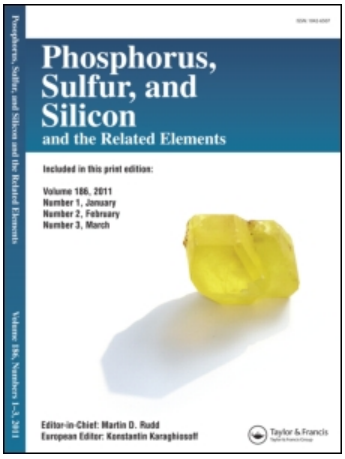

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Novel 1,2,4-Triphosphole, 1,2,3-Triphosphetene and Azaphospholene Derivatives from N -Heterocyclic Carbenes and Phosphaalkynes

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NOVEL 1,2,4-TRIPHOSPHOLE, 1,2,3-TRIPHOSPHETENE AND AZAPHOSPHOLENE DERIVATIVES FROM *N*-HETEROCYCLIC CARBENES AND PHOSPHAALKYNES

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The stable singlet carbenes N,N′*-bis(2,2-dimethylpropyl)-benzimidazolin-2-ylidene* ***1*** *and 1,3,4,5-tetramethylimidazol-2-ylidene* ***2*** *react with phosphaalkynes P≡C–tBu (**3a**) or P≡C–NiPr$_2$ (**3b**) regioselective to give the aromatic 1,2,4-triphosphole derivatives (**1** or **2** + **3a** → **6a** or **6b**, respectively) or 1,2,3-triphosphetene (**1** + **3b** → **7**) or azaphospholene (**2** + **3b** → **9**) in almost quantitative yields. The mechanisms of the surprising formation of compound **9** under C–H-activation was studied by quantum chemical DFT calculations.*

Keywords: Carbenes; phosphaalkynes; phosphorus heterocycles

The reactivity of halocarbenes or phosphanylsilylcarbenes (Bertrand carbenes) towards phosphaalkynes P≡CR is well documented.[1] Here, we present the interesting results of the reactions of the stable N-heterocyclic carbenes (**1, 2**) with the phosphaalkynes P≡C–*t*Bu (**3a**) or P≡C–N*i*Pr$_2$ (**3b**).

Treatment of carbene **1**[2] with the phosphaacetylene **2a** at room temperature affords the crystalline adduct **6a** in near quantitative yield.[3] Similarly, Nixon et al.[4] have synthesized the 1,2,4-triphosphole derivative **6b** by reacting the Arduengo carbene 1,3,4,5-tetramethylimidazol-2-ylidene **2** with the 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene. We now found that the compound **6b** can be also produced easily by reaction

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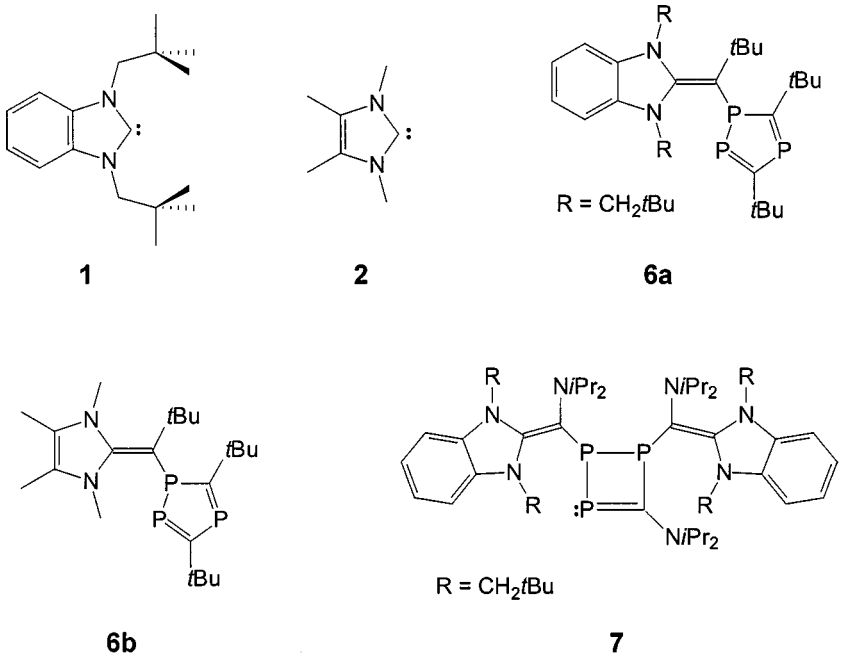

FIGURE 1

of carbene **2** with **3a**.[5] The structural parameters of **6a** indicate a completely delocalized 1,2,4-triphospha-cyclopentadiene system. In contrast to the triphospholes previously described, **6a** and **6b** have mesomerically stabilizing substituents on the tricoordinate phosphorus atom. However, the molecular structure of **6a** shows a strong twisting (ca. 60°) of the benzimidazol-2-ylidene plane towards the C═C(P)*t*Bu plane, which in turn is twisted with respect to the plane of the triphosphole ring. An effective conjugation between these sections of the molecule seems to be out of the question (Figure 1).

Under comparable reaction conditions, the aminophosphaalkyne **3b** behaves differently than **3a** toward **1**. In the reaction of **3b**, the time taken for its complete consumption was only about 15 min, while the air-sensitive 1,2,3-triphosphetene **7** crystallized out as the only product. As expected, the four-membered heterocycle **7** is not planar, and the structural parameters show a π-delocalization in the P═C–N fragment.

While no intermediates were detected by ^{31}P NMR monitoring of the reaction of the annelated carbene **1** with **3a**, the analogous reaction with **3b** yielded the nonisolable 1*H*-diphosphirene **5b** as an (^{31}P NMR $\delta(\sigma^2\text{P}) = -66.3$ ppm, $\delta(\sigma^3\text{P}) = -182.2$ ppm, $J_{PP} = 97.7$ Hz) intermediate. It is plausible that the reaction commences with the addition of

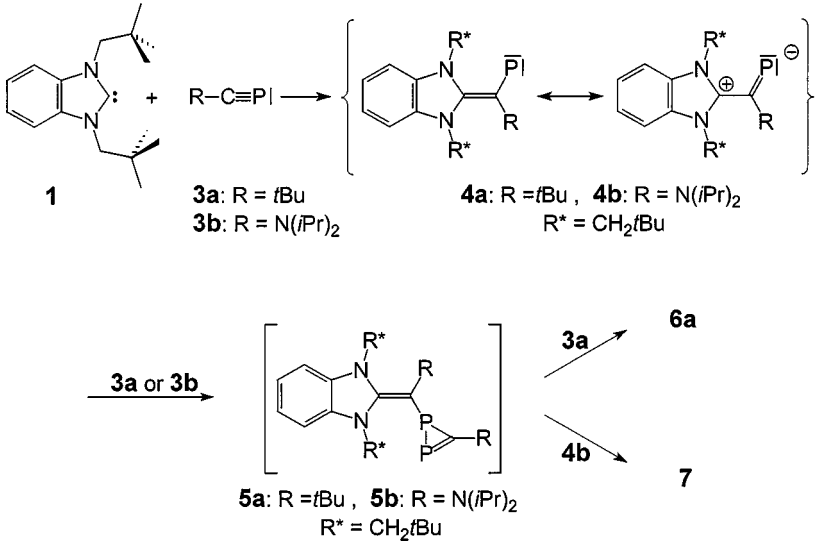

FIGURE 2

the nucleophilic carbene **1** to **3a** or **3b** to form the highly reactive phosphinidene **4a** or **4b**. The ensuing [2 + 1] cycloaddition of these species to a further molecule of the phosphaalkyne delivers the 1*H*-diphosphirene **5a** or **5b**, respectively. Compound **5a** is capable, after ring opening, of undergoing a [3 + 2] cycloaddition with the phosphaacetylene **3a** to form **6a**. In the case of **5b**, the insertion of phosphinidene **4b** into the P—P diphosphirene bond leads to the 1,2,3-triphosphetene **7**. The cause of the difference in the end products obtained from the reaction of **1** with **3a** or **3b** lies clearly in the distinction of the polarity between the two related phosphaalkynes (Figure 2).

The reaction of the Arduengo carbene **2** with the aminophosphaalkyne **3b** affords surprisingly the isolable 1:1 adduct **9** in almost quantitative yield. The bonding situation in the new azaphosphole **9** is best described by the two resonance structures **9A** and **9B**, in which **9B** represents an inversely polarized phosphaalkene with a π-electron distribution $P^{\delta-}$–$C^{\delta+}$ at the P—C double bond. This interpretation is supported by the derivatisation of **9** with the Lewis acid BH_3·THF, which yields the complex **10** with two coordinated BH_3 groups on the phosphorus atom.[5]

DFT calculations show that **9** is the result of the stabilization of the intermediate **8** through intramolecular C—H insertion into the methyl group of the amino substituent of carbene **2**. Interestingly, both P—C bonds in the newly formed carbene **8** as well as in the bicyclus **9** are

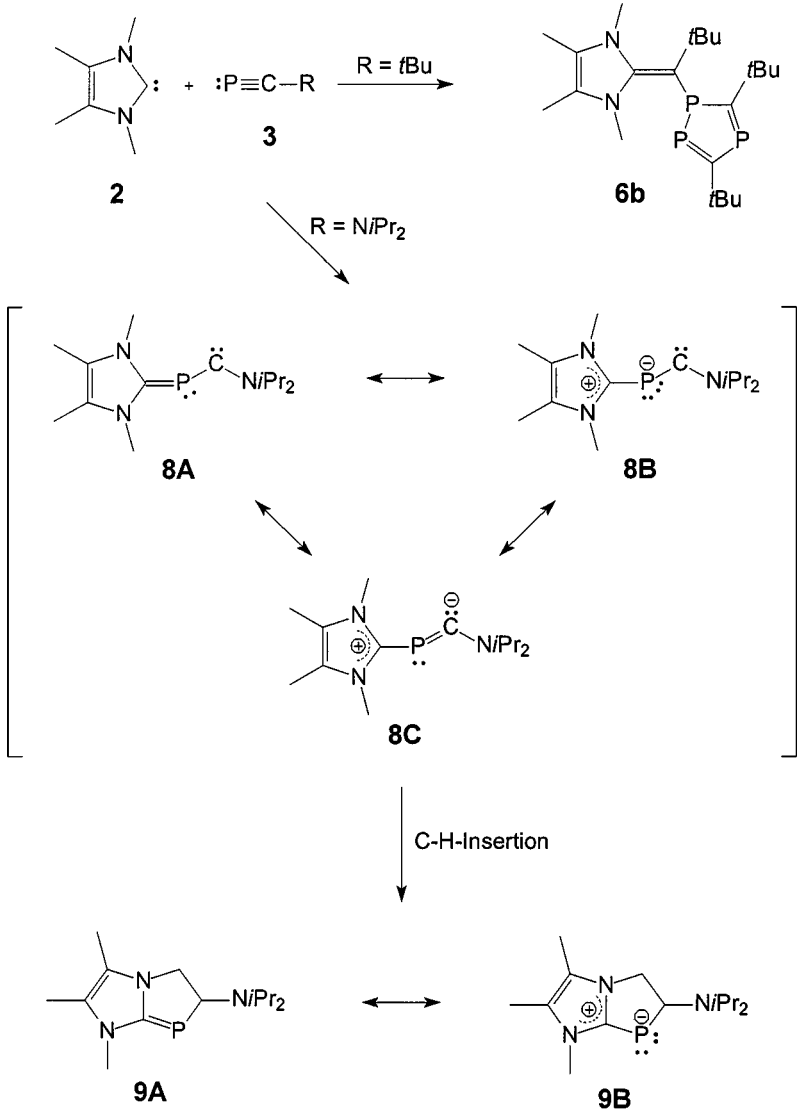

FIGURE 3

calculated to be unsually long [P-heterocycle: 1.82 Å (**8**), 1.76 Å (**9**), P—$C_{carbene}$: 1.77 Å (**8**), P—CH: 1.96 Å (**9**, a rare example for compounds with bond-no bond resonance)] (Figure 3).

According to the DFT calculations benzimidazol-2-ylidene **1′**(CH_3 instead of neopentyl group in **1**) is a harder nucleophile than **2′** (H instead

of CH_3 at C═C in **2**). It undergoes exclusively the thermodynamically favored P≡*C*-attack.

In conclusion, the electronic structures of the phosphaalkynes (with or without π-donor substituents), as well as those of the *N*-heterocyclic carbenes, determine the reaction pathway of the adduct formation. Generally, the formation of three different types of phospha-heterocycles (type **6**, **7**, or **9**) may be expected. By reacting a soft carbene (**2**) with an electron rich phosphaalkyne (**3b**), we can direct the course of the reaction towards a primary attack of the carbene carbon atom at the phosphorus atom of the phosphaalkyne. This allows for the unusual CH-activation at the nitrogen substituent of the Arduengo carbene.

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