Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2016, **45**, 6060

The carboboration of Me_3Si-substituted alkynes and allenes with boranes and borocations†

James R. Lawson, Valerio Fasano, Jessica Cid, Inigo Vitorica-Yrezabal and Michael J. Ingleson*

Received 4th August 2015,
Accepted 8th September 2015

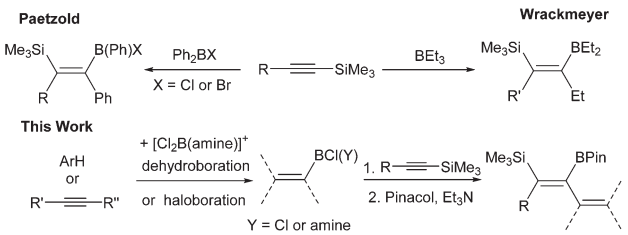
DOI: 10.1039/c5dt03003j

www.rsc.org/dalton

The 1,1-carboboration of 1-Me_3Si-1-alkynes is the dominant reaction observed using [PhBCl(2-DMAP)][$AlCl_4$], **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_3Si-1-alkynes, with desilylboration more prevalent. $PhBCl_2$ converts Me_3Si-substituted allenes to allylboranes *via* a formal 1,3-carboboration with Me_3Si-migration. [Cl_2B(2-DMAP)][$AlCl_4$] reacts with a number of 1-Me_3Si-1-alkynes by desilylboration, whilst with Me_3Si-ethyne a 1,1-boroamination reaction proceeds, which with excess boron electrophile is followed by an intermolecular desilylboration to form a tricationic-borate. The use of excess 1-Me_3Si-1-propyne relative to **1** (and a thienyl congener of **1**) formed 2-boradienes in low yields from the reaction with two equivalents of alkyne. Vinyl borocations ligated by 2,6-lutidine of the general formula, [(vinyl)BCl(2,6-lutidine)][$AlCl_4$] formed 1-boradienes with 1-Me_3Si-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 $RB(C_6F_5)_2$ (R = C_6F_5, alkyl).[1] Addition of $RB(C_6F_5)_2$ 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.[2] This reaction has been developed into a useful route to arylboranes by benzannulation,[3] and to highly substituted vinyl boranes that are complementary to those obtained from hydroboration.[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_3Pb > R_3Sn > R_3Ge > R_3Si (TMS), with R_3C-substituted alkynes not amenable.[5] These studies predominantly used trialkylboranes; in contrast, the utilisation of vinyl and aryl boranes (excluding $B(C_6F_5)_3$) for the 1,1-vinyl-boration or 1,1-aryl-boration of alkynes is rare with only limited examples reported using BPh_3 or $PhB(C_6F_5)_2$.[6,7] One report particularly relevant to this work showed that Ph_2BX (X = Cl or Br) effected the 1,1-carboboration of 1-TMS-1-hexyne (Scheme 1, top).[8] It should be noted that with $(chloro)_x(aryl)_{3-x}B$ compounds TMS substitution appears essential for 1,1-carboboration, with $PhBCl_2$ and terminal alkynes reacting *via* 1,2-halo- or 1,2-carboboration instead.[9] 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 alkyne haloboration,[11] using BCl_3 derived borocations (to produce $arylBCl_2$ and [vinylBCl(amine)]$^+$, 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 organo-

School of Chemistry, University of Manchester, Manchester, M13 9PL, UK.
E-mail: Michael.ingleson@manchester.ac.uk

†Electronic supplementary information (ESI) available: Copies of NMR spectra, coordinates for calculated structures and crystallographic data. CCDC 1416375 and 1416376. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03003j

BCl_2 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.[11,13] For example, terminal alkynes and the boronium salt [(Ph)ClB(2-DMAP)][$AlCl_4$] (2-DMAP = 2-*N*,*N*-dimethylamino-pyridine) react only by 1,2-chloroboration.[11] Based on the previous 1,1-carboboration 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_2 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 such as (NHC)BH_2(NTf)$_2$.[14] Herein is reported our studies using arylBCl_2 and aryl and vinyl containing borocations synthesised by electrophilic borylation to effect the carboboration of TMS-substituted alkynes.

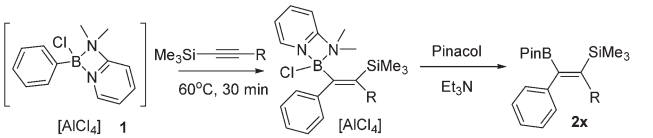
Results and discussion

Vinylboronate ester formation

Studies commenced with the boronium cation [Ph(Cl)B(2-DMAP)][$AlCl_4$], **1**.[11] 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 (δ_{29Si} −6.05) with minimal desilylboration observed (only a low intensity TMSCl resonance present in the ^{1}H NMR spectra). Heating the reaction to 60 °C in CH_2Cl_2 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/Et_3N 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 ^{1}H NMR spectroscopy).

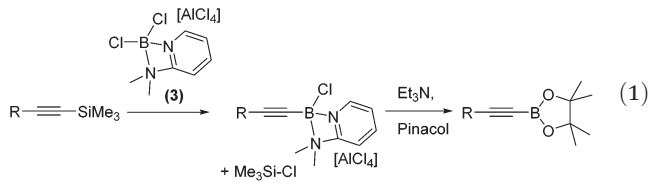
With 1,1-carboboration observed from the combination of **1** and 1-TMS-1-alkynes the reaction of 1-TMS-1-propyne and [Cl_2B(2-DMAP)][$AlCl_4$], **3**, was explored to determine if any 1,1-chloroboration occurred. Instead, this led to formation of TMSCl (by ^{1}H and ^{29}Si NMR spectroscopy) and a major new ^{11}B resonance at +6.5 ppm. Esterification enabled identification of the alkynyl pinacol boronate ester confirming desilylboration (eqn (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.[11]

Table 1 1,1-Carboboration with **1**,[a] followed by esterification with pinacol



Entry	Electrophile	T^a (°C)	Compound no.	R	Isolated yield (%)
1	**1**	**60**	**2a**	Me	63
2	**1**	**60**	**2b**	Bu	61
3	**1**	**60**	**2c**	C(Me)=CH_2	55
4	**1**	**60**	**2d**	Ph	65
5	**1**	**60**	**2e**	*p*-Br-C_6H_4	56

[a] Performed in CH_2Cl_2 in sealed tubes fitted with J. Young valves.



(1)

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 ^{1}H NMR spectrum consistent with alkyne elemento-boration. Crystalline solid spontaneously deposited from CH_2Cl_2 solutions as the reaction proceeded with a concomitant increase in the quantity of TMSCl and a decrease in the vinylic singlet (by ^{1}H 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 (Fig. 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.

Compound **4** was confirmed as the major component of the CH_2Cl_2 insoluble material by elemental microanalysis. Furthermore, on dissolution of the crystalline solid in CD_3CN two major resonances at +3.9 ppm and −15.4 ppm in the ^{11}B NMR spectrum were observed consistent with four coordinate cationic and anionic boron centres, respectively. The formation of **4** suggested that the CH_2Cl_2 soluble product formed is **5**, the product from 1,1-boroamination of TMS-ethyne prior to intermolecular desilylboration (Fig. 1). Whilst **5** could not be isolated analytically pure (due to contamination with **4**, the alkynyl-borocation and [H(2-DMAP)][$AlCl_4$]) multinuclear NMR

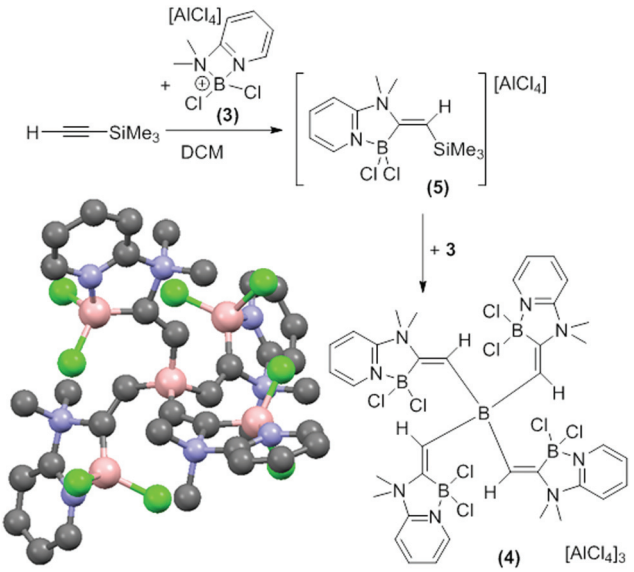
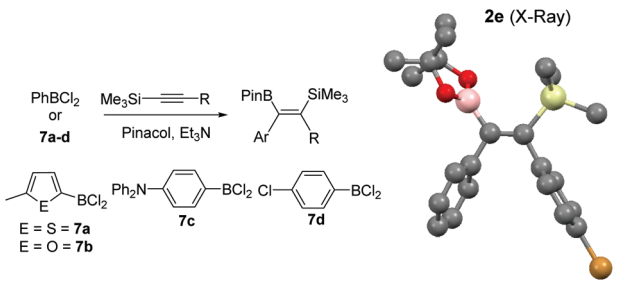


Fig. 1 Formation of the tricationic borate **4** by 1,1-boroamination. Bottom left, solid state structure of **4** (anions and hydrogens omitted).

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 [Cl_2B(2,6-lutidine)][$AlCl_4$], **6**, a borocation where the amine does not contain a pendant nucleophile, with 1-TMS-alkynes, including TMS-ethyne, led predominantly to desilylboration in all cases.

Whilst the reactivity of 1-TMS-1-alkynes with BCl_3 proceeds by desilylboration[15] the analogous reactivity with $PhBCl_2$ has not been explored to the best of our knowledge. To determine if $PhBCl_2$ and **1** react comparably with 1-TMS-1-alkynes equimolar 1-TMS-1-propyne and $PhBCl_2$ were combined in CH_2Cl_2 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 $PhBCl_2$ 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)silane (entry 7) resulted in only 1,1-carboboration with no 6-*endo*-dig cyclisation as recently reported for related alkynes and BCl_3.[16] The facile formation of **2a–2h** by 1,1-carboboration represents an alternative to transition metal catalysed borosilyation of alkynes for accessing these versatile intermediates.[17] Attempts to extend this reaction to 1-triisopropylsilyl-1-propyne resulted in no reaction, whilst combining $PhBCl_2$ and 1-($PhMe_2Si$)-1-propyne resulted predominantly in desilyl-

Table 2 1,1-Carboboration using (hetero)arylBCl_2 (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	$PhBCl_2$	1	20	**2a**	Me	88
2	$PhBCl_2$	6	20	**2b**	Bu	79
3	$PhBCl_2$	24	20	**2c**	C(Me)=CH_2	77
4	$PhBCl_2$	20	20	**2d**	Ph	85
5	$PhBCl_2$	20	20	**2e**	*p*-Br-C_6H_4	68
6	$PhBCl_2$	2	20	**2f**	^{i}Pr	76
7	$PhBCl_2$	1	20	**2g**	CH_2CH_2Ph	37
8	$PhBCl_2$	1	60	**2h**	H	30
9	**7a**	1	20	**2i**	Me	—[a]
10	**7b**	0.5	20	**2j**	Me	—[a]
11	**7c**	1	20	**2k**	Me	68
12	**7d**	1	20	**2l**	Me	61

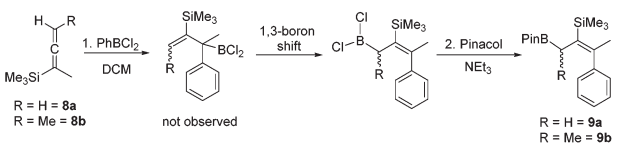
[a] Isolated yield not obtained due to intractable minor contaminants of (heteroaryl)BPin.

boration products (by observation of $PhMe_2SiCl$ by ^1H and ^{29}Si NMR spectroscopy) and multiple other currently unidentified products.

To increase the scope, variation of the aryl substituent on the borane was explored. $ArylBCl_2$ and $heteroarylBCl_2$ species are readily accessible by electrophilic arene borylation.[10] Using established methodologies 2-methylthiophene, 2-methylfuran, chlorobenzene and triphenylamine were all borylated to produce the respective (hetero)$arylBCl_2$ compounds **7a–7d** (Table 2) in good conversion as determined by multi-nuclear NMR spectroscopy.[10a,b] Removal of reaction solvent (CH_2Cl_2 or $1,2\text{-}Cl_2C_6H_4$) 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 heteroarylBPin (from esterfication 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.

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)silane, instead led to desilylboration being the dominant reaction pathway (by ^1H, ^{11}B and ^{29}Si NMR spectroscopy). To preclude the disparity between $PhBCl_2$ and the four (hetero)$arylBCl_2$ compounds **7a–d** being due to any impurities in commercially sourced $PhBCl_2$ or impurities in (hetero)$arylBCl_2$ synthesised by electrophilic borylation, benzene was borylated in $1,2\text{-}Cl_2C_6H_4$ using 4-*N*,*N*-trimethylaniline, BCl_3 and two equivalents of $AlCl_3$ to form $PhBCl_2$.[10c] This reaction mixture was dried and $PhBCl_2$ extracted into hexane and found to form **2f** on addition of trimethyl(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)$arylBCl_2$ compounds is somewhat limited in scope.

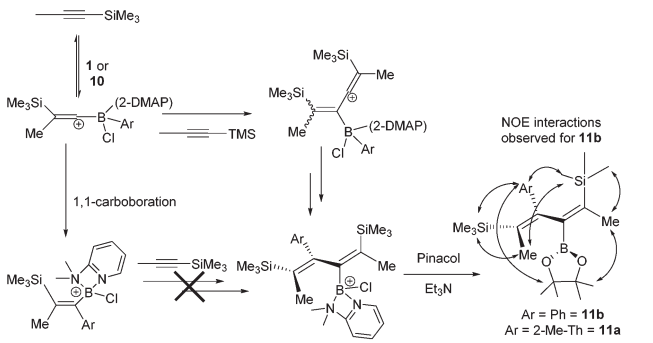
$PhBCl_2$ was effective for the carboboration of silylated allenes with **8a** and **8b** (Scheme 2) undergoing carboboration with TMS migration producing only a single $allylBCl_2$ product (by *multinuclear* NMR spectroscopy). With no intermediates observed we attribute the reaction outcome to a 1,1-carboboration followed by a rapid intramolecular sigmatropic 1,3-boron shift to form the more thermodynamically stable less hindered $allylBCl_2$ species.[18] 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 hydroboration of closely related TMS-allenes where TMS migration does not occur.[19]



Scheme 2 The carboboration of TMS-allenes with $PhBCl_2$.

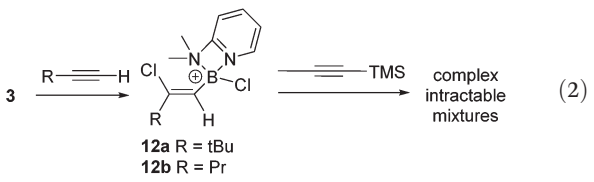
Boradiene formation using borocations

To explore potential scope expansion further [5-methyl-2-(BCl-(2-DMAP))-thiophene][$AlCl_4$], **10**, was synthesised by addition of 2-DMAP and $AlCl_3$ 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, ^{11}B and ^{29}Si 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 (Scheme 3). 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 $PhBCl_2$ 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 BEt_3 with two equivalents of 1-R_3Sn-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-bor-



Scheme 3 2-Boradiene formation from **1** and **10** and 1-TMS-1-propyne (shown as vinyl cation intermediates, π complexes of $\{Me_3Si\}^+$ are also feasible).

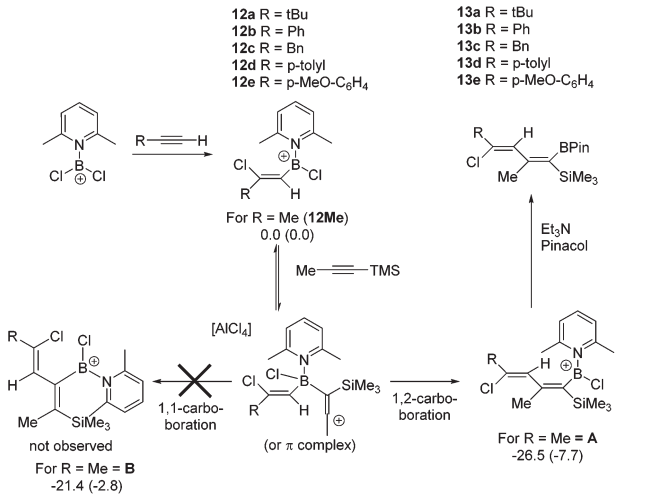
adiene. This is in contrast to that in **2x** suggesting that 1,1-carboboration is not the first step in 2-boradiene formation, a hypothesis supported by the fact that resonances for the 1,1-carboboration products increase in intensity as the reaction progresses, suggesting it is not an intermediate 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 borocation and this ultimately leads to the observed 2-boradiene structures. Related borane activation of alkynes towards external π nucleophiles have been reported previously.[2b,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**.



(2)

Subsequently, the one pot, two step reaction of **3** with terminal alkynes (proceeding by 1,2-haloboration as previously reported to form **12x**, eqn (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 ^{1}H NMR spectrum, including $[(2\text{-DMAP})H]^{+}$, as well as four new ^{29}Si resonances (one corresponding to TMSCl) and new ^{11}B 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-borocation 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 $[(\text{vinyl})BCl(2,6\text{-lutidine})]^{+}$ cations, made *via* haloboration of alkynes with **6**, with 1-TMS-1-alkynes was explored.

In a one pot two step reaction **6** was used to separately haloborate ^{t}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 carboboration products (Scheme 4). Running the reaction for longer times at 20 °C (≥2 h) resulted



Scheme 4 1-Boradiene formation by haloboration and 1,2-carboboration. Electronic energies (Gibbs free energies at 293 K) shown in kcalmol^{-1} for the model system where R = Me (all energies relative to **12Me** and 1-TMS-1-propyne at infinite distance).

in significant TMSCl formation, whilst attempts to use greater equivalents of 1-TMS-1-propyne also led to more TMSCl formation; thus optimized 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 $^{4}J_{HH}$ coupling of 1 Hz is observed between the methyl and the vinyl-H in both **13a** and **13b** confirming the connectivity as this coupling 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,[22] 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) borocations 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) which show that the 2-boradiene **B** is 5 kcal mol^{-1} higher in energy than the 1-boradiene isomer **A** (Scheme 4). Furthermore, in contrast to 1,1-carboboration reactions with BEt_3,[5] the 1,2-vinylboration to form **A** is unlikely to be reversible at 20 °C. This is indicated by the conversion of the model compound **12Me** (where R = Me) to **A** being

found to be exergonic by 7.7 kcal mol^{-1}, thus the barrier to the reverse process (retro-vinylboration) will be significantly higher than that for the forward reaction (which requires at least 1 h for significant conversion).

As bora-dienes 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 as previously reported underwent 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 desilylboration.

Conclusions

The carboboration of 1-TMS-1-alkynes with aryldichloroboranes and aryl-substituted and vinyl-substituted borocations has been demonstrated to yield highly substituted vinyl and dienyl boronate esters post esterification. However, due to carboboration occurring in competition with desilylboration and diene formation, coupled with further reactions proceeding subsequent to the initial carboboration (*e.g.*, desilylboration), complex mixtures are often produced that limit the overall utility of this reaction. Variation in borane and borocation structure is therefore essential to preclude desilylboration 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 under vacuum before use. Hexane, *ortho*-dichlorobenzene, d_1-chloroform, d_2-dichloromethane, 2,6-lutidine, Et_3N 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 SPS800 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.[11] All other materials were purchased from commercial vendors and used as received. NMR spectra were recorded with a Bruker AV-400 spectrometer (400 MHz ^{1}H; 100 MHz ^{13}C; 128 MHz ^{11}B; 376.50 MHz ^{19}F; 104.3 MHz ^{27}Al; 79.5 MHz ^{29}Si). ^{1}H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents and ^{13}C NMR using the solvent resonances unless otherwise stated. ^{11}B NMR spectra were referenced to external $BF_3:Et_2O$, ^{19}F to Cl_3CF, ^{27}Al to $Al(NO_3)_3$ in D_2O ($Al(D_2O)_6^{3+}$), ^{29}Si to $Si(CH_3)_4$. Resonances for the carbon directly bonded to boron are not observed in the $^{13}C\{^1H\}$ NMR spectra due to quadrupolar effects. GC-MS analysis was performed on an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD with triple axis detector. The column employed was an Agilent J&W HP-5 ms ((5%-phenyl)-methylpolysiloxane) of dimensions: length, 30 m; internal diameter, 0.250 mm; film, 0.25 μm. Mass spectra were recorded on a Waters QTOF mass spectrometer. X-ray data for compounds **2e** and **4** was collected at a temperature of 150 K using Mo-K_α radiation on an Agilent Supernova, equipped with an Oxford Cryosystems Cobra nitrogen flow gas system. 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_2O_5 as an additional oxidant.

General procedures for 1,1-carboboration 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.

*(E)-(1-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl) trimethylsilane (**2a**).* The product was isolated as a yellow oil (Route 1: 24 mg, 63%). (Route 2: 424 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, 2H, ^3J(H,H) = 7.2 Hz), 7.18 (t, 1H, ^3J(H,H) = 7.2 Hz), 7.06 (d, 2H, ^3J(H,H) = 7.2 Hz),

1.68 (s, 3H), 1.23 (s, 12H), 0.23 (s, 9H); $^{13}C\{^1H\}$ NMR (100.06 MHz, $CDCl_3$) δ 150.92, 143.54, 128.42, 127.86, 125.55, 83.50, 25.05, 20.58, 0.00; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.2; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −4.22 ppm. MS: (M + Na^+ *m*/*z*) calculated for $C_{18}H_{29}O_2SiBNa$ = 339.1928 Found = 339.1923.

*(E)-(1-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-2-yl) trimethylsilane (**2b**).* The product was isolated as a yellow oil (Route 1: 27 mg, 61%). (Route 2: 431 mg, 79%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, 2H), 7.18 (t, 1H), 7.07 (d, 2H), 2.07–2.03 (m, 2H), 1.21 (s, 12H), 1.19–1.10 (m, 4H), 0.72 (t, 2H), 0.26 (9H); $^{13}C\{^1H\}$ NMR (100.06 MHz, $CDCl_3$) δ 155.70, 143.59, 128.16, 127.67, 125.35, 83.42, 33.49, 32.49, 24.90, 22.81, 13.77, 0.81; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.4; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −4.60 ppm. MS: (GC, M + H^+, *m*/*z*) 359.3.

*(E)-(3-Methyl-1-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-2-yl)trimethyl silane (**2c**).* The product was isolated as a yellow oil ((Route 1: 23 mg, 55%). (Route 2: 403 mg, 77%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.24–7.15 (m, 5H), 4.69 (m, 1H), 4.38 (m, 1H), 1.42 (s, 1H), 1.23 (s, 12H), 0.24 (s, 9H); $^{13}C\{^1H\}$ NMR (100.06 MHz, $CDCl_3$) δ 158.70, 147.58, 142.92, 134.70, 128.37, 127.19, 125.58, 83.72, 25.00, 24.17, 0.27; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 31.1; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −6.59 ppm. MS: (GC, M + Na^+ *m*/*z*) 365.3.

*(E)-(1,2-Diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-vinyl)trimethylsilane (**2d**).* The product was isolated as a yellow oil (Route 1: 29 mg, 65%). (Route 2: 489 mg, 85%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.06–7.00 (m, 4H), 6.96–6.93 (m, 4H), 6.75–6.73 (m, 2H), 1.29 (s, 12H), 0.17 (s, 9H); $^{13}C\{^1H\}$ NMR (100.06 MHz, $CDCl_3$) δ 156.92, 144.48, 142.51, 128.84, 128.10, 127.19, 127.11, 125.22, 124.57, 83.91, 25.11, 0.36; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.6; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −5.00 ppm. MS: (GC *m*/*z*) 378.2 MS: (M + Na^+ *m*/*z*) 401.4.

*(E)-(1-(4-Bromophenyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (**2e**).* The product was isolated as a yellow oil (Route 1: 31 mg, 56%). (Route 2: 102 mg, 68%, reaction performed on a 1/4 scale of the general procedure).

^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, 2H, ^3J(H,H) = 8.2 Hz), 7.07–6.91 (m, 5H), 6.63 (d, 2H, ^3J(H,H) = 8.2 Hz), 1.28 (s, 12H), 0.17 (s, 9H); $^{13}C\{^1H\}$ NMR (100.06 MHz, $CDCl_3$) 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; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.0; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −4.92 ppm. MS: (GC, M + H^+ *m*/*z*) 458.0.

*(E)-(3-Methyl-1-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-2-yl)trimethylsilane (**2f**).* The product was isolated as orange crystals (100 mg, 76%, reaction performed on a 1/4 scale of the general procedure.

^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, 2H, ^3J(H,H) = 7.0 Hz), 7.03 (t, 1H, ^3J(H,H) = 7.0 Hz), 6.94 (d, 2H, ^3J(H,H) = 7.0 Hz), 2.57 (septet, 1H, ^3J(H,H) = 7.0 Hz), 1.02 (s, 12H), 0.81 (d, 6H, ^3J(H,H) = 7.0 Hz), 0.16 (s, 9H); $^{13}C\{^1H\}$ NMR (100.06 MHz, $CDCl_3$) δ 157.97, 143.70, 128.05, 127.89, 125.57, 83.56, 33.79, 24.92, 22.28, 2.67; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.5; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −5.83 ppm. MS: (GC, M + Na^+ *m*/*z*) 367.4.

*(E)-(1,4-Diphenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-but-1-en-2-yl)trimethylsilane (**2g**).* Trimethyl(4-phenylbut-1-yn-1-yl)silane (45 μL, 0.20 mmol, 1.0 eq.) was dissolved in DCM (0.6 ml) in a J. Youngs tube, $PhBCl_2$ (29 μL, 0.22 mmol, 1.1 eq.) was then added and the reaction sealed and rotated. After 1 h, a cooled solution of pinacol (26 mg, 0.22 mmol, 1.1 eq.) and excess of triethylamine were added to the reaction mixture. The reaction mixture was then concentrated under reduced pressure, the resultant crude was dissolved in pentane, filtered and concentrated. The residue was then purified by flash chromatography (petroleum ether : DCM 70 : 30), affording **2g** (30 mg, 37%) as a white solid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.34 Hz, 1H), 7.13–7.18 (m, 2H), 7.07–7.12 (m, 3H), 6.85 (d, *J* = 7.0 Hz, 2H), 2.40–2.47 (m, 2H), 2.28–2.36 (m, 2H), 1.22 (s, 12H), 0.31 (s, 9H); $^{13}C\{^1H\}$ NMR (100.06 MHz, $CDCl_3$): δ 154.4, 143.2, 142.4, 128.1, 128.0, 127.9, 127.8, 125.6, 125.5, 83.5, 36.6, 36.2, 24.9, 0.7; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.9 (s) ppm; ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ −4.4 (s) ppm; MS (GC, $[M - CH_3]^+$, *m*/*z*) 391.3; accurate mass: ($[M + H]^+$ 407.2583).

*(Z)-Trimethyl(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (**2h**).* Trimethylsilylacetylene (48 μL, 0.33 mmol, 1.0 eq.) was dissolved in DCM in a J. Youngs tube, $PhBCl_2$ (49 μL, 0.37 mmol, 1.1 eq.) was then added and the tube sealed. After 1 h at 60 °C a cooled solution of pinacol (44 mg, 0.37 mmol, 1.1 eq.) and excess of triethylamine were added to the reaction mixture. The reaction mixture was then concentrated under reduced pressure and the crude was dissolved in pentane, filtered and concentrated. The residue was then purified by flash chromatography (petroleum ether : DCM 70 : 30), affording **2h** (30 mg, 30%) as a colourless oil.

^1H NMR (400 MHz, $CDCl_3$) 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); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.6, 145.5, 128.0, 126.9, 126.7, 83.8, 25.1, 0.3; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.2 (s) ppm; ^{29}Si NMR (79 MHz, CDCl3): δ −9.2 (s) ppm; MS (GC, $[M - CH_3]^+$, *m*/*z*) 287.1; accurate mass: ($[M - CH_3]^+$ 287.1635).

*(E)-(1-(5-Methylthiophen-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)trimethylsilane (**2i**).* $[BCl_2(2\text{-DMAP})][AlCl_4]$ (100 mg, 2.7 mmol, 1 eq.) was 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 sealed and heated at 60 °C for 1 hour. NMR spectroscopy confirmed formation of 2-methylthiophene-BCl_2 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 Et_3N (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 **2i** with resonances for the minor by-product omitted.

^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100.06 MHz, $CDCl_3$) δ 148.27, 139.11, 135.82, 126.00, 122.91, 83.22, 25.01, 20.37, 15.86, 0.02 ppm; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.0; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −3.92 ppm. MS (GC, M^+, m/z): 336.4.

(E)-(1-(5-Methylfuran-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)trimethylsilane ***(2j).*** $[BCl_2(2\text{-DMAP})][AlCl_4]$ (100 mg, 2.7 mmol, 1 eq.) was combined with 2-methylfuran (24 μl, 2.7 mmol, 1 eq.) in DCM (0.5 ml) in a J. Youngs NMR tube. NMR spectroscopy confirmed formation of 2-methylfuran-BCl_2 in <5 min which was then extracted into hexane (10 ml). To this 1-TMS-1-propyne (40 μl, 2.7 mmol, 1 eq.) was added with the reaction turning deep orange. The reaction mixture was esterified after 30 minutes with excess Et_3N (0.1 ml) and pinacol (96 mg, 3 eq.). The crude product was extracted into pentane and filtered through a 1 inch plug of silica affording the desired product contaminated with 2-methyl-5-BPin-furan. The data below are for **2j** with resonances for the minor by-product omitted.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (d, 1H, ^3J(H,H) = 3.2 Hz), 5.99 (m, 1H), 2.28 (s, 3H), 2.02 (s, 3H), 1.37 (s, 12H), 0.21 (s, 9H); ^{13}C{^{1}H} NMR (100.06 MHz, $CDCl_3$) δ 155.78, 153.22, 152.09, 109.07, 102.72, 82.98, 25.03, 21.25, 14.76, 0.98 ppm; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.2; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −3.92 ppm. MS (GC, M^+, m/z): 320.3.

(E)-N,N-Diphenyl-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)prop-1-en-1-yl)aniline ***(2k).*** $[2,6\text{-lutBCl}_2][AlCl_4]$ (80 mg, 2.2 mmol, 1 eq.) was generated *in situ* (from lut-BCl_3 and $AlCl_3$) 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_2, 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 Et_3N (0.1 ml) and pinacol (78 mg, 3 eq.). The crude product was extracted into pentane (20 ml) and filtered through a 1 inch plug of silica afforded the product. (74 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07–6.77 (m, 14H), 1.58 (s, 3H), 1.07 (s, 12H), 0.05 (s, 9H); ^{13}C{^{1}H} NMR (100.06 MHz, $CDCl_3$) δ 150.41, 147.97, 145.25, 137.85, 129.38, 129.08, 123.97, 123.69, 122.35, 83.49, 25.04, 20.63, −0.03; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.3; ^{29}Si NMR (MHz, $CDCl_3$) δ −4.29 ppm. MS: (GC, M^+, m/z) 483.3.

(E)-(1-(4-Chlorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)trimethylsilane ***(2l).*** DMT-BCl_3 (100 mg, 1 eq.) and $AlCl_3$ (111 mg, 2.1 eq.) were combined in dichlorobenzene (0.5 ml) in a J. Youngs NMR tube which was then sealed and heated to 100 °C for 18 h. NMR spectroscopy confirmed formation of 4-chloro-phenyl-BCl_2, 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 Et_3N (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%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, 2H, ^3J(H,H) = 8.2 Hz), 6.75 (d, 2H, ^3J(H,H) = 8.2 Hz), 1.44 (s, 3H), 1.00 (s, 12H), 0.00 (s, 9H); ^{13}C{^{1}H} NMR (100.06 MHz, $CDCl_3$) δ 152.57, 136.11, 131.30, 129.82, 128.03, 83.59, 24.99, 20.77, 0.00; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.0; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −4.04 ppm. MS: (GC, M^+, m/z) 350.1.

Compound ***4.*** A 5 : 4 ratio of $[BCl_2(2\text{-DMAP})][AlCl_4]$ (100 mg, 0.27 mmol, 5 eq.), to trimethylsilylacetylene (31 μl, 0.22 mmol, 4 eq.) was dissolved in CH_2Cl_2 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).

^{1}H NMR (400 MHz, CD_3CN, −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); ^{11}B NMR (128.4 MHz, CD_3CN): δ 3.90, −15.44; ^{13}C{^{1}H} NMR (100.6 MHz, CD_3CN): δ 154.09, 150.15, 143.80, 130.47, 119.85 ppm. Expected (%) for $C_{36}H_{44}Al_3B_5N_8Cl_{20}$ C = 30.18 H = 3.10 N = 7.82, Found (%) C = 29.94, H = 2.97, N = 7.65.

Compound ***5.*** To a 1 : 1 suspension of $[BCl_2(2\text{-DMAP})][AlCl_4]$ (100 mg, 0.27 mmol, 1 eq.) in CH_2Cl_2 in a J. Young's NMR tube was added trimethylsilylacetylene (38 μl, 0.27 mmol, 1 eq.) and tube was sealed and rotated at room temperature for 18 hours. The solvent was removed under reduced pressure, and the product redissolved in DCM.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.99 (d, 1H), 8.88 (t, 1H), 8.56 (d, 1H), 8.25 (t, 1H), 6.65 (s, 1H), 3.80 (s, 6H), 0.38 (s, 9H); δ ^{11}B NMR (128.4 MHz, CD_2Cl_2): δ 2.5 (s); ^{29}Si NMR (79.5 MHz, CH_2Cl_2) δ −3.6 ppm. Due to difficulties in purifying this compound, the ^{13}C NMR spectra were complicated by numerous minor species. Accurate elemental analysis could not be obtained due to the impure nature of the material from each attempt to isolate this product.

(E)-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-2-yl)trimethylsilane ***(9a).*** 3-(Trimethylsilyl)-1,2-butadiene (25 μL, 0.15 mmol, 1.0 eq.) was dissolved in DCM in a J. Youngs tube and $PhBCl_2$ (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 **9a** (21 mg, 43%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.0, 145.1, 131.3, 128.0, 127.6, 125.9, 82.9, 25.3, 24.8, 0.4; ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.7 (s) ppm; ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ −5.8 (s) ppm. MS: (GC, M^+, m/z) 330.2, 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 ***(9b).*** 2-(Trimethylsilyl)-2,3-pentadiene (25 μL, 0.13 mmol, 1.0 eq.) was dissolved in DCM in a

J. Youngs tube and $PhBCl_2$ (20 μL, 0.14 mmol, 1.1 eq.) was added. The reaction mixture was heated at 60 °C and after 24 h a cooled solution of pinacol (17 mg, 0.14 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 **9b** (10 mg, 22%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 7.2 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.14 (d, J = 6.9 Hz, 2H), 2.08 (s, 3H), 2.04 (q, J = 7.5 Hz, 1H), 1.22 (s, 12H), 0.92 (d, J = 7.5 Hz, 3H), 0.26 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.4, 145.8, 138.4, 128.0, 127.8, 125.8, 82.9, 25.8, 25.3, 24.7, 16.3, 1.6; ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.5 (s) ppm; ^{29}Si NMR (79 MHz, $CDCl_3$): δ −6.6 (s) ppm. MS: (GC, $[M - CH_3]^+$, m/z) 329.2, accurate mass: $[M]^+$ 344.2337.

*((2Z,4Z)-3-(5-Methylthiophen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-2,4-diene-2,5-diyl)bis(trimethylsilane) (**11a**).* To a suspension of [Cl_2B(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, 1.1 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 $AlCl_3$ then generated [ClB2-methylthiophene(2-DMAP)]-[$AlCl_4$]. To this 1-TMS-1-propyne (90 μl, 0.6 mmol, 5 eq.) was addedand 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%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (d, 1H, ^3J(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{^{1}H} NMR (100.06 MHz, $CDCl_3$) δ 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, $CDCl_3$): δ 30.0; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −5.98 ppm. MS: (GC, M^+, m/z) 448.6 g mol^{-1}.

*((2Z,4Z)-3-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-hexa-2,4-diene-2,5-diyl)bis(trimethylsilane) (**11b**).* 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-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%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.20 (m, 5H), 1.98 (s, 3H), 1.85 (s, 3H), 1.16 (s, 6H), 1.11 (s, 6H), 0.09 (s, 9H), −0.15 (s, 9H) ppm; ^{13}C NMR (100.06 MHz, $CDCl_3$) δ 144.00, 133.75, 130.67, 129.96, 127.37, 126.72, 125.59, 83.08, 24.72, 22.40, 20.86, 0.01 (TMS resonances coincident); ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 29.6; ^{29}Si NMR (MHz, $CDCl_3$) δ −6.00 ppm. MS: (m/z): Calculated $[M]^+$ = 429.2811. Measured = 429.2812.

General procedure for vinylboration with 6

LutBCl_3 (50 mg, 0.22 mmol) was suspended in anhydrous CH_2Cl_2 (5 ml) in a J. Young's NMR tube and $AlCl_3$ (30 mg, 0.22 mmol) added causing dissolution to form a yellow solution. To this the appropriate alkyne (0.22 mmol) was added. The reaction mixture was then sealed and rotated at room temperature. After 10 min 1-TMS-1-propyne (40 μl, 0.26 mmol) was added and the tube resealed and rotated for a further 45 minutes. Then the solution was esterified with excess triethylamine (0.5 ml) and pinacol (2 eq.). The solvent was removed under reduced pressure, leaving a yellow oil. Hexane (30 ml) was used to extract the product, which was filtered. This left a mixture of the desired diene and the haloboration derived vinyl by-product used to determine NMR conversion before purification by column chromatography.

((1*E*,3*Z*)-4-Chloro-2,5,5-trimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,3-dien-1-yl)trimethylsilane (13a). This crude product (65% yield by NMR spectroscopy) was purified with column chromatography using 2 : 1 hexane : DCM eluent and isolated as a yellow oil (18 mg, 23%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (q, 1H, ^4J (H,H) = 1 Hz), 1.78 (d, 3H, ^4J (H,H) = 1 Hz), 1.29 (s, 12H), 1.22 (s, 9H), 0.19 (s, 9H); ^{13}C{^{1}H} NMR (100.06 MHz, $CDCl_3$) δ 154.05, 144.78, 123.72, 83.26, 38.72, 28.94, 25.36, 20.73, 0.28; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 29.41; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −4.64 ppm. MS: (GC, M^+ m/z) 356.3 g mol^{-1}.

((1*E*,3*Z*)-4-Chloro-2-methyl-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)trimethylsilane (13b). This crude product (71% conversion by NMR spectroscopy) was purified with column chromatography using 2 : 1 hexane : DCM eluent and isolated as a yellow oil (49 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.38–7.30 (m, 3H), 6.94 (q, 1H, ^4J (H,H) = 1.2 Hz), 1.91 (d, 3H, ^4J (H,H) = 1.2 Hz), 1.33 (s, 12H), 0.25 (s, 9H); ^{13}C{^{1}H} NMR (100.06 MHz, $CDCl_3$) δ 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, $CDCl_3$): δ 29.16 ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −4.18 ppm. MS: (GC, M^+, m/z) 376.2.

((1*E*,3*Z*)-4-Chloro-2-methyl-5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-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%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.23 (m, 5H), 6.37 (q, 1H, ^4J (H,H) = 1 Hz), 3.74 (s, 2H), 1.84 (d, 3H, ^4J (H,H) = 1 Hz), 1.30 (s, 12H), 0.20 (s, 9H); ^{13}C{^{1}H} NMR (100.06 MHz, $CDCl_3$) δ 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, $CDCl_3$):

δ 29.5 ppm; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −4.40 ppm. MS: (GC, M^+, m/z) 390.2.

((1*E*,3*Z*)-4-Chloro-2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(*p*-tolyl)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.

^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$): δ 29.5; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −4.24 ppm.

((1*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.

^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 30.0; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −4.28 ppm.

((1*E*,3*Z*)-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 (13f). 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%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50–2.39 (m, 2H), 2.26–2.16 (m, 2H), 1.74 (s, 3H), 1.24 (s, 12H), 1.14 (t, 3H), 0.95 (t, 3H), 0.19 (s, 9H); ^{13}C{^{1}H} NMR (100.06 MHz, $CDCl_3$) δ 153.05, 139.87, 128.54, 82.65, 27.98, 26.10, 24.62, 24.39, 20.72, 12.65, 12.30; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ 29.30; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −4.75 ppm.

Acknowledgements

The research leading to these results has received funding from the University of Manchester, the EPSRC (EP/J000973/1 and EP/K03099X/1) and the European Research Council (FP/2007–2013/ERC Grant Agreement 305868). MJI acknowledges the Royal Society (for the award of a University Research Fellowship) The authors would also like to acknowledge the use of the EPSRC UK National Service for Computational Chemistry Software (NSCCS) at Imperial College London in carrying out this work.

Notes and references

1 For initial reports on 1,1-carboboration using fluorinated boranes see: (*a*) C. Chen, F. Eweiner, B. Wibbeling, R. Fröhlich, S. Senda, Y. Ohki, K. Tatsumi, S. Grimme, G. Kehr and G. Erker, *Chem. – Asian J.*, 2010, 4711; (*b*) C. Jiang, O. Blacque and H. Berke, *Organometallics*, 2010, **29**, 125; (*c*) C. Fan, W. E. Piers, M. Parvez and R. McDonald, *Organometallics*, 2010, **29**, 5132; (*d*) C. Chen, G. Kehr, R. Fröhlich and G. Erker, *J. Am. Chem. Soc.*, 2010, **132**, 13594.

2 For recent reviews see: (*a*) G. Kehr and G. Erker, *Chem. Commun.*, 2012, **48**, 1839; (*b*) R. Melen, *Chem. Commun.*, 2014, **50**, 1161.

3 For a recent synthetic use of 1,1-carboboration for benzannulation see: (*a*) R. Liedtke, F. Tenberge, C. G. Daniliuc, G. Kehr and G. Erker, *J. Org. Chem.*, 2015, **80**, 2240.

4 C. Chen, T. Voss, R. Fröhlich, G. Kehr and G. Erker, *Org. Lett.*, 2011, **13**, 62.

5 (*a*) B. Wrackmeyer, *Coord. Chem. Rev.*, 1995, **145**, 125; (*b*) B. Wrackmeyer, *Heteroat. Chem.*, 2006, **17**, 188.

6 For select reactions of BPh_3 in 1,1-carboborations: With 1-TMS-1-alkynes see: (*a*) R. Köster, G. Seidel and B. Wrackmeyer, *Chem. Ber.*, 1989, **122**, 1825. With stannylated alkynes see: (*b*) B. Wrackmeyer, O. L. Tok and W. Milius, *Z. Naturforsch., B: Chem. Sci.*, 2007, **62**, 1509; (*c*) B. Wrackmeyer, P. Thoma, S. Marx, T. Bauer and R. Kempe, *Eur. J. Inorg. Chem.*, 2014, 2103. With Te-alkynes see: (*d*) F. A. Tsao, A. J. Lough and D. W. Stephan, *Chem. Commun.*, 2015, **51**, 4287; (*e*) F. A. Tsao and D. W. Stephan, *Dalton Trans.*, 2015, **44**, 71.

7 For an example with $PhB(C_6F_5)_2$: R. Liedtke, M. Harhausen, R. Fröhlich, G. Kehr and G. Erker, *Org. Lett.*, 2012, **14**, 1448.

8 R.-J. Binnewirtz, H. Klingenberger, R. Welte and P. Paetzold, *Chem. Ber.*, 1983, **116**, 1271.

9 M. Lappert and B. Prokai, *J. Organomet. Chem.*, 1963, **1**, 384.

10 (*a*) A. Del Grosso, M. D. Helm, S. A. Solomon, D. Caras-Quintero and M. J. Ingleson, *Chem. Commun.*, 2011, **47**, 12459; (*b*) V. Bagutski, A. Del Grosso, J. Ayuso-Carrillo, I. A. Cade, M. D. Helm, J. R. Lawson, P. J. Singleton, S. A. Solomon, T. Marcelli and M. J. Ingleson, *J. Am. Chem. Soc.*, 2013, **135**, 474; (*c*) A. Del Grosso, J. Ayuso Carrillo and M. J. Ingleson, *Chem. Commun.*, 2015, **51**, 2878.

11 J. R. Lawson, E. R. Clark, I. A. Cade, S. A. Solomon and M. J. Ingleson, *Angew. Chem., Int. Ed.*, 2013, **52**, 7518.

12 For synthetic applications of boronic acid derivatives see: *Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine*, ed. D. G. Hall, Wiley-VCH, Weinheim, New York, 2011.

13 I. A. Cade and M. J. Ingleson, *Chem. – Eur. J.*, 2014, **20**, 12874.

14 A. Boussonniere, X. Pan, S. J. Geib and D. P. Curran, *Organometallics*, 2013, **32**, 7445.

15 D. A. Singleton and S.-W. Leung, *J. Organomet. Chem.*, 1997, **544**, 157.

16 A. J. Warner, J. R. Lawson, V. Fasano and M. J. Ingleson, *Angew. Chem., Int. Ed.*, 2015, **54**, 11245.

17 For metal catalysed alkyne borosilylation see: (*a*) T. Ohmura, K. Oshima, H. Taniguchi and M. Suginiome, *J. Am. Chem. Soc.*, 2010, **132**, 12194; (*b*) J. Jiao, K. Hyodo, H. Hu, K. Nakajima and Y. Nishihara, *J. Org. Chem.*, 2014, **79**, 285 and references therein.

18 A related 1,1-carboboration followed by a 1,3-boron shift has been observed previously with $B(C_6F_5)_3$: M. M. Hansmann, R. L. Melen, F. Rominger, A. S. K. Hashmi and D. W. Stephan, *J. Am. Chem. Soc.*, 2014, **136**, 777.
19 K. K. Wang, Y. G. Gu and C. Liu, *J. Am. Chem. Soc.*, 1990, **112**, 4424.
20 B. Wrackmeyer and R. Zentgraf, *J. Chem. Soc., Chem. Commun.*, 1978, 402.
21 (*a*) M. A. Dureen, C. C. Brown and D. W. Stephan, *Organometallics*, 2010, **29**, 6422; (*b*) B.-H. Xu, G. Kehr, R. Fröhlich and G. Erker, *Organometallics*, 2011, **30**, 5080.
22 S. Roscales and A. G. Csaky, *Org. Lett.*, 2015, **17**, 1605.
23 M. Devillard, R. Brousses, K. Miqueu, G. Bouhadir and D. Bourissou, *Angew. Chem., Int. Ed.*, 2015, **54**, 5722.
24 L. Eberlin, F. Tripoteau, F. Carreaux, A. Whiting and B. Carboni, *Beilstein J. Org. Chem.*, 2014, **10**, 237.