# Journal Name

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## COMMUNICATION

# Expanding the chemistry of tricyclic 1,4-diphosphinines by stable mono anion formation

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**A new sulfur-enriched tricyclic 1,4-diphosphinine (2) was synthesized and novel reactivity studies on the phosphorus heterocycle was performed: A weak anionic nucleophile (KHMDS) adds selectively thus forming a stable anionic 1,4-diphosphinine derivative (3b) which was fully characterized. The substitution potential of 3b was demonstrated using Ph₂PCl to give 4b, while oxidation of 3b using elemental iodine furnished cleanly the P-P coupling product 5.**

Heteroatom-substituted benzene derivatives **I** (Fig. 1) have had a great impact on the chemistry of arenes.[1] By contrast, the properties and reactivity of phosphinines **II**[2] are largely dominated by the presence of aryl substituents,[3] and heteroatom persubstitution is completely unknown; 2-hydroxy derivatives have been described recently.[4] Phosphinine, the heavy homologue of pyridine, possesses about 90 % of the aromaticity of benzene.[5] These alluring species (**II**) have initiated intense research for more than five decades,[6] and, nowadays, the spectrum of applications range from luminescent materials, to polymer precursors and ligands in

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catalysis.[7] A broad spectrum of studies have revealed complexation,[8] P-alkylation,[9] P-oxidation,[10] P-reduction[11] and cycloaddition reactions.[12] Interestingly, most of the chemical disparities of pyridines and phosphinines can be attributed to the lower lying LUMO energies and, consequently, increased electron affinity of the latter.[13]
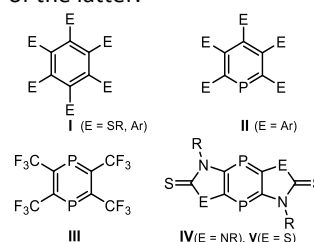


**Figure 1.** Benzenes (**I**) and phosphinines (**II**) having a complete set of substituents as well as electron-poor (**III**) and -rich (**IV,V**) 1,4-diphosphinines.

In particular, phosphinines have interesting π-ligand accepting properties, and a decidedly electrophilic phosphorus center. Therefore, they readily react with Grignard and lithio compounds to furnish dihydrophosphinine anions; the latter offer access to regiochemically different substitution products, *i.e.,* 1,1- or 1,2- or 1,4-regioisomers, depending on the nature of the electrophile used in the next step.[14]

In contrast, the chemistry of 1,4-diphosphinines is almost unexplored and, until recently, only a single derivative (**III**) of a 1,4-diphosphinine had been reported.[15] Synthesis of **III** is very laborious, the compound is not isolable and, hence, only a few physical properties and reactions are known, including formal [4+1] and [4+2] cycloaddition, and one example of a photoisomerization.[16] The easy access to imidazole-2-thione-based tricyclic 1,4-diphosphinines **IV**[17] has now reopened this area of research. This compound possess a high degree of aromaticity: NICS(1) value of the central ring = −9.5. Another very remarkable feature was revealed by voltammetry which showed a double reduction with an unresolved cathodic peak at −1.87 V to form the dianion.[17] Initial reactivity studies demonstrated that **IV** undergo [4+2] cycloaddition reactions to give 1,4-diphosphabarrelenes in high yield, but also react with dichalcogenides PhCh-ChPh (Ch = S, Se) in (rare) [4π+2σ] cycloaddition reactions, followed by inversion at the phosphorus center.[18] To investigate if the new 1,4-diphosphinine synthetic protocol could be transferred to other five-membered unsaturated heterocycles, we have started to examine the accessibility of tricyclic 1,4-diphosphinines **V** (Fig. 1), having a sulfur atom instead of an NR unit in the ring, and explore their chemistry. The required starting material, the 1,3-thiazole-2-thiones, have been previously used in coordination chemistry[19] and, sparingly, in N-heterocyclic carbene chemistry.[20] Herein, synthesis and characterization of a new sulfur-containing tricyclic 1,4-diphosphinine is described, including first ex-

amples of nucleophilic reactions, thus revealing the huge synthetic potential to access novel multi-topic hetero-cyclic ligand arrays.

Using the recently published ring closing protocol with subsequent facile conversion of the $P$-NEt$_2$ into the $P$-Cl group (see ESI),[17] the dichloro derivative **1** was obtained in high yield as *cis/trans* mixture (53:47); the identity of the *trans* isomer has been confirmed by a single crystal X-ray structure determination (see S1 in the ESI). Interestingly, our DFT calcu-lations reveal only a marginal energy difference (0.3 kcal/mol at M06-2X-6-311+G**) in favor of the *trans* isomer. The 1,4-dihydro-1,4-diphosphinine **1** was then used to obtain 1,4-diphosphinine **2** which, upon treatment of **1** with $^nBu_3P$, was cleanly formed (Scheme 1) and isolated in good yields (77 %) (see ESI). The $^{31}P\{^1H\}$ NMR spectrum of an aliquot shows resonances for **2** (134.7 ppm) and the (known) chlorophos-phonium salt (105 ppm).
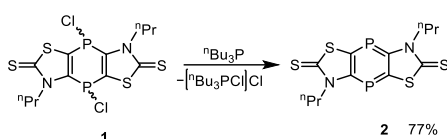
**Scheme 1.** Reduction of 1,4-dichloro-1,4-diphosphinine **1** with $^nBu_3P$ to yield 1,4-diphosphinine **2**.

Single crystal X-ray diffraction analysis of **2 in good agreement with the calculated structure (see ESI)** reveals an all-planar tricycle having the $^n$propyl groups *trans*. Two molecules of **2** in the unit cell are oriented so that each independent 1,4-diphosphinine unit is facing the thiazole-2-thione unit of the neighbouring molecule. The interplanar distance of 3.595 Å indicates effective $\pi-\pi$ interactions. The P-C (P-C1 1.7390(15) Å, P-C3 1.7494(15) Å) and C-C bond lengths (1.406(2) Å) in the six-membered good agreement with the literature values for phosphinines[6e, 6f, 21] and benzene (1.397 Å),[22] respectively, suggesting a high degree of aromaticity in **2**.
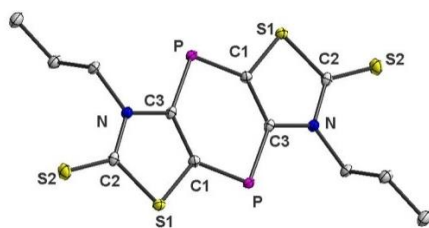
**Figure 2.** Displacement ellipsoids plot (50% probability) of molecular structure of **2** in the solid state. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) P-C1 1.7390(15), P-C3 1.7494(15), C1-C3 1.406(2), C1-P-C3 100.02(7).

According to the calculated NICS(1) values (M06-2X/6-311+G**) all three rings of **2'** (the notation **'** stands for using Me substituents instead of $^nPr$) are aromatic, but the central 1,4-diphosphinine moiety (NICS(1) = −8.8) is more aromatic than the outer rings (NICS(1) = -4.9) (cf. benzene −12.8).[23] Strong absorption in the UV/Vis spectrum of **2** is observed in dichloromethane solution ($\lambda_{max}$ = 497 nm). This value is found to be in a very good agreement with the TD DFT calculated 502 nm (B3LYP/6-311+G**//M06-2X-6-311+G** for **2'**), which is

basically the HOMO($\pi$)–LUMO($\pi$*) transition (Figure S4 in the ESI), with high transition probability (Table S4 in ESI).

Solution voltammetry on **2** in THF/[nBu$_4$N][PF$_6$] at Pt (Fig. 3) and Au working electrodes identifies two central reduction processes that are very closely spaced ($E_p^c$(2) = -1.28 V and $E_p^c$(3) = -1.45 V vs. the ferrocene/ferrocenium redox couple,[24] hereafter Fc$^{+/0}$) and are not electrochemically reversible. Nevertheless, return peaks $E_p^a$(3) and $E_p^a$(2) are observed and the general appearance of the solid trace (——) in Fig. 3, including off-set re-oxidation $E_p^a$('), is constant over multiple cycles and variation in scan rates from 0.1–1.0 V·s$^{-1}$, except that the re-oxidation peak $E_p^a$('') increases in intensity with slower scanning but loses intensity with multiple cycles that do not go negative of the starting potential.

Oxidation process $E_p^a$(1) is irreversible at +0.70 V vs. Fc$^{+/0}$ and no further processes can be observed before the solvent limit is reached (compound reactivity limits solvent selection.) There are also further reduction processes observable at much more negative potentials. (A detailed description of this complex behaviour is provided in the ESI).
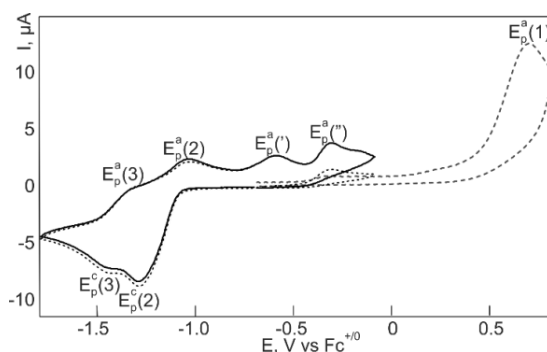
**Figure 3.** Composite CVs obtained on **2** 2.0 mM in THF (0.2 M [nBu$_4$N][PF$_6$], $v$ = 0.2 V·s$^{-1}$; scans start from o.c.p. = −0.69 V). (−−−) Anodic scan through E(1). (——) Cycle in cathodic direction through E(2,3); (·····) same but starting anodic.

The most important feature of the voltammetry is that $E_p^c$(2) and $E_p^c$(3) are at significantly *lower* potential than in **IV** (by 0.52 and 0.50 V). This is in full agreement with the calculated LUMO energies of the two compounds, which are −3.20 eV and −2.93 eV at B3LYP/6-311+G**(PCM:THF) − see Fig. S3 in the ESI. Also the M06-2X/6-311+G** (PCM:THF) anion and dianion is more stable for **2'** than for **IV'** by 0.30 and 0.44 eV, respectively (see Table S2 in the ESI).

To examine the scope of nucleophilic additions, we decided to test the well-known strong nucleophile ($^nBuLi$) and, by contrast, a rather weak nucleophile (KHMDS) (Scheme 2). Upon treatment of an ether suspension of **2** with $^nBuLi$ at −78 °C, a dark red solution was formed, and the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed two signals at $\delta$ = −59.1 and −21.1, assigned to the anionic (−59.1) and neutral (-21.1) phosphorus centers of product **3a**. Quenching of freshly prepared **3a** with $^nBuI$ at −78 °C led to an immediate color change from red to yellow. $^{31}P\{^1H\}$ NMR spectroscopic reaction monitoring indicated fast and clean conversion to **4a** (Scheme 2). The two signals in the $^{31}P\{^1H\}$ NMR spectrum of **4a** ($\delta$ = −44.1 and −38.3) are assigned to two isomers of **4a** which are isolated in good yields in a 2:1 ratio (see ESI). This outcome

represents a noteworthy contrast to a similar reaction sequence of 2,4,6-tri-$^t$Bu-1,3,5-triphosphabenzene (step 1, $^n$BuLi; step 2, MeI) that resulted in dialkylation of the *same* phosphorus atom yielding the corresponding $1\lambda^5,3\lambda^3,5\lambda^3$-triphosphabenzene derivative.[25] Noteworthy here is that the calculated energy difference between the (methyl analogue) of **4a'** and its mixed valence isomer ($1\lambda^5,4\lambda^3$-diphosphinine) reveals that the latter is less stable by 14.7 kcal/mol (M06-2X/6-311+G**).
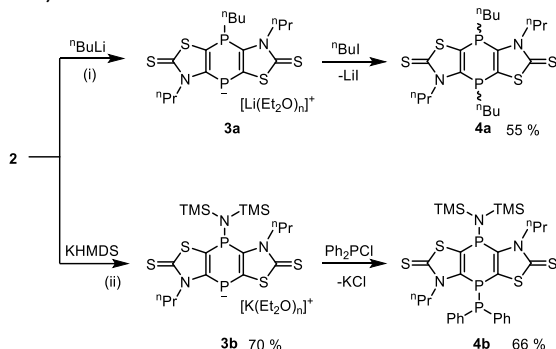


**Scheme 2.** Sequential addition of nucleophiles and electrophiles to 1,4-diphosphinine **2**.

In the second case, treatment of **2** with KHMDS in diethyl ether at ambient temperature resulted in a sequence of colour changes from red to green and, after a few minutes, to bright red. The appearance and subsequent fast disappearance of the green colour is likely to be attributed to the formation of an intermediate radical anion **2$^{•-}$**, which could form easily due to the low lying LUMO of **2**. In agreement with this assumption, the calculated TD-DFT spectra of the radical **2'$^{•-}$** suggests a green colour (Table S4 B3LYP/6-311+G**//M06-2X/6-311+G**). Finally, the bright red color can be attributed to the anion **3b** (for the TD DFT B3LYP/6-311+G**//M06-2X/6-311+G** excitation energies of **3b'** see Table S5). The $^{31}$P{$^1$H} NMR spectrum of the reaction mixture shows two rather broad singlets at −28.6 and 6.7 ppm, which can be assigned to the anionic and neutral phosphorus nuclei of product **3b**, respectively. Compound **3b** was isolated as a red powder in good yields (70%) if the solvent was removed rapidly. The negative ESI-MS experiment shows a peak at *m/z* 538.0453 (calc. 538.0451) which confirms the composition of the product as **3b**. A single crystal X-ray structure determination confirms the geometry but also the presence of three solvent molecules per unit cell. Within a 1D-coordination polymer, each potassium cation is coordinated to the thione sulfur centers of two neighbouring molecules and three solvent molecules (Fig. 3). Having the isolated ionic compound **3b** in hand, its reactivity was investigated starting with the reaction of Ph$_2$PCl, representing a rather common main group element electrophile (Scheme 2). Upon addition of Ph$_2$PCl to a freshly prepared, pre-cooled Et$_2$O solution of **3b** immediate colour change from red to yellow was observed. The $^{31}$P{$^1$H} NMR spectrum showed three signals of an ABM spin habitus with three different $J_{P,P}$ couplings, *i.e.,* -50.8 ppm (dd, $^1J_{P,P}$ = 294.2 Hz, $^4J_{P,P}$ = 15.9 Hz), 9.5 ppm (dd, $^1J_{P,P}$ = 294.2 Hz, $^3J_{P,P}$ = 18.4 Hz),

15.0 ppm (t, $^JJ_{P,P}$ = 17.1 Hz)}, thus also revealing that the $^3J_{P,P}$ and $^4J_{P,P}$ coupling constant magnitudes are very similar.

Compound **4b** was isolated in good yield (65%) after filtration.Crystals were grown for **4b** and characterized via single crystal X-ray analysis, will be discussed later. (for details see ESI, S2).
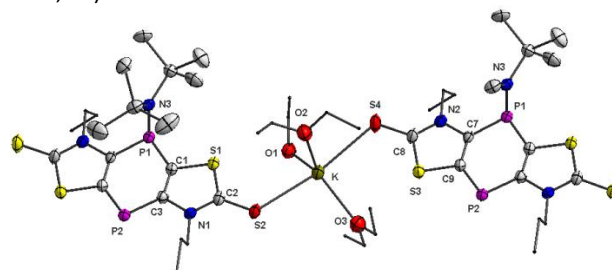


**Figure 3.** Displacement ellipsoids plot (50%) of the polymeric structure of **3b** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.807(4), P1-C7 1.805(4), P2-C3 1.776(4), P2-C9 1.777(4), C1-C3, 1.376(6), C7-C9 1.373(6), P1-N3 1.744(4). C1-P1-C7 95.24(19), C3-P2-C9 96.6(9).

An ethereal solution of **3b** was then treated with half an equivalent of elemental iodine at low temperature (−70 °C) resulting in an immediate color change from red to green and finally to yellow, suggesting a short-lived radical. Unfortunately, first attempts to achieve EPR characterization were not successful, but the calculated spin density distribution showed that the radical is localized mainly at the phosphorus atom (Figure S5). As in case of **4b** the *trans* isomer forms overwhelmingly, which suggests a rather strong directional effect of the N(SiMe$_3$)$_2$ moiety onto the incoming group. The final product **5** is isolated by dissolving the reaction mixture in toluene and filtering it via canula to remove the KI byproduct (for more details, see the SI). The $^{31}$P{$^1$H} NMR spectrum of **5** shows two sets of signals for a major (98 %) and a minor (2 %) isomer, which have been assigned to **5** {−42.1 ppm (t, $^{3/4}J_{P,P}$ = 20.1 Hz) −40.4 ppm (t, $^{3/4}J_{P,P}$ = 20.4 Hz), 17.9 ppm (t, $^{3/4}J_{P,P}$ = 20.2) 19.9 ppm (t, $^{3/4}J_{P,P}$ = 20.8)}.
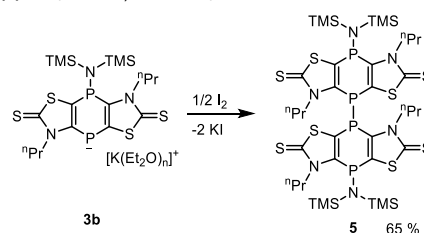


**Scheme 3.** Oxidation of mono anion **3b** with I$_2$ to generate **5**.

Single crystal X-ray diffraction studies of **4b** and **5** show very similar P-C bond lengths in the central 1,4-dihydro-1,4-diphosphinine rings. However, a slightly longer P1-P3 bond distance of 2.2893(7) Å is found in **5** (Fig. 5), compared to 2.246(6) Å in **4b**. Furthermore, one of the phenyl groups in **4b** is observed to have π−π interactions with the central 1,4-dihydro-1,4-diphosphinine ring on the same molecule. The molecular structure of **5** shows a dispersion forces inducated (see ESI) orientation of the two tricyclic units with a torsion angle of 60.5° between the P1-P3-C1 and P1-P3-C19 planes. It seems that dispersive forces are responsible for the observed arrangement of

substituents in **5'** (which is similar to that in **5**) since there was no sign of secondary orbital interactions in a second-order perturbation theory analysis made on the NBO basis.
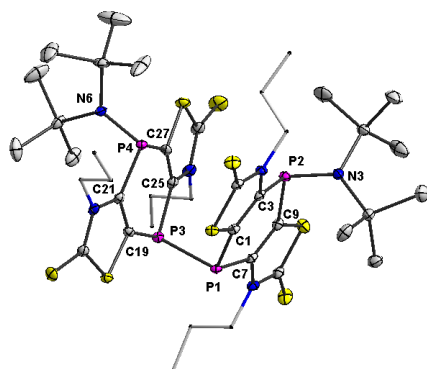


**Figure 5.** Displacement ellipsoids plot (50%) of the molecular structure of **5** in the crystal lattice. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.793(2), P1-C7 1.811(2), P1-P3 2.2893(7), P2-N3 1.7048(18), P2-C3 1.831(2), P2-C9 1824(2), C1-C3, 1.364(3). C1-P1-C7 99.43(9), C3-P2-C9 97.55(9), C1-P1-P3 101.64(7), P1-P3-C25 105.88(7).

In conclusion, a multigram scale synthesis of a new, sulfur-enriched tricyclic 1,4-diphosphinine was described. The key property of the 1,4-diphosphinine is its high electrophilicity as revealed by cyclic voltammetry and DFT calculations. Accordingly, reactivity studies with nucleophiles show interesting differences to phosphinines and the first stable anionic 1,4-diphosphinine derivative was obtained via reaction with the weak anionic nucleophile KHMDS. It was illustrated that the latter represents an interesting starting material for selective 1,4-disubstitution or for oxidation to give a P-P coupling product.

## Acknowledgements

## Conflicts of interest

There are no conflicts to declare.

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