## Using the Wittig reaction to produce alkenylcarbaboranes<sup>†</sup>

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## This communication reports the first use of the Wittig reaction to produce alkenylcarbaboranes.

o-Carbaboranes are cluster compounds with ten boron and two adjacent carbon atoms in an icosahedral arrangement. Different methods for incorporating this unit into various substrates have been developed and their properties studied.<sup>1</sup> Therefore, it is very useful to develop efficient methodologies that lead to the formation of carbaborane derivatives functionalized either through C or B that can be used for applications. Although carbaborane moieties have been successfully attached to a wide range of residues, the connection of o-carbaborane as a reagent to aromatic or conjugated systems has turned out to be particularly difficult.<sup>2</sup> However, some molecules containing a carbaborane moiety linked to an organic fragment through a conjugated spacer exhibit nonlinear optical behaviour and have attracted great interest due to their applications.<sup>3–5</sup> The conjugated linker is very important as it provides electronic coupling between the bridged units, thus permitting intercomponent processes. Several alkenyl linkers between the carbaborane unit and the donor group have been investigated.<sup>4,5</sup> The Wittig reaction allows the preparation of an alkene by the reaction of an aldehyde or ketone with a triphenyl phosphonium ylide. The phosphonium ylide is prepared *in situ* by deprotonation of the corresponding phosphonium halide, which is in turn prepared by the reaction of triphenylphosphine with an alkyl halide. Despite the possibilities the Wittig reaction offers in organic chemistry, it has never been used to generate an alkenyl group bonded to the o-carbaborane. The strong electronwithdrawing character of the carboranyl group could have prevented this reaction. With this communication we provide first evidence that this is not the case and that the Wittig reaction is a real option to produce (C)-carbaborane alkenyl moities. The preparation of the anthracene derivative 1 is reported (Scheme 1). As an additional measure of the feasibility of this reaction it has been applied on the bis-ylide of anthracene in a single step, producing the sought disubstitution leading to 2. There are indeed ways to produce alkenyl groups connected to the carbaborane moiety. Most of them, however, rely on the typical reaction of assembling the

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carbaborane cluster upon the reaction of the appropriate alkyne, that already incorporates the alkene function, with decaborane(14);<sup>6</sup> or in E2 reactions.<sup>7</sup> Recently, a method that starts from the carboryne complex has been used for the synthesis of cyclic alkenylcarbaboranes.<sup>8</sup> Therefore methods that could start either from C mono-substituted or from pristine carbaborane leading to the alkenylcarbaborane could be very advantageous.

The recent publication of a single-step high-yield preparation of C-formyl-o-carbaborane9 has encouraged us to investigate the use of this aldehyde in the Wittig reaction to produce the anthracene derivatives 1 and 2. In the case of compound 1, the phosphonium salt 9-(triphenylphospho-niumchloride)methylanthracene was prepared from 9-(chloromethyl)anthracene.<sup>10</sup> Starting from the phosphonium chloride precursor, the target compound was prepared using the Wittig methodology as shown in the reaction Scheme 2.

Following this one-pot synthesis the desired product 1 was isolated. The yield of this reaction is quite high, around 70%. although it was not optimized. However, the yield refers to the combined yield for the E and Z diastereoisomers. This mixture of isomers was isolated from the reaction mixture by column chromatography and studied by <sup>1</sup>H NMR. The signal of the proton of the spacer closer to the anthracene moiety is very informative. This signal appears for both isomers between 6 and 6.5 ppm as a doublet. Analysis of the coupling constants, <sup>3</sup>J<sub>HH</sub>, between the protons of the spacer of both forms enables the distinction of both isomers. These constants were 15.9 Hz and 12.3 Hz which were assigned respectively to the E and Z forms. Comparison between the integrals of these doublets gives the E: Z ratio, which was 60: 40. The mixture of E and Z isomers was separated by successive preparative TLC using hexane as eluent. After separation, the E isomer was crystallized from a THF-hexane solution and studied by X-ray crystallography<sup>11</sup> that revealed a very interesting supramolecular helical structure (see Fig. 1).

The success of the Wittig methodology in preparing both isomers of compound 1 led us to attempt the synthesis of the isomers of the disubstituted anthracene 2. Starting from the



Carbaborane derivatives obtained using the Wittig reaction.

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<sup>&</sup>lt;sup>b</sup> On leave from Universidad de Santiago de Compostela, Spain † Electronic supplementary information (ESI) available: Synthesis and characterization of E-1, Z-1 and 2 and crystal structure and packing of compound E-1 and E,E-2. CCDC 746811 & 746812. For ESI and crystallographic data in CIF or other electronic format see



Scheme 2 Synthetic route to compound 1.



Fig. 1 Crystal packing of E-1 along the crystallographic b axis.

phosphonium salt 9,10-bis(triphenylphosphoniumchloride)di-methylanthracene,<sup>9</sup> obtained from 9,10-bis(chloromethyl)anthracene,<sup>12</sup> the reaction was done in a similar way as for compound **1**. After purification, the reaction yielded the mixture of all possible isomers of compound **2**. All attempts to separate the mixture were unsuccessful, although single crystals of the major E,E isomer could be obtained from a THF–hexane solution of the isomer mixture.<sup>13</sup> These studies show, however, that the Wittig reaction can be successfully used to prepare the isomers of the disubstituted compound **2**.

The Wittig methodology presents some advantages compared to the methods already described in the literature (*vide supra*). The major advantage is the fact that it forms the double bond in one position with no ambiguity, unlike elimination reactions which produce mixtures of alkene regioisomers. Another advantage is the possibility of forming all possible isomers of the double bond, while the other available methods only produce the *trans* isomer. Although this may seem like an experimental drawback, it enables the possibility of obtaining the elusive Z isomers. However, the Wittig reaction has been extensively studied and there are known variations of the reaction that favours the formation of only one of the isomeric forms.<sup>14</sup> More research is on the way to show how these known modifications can affect the ratio of the alkenylcarbaborane isomers.

The Wittig reaction can thus provide an efficient method to prepare compounds with *o*-carbaborane moieties linked to an aromatic organic residue through an ethylene spacer. As mentioned before, these materials are very promising as technology oriented materials, especially in the field of NLO materials. One limitation is that, in the solid state, a non-centrosymmetric arrangement of the molecules is an essential prerequisite, if the molecular NLO response is to contribute to an observable bulk nonlinearity.<sup>3</sup> One of the molecules prepared using the Wittig reaction, **E-1**, fulfills this condition. Compound **E-1** crystallizes in the non-centrosymmetric space group Pn. The main secondary



Fig. 2 Molecular structure of E,E-2 with 30% thermal ellipsoid probability.

interaction in the crystal packing of this compound is a  $\pi$ -stacking interaction among the anthracene groups. Thus, the anthracene groups stack along the crystallographic *b* axis, as shown in Fig. 1. If we take a close look at one of those chains, we see that the ethylene-carboranyl side groups on the anthracene moieties spiral along the anthracene row, forming a helix. This helical structure is responsible for the non-centrosymmetry of the crystal packing.

Compound **E,E-2** crystallizes in the centric space group P21/c. The molecular structure of this compound is shown in Fig. 2. The complete descriptions of the molecular structures of compounds **E-1** and **E,E-2**, along with a full discussion of their crystal packing, can be found in the ESI.†

In conclusion, we have shown that the Wittig reaction is an efficient and simple method for preparing alkenylcarbaborane derivatives. We have also shown that some of the final compounds are potentially interesting for technological applications. Compound **E-1** is a good example of the structurally interesting materials that can be prepared using this methodology.

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collected/unique =  $36376/7889 [R_{int} = 0.0650]$ ; Data/parameters = 7889/1009;  $R_1 = 0.0589$  and wR<sup>2</sup> = 0.1242 for 5405 reflections with  $I > 2\sigma(I)$ ;  $R_1 = 0.0911$  and wR<sup>2</sup> = 0.1386 for all 7889 unique reflections. CCDC 746812.

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