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Phosphorus derivatives of mesoionic carbenes: synthesis and characterization of triazaphosphole-5-ylidene → BF_3 adducts†‡

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Trimethylsilyl-substituted triazaphospholes were synthesized by a [3+2] cycloaddition reaction between organic azides and $(CH_3)_3Si–C\equiv P$. In an attempt to isolate their *N*-alkylated products, the formation of BF_3 adducts of unprecedented triazaphosphol-5-ylidenes was found. The nature of the carbon$_{carbene}$–boron bond was investigated within the DFT framework, revealing a strong donation of electrons from the carbene carbon atom to the boron atom combined with weak back-bonding.

According to the isolobal relationship between a trivalent phosphorus atom and a C–H fragment, 3*H*-1,2,3,4-triazaphosphole derivatives **A** are phosphorus analogues of the well-known 1,4-disubstituted 1,2,3-triazoles **B** (Fig. 1), which play a prominent role in the field of "click"-chemistry.[1] These heterocycles possess a high degree of aromaticity and can be obtained in a modular [3+2] cycloaddition reaction, starting from organic azides and phosphaalkynes.[2,3]

Although triazaphospholes were first synthesized as early as 1984, reports of their coordination chemistry were first published almost 30 years later.[3,4] Our group reported the coordination chemistry and photoluminescence properties of conjugated, pyridyl-functionalized triazaphospholes, bearing either ^{t}Bu or $Si(CH_3)_3$-substituents at the 5-position of the heterocycle.[5]

Little is known about the chemical reactivity of triazaphospholes. In addition to our observation that they undergo cycloaddition–cycloreversion reactions with $CF_3C\equiv CCF_3$ forming **C**, we found that triazaphospholenium salts **D** are accessible by alkylation of triazaphospholes with Meerwein salts.[6,7] Because a negatively charged carbon atom is valence isoelectronic to a phosphorus atom, these cationic phosphorus heterocycles are formally phosphorus congeners of the well-known mesoionic 1,2,3-triazolylidenes **E** and show an interesting coordination chemistry.[7,8]

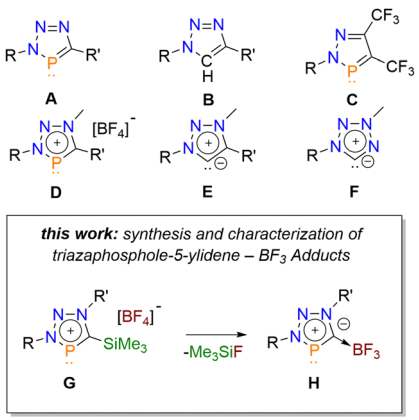

Fig. 1 Selected phosphorus and nitrogen based heterocycles and brief summary of this work (*R*/*R*′: alkyl-, aryl-group).

Inspired by our recent investigations on 6-membered, 2-$Si(CH_3)_3$-substituted aromatic phosphorus heterocycles (phosphinines), we became interested in reinvestigating $Si(CH_3)_3$-substituted triazaphospholes (**A**, R' = $Si(CH_3)_3$), particularly with respect to the formation of the corresponding triazaphospholenium salts (**D**, R' = $Si(CH_3)_3$).[5,9] As $Si(CH_3)_3$-groups linked to an aromatic system generally provide interesting electronic effects to the aromatic ring, we anticipated that these compounds might also undergo chemical transformations, such as protodesilylations or C–Si bond cleavage reactions.[10]

Much to our surprise, we now found that BF_4^--salts of $Si(CH_3)_3$-substituted triazaphospholenium cations (**G**) undergo elimination of $FSi(CH_3)_3$ to form selectively BF_3 adducts of unprecedented triazaphosphol-5-ylidenes (**H**). Interestingly,

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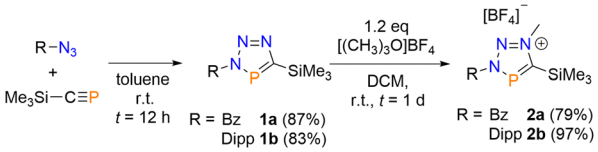
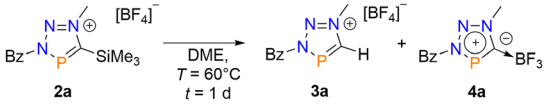
† Dedicated to Prof. Peter Jutzi on the occasion of his 85th birthday.

‡ Electronic supplementary information (ESI) available. CCDC 2279453–2279457. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3cc03268j



Scheme 1 Synthesis of the triazaphospholenium salts **2a/2b**.



Scheme 2 Formation of **3a** and **4a** upon heating of **2a** in DME.

these heterocycles are the phosphorus congeners of tetrazol-5-ylidene carbenes (**F**) with an abnormal substitution pattern.[11]

The $Si(CH_3)_3$-substituted triazaphospholes **1a/b** were synthesized by [3+2] cycloaddition reactions from $Si(CH_3)_3$–C≡P and benzyl azide (Bz-N_3) or diisopropylphenyl azide (Dipp-N_3), respectively in good yields (**1a**: 87%, **1b**: 83%, Scheme 1). As expected, both compounds show resonances in the downfield region of the $^{31}P\{^1H\}$ NMR spectrum, at δ(ppm) = 214.8 (**1a**) and δ(ppm) = 222.9 (**1b**).

Subsequently, we intended to convert **1a/b** into the corresponding $Si(CH_3)_3$-substituted triazaphospholenium salts of type **G** (Fig. 1). Using an analogous methodology to that of the ^{t}Bu-substituted derivatives, an equimolar mixture of compound **1a** and $[Me_3O][BF_4]$ was vigorously stirred in dichloromethane at T = 55 °C and the course of the reaction was followed by means of $^{31}P\{^1H\}$ NMR spectroscopy (Fig. S1, ESI†). After one hour, the formation of a new species was observed, which we attribute to the desired alkylated triazaphospholenium salt **2a**, due to its characteristic chemical shift at δ(ppm) = 239.3.

However, considerable amounts of starting material were still present, while longer reaction times led to the formation of two more side-products. With the aim of preventing the formation of any side-products, $[Me_3O][BF_4]$ was used in a slight excess and the reaction was kept at room temperature. After one day, **2a** was obtained as the sole product in an isolated yield of 79% (Scheme 1). Similarly, the triazaphospholenium salt **2b** was obtained in 97% isolated yield after washing the product with dry diethyl ether. **2b** shows a resonance at δ(ppm) = 249.1 in the $^{31}P\{^1H\}$ NMR spectrum. In the ^1H NMR spectrum of the triazaphospholenium salts, the introduced CH_3-group can be detected as a characteristic singlet at δ(ppm) = 4.52 (**2a**) and δ(ppm) = 4.69 (**2b**), respectively.

Even though the $Si(CH_3)_3$-substituted triazaphospholenium salts **2a/b** were finally synthesized in high yields, we were still wondering about the formation of the observed side products (*vide supra*), particularly at higher reaction temperatures. Consequently, we investigated the thermal stability of **2a** by heating a solution of this compound in dimethoxyethane (DME) to T = 60 °C. Interestingly, the complete conversion of **2a** to two new species (**3a**, **4a**) was observed by $^{31}P\{^1H\}$ spectroscopy after one day.

We were able to separate both compounds by means of either extraction (**3a**) or flash column chromatography (**4a**). Compound **3a** shows a resonance at δ(ppm) = 206.7 in the $^{31}P\{^1H\}$ NMR spectrum, which corresponds to a chemical shift difference of $\Delta\delta$ = 32.6 ppm compared to the starting material **2a** (δ(ppm) = 239.3). Interestingly, a new signal can be observed in the ^1H NMR spectrum at δ(ppm) = 9.26. This resonance appears as a doublet with a coupling constant of $^2J_{H-P}$ = 37.5 Hz, which is typical of protons in the α-position to a phosphorus atom. We therefore concluded that **3a** must have been formed by protodesilylation of **2a**, according to Scheme 2. The crystallographic characterization of **3a** indeed confirmed that protodesilylation of **2a** had occurred (Table S1, ESI†). Note, that the access to this compound would otherwise only be possible by cycloaddition reaction between an azide and hydrogen cyaphide (H–C≡P), or the cyaphido ligand (C≡P^-), followed by a subsequent quaternization with Meerwein salt.[12]

Up to this point, the source of the proton still remains unknown. It should be noted, however, that protonated side-products have also been observed in the thermal degradation of free 1,2,3-triazol-5-ylidenes.[13]

Next, we turned our attention to the identification of the second species **4a**. Surprisingly, this compound shows a quartet in the $^{19}F\{^{31}P\}$ NMR spectrum at δ(ppm) = −140.5 (q, $^1J_{F-B}$ = 37.7 Hz, Fig. S2, ESI†). Likewise, a quartet of doublets is observed in the corresponding ^{11}B NMR spectrum at δ(ppm) = 0.6 (d, $^2J_{B-P}$ = 15.9 Hz, q, $^1J_{B-F}$ = 37.9 Hz). The chemical shifts and the coupling pattern is in line with the presence of a BF_3-carbene adduct. For instance, the classical Arduengo carbene adduct IMes → BF_3 (IMes = 1,3-dimesitylimidazol-2-ylidene) shows a resonance in the ^{19}F NMR spectrum at δ(ppm) = −142.44 (q, $^1J_{F-B}$ = 34.6 Hz) and at δ(ppm) = −1.36 (q, $^1J_{B-F}$ = 34.6 Hz) in the corresponding ^{11}B NMR spectrum.[15] A coupling to the phosphorus nucleus in **4a** would provide an additional splitting of the otherwise similar signals as can indeed be noticed in the ^{19}F NMR and the ^{11}B NMR spectra of **4a** (^{19}F NMR: δ(ppm) = −140.5 (d, $^2J_{F-P}$ = 14.6 Hz), ^{11}B NMR: δ(ppm) = 0.6 ppm (d, $^1J_{B-P}$ = 15.9 Hz), Fig. S2, ESI†). Accordingly, the decoupled $^{11}B\{^{19}F\}$ NMR spectrum of **4a** shows only a doublet due to the $^1J_{B-P}$ coupling ($^{11}B\{^{19}F\}$ NMR: δ(ppm) = 0.7 ($^1J_{B-P}$ = 15.8 Hz), Fig. S2, ESI†). Compound **4b** was synthesized in an analogous manner.

Single crystals of **4a**, suitable for X-ray diffraction, were obtained by layering a concentrated dichloromethane solution of **4a** with *n*-pentane and the molecular structure of **4a**, along with selected bond lengths and distances, is depicted in Fig. 2 (**4b**: Table S3, ESI†). The crystallographic characterization of **4a** indeed reveals the presence of an abnormal carbene → BF_3-adduct (Scheme 2). Compared to the protodesilylated triazaphospholenium salt **3a**, the P(1)–C(1) bond in **4a** is slightly elongated (**4a**: 1.711(2) Å; **3a**: 1.706(2) Å), while the N(1)–P(1)–C(1) bond angle is somewhat larger and closer to 90° (**4a**: 87.31(8)°; **3a**: 85.75(6)°). The C(1)–B(1) bond length of 1.640(3) Å) is very similar to the one found for the C–B-bond distance in the Lewis pairs of classical Arduengo carbenes (1.635(5) Å for IMes → BF_3 and 1.669(6) Å for 4,5-dichloro-IMes → BF_3).[14] Similar bond lengths and distances were observed also for **4b** (Table S3, ESI†). **4a** can be described as a BF_3 adduct of an unprecedented

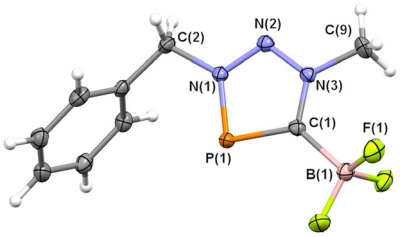
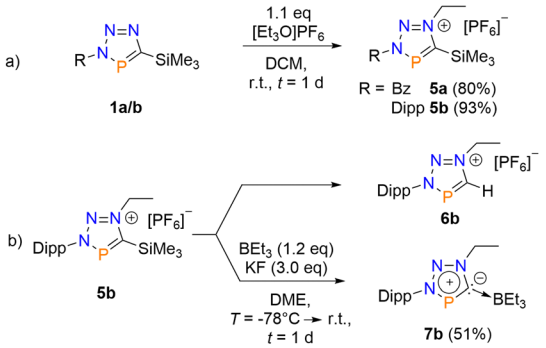


Fig. 2 Molecular structure of **4a** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected experimental and theoretical [B3LYP-D3(BJ)/def2-SVP] bond lengths (Å) and angles (°): P(1)–C(1): 1.711(2) [1.722], P(1)–N(1): 1.705(2) [1.755], N(1)–N(2): 1.309(2) [1.301], N(2)–N(3): 1.320(2) [1.316], N(3)–C(1): 1.354(2) [1.357], C(1)–B(1): 1.640(3) [1.667], N(1)–P(1)–C(1): 87.31(8) [86.2].



Scheme 3 Synthesis of the triazaphospholenium salts **5a**/**5b** (a). Preparation of the BEt_3-adduct **7b** and the protodesilylated compound **6b** (b).

triazaphosphol-5-ylidene and thus as a phosphorus congener of the known tetrazol-5-ylidenes with an abnormal substitution pattern (**F**, Scheme 1).[11] Moreover, **4a**/**b** is again isoelectronic to the cationic part of the triazaphospholenium salt **D** (Fig. 1).

From a mechanistic point of view, **4a**/**b** is formed by elimination of $FSiMe_3$ from **2a**/**b**, which initially forms the carbene intermediate, that subsequently reacts with the remaining BF_3. This would be in line with observations reported by Borozov and co-workers for 1-ethyl-3-methyl-1*H*-imidazolium BF_4^- (and respectively PF_6^-), which results in the formation of the corresponding NHC-based BF_3 and PF_5 Lewis pairs under rather harsh conditions.[15] In this respect, **4a**/**b** are also related to the $GaCl_3$ adducts of neutral tetrazaphospholes, reported by Schulz and co-workers.[16]

In case of the formation of **4a**/**b** the free carbene could not be observed spectroscopically, probably due to a rapid Lewis pair formation. However, the by-product $FSiMe_3$ was detected by means of ^{1}H–, ^{19}F– and ^{29}Si–^{1}H-HMQC NMR spectroscopy and can easily be removed under vacuum. It is likely that the protonation of the carbene leads to the formation of **3a**. This would be in agreement with observation that 1,2,3-triazlylidenes can undergo migration of an alkyl group, that is bound to the most nucleophilic nitrogen atom, to the carbene carbon atom, while the formation of a protodesilylated side-product is also observed.[13]

Because **3a** and **4a** are apparently formed by competing reactions, the isolated yields were moderate. We therefore anticipated targeted syntheses of both compounds. While other electrophiles, such as CH_3I or CH_3OTf, are not suitable for quaternization reactions at triazaphospholes, we chose triethyloxonium hexafluorophosphate instead. This indeed yielded the corresponding triazaphospholenium salts **5a**/**b** in good isolated yields (**5a**: 80%, **5b**: 93%, Scheme 3a). Compounds **5a**/**b** provide again characteristic signals in the ^{31}P{^{1}H} NMR spectra at δ(ppm) = 238.1 (**5a**) and δ(ppm) = 249.0 (**5b**), respectively. Additionally, the introduced ethyl group shows typical signals in the ^{1}H NMR spectra (**5a**: δ(ppm) = 4.73 (q, J = 7.5 Hz), 1.74 (t, J = 7.3 Hz,); **5b**: δ(ppm) = 4.84 (q, J = 7.1 Hz), 1.69 (t, J = 7.1 Hz)).

We also anticipated that the addition of potassium fluoride (KF) in the presence of a Boron-based Lewis acid BR_3 should facilitate the formation of $FSiMe_3$ and the abnormal carbene → BR_3 adduct, while K[PF_6] might precipitate from the solution. For this purpose, $BH_3{\cdot}SMe_2$, $BH_3{\cdot}THF$, $BF_3{\cdot}SMe_2$, $BF_3{\cdot}OEt_2$, and BEt_3, were used in combination with **5b**. Interestingly, except for BEt_3, the selective formation of the protodesilylated product **6b** was observed, most likely due to contaminations with H_2O/HF. On the other hand, in the presence of BEt_3, the BEt_3-adduct **7b** was selectively formed (Scheme 3b). This was confirmed by an X-ray structural analysis (Fig. 3). Compound **6b** was also independently synthesized and characterized crystallographically (see Table S4, ESI†).

Finally, we investigated the nature of the C_{carb} → B bond by means of DFT calculations at the B3LYP-D3(BJ)/def2-SVP level of theory (see ESI† for details). We were particularly interested in the effect of the phosphorus atom on the donor–acceptor abilities of the abnormal carbene moiety.[17] The optimized structures are in good agreement with the experimentally measured ones (Fig. 2, 3 and Table S3 and Fig. S43, ESI†), with the C_{carb}–B bond lengths being slightly longer than those observed experimentally (**4a** 1.667 Å and **4b** 1.668 Å). The natural bond orbital analysis (Table S6 and Fig. S44, ESI†) indicates a strong donation of electrons as the BF_3 bears a negative partial charge of −0.47 (**4a**) and −0.46 (**4b**). The Wiberg bond orders indicate a single bond character with 0.71 au in **4a** and **4b**. The Bader topological analysis[18] reveals an electron accumulation between the carbene carbon atom and the boron atom with a bond critical point that possesses a

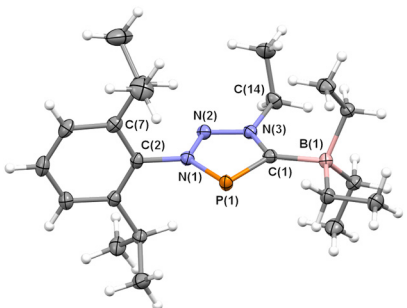


Fig. 3 Molecular structure of **7b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Only one independent molecule in the asymmetric unit is shown. Selected bond lengths (Å) and angles (°): P(1)–C(1): 1.7306(10), P(1)–N(1): 1.7110(9), N(1)–N(2): 1.3146(12), N(2)–N(3): 1.3310(12), N(3)–C(1): 1.3629(13) C(1)–B(1): 1.6468(15); N(1)–P(1)–C(1): 88.26(4).

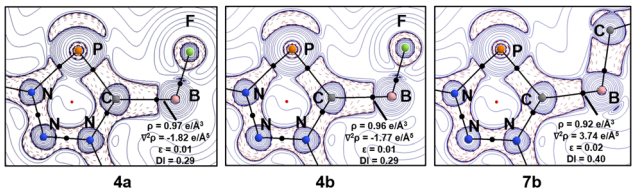


Fig. 4 Laplacian distribution of the electron density of compounds **4a/b** and **7b** (B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP). Contour line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ in the PHC ring plane. Dashed red lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) while solid blue lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The thick solid lines connecting the atomic nuclei are the bond paths and the small dots are the critical points. Bond Critical Points (in black), Ring Critical Points (in red).

relatively small electron density value ($\rho(r)$ 0.97 e Å^{-3} **4a**, 0.96 e Å^{-3} **4b**, and 0.92 e Å^{-3} **7b**) with negative Laplacian values of $\nabla^2\rho(r)$ = −1.82 e Å^{-5} (**4a**) and $\nabla^2\rho$(r) = −1.77 e Å^{-5} (**4b**), respectively a positive value of $\nabla^2\rho(r)$ = 3.74 e Å^{-5} for **7b** (Fig. 4). Additionally, we have performed energy decomposition analysis (EDA-NOCV)[19] to quantitatively assess the chemical bonding situation in these adducts, taking as fragments the neutral triazaphosphol-5-ylidenes (**4a/b**, **7b**) and BF_3 moieties (Table S7 and Fig. S45, ESI†). The bond dissociation energy is slightly weaker than in other borane adducts, with energies of 38.4 (**4a**), 37.5 (**4b**) and 40.0 (**7b**) kcal mol^{-1}.[20] However, the dissection into preparation energy and interaction energy suggests that the geometrical deformation of BF_3 or BEt_3 brings a significant energy penalty (31.0 and 26.0 kcal mol^{-1}).

The interaction energy is comparable to other known $C_{carbene}$ → B adducts, counting −72.1 (**4a**), −70.7 (**4b**) and −68.4 (**7b**) kcal mol^{-1}.[21] Further decomposition reveals an ionic nature of the bond with approximately 53% electrostatic interaction and 45% orbital interaction. Note that the electrostatic interaction refers to the electrostatic attraction between the charge distribution of the fragments, differentiating from the VB ionic bonds (for further details see ref. 20). The orbital term can be analysed with the Natural Orbitals for Chemical Valence (NOCV), where the σ-donation counts for ∼80% of the orbital interaction, while the π-back donation is only ∼5%. Fig. S46 (ESI†) shows a comparison of the frontier molecular orbital energies of the model systems 1,2,3-triazolylidene, tetrazol-5-ylidene and triazaphosphole-5-ylidene.

The energy of the σ-lone pair on the carbene carbon atom is comparable to the triazole analogue and agrees with the strong donor properties towards BF_3 or BEt_3. On the other hand, the presence of a phosphorus atom provides less stabilization of the π* orbital, leading to relatively high π-acceptor properties.

In summary, we have found an access to BF_3 adducts of hitherto unknown triazaphosphol-5-ylidenes, which are the phosphorus analogs of tetrazol-5-ylidene carbenes with abnormal substitution pattern. Quantum chemical calculations reveal a strong σ-donor property and marginal π-accepting ligand properties. The access to transition metal complexes containing our novel triazaphosphole-5-ylidenes as ligands are currently performed in our laboratories.

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Conflicts of interest

There are no conflicts to declare.

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