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Phosphorus Heterocycles

The 1,1-Carboboration of Bis(alkynyl)phosphanes as a Route to Phosphole Compounds**

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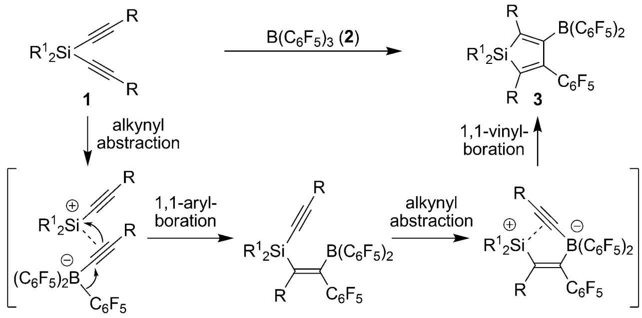
Dedicated to Professor Dieter Hoppe on the occasion of his 70th birthday

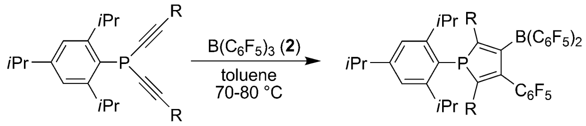
Phospholes have been receiving increasing interest as a class of compounds. They possess a planar five-membered heterocyclic framework that has the heavy Group 15 element incorporated in a markedly nonplanar coordination geometry. Consequently, in contrast to the other first-row five-membered heteroarenes, the phospholes are only weakly aromatic.[1] There are far fewer established synthetic pathways to phospholes compared to their first-row-element relatives. The classical elimination pathway described by Mathey et al.[2] has been augmented by some Group 4 metallocene alkyne coupling/phosphorylation pathways and related syntheses.[3] Nevertheless, the phosphole framework is increasingly being used, for example, in materials science,[4] especially in conjunction with boron-based acceptor substituents in conjugation with the P donor.[5] Also rigid conjugated zwitterionic phosphonium/borate frameworks have recently been studied and found considerable interest.[6] We have now found a new very simple synthesis that directly makes 3-boryl substituted phospholes available from suitable bis(alkynyl)phosphanes in a one-pot reaction. Several representative examples are described and characterized herein and their synthetic utilization explored.

We have recently shown that bis(alkynyl)silanes **1** undergo a special variant of the "Wrackmeyer 1,1-carboboration reaction" sequence[7] under very mild reaction conditions upon treatment with the strong Lewis acid tris(pentafluorophenyl)borane (**2**) to give the respective borylsiloles **3**.[8,9] The reaction probably involves a sequence as depicted in Scheme 1, involving a typical series of 1,1-carboboration reactions of activated alkynes.[10]



Scheme 1. Formation of silols by 1,1-carboboration.

The arylbis(alkynyl)phosphanes **5a–c** were prepared by treatment of the (tipp)PX_2 compounds **4** (X = Cl, Br; tipp = 2,4,6-triisopropylphenyl) with the respective alkynyl lithium reagents LiC≡C-R (R = $SiMe_3$ (**a**), *n*-C_3H_7 (**b**), Ph (**c**)). The mesitylP(C≡C-$SiMe_3$)$_2$ starting material **6a** was prepared analogously. The bis(alkynyl)phosphane **5a** was treated with one equivalent of $B(C_6F_5)_3$ in toluene solution at 70 °C (2 h) to give the phosphole **7a** in 79 % yield (Scheme 2). Compound **7a** shows the typical broad ^{11}B NMR resonance of a trivalent R-$B(C_6F_5)_2$ boron Lewis acid at $\delta = 63$ ppm, a ^{31}P NMR signal at $\delta = 59.1$ ppm and a pair of ^{29}Si NMR resonances at $\delta = -7.8$ and -8.2 ppm. The X-ray crystal-structure analysis of **7a** (Figure 1) shows the planar central five-membered ring. Typically, the phosphorus–carbon distances P1–C1 and P1–C4 inside the weakly aromatic heterocycle are markedly shorter than the exocyclic P–C(aryl) bond (Table 1), but the coordination geometry at phosphorus is markedly nonplanar. The coordination plane of the trigonal-planar boron moiety is rotated markedly from the central ring plane (dihedral angle C1-C2-B1-C51: −52.0(6)°).



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7a: R = $SiMe_3$, 79%
7b: R = *n*Pr, 97%
7c: R = Ph, 89%

Scheme 2. Preparation of phospholes by 1,1-carboboration.

The reaction of **5b** with $B(C_6F_5)_3$ proceeded analogously at 80 °C (1 h) to give **7b** in near to quantitative yield (97 %, NMR: $\delta = 62$ (^{11}B), $\delta = 16.5$ ppm (^{31}P))[11a] and we prepared the phosphole **7c** similarly from **5c** and $B(C_6F_5)_3$. Both phospholes were also characterized by X-ray crystal structure

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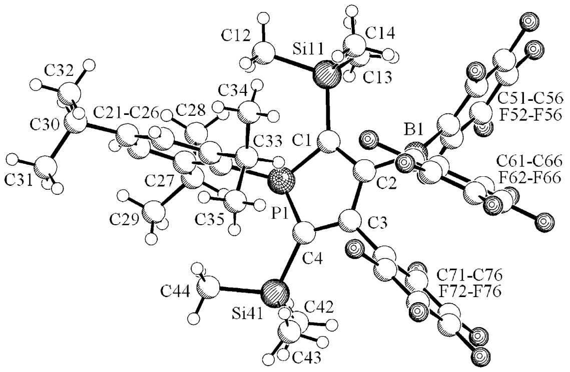


Figure 1. A view of the crystal structure of the phosphole **7a**. See Table 1 for selected bond lengths and angles.

Table 1: Selected structural data of the phospholes **7** and **10**.[a]

Parameter	**7a**	**7b**	**10c**
P1–C1	1.772(4)	1.774(2)	1.788(2)
P1–C4	1.769(4)	1.779(3)	1.788(2)
P1–C21	1.821(4)	1.823(2)	1.836(2)
C1–C2	1.391(6)	1.387(3)	1.369(2)
C3–C4	1.380(5)	1.362(3)	1.369(3)
C2–C3	1.462(6)	1.464(3)	1.457(2)
C2–B1	1.550(6)	1.541(4)	–
Angles			
Σ at P	328.1	321.5	314.7
Σ at B	359.9	360.0	–

[a] Bond lengths [Å], angles [°].

analysis (for details see Table 1 and the Supporting Information).

In each case the reaction course was monitored by ^{31}P NMR spectroscopy. The reaction of **5b** with $B(C_6F_5)_3$ is a representative example. After 1 min at 318 K in [D$_6$]benzene solution the **5b**/$B(C_6F_5)_3$ pair had converted quantitatively into a single new product (**8b**) characterized by a typical ^{31}P NMR signal at $\delta = -166.2$ ppm.[12]

Upon standing of the product solution at 318 K, two products were formed from **8b**, namely the phosphole **7b** and a new product (**9b**, ^{31}P NMR: $\delta = -35.5$ ppm, t, $J_{PF} \approx 41$ Hz). Both the secondary products **7b** and **9b** are initially formed at about the same rate, but after some time **9b** is also consumed to eventually yield the stable phosphole **7b** (Figure 2). The reaction systems **5a**/$B(C_6F_5)_3$ and **5c**/$B(C_6F_5)_3$ show a similar behavior.

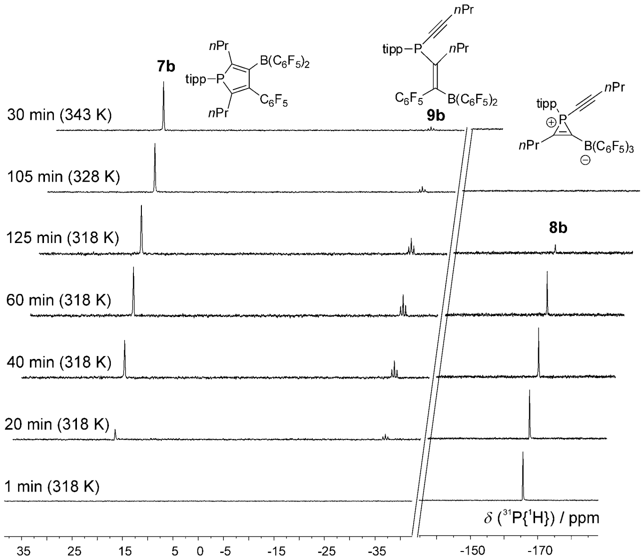
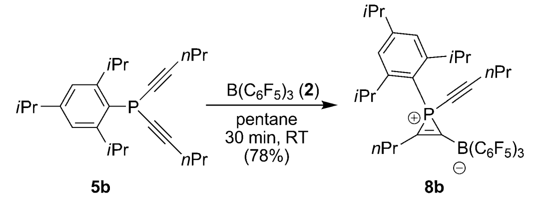


Figure 2. The reaction course of the **5b**/$B(C_6F_5)_3$ system monitored by ^{31}P NMR spectroscopy ([D$_6$]benzene, 81 MHz, 318 K to 343 K).



Scheme 3. Formation of phosphirenium borate zwitterion **8b**.

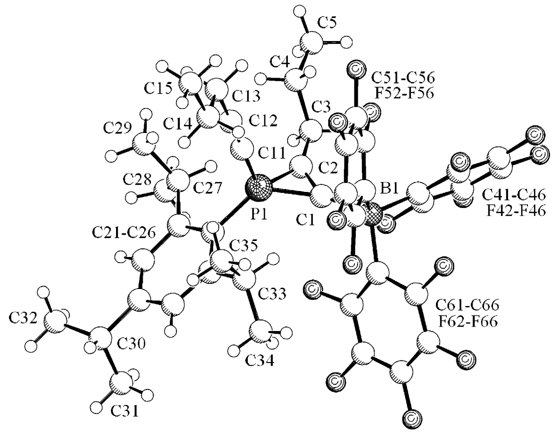
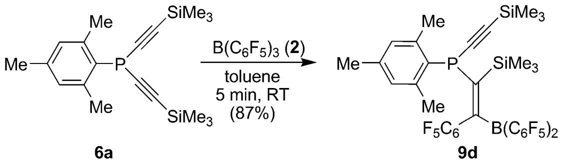


Figure 3. A view of the crystal structure of the zwitterionic phosphirenium borate **8b**. Selected bond lengths [Å] and angles [°]: P–C1 1.771(2), P–C2 1.734(2), P1–C11 1.726(2), P1–C21 1.793(2), C1–C2 1.323(3), C1–B1 1.623(3); C1-P1-C2 44.3(1), C11-P1-C21 110.4(1).

We were able to isolate compound **8b** by performing the reaction of **5b** with $B(C_6F_5)_3$ under strict kinetic control (Scheme 3).[11b] The **5b**/$B(C_6F_5)_3$ reaction mixture was stirred in pentane solution for 30 min at room temperature and the product crystallized at −35 °C. The product was isolated in 78 % yield (^{31}P NMR: $\delta = -166.2$ ppm, ^{11}B NMR: $\delta = -17.7$ ppm) and identified as the phosphirenium borate zwitterion **8b**. The X-ray crystal structure analysis (Figure 3) revealed the formation of a central three-membered phosphorus containing heterocycle. It contains P–C1 and P–C2 σ-bonds. The phosphorus atom is tetracoordinate and the $B(C_6F_5)_3$ substituent is attached at carbon atom C1 of the central three-membered ring.

The follow-up product **9b** was not isolated directly but it was identified by comparison with an analogous product in a closely related mesityl–phosphorus system. Treatment of mesitylP(C≡C-SiMe$_3$)$_2$ (**6a**) with $B(C_6F_5)_3$ for 5 min in



Scheme 4. Formation of product **9b**.

toluene at room temperature and crystallization (from *n*-pentane) gave **9d** in 87 % yield (Scheme 4). The X-ray crystal-structure analysis revealed that this product was formed by 1,1-carboboration at one of the P-bound alkynyl groups (Figure 4). The resulting phosphinoalkene moiety is *Z*-configured and the other alkynyl unit at the phosphorus atom has remained intact.

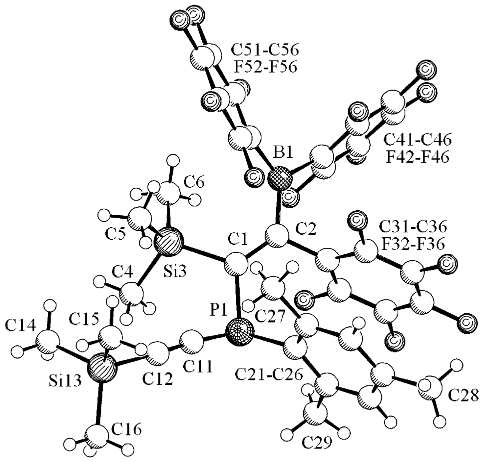
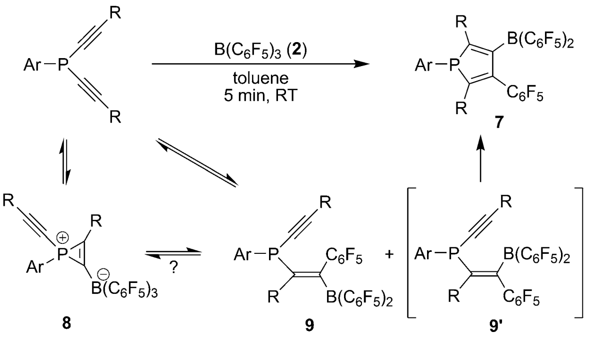


Figure 4. A view of the crystal structure of compound **9d**. Selected bond lengths [Å] and angles [°]: P1–C1 1.838(3), P1–C11 1.762(3), C1–C2 1.364(4), C11–C12 1.206(5), C2–B1 1.545(4), C1–Si3 1.931(3); P1-C1-C2 122.7(2), C1-C2-B1 128.6(3); sum of bond angles at P1: 313.8.

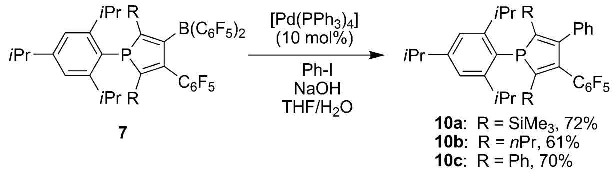
Product **9d** shows a typical ^{11}B NMR resonance at $\delta = 59$ ppm. It shows a set of ^{19}F NMR features of the $B(C_6F_5)_2$ functional group at $\delta = -126.3$ (*o*), -146.1 (*p*), -161.2 ppm (*m*) and a separate set of signals of the C_6F_5 group at carbon C2 ($\delta = -136.5$ (*o*), -155.6 (*p*), -162.6 ppm (*m*)). Most significantly, compound **9d** exhibits a $^{31}P\{^1H\}$ NMR signal at $\delta = -33.5$ ppm[13] (t, $J_{PF} \approx 34$ Hz), that is characteristic for this class of compounds. Heating of **9d** in [D$_6$]benzene (90 °C, 1.5 h) gave the corresponding phosphole **7d** (for details see the Supporting Information).

These observations indicated to us that phosphanyl groups may serve as "activating" migrating groups in 1,1-carboboration reactions (Scheme 5). This may be due to stabilization of the phosphirenium subunit in the zwitterionic intermediates (**8**) by their alleged "σ*-aromaticity" features as has been proposed for their analogous cationic parent compounds.[14]

The phospholes (**7**) that are formed so readily from the arylbis(alkynyl)phosphanes **5** and $B(C_6F_5)_3$ are not only interesting P/B systems, but they are also reagents for metal-catalyzed cross-coupling reactions.[9] Treatment of the borylphosphole **7a** with iodobenzene at 65 °C in THF under typical Suzuki–Miyaura conditions (10 mol % [Pd(PPh$_3$)$_4$] catalyst, NaOH base) resulted in the formation of the cross-coupling product **10a** (Scheme 6). The analogous treatment of the phospholes **7b** and **7c** gave the products **10b** and **10c**, respectively. Both the compounds **10a** and **10c** were characterized by X-ray diffraction (for details see the Supporting Information). The phosphole derivative **10c** (Figure 5) shows a fivefold substituted central phosphole framework with the phenyl groups at the carbon atoms C1 and C4 originating from the alkynyl moieties of the starting material (**5c**), the pentafluorophenyl group at C3 having been introduced by the $B(C_6F_5)_3$ reagent during the 1,1-carboboration reaction, and the phenyl group at carbon atom C2 having been attached in the final palladium-catalyzed cross-coupling reaction (for details see Figure 4 and Table 1).



Scheme 5. Proposed reaction mechanism of the 1,1-carboboration reaction sequence leading to the phospholes **7**.



Scheme 6. Cross-coupling reactions of borylphospholes.

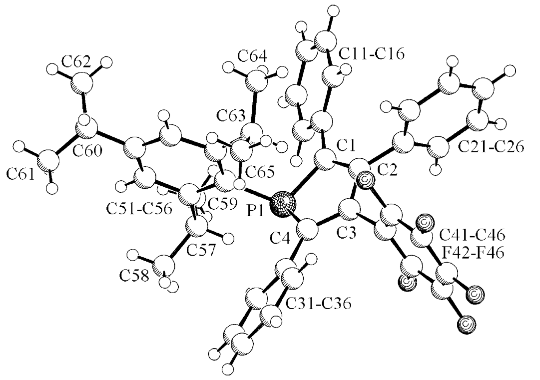


Figure 5. Molecular structure of the phosphole **10c**. See Table 1 for selected bond lengths and angles.

Our study shows that our new variant of the 1,1-carboboration sequence[9] can be applied to the synthesis of new phosphole derivatives. This result indicates that the 1,1-carboboration reaction may have an even greater potential for preparing useful olefinic and heterocyclic borane derivatives than previously thought. We are actively pursuing the extension of this development.

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[11] a) Preparation of **7b**: Compound **6b** (0.52 mmol, 1 equiv) and $\mathrm{B(C_6F_5)_3}$ (0.52 mmol, 1 equiv) were mixed in toluene (25 mL) and the solution heated to 80 °C for 1 h. Evaporation of the volatiles, redissolving in pentane (10 mL), removal of solids by filtration, and removal of solvents in vacuo yielded **7b** (0.50 mmol, 97 %) as orange oil which crystallized when left standing. Crystal data of $\mathrm{C_{43}H_{37}BF_{15}P}$, $M_r = 880.51$, monoclinic, $P2_1/c$ (No. 14), $a = 13.4531(3)$, $b = 32.5343(7)$, $c = 9.3758(2)$ Å, $\beta = 90.246(1)°$, $V = 4103.63(15)$ Å^3, $\rho_{\text{calcd}} = 1.425\ \text{g cm}^{-3}$, $\mu = 0.166\ \text{mm}^{-1}$, $F(000) = 1800$, $Z = 4$, $\lambda = 0.71073$ Å, $T = 223(2)$ K, 33333 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å^{-1}, 9543 independent ($R_{\text{int}} = 0.036$), and 6764 observed reflections $[I \geq 2\sigma(I)]$, 557 refined parameters, $R = 0.062$, $wR^2 = 0.158$, GOF = 1.054. b) Preparation of **8b**: Compound **6b** (1.2 mmol, 1 equiv) and $\mathrm{B(C_6F_5)_3}$ (1.2 mmol, 1 equiv) were mixed in pentane (8 mL), the solution stirred for 30 min at room temperature and precipitated at −35 °C. Removal of the supernatant solution, washing of the solid with cold pentane (5 mL) and drying in vacuo gave **8b** (1.0 mmol, 78 %) as pale yellow solid. Crystal data for $\mathrm{C_{43}H_{37}BF_{15}P}$, $M_r = 880.51$, triclinic, $P\bar{1}$ (No. 2), $a = 10.7736(7)$, $b = 11.1932(5)$, $c = 19.2748(4)$ Å, $\alpha = 74.564(2)$, $\beta = 80.781(4)$, $\gamma = 69.127(4)°$, $V = 2087.96(17)$ Å^3, $\rho_{\text{calcd}} = 1.401\ \text{g cm}^{-3}$, $\mu = 1.464\ \text{mm}^{-1}$, $F(000) = 900$, $Z = 2$, $\lambda = 1.54178$ Å, $T = 223(2)$ K, 25680 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 7119 independent ($R_{\text{int}} = 0.044$), and 6360 observed reflections $[I \geq 2\sigma(I)]$, 549 refined parameters, $R = 0.044$, $wR^2 = 0.121$, GOF = 1.021.

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