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Phosphorus Heterocycles

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Redox-Triggered Reversible Interconversion of a Monocyclic and a Bicyclic Phosphorus Heterocycle**

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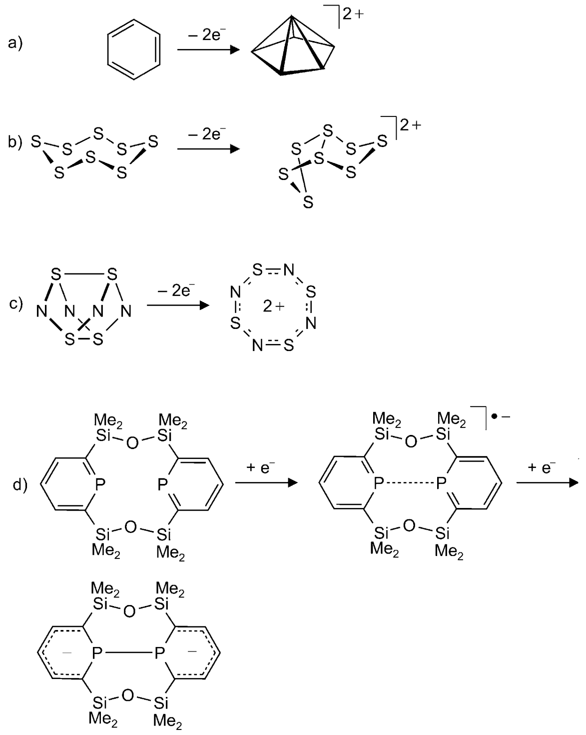
In memory of Pascal Le Floch

Abstract: *Molecules which change their structures significantly and reversibly upon an oxidation or reduction process have potential as future components of smart materials. A prerequisite for such an application is that the molecules should undergo the redox-coupled transformation within a reasonable electrochemical window and lock into stable redox states. Sodium phosphaethynolate reacts with two equivalents of dicyclohexylcarbodiimide (DCC) to yield an anionic, imino-functionalized 1,3,5-diazaphosphinane [**3a**]$^-$. The oxidation of this anion with elemental iodine causes an intramolecular rearrangement reaction to give a bicyclic 1,3,2-diazaphospholenium cation [**6**]$^+$. This umpolung of electronic properties from non-aromatic to highly aromatic is reversible, and the cation [**6**]$^+$ is reduced with elemental magnesium to reform the 1,3,5-diazaphosphinanide anion [**3a**]$^-$. Theoretical calculations suggest that phosphinidene species are involved in the rearrangement processes.*

Selected archetypical examples for redox processes which are accompanied by significant structural changes[1] are shown in Scheme 1. The two-electron oxidation of the delocalized π-system of benzene forms the dication $[C_6H_6]^{2+}$, which converts to a Wade–Mingos cluster with a nido-structure (Scheme 1a). While this dication has not been directly observed in the gas phase,[2,3] the $[S_8]^{2+}$ ion, with a rather weak *trans*-annular S–S bond, can be formed from the two-electron oxidation of the non-bonding electron pairs of S_8 and has been isolated and structurally characterized (Scheme 1b).[4] In addition, the two-electron oxidation of the cage compound S_4N_4 forms the planar aromatic dication $[S_4N_4]^{2+}$ (Scheme 1c).[5] Although π-conjugated heterocycles with low-valent phosphorus centers in the ring skeleton[6a] have potential as candidates to study redox-promoted structural changes because of their expected relatively low oxidation potentials,[6b] they have been little investigated. A rare example is the reductive annulation reaction of siloxy-bridged diphosphinines which was observed by Le Floch et al. (Scheme 1d).[6c] Remarkably, the one-electron reduced intermediate with a 2-center-1-electron bond could be fully characterized. However, the chemical reversibility of these oxidation or reduction processes was not reported for any of these examples.



Scheme 1. Examples of molecules in which structural changes are promoted by two-electron oxidation or reduction processes.

Herein, we describe the chemically reversible redox-induced annulation of a monocyclic phosphide anion to a bicyclic phosphenium cation, which involves the making and breaking of four bonds. These heterocycles were prepared using simple, easily accessible chemicals, and relatively mild reagents were used for the oxidation (I_2, $E°[I_2/2I^-] = 0.54$ V vs NHE; NHE = normal hydrogen electrode) and reduction processes (Mg, $E°[Mg^{2+}/Mg] = -2.36$ V vs NHE).[7]

When $[Na(OCP)\cdot(dioxane)_x]$ (**1**; $x \approx 2.5$, abbreviated as Na(OCP) herein)[8] and carbodiimides **2a–c** were allowed to react in a 1:2 ratio in THF, a clean reaction occurred in each case to yield one product [**3a–c**]$^-$. Products **3a–c** show a singlet resonance in their ^{31}P NMR spectra ([**3a**]$^-$ $\delta =$

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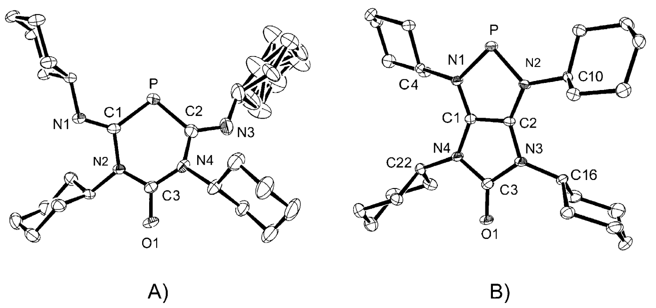
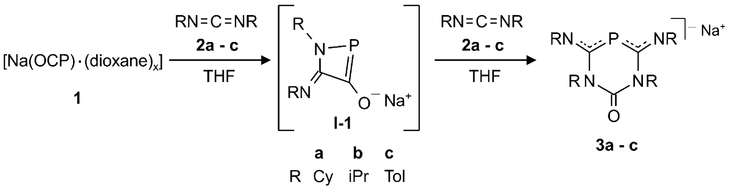


Figure 1. A) ORTEP plot of Na[**3a**]·(THF)$_4$ (thermal ellipsoids set at 50% probability). Hydrogen atoms, the sodium counterion and THF molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P-C1 1.802(2), P-C2 1.798(2), C2-N4 1.445(3), N4-C3 1.374(3), C3-O1 1.245(3), C3-N2 1.365(3), N2-C1 1.441(2), C1-N1 1.286(3), C2-N3 1.280(3); C1-P-C2 98.7(1), P-C2-N4 119.7(2), C2-N4-C3 121.8(2), N4-C3-N2 119.7(2), C3-N2-C1 123.1(2), N2-C1-P 118.2(1); B) ORTEP plot of [**6**][I$_3$] (thermal ellipsoids set at 50% probability). Hydrogen atoms and the triiodide counterion have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P-N1 1.699(3), N1-C1 1.354(4), C1-N4 1.381(4), N4-C3 1.411(4), C3-O1 1.217(4), C3-N3 1.409(4), N3-C2 1.374(5), C2-N2 1.360(5), N2-P 1.707(3), C1-C2 1.379(5), N1-C4 1.502(4), N2-C10 1.495(4), N3-C16 1.490(4), N4-C22 1.481(4); N1-P-N2 90.6(2), C1-N1-P 112.2(2), C2-N2-P 112.0(2), C1-N4-C3 107.1(3), N3-C3-N4 107.3(3).

−44.2 ppm; [**3b**]$^-$ $\delta = -49.3$ ppm; [**3c**]$^-$ $\delta = -53.7$ ppm). Further spectroscopic analyses and in particular, a single-crystal X-ray diffraction structure of Na[**3a**] (Figure 1 A), reveal that these compounds are the sodium salts of anionic 4,6-diimino-1,3,5-diazaphosphinan-2-ones (Scheme 2).



Scheme 2. Formation of the six-membered heterocyclic anion [**3a–c**]$^-$. Reaction temperatures used in the formation of [**3a**]$^-$ and [**3b**]$^-$: 80 °C, [**3c**]$^-$: 25 °C. Cy = cyclohexyl (C_6H_{11}), *i*Pr = isopropyl (C_3H_7), Tol = *p*-tolyl (4-CH_3-C_6H_4).

We assume that the four-membered heterocycle [**I-1**]$^-$ is an intermediate in this reaction, although it was not observed. However, Jupp and Goicoechea recently reported the formation and isolation of a closely related [2+2] adduct between [K([18]crown-6)](OCP) and the bulky bis(2,6-diisopropylphenyl)carbodiimide (DippN=C=NDipp).[9] Theoretical calculations were used to elucidate the reaction mechanism and the minimum-energy reaction pathway (MERP) for the reaction between Na(OCP) and dimethylcarbodiimide (**2′**; 2 equiv), used as the model compound (Figure 2).[10]

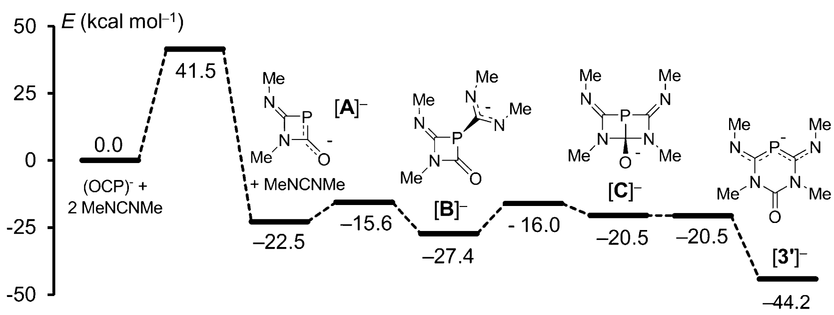
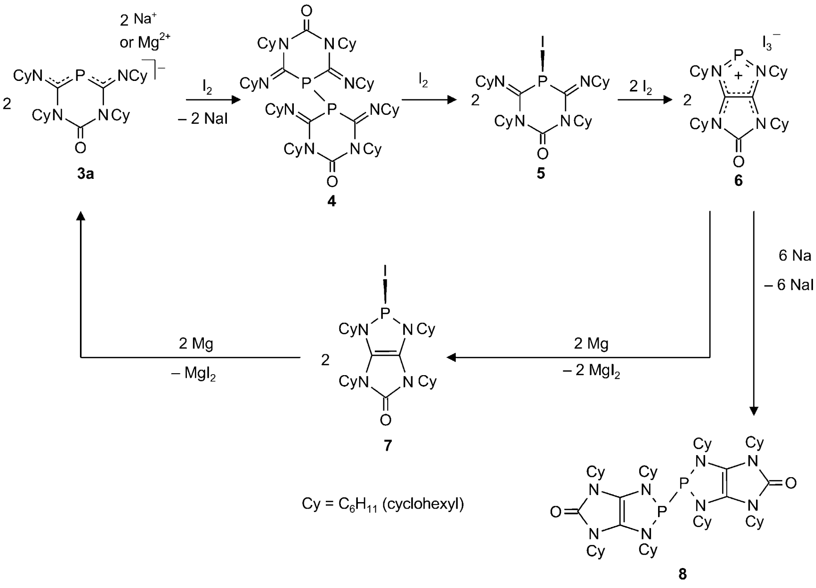


Figure 2. MERP of the reaction between Na(OCP) and dimethylcarbodiimide (**2′**; 2 equiv) to form [**3′**]$^-$ at the CBS-QB3 level. Na$^+$ ions were included in the computations but are not shown.

The anionic heterocycle [**A**]$^-$ forms in an exothermic [2+2] cycloaddition reaction in the first reaction step. Subsequently, the nucleophilic phosphorus center of [**A**]$^-$ attacks the central carbon atom of a second carbodiimide molecule **2′** to give adduct [**B**]$^-$. Through an intramolecular nucleophilic attack of one of the nitrogen centers of the exocyclic MeNCNMe moiety on the carbonyl-carbon atom, [**B**]$^-$ undergoes a rearrangement to form the Dewar-benzene-type intermediate [**C**]$^-$. Finally, product [**3′**]$^-$ is formed in an essentially barrierless reaction step. After the formation of [**A**]$^-$, the reaction profile is shallow (all activation barriers below 10 kcal mol^{-1}), which explains why no intermediates were observed and [**A**]$^-$ immediately reacts to form the final product [**3′**]$^-$. Only the formation of [**A**]$^-$, the rate-determining step, requires a rather high activation energy (41.5 kcal mol^{-1}). This is in agreement with the experimental conditions, in which elevated temperatures and longer reaction times are required with the alkyl-substituted carbodiimides **2a**,**b**. Note that the formation of the aryl-substituted Na[**3c**] proceeds at room temperature, in agreement with the results of calculations on the reaction between Na(OCP) and diphenylcarbodiimide. In this case, the activation barrier of the [2+2] cycloaddition is remarkably lower (14.3 kcal mol^{-1}) than in the case of [**3′**]$^-$.

The anion in Na[**3a**] shows an irreversible oxidation peak at $E_{\text{peak,ox}} = -0.78$ V versus the ferrocenium/ferrocene couple (Fc$^+$/Fc; Fc = [(η-$C_5H_5)_2$Fe]) in THF as solvent.

With stoichiometric amounts of oxidizing reagents, such as ferrocenium hexafluorophosphate or trityl chloride, Na-[**3a**] is converted into the diphosphane **4** ($\delta(^{31}P) = -84.8$ ppm). Compound **4** is EPR silent and shows no indication of dissociation into radicals up to 323 K.[11] Upon titration of a solution of 1,3,5-diazaphosphinanide Na[**3a**] in THF with small portions of iodine as oxidant, diphosphane **4** is formed as the first product (Scheme 3). Further addition of I_2 cleaves the P–P bond[12] to give the iodophosphane **5** ($\delta(^{31}P) = -87.4$ ppm). Addition of another equivalent of iodine as a weak Lewis acid causes the heterolytic dissociation of the P–I bond[13] in **5** to cleanly afford the final product [**6**][I$_3$]. The ^{31}P NMR spectrum of [**6**][I$_3$] is remarkably different, with the ^{31}P resonance appearing at $\delta = 196.3$ ppm. The shift of resonance signal indicates a substantial structural change with respect



Scheme 3. Oxidation of Na[**3a**] with iodine to form [**6**][I_3] and reduction of [**6**][I_3] with Mg to regenerate anion [**3a**]$^-$. The reduction of [**6**][I_3] with Na leads to the diphosphane **8**.

to Na[**3a**], **4**, and **5**. A single crystal X-ray diffraction study (Figure 1b) allowed us to characterize the product as the annulated 1,3,2-diazaphospholenium cation [**6**]$^+$ with triiodide, [I_3]$^-$, as the counteranion.

Using elemental sodium or potassium as the reductant, the reduction of [**6**]$^+$ ($E_{\text{peak,red}} = -1.84$ V vs Fc^+/Fc) leads to the formation of the diphosphane **8** ($\delta(^{31}\text{P}) = 122.7$ ppm).[12,14] Further reduction with these strong reagents yielded only small amounts of anion [**3a**]$^-$ along with a black precipitate, which we could not characterize. Cation [**6**][I_3] was cleanly reduced using magnesium turnings to the magnesium salt of anion [**3a**]$^-$ (Scheme 3). Monitoring the reaction by ^{31}P NMR spectroscopy revealed the formation of resonance signals due to the bicyclic P-iododiazaphospholene **7** ($\delta(^{31}\text{P}) = 186.7$ ppm) as an intermediate, while there was no evidence for the formation of bis(diazaphosphane) **8**.

The structures of Na[**3a**]·$(\text{THF})_4$ and [**6**][I_3] were determined by single-crystal X-ray diffraction[15] and the anion [**3a**]$^-$ and cation [**6**]$^+$ are displayed in Figure 1A and B, respectively. Both compounds can be described as close-contact ion pairs with cation–anion interactions of less than 4 Å (see Supporting Information). The six-membered ring of the anionic 1,3,5-diazaphosphinane ring [**3a**]$^-$ is not planar and has a maximum deviation from planarity of 0.254 Å.[16] In [**3a**]$^-$, the P−C bond lengths (1.802(2), 1.798(2) Å) and C=N bond lengths (1.286(3), 1.280(3) Å) indicate π-delocalization within the N=C−P−C=N moiety resulting from donor–acceptor interactions between the out-of-plane phosphorus lone-pair and the π*(C=N) orbitals. The two fused five-membered rings in [**6**]$^+$ are coplanar. The bond lengths in the C_2N_2P ring of cation [**6**]$^+$ are very similar to those of known 1,3,2-diazaphospholenium cations, for example in 1,3-dicyclohexyl-1,3,2-diazaphospholenium triiodide.[17] The endocyclic C−N bond lengths (1.354(4)–1.381(4) Å) are significantly shorter than the exocyclic ones (1.481(4)–1.502(4) Å) and together with the slightly elongated central C=C bond (1.379(5) Å), indicate extensive π-conjugation within both five-membered rings.

Both heterocycles [**3a**]$^-$ and [**6**]$^+$ are further stabilized by extensive charge alternation because of the electronegativity differences between the neighboring atoms. This is illustrated in Figure 3, which shows the molecular electrostatic potential maps and computed natural partial charges for the model species [**3′**]$^-$ and [**6′**]$^+$ (Cy groups replaced with Me substituents).[10] The extent of π-conjugation and the associated electronic structure is very different in heterocycles [**3′**]$^-$ and [**6′**]$^+$. The six-membered ring in the anionic 1,3,5-diazaphosphinane ring [**3′**]$^-$ is non-aromatic as indicated by the small negative value of the nucleus independent chemical shift 1 Å above the ring center (NICS(1) = −1.5 ppm at the B3LYP/6-311 + G** level, for further NICS values see the Supporting Information).[18] On the other hand, the PN_2C_2 diazaphospholenium moiety in cation [**6′**]$^+$ shows a significant aromatic delocalization with a computed NICS(1) value of −8.1 ppm. The annulated C_2N_2(CO) fragment is less aromatic (NICS(1) = −5.7 ppm).[19]

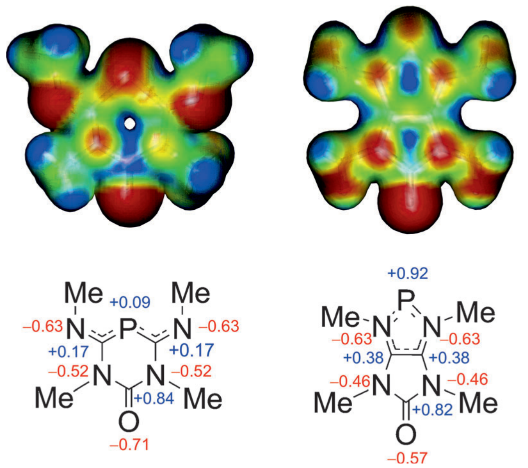


Figure 3. Molecular electrostatic potential maps and partial charges of ions [**3′**]$^-$ (left) and [**6′**]$^+$ (right) at the B3LYP/6-311 + G** level.

Computations with model compounds[10] (Cy groups replaced by Me substituents) were performed to gain insight into the rearrangement of [**3a**]$^-$ to form [**6**]$^+$ and the backward process ([**6**]$^+$→[**3a**]$^-$). As iodophosphane **5**, the final intermediate to [**6**]$^+$, has the monocyclic structure of the starting material [**3**]$^-$, we assume that the rearrangement to [**6**]$^+$ takes place within a cation such as [**D**]$^+$. Equally, because the iodophosphane **7**,[20] as a possible direct precursor to [**3a**]$^-$, still has a bicyclic structure, we propose that the diazaphospholenide anion [**G**]$^-$ undergoes the rearrangement to form the monocycle [**3′**]$^-$ as model for [**3a**]$^-$ (see Figure 4). The first step in the rearrangement of the free ion [**D**]$^+$

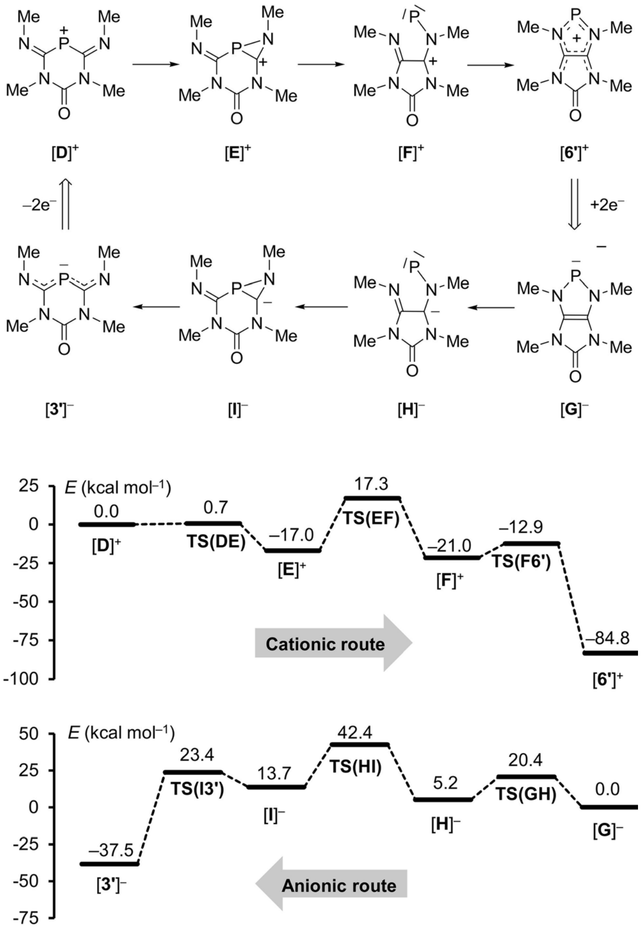


Figure 4. Possible rearrangement processes leading to [6′]$^+$ and [3′]$^-$, and calculated relative energies (ΔE, kcal mol^{-1}) compared to [D]$^+$ and [G]$^-$, respectively, at the CBS-QB3 level.[10] TS = transition state.

involves an exothermic ring closure to the annulated azaphosphirane [**E**]$^+$. Given the remarkably low activation barrier, this cyclization should proceed almost spontaneously. The subsequent transformation from [**E**]$^+$ to the amino phosphinidene[21] [**F**]$^+$ has the highest activation barrier and is the rate-determining step. The strongly exothermic cyclization of [**F**]$^+$ to the [**6′**]$^+$ ion completes the rearrangement and provides the thermodynamic driving force for this process.

After the two-electron reduction of [**6′**]$^+$ (experimentally achieved through the formation of iodophosphane **7**), the anion [**G**]$^-$ is the starting point for the rearrangement sequence leading to anion [**3′**]$^-$ (Figure 4). This process is remarkably similar to the formation of [**6′**]$^+$ from [**D**]$^+$. The structures of anionic amino phosphinidene [**H**]$^-$ and anionic bicyclic azaphosphirane [**I**]$^-$ are analogous to those of [**F**]$^+$ and [**E**]$^+$, respectively. The rearrangement of the phosphinidene intermediate [**H**]$^-$ to [**I**]$^-$, which involves the cleavage of the central C−C bond, is the rate-determining step. In the final step, the three-membered azaphosphirane ring is opened and the monocyclic anion [**3′**]$^-$ is obtained in a strongly exothermic reaction ($\Delta_r E = -37.5$ kcal mol^{-1}). Although this computation is valid for the isolated ions in the gas phase only, the species encountered along the MERP are reasonable intermediates and no unrealistically high barriers were found.[10]

In summary, a simple and straight-forward synthesis of anionic and cationic phosphorus heterocycles using Na(OCP) as the phosphorus building block has been discovered. Using iodine and magnesium as relatively mild two-electron oxidative and reductive switches, the heterocycles can be mutually interconverted. Remarkably, the anion [**3**]$^-$ ($E_{\text{peak,ox}} = -0.78$ V) and the cation [**6**]$^+$ ($E_{\text{peak,red}} = -1.84$ V) are thermodynamically stable redox states and do not react with each other. In addition to the substantial structural change from the monocyclic anion [**3**]$^-$ to the bicyclic cation [**6**]$^+$, a significant change of the electronic structure from linearly N=C−P−C=N-conjugated and non-aromatic [**3**]$^-$ to strongly delocalized and aromatic [**6**]$^+$ is achieved. This explains why both structures—the reduced [**3**]$^-$ and oxidized [**6**]$^+$—are stable and coexist in solution, making them potentially interesting for application in materials. Given that carbodiimides, RN=C=NR, can be prepared with a broad range of substituents R, the redox-active phosphorus heterocycles introduced here as prototypes may be envisioned as components for functional materials.

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[15] CCDC 980820 ($\mathrm{Na}[\mathbf{3a}]\cdot(\mathrm{THF})_4$) and 980821 ($[\mathbf{6}][\mathrm{I}_3]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] The non-planarity results from steric interactions between the bulky Cy-substituents. The computed structure, with R = H instead of R = Cy, is planar.

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[20] The reduction of halophosphanes to phosphides with alkaline and alkaline-earth metals is well established, see Ref. [12].

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