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The carboboration of Me$_3$Si-substituted alkynes and allenes with boranes and borocations.

James R. Lawson,$^3$ Valerio Fasano,$^3$ Jessica Cid,$^4$ Inigo Vitorica-Yrezabal,$^3$ and Michael J. Ingleson$^{*5}$

The 1,1-carboboration of 1-Me$_3$Si-1-alkynes is the dominant reaction observed using PhBCl(2-DMAP)[AlCl$_3$], 1, and PhBCl$_2$ electrophiles, with highly substituted vinyl pinacol boronate esters isolated post esterification. Other aryl and heteroaryl congeners of both 1 and PhBCl$_2$ have a limited scope in the 1,1-carboboration of 1-Me$_3$Si-1-alkynes, with desilylboration more prevalent. PhBCl$_2$ converts Me$_3$Si-substituted allenes to allylboranes via a formal 1,3-carboboration with Me$_3$Si-migration. [Cl$_3$B(2-DMAP)][AlCl$_3$] reacted with a number of 1-Me$_3$Si-1-alkynes by desilylboration, whilst with 1-Me$_3$Si-ethyne a 1,1-boroamination reaction proceeds, which with excess boron electrophile is followed by an intramolecular desilylboration to form a tricationic-borate. The use of excess 1-Me$_3$Si-1-propyne relative to 1 (and a thienyl congener of 1) formed 2-boradienes in low yields from the reaction with two equivalents of alkyn. Vinyl borocations ligated by 2,6-lutidine of the general formula, [(vinyl)BCl(2,6-lutidine)][AlCl$_3$] formed 1-boradienes with 1-Me$_3$Si-1-alkynes.

Introduction

The 1,1-carboboration of alkynes has received increased interest in recent years following the discovery of the 1,1-carboboration of terminal and internal alkynes with the strong electrophile RB(C$_3$F$_3$)$_2$ (R = C$_3$F$_5$, alkyl).$^3$ Addition of RB(C$_3$F$_3$)$_2$ to a terminal alkyne induces a 1,2-shift of H (or a hydrocarbyl for internal alkynes) along the alkynyl backbone with subsequent migration of the R group from boron to carbon resulting in 1,1-carboboration.$^5$ This reaction has been developed into a useful route to arylboranes by benzannulation,$^5$ and to highly substituted vinyl boranes that are complementary to those obtained from hydroboronation.$^4$ 1,1-carboboration was pioneered by Wrackmeyer albeit with weaker boron electrophiles, such as trialkylboranes, for the 1,1-carboboration of activated alkynes, e.g., alkynes substituted with heavier group 14 substituents (Scheme 1, top).$^5$ Wrackmeyer and co-workers reported extensively on this topic and determined the relative reactivity of a range of substituted alkynes toward BET$_3$ to be R$_2$Pb > R$_2$Sn > R$_2$Ge > R$_2$Si (TMS), with R$_2$C-substituted alkynes not amenable.$^5$ These studies predominantly used trialkylboranes; in contrast, the utilisation of vinyl and aryl boranes (excluding B(C$_3$F$_3$)$_2$) for the 1,1-vinylboration or 1,1-aryl-boration of alkynes is rare with only limited examples reported using BPh$_3$ or PhB(C$_3$F$_3$)$_2$.$^6$ One report particularly relevant to this work showed that Ph$_2$BX (X = Cl or Br) effected the 1,1-carboboration of 1-TMS-1-hexyne (Scheme 1, top).$^6$ It should be noted that with (chloro)aryl)$_x$B compounds TMS substitution appears essential for 1,1-carboboration, with PhBCl$_2$ and terminal alkynes reacting via 1,2-halo- or 1,2-carbo-boration instead.$^6$ To the best of our knowledge the outcome from combining TMS-alkynes and (hydrocarbyl)BCl$_2$ has not been reported to date.

Scheme 1: Relevant early 1,1-carboborations and the approach in this work

We envisaged combining arene borylation,$^{10}$ or alkyn haloboration,$^{11}$ using BCl$_3$ derived borocations (to produce arylicl$_2$ and [vinyl]BCl(amine))$_x$, respectively) with 1,1-carboboration to generate synthetically useful highly substituted vinyl (or dienyl) boronate esters after esterification (Scheme 1, bottom).$^{12}$ This process may proceed directly from the organoBCl$_3$ or require enhancement of electrophilicity at boron by formation of a borocation. We have previously demonstrated that borocations are effective for the 1,2-haloboration and 1,2-carboboration of alkynes, with no 1,1-elementoboration observed.$^{11}$ For example, terminal alkynes and the boronium salt [(Ph)ClB(2-DMAP)][AlCl$_3$] (2-DMAP = 2-N,N-dimethylamino-pyridine) react only by 1,2-chloroboration.$^{11}$ Based on the previous 1,1-carboboration

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studies with neutral boranes it was hypothesised that TMS-substituted alkynes would preferentially undergo 1,1-elementoboration over 1,2-elementoboration when combined with organoBCl or borocation compounds. Support for this comes from the work of Curran and co-workers on the 1,1-hydroboration of 1-TMS-1-alkynes using borenium equivalents (NHC)BHCl(NTf2). Herein is reported our studies using aryliBCl and aryl and vinyl containing borocations synthesised by electrophilic borylation to effect the carboboration of TMS-substituted alkynes.

Results and discussion

Vinylboronate ester formation

Studies commenced with the boronium cation [Ph(Cl)B(2-DMAP)][AlCl4], 1. The combination of 1 and equimolar 1-TMS-1-propyne at 20°C resulted in a slow reaction generating a single new silicon containing compound (δ29Si -6.05) with minimal desilylboration observed (only a low intensity TMSCl resonance present in the 1H NMR spectra). Heating the reaction to 60°C in CH2Cl2 in a sealed tube for extended periods (> 1 h) led to complex mixtures, however heating for 30 minutes at 60°C led to one major new product possessing identical resonances to that observed in the 20°C reaction, with unreacted 1 also remaining. Esterification of the reaction mixture after 30 minutes with pinacol / Et2N led to two major boron containing products, PhBPin (derived from unreacted 1) and a new product isolable by column chromatography. NMR and mass spectroscopy confirmed this to be the product from the 1,1-carboboration of 1-TMS-1-propyne, formed as the E-isomer exclusively, 2a (Table 1). This reactivity was extended to a number of other 1-TMS-1-alkynes to yield 2b to 2e. Using these conditions PhBPin was observed as a minor product from esterification of unreacted 1 in all cases and required separation by column chromatography. The reaction of 1 with TMS-ethyne and trimethyl[3-methylbut-1-yn-1-yl]silane under analogous conditions led to complex intractable mixtures containing significant TMSCl (by 1H NMR spectroscopy).

With 1,1-carboboration observed from the combination of 1 and 1-TMS-1-alkynes the reaction of 1-TMS-1-propyne and [Cl2B(2-DMAP)][AlCl4], 3, was explored to determine if any 1,1-chloroboration occurred. Instead, this led to formation of TMSCI (by 1H and 29Si NMR spectroscopy) and a major new 11B resonance at +6.5 ppm. Esterification enabled identification of the alkynyl pinacol boronate ester confirming desilylboration (equation 1). Desilylboration was observed also on combination of 3 with 1-phenyl-2-TMS-acetylene and with 1-TMS-1-hexyne. Whilst in-situ NMR spectra pre-esterification indicated desilylboration and alkynylborane formation is the dominant reaction outcome, the isolated yields post pinacol esterification were consistently low due to the susceptibility of alkynyl-B species to protodeboronation.

\[
\text{R} = \text{SiMe}_3 \quad \text{R} = \text{Cl} \quad \text{Cl} = \text{B(2-DMAP)} \quad \text{AlCl}_4
\]

In contrast, the combination of 3 and TMS-ethyne only formed the alkynyl-borocation as a minor species (by NMR spectroscopy). The major soluble product contained a vinylic singlet at 6.65 ppm in the 1H NMR spectrum consistent with alkyn elemento-boration. Crystalline solid spontaneously deposited from CH2Cl2 solutions as the reaction proceeded with a concomitant increase in the quantity of TMSCI and a decrease in the vinylic singlet (by 1H NMR spectroscopy). The amount of precipitate was increased by using an excess of 3 (5 : 4 ratio of 3 : TMS-ethyne). X-ray diffraction studies on multiple crystals consistently produced poor quality data due to low crystal quality but an unambiguous connectivity map was obtained (Figure 1, bottom left). This revealed the compound to be the tricationic borate, 4 formed from 1,1-boroamination of TMS-ethyne and desilylboration. Due to the low data quality detailed discussion of structural metrics of 4 is not warranted.

Table 1: 1,1-carboboration with 1, followed by esterification with pinacol

| Entry | Electrophile | T°C | Compound No. | R | Isolated Yield (%) |
|-------|-------------|-----|--------------|---|--------------------|
| 1     | 1           | 60  | 2a           | Me | 63                 |
| 2     | 1           | 60  | 2b           | Bu | 61                 |
| 3     | 1           | 60  | 2c           | C(Me)=CH2 | 55               |
| 4     | 1           | 60  | 2d           | Ph | 65                 |
| 5     | 1           | 60  | 2e           | p-Br-C6H4 | 56               |

\(a = \text{performed in CH}_2\text{Cl}_2 \text{in sealed tubes fitted with J. Young valves.}\)

Figure 1. Formation of the tricationic borate 4 by 1,1-boroamination. Bottom left, solid state structure of 4 (anions and hydrogens omitted).
Compound 4 was confirmed as the major component of the CH₂Cl₂ insoluble material by elemental microanalysis. Furthermore, on dissolution of the crystalline solid in CD₂CN two major resonances at +3.9 ppm and -15.4 ppm in the ¹H NMR spectrum were observed consistent with four coordinate cationic and anionic boron centres, respectively. The formation of 4 suggested that the CH₂Cl₂ soluble product formed is 5, the product from 1,1-boronation of TMS-ethyne prior to intermolecular desilylboration (Figure 1). Whilst 5 could not be isolated analytically pure (due to contamination with 4, the alkynyl-borocation and [H₂(2,6-DMAP)[AlCl₄]]) multinuclear NMR spectroscopy is fully consistent with this formulation with NOE spectroscopy confirming the regio- and stereo-chemistry and indicating that the desilylboration of 5 to form 4 occurs with retention. The reactivity disparity between TMS-ethyne and other 1-TMS-1-alkynes studied is attributed to a less stabilised vinyl cation formed on interaction of 3 with TMS-ethyne which presumably favours rapid TMS-migration leading to 5 as the initial product and not the alkynyl-borocation from desilylboration. It is noteworthy that the reaction of [Cl₂B(2,6-lutidine)][AlCl₄], 6, a borocation where the amine does not contain a pendant nucleophile, with 1-TMS-1-alkynes, including TMS-ethyne, led predominantly to desilylboration in all cases.

Whilst the reactivity of 1-TMS-1-alkynes with BCl₃ has not been explored to the best of our knowledge. To determine if PhBCl₂ and 1 react comparably with 1-TMS-1-alkynes equimolar 1-TMS-1-propyne and PhBCl₂ were combined in CH₂Cl₂ at 20°C. This resulted in a rapid reaction producing a single new product identified by multinuclear NMR spectroscopy as the product from 1,1-carboboration. Post esterification 2a was isolated in a higher yield than when using 1. A substrate scope exploration (Table 2) confirmed that the 1,1-carboboration of 1-TMS-1-alkynes with PhBCl₂ consistently proceeds in higher yield than when using 1 and does not require purification by chromatography post esterification. Furthermore, the structure of 2e was also confirmed by a single crystal X-ray diffraction study (Table 2, right). It is noteworthy that trimethyl(4-phenylbut-1-yn-1-yl)disilane (entry 7) resulted in only 1,1-carboboration with no 6-endo-dig cyclisation as recently reported for related alkynes and BCl₃.15 The facile formation of 2a – 2h by 1,1-carboboration represents an alternative to transition metal catalysed borosilylation of alkynes for accessing these versatile intermediates.17 Attempts to extend this reaction to 1-trisopropylsilyl-1-propyne resulted in no reaction, whilst combining PhBCl₂ and 1-(PhMe₂Si)-1-propyne resulted predominantly in desilylboration products (by observation of PhMe₂SiCl by ¹H and ²⁹Si NMR spectroscopy) and multiple other unidentified products.

To increase the scope, variation of the aryl substituent on the borane was explored. ArylBCl₂ and heteroarylBCl₂ species are readily accessible by electrophilic arene borylation.18 Using established methodologies 2-methylthiophene, 2-methylfuran, chlorobenzene and triphenylamine were all borylated to produce the respective (hetero)arylBCl₂ compounds 7a – 7d (Table 2) in good conversion as determined by multinuclear NMR spectroscopy.19, 20 Removal of reaction solvent (CH₂Cl₂ or 1,2-C₂H₄) and extraction of 7a - d into hexanes was sufficient to enable subsequent reaction with 1-TMS-1-propyne without any additional purification steps. This led to the formation of the desired 1,1-carboboration products which were esterified to form a single regio- and stereo-isomer of the respective vinyl pinacol boronate esters (entries 9 – 12). The products derived from carboboration using 7a and 7b were repeatedly contaminated with minor quantities of heteroarylBP (from esterification of unreacted 7a and 7b) which in our hands proved challenging to separate from 2i and 2j. The 1,1-carboboration reaction using longer times (3 h) for 7a and 1-TMS-1-propyne led to considerably more complex NMR spectra and intractable products post esterification.

Table 2: 1,1-carboboration using (hetero)arylBCl₂ (right, solid state structure of 2e, hydrogens and one component of the disordered pinacol omitted for clarity).

| Entry | Electrophile t (h) | T (°C) | Compound No. | R | Isolated Yield [%] |
|-------|-------------------|--------|--------------|----|--------------------|
| 1     | PhBCl₂            | 20     | 2a           | Me | 88                 |
| 2     | PhBCl₂            | 20     | 2b           | Bu | 79                 |
| 3     | PhBCl₂            | 20     | 2c           | C(Me)CH₂ | 77       |
| 4     | PhBCl₂            | 20     | 2d           | Ph | 85                 |
| 5     | PhBCl₂            | 20     | 2e           | p-Br-CH₂ | 68       |
| 6     | PhBCl₂            | 20     | 2f           | 'Pr | 76                 |
| 7     | PhBCl₂            | 20     | 2g           | CH₂CH₂Ph | 37       |
| 8     | PhBCl₂            | 60     | 2h           | H  | 30                 |
| 9     | PhBCl₂            | 20     | 2i           | Me | *                  |
| 10    | 7b                | 0.5    | 2j           | Me | *                  |
| 11    | 7c                | 20     | 2k           | Me | 68                 |
| 12    | 7d                | 20     | 2l           | Me | 61                 |

a = Isolated yield not obtained due to intractable minor contaminants of (hetero)arylBP.

Attempts to extend 1,1-carboboration using 7a – 7d to other 1-TMS-1-alkynes, specifically 1-TMS-2-phenylacetylene and trimethyl(3-methylbut-1-yn-1-yl)disilane, instead led to desilylboration being the dominant reaction pathway (by ¹H, ¹³C and ²⁹Si NMR spectroscopy). To preclude the disparity between PhBCl₂ and the four (hetero)arylBCl₂ compounds 7a - d being due to any impurities in commercially sourced PhBCl₂ or impurities in (hetero)arylBCl₂ synthesised by electrophilic borylation, benzene was borylated in 1,2-C₂H₄ using 4,N,N-trimethylaniline, BCl₃ and two equivalents of AlCl₃ to form PhBCl₂.116 This reaction mixture was dried and PhBCl₂ extracted into hexane and found to form 2f on addition of...
trihexyl(3-methylbut-1-yn-1-yl)silane, a substrate that 7a – d react with predominantly by desilylboration. Therefore the greater prevalence for desilylboration using 7a-d is attributed to the modified electrophilicity of the borane and the different migratory propensity of the (hetero)aryl group (relative to phenyl), indicating that the 1,1-carboboration of 1-TMS-1-alkynes using (hetero)arylBCl3 compounds is limited in scope.

PhBCl3 was effective for the carboxaboration of silylated allenes with 8a and 8b (Scheme 2) undergoing carboxaboration with TMS migration producing only a single allylBCl3 product (by multinuclear NMR spectroscopy). With no intermediates observed we attribute the reaction outcome to a 1,1-carboboration followed by a rapid intramolecular sigmatropic 1,3-boron shift to form the more thermodynamically stable less hindered allylBCl3 species. This can be subsequently pinacol protected and the resultant boronate esters 9a and 9b isolated. This enables access to complementary boronate ester isomers to that produced by the hydroboraboration of closely related TMS-alkynes where TMS migration does not occur.29

Scheme 2: The carboxaboration of TMS-alkynes with PhBCl3.

**Boradiene formation using borocarbons**

To explore potential scope expansion further [5-methyl-2-(BCl2(2-DMAP))-thiophene][AlCl3], 10, was synthesised by addition of 2-DMAP and AlCl3 to 7a. The addition of 1-TMS-1-propyne to 10 resulted in a slow reaction at 20°C that after 18 hours produced four new TMS resonances one of which was attributable to the 1,1-carboboration product (by 1H, 11B and 29Si NMR spectroscopy). One of the other new compounds derived from 10 / 7a could be formed as a greater component of the reaction mixture when an excess of 1-TMS-1-propyne (5 equivalents) was used with heating to 60°C for 18 h. Post esterification, isolation by column chromatography and analysis by NMR and mass spectroscopy enabled it to be identified as the 2-boradiene 11a, from reaction of 10 with two equivalents of 1-TMS-1-propyne. Under identical conditions 1 also reacted with excess 1-TMS-1-propyne to produce the 2-boradiene 11b as a minor product. In contrast, heating PhBCl3 with excess (5 equiv.) 1-TMS-1-propyne led to no observable 2-boradiene after esterification with pinacol, instead complex mixtures were produced with significant TMSCl observed in-situ indicating desilylboration. Under a range of conditions 11a and 11b were formed only as minor products from 10 and 1 (with a maximum 13 and 15% isolated yield, respectively) with the 1,1-carboboration products, 2i and 2a, being the major species isolated post esterification. 2-Boradienes related to 11x have been previously synthesised by Wrackmeyer and co-workers from the reaction of BEt3 with two equivalents of 1-R5Sn-1-alkynes.20 Precise isomer assignment for 11x was based on 1D and 2D NMR spectroscopy, most notably NOESY indicated a trans-disposition of TMS and PinB moieties in the 2-boradiene. This is in contrast to that in 2x suggesting that 1,1-carboboration is not the first step in 2-boradiene formation, a hypothesis supported by the fact that resonances for the 1,1-carboboration products increase in intensity as the reaction progresses, suggesting it is not an intermediate in diene formation. Instead we propose that 1-TMS-1-propyne is activated to an intermolecular attack by a second equivalent of alkyne by interaction with the borocarboxon and this ultimately leads to the observed 2-boradiene structures. Related borane activation of alkyne towards external π nucleophiles have been reported previously.20, 21 As repeated attempts to crystallise 11a and 11b failed in our hands to support the proposed diene structure, particularly correlating the structure with the multiple NOE interactions observed, the structure of 11b was optimised at the M06-2X/6-311G(d,p)(PCM:DCM) level. This revealed that steric bulk forces a significant dihedral angle in the diene (C=C-C=C = 60.24°) and thus short distances (< 4 Å) were observed in the calculated structure for all the observed NOE interactions, supporting this isomer assignment. Attempts to form other 2-boradienes using different (hetero)arylboronium cations or different TMS-alkynes all led to complex mixtures and lower conversions than that observed for 11a and 11b.

Scheme 3: 2-boradiene formation from 1 and 10 and 1-TMS-1-propyne (shown as vinyl cation intermediates, π complexes of [Me3Si]+ are also feasible).

Subsequently, the one pot, two step reaction of 3 with terminal alkynes (proceeding by 1,2-haloboration as previously reported to form 12x, equation 2)11 followed by addition of 1-TMS-1-propyne was explored as an alternative route to 2-boradienes. The addition of 1-TMS-1-propyne to 12a or 12b gave no reaction (by NMR spectroscopy) at room temperature after 18 hours. When the reaction mixture was heated to 60°C for 1 h multiple new species were observed in the 1H NMR spectrum, including [(2-DMAP)H]+, as well as four new 29Si resonances (one corresponding to TMSCl) and new 11B
resonances at +55 and +66 ppm. Esterification and attempts to purify the resultant complex mixture failed to deliver pure products in our hands. A more electrophilic vinyl-bororation was targeted to enable room temperature reactivity with 1-TMS-1-alkynes and potentially avoid the complex mixtures observed with 12x at 60°C. Thus the reactivity of [(vinyl)BCl(2,6-lutidine)]⁺ cations, made via haloboration of alkynes with 6, with 1-TMS-1-alkynes was explored.

![Scheme 4: 1-boradiene formation by haloboration and 1,2-carboboration.](image)

In a one pot two step reaction 6 was used to separately haloborate "Bu-acetylene and phenylacetylene followed by addition of one equivalent 1-TMS-1-propyne, which did not lead to any significant TMSCl formation at short reactions times (< 1 h by NMR spectroscopy) in each case. The initial haloboration step is rapid (complete in < 5 minutes with both terminal alkynes) whilst the subsequent reaction with 1-TMS-1-propyne is slower it did proceed to form carboxoration products (Scheme 4). Running the reaction for longer times at 20°C (≥ 2 h) resulted in significant TMSCl formation, whilst attempts to use greater equivalents of 1-TMS-1-propyne also led to more TMSCl formation; thus optimised conditions of 1.2 equivalents of 1-TMS-1-propyne and a 1 h reaction duration were found to minimise the amount of unreacted haloboration compounds (12a-b) remaining and TMSCl formation. Post esterification the boradiene products 13a-b could be separated from the vinyl-pinacol boronate esters (formed from esterification of unreacted 12a-b) with NMR spectroscopy consistent with a 1-boradiene formulation formed from a 1,2-carboboration reaction (Scheme 4). Notably a JHH coupling of 1 Hz is observed between the methyl and the vinyl-H in both 13a and 13b confirming the connectivity as this couple would not be observed in the 1,1-carboboration products. Whilst 1,2-carboboration is less documented that 1,1-carboboration several recent examples have been reported, including using borocations.13, 23 The diene structure (Scheme 4) expected from 1,2-carboboration was confirmed by NOESY and in the absence of crystalline material (which was unobtainable in our hands) supported by optimising the structure of 13b at the M06-2X/6-311G(d,p)(PCM:DCM) level. This indicated that 13b is a non-planar diene (C=C-C=C = 39.93°) and that all observed NOE interactions correspond to calculated H---H distances of < 4 Å. We attribute the reactivity disparity between 2-DMAP (2-boradienes) and 2,6-lutidine (1-boradienes) bororations to the greater steric demand of 2,6-lutidine which disfavours formation of a more sterically hindered 2-boradiene. This is consistent with calculations on a model complex (at the M06-2X/6-311G(d,p)(PCM:DCM) level) that show the 2-boradiene B is 5 kcalmol⁻¹ higher in energy than the 1-boradiene isomer A (Scheme 4). Furthermore, in contrast to 1,1-carboboration reactions with BTs, the 1,2-vinylbororation to form A is unlikely to be reversible. This is indicated by calculations for the conversion of the model compound 12Me (where R = Me) to A which is found to be exergonic by 7.7 kcalmol⁻¹, thus the barrier to the reverse process (retro-vinylbororation) will be significantly higher than that for the forward reaction (which requires at least 1 h for significant conversion).

As boradienes are useful species for a range of subsequent synthetic transformations,24 the broader applicability of this reaction was explored initially looking at other terminal alkynes. 12c-12e were all readily produced by haloboration with 6 and underwent 1,2-carboboration to form 13c-13e, however the isolated yields of 13x are poor to moderate (23 – 59 %), whilst 13d and 13e could not be separated from reaction by-products. The propensity of other 1-TMS-1-alkynes to undergo 1,2-carboboration, specifically 1-TMS-2-phenylacetylene and 1-TMS-1-hexyne, were investigated using 12a, however the reaction was slower (by in-situ NMR spectroscopy) and resulted in lower conversions to the desired boradiene and more unidentified by-products. Finally, the use of an internal alkyne, 3-hexyne, was investigated, which was previously reported undertaken facile haloboration with 6,11 but subsequent reaction with 1-TMS-1-propyne resulted in a low conversion to the 1-boradiene product which was isolated as the pinacol boronate ester, 13f in only 10% yield. The low conversions with more substituted systems is presumably due to the increased steric crowding resulting in the slower formation of the 1,2-carboboration products and thus increased formation of by-products derived from desilyloboration.

Conclusions

The carboxoration of 1-TMS-1-alkynes with arylidichloroboranes and aryl-substituted and vinyl-substituted bororations has been demonstrated to yield highly substituted vinyl and dienyl boronate esters post esterification. However, due to carboxoration occurring in competition with desilyloboration and diene formation, coupled with further reactions proceeding subsequent to the initial carboxoration (e.g., further desilyloboration), complex mixtures are often produced that limit the overall utility of this reaction. Variation
in borane and boronation structure is therefore essential to preclude desilylation to generate more general and higher yielding 1-TMS-1-alkyne carboboration protocols.

**Experimental**

**General Considerations:** All manipulations of air and moisture sensitive species were performed under an atmosphere of argon or nitrogen using standard Schlenk and glovebox techniques. Glassware was dried in a hot oven overnight and heated before use. Hexane, ortho-dichlorobenzene, d_{2}-chloroform, d_{2}-dichloromethane, 2,6-lutidine, Et,N and were dried over calcium hydride and distilled under vacuum. Pentane and dichloromethane were dried by passing through an alumina drying column incorporated into an MBraun SP5800 solvent purification system. All solvents were degassed and stored over molecular sieves (3 Å) under an inert atmosphere. Compounds 1 and 3 were synthesised according to the published procedures. All other materials were purchased from commercial vendors and used as received.

**NMR Spectrometry:** NMR spectra were referenced to external BF_{3}:Et,O, F to Cl, CF, 27Al to Al(NO)_{3} in D_{2}O (Al(D_{2}O)_{6})^{3-}, Si to Si(CH_{3})_{4}. Resonances for the carbon directly bonded to boron are not observed in the ^{13}C NMR spectra due to quadrupolar effects. GC-MS analysis was performed on a Waters QTOF mass spectrometer. X-ray data for compounds 2e and 4 was collected at a temperature of 150 K using a using Mo-Kα radiation on an Agilent Supernova, equipped with an Oxford Cryosystems Cobra nitrogen flow gas system. Data were measured using CrysAlisPro suite of programs. Elemental analysis of air sensitive compounds was performed by London Metropolitan University service. Repeated attempts to obtain satisfactory elemental analyses for a range of the pinacol boronate esters repeatedly gave results with low carbon content, even when using V_{2}O_{5} as an additional oxidant.

**General procedures for 1,1-carboration reactions:** With [PhBCl(2-DMAP)][AlCl_{4}] (Route 1) To a suspension of [PhBCl(2-DMAP)][AlCl_{4}] (50 mg, 0.12 mmol, 1 eq) in DCM (0.5 ml) in a J. Youngs NMR tube was added 1-TMS-1-alkyne (0.12 mmol, 1 eq). This was sealed and the mixture heated for 30 minutes after which time an excess of triethylamine (0.1 ml) and pinacol (30 mg, 0.24 mmol, 2 eq) were added and the solvent was removed under reduced pressure to leave an oil. Pentane was used to extract the product, which was passed through a 1 inch plug of silica to remove pinacol impurities. Column chromatography (DCM:hexane, 1:1) was used to separate the desired product from the by-products.

**With PhBCl_{2} (Route 2)**

To a solution of PhBCl_{2} (200 µl, 1.5 mmol, 1 eq) in DCM (5 ml) in a Schlenk was added 1-TMS-1-alkyne (1.5 mmol, 1 eq). After x hours an excess of triethylamine (0.5 ml) and pinacol (350 mg, 3.0 mmol, 2 eq) were added, and the solvent was removed under reduced pressure to leave an oil. Filtration through a 1 inch plug of silica afforded the product in good purity without column chromatography.

**References**

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22.28, 2.67; = 7.0 Hz), 0.16 (s, 9H); the product was then purified by flash chromatography (petroleum ether: DCM 70:30), affording 2h (30 mg, 30%) as a colourless oil.

1H NMR (400 MHz, CDCl3) δ 7.41 (d, J = 8.1 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.21-7.26 (m, 1H), 6.74 (s, 1H), 1.34 (s, 12H), 0.23 (s, 9H); 13C{1H} NMR (100 MHz, CDCl3) δ 150.6, 145.5, 128.0, 126.9, 126.7, 83.8, 25.1, 0.3; 11B NMR (128 MHz, CDCl3) δ 30.2 (s ppm); 25Si NMR (79 MHz, CDCl3): δ = 9.2 (s ppm); MS (GC, [M-CH3]1 m/z) 287.1; Accurate Mass: ([M-CH3]1 287.1635).

- (E)-1-(5-methylthio phen-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)trimethylsilane (2i)

The product was isolated as orange crystals (100 mg, 68%, reaction performed on a ¼ scale of the general procedure)

1H NMR (400 MHz, CDCl3) δ 7.17 (d, 2H, 3J(H,H) = 7.0 Hz), 7.07-6.91 (m, 5H), 6.63 (d, 2H, 4J(H,H) = 8.2 Hz), 1.28 (s, 12H), 0.17 (s, 9H); 13C{1H} NMR (100.06 MHz, CDCl3) δ 155.55, 143.50, 142.16, 130.36, 129.80, 128.68, 128.08, 127.33, 125.47, 83.98, 25.08, 0.34; 11B NMR (128.4 MHz, CDCl3); δ 30.0; 25Si NMR (79.5 MHz, CDCl3) δ -4.92 ppm. MS: (GC, M + Na+) m/z 458.0.

- (E)-1-(4-diphenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-2-yl)trimethylsilane (2j)

The product was isolated as yellow crude oil (Route 1: 31 mg, 56%).

- (Z)-trimethyl(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (2k)

The product was isolated as a white solid.

1H NMR (400 MHz, CDCl3) δ 7.13 (t, 2H, 3J(H,H) = 8.2 Hz), 7.03 (t, 1H, 4J(H,H) = 7.0 Hz), 6.94 (d, 2H, 5J(H,H) = 7.0 Hz), 2.57 (septet, 1H, 6J(H,H) = 7.0 Hz), 1.02 (s, 12H), 0.81 (d, 6H, 7J(H,H) = 7.0 Hz), 0.16 (s, 9H); 13C{1H} NMR (100.06 MHz, CDCl3) δ 157.97, 143.70, 124.05, 127.89, 125.57, 83.56, 33.79, 24.92, 22.28, 2.67; 11B NMR (128.4 MHz, CDCl3); δ 30.5; 25Si NMR (79.5 MHz, CDCl3) δ -5.83 ppm. MS (GC, M + Na+) m/z 367.4.

1H NMR (400 MHz, CDCl3) δ 6.63 (m, 1H), 6.57 (d, 1H, 3J(H,H) = 7.1 Hz), 2.46 (s, 3H), 1.93 (s, 3H), 1.29 (s, 12H), 0.22 (s, 9H); 13C NMR (100 MHz, CDCl3) δ 148.27, 139.11, 135.82, 126.00, 122.91, 83.22, 25.01, 20.37, 15.86, 0.02 ppm; 11B NMR (128.4 MHz, CDCl3); δ -3.92 ppm; 25Si NMR (79.5 MHz, CDCl3) δ -3.92 ppm. MS (GC, M, m/z): 336.4.

- (E)-1-(5-methylfur an-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (2l)

The product was isolated as orange crystals (100 mg, 2.7 mmol, 1 eq) combined with 2-methylthiophene (26 µl, 2.7 mmol, 1 eq) in DCM (0.5 ml) in a J. Youngs NMR tube which was then heated and stirred at 60°C for 1 hour. NMR spectroscopy confirmed formation of 2-methylthiophene-BCl which was extracted into hexane (10 ml). To this, 1-TMS-1-propyne (80 µl, 5.4 mmol, 2 eq) was added with the reaction mixture turning deep orange. The reaction mixture was esterified after 1 hour by addition of excess Et2N (0.1 ml) and pinacol (96 mg, 3 eq). The crude product was extracted into pentane (20 ml) and filtered through a 1 inch plug of silica affording the desired product contaminated with 2-methyl-5-BPin-thiophene. The data below are for 2l with resonances for the minor by-product omitted.

1H NMR (400 MHz, CDCl3) δ 2.79 (m, 2H), 2.70 (d, 1H, 3J(H,H) = 7.8 Hz, 2H), 2.46 (s, 3H), 1.93 (s, 3H), 1.29 (s, 12H), 0.22 (s, 9H); 13C NMR (100 MHz, CDCl3) δ 148.27, 139.11, 135.82, 126.00, 122.91, 83.22, 25.01, 20.37, 15.86, 0.02 ppm; 11B NMR (128.4 MHz, CDCl3); δ -3.92 ppm; 25Si NMR (79.5 MHz, CDCl3) δ -3.92 ppm. MS (GC, M, m/z): 336.4.

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[2,6-lutBCl][AlCl4] (80 mg, 2.2 mmol, 1 eq) was generated in-situ (from lut-BCl and AlCl3) and combined with triphenylamine (55 mg, 2.2 mmol, 1 eq) in DCM (0.5 ml) in a J. Youngs NMR tube which was then sealed and rotated at room temperature for 2 hours resulting in the solution turning brown. NMR spectroscopy confirmed formation of triphenylamine-BCl, which was extracted into hexane (10 ml). To this 1-TMS-1-propyne (66 μl, 4.5 mmol, 2 eq) was added. After 30 minutes the reaction mixture was esterified with excess Et3N (0.1 ml) and pinacol (78 mg, 0.8 eq). The crude product was extracted into pentane (20 ml) and filtered through a 1 inch plug of silica affording the product. (74 mg, 68%).

1H NMR (400 MHz, CDCl3) δ 7.07-6.77 (m, 14H), 1.58 (s, 3H), 1.07 (s, 12H), 0.05 (s, 9H); 13C1[H] NMR (100.06 MHz, CDCl3) δ 150.41, 147.95, 145.25, 137.85, 129.38, 129.08, 123.97, 123.69, 122.35, 83.49, 25.04, 20.63, -0.03; 11B NMR (128.4 MHz, CDCl3): δ 30.3; 29Si NMR (MCH3, CDCl3) δ -4.29 ppm. MS: (GC, M+): 330.2181

(E)-(1-(4-chlorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-yl)trimethylsilane (2l)

DMMBCl (100 mg, 1 eq) and AlCl3 (111 mg, 2.1 eq) were combined in dichlorobenzene (0.5 ml) in a J. Young's NMR tube. On standing a brown. NMR spectroscopy confirmed formation of 4-chlorophenyl-BCl, which was extracted into hexane (10 ml). To this hexane solution 1-TMS-1-propyne (117 μl, 2 eq) was added turning the solution brown. After 40 minutes the reaction mixture was then esterified with excess Et3N (0.1 ml) and pinacol (140 mg, 3 eq). The crude product was extracted into pentane (20 ml) and filtered through a 1 inch plug of silica affording the product. (85 mg, 61%).

1H NMR (400 MHz, CDCl3) δ 7.03 (d, 2H, J[H,H] = 8.2 Hz), 6.75 (d, 2H, J[H,H] = 8.2 Hz), 1.44 (s, 3H), 1.00 (s, 12H), 0.00 (s, 9H); 13C1[H] NMR (100.06 MHz, CDCl3) δ 152.57, 136.11, 131.30, 129.82, 128.03, 83.59, 24.99, 20.77, 0.00; 11B NMR (128.4 MHz, CDCl3): δ 30.0; 29Si NMR (79.5 MHz, CDCl3) δ -4.04 ppm. MS: (GC, M+): 305.1.0

Compound 4
A 5:4 ratio of [BCl3(2-DMAP)][AlCl4] (100 mg, 0.27 mmol, 5 eq), to trimethylsilylacetylene (31 μl, 0.22 mmol, 4 eq) was dissolved in CH2Cl2 in a J. Young’s NMR tube. On standing a crystalline solid precipitated out of solution. Removal of the solvent and washing with pentane allowed isolation of the crystals 21 mg, 27% (based on boron content).

1H NMR (400 MHz, CD3CN, -40°C): δ 8.91 (d, 1H, 8.71 (t, 1H), 8.28 (d, 1H), 8.16 (t, 1H), 7.89 (s, 1H), 3.78 (s, 3H), 3.45 (s, 3H); 11B NMR (128.4 MHz, CD3CN): δ 3.90, -15.44; 13C1[H] NMR (100.6 MHz, CD3CN): δ 154.09, 147.95, 145.1, 131.30, 128.02, 127.8, 82.9, 25.8, 25.3, 24.7, 16.3, 1.6; 29Si NMR (79 MHz, CD3CN): δ 34.5 (s) ppm; 30Si NMR (79 MHz, CD3CN): δ -6.6 (s) ppm. MS: (GC, [M-CH3]+): 329.2. Accurate Mass: [M]+: 330.2181

(E)-(2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-3-yl)trimethylsilane (2b)

2-(trimethylsilyl)-2,3-pentadiene (25 μl, 0.13 mmol, 1.0 eq) was dissolved in DCM in a J. Youngs tube and PhBCl2 (22 μl, 0.16 mmol, 1.1 eq) was added. After 1 h a cooled solution of pinacol (19 mg, 0.16 mmol, 1.1 eq) and excess triethylamine were added to the reaction mixture. The reaction mixture was then dried under reduced pressure and the crude was dissolved in pentane, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether: DCM 60:40), affording 2b (21 mg, 43%) as a white solid.

1H NMR (400 MHz, CDCl3) δ 7.29 (t, J = 7.2 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 7.0 Hz, 2H), 2.10 (s, 3H), 1.57 (s, 2H), 1.23 (s, 12H), 0.23 (s, 9H); 13C1[H] NMR (100 MHz, CDCl3): δ 146.0, 145.1, 131.3, 128.0, 127.6, 125.9, 82.9, 25.3, 24.8, 0.4; 11B NMR (128 MHz, CDCl3): δ 33.7 (s) ppm; 29Si NMR (79.5 MHz, CDCl3): δ 5.8 (s) ppm. MS: (GC, M+, m/z) 330.2. Accurate Mass: [M]+: 330.2181

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To a suspension of [Cl\(_2\)B(2-DMAP)][AlCl4] (50 mg, 0.14 mmol, 1 eq) in DCM (0.5 ml) in a J. Youngs NMR tube was added 2-methylthiophene (14 µl 0.15 mmol, 1 eq). The reaction was heated at 60°C for 1 h when borylation was confirmed by NMR spectroscopy. Sequential addition of equimolar 2-DMAP and AlCl3 then generated [CIB2-methylthiophene(2-DMAP)][AlCl4]. To this 1-TMS-1-propyne (90 µl, 0.6 mmol, 5 eq) was added and the tube was sealed and heated to 60°C. After 18 h an excess of triethylamine (0.1 ml) and pinacol (30 mg, 0.24 mmol, 2 eq) were added and the solvent was removed under reduced pressure. Pentane (20 ml) was used to extract the product which was then passed through a 1 inch plug of silica. Column chromatography (DCM:hexane, 1:1) was used to separate the desired diene from the 1,1-carboboration product. The product was isolated as a yellow oil (8 mg, 22%).

\(^{13}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\ 6.59 (d, 1H, ^{3}J(H,H) = 3.5 Hz), 6.51 (m, 1H), 2.42 (s, 3H), 1.96 (s, 3H), 1.81 (s, 3H), 1.20 (s, 6H), 1.17 (s, 6H), 0.08 (s, 9H), -0.03 (s, 9H); ^{13}C\) NMR (100.06 MHz, CDCl\(_3\)) \(\delta\ 147.42, 146.02, 144.67, 139.85, 135.77, 126.83, 123.83, 83.06, 24.65, 24.59, 22.23, 20.49, 15.44, -0.13, -0.54; ^{11}B\) NMR (128.4 MHz, CDCl\(_3\)) \(\delta\ 30.0; ^{29}Si\) NMR (79.5 MHz, CDCl\(_3\)) \(\delta\ -5.98 ppm. MS: (GC, M\(^{+}\), m/z) 448.6 gmol\(^{-1}\).

\(\text{Z}^{1}\text{E,3}\) Z-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-2,4-diene-2,5-diylbis(trimethylsilane) (11b)

To a suspension of [PhBC(2-DMAP)][AlCl4] (50 mg, 0.12 mmol, 1 eq) in DCM (0.5 ml) in a J. Youngs NMR tube was added 1-TMS-1-propyne (90 µl, 0.6 mmol, 5 eq). The tube was sealed and then heated to 60°C. After 18 h an excess of triethylamine (0.1 ml) and pinacol (30 mg, 0.24 mmol, 2 eq) were added and the solvent was removed under reduced pressure leaving a yellow/orange oil. Pentane (20 ml) was used to extract the product which was then passed through a 1 inch plug of silica. Column chromatography (DCM:hexane, 1:1) was used to separate the desired diene from the 1,1-carboboration product. The product was isolated as a yellow oil (8 mg, 15%).

\(^{13}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\ 6.51 (d, 1H, ^{3}J(H,H) = 3.5 Hz), 6.49 (q, 1H, ^{3}J(H,H) = 1 Hz), 1.91 (d, 3H, ^{3}J(H,H) = 1 Hz), 1.33 (s, 12H), 0.25 (s, 9H); ^{13}C\) NMR (100.06 MHz, CDCl\(_3\)) \(\delta\ 155.01, 147.37, 136.44, 129.00, 128.31, 127.32, 120.10, 84.07, 24.25, 22.87, 0.41; ^{11}B\) NMR (128.4 MHz, CDCl\(_3\)) \(\delta\ 29.16; ^{29}Si\) NMR (79.5 MHz, CDCl\(_3\)) \(\delta\ -4.18 ppm. MS: (GC, M\(^{+}\), m/z) 376.2.

\(\text{Z}^{1}\text{E,3}\) Z-2-methyl-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl(trimethylsilane) (13b)

The crude product (15% conversion by NMR spectroscopy) was purified with column chromatography using 2:1 hexane:DCM eluent and isolated as a yellow oil (49 mg, 59%).

\(^{13}H\) NMR (400 MHz, CDCl\(_3\)) \(67.69 (m, 2H), 7.38-7.30 (m, 3H), 6.94 (q, 1H, ^{3}J(H,H) = 1 Hz), 1.91 (d, 3H, ^{3}J(H,H) = 1 Hz), 1.33 (s, 12H), 0.25 (s, 9H); ^{13}C\) NMR (100.06 MHz, CDCl\(_3\)) \(\delta\ 154.05, 144.78, 123.72, 120.10, 83.08, 24.25, 22.87, 0.41; ^{11}B\) NMR (128.4 MHz, CDCl\(_3\)) \(\delta\ 29.16; ^{29}Si\) NMR (79.5 MHz, CDCl\(_3\)) \(\delta\ -4.18 ppm. MS: (GC, M\(^{+}\), m/z) 376.2.

\(\text{Z}^{1}\text{E,3}\) Z-2-methyl-5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,3-dien-1-yl(trimethylsilane) (13c)

The crude product (70% conversion by NMR spectroscopy) was purified with column chromatography using 2:1 hexane:DCM eluent and isolated as a yellow oil (27 mg, 31%).

\(^{13}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\ 67.37-7.23 (m, 5H), 6.37 (q, 1H, ^{3}J(H,H) = 1 Hz), 3.74 (s, 2H), 1.84 (d, 3H, ^{3}J(H,H) = 1 Hz), 1.30 (s, 12H), 0.20 (s, 9H); ^{13}C\) NMR (100.06 MHz, CDCl\(_3\)) \(\delta\ 156.72, 138.00, 132.80, 129.37, 128.85, 128.28, 126.56, 83.41, 45.64, 25.32, 21.43, 0.36; ^{11}B\) NMR (128.4 MHz, CDCl\(_3\)) \(\delta\ 29.55 ppm; ^{29}Si\) NMR (79.5 MHz, CDCl\(_3\)) \(\delta\ -4.40 ppm. MS: (GC, M\(^{+}\), m/z) 390.2

\(\text{Z}^{1}\text{E,3}\) Z-2-chloro-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl(trimethylsilane) (13d)

Attempts at purifying the crude product (70% conversion by NMR spectroscopy) by column chromatography failed. NMR data are given with the vinylboronate ester resonances omitted.

\(^{13}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\ 7.42-7.38 (m, 2H), 7.01-6.99 (m, 2H), 6.72 (m, 1H), 1.72 (m, 3H), 1.21 (s, 3H), 1.15 (s, 12H), 0.07 (s, 9H); ^{11}B\) NMR (128.4 MHz, CDCl\(_3\)) \(\delta\ 29.5; ^{29}Si\) NMR (79.5 MHz, CDCl\(_3\)) \(\delta\ -4.24 ppm.

\(\text{Z}^{1}\text{E,3}\) Z-4-chloro-4-(4-methoxyphenyl)-2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl(trimethylsilane) (13e)
Attempts at purifying the crude product (67% conversion by NMR spectroscopy) by column chromatography failed. NMR data are given with the vinylboronate ester resonances omitted.

1H NMR (400 MHz, CDCl3) δ 7.61-7.59 (m, 2H), 6.89-6.87 (m, 2H), 6.81 (m, 1H), 3.83 (s, 3H), 1.88 (m, 3H), 1.32 (s, 12H), 0.23 (s, 9H); 11B NMR (128.4 MHz, CDCl3): δ 30.0; 29Si NMR (79.5 MHz, CDCl3) δ -4.28 ppm.

((1E,3Z)-4-chloro-3-ethyl-2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,3-dien-1-yl)trimethylsilane

Following the general procedure but allowing 4 h for haloboration. The crude product was then purified with column chromatography using 2:1 hexane:DCM eluent and isolated as a yellow oil (8 mg, 10%)

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