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Phosphirenium-borate zwitterion: formation in the 1,1-carboboration reaction of phosphinylalkynes†‡

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Reaction of the acetylene $Mes_2P–C{\equiv}C–Ar$ with $B(C_6F_5)_3$ at rt gives a zwitterionic phosphirenium product, which reacts further at >100 °C to complete the 1,1-carboboration reaction.

1,1-Carboboration[1] of alkynes is increasingly becoming synthetically useful. It was recently shown that using strongly electrophilic $RB(C_6F_5)_2$ type boranes has allowed carrying out facile 1,1-carboboration reactions of simple 1-alkynes.[2–4] In these cases the boron bonded alkyl groups R migrate preferentially (Chart 1). The resulting alkenylboranes (**1**) are interesting strong Lewis acids in themselves and they have served as useful substrates in palladium catalyzed cross-coupling reactions. Thus, such 1,1-carboboration reactions of terminal acetylenes are increasingly becoming useful conceptual alternatives to the ubiquitous 1,2-hydroboration of alkynes.[3]

Recently it was shown that the 1,1-carboboration reaction can even be used for carbon–carbon σ-bond activation. We found that the internal acetylene 4-octyne reacted with $B(C_6F_5)_3$ at elevated temperatures to cleanly give the 1,1-carboboration product (**2**), formed by cleavage of a strong $C(sp^3)–C(sp)$ σ-bond and 1,2-migration of the *n*-propyl substituent. Several additional related examples were reported.[5,6] Carbon–phosphorus σ-bonds can be cleaved analogously. We recently described the 1,1-carboboration reaction of phosphinylalkynes[7] at elevated temperature as a synthetic alternative to the previously described nucleophilic routes[8] to 1,2-phosphinyl/boryl-substituted alkenes (**4**), compounds that are of considerable interest *e.g.* due to their photophysical properties.[9] We have now found that the reaction of $B(C_6F_5)_3$ with a phosphinylalkyne proceeds rapidly even at low temperature, but to a different outcome. A first example of an interesting novel class of compounds has become readily available in this way.

Starting material for our study was the 1-dimesitylphosphinyl-2-*p*-tolylacetylene **3c**.[10] This compound was prepared by treating *p*-tolylacetylene with *n*-butyl lithium followed by Mes_2PCl. The product (**3c**) was isolated in 40% yield. It features a ^{31}P NMR resonance at δ −55.7 and ^{13}C NMR signals of the central acetylene unit at δ 107.6 ($^2J_{PC}$ = 8.4 Hz) and δ 87.8 ($^1J_{PC}$ = 6.2 Hz). The X-ray crystal structure analysis of **3c** shows the presence of a linear central framework (P1–C1: 1.766(2) Å, C1–C2: 1.204(3) Å, C2–C3: 1.433(3) Å, angles P1–C1–C2: 165.0(2)°, C1–C2–C3: 176.1(2)°; see Fig. 1).

We had previously shown that dimesitylphosphinylalkynes undergo 1,1-carboboration with $B(C_6F_5)_3$ at temperatures >100 °C. Consequently, the Mes_2P-substituted acetylene (**3c**) reacted cleanly with $B(C_6F_5)_3$ at 105 °C for 6 h to give

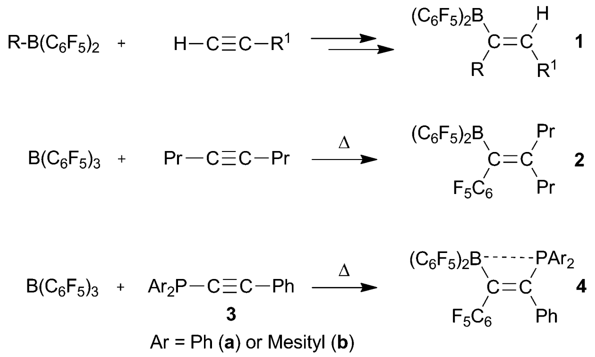

Chart 1

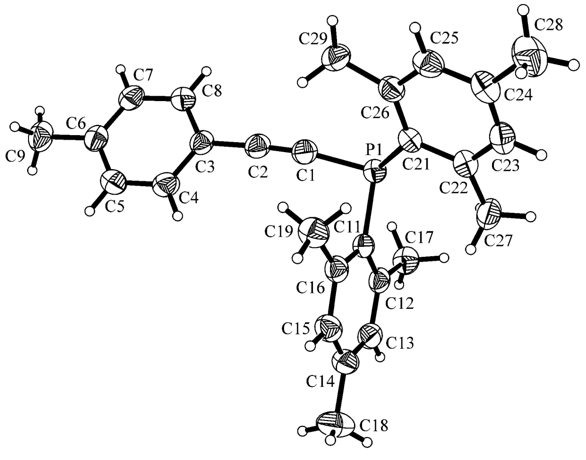

Fig. 1 A view of the molecular geometry of compound **3c** ¶.

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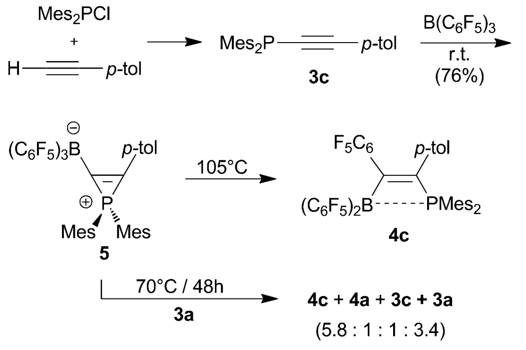
† Dedicated to Professor Heinz Berke on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Additional experimental and spectroscopic data. CCDC 826907–826909. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc13008k

§ X-Ray structure analyses.



Scheme 1

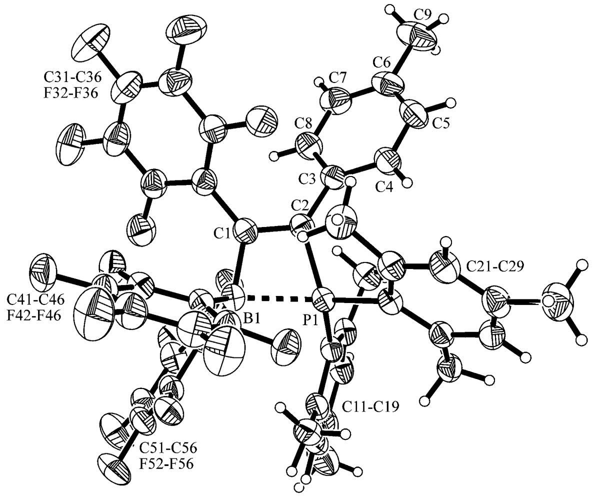


Fig. 2 A view of the molecular structure of compound **4c** ¶.

the product **4c** that was isolated in 65% yield. Compound **4c** features a ^{11}B NMR resonance at δ 0 and a ^{31}P NMR signal at +14.6. It shows sets of each three ^{19}F NMR signals of the C_6F_5 substituent at carbon [δ −136.7 (*o*), −156.3 (*p*), −163.7 (*m*)] and the pair of C_6F_5 substituents at boron [δ −127.3 (*o*), −158.0 (*p*), −165.2 (*m*)]. The X-ray crystal structure analysis of compound **4c** shows a central four-membered heterocyclic framework [C1–C2: 1.353(2) Å, B–C1: 1.634(2) Å, P1–C2: 1.827(2) Å, angles C2–C1–B: 107.9(1)°, C1–C2–P1: 97.0(1)°]. The B···P bond is long at 2.094(2) Å (see Scheme 1 and Fig. 2).

At room temperature the reaction of the Mes$_2$P-substituted alkyne **3c** with the boron Lewis acid B(C_6F_5)$_3$ stops at the intermediate **5**. Stirring of **3c** with B(C_6F_5)$_3$ in pentane at ambient temperature for 30 min gave a white precipitate of the new product **5** that was isolated in 76% yield.‖ Compound **5** was characterized spectroscopically, by C,H elemental analysis and by X-ray diffraction (see Scheme 1 and Fig. 3).

It revealed the formation of a central three-membered heterocyclic phosphirenium ring system, with pertinent bonding parameters of the pair of crystallographically independent molecules of C1–C2: 1.325(6) Å [1.330(6) Å], C1–P1: 1.793(5) Å [1.799(5) Å] and C2–P1: 1.755(5) Å [1.746(4) Å]. The latter bond is markedly shorter than the C(sp^2)–P bonds to the mesityl substituents [P1–C11: 1.802(5) Å [1.809(4) Å], P1–C21: 1.809(5) Å [1.807(5) Å], which might indicate some extra-stabilisation of the unsaturated three-membered ring system *e.g.* by "σ*-conjugation" as it had been discussed for some 1H-phosphirenium cations in the literature.[11] The bond angles inside the central phosphirenium ring of compound **5** amount to 66.6(3)° [65.8(3)°] (C2–C1–P1), 69.6(3)° [70.1(3)°] (C1–C2–P1) and 43.8(2)° [44.0(2)°] (C1–P1–C2), respectively. The bulky (C_6F_5)$_3$B-substituent is attached at carbon atom C1 of the central core of compound **5** (C1–B: 1.647(7) Å [1.629(7) Å]). The *p*-tolyl substituent at the ring carbon atom C2 (C2–C3: 1.464(7) Å [1.477(6) Å]) is rotated markedly out of the plane of the unsaturated phosphirenium system (*Θ* C1–C2–C3–C4: 123.5(7)° [35.2(9)°]).

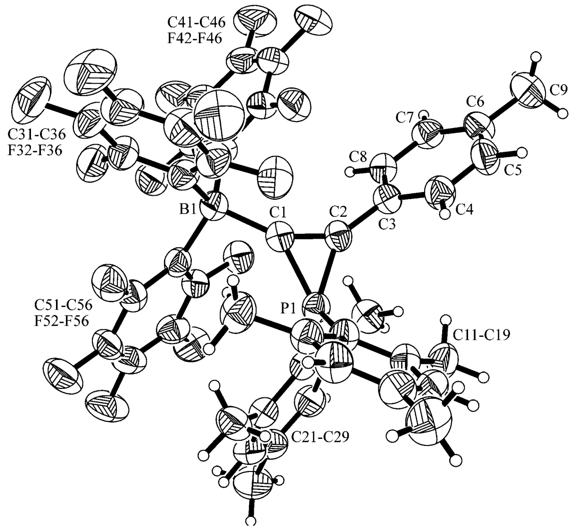


Fig. 3 Molecular structure of the zwitterionic compound **5** ¶.

Compound **5** features a ^{11}B NMR signal at δ −16.5 and ^{19}F NMR signals of the three symmetry-equivalent adjacent C_6F_5 groups in a typical borate range [δ −130.3(*o*), −159.5(*p*), −164.5(*m*)]. The ^{31}P NMR signal at δ −137.8 corresponds well with the phosphirenium character[12] of the central unit of the zwitterion **5**. The adjacent phosphirenium carbon atoms show ^{13}C NMR resonances at δ 151.6 ([B]C=) and δ 136.7 (=C[tolyl]), respectively.

Upon heating to 105 °C compound **5** rearranges to the 1,1-carboboration product **4c**. A crossover experiment revealed that the formation of the phosphirenium borate zwitterion **5** is at least partly reversible. Heating of **5** for prolonged time at 70 °C in the presence of Ph$_2$P–C≡C–Ph (**3a**) (**5** : **3a** ≈ 1 : 1.3) gave the intramolecular 1,1-carboboration product **4c** admixed with a small amount of the crossover product **4a** and the free Mes$_2$P–C≡C–p-tol acetylene derivative (**3c**). In a typical experiment these three products and remaining **3a** were obtained in a ratio of **4c**, **4a**, **3c** and **3a** of *ca.* 5.8 : 1 : 1 : 3.4.

These results show that treatment of a phosphinylacetylene with B(C_6F_5)$_3$ results in the migration of the diorganylphosphinyl group at ambient conditions. The reaction proceeds to a phosphirenium type product that provides sufficient internal stabilisation for the system to serve as a resting stage of this cooperative rearrangement process. It shows that the modern variants of the 1,1-carboboration reactions have synthetic power making interesting organic main group element compounds readily available. The observation that the title compounds of this study, the phosphirenium-borate zwitterions, are easily obtained even at room temperature lets us hope that a specific chemistry of these neutral derivatives of the phosphirenium cations will be developed.

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Notes and references

¶ Crystal data: **3c**: $C_{27}H_{29}P$, $M = 384.47$, triclinic, $P\bar{1}$, (No. 2), $a = 10.1751(5)$, $b = 10.6783(4)$, $c = 11.6493(7)$ Å, $\alpha = 96.462(2)°$, $\beta = 107.570(4)°$, $\gamma = 109.165(4)°$, $V = 1107.87(10)$ Å^3, $D_c = 1.153$ g cm^{-3}, $\mu = 1.142$ mm^{-1}, $F(000) = 412$, $Z = 2$, $\lambda = 1.54178$ Å, $T = 223(2)$ K, 15 949 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 3784 independent ($R_{int} = 0.048$), and 3388 observed reflections [$I \geq 2\sigma(I)$], 260 refined parameters, $R = 0.044$, w$R^2 = 0.123$, GoF = 1.039. CCDC 826907.

4c: $C_{45}H_{29}BF_{15}P$, $M = 896.46$, triclinic, $P\bar{1}$, (No. 2), $a = 12.4342(5)$, $b = 13.4995(6)$, $c = 14.2303(6)$ Å, $\alpha = 82.805(2)°$, $\beta = 66.678(2)°$, $\gamma = 64.037(2)°$, $V = 1968.75(14)$ Å^3, $D_c = 1.512$ g cm^{-3}, $\mu = 1.570$ mm^{-1}, $F(000) = 908$, $Z = 2$, $\lambda = 1.54178$ Å, $T = 223(2)$ K, 28 030 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 6739 independent ($R_{int} = 0.038$), and 6261 observed reflections [$I \geq 2\sigma(I)$], 566 refined parameters, $R = 0.037$, w$R^2 = 0.109$, GoF = 1.034. CCDC 826908.

5: $C_{48}H_{36}BClF_{15}P$, $M = 975.00$, orthorhombic, $Pca2_1$ (No. 29), $a = 21.7497(6)$, $b = 22.5390(4)$, $c = 17.9477(6)$ Å, $V = 8798.3(4)$ Å^3, $D_c = 1.472$ g cm^{-3}, $\mu = 1.998$ mm^{-1}, $F(000) = 3968$, $Z = 8$, $\lambda = 1.54178$ Å, $T = 223(2)$ K, 47 800 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 14 469 independent ($R_{int} = 0.074$), and 12 099 observed reflections [$I \geq 2\sigma(I)$], 1206 refined parameters, $R = 0.059$, w$R^2 = 0.157$, GoF = 1.033. CCDC 826909.

‖ Preparation of compound **5**: $B(C_6F_5)_3$ (0.400 g, 0.780 mmol) and **3c** (0.300 g, 0.780 mmol) were suspended in pentane (15 ml) and stirred for 30 minutes at room temperature. After filtration **5** (0.534 g, 0.596 mmol, 76%) was obtained as a white solid. Crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **5** in dichloromethane at −36 °C. [Elemental analysis, found: C, 60.37; H, 3.51%; calcd. for $C_{45}H_{29}BF_{15}P$: C, 60.29; H, 3.26%; ^{13}C NMR $\delta = 151.6$ (br, $^{B}C^{-}$), 136.7 ($^{Tol}C^{-}$); ^{19}F NMR $\delta = -130.3$ (*o*), −159.5 (*p*), −164.5 (*m*); ^{11}B NMR $\delta = -16.5$; ^{31}P NMR $\delta = -137.8$.]

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