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Synthesis of Azaphosphinines by Directed Inverse Electron Demand Hetero-Diels-Alder Reactions with Na(OCP)

Max M. Hansmann*

Abstract: Herein, a straightforward synthetic approach towards azaphosphinines is reported. The synthesis of 1,3- and 1,4-aza-λ^3-phosphinines as well as 1,2,4-diaza-λ^3-phosphinines by inverse electron demand hetero-Diels-Alder reactions of sodium 2-phosphaethynolate [NaOCP] with triazines and tetrazines is studied. In the case of 1,2,4-triazines a hetero-D.A. reaction was developed which relies on a new directing group approach based on the complexation of sodium to form an ionic Do->Na-OCP tether. The first X-ray characterization data for aza-λ^3-phosphinines as well as the first phosphinine triflates are presented.

λ^3-Phosphinines (**I**), the higher homologs of pyridines, first synthetized by Märkl in 1966,[1] have found various applications ranging from ligands, due to their excellent π-acceptor abilities, to applications in material science.[2] Based on the analogy between pyridine and phosphinine, the mixed six-membered N/P heteroaromatic systems, the aza-phosphinines, have been much less investigated and remain a lab curiosity, presumably a result of their challenging synthetic access. Shortly after the discovery of phosphinines, Märkl described the first synthesis of a 1,4-aza-λ^3-phosphinine (**II**) by flash vacuum thermolysis (Figure 1).[3] Besides an additional single example by Regitz in 1990,[4] the 1,4-aza-λ^3-phosphinine scaffold and its reactivity remained unexplored.[5] Furthermore, there have been only two reports on the synthesis of 1,3-aza-λ^3-phosphinines such as **III** starting from 1,3-azapyrylium compounds[6] or an amino-phosphaalkyne.[7] While 1,2-aza-λ^5-phosphinines have found applications in material science,[8] only very few 1,2-aza-λ^3-phosphinines such as **IV** were synthesized by flash vacuum pyrolysis,[9] or from 1,3,2-diazaphosphinine.[10] Considering the importance of N and P-heterocyclic compounds, it seems remarkable that no coordination complex or X-ray structure has been reported for any isomer of the aza-λ^3-phosphinine.

The phosphaethynolate anion [PCO]$^-$ first described as its lithium salt in 1992 by Becker et al.,[11] remained unexplored until the recent novel one-step preparation.[12] Since then NaOCP has found applications in the synthesis of a range of previously unknown phosphorus heterocycles,[13] such as **V**,[14] **VI**,[15] **VII**,[16] or **VIII**.[17] Importantly, Grützmacher et al. could show that the reaction of α-pyrone with NaOCP at 60°C affords the sodium salt of 2-phosphininol (**V**) with concurrent loss of carbon dioxide.[14a]

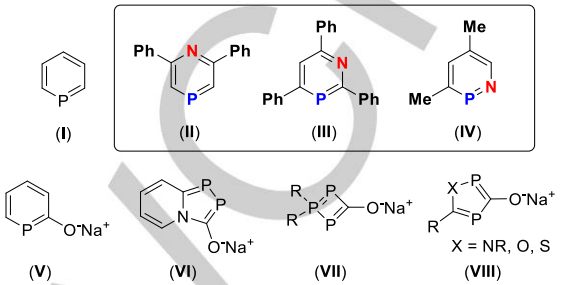
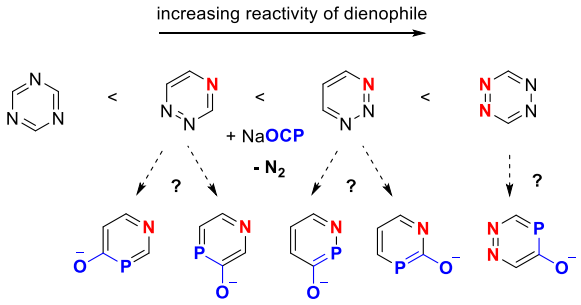


Figure 1. Phosphinine (**I**), literature known examples of aza-λ^3-phosphinines (**II-IV**) as well as P-heterocycles derived from NaOCP (**V-VIII**).

This approach raised my interest in the synthesis of novel phosphorus ligands, namely azaphosphinines, by an inverse electron demand hetero-Diels-Alder (D.A.) reaction with subsequent retro-D.A. under loss of N_2. Note, during the preparation of this manuscript, Grützmacher et al. reported one example of a phosphanaphthalene via N_2 elimination, however, the synthesis requires reaction times over several weeks to months at 80°C.[18] For accessing azaphosphinines triazines and tetrazines should be ideal starting materials as they are electron-deficient, known to undergo inverse electron demand hetero-D.A. reactions with electron rich partners.[19] Depending on the regioselectivity, the reaction of NaOCP with the three isomers of triazines, as well as tetrazines should lead to a variety of new azaphosphinines (Scheme 1). Herein a straightforward synthesis of some of these new heterocycles utilizing NaOCP is presented.



Scheme 1. Targeted approach towards aza-phosphinines via hetero-D.A.

In the following aza-dienophiles are studied in the order of increasing reactivity. While ^{31}P {^{1}H} NMR spectroscopy at room temperature indicated no reaction between 3,5,6-triphenyl-1,2,4-triazine (**1a**) with NaOCP in THF, elevated temperatures (90°C; the reaction was performed in a closed pressure tube with large headspace volume) and prolonged reaction times (5 days) led to the generation of two new compounds with their ^{31}P {^{1}H} NMR resonances at δ = 178 and 123 ppm in a 4:1 ratio (Scheme 2). Both compounds were assigned based on ^{31}P {^{1}H} NMR as a mixture of 1,4 (**2a**) and 1,3-azaphosphinines (**3a**) compared to

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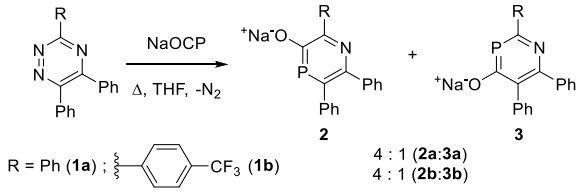
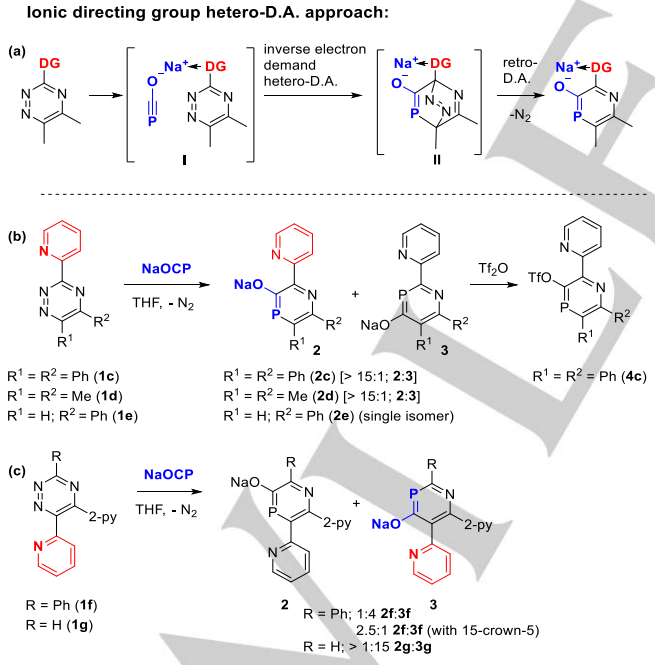
calculated data. DFT calculations of **2a** and **3a** at the GIAO-PBE1PBE/6-311G(2d,2p)//B3LYP-D3BJ/def2-TZVP level[20] predict ^{31}P {^{1}H}: δ = 194 ppm (**2a**) and 137 ppm (**3a**) in good agreement with the experimental data. Calculations indicate no significant difference in thermodynamic product stabilities between 1,4 and 1,3-regioisomers, slightly favoring the 1,3-azaphosphinine **3a** by 1.7 kcal/mol (B3LYP-D3BJ/def2-TZVP; *vide intra*). As the reaction proceeded very slowly and reaction times > 4d were required, we investigated enhancing the reactivity by increasing the electron-deficiency of the triazine. Indeed, 1,2,4-triazine **1b** featuring a *para*-CF_3 group reacts faster with NaOCP (4 days at 65°C) but still leads to a poor regioselectivity [4:1 mixture: ^{31}P {^{1}H}: δ = 185/130 ppm].[21]



Scheme 2. Synthesis of aza-λ^3-phosphinines from 1,2,4-triazines.

As a result of the poor regioselectivity and reactivity a directed D.A. approach was investigated. The interaction of the sodium cation with a nitrogen directing group was planned to generate an ionic tether group **I** [py-Na-OCP] thereby increasing rate and selectivity for the generation of the transient diazaphospha-barrelene **II** (Scheme 3a).



Scheme 3. Transient ionic [donor-Na-OCP] tether strategy for the inverse electron demand D.A. reaction of 1,2,4-triazines.

Indeed **1c** and **1d** featuring an *ortho*-pyridine directing group react with NaOCP at a dramatically higher reaction rate (14-16h at 60°C) and excellent selectivity (> 15:1) leading to sodium salts **2c** and **2d** [^{31}P {^{1}H} NMR: δ = 193.2 (**2c**); 192.8 ppm (**2d**)]. Note, typically inverse electron D.A. reactions of triazines require harsh conditions and are poorly regioselective.[22] Interestingly, switching to **1e** further boosts the reaction rate (< 30 min at rt) and selectivity to give **2e** as single isomer. The proton in the 1,4-azaphosphinine **2e** shows a large $^{3}J_{HP}$-coupling constant [^{1}H NMR (d_8-THF): δ = 8.85 ppm (d, $^{3}J_{HP}$ = 31 Hz)]. The ^{13}C for the 3-oxo carbon is at δ = 201.1 ppm (d, J_{CP} = 44 Hz) significantly downfield shifted compared to the other three carbon atoms in the heterocycle [δ [ppm]: 147.2 (d, J_{CP} = 53 Hz), 145.0 (d, J_{CP} = 19 Hz), 141.3 (d, J_{CP} = 13 Hz)], indicating a partial phospha-acyl contribution and disruption of the aromaticity (*vide infra*). The ^{1}H-^{15}N HMBC spectrum allows assignment of the nitrogen atoms: ^{15}N δ = -82.7 (pyridine) and -65.8 ppm (1,4-azaphosphinine; **2e**); -83.2 and -56.4 ppm (**2d**).[23] In case of **2d** it was possible to grow single crystals suitable for X-ray diffraction (Figure 2).[24]

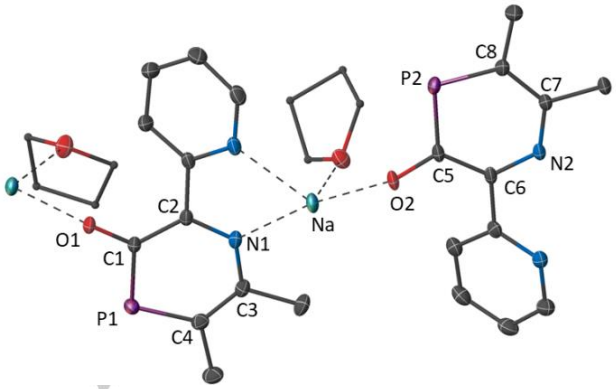


Figure 2. X-ray solid state structure of **2d**. Ellipsoids are drawn at the 50% probability level. Selected bond parameters in [Å] and [°]: P1-C1 1.770(2); C1-C2 1.442(2); C2-N1 1.342(2); N1-C3 1.339(2); C3-C4 1.399(2); C4-P1 1.731(2); C1-O1 1.288(2); P2-C5 1.769(2); C5-C6 1.437(2); C6-N2 1.344(2); N2-C7 1.341(2); C7-C8 1.399(2); C8-P2 1.726(2); C4-P1-C1 102.83(8); C2-N1-C3 124.6(1).

In the solid-state **2d** contains two independent molecules in the unit cell, forming a polymer bridged by sodium cations in between the 1,4-azaphosphinin-3-olate and the bipyridine moieties. Interestingly, C1-P1 [1.770(2) Å] is elongated compared to P1-C4 [1.731(2) Å], reflecting some contribution of the acyl/ketone resonance structure. Furthermore, the six-membered ring is slightly distorted from the planar geometry [deviation of C1 from the least-square plane by 0.062(1)Å]. While, previously it was shown that 2-oxo-phosphinine (**V**) could be alkylated and protonated,[14a] we were curious to transform the oxolate-moiety into a leaving group by triflation. Note, phosphinine derived triflates are unknown compounds, which however, should be valuable precursors for applications in cross-coupling chemistry.[25] Indeed, sodium salt **2c** reacts with Tf_2O to afford the corresponding triflate, indicated by a downfield shifted ^{31}P {^{1}H} NMR signal with fluorine coupling [**2c**: δ = 219.3 ppm (q, J_{PF} = 20 Hz)]. Upon triflation the "acyl"-carbon atoms shifts from δ = 201.4 ppm into a more typical aromatic region [δ = 172.1 ppm (d, J_{CP} = 54 Hz)]. Importantly, it was possible to obtain single crystals of triflate **4c** (Figure 3).[24] In comparison to **2d** the heterocyclic core in **4c** is highly symmetrical and planar [max. derivation from the least-square plane 0.024(1)] with equal C-P [1.732(2) vs. 1.733(2)] and similar C-N [1.345(2) vs.

1.339(2)] bond lengths, while the C-O bond elongates upon triflation [1.288(2) (**2d**) vs. 1.436(2) (**4c**)].

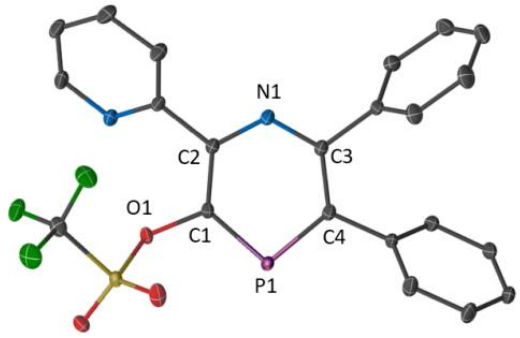


Figure 3. X-ray solid state structure of **4c**. Ellipsoids are drawn at the 50% probability level. Selected bond parameters in [Å] and [°]: P1-C1 1.732(2); C1-C2 1.399(2); C2-N1 1.345(2); N1-C3 1.339(2); C3-C4 1.411(2); C4-P1 1.733(2); C1-O1 1.436(2); C4-P1-C1 98.70(7); P1-C1-C2 127.2(1); C1-C2-N1; C3-C4-P1 123.2(1).

Importantly, upon reaction of NaOCP with **1f**, featuring a pyridine directing group in 6- instead of the 3-position, at 60°C the previously observed > 15:1 regioselectivity inverted to a 1:4 ratio [^{31}P {^{1}H} NMR: δ = 183: 138 ppm] favoring the 1,3-azaphosphinine (Scheme 3c). Notably, **1g** containing a H-atom at the 3-position, reacts selectively (> 15:1) and fast (3h at rt) to give the 1,3-azaphosphinine **3g** (^{31}P {^{1}H} NMR: δ = 148.3 ppm). The proton shows a large P-coupling constant [^{1}H NMR: δ = 9.73 ppm (d, $^{2}J_{HP}$ = 51 Hz)], while both ^{13}C NMR signals adjacent to phosphorus are downfield shifted [210.1 ppm (d, J_{CP} = 46 Hz), 185.1 ppm (d, J_{CP} = 70 Hz)]. The ^{15}N NMR for the 1,3-azaphosphinine (δ = -90.5 ppm) is downfield shifted by 25-34 ppm compared to the 1,4-isomers. To support the idea of the ionic tethered hetero-D.A. the reaction to form **3f** was performed under identical conditions but in the presence of 15-crown-5 inhibiting coordination of the sodium cation to the directing group. Indeed, a reversal in regioselectivity from 1:4 to 2.5:1 was observed, favoring the 1,4-azaphosphinine. In line with the tether strategy, DFT calculations show that the sodium cation features short (py)-Na-(OCP) distances in the transition state and in the diazaphospha-barrelene intermediate (Figure 4).

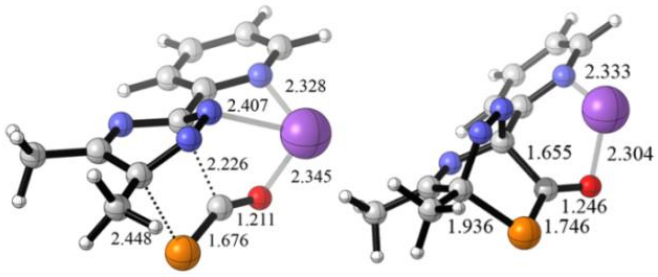
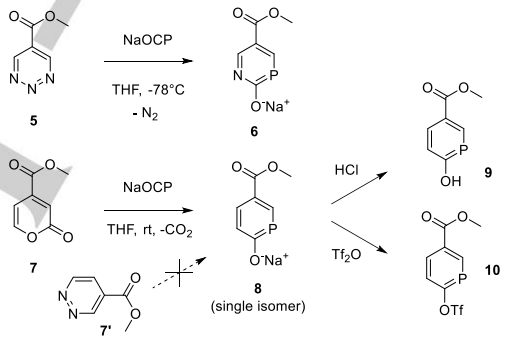


Figure 4. DFT-calculated structures for the transition state (left) and the .diazaphosphabarrelene intermediate (right) to form **2d**.

Compared to phosphinin-2-olate and its methylated derivative, introduction of nitrogen atoms has a significant influence on the charge distribution, dipole moment, as well as on the frontier orbitals (see Figure S1-2 in SI).[26] Calculated nucleus independent chemical shifts [NICS(1)][27] indicate a low aromaticity for all the sodium salts with a slight increase from phosphinin-2-olate (-4.8) to 1,3-azaphosphinin-4-olate (-5.0) to 1,4-azaphosphinin-3-olate (-5.2). Note, upon triflation or alkylation the NICS values are shifted by ca. 4-5 ppm indicating a large aromatic stabilization, although still lower than in pyridine.[28]

1,2,3-trazines are known to be more reactive dienophiles than 1,2,4-triazines.[29] Unfortunately, the reaction of NaOCP with the parent 1,2,3-triazine as well as 5-phenyl-1,2,3-triazine led to intense dark solutions with no new ^{31}P {^{1}H} NMR signal. However, the more reactive 1,2,3-triazine **5**, reacts with NaOCP at -78°C to turn from a yellow to a bright red solution with concurrent gas formation (Scheme 4). ^{31}P {^{1}H} NMR (δ = 123 ppm) indicates the formation of a single new product. Calculated NMR shifts clearly favor the 1,3-isomer (127 ppm) over the 1,2-isomer (278 ppm). Unfortunately, **6** shows poor solubility, however, ^{1}H NMR of a suspension in d_8-THF shows for the aromatic signals: δ [ppm] = 9.47 (dd, J = 32 Hz, 2.9 Hz), 8.57 (dd, J = 3.0 Hz, 2.9 Hz) in good agreement with **6**.



Scheme 4. Synthesis of 1,3-aza-phosphinine **6** and its analog without nitrogen.

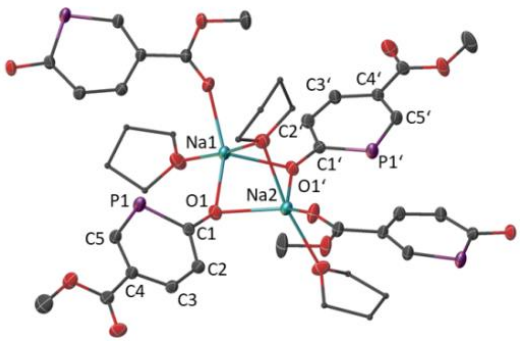
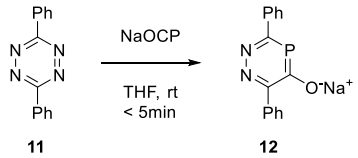


Figure 5. X-ray solid state structure of **8**. Ellipsoids are drawn at the 50% probability level. Selected bond parameters in [Å] and [°]: P1-C1 1.792(1); C1-C2 1.435(2); C2-C3 1.379(2); C3-C4 1.407(2); C4-C5 1.395(2); C5-P1 1.724(1); C1-O1 1.277(1); C5-P1-C1 101.79(5); P1-C1-C2 120.78(8); C4-C5-P1 126.70(8).

In order to compare the electronic structure of **6** with its non-aza derivative **8** the reaction of methyl coumalate (**7**) with NaOCP was studied. Notably, from the two potential regioisomers only **8** [^{31}P {^{1}H}: δ [ppm] = 149] is formed selectively and fast (<10 min at rt) and could be structurally characterized (Figure 5).[24] In the solid-state structure two

sodium cations are bridged between the phosphinin-2-olate and the ester moieties forming a polymeric network. Note, the reaction of NaOCP with pyridazine derivative **7'** does not lead to **8**. Sodium salt **8** can be protonated (**9**) or triflated (**10**). Interestingly, both compounds are remarkably stable and can be purified by column chromatography in air.

1,2,4,5-tetrazines are known to be superiorly suited for inverse electron demand D.A. reactions.[30,31] Upon addition of NaOCP to a solution of 1,2,4,5-tetrazine **11** the instant formation of a gas is detected with a color change from pink to orange (Scheme 5). ^{31}P {^{1}H} NMR spectroscopy indicates a clean and rapid (< 10min) reaction to a new compound [^{31}P {^{1}H}: δ = 130 ppm]. An X-ray diffraction study proved it to be the sodium salt of 1,2,4-diazaphosphinin-5-olate (**12**), a previously unknown heterocycle (Figure 6).[31,32] In the solid-state structure sodium is coordinated to the two nitrogen atoms of the 1,2-diaza moiety, while the heterocyclic core is surprisingly planar [max. derivation 0.03(1) Å at C1; calc. NICS value -5.3 ppm]. Similar to **2d** the P-C bonds are significantly different in length [1.776(2) vs. 1.743(2)], further supported by ^{13}C NMR data [δ [ppm] = 201.0 (J_{CP} = 46 Hz); 190.2 (J_{CP} = 72 Hz); 148.8 (J_{CP} = 22 Hz)].



Scheme 5. Inverse electron demand D.A. with 1,2,4,5-tetrazines.

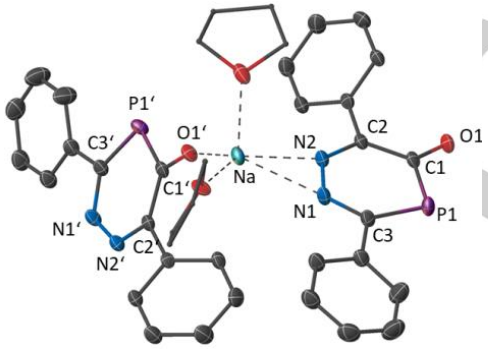


Figure 6. X-ray solid state structure of **12**. Ellipsoids are drawn at the 50% probability level. Selected bond parameters in [Å] and [°]: P1-C1 1.776(2); C1-C2 1.453(3); C2-N2 1.327(2); N2-N1 1.345(2); N1-C3 1.343(3); C3-P1 1.743(2); C1-O1 1.258(2); C3-P1-C1 100.09(9); N2-N1-C3 121.7(2); N1-C3-P1 127.7(2).

In summary, an inverse hetero-D.A. reaction with tri and tetrazines was developed leading to new aza-λ^3-phosphinines as well as diaza-λ^3-phosphinines, proven by the first X-ray data for these compound classes. The concept of an ionic directed hetero-D.A. was introduced and the directed reactions proceed under remarkably mild conditions with high regioselectivity, allowing to selectively access 1,4 and 1,3-azaphosphinines depending on the position of the directing group. Even though transient tether strategies for D.A. reactions are known,[33] tethers with tight ion contact pairs are unprecedented. This is especially interesting as counter-cations are often neglected in reactions with NaOCP. The here developed approach might be an interesting concept for broader applications with other ionic reagents. We are currently exploring the scope of the directed hetero-D.A. reactions as well as reactivity and coordination chemistry of the new heterocycles. The functional moiety of a phosphinine triflate should also pave the way for further functionalization chemistry, such as cross-coupling strategies with a wide array of applications.

Acknowledgements

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Keywords: phosphinine • Diels-Alder reaction • P-heterocycles

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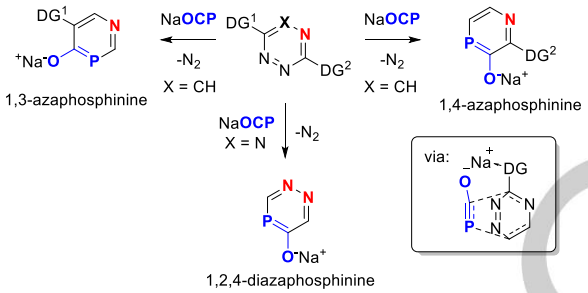
COMMUNICATION

A directed inverse electron demand Diels-Alder reaction of triazines and tetrazines leads to novel aza-λ^3-phosphinines with concurrent loss of N_2. We introduce the concept of an ionic bound tether for D.A. reactions and present the first x-ray characterization data for azaphosphinines as well as the first (aza)phosphinine triflates.



*Max M. Hansmann**

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