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Carbaborane-based alkynylphosphanes and phospholes†

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The reaction of 1,2-bis(N,N-dimethylaminochloro-phosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) and lithiated phenylacetylene gives a five-membered dihydrophosphole derivative with an exocyclic phosphanyl group. This unexpected reaction opens new possibilities for the synthesis of carbaborane-containing phosphorus heterocycles. P,P′-alkynylated 1,2-bis(phosphanyl)-1,2-dicarba-*closo*-dodecaborane(12)s are obtained from alkynylchlorophosphanes and dilithiated carbaborane. This new class of alkynes can be used for future applications in cyclizations and polymerizations.

Alkynylphosphanes [>P–C≡C–] have attracted considerable attention, not only due to their unique electronic properties that arise from interactions of phosphorus-based orbitals with the π system of the alkyne unit, but also because of their interesting spectroscopic and thermodynamic properties.[1] Furthermore, owing to the well-established coupling chemistry of the acetylene moiety, they are appealing building blocks for more elaborate molecular architectures such as phospha-pericyclynes and oligomers.[2] In addition, the acetylenes can be engaged in subsequent chemistry, and allow, for example, the formation of a variety of hetero- and carbocycles, such as phospholes[3a] and diphosphinidenecyclobutenes.[3b,c]

The combination of acetylenes with electron-deficient moieties offers the possibility to prepare monodisperse oligomers or polymers with high electron-acceptor capacities. Acetylenic scaffolds with fullerene units[4] and cyanoethynylethenes[5] are probably the best studied compounds in this context. The combination of

alkynylphosphanes with *ortho*-carbaborane would be an interesting addition to this field, as such structures would merge the electron-withdrawing and -delocalizing properties of an *ortho*-carbaborane[6] with the electronic properties and reactivity of the alkynylphosphane moiety. Such combinations of carbaboranes with alkynylphosphanes would make fascinating building blocks for new polymeric or heterocyclic systems.

There are several synthetic approaches for alkynylphosphanes, the most widely applied of which is the nucleophilic attack of an acetylide at halophosphanes.[7] Therefore, in a first attempt to obtain P,P′-alkynylated 1,2-bis(phosphanyl)-1,2-dicarba-*closo*-dodecaborane(12)s, 1,2-bis(N,N-dimethylaminochlorophosphanyl)-1,2-dicarba-*closo*-dodecacaborane (1)[8] was treated with two equivalents of lithiated phenylacetylene (Scheme 1).[9]

The ³¹P NMR spectrum of the reaction mixture showed the formation of the proposed product (6a, see Scheme 3) as well as many other products. Attempts to isolate 6a failed; however, yellow crystals of the highly substituted five-membered heterocycle 2 were isolated in 20% yield (Scheme 1). Compound 2 is a highly functionalized dihydrophosphole to which a carbaborane unit is fused *via* two carbon centers, with a dimethylamino group at the phosphole P atom as well as an exocyclic alkynyl-phosphanyl substituent.
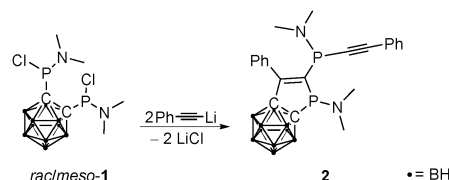
The $^{31}P\{^{1}H\}$ NMR spectrum of 2 (in C_6D_6) exhibits two doublets at 35.3 (P2, see Fig. 1) and 87.6 ppm (P1, $^{2}J_{PP}$ = 20.7 Hz). The exocyclic alkynyl group is observed in the $^{13}C\{^{1}H\}$ NMR spectrum as two doublets at 78.1 ($^{1}J_{CP}$ = 90.0 Hz) and 108.3 ppm ($^{3}J_{CP}$ = 4.2 Hz), and the signals for C3 and C4 (Fig. 1) of the

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Scheme 1 Synthesis of carbaborane-based alkynylphosphane-substituted phosphole 2.
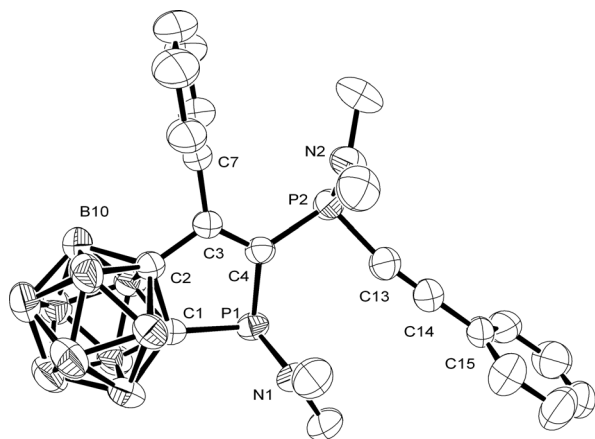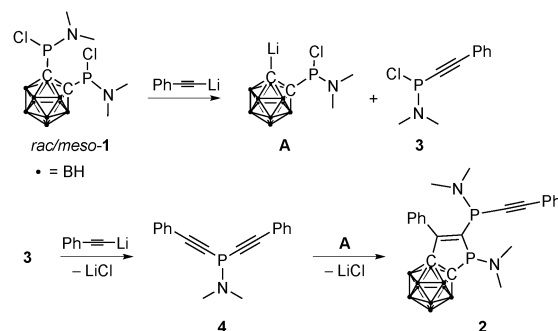
Fig. 1 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): C1–C2 1.624(3), C2–C3 1.506(3), C3–C4 1.342(2), C1–P1 1.878(2), P1–C4 1.842(2), C4–P2 1.836(2), P2–C13 1.776(3), C13–C14 1.198(3), B–B 1.749–1.785, B–C 1.706–1.733, C1–C2–C3 118.1(2), C2–C3–C4 116.1(2), C3–C4–P1 116.8(2), C4–P1–C1 89.58(9), P1–C1–C2 108.9(1), P1–C4–P2 118.3(1) (hydrogen atoms have been omitted for clarity; ellipsoids are shown at 50% probability). Only the S_P, S_P isomer is shown.

Scheme 2 Proposed mechanism for the formation of **2** and the observed byproduct **4**.

endocyclic double bond are observed as two doublets of doublets at 149.2 ($^1J_{CP}$ = 43.1, 43.3 Hz) and 150.0 ppm ($^2J_{CP}$ = 5.1, 5.6 Hz). Furthermore two doublets are observed for the carbon cluster atoms of the heterocycle at 84.6 ($^1J_{CP}$ = 20.5 Hz) and 88.0 ppm ($^2J_{CP}$ = 6.8 Hz). The $^{11}B\{^1H\}$ NMR spectrum shows five signals in the ratio 1 : 1 : 2 : 2 : 4.

An X-ray structure analysis was carried out for **2** (Fig. 1).[10] Yellow crystals of **2** were obtained at −20 °C from *n*-hexane. The endocyclic C2–C3, C3–C4, C1–P1, and P1–C4 bond lengths (1.506(3), 1.342(2), 1.878(2), and 1.842(2) Å) in 1-diethylamido-2,3-dihydro-1*H*-phosphole **2** compare well with the corresponding bonds found in 1*H*-phosphindole-1-sulfides[11] or pentaphenyl-2,3-dihydro-1*H*-phosphole.[12] The C1–C2 bond (1.624(3) Å) is longer than in these heterocycles (1.391(4), 1.523(3) Å),[9,10] but similar to those of carbaborane-substituted 1,2-diphosphetanes (1.645(4), 1.631(5) Å).[13] The P2–C13 and C13–C14 bond lengths (1.776(3), 1.198(3) Å) are in the same range as found in [8-(dimethylamino-κN)-1-naphthalenyl-κC]-diphenylethynylphosphorus (1.786(9), 1.184(9) Å).[14] The phosphorus atoms P1 and P2 in the isolated *rac* isomer of compound **2** have a pyramidal, and the nitrogen atoms N1 and N2 a trigonal-planar environment.

A mechanism for the formation of **2** was proposed on the basis of computational and ^{31}P NMR spectroscopic studies. The first step of the sequence is the cleavage of one P–C bond in **1** by lithiated phenylacetylene, resulting in intermediates **A** and **3** (Scheme 2 and ESI†). Such *exo*-polyhedral C–E bond (E = P, C) cleavage in mono- and disubstituted dicarba-*closo*-dodecaborane(12)s has been reported earlier.[15] The second equivalent of lithiated phenylacetylene reacts with **3** to give the dialkynyl(amido)phosphane **4** (Scheme 2). Subsequently, the Li–$C_{cluster}$ bond of **A** inserts into one of the carbon–carbon triple bonds of **4**, and **2** is formed after LiCl elimination. The addition of organolithium compounds to carbon–carbon triple bonds has been described in the literature.[16] For the investigation of the proposed mechanism
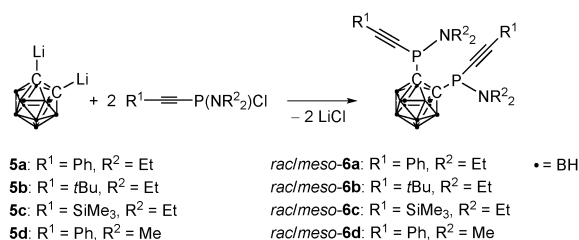
(Scheme 2), alkynylphosphanes **3** and **4** were synthesized independently and fully characterized. On the basis of their ^{31}P NMR shifts, both species could be identified in the reaction solution, and the formation of **4** by reaction of **1** and lithiated phenylacetylene was thus verified. Compound **4** polymerizes very fast above 0 °C and seems to be responsible for the dark color of the reaction solution. Polymerization of **4** is presumably also responsible for the moderate yield of **2**.

While the unexpected reactivity of **1** towards lithium acetylides gives rise to the unusual phosphole **2**, the initially desired bis(alkynylphosphanyl)carbaboranes remain elusive by this synthetic strategy. They can, however, be prepared in a different procedure from alkynylchlorophosphanes **5a–5d** and lithiated *ortho*-carbaborane (Scheme 3) in a twofold nucleophilic substitution reaction. The bis(alkynylphosphanyl)carbaboranes **6a–6d** are stable under ambient conditions and were obtained in moderate to good yields.

Compounds **1**, **2**, and **6d** were investigated by cyclic voltammetry (CV) to elucidate the electronic communication between the different *P*-substituents in the three compounds and the carbaborane unit. Phosphole **2** features one irreversible oxidation at $E_{p,a}$ = 0.85 V *vs.* Fc$^{+/0}$, and thus at a potential that is very similar to that found for **6d** ($E_{p,a}$ = 1.00 V). It is thus tempting to assign this process to an oxidation of mainly the P(NMe$_2$)(CCR) substituent, which is present in both compounds. Supporting this assignment is the notion that the oxidation potential of the P(NMe$_2$)(CCR) group in **2** can be expected to be somewhat lower than that of **6d** due to the presence of the conjugated endocyclic double bond in the former. Neither CV of the two compounds shows a reductive feature within the solvent window down to −2.3 V *vs.* Fc$^{+/0}$, in analogy to the reported reduction

Scheme 3 Synthesis of *P,P'*-alkynylated 1,2-bis(*N,N*-dialkylaminophosphanyl)-1,2-dicarba-*closo*-dodecaborane(12)s **6a–6d**.

potential of the unsubstituted, parent dicarba-*closo*-dode-caborane(12).[17] The only cathodic process that is observed for the three compounds is an irreversible reduction of *rac/meso-***1** at $E_{p,c}$ = 2.20 V (see ESI†) which is assigned to the electron-deficient phosphane units, rather than to processes that are localized on the carborane core.[17]

In conclusion, the reaction of 1,2-bis(*N*,*N*-dimethyl-amino-chlorophosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (**1**) and lithiated phenylacetylene gave an unusual five-membered heterocycle **2** containing an exocyclic alkynylphosphane unit and a dimethylamino group at the phosphole P atom. The high degree of functionalization should offer multiple possibilities for the synthesis of future carbaborane-containing phos-phorus heterocycles. 1,2-Bis(phosphanyl)-1,2-dicarba-*closo*-dodecaborane(12)s **6a–6d** are accessible from the reaction of alkynylchlorophosphanes and dilithiated *ortho*-carbaborane. Comparative cyclic voltammetric studies show that the HOMO of **2** is localized mainly on the P(NMe₂)(CCR) group. The dihydro-phosphole unit is thus rather inert to oxidation, an effect that could point towards strong electronic coupling to the electron-deficient carbaborane that is fused onto the phosphole ring. Further studies on the reactivity of this new class of alkynyl-phosphanes are underway.

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