinines in the early 80s to the most recent and promising achievements of tricyclic 1,4-dihydro-1,4-diphosphinines and tricyclic 1,4-diphosphinines. Theoretical aspects are presented for 1,4-dihydro- and 1,4-diphosphinines considering HOMO LUMO situations as well as the degree of aromaticity. Moreover, fundamental characteristics of analytical data of these compounds are highlighted with special focus on substituent effects, structural aspects and trends of electrophilicity. The two P-centers and the heterocyclic rings of 1,4-dihydro- and 1,4-diphosphinines constitute a broad platform for substitution, reduction/oxidation, alkylation, complexation and cycloaddition reactions, i.e., a comprehensive compilation of reactivity aspects is presented. Furthermore, very recent developments in the synthesis and reactivity of tricyclic PV/V- and PIII/III-bridged bis(imidazole-2-ylidenes) will be discussed together with new perspectives derived from an antiaromatic middle ring. In total, our intention is to show new frontiers, i.e., new synthetic paths, thus creating novel opportunities for potential applications in molecular and materials chemistry.

1. Introduction

The research of low-coordinate phosphorus compounds has opened up new avenues for a broad and systematic exploration towards diverse applications in main group element and coordination chemistry. With the synthesis of the first \(\sigma^2\lambda^3\)-phosphinine derivative 1 (Fig. 1) in 1966 by Märkl, a remarkable expansion of P–C heterocyclic chemistry has started. Several years later, the synthesis of the parent compound 2 by a tin-based route was achieved by Ashe III in 1971. Since then different synthetic approaches have been utilized towards synthesis of a large variety of differently substituted phosphinines, e.g., pyridyl-functionalized phosphinines, OH-functionalized phosphinines, NR\(_2\)-substituted phosphinines, thienyl-substituted phosphinines. P-Halogen substituted phosphinines (X = Cl, Br) are also reported to give V. One electron reduction and oxidation products have also been reported for phosphinines. Nucleophilic substitution using Grignard or organolithium reagents result in \(\lambda^4\)-phosphinines VI. Treating a \(\lambda^4\)-phosphinine with hexachloroethane and, subsequently, abstracting a chloride with GaCl\(_3\) results in phosphinium cations VII. Phosphinines also undergo [4 + 2] (Fig. 2) only if very strong, non-oxidizing acids with weakly coordinating anions are employed. A large number of oxidized \(\sigma^4\lambda^5\)-phosphinine derivatives has been reported using oxidation with H\(_2\)O\(_2\), Hg(OAc)\(_2\), diols and amines leading to the formation of II and III. Several phosphinines have been oxidized by heating their toluene solutions and elemental sulfur to give IV. P-Halogen substituted phosphinines (X = Cl, Br) are also reported to give V. One electron reduction and oxidation products have also been reported for phosphinines. Nucleophilic substitution using Grignard or organolithium reagents result in \(\lambda^4\)-phosphinines VI. Treating a \(\lambda^4\)-phosphinine with hexachloroethane and, subsequently, abstracting a chloride with GaCl\(_3\) results in phosphinium cations VII. Phosphinines also undergo [4 + 2]
cycloadditions with activated alkyne to yield phosphabarrelenes VIII. A very recent development of these phosphabarrelenes is selective photochemical rearrangement to result phosphasemibullvalenes IX. Others are extensively described in the literature including coordination chemistry. With significant advances made on $\lambda^3$- and $\lambda^5$-phosphinines, during the past decade, only few reviews are devoted to the chemistry of $\lambda^3$-phosphinines and their $\lambda^5$ derivatives with the emphasis on synthesis and reactivity, coordination chemistry and catalysis. Specific functionalization and derivatization of phosphinines has led to the development of polydentate derivatives with tailor-made properties for homogenous catalysis and, more recently, new optoelectronic devices.

While phosphinines are well known, diphosphinines have been much less studied and present some intriguing features. Of the three regioisomers reported in the literature, only a couple of examples of the synthesis of 1,2-diphosphinines is known to date. The discovery of X ($R = \text{CF}_3$) (Fig. 3) by Kobayashi and co-workers started the chemistry of 1,4-

Within the present mini-review, we aim to emphasize the most recent and promising achievements of 1,4-dihydro-1,4-diphosphinines and tricyclic 1,4-diphosphinines that are likely to lead to interesting and rewarding applications in a near future. Furthermore, a comprehensive up-to-date account of important theoretical aspects of bonding, physical properties such as NMR, UV/vis, solid state X-ray diffraction data and electrochemical data. Synthesis and reactivity of the tricyclic 1,4-diphosphinines and derived tricyclic P$^{V/\text{I}}$ and P$^{V/\text{II}}$ bridged bis(imidazole-2-ylidenes) will also be discussed along with new perspectives.

2. Synthesis

2.1 Synthesis of 1,4-dihydro-1,4-diphosphinines

2.1.1 Monocyclic 1,4-dihydro-1,4-diphosphinines. Only a couple of synthetic protocols are known for monocyclic 1,4-dihydro-1,4-diphosphinines to date. Märkl et al. reported the double hydrophosphinations of alkyldiethinylphosphane with alkylphosphanes to yield the corresponding monocyclic 1,4-dihydro-1,4-diphosphinines 8 (Scheme 1) as cis and trans isomers (55 : 45 ratio). cis-8 was obtained in pure form by recrystallization from acetonitrile, however it converted to the 82 : 18 mixture at 150 °C; chromatography and distillation resulted in a 77 : 23 mixture.

Reaction of thio- or dithiocarbonic acids with ethinylamino-phosphanes led to 1,4-dihydro-$1\lambda^3,4\lambda^5$-diphosphinines-

Fig. 3 Mono and tricyclic 1,4-diphosphinines and related 1,4-dihydro derivatives.
1,4-disulfides. Tri-\textit{n}-butylphosphane was used for a desulfurization and yellow crystals of 9 (Scheme 2) were isolated in quantitative yield, and NMR spectroscopy confirmed the formation of \textit{cis} and \textit{trans} isomers.

2.1.2 Benzo-fused tricyclic 1,4-diphosphinines. Benzo-fused tricyclic 1,4-diphosphinines were mainly synthesized by employing stepwise ring closing reactions with dichloro(organo)phosphanes. The first tricyclic benzene fused 1,4-dihydro-1,4-diphosphinine was synthesized by Davis and Mann in 1964 starting with \textit{o}-bromochlorobenzene and magnesium (Scheme 3). The Grignard reagent was then reacted with dichloro(ethyl)phosphane to result in the crystalline bridging phosphinine intermediate which, upon reaction with Li and subsequent addition of EtPCl\textsubscript{2}, yielded the 1,4-diethyl-1,4-diphosphinine 10; Akutsu later reported the structure and characterization of this compound.

The similar fluorinated analogue 11, reported by Cullen \textit{et al.} was formed by reacting 1,2-diiodotetrafluorobenzene with MeLi, followed by the addition of PhPCl\textsubscript{2} (Scheme 4).

Synthesis of 1,4-dihydro-1,4-diphosphinine 12 was accomplished by Uchiyama \textit{et al.} via reaction of 4,5-dibromo-\textit{o}-xylene with \textit{n}-butyllithium (\textit{n}BuLi) and PhPCl\textsubscript{2} (Scheme 5). Spontaneous oxidation of 12 and the isomerization products will be discussed in section 5.1.

2.1.3 Five-membered heterocycle-fused tricyclic 1,4-diphosphinines. Backbone lithiation strategy of the corresponding heterocycle, followed by reaction with dichloro(organo)phosphanes has been the commonly used protocol to synthesize heterocycle-fused 1,4-diphosphinines. The synthesis of tricyclic antiaromatic heterocycle 13 (Scheme 6) was reported by Schardt \textit{et al.} Treatment of lithium \textit{1,3-di-\textit{t}}-\textit{butylcyclopentadienide} with PCl\textsubscript{3} led to diphosphinine-related 13 which was obtained as a blue-black, fine crystalline solid.

Ren \textit{et al.} demonstrated the synthesis of ladder-type \textpi-conjugated 1,4-dihydro-1,4-diphosphinine, 14. Repeated lithiation followed by the addition of PhPCl\textsubscript{2} resulted in good yield (Scheme 7) and different solvent ratios of THF:Et\textsubscript{2}O resulted in \textit{cis} and \textit{trans}-isomers. A similar protocol was employed for the synthesis of 15 (Scheme 8).

A unique synthetic approach for the synthesis of heterocycle-fused 1,4-diphosphinine 16 (X = O, S) was reported by Fenske and co-workers via elimination of chlorotrimethylsilane. Dichloromaleic anhydride and thioanhydride was reacted with bis(trimethylsilyl)phenylphosphane (Scheme 9) to yield 16 (X = O) as intense yellow colour crystalline compound.

Introducing P-containing substituents to a heterocycle with P\textsuperscript{III} halides in basic media has enabled synthetic access to \textit{C}-phosphorylated five-membered heterocycles. Especially this idea has been implemented for the synthesis of hetero-condensed 1,4-diphosphinines. Using 2,5-dimethyl-N-aryl-pyr-
roles as the starting material, Ivonin and co-workers synthesized the first N-containing 1,4-diphosphinine 17 by reacting with PBr₃ in pyridine (Scheme 10).³⁹

Having two N-heterocycles in the tricyclic framework illustrate the potential synthetic diversity. Synthetic strategies developed for electrophilic substitution at the 4-position of the imidazole rings has led the way towards the synthesis of 1,4-dihydro-1,4-diphosphinines.⁴⁰ Reaction of 4-phosphorylated imidazoles with PCl₃ in pyridine gives rise to 1,4-dichloro-1,4-diphosphinine and subsequent addition of dimethylamine resulted in the tricyclic heterocyclic scaffold in 18 (Scheme 11).⁴¹ Oxidation reactions of 18 will be discussed in section 5.1.

In recent years, we have developed the chemistry of acyclic bis(imidazole-2-thione-4-yl)phosphanes, including their P-substitution chemistry.⁴²⁻⁴⁴ It has also been demonstrated that such acyclic imidazole-2-thiones can be converted into imidazole-2-ylidenes.⁴³,⁴⁴ Thus the chemistry of P and S centres of acyclic imidazole-2-thiones have been investigated thoroughly in these reports.⁴³⁻⁴⁵ Based on this background knowledge, Koner et al. reported the synthesis and reactivity of the first example of tricyclic imidazole-2-thione 19 (Scheme 12).⁴⁶ The phosphorylated imidazole-2-thione was reacted with lithium diisopropylamide (LDA) as the base to result in 19 obtained as mixture of cis/trans stereoisomers. Further utilization of this molecule was enabled by targeting the tricyclic P-Cl substituted derivative 20 with the reaction of 19 with PCl₃ in dichloromethane (DCM). 20 was formed as isomeric mixture in the form of yellow-orange solid.

Soon after, Koner et al. described a detailed investigation on the optimized synthetic protocols and broad reactivity study of P-functional tricyclic 1,4-dihydro-1,4-diphosphinines.³⁷ The findings reveal that backbone phosphanylation of imidazole-2-thione using ⁷⁷BuLi, and dichloro(dimethylamino)phosphane result in a mixture of acyclic derivative 21 and the tricyclic 1,4-dihydro-1,4-diphosphinine 22 (Scheme 13). When R = Et, 21 and 22 was obtained in a 3 : 1 ratio, and the isomers were separable by column chromatography. They further investigated the ring formation process to develop high-yield access to 1,4-dihydro-1,4-diphosphinine derivatives using 4-[amino(chloro)phosphanyl]imidazole-2-thione and backbone-lithiated 1,3-dimethylimidazole-2-thione (Scheme 14). The reaction was started at −78 °C and led to two stereoisomers of the 1,4-dihydro-1,4-diphosphinine 19 as determined by ³¹P NMR spectroscopy (at room temperature).

With this knowledge, the heterocycle-fused 1,4-diphosphinine research expanded to the chemistry of C-phosphanylated thiazol-2-thiones. High yield synthesis of 23 was reported by Begum et al. following the concept of deprotonation of the backbone C⁴-H of amino(chloro)phosphanyl thiazol-2-thione and intermolecular nucleophilic substitution reaction.⁴⁸ Reaction was optimized using the bases potassium hexamethyl-disilazide (KHMDS) and LDA (Scheme 15), and the isomeric mixtures of 23 were obtained in excellent yields with THF as the solvent and LDA as the base at ambient temperature. PCl₃-initiated P–N bond cleavage of 23 was achieved using PCl₃ in dichloromethane to yield 24 as a mixture of cis/trans isomers in a 1 : 1.1 ratio identified by ³¹P{¹H} NMR spectroscopy (Scheme 15).⁴⁹
The next step of this broader program targeted 1,3-dithiol-2-thione-based tricyclic 1,4-dihydro-1,4-diphosphinine system. Gese et al. reported the synthesis of 25 (Scheme 16), using the reaction of phosphanylated dithiol-2-thione with LDA.50 25 was observed in cis/trans isomer mixture in a ratio of 1:1.3. Subsequent reaction with PCl₃ in DCM resulted in the precipitation of dichloro derivative 26 as a lemon-yellow solid.

Avarvari et al. reported the synthesis of 1,4-dihydro-1,4-diphosphinine heterocycle being fused with two tetrathiafulvalene (TTF) moieties.51 Redox-active 1,4-dihydro-1,4-diphosphinine 27 was achieved in a one-pot procedure via bis-lithiation of o-dimethyltetraphiafulvalene (o-DMTTF) with LDA, followed by trapping of the resulting dianion with one equivalent of phenyl-dichlorophosphine (PhPCl₂) (Scheme 17). 27 is thus obtained as a cis/trans mixture, in which the cis isomer is largely pre-dominant with a cis:trans ratio of about 15:1, as determined by ³¹P NMR spectroscopy.

2.2 Synthesis of 1λ⁵,4λ⁵-diphosphinines

Synthesis of the first (high-coordinate) 1λ⁵,4λ⁵-diphosphinines was first attempted by Aguiar et al. in 1966 from the reaction of cis-vinylenebis(diphenylphosphine) with 1,2-dibromoethane (Scheme 18).52 However, attempts to produce the aromatic, conjugated diylide, 28, by proton abstraction using the bases butyllithium and phenyllithium have led to ring opening (Scheme 18). They further described the synthesis of 29 (60% yield) using phenylethynyl(diphenyl)phosphine and hydrogen bromide in glacial acetic acid at room temperature (Scheme 18).53

1λ⁵,4λ⁵-Diphosphinine, 30 was synthesized by Davies et al. using [4 + 2]-cyclization reaction between Z-1,2-bis(diphenylphosphino)ethene and dimethyl acetylenedicarboxylate (DMAD) (Scheme 19).54 Diphospha-substituted benzoquinone-type compound 31 was synthesized via the reaction of pivaloylethoxyacetylene and Ph₂PCl through a ketene intermediate – in a [3 + 3]-cyclization reaction (Scheme 20).55

2.3 Synthesis of σ³λ³-diphosphinines

The first thermally stable 1,4-diphosphinine was synthesized by Kobayashi and co-workers by addition of methanol to hexakis(trifluoromethyl)-1,4-diphosphabarrelene in the presence of rhodium trichloride as catalyst. After refluxing in n-hexane, in a stream of argon, 32 was formed but could only be obtained as n-hexane solution (Scheme 21).26
Many years later, stable tricyclic $\sigma^2\lambda^3$-diphosphinines were synthesized by our group via selective reduction of the respective tricyclic $P$-Cl-substituted derivatives (Scheme 22). Stereoisomeric mixtures of 30 were reacted with $^\text{t}$Bu$_3$P in DCM and the yellow-orange colour of the solution changed immediately to dark red, indicating the conversion.46 The same synthesis protocol was applied to 1,3-thiazole-2-thiones based 1,4-dichloro-1,4-diphosphinine, 24 as well as for 1,3-dithiol-2-thione-based tricyclic 1,4-chloro-1,4-diphosphinine 25. The respective $\sigma^2\lambda^3$-diphosphinine 34 formed in good yield; raw 35 was obtained as reddish-brown solid containing 35 as the major component.

3. Theoretical methods

3.1 1,4-Dihydro-1,4-diphosphinines

Quantum chemical calculations have been accompanying the syntheses of 1,4-dihydro- and 1,4-diphosphinines in order to get deeper insight into reaction pathways, structures and electronic properties. For 1,4-dihydro-1,4-diphosphinines the focus of theoretical investigations has largely been on the structures of different isomers (Fig. 5). Energy differences between cis and trans isomers were reported to be very small and below the limit of accuracy in all studied cases. This also holds true for the majority of interconversion barriers between the respective isomers, the exception being compound 26 ($\Delta G^\ddagger = 38.56 \text{ kcal mol}^{-1}$) which underlines the observation of two distinct isomers. Model calculations of the parent compound XIV showed the existence of two trans isomers (Fig. 5), the trans-boat and trans-chair structures being virtually identical in energy.50 Theoretical investigations on experimentally observed trans-boat isomers of 15 and 26 reveal broad similarities to XIV regarding relative stabilities and interconversion barriers of different isomers.

3.2 1,4-Diphosphinines

Two of the most striking characteristics of 1,4-diphosphinines with regard to predicting their reactivity are the HOMO/LUMO symmetries and energies, as well as the degree of aromaticity compared to benzene.

Very well comparable theoretical investigations have very recently been carried out for the tricyclic 1,4-diphosphinines 33–35. Being $\pi$-symmetric, both the HOMOs and LUMOs of the three compounds show similar geometries (Fig. 4). The HOMOs lie relatively high in energy and consist of the antibonding combination of the HOMOs of the respective five-membered rings, i.e., imidazole-2-thione, thiazole-2-thione or...
dithiole-2-thione, respectively. Consequently, they bear no contribution at the phosphorus atoms. The LUMOs are stabilized and have the π*-symmetry of the LUMO of parent 1,4-diphosphine H-X (R = H), \(^{16,50}\) while the large contribution at phosphorus makes the good acceptor abilities of these compounds easily understandable. A comparison of the HOMO/LUMO gaps which amount to 2.73 eV (Me-33), 2.86 eV (Me-34) and 3.01 eV (35) show a clear trend towards a larger gap with higher amount of sulfur in the annulated five-membered rings. Moreover both the HOMO and LUMO of 35 possess the lowest energy compared to Me-33 and Me-34 implying a comparatively more facile reduction. The lone pairs at phosphorus are very low in energy in all three cases, being represented by the HOMO–6 (Me-33, \(\varepsilon = -8.40\) eV), HOMO–7 (Me-34, \(\varepsilon = -8.85\) eV) and HOMO–5 (35, \(\varepsilon = -8.89\) eV), respectively. This underlines a poor σ-donor strength of this class of compounds, but we are currently looking into this.

A commonly used indicator for the degree of aromaticity is the calculation of the nucleus-independent chemical shift (NICS), \(^{46}\) i.e., the NICS(1) value of benzene is \(-12.8\) ppm. \(^{50}\) Selected values given in Table 1 show the trend of diminished aromaticity upon substitution of CH-units in benzene by phosphorus, affording phosphinine and 1,4-diphosphinine. However, a relatively high degree of aromaticity is still preserved in the latter systems.

The same (linear) trend of decreasing aromaticity can be observed for the tricyclic 1,4-diphosphinines 33–35 at higher sulfur contents, the NICS values being lower than those of H-X throughout. \(^{50}\) A comparison of NICS values of the central six-membered rings to the five-membered rings of all three tricyclic cases reveals a higher aromaticity of the central rings, however also showing a π-delocalization over the entire scaffold.

The substituent effect on stability and aromaticity of 1,4-diphosphinines was theoretically investigated via isodesmic reactions (Table 2) for different substituents including thiourea. \(^{46}\) The effect was found to be weak, stabilizations being in the range of a few kcal mol\(^{-1}\) and NICS(1) values being very similar. An exception is the CF\(_3\)-substituted compound CF\(_3\)-X which is notably destabilized and more aromatic compared to the other calculated examples.

### Table 1 Computed NICS(0) and NICS(1) values (ppm) for benzene,\(^{55}\) phosphinine and 1,4-diphosphinines H-X.\(^{36,33–35,45}\)

<table>
<thead>
<tr>
<th>Central ring</th>
<th>Outer ring</th>
<th>NICS(0)</th>
<th>NICS(1)</th>
<th>NICS(0)</th>
<th>NICS(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_6)H(_6)</td>
<td></td>
<td>-12.8(^{26})</td>
<td>-18.7(^{26})</td>
<td>-10.4(^{26})</td>
<td>-16.1(^{26})</td>
</tr>
<tr>
<td>C(_6)H(_5)P</td>
<td></td>
<td>-11.4(^{b})</td>
<td>-16.1(^{b})</td>
<td>-10.4(^{b})</td>
<td>-15.1(^{b})</td>
</tr>
<tr>
<td>H-X</td>
<td></td>
<td>-7.9(^{c})</td>
<td>-10.4(^{c})</td>
<td>-8.5(^{c})</td>
<td>-10.4(^{c})</td>
</tr>
<tr>
<td>Me-33</td>
<td></td>
<td>-6.7(^{c})</td>
<td>-8.5(^{c})</td>
<td>-8.5(^{c})</td>
<td>-10.4(^{c})</td>
</tr>
<tr>
<td>Me-34(^{a})</td>
<td></td>
<td>-5.8(^{c})</td>
<td>-7.6(^{c})</td>
<td>-5.3(^{c})</td>
<td>-7.6(^{c})</td>
</tr>
<tr>
<td>35</td>
<td></td>
<td>-4.8(^{c})</td>
<td>-6.6(^{c})</td>
<td>-2.9(^{c})</td>
<td>-4.8(^{c})</td>
</tr>
</tbody>
</table>

\(^{a}\) N-Me substituted structure was calculated. \(^{b}\) Values at B3LYP/6-311++G(d,p).\(^{55}\) Values at M06-2X/cc-pVTZ/B3LYP/cc-pVTZ.\(^{45}\)

### 4. Analytical data

#### 4.1 \(^{31}\)P NMR spectroscopy

\(^{31}\)P NMR spectroscopic studies corroborated significant structural aspects of 1,4-dihydro-1,4-diphosphinines and 1,4-diphosphinines, substituent effects on the phosphorus nuclei and, especially, the nature of the fused heterocycles. In case of 1,4-dihydro-1,4-diphosphinines, the P-substitution is immediately evident and also the presence of cis and trans isomers (Table 3).

Monocyclic 1,4-dihydro-1,4-diphosphinines 8 without any fused heterocycles, having alkyl and aryl groups, can be used as a good case in point: the resonances for cis and trans isomers\(^{27}\) are in a chemical range of \(-18.7\) to \(-44.1\) ppm. Asymmetrically substituted derivatives show \(J_{\text{P,P}}\) coupling constants between 52–55 Hz (cis) and 42–46 Hz for the trans isomers. The rather unusual structure of compound 13 is immediately revealed by its \(^{31}\)P chemical shift at 275.6 ppm.\(^{33}\) The deshielding of the phosphorus nuclei can be partly explained by the mesomeric structures of 13 in which a positive charge at phosphorus can be assumed. For compound 17, having a PBr substitution, only one \(^{31}\)P NMR signal at

### Table 2 Computed isodesmic reaction energies (kcal mol\(^{-1}\)) and NICS(1) values (ppm) for different substituents. Values at M06-2X/6-311+G**\(^{42}\)

<table>
<thead>
<tr>
<th>Substituent</th>
<th>(\Delta E/k\text{cal mol}^{-1})</th>
<th>NICS(1)</th>
</tr>
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<tbody>
<tr>
<td>-NC(=S)N-</td>
<td>-2.2</td>
<td>-8.7</td>
</tr>
<tr>
<td>-F</td>
<td>8.1</td>
<td>-9.4</td>
</tr>
<tr>
<td>-CF(_3)</td>
<td>17.8</td>
<td>-10.5</td>
</tr>
<tr>
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<td>-9.4</td>
</tr>
<tr>
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<td>-8.6</td>
</tr>
<tr>
<td>-SiH(_3)</td>
<td>0.1</td>
<td>-8.8</td>
</tr>
</tbody>
</table>

#### 4.2 \(^{31}\)P CH FIS spectra of 1,4-dihydro-1,4-diphosphinines 19–26

Chemical shifts are given for cis and trans (in brackets) isomers

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>R’</th>
<th>(^{31})P((^{1})H)/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>Me</td>
<td></td>
<td>3.3 (3.9)</td>
</tr>
<tr>
<td>20</td>
<td>n-Bu</td>
<td></td>
<td>0.2 (3.6)</td>
</tr>
<tr>
<td>22</td>
<td>n-Bu</td>
<td></td>
<td>2.6 (10.9)</td>
</tr>
<tr>
<td>23b</td>
<td>n-Pr</td>
<td>NEt(_2)</td>
<td>18.8 (19.5)</td>
</tr>
<tr>
<td>23c</td>
<td>Me</td>
<td>Ph</td>
<td>16.5 (19.3)</td>
</tr>
<tr>
<td>23d</td>
<td>n-Pr</td>
<td>Ph</td>
<td>-39.8 (40)</td>
</tr>
<tr>
<td>24</td>
<td>n-Pr</td>
<td></td>
<td>12.7 (21.3)</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
<td>29.8 (23.5)</td>
</tr>
<tr>
<td>26(^{a})</td>
<td></td>
<td></td>
<td>17.8 (21.8)</td>
</tr>
</tbody>
</table>

\(^{a}\) Due to the low solubility of 26, a solid-state CP/MAS\(^{31}\)P \(^{1}\)H-NMR spectrum was recorded.
39.1 ppm was reported; and the low-field shift can be attributed to the effect of the electron withdrawing group.\textsuperscript{38} The ensemble of 1,4-dihydro-1,4-diphosphinines, having fused imidazole-2-thione, thiazole-2-thione or dithiol-2-thione units, appear as \textit{cis} and \textit{trans} mixtures, and the heterocycle exerts a strong effect on the chemical shift.\textsuperscript{46-48,50} The P-Cl compounds 20, 24 and 25 show the same trend as that of 17 but appear more highfield-shifted compared to 17. Compound 27 is an interesting example as only carbocycles are fused to the middle ring while the phosphorus atoms are similarly constrained in a rigid scaffold; resonances of their isomers appear at \(-21.5\) and \(-25.6\) ppm in the \(31^P\) NMR spectrum\textsuperscript{31} and, hence, revealing the influence of the heteroatoms in the other tricyclic derivatives.

For a double phosphonium such as 29 a 31P chemical shift of 3.5 ppm points to rather shielded phosphorus nuclei, but no solid state structure was reported.\textsuperscript{52} The derivative 31 is significant as to be the only example of a phosphorane-type derivative, for which a 31P NMR value of 8.82 ppm was reported but, again, not further confirmed.\textsuperscript{55}

As discussed beforehand, we could use 1,4-dihydro-1,4-diphosphinines as precursors for 1,4-diphosphinines 33\textsuperscript{Bu} and 34, stimulated by the early advent of mononuclear 32,\textsuperscript{26} and they have been well characterized by NMR spectroscopic studies.\textsuperscript{46,56} Unfortunately, 35 had such a low solubility that solution NMR data could not be obtained, but GIAO calculations predict a 31P NMR chemical shift of 138.2 ppm for 35\textsuperscript{50} (Table 4).

### 4.2 UV/vis spectroscopy

Due to the intensely red colors of 1,4-diphosphinines of 33-35 UV/vis studies have been measured. The UV/vis spectrum of 32 shows a strong peak at 282 nm (\(\varepsilon > 4000-5000\) in n-hexane in an argon atmosphere).\textsuperscript{26} For 33-35 two absorption bands are the most prominent, being around 300 nm and 500 nm, respectively (Table 5).\textsuperscript{46,50,56} As accompanying calculations, being in good agreement with the experiments, revealed, the latter absorption corresponds to the HOMO/LUMO excitation of the 1,4-diphosphinines, while the former can be assigned to different excitations for different 1,4-diphosphinines. In the case of 33 the absorption at 285 nm was assigned to the HOMO \(\rightarrow\) LUMO+1 excitation, while for 34 the respective absorption consists of the HOMO–4 \(\rightarrow\) LUMO+1 excitation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption (\lambda/\text{nm})</th>
<th>Excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me-33</td>
<td>282, 283\textsuperscript{a}</td>
<td>HOMO (\rightarrow) LUMO+1</td>
</tr>
<tr>
<td>9-Bu-33</td>
<td>286</td>
<td>HOMO (\rightarrow) LUMO</td>
</tr>
<tr>
<td>34</td>
<td>313</td>
<td>HOMO–4 (\rightarrow) LUMO+1</td>
</tr>
<tr>
<td></td>
<td>341, 330\textsuperscript{b}</td>
<td>HOMO (\rightarrow) LUMO+1</td>
</tr>
<tr>
<td>35</td>
<td>497, 496\textsuperscript{b}</td>
<td>HOMO (\rightarrow) LUMO</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Values at B3LYP/6-311+G** [PCM: CH\(_2\)Cl\(_2\)].\textsuperscript{46} \textsuperscript{b} Values at B3LYP/6-311+G*/B3LYP/6-311+G**.\textsuperscript{56} \textsuperscript{c} Values at B3LYP/cc-pVTZ/B3LYP/cc-pVTZ.\textsuperscript{50}

#### 4.3. X-ray diffraction analysis

Single crystal X-ray diffraction analyses unveiled molecular structures of 1,4-dihydro-1,4-diphosphinines and 1,4-diphosphinines including stereochemical information on the orientation of P-bound groups. In case of compound 8 with \(R = \text{CMe}_3\) and \(R = \text{Ph}\), the \textit{cis}(e,e)-tub form was observed. The P-C bond distances of about 1.80 \(\text{Å}\) and the P-C-P bond angles of about 101° were in good agreement with data published for acrylic tertiary phosphines.\textsuperscript{27} The X-ray crystallographic analysis of different derivatives of compound 15 showed the existence of different configurations depending on the steric demand of the P-substituent. The isomers, \textit{trans}-15\textsuperscript{Ph} and \textit{cis}-15\textsuperscript{Ph} possessed a butterfly structure of the tricyclic ring. On the other hand, \textit{trans}-15\textsuperscript{Mes} possesses a planar structure. The sum of the internal angles in the central diphosphinine rings were calculated to be 680.2°, 708.2°, and 717.2° for \textit{trans}-15\textsuperscript{Ph}, \textit{cis}-15\textsuperscript{Ph} and \textit{trans}-15\textsuperscript{Mes}, respectively, which was proposed to describe as the deviation of the ring structure from planarity; the least deviation was observed for \textit{trans}-15\textsuperscript{Mes} and the most for \textit{trans}-15\textsuperscript{Ph}.

Most of the crystal structures showed a common trend where the \textit{cis}-isomers were non-planar with the out-of-plane orientation of phosphorus atoms and \textit{trans} isomers were generally planar, even though the \textit{trans}-15\textsuperscript{Ph} is an exception. Having said this, \textit{cis}-22\textsuperscript{rf} had the two P atoms slightly out of plane (N–P–C bond angle showed a difference of 3.5°) and \textit{trans}-22\textsuperscript{Me} showed a planar structure.\textsuperscript{47} Same trend was observed for 23, where a non-planar 6-membered ring was observed for \textit{cis}-23\textsuperscript{a} and a planar six-membered ring for \textit{trans}-23\textsuperscript{b}.\textsuperscript{48} The absence of functional groups in the fused rings gave a slight boat-shaped conformation (folding angle along the P–P axis = 18.7°) for \textit{trans}-25 and \textit{cis}-26 (folding angle along the P–P axis = 38.7°) and an almost planar, tricyclic system for \textit{trans}-25 following the previous trend.\textsuperscript{50}

\textit{cis}-27 also showed a boat type conformation, pointing to the same reason as that of \textit{trans}-25 and \textit{cis}-26 (folding angle along the P–P axis = 30.4°).\textsuperscript{51} X-ray crystal structure of 33\textsuperscript{Bu} revealed a planar tricyclic systems with the crystallographic center of symmetry oriented in the middle of the central ring.
(Fig. 6). The structure of 33Bu revealed the trans-orientation of the Bu groups owing to dispersive interactions with the next molecules. The P–C bonds in the 1,4-diphosphine ring unit were found to be in the range of 1.743 Å (P–C1) and 1.745 Å (P–C3) in 33Bu. The C–C bond lengths in the rings were in good agreement with that of benzene with the value of 1.400 Å in 33Bu.46,61 These structural parameters confirmed the aromaticity of the central six-membered ring. In the same way, X-ray crystal structure analysis of 34 confirmed the trans-oriented n-propyl groups (Fig. 7). The P–C and C–C bond lengths of the central ring were quite similar to 33Bu (P–C1 = 1.7390, P–C3 = 1.7494 and C1–C3 1.406 Å) and, hence, consistent with a high degree of aromaticity in 34.56,61

4.4 Electrochemical analysis

Electrochemical studies helped to investigate the quest of reversibility of a redox process and, also, the electrochemical stability of the species involved. This, together with theoretical studies, helped to understand the feasibility of the formation of ionic/radical species by calculating ionization energies from peak potential differences and also, orbital energy studies. It’s evident from these examples that the fused cycles also play major roles in the redox properties of the compounds. Selected examples of 1,4-dihydro-1,4-diphosphinines and 1,4-diphosphinines are provided below (Table 6).

Electrochemical analysis proved that 10 had a predominant donating behaviour as well as its irreversibility (Table 6).30 cis-27 was a really good example to showed that the interaction between the fused and the middle rings could largely affect the cyclic voltammogram behaviour. Here, large potential differences were observed between the first and second (120 mV), but also between the third and fourth waves (120 mV) and this striking splitting of both oxidation waves indicated a significant interaction between the two TTF moieties through the almost planar middle ring (Table 6).31 The feasibility of the formation of monoanion and dianion was investigated thoroughly with the help of cyclic voltammetry studies for 1,4-diphosphinines 33Bu and 34. Along with the theoretical calculations and orbital energy studies helped to investigate upon the stability of these anions.46,56 This was evident when 33Bu showed two pseudo-reversible redox waves representing a two-electron reduction and one-electron reduction (Table 6) and the theoretical studies confirmed the stability of the first radical anionic state.30 Same was observed for 34 also, but Epc(2) and Epc(3) were at significantly lower potential than in 33Bu (Table 6) pointing to the easily reducible nature of 34. Also, it was found that monoanion and dianion were more stable for 34 than for 33Bu. All these findings were further supported by theoretical calculations.56 The aforementioned findings for 33Bu were experimentally investigated via synthesis and isolation of mono anionic compound 33Bu+, and this showed a redox cycle where the oxidation led to the formation of a formal radical dimer, i.e., having a P–P bond linkage, the “Dim-33” (see Scheme 23).62 This process was studied and performed via cyclic voltammetry and, hence, we were able to establish the cyclic redox nature of this system. This redox process (Table 6) point to the remarkable stability of a redox couple involving phosphanide 33Bu+ and diphosphone-type compound Dim-33. Especially the multi-cycle stability of this system could enable its use as battery material.62

Table 6 Oxidation and reduction peak potentials of different 1,4-dihydro-1,4-diphosphinines and 1,4-diphosphinines

<table>
<thead>
<tr>
<th>Compound</th>
<th>Epa (V)</th>
<th>Epc (V)</th>
<th>Redox process reversibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Bu</td>
<td>0.63</td>
<td></td>
<td>Ambiguous signal</td>
</tr>
<tr>
<td>25Bu</td>
<td>−1.3, −1.4, −1.6, −1.8</td>
<td>−0.1, 0.6</td>
<td>Irreversible</td>
</tr>
<tr>
<td>26</td>
<td>−1.37 (broad)</td>
<td></td>
<td>Irreversible</td>
</tr>
<tr>
<td>cis-27</td>
<td>0.43, 0.55, 0.93, 1.05</td>
<td></td>
<td>Irreversible</td>
</tr>
<tr>
<td>33Bu</td>
<td>−0.61, −0.34</td>
<td>−1.74, −2.59</td>
<td>Reversible</td>
</tr>
<tr>
<td>34Bu</td>
<td>−0.959</td>
<td>−1.715</td>
<td>Irreversible</td>
</tr>
<tr>
<td>34</td>
<td>−1.042, −1.343, 0.698</td>
<td>−1.28, −1.45</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

*Calibrated vs. Ag/AgCl. **Calibrated vs. Fe3+/0 = 0.9 V, rest are calibrated vs. Fe3+/0 = 0 V.
5. Reactivity

5.1 Reactivity of 1,4-dihydro-1,4-diphosphinines

5.1.1. Nucleophilic reactions of the P centers. The first example of a nucleophilic substitution reaction of a 1,4-dihydro-1,4-diphosphinine was reported by Märkl et al.27 Reaction of cis-8 and 1,2-dibromoethane in boiling n-propanol resulted in the formation of the bridging bis-phosphonium salt 36 (Scheme 24).

Nucleophilic substitution reactions at phosphorus were studied using 1,4-dichloro-1,4-dihydro-1,4-diphosphinines with carbon-based nucleophiles (Scheme 25).47 A mixture of isomers of 20 in THF was treated with n-BuLi at −78 °C, and the colour of the reaction mixture changed from yellow to brown. The two products 37a, b (singlets at −56.5 and −63.5 ppm) were obtained as cis/trans mixture (1 : 2.9), isolated and fully characterized.

In order to benefit from post-functionalization of the P-center, nucleophilic substitution was carried out with lithium (trimethylsilyl)acetylide leading to an isomeric mixture of 37c. Nucleophilic substitution of 25 was also accomplished using weak nucleophiles such as KHMDS which led to the formation of 38 in a 1 : 1 isomeric ratio as confirmed by 31P NMR spectroscopy (Scheme 26).50 Alkoxy-functionalized 1,4-dihydro-1,4-diphosphinines 39 were synthesized using alcohols of different steric demand. In all cases, the two isomers were determined in the reaction mixtures with a ratio of 1.5 : 2.

5.1.2. Oxidation reactions at P. To date, selective oxidation reactions of both P-centers of the 1,4-dihydro-1,4-diphosphinines were successfully conducted leading to bis(P-chalcogenide) derivatives (Ch = O, S, Se).

5.1.2.1 P=O derivatives. Oxidation of cis-8 in ethanol with atmospheric oxygen, the cis-dioxide 40 was obtained quantitatively, by fractional recrystallization of the P-oxides of the cis/trans-isomer mixture in acetonitrile (Scheme 27).27

As proven by Uchiyama and co-workers, 1,4-dihydro-1,4-diphosphinine 12 is spontaneously oxidized in air during workup to afford the dioxide 41 as identified by 31P NMR spectroscopy (Scheme 28).32 Signals observed for the 1 : 1 stereoisomers at −15.3 and −15.1 ppm were shifted to 9.11 and 10.3 ppm with the formation of 41. Reaction of trans-41 with HSiCl3 gave trans-12 that have two 31P signals at −15.7 and −16.6 ppm indicating that cis/trans isomerization had occurred (most probably via vertex inversion) at the phosphorus to provide a mixture. However, cis-12 did not undergo oxidation under the same conditions to produce cis-41, maybe because of large(r) steric repulsion between phenyl groups at 5, 10-positions (Scheme 28).

13, having a double ylidic mesomeric structure, readily adds two oxygen and water thus resulting in quantitative yields of the bis-phosphinic acid 42 (Scheme 29).33

Ren et al. demonstrated that the trivalent phosphorus species, 14 can be oxidized with hydrogen peroxide in situ to provide dioxide 43 (Scheme 30).34 Clean separation of cis- and trans-43 species was achieved by column chromatography, owing to their significantly different dipole moments.64
With the accessibility of dibromo-1,4-diphosphinine, \(17\) Ivonin and co-workers synthesized differently oxidized derivatives (Scheme 31).\(^\text{39}\) \(17\) was readily converted to bis-phosphinous acid \(44\) via reaction with water. By the Todd–Atherton reaction, bis-phosphinous acid \(44\) was converted to obtain bis-phosphinic acid \(45\) and bis-aminophosphinates \(46\) in good yields.

Oxidation of the P-center, while keeping the thione moieties intact, is an important aspect of the chemistry of the tricyclic 1,4-dihydro-1,4-diphosphinines of the Streubel group. Facile and selective P-oxidation was achieved by treatment of \(20\), \(24\) and \(25\) with the mild oxidant hydrogen peroxide-urea adduct in dichloromethane leading to a clean formation of \(\text{P}^{\text{V}}\)/\(1\),4-dihydro-1,4-diphosphinines \(47\), \(48\) and \(49\) (Scheme 32).\(^\text{47,48,50}\)

### 5.1.2.2 \(P=E\) derivatives

With the knowledge of the versatility of dibromo-1,4-diphosphinine \(17\), Ivonin et al. synthesized many oxidized products with elemental sulfur (Scheme 33)\(^\text{39}\) to give the dibromo-diphosphinine \(P\)-sulfide \(50\), and a library of compounds \(51–54\) via multi-component reactions. Interestingly, one C–P bond is cleaved with excess of methanol to form a phosphonate which upon oxidation with sulfur formed \(55\).

1,4-Dihydro-1,4-diphosphinine-1,4-diamine \(18\) was oxidized by selenium and sulfur under mild conditions to yield 1,4-dihydro-1,4-diphosphinine-1,4-diamine-1,4-diselenide \(56a\) and -sulfide \(56b\), respectively (Scheme 34).\(^\text{41}\) This was the first example of a \(PP\)′-diselenide known for 1,4-dihydro-1,4-diphosphinines. Isomeric mixtures (\(E\) and \(Z\)) of the compounds in a 3:1 ratio was detected by HPLC-MS. 1,4-Diamine-diphosphinines \(18\) were obtained in analytically pure state by reduction of selenides/sulfides \(56\) with elemental sodium in toluene.

Koner et al. demonstrated that the P centers in \(20\) can also be converted into \(P\)-sulfides via heating in toluene with elemental sulfur (Scheme 35). The final products, \(i.e.,\) the bis-sulfides, \(57\) were isolated as white to light-yellow powders in moderate to good yields.\(^\text{47}\)

Similarly the reactivity of 1,3-thiazole-2-thione and 1,3-dithiol-2-thione-based tricyclic 1,4-chloro-1,4-diphosphinines were studied for their reactivity towards oxidation. Isomeric mixture of \(24\) upon oxidation with sulfur led to \(58a\) with \(cis/\text{trans}\) ratio of 1:1 and with selenium, resulted \(58b\) with 1.2:1 isomeric ratio indicated by \(^{31}\)P NMR spectroscopy.\(^\text{48}\) Compound \(25\) also yielded the corresponding sulfides and
selenides, 59 in moderate yield as an isomeric mixture (Scheme 35).

The reactivity of cis/trans mixtures of 27 towards oxidation was investigated by Avarvari and co-workers (Scheme 36). Reaction of 27 with a large excess of sulfur in THF (under reflux) during 24 h provided a mixture of phosphine sulfides cis-60 and trans-60 in a ratio of 1.5:1, difficult to separate by column-chromatography.

5.1.2.3 Five-coordinate derivatives. Oxidation of 1,4-dihydro-1,4-diphosphinines was further investigated by Koner and Begum using ortho-chloranil, a reagent which provides access to new spirocyclic diphosphinine derivatives as well as opening a potential path towards synthesis of polymers. The reaction affords stereoselective access to 61 and 62 having two spirobenzo-dioxaphospholane units each (Scheme 37). They were isolated as a mixture of two isomers in good yield and these molecules represent unique examples of tricyclic bis (spirocyclic) P-heterocycles reported to date.

5.1.3. Reductive P–C bond cleavage. P-Ph substituted tricyclic derivatives 63 were successfully used to generate tricyclic bisphosphanides 64 which was proven via quenching with an electrophile. This two-fold reductive P–C bond cleavage of the P–Ph bond was accomplished by employing potassium metal to a THF solution of 63 (Scheme 38). Formation of an orange color precipitate was indicative of the dianionic species formed. Complete disappearance of the two resonances of
compound 63 and appearance of a new singlet resonance in $^{31}$P NMR spectroscopy confirmed the formation of symmetrical structure of the dianionic derivative 64. To prove the existence of 64, it was reacted in situ with $n$-butyl iodide (where $R = \text{^7}Bu$) at $-80 \, ^\circ\text{C}$ and as the reaction progressed, the orange turbid reaction mixture immediately turned clear and became light yellow. The reaction mixture showed two singlet resonances in the $^{31}$P NMR spectrum for compound 65, for which all the analytical data were in accordance with previously reported compound 37b.

### 5.1.4. Alkylation of the thione S-centers.
Selective methylation at the S-center was achieved using carbon-based hard electrophiles such as methyl trifluoromethane sulfonate (methyl triflate), leaving the phosphorus centers untouched. Twofold S-methylated derivatives were synthesised from 1,4-dihydro-1,4-diphosphinine derivatives 20 and 25 in DCM to furnish 66 and 67 characterized by the turbid solution followed by formation of white precipitate of bis(imidazolium) salt (Scheme 39).47,50 The $^{13}$C{$^1$H} NMR spectrum of 66 and 67 confirmed the disappearance of the thione carbon atom resonance and the appearance of a new singlet characteristic of a C2-carbon nucleus of doubly S-methylated product. ESI-MS data also provides proof for the formation of the cation by the molecular ion peaks of 66 and 67.

### 5.1.5. Metal coordination via the P-center.
The ability to control the photophysical properties and the molecular scaffold through simple modification at the hetero-atom has been a key feature of main-group element-based electronic materials. The 1,4-dihydro-1,4-diphosphinine-based pentacene, 14 synthesized by Ren et al. demonstrates complexation with [Au(tht)Cl] using a mixture of cis/trans-14 containing about 90% cis-14 (Scheme 40).34 The cis-configured gold complex cis-68 was isolated by washing the product mixture with acetone. The optical/electronic properties, as well as the solid-state organization of cis-68 were studied in detail.

The TTF-based bimetallic complexes cis/trans-69 were synthesized by thermal displacement of the THF ligand in M(CO)$_5$(thf) (Scheme 41).64 Here, the Mo complex was less reactive than the W counterpart, thus longer heating periods were necessary and this afforded reaction mixtures with different cis/trans ratio.

Coordination properties of the amino-substituted tricyclic 1,4-dihydro-1,4-diphosphinines were evaluated using borane-dimethyl sulfane adduct in DCM (Scheme 42).47 The reaction was monitored by $^{31}$P NMR spectroscopy and the formation of P-borane adducts 70 detected; these were isolated as white powders in good yields. Similarly, the reactivity of 1,3-dithiol-2-thione-based tricyclic 1,4-dihydro-1,4-diphosphinine 25 towards the same boron reagent was investigated,50 and the two new main signals in the $^{31}$P NMR spectrum indicated the formation of 71 as an isomeric mixture, but the product could not be isolated in this case.
5.2 Reactivity of tricyclic 1,4-diphosphinines

5.2.1. Sequential reactions with nucleophiles and electrophiles. Begum et al. demonstrated the sequential addition of nucleophiles and electrophiles to 1,4-diphosphinine 34 (Scheme 43) using n-BuLi as strong nucleophile, thus creating a dark red solution.

The NMR spectrum of which exhibited two signals corresponding to anionic and neutral phosphorus centers of 72. Subsequent quenching of 72 with n-BuI resulted in a clean conversion to give an isomeric mixture of 73 (2:1 ratio, by 31P NMR integration). Reaction of 34 with a weak nucleophile such as KHMDS afforded also a color change from red to green, maybe indicating some kind of intermediate radical, and then to bright red, due to the formation of 74 (Scheme 44).

The reactivity of 74 was investigated further, using first Ph2PCl which cleanly formed 76 accompanied by the red to yellow color change and the appearance of three new signals in the 31P NMR spectrum. But 74 was also treated with a mild oxidant, i.e. half an equivalent of elemental iodine, resulting, again, in a color change from red to green, and finally to yellow (Scheme 44). The final product, compound 76, bearing a P–P bond resulting from the homo-coupling of the transient P-centered radical was isolated as isomers (98:2 ratio) and confirmed by X-ray crystallography.

5.2.2. Cycloaddition reactions

5.2.2.1 [4 + 2] cycloaddition reactions. The presence of the conjugated π-system in 1,4-diphosphinines together with the highly electrophilic P-center facilitate interesting reactions. Especially, the dienic nature of the π-system has enabled a variety of cycloadditions, some of which allowed to access diphosphabarrelenes. This is of special interest as (mono) phosphabarrelenes are considered as important ligands in hydrogenation of alkenes and rhodium-catalyzed hydroformylation. The first reported 1,4-diphosphabarrelene was synthesized by Krespan in one step reaction heating red phosphorus with hexafluoro-2-butyne and a catalytic amount of elemental iodine at 200 °C under pressure. Years later, the same 1,4-diphosphabarrelene 77 was synthesized by Kobayashi and co-workers using a more efficient synthetic protocol and the reaction of tetrakis(trifluoromethyl)-1,4-diphosphabenzene 32 with various alkynes to give diphosphabarrelenes 77–79 (Scheme 45). However, 1,4-diphosphinine 32 was unstable in pure form, and its synthesis was a tedious process which limited the usage of this synthetic protocol.

Since then, several other 1,4-diphosphabarrelenes were reported using different synthetic approaches. Weinberg and co-workers described the synthesis of 80 in one-step process by treating o-dichlorobenzene and white phosphorus in the presence of catalytic amounts of ferric chloride (Scheme 46), however, the yield was only 20%. Further efforts to improve this synthetic protocol by Uchiyama et al. was not successful as their yield was only 7%. Ishii and co-workers reported the synthesis of thiophene-based 1,4-diphosphabarrelene 81 in 85% yield by the reaction of lithiation of thiophene rings with n-BuLi followed by oxidation with large excess of P(OPh)3 and...
subsequent reduction with an excess and amount of trichlorosilane in refluxing benzene (Scheme 47). As our group has been able to access stable, tricyclic imidazole- and thiazole-2-thione-based 1,4-diphosphinines, we have thoroughly investigated their reactivity in bond activation reactions using an array of C,C-based dienophiles, and the thermal reactivity of the $4\pi$-system was established in $[4\pi+2\sigma]$ cycloaddition reactions. 1,4-Diphosphinines 33–35 reacted with the electron-deficient alkyne dimethyl acetylenedicarboxylate (DMAD) in toluene to achieve a clean conversion to 82–84 at elevated temperatures (Scheme 48), although 35 couldn’t be used in pure form. To investigate electron-deficient alkenes as a $2\pi$ system, N-phenyl maleimide was used as case in point. Although 33 and 34 reacted with N-phenyl maleimide in toluene at very different temperatures, i.e. 110 °C and r.t., respectively, both resulted in 7,8-dihydro-1,4-diphosphanorbornadienes 85 and 86 in good yields (Scheme 48). Remarkable was the discovery that visible light leads to a retro-reaction in case of 86, i.e. only in the dark a quantitative reaction could be obtained. This finding is of importance as it can be regarded as potential 1,4-diphosphinine protecting group strategy.

A unique new example of $\sigma$-bond activation of tricyclic imidazole-2-thione-based 1,4-diphosphinines was observed when diphenyldisulfane and -diselane was heated with 33 in toluene at 110 °C, thus yielding selectively trans 1,4-addition products 87a,b via a unique $[4\pi+2\sigma]$-type cycloaddition (Scheme 49).

5.2.2.2 $[4 + 1]$ cycloaddition reactions. Several $[4 + 1]$ cycloaddition reactions were reported by Kobayashi et al. When the 1,4-diphosphinine 32 was heated in carbon tetrachloride in a sealed NMR tube at 130 °C, the diphosphanorbornadiene 88 was formed and confirmed by $^{19}$F NMR spectroscopy (Scheme 50). Upon treatment of 32 with excess sulfur or the bicyclic thiirane, the hetero-norbornadiene 89 was obtained in quantitative yield as estimated by $^{19}$F NMR spectroscopy (Scheme 50).

The first examples 7-metallo-1,4-diphosphanorbornadienes were reported by our group, recently, taking advantage of the dienophilic monovalent group-13 (NacNac)M complexes (Scheme 51; formal charges are not shown).
When tricyclic 1,4-diphospinine 33 was treated with (NacNac)Ga and (NacNac)Al the 7-galla-1,4-diphosphenorbornadiene 90 and 7-aluma-1,4-diphosphenorbornadiene 91 were formed, confirmed by $^{31}$P NMR spectroscopy and X-ray diffraction studies. Both reactions proceeded fast at low temperatures and showed a color change of bright-red to yellow. The Ga case was special as a reversible product formation was observed, thus leading to an equilibrium.

5.3 Synthesis and reactivity of tricyclic $^{3\text{V/V}}$- and $^{\text{PIII/III}}$-bridged bis(imidazole-2-yldenes)

Imidazol based N-heterocyclic carbenes (NHCs) are considered as prominent species that contribute to the synthesis of complex ligands with catalytic properties and coordinating properties. Therefore, fine tuning of the electronic properties of the NHC back bone via different substituents is of particular interest in this context. Mono NHCs (Fig. 8) which are bearing heteroatomic substituents have been studied to exert electronic influence and modulate the properties. Janus-type bis(NHCs) (Fig. 8) which were investigated to build organometallic architectures and create molecular squares and quadrilaterals in supramolecular assemblies. The first tricyclic, rigid, hetero-atom-linked bis(NHCs) and XIX are recently developed from our group based on the knowledge gained through the previous study of tricyclic 1,4-dihydro-1,4-diphosphines bearing dithione functionalities. Deprotonation of tricyclic P/V/V-bridged bis(imidazolium) salts cis/trans mixture of diselone 92 with H$_2$O$_2$ in dichloromethane produced the isomeric P/V/V-bridged bis(imidazolium) salts (1 : 0.9) via oxidative deselenization. Immediate treatment with BaCl$_2$·2H$_2$O led to the cis/trans mixture of chloride salts 93 (Scheme 52) evidenced by the high-field shift of the $^{31}$P resonances to $\delta = -6.2$ (cis) and $-5.6$ ppm (trans) due to the oxidation of the P/III to P/V centres. Formation of the P/V/V (imidazolium) derivative 93 was confirmed by various analytical methods and further supported by single crystal analysis. Deprotonation of tricyclic P/V/V-bridged bis(imidazolium) salts 93cis/trans using two eq. of KHMD in THF resulted P/V/V-bis(NHCs) 94cis/trans (1 : 0.2) in 88% yield (Scheme 51). The biscarbene formation was evidenced by a disappearance of the C$_2$-proton resonance in the $^1$H NMR spectrum and the downfield shift of the C$^2$-carbon resonance in the $^{13}$C NMR spectrum.

Moreover, those complexes established enhanced catalytic activity and solubility compared to the classical cationic metal complexes of the neutral NHCs. To further investigate on these advantageous properties of anionic bis(NHC)s, we have synthesized novel anionic low-coordinate P-linked bis(NHCs) XX and XXI (Fig. 8) and studied the modulation of electronic communication and redox activity. 

5.3.1 Tricyclic P$^{3\text{V/V}}$- and P$^{\text{PIII/III}}$-bridged bis(imidazole-2-yldenes)

5.3.1.1 Synthesis. The tricyclic P$^{\text{PIII/III}}$-bridged diselone 92 was obtained as cis/trans mixture (1 : 0.7) in good yields according to the previously published protocols. Reaction of cis/trans mixture of diselone 92 with H$_2$O$_2$ in dichloromethane produced the isomeric P/V/V-bridged bis(imidazolium) salts (1 : 0.9) via oxidative deselenization. Immediate treatment with BaCl$_2$·2H$_2$O led to the cis/trans mixture of chloride salts 93 (Scheme 52) evidenced by the high-field shift of the $^{31}$P resonances to $\delta = -6.2$ (cis) and $-5.6$ ppm (trans) due to the oxidation of the P/III to P/V centres. Formation of the P/V/V (imidazolium) derivative 93 was confirmed by various analytical methods and further supported by single crystal analysis. Deprotonation of tricyclic P/V/V-bridged bis(imidazolium) salts 93cis/trans using two eq. of KHMD in THF resulted P/V/V-bis(NHCs) 94cis/trans (1 : 0.2) in 88% yield (Scheme 51). The biscarbene formation was evidenced by a disappearance of the C$_2$-proton resonance in the $^1$H NMR spectrum and the downfield shift of the C$^2$-carbon resonance in the $^{13}$C NMR spectrum.

To access free P$^{\text{PIII/III}}$-bridged bis(NHCs), twofold Se-methylation was employed. When trifluoromethyl sulfonate (MeOTf) was employed, the salt 95cis/trans was easily obtained in good yields (84%, ratio 1 : 0.33) (Scheme 53). Subsequent treatment of 95cis/trans with NaBH$_4$ in methanol resulted in the formation of P$^{\text{PIII/III}}$-bridged bis(imidazolium) salts 96cis/trans which could be isolated as orange liquid (61%, 1 : 0.3) and fully characterized. The P$^{\text{PIII/III}}$-bridged bis(NHC) 94cis/trans was then targeted by using KHMD in THF and the reaction mixture showed a slight down-field shift for the resonances in the $^{31}$P$^1{H}$ NMR spectrum.
5.3.1 Formation of dinuclear coinage metal(I) complexes. To understand the coordination properties of the tricyclic PV/V- and PIII/III-bridged bis(imidazole-2-ylidenes), they were reacted with coinage metals. Reaction of \(93^\text{cis}/\text{trans}\) with one eq. of \(\text{M}_2\text{O}\) (\(\text{M} = \text{Cu}, \text{Ag}\)) in DCM led to PV/V-bridged bis(NHC) complexes \(97^\text{cis}/\text{trans}\) (Scheme 54). The complexes \(98^\text{cis}/\text{trans}\) produced by the metal exchange reactions using dimethyl sulfide gold(I) chloride were isolated as white powders and characterized by NMR spectroscopy and X-ray diffraction. The same coinage metals were employed to examine the different coordination sites of bis(NHC) \(94^\text{cis}/\text{trans}\). They were treated with \(\text{M}_2\text{O}\) (\(\text{M} = \text{Cu}, \text{Ag}\)) to emphasize the transition metal bonding at the C2 carbon sites of the PIII/III-bridged bis(imidazolium) salts \(96^\text{cis}/\text{trans}\) (Scheme 55). Clean formation of PIII/III-bridged bis(NHC) complexes \(99^\text{cis}/\text{trans}\) were evidenced by the resonance in the \(31\text{P}\{\text{1H}\}\) NMR spectra. \(98^\text{cis}/\text{trans}\) was similarly obtained by metal exchange reaction. It was evident that as the reaction proceeds with no binding to the PIII/III-centers, the complex \(98^\text{cis}/\text{trans}\) allows second complexation at phosphorus center with a different metal.

5.3.2 Anionic Janus-type tricyclic bis(NHC)s and mixed substituted PIII/III-bridged bis(NHCs)

5.3.2.1 Synthesis. Tricyclic 1,4-diphosphinine diselone 100 has been treated with trifluoromethyl methylsulfonate (MeOTf) in dichloromethane to afford the doubly Se-methylated salt 101 which was isolated as a yellow solid and fully characterized (Scheme 56). Reductive deselenization of doubly Se-methylated salt 101 with Na[BH4] in the presence of [2.2.2]-cryptand in methanol afforded bis(imidazolium) salt 102 with an anionic phosphorus centre.

The salt 102, obtained in pure form was confirmed by two resonance signals in a 1:1 ratio in the \(31\text{P}\) NMR spectrum. Further confirmation for 102 was obtained from NMR, MS experiments and elemental analysis. Deprotonation of the bis
(imidazolium) salt 102 was performed in THF using two equivalents of KHMD (Scheme 56) to yield anionic P-functional bis(NHC) 103. The latter was isolated as a dark orange solid and confirmed by two resonances in its $^{31}$P NMR spectrum. We further extended our efforts towards the synthesis of mixed substituted PIII/III bridged bis(NHC)s 105cis/105trans by treating 102 with MeI in diethyl ether which resulted in a clean formation of bis(imidazolium) salt 104cis/104trans with an isomeric ratio of 1 : 0.3 confirmed by two sets of signals for two isomers. Subsequent deprotonation of 104 using two equiv. of KHMD in THF afforded the mixed-substituted bis(NHC)s 105cis/105trans in 1 : 0.3 ratio.

A very recent, highly interesting observation was the formation of the dianionic bis(NHC) 106 by Rauf Naz using a multifold reduction using KC8 (Scheme 57).89 Dithione derivative of imidazole based 1,4-diphosphinine 33 was reduced twofold using potassium graphite in Et2O at room temperature. The dianionic product 64, a dark brown solid, precipitated from the reaction mixture after one day of stirring. When compound 64 was then treated with an excess of KC8 the dianionic bis(NHC) 106 was formed as a dark red-brown solid identified by two major signals in the $^{31}$P{1H} NMR spectrum and a broad signal in the $^{13}$C{1H} NMR spectrum (Scheme 57).89 It should be noted that 106 represents the first combination of a bis(NHC) with an annelated antiaromatic core. Studies on this chemistry are currently underway in our group.

5.3.2.2 Reactivity of tricyclic bis(imidazolium) salt. The coordination properties of 102 was studied using 0.5 equiv. and 0.75 equiv. of rhodium dimer complex, [Rh(cod)Cl]$_2$ (Scheme 58). The reaction with a half equiv. of [Rh(cod)Cl]$_2$ afforded exclusively the mono rhodium(i) complex 107 co-ordinated to the neutral phosphorus atom as indicated by the $^{31}$P NMR spectroscopy; high-field shift of the anionic P and rhodium-phosphorus coupling of the neutral phosphorus atom. When treated with 1.5 equiv. of the rhodium dimer, it formed a selective isomeric mixture of trinuclear phosphanido complexes 108cis/108trans (ratio 0.9 : 1) (Scheme 58) and coordination was confirmed by two sets of signals in the $^{31}$P NMR spectrum.

5.4 Synthesis and reactivity of tricyclic 1,4-diphosphinine-1,4-diides

Based on the previous knowledge developed on anionic di-carbenes90 Rottschäfer et al. recently synthesized the first 1,4-diphosphinine-1,4-diide 110 and demonstrated its reactivity.91 Double deprotonation of the C'-arylated 1,3-imidazolium salts with 4BuLi followed by reaction with TmsCl afforded the bis-silylated derivatives in almost quantitative yields (Scheme 59). The bis-silylated compound yielded the desired chloride 109 upon treatment with PCl$_3$. Reacting a THF suspension of 109 with magnesium turnings or potassium graphite (KC8) led to the formation of a dark red suspension of double-zwitterionic compound 110 isolated as a red crystalline solid in 97% yield; a similar result was obtained before by Rauf Naz (see section 5.3.2.1).89

The two lone-pairs of each phosphorus atoms which reside in $\sigma$ and $\pi$ orbitals constitute the key feature of the reactivity of

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**Scheme 57**

**Scheme 58**

**Scheme 59**
110. Indeed, the tricyclic 1,4-diphosphinine-1,4-diide 110 readily reacts with (Me₂S)AuCl at room temperature to form the complex 111 in which each phosphorus atom binds to two AuCl entities (Scheme 60). Given the fact that a two-electron oxidation of the antiaromatic 8π electron C₄P₂ ring to form the 6π-electron C₆P₂ ring is a thermodynamically favorable process, they employed 110 as the reducing species for 109. When a 1:1 mixture of 109 and 110 was reacted in the presence of MgCl₂, it smoothly undergoes comproportionation to form rather stable molecule 112 which is comprising a 14π electron aromatic system isolated as an orange crystalline solid (Scheme 60).

6. Conclusions and outlook

We have described the development of the research field of saturated and unsaturated 1,4-diphosphinine-type compounds including P-bridged bis(NHCs). After a slow start, it has picked up steam in the past 20 years and has reached a remarkable synthetic diversity, and this enables a novel fascinating chemistry largely facilitated by phosphorus. While the first developments can be classified as (more) traditional heterocyclic organophosphorus chemistry, the new developments unveil bright and unprecedented perspectives. Especially the facile access to a manifold of tricyclic structures with two (or more) Lewis basic and/or acidic centers has widened the field and, in particular, has allowed for a straightforward large scale synthesis of stable aromatic tricyclic 1,4-diphosphinines. The latter show a broad range of 1,4-additions and [4 + n] cycloadditions to form, e.g. (rigid) diphosphabarrelenes; the reversible cycloadditions can pave the way towards a protection/de-protection strategy. Furthermore, the more recent advent of P³⁺- and P⁵⁺-bridged bis(NHCs) will stimulate (further) the rapidly developing field of NHC main group element adducts. A remarkable counterpoint to their N-congeners are the exceptional redox and electrophilic properties of the 1,4-diphosphinine moiety, thus being a perfect conceptual extension.

To our opinion current frontiers are (1) to achieve umpolung of 1,4-diphosphinine P-centers so that they possess nucleophi-lic ligand properties, (2) to access (aromatic) 1,4-diphosphinine-fuzed bis(NHCs) and (3) dianionic (antiaromatic) 1,4-diphosphinine-fuzed bis(NHCs). Especially the latter two lines of research would aim at tetrapodal and orthogonal ligand systems, representing an unprecedented scaffolds, which could find many applications in vastly different areas such as co-ordination (polymer), catalysis, and materials chemistry.

Author contributions

The manuscript has been written by all authors with a leading contribution of D.W. The concept was designed by R.S.

Conflicts of interest

There are no conflicts to declare.

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