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Reactivity of Yellow Arsenic towards Cyclic (Alkyl)(Amino) Carbenes (CAACs)

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Dedicated to Prof. A. Filippou on the occasion of his 65th birthday

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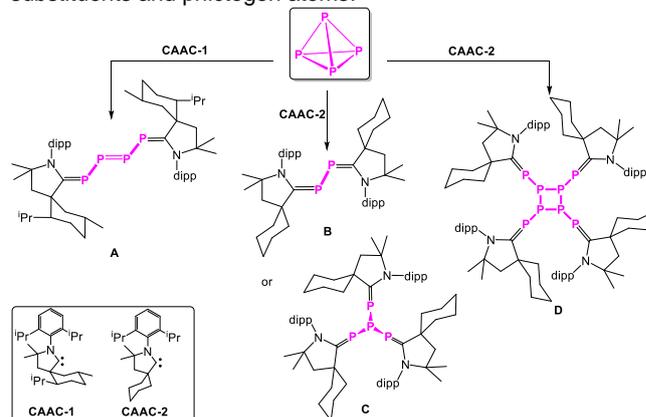
Abstract: Different cyclic (alkyl)(amino)carbenes (CAACs) were reacted with yellow arsenic. Several products [(CAAC-*n*)₂(μ,η^{1:1}-As₂)] (*n* = 1 (1), 4 (2)), [(CAAC-2)₃(μ₃,η^{1:1:1}-As₄)] (3) and [(CAAC-3)₄(μ₄,η^{1:1:1:1}-As₈)] (6) were isolated due to the differing steric properties of CAAC-1-4. The products contain As₂, As₄ or As₈ units and represent the first examples of CAACs-substituted products of yellow arsenic. The reactivity of As₄ was compared with the reactivities of P₄ and the interpnictogen compound AsP₃, which led to a series of phosphorus-containing derivatives such as [(CAAC-3)₃(μ₃,η^{1:1:1}-P₄)] (4) and [(CAAC-3)₄(μ₄,η^{1:1:1:1}-P₈)] (7) and the [(CAAC-3)₃(μ₃,η^{1:1:1}-AsP₃)] (5). The products were characterized by spectroscopic and crystallographic methods and DFT computations were performed to clarify their formation pathway.

Introduction

Since their discovery in 2005, cyclic (alkyl)(amino)carbenes (CAACs) have attracted increasing attention and their use as starting materials and co-substituents is a topical field of interest.^[1] These carbenes are both more nucleophilic and electrophilic than their NHC counterparts.^[2] Their versatile application ranges from coordination chemistry to transition metal catalysis and to the activation of small molecules such as H₂,^[3] NH₃,^[3] CO^[4] and, most interestingly, P₄.^[5] Among others, CAACs have the potential to aggregate and fragmentate white phosphorus. In 2007, Bertrand *et al.* reported the first example of a 2,3,4,5-tetraphosphatriene derivative (A), stabilized by two menthyl-substituted CAACs (CAAC-1) (Scheme 1).^[6] Depending on the reaction conditions, the reaction of the less sterically protected cyclohexyl-substituted CAAC (CAAC-2, Scheme 1) with P₄ leads to three different products: the P₂-dicarbene adduct (B),^[5a] an isotetraphosphine adduct stabilized by three CAAC molecules (C)^[5a] and the P₈ tetracarbenes compound (D)^[5b] (Scheme 1). For D, a dimerization reaction of two molecules of type A was postulated.

While the reactivity of white phosphorus towards transition metal and main group compounds was extensively studied,^[7] the related research regarding the conversion of yellow arsenic is limited by its toxicity, light- and air-sensitivity, and the impossibility to carry out stoichiometric reactions due to the autocatalytic conversion to

grey arsenic. While there have been several studies of the conversion of yellow arsenic with transition metal complexes containing e.g. Cp^R or nacnac ligands,^[8] there have only been few examples of conversions by main group element compounds.^[8-9] Arsenic-arsenic bonds are weaker than phosphorus-phosphorus bonds, which results in less stable intermediates. In the case of yellow arsenic, most likely only the thermodynamically most stable compounds are formed, but there are a few examples of transient species that could be characterized.^[9a] Interestingly, there have been efforts to find other ways to prepare arsenic-containing compounds stabilized by CAACs. Hudnall *et al.* synthesized the dicarbene-substituted diarsenic compound [(CAAC-3)₂(μ,η^{1:1}-As₂)] (E) by reacting CAAC-3 with AsCl₃ and subsequent reduction.^[11] There is also one example that has been reported with the heavier analog antimony which is isostructural to [(CAAC-*n*)₂E₂] (E = P (B), *n* = 2; As (E), *n* = 3).^[12] This product was synthesized by the stepwise reduction of [(CAAC-2)SbCl₃] with potassium graphite. Importantly, only a few direct comparisons of P₄/As₄ reactivity have been reported.^[9c,10] For example, the reaction of E₄ (E = P, As) with silylene [PhC(N^tBu)₂SiN(SiMe₃)₂] and disilene [(Me₃Si)₂NCp*Si=SiCp*N(SiMe₃)₂] (Cp* = C₅Me₅) leads to products with different topologies as well as different numbers of substituents and pnictogen atoms.^[9c,10c]



Scheme 1. Conversion of white phosphorus by different CAACs.

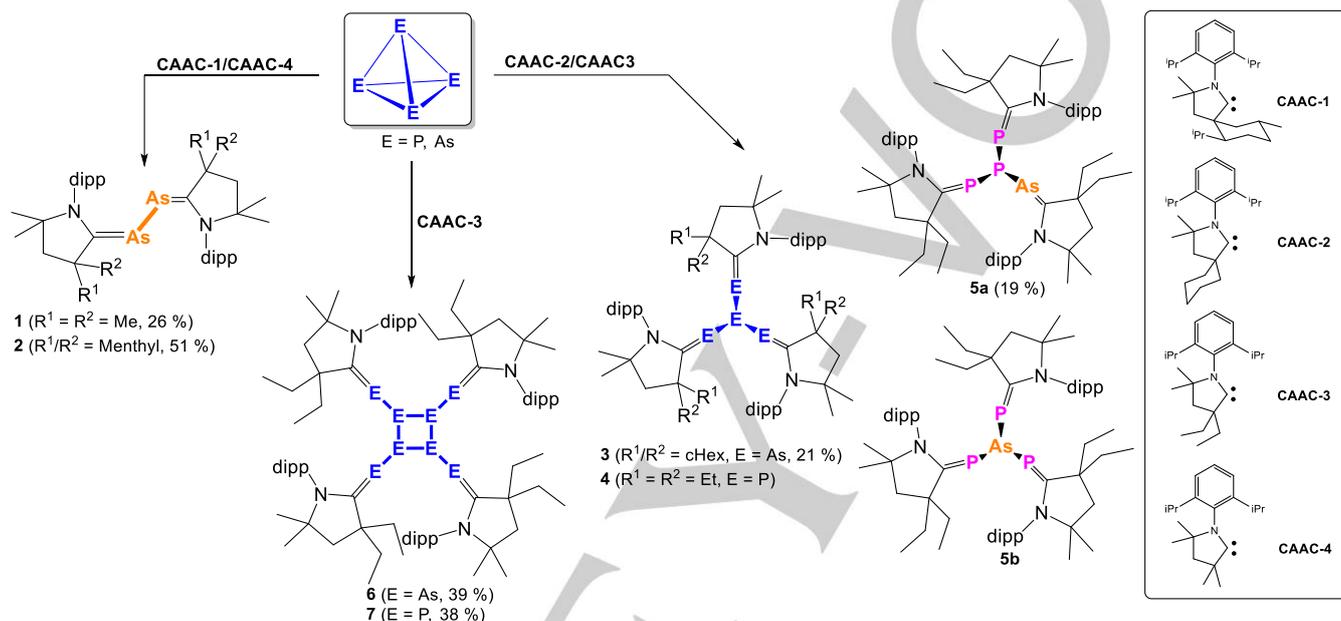
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Based on the known reaction behavior of CAACs with white phosphorus, the question arose as to whether CAACs could also induce conversions, aggregations, and fragmentations of yellow arsenic as well as to what similarities or differences could be found between the reactivities of P_4 and As_4 .

In contrast to yellow arsenic, the binary isolobal interpnictogen compound AsP_3 ^[13] is stable, and can be handled in a way similar to P_4 . Interestingly, only few examples of the conversion of AsP_3 with main group and transition metal compounds have been reported,^[14a-e] however, there is a rising interest in nanomaterials containing both phosphorus and arsenic.^[14f-h] Therefore, this compound might serve as starting materials for phosphorus-

based materials by alloying them with arsenic nuclei. Furthermore, AsP_3 might close the gap between white phosphorus and yellow arsenic and, in principle, the reaction behavior of phosphorus and arsenic could be investigated at the same time. With such tools in hand, it is possible to monitor the formation of the products by ^{31}P NMR spectroscopy, which is impossible for yellow arsenic.

Herein, we present a comparative experimental and computational study of the conversion of As_4 by different CAACs (**CAAC-1** – **CAAC-4**, Scheme 2). During our investigations, we were also able to synthesize and characterize some new phosphorus containing products and an interpnictogen compound by the reaction of **CAAC-3** with P_4 and AsP_3 , respectively.



Scheme 2. Conversion of E_4 ($E_4 = P_4, As_4, AsP_3$) by different CAACs (dipp = 2,6-diisopropylphenyl). Yields are given in parentheses (those for **5b** and **4** are included in those of **5a**).

Results and Discussion

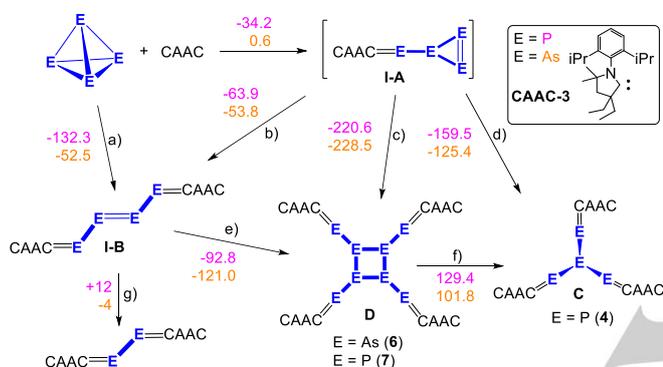
The reactions of **CAAC-1**, **CAAC-2**, **CAAC-3** and **CAAC-4** with an excess of yellow arsenic in toluene at room temperature led to the formation of the 2,3-diarsabutadiene derivatives $[(CAAC-4)_2(\mu, \eta^{1:1}-As_2)]$ (**1**) and $[(CAAC-1)_2(\mu, \eta^{1:1}-As_2)]$ (**2**), the isotetraarsine adduct stabilized by three CAAC molecules (**3**) and $[(CAAC-3)_4(\mu_4, \eta^{1:1:1:1}-As_8)]$ (**6**) (Scheme 2). The formation of **3** and **6** from the reaction of yellow arsenic with **CAAC-3** is independent of the stoichiometry used. These products are isolated as air-, moisture- and light-sensitive yellow to red crystalline solids in 26 % (**1**), 51 % (**2**), 21 % (**3**), 39 % (**6**) yields, respectively (Scheme 2). Changing the reaction conditions (e.g. temperature)^[15a] leads to the same products. The reaction between **CAAC-3** and P_4 results in the formation of both the isotetraphosphine $[(CAAC-3)_3(\mu_3, \eta^{1:1:1}-P_4)]$ (**4**, 54%, cf. SI) and the P_8 tetracarbeno derivative $[(CAAC-3)_4(\mu_4, \eta^{1:1:1:1}-P_8)]$ (**7**) (Scheme 2). **7** was isolated as crystals in 38 % yield. Furthermore, the reaction of AsP_3 with **CAAC-3** led to the formation of a yellow air-sensitive crystalline solid. NMR as well as X-ray analyses revealed that this solid consists of a mixture of three products, namely $[(CAAC-3)_3(\mu_3, \eta^{1:1:1}-AsP_3)]$ (**5a**), $[(CAAC-3)_3(\mu_3, \eta^{1:1:1}-P_2AsP)]$ (**5b**) and $[(CAAC-3)_3(\mu_3, \eta^{1:1:1}-P_4)]$ (**4**) (Scheme 2). In the $^{31}P\{^1H\}$ NMR spectrum of **5**, a doublet at $\delta = 65.4$ ppm and a triplet

at $\delta = -58.9$ ppm ($J_{PP} = 242$ Hz) in an integral ratio of 2:1 for the major isomer **5a** and a singlet at $\delta = 74.18$ ppm for the minor isomer **5b** can be detected (there are also signals for **4** visible pointing to a small amount of P_4 within an AsP_3 sample, vide infra). While the reaction of **CAAC-1** with P_4 leads to a carbene-stabilized P_4 chain (**A**, Scheme 1), the reaction with yellow arsenic results in a carbene-stabilized As_2 unit (**2**, Scheme 2). In order to clarify the difference in the reactivity, DFT computations at the B3LYP/def2-SVP level of theory were carried out (see SI for details). The formation of *trans* isomers of compounds **A**, featuring an E_4 chain, is *exergonic* by 81 and 3 kJ mol⁻¹ for P and As, respectively. However, the subsequent fragmentation of $[(CAAC-1)_2E_4]$ (**I-B**, Scheme 3) to $[(CAAC-1)_2E_2]$ and $\frac{1}{2} E_4$ is *endergonic* by 12 kJ mol⁻¹ for P, but *exergonic* by 4 kJ mol⁻¹ for As. Thus, the P_4 chain and the As_2 unit are thermodynamically the most favorable products.

Via trapping reactions, *Bertrand et al.* showed that by reacting a CAAC with P_4 an unstable monocarbene adduct **I-A** (Scheme 3) is formed as an intermediate.^[5b] The formation of this intermediate and the following products (Scheme 3) were also computationally studied for **CAAC-2** and **CAAC-3** (Scheme 3). Experimentally, the reaction of **CAAC-2** with P_4 leads to the formation of **B**, **C** and **D** (Scheme 1). In contrast, the reaction between **CAAC-3** and P_4

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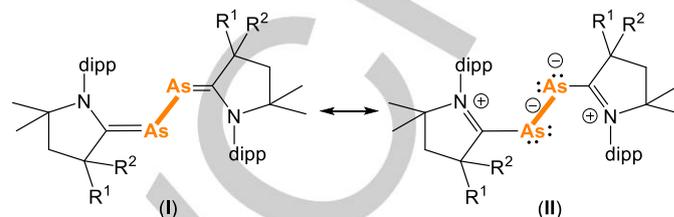
leads to **4** and **7**. In the case of arsenic, the formation of other products during the reaction cannot be precluded but is hard to monitor due to the poor NMR features of arsenic compounds. For the formation of **6** and **7**, two different reaction pathways can be proposed (Scheme 3). The first one includes the formation of the **I-B** intermediate which is exergonic both for P and As (Scheme 3). The subsequent dimerization of two molecules of **I-B** to **6** and **7** is also exergonic by 93 and 121 kJ mol⁻¹, respectively. The second pathway includes the formation of **I-A** as the first step and, afterwards, a direct formation of **6** and **7** or an indirect route via **I-B** (Scheme 3). By changing the stoichiometry, it was also possible to synthesize **4**, but not its arsenic analog [(CAAC-3)₃As₄]. [(CAAC-3)₃E₄] is expected to be built via an **I-A** intermediate. Since the **I-A** formation is slightly *endergonic* for As, this reaction pathway would be less favorable than the formation of **6** via an **I-B** intermediate. This could explain the sole formation of **6** in the case of the reaction with As₄.



Scheme 3. Standard Gibbs energies for the suggested reaction pathways (ΔG°_{298} values are in kJ mol⁻¹ for **CAAC-3**, values for **CAAC-2** see SI). a) + 2 CAAC; b) 2x **I-A**, - P₄; c) 4x **I-A**, - 2 P₄; d) + 2 CAAC; e) 2x **I-B**; f) for the reaction **D** = **C** + **I-A**; g) values for **CAAC-1**, -1/2 E₄.

The ¹H NMR spectra of **1**, **6** and **7** reveal a high symmetry with one set of signals for the CAAC units. The ³¹P{¹H} NMR spectrum of **4** in C₆D₆ at room temperature reveals a doublet at δ = 69.9 ppm (¹J_{PP} = 236 Hz) and a quartet at δ = -57.6 ppm (¹J_{PP} = 236 Hz), matching the AM₃ pattern expected for **C**. In the case of **5**, two isomers are visible in the ³¹P{¹H} NMR spectrum indicating a different chemical and magnetic environment, which can be explained by the position of the arsenic atom. Which isomer is formed, depends on the subsequent bond cleavage within the AsP₃ tetrahedron by the carbene. The bond cleavage of an As-P bond in AsP₃ is by 6 kJ·mol⁻¹ less energy-demanding than a P-P bond cleavage.^[14d] Two As-P and one P-P bond cleavages lead to the formation of the major isomer **5a** with the carbene-coordinated arsenic atom (Scheme 2). Three P-P bond cleavages of the AsP₃ tetrahedron lead to the minor isomer **5b**, where the arsenic atom is in the middle of the E₄ unit (Scheme 2). Furthermore, the ³¹P{¹H} NMR spectrum of **7** shows two multiplets at δ = 52.7 ppm and -54.9 ppm (comparable to **D**). In the LIFDI-MS spectra of **1**, **2**, **5** and **7**, respectively, the corresponding molecular ion peaks are detected. Compound **3** is visible in traces in the LIFDI-MS spectrum and, for **6**, the LIFDI-MS spectrum shows different fragments of ((CAAC-3)₃As₇), (CAAC-3)₂As_n (n = 2, 3, 5)), but not the molecular ion peak, which emphasizes the high sensitivity of arsenic-rich compounds.

For **2**, cyclic voltammetry measurements in thf were performed (cf. SI). Compound **2** reveals a first reversible oxidation at -658 mV and a second irreversible oxidation at -350 mV (against [Cp₂Fe]/[Cp₂Fe]⁺). Compared to the corresponding phosphorus analogs of **2**, **B** shows a reversible oxidation at -536 mV.^[15b] Thus, **2** can more easily be oxidized. This could be explained by the resonance form **II** shown in scheme 4. Due to arsenic being less prone to form double bonds, the canonical form (**I**) might be less important than form (**II**) which contains an electron-rich As₂ unit.



Scheme 4. Canonical forms of 2,3-diarsabutadiene (**I**) and a charge-separated diarsenediide (**II**).

The molecular structures of **1** and **2** reveal a central As₂ unit binding in η^{1:1} fashion to two CAAC fragments (Figure 1). The C2-As1-As2-C21/C28 dihedral angle amounts to 175.6(1)° (**1**) and 165.7(1)° (**2**), respectively. Furthermore, the carbene carbon atoms reveal a typical planar geometry for sp²-hybridized carbon atoms (sum of angles; **1**: 360° for C1 and C21; **2**: 359.8° for C1 and 359.9° for C28). While in **1** the diisopropylphenyl groups of the CAAC groups point away from the As₂ unit, they point towards the As₂ unit in **2**. This could be explained by the steric effect of the bulky menthyl group being larger than the one of the diisopropylphenyl groups in **2** (buried volume for **CAAC-1**: 77.4 %, for **CAAC-4**: 71.9 %).^[16] The As1-As2 bond distance amounts to 2.4175(2) Å (**1**) and 2.4423(4) Å (**2**), respectively, which is in the typical range of an As-As single bond (determined by electron diffraction:^[17] 2.435(4) Å, by DFT computations:^[18] 2.437 Å, by the sum of covalent radii:^[19] 2.42 Å). The C-As bond distances are halfway between a single^[19] and a double bond^[20] (**1**: 1.8520(14) and 1.8528(14) Å; **2**: 1.856(3) and 1.859(3) Å). The C1-N1 and C21/C28-N2 bond distances with 1.3645(17) Å and 1.3621(17) Å for **1**, 1.371(4) Å and 1.364(4) Å for **2**, respectively, are slightly shorter than the corresponding C-N bond distances in **B** (1.387(9) Å).^[5a]

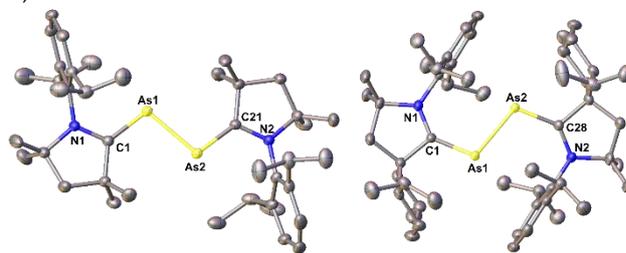


Figure 1. Molecular structures of **1** (left) and **2** (right) in the solid state. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

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The molecular structures of **3** and **5** reveal an iso-tetrapnictogen unit ($E = \text{As}$ (**3**), AsP_3 (**5**)) that is stabilized by three CAAC substituents (Figure 2). The arsenic atom in **5** is disordered over all four pnictogen positions. The major isomer **5a** with the carbene-coordinated arsenic atom as well as the minor isomer **5b** with the arsenic atom at position E4 are found to be in a ratio of 79:5 (16 % corresponds to compound **4**) in the solid state (Scheme 2). DFT computations indicate that, in the gas phase, the standard Gibbs energy for the equilibrium **5a** to **5b** is exergonic by 22.1 kJ mol⁻¹, indicating that isomer **5b** is the thermodynamically stable product (see SI). The higher amount of **5a** in the experiment is most likely due to kinetic reasons. To understand the formation of both isomers, the energy associated with the initial reaction between **CAAC3** and AsP_3 was calculated. We found that the attack of the carbene at a P atom is more exergonic by 24.6 kJ mol⁻¹ than the attack at the As atom. The breaking of the P-As bond in the (CAAC-3)PAsP₂ intermediate is expected to proceed more easily than that in the P-P bond, resulting in **5a** rather than in **5b**. The formation of **4** upon reaction with AsP_3 can be explained by the thermodynamic favorability of the disproportionation of AsP_3 : $4 \text{AsP}_3 = 3 \text{P}_4 + \text{As}_4$ (computed gas phase $\Delta G^\circ_{298} = -13.6 \text{ kJ mol}^{-1}$). The formed As_4 can isomerize into unreactive grey arsenic and quit the reaction.

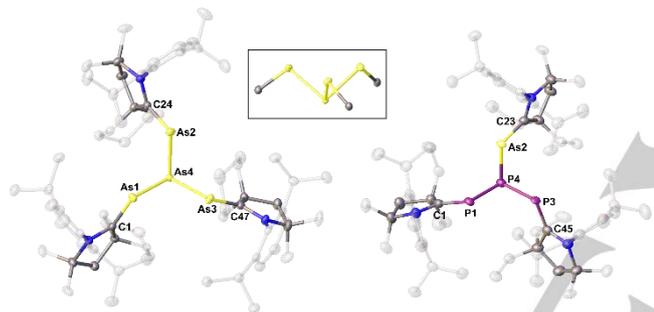


Figure 2. Molecular structure of **3** (left) and **5a** (right, one isomer of **5**) in the solid state, side view of the E₄ unit (box). Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Table 1. Occupation of the phosphorus and arsenic positions in compound **5**.

Atom	1	2	3	4
P	70	76	75	95
As	30	24	25	5

The angles around the central atom E4 are in the range of 89.28(1)° to 92.24(1)° for **3**, 86.81(1)° to 92.88(1)° for **5a** and 86.54(1)° to 86.99(1)° for **5b**. In comparison to **C** which has all three angles at 90.15(2)°, **3** and **5** show more deviation from the perfect local C_{3v} symmetry. In both structures, the diisopropylphenyl groups of the CAAC substituents point away from the central atom E4, and the CAAC fragments themselves are bent counter clockwise in the case of **3** and clockwise in the case of **5** (**C**: clockwise). In the case of arsenic, the CAAC fragments are bent in the opposite direction than in the case of phosphorus. Interestingly, the CAAC units in the mixed interpnictogen compound **5** and in the phosphorus analogue **C** have the same orientation. The As-As bond distances of **3** are in between 2.4479(2) and 2.4520(2) Å which is in the range of an arsenic single bond.^[19] The E-E bond distances of **5** are in the

range of normal single bonds (P-P: 2.212(10) to 2.263(8) Å, P-As: 2.289(11) to 2.40(4) Å). The C-E bond distances are in between a single and a double bond (**3**: 1.862(2) to 1.866(2) Å; **5**: C-P: 1.714(8) to 1.748(10) Å, C-As: 1.856(9) to 1.891(10) Å).

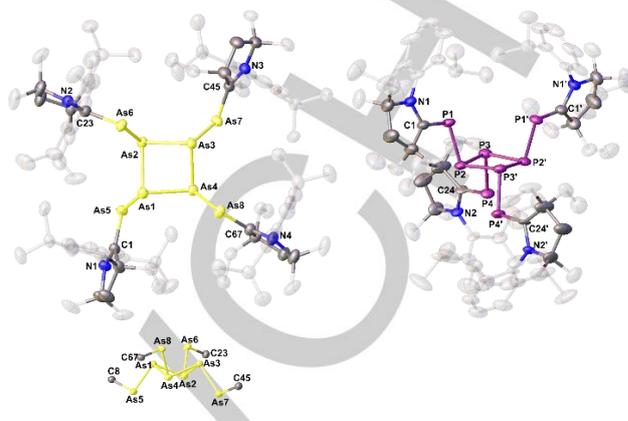


Figure 3. Molecular structures of **6** (left) and **7** (right) in the solid state (bottom: side view of the As₄ unit). Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity.

The molecular structure of **6** and **7** reveals a tetra(carbene)E₈ cage compound ($E = \text{As}$ (**6**), P (**7**)) which contains a four-membered E₄ ring with each pnictogen atom being connected to a further pnictogen atom and stabilized by four CAAC fragments. For the phosphorus compound **7**, the P₄ cycle is nearly planar (torsion angle: 171.8°) possessing almost right angles (P2-P3-P2' 89.70(3)° and P3-P2-P3' 90.01(3)°), which is in contrast to the reported compound **D** that has a similar structural P₈ motif, with the P₄ cycle, however, being folded by 47.90°. In compound **6**, the As₄ cycle is folded by 55.54° (As1-As2-As3 plane: As2-As3-As4 plane). The diisopropylphenyl groups of both compounds point away from the E₈ unit. The E-E-C angles are very similar for both compounds (**6**: 102.71(9) - 104.05(10)°; **7**: 101.01(4)/104.66(7)°). So here the main difference is the inner E₄ cycle. The E-E bond distances in the *cyclo*-E₄ unit are between 2.4538(5) and 2.4741(5) Å (**6**), 2.2335(8) and 2.2354(8) Å (**7**), respectively, representing elongated single bonds. The other E-E bond distances are in the range of ordinary single bonds (**6**: 2.4237(5) - 2.4334(5) Å, **7**: 2.1975(7) and 2.1987(7) Å). The C-E bond distances of **6** (between 1.862(3) and 1.864(3) Å) and **7** (1.731(2), 1.797(13) Å) are also halfway between a single and a double bond.

Conclusion

In summary, the first investigations of the reactivity of yellow arsenic towards carbenes are presented. This work demonstrates that the reaction of yellow arsenic with CAACs leads to aggregation, fragmentation, and rearrangement of As₄. The reaction outcome depends on the sterics of the respective CAAC. By reacting different CAACs with As₄, the compounds [(CAAC-4)₂(μ,η^{1:1}-As₂)] (**1**), [(CAAC-1)₂(μ,η^{1:1}-As₂)] (**2**), [(CAAC-2)₃(μ₃,η^{1:1:1}-As₄)] (**3**) and [(CAAC-3)₄(μ₄,η^{1:1:1:1}-As₈)] (**6**) were obtained. These products represent the first examples of polyarsenic units containing CAACs entities. By the conversion of yellow arsenic with CAACs, only the thermodynamically most stable products could be isolated. These products are less stable

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than their phosphorus analogues, which also affects the isolated yields. DFT computations are in qualitative agreement with the experimental observations. Furthermore, the products [(CAAC-3)₃(μ₃,η^{1:1:1}-P₄)] (**4**), [(CAAC-3)₄(μ₄,η^{1:1:1:1}-P₈)] (**7**) and [(CAAC-3)₃(μ₃,η^{1:1:1}-AsP₃)] (**5**) were synthesized. The latter represents the first product of the reactivity of AsP₃ towards CAACs. Moreover, the different reaction outcomes and structural differences of the reactions with white phosphorus, yellow arsenic and the interpnictogen compound AsP₃ were discussed, most reflected by the instability of kinetically formed products and their subsequent reactions in case of the As₄ reactions. Furthermore, the use of AsP₃ might open a new modification strategy for phosphorus-based materials doped with arsenic.

Experimental Section

Experimental procedures for the synthesis of all compounds, analytical data, quantum chemical calculations and X-ray crystallography are described in the Supporting Information.

Deposition numbers 2205186 (for **1**), 2205187 (for **2**), 2205188 (for **3**), 2205189 (for **5**), 2205190 (for **6**) and 2205191 (for **7**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Keywords: CAAC • interpnictogen compound • yellow arsenic • polyarsenic compounds

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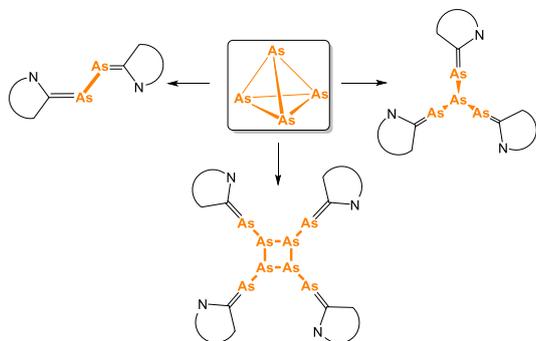
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Cyclic (alkyl)(amino)carbenes (CAACs) are reacted with yellow arsenic. Depending on the CAAC used, aggregation, fragmentation and/or rearrangement of yellow arsenic occur to form novel As_2 -, *iso*- As_4 - and As_8 -units substituted by CAAC units.