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Alkyne Carboboration

# *syn*-1,2-Carboboration of Alkynes with Borenium Cations

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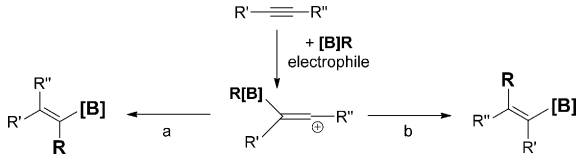
**Abstract:** The reaction of 8-(trimethylsiloxy)quinoline (**QOTMS**) with $BCl_3$ and (aryl)$BCl_2$ forms **QOBCl$_2$** and QOBCl(aryl). The subsequent addition of stoichiometric $AlCl_3$ follows one of two paths, dependent on the steric demands of the QO ligand and the electrophilicity of the resulting borenium cation. The phenyl- and 5-hexylthienylborenium cations, **QOBPh$^+$** and **QOBTh$^+$**, are formed, whereas **QOBCl$^+$** is not. Instead, $AlCl_3$ preferentially binds with **QOBCl$_2$** at oxygen, forming **QOBCl$_2$·AlCl$_3$**, rather than abstracting chloride. A modest increase in the steric demands around oxygen, by installing a methyl group at the 7-position of the quinolato ligand, switches the reactivity with $AlCl_3$ back to chloride abstraction, allowing formation of **$^{Me_2}$QOBCl$^+$**. All the prepared borenium cations are highly chlorophilic and exhibit significant interaction with $AlCl_4^-$ resulting in an equilibrium concentration of Lewis acidic "$AlCl_3$" species. The presence of "$AlCl_3$" species limits the alkyne substrates compatible with these borenium systems, with reaction of **[QOBPh][AlCl$_4$]** with 1-pentyne exclusively yielding the cyclotrimerised product, 1,3,5-tripropylbenzene. In contrast, **QOBPh$^+$** and **QOBTh$^+$** systems effect the *syn*-1,2-carboboration of 3-hexyne. DFT calculations at the M06-2X/6-311G(d,p)/PCM(DCM) level confirm that the higher migratory aptitude of Ph versus Me leads to a lower barrier to 1,2-carboboration relative to 1,1-carboboration.

## Introduction

The carboboration of alkynes concomitantly installs a C–B and C–C bond and represents an attractive synthetic route to substituted alkenes, provided it proceeds with high regio- and stereoselectivity. The di- and tri-substituted vinyl boronates produced are synthetically desirable for subsequent transformations, most notably C–C bond formation.[1] Significant advances in metal-catalysed carboborations have been reported using Cu, Ni and Pd complexes.[2] The majority of these protocols form the vinyl–boron moiety by boro-metallation of the alkyne using a transition-metal boryl complex; a subsequent step (reductive elimination or addition of a carbon electrophile) then installs the new C–C bond. Direct electrophilic carboboration (Scheme 1) is a transition-metal-free alternative that requires a boron Lewis acid that contains a B–C bond into which the alkyne formally inserts. Until recently this was limited to the "Wrackmeyer" reaction between trialkylboranes and alkynes containing $ER_3$ (E = Si, Ge, Sn or Pb) or transition-metal substituents.[3] Due to the propensity of the $ER_3$ moieties to undergo formal 1,2-migration the 1,1-carboboration products do-




**Scheme 1.** Reactions of internal alkynes with boron-based electrophiles, groups in bold indicate those that have been added to the alkyne. a) 1,1-Carboboration with, for example, $Et_3B$, R′ = Me and R″ = Si/Ge/Sn/$PbMe_3$. b) The alternative 1,2-carboboration as observed with allylboranes.[10]

minated. However, no reactivity was observed with hydrocarbyl-substituted terminal or internal alkynes presumably due to the limited electrophilicity of trialkylboranes, such as $BEt_3$. In 2010 Erker et al.[4] and Berke et al.,[5] extended 1,1-carboboration to terminal alkynes by using stronger boron Lewis acids, $RB(C_6F_5)_2$ (R = 1° alkyl or $C_6F_5$), with 1,2-hydride migration rapid even at room temperature. Since this breakthrough 1,1-carboboration has been applied to a range of heteroatom substituted alkynes[6] and even to internal alkynes.[7] The 1,1-carboboration of internal alkynes with $B(C_6F_5)_3$ or the perfluorinated pentaphenylborole[8] is remarkable as it requires cleavage of a strong C–C σ bond prior to B–C cleavage. To the best of our knowledge, 1,1-carboboration of alkynes occurs exclusively with $RB(C_6F_5)_2$ with no competitive 1,2-carboboration reported to date.

Alkyne 1,2-carboborations are in fact surprisingly rare in contrast to the ubiquitous 1,2-hydroboration and 1,2-haloboration. Notable exceptions include 1,2-allylborations[10] and one report on the reaction of $Ph_{3-x}BCl_x$ ($x$ = 1 or 2) with terminal alkynes.[11] Clearly concerted B–Y addition leads to 1,2-products,

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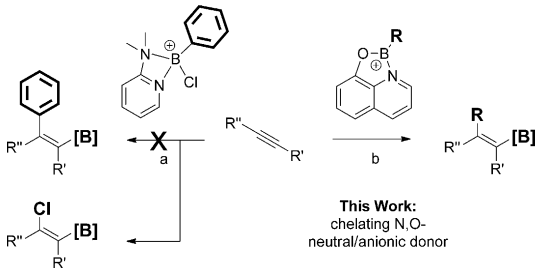
whereas a stepwise process via vinyl cation intermediates permits both outcomes depending on relative barriers to migration. If the barrier to internal group transfer prior to B–C activation is lower than B–C activation this results in an overall 1,1-addition. We surmised that the relative rarity of 1,2-carboborations is due to the use, historically, of R groups with an intrinsically low migratory aptitude (e.g., R = 1° alkyl or $C_6F_5$ in $RB(C_6F_5)_2$)[6] and it is this low migratory propensity that leads to high barriers to 1,2-carboboration. If so, it would suggest strong boron Lewis acids, containing groups that more readily undergo migration, will react with alkynes to give 1,2-carboboration. Migratory aptitude is particularly well-defined in the Baeyer–Villager reaction (also involving a cationic transition state and formal migration of a hydrocarbyl anion) and corresponds to the availability of bonding electrons in the moiety undergoing migration to donate into a σ* orbital (in carboboration, it is donation to the formally empty $p_z$ orbital in the vinyl cation). Thus, for migratory aptitude phenyl ≫ $C_6F_5$ and 1° alkyl. Borenium cations are ideal to probe this hypothesis, as a range of highly Lewis acidic structures containing B–(aryl) moieties can be readily accessed. Guided by previous work on $[PhBCl(2\text{-}DMAP)]^+$ and $[vinylBCl(2\text{-}DMAP)]^+$,[11] in which chloride migrates in preference to the hydrocarbyl (Scheme 2), herein we report borocations that are designed to permit only hydrocarbyl migration. These borocations undergo 1,2-carboboration of alkynes as the only observed carboboration mode of reaction with phenyl and thienyl migrating groups.

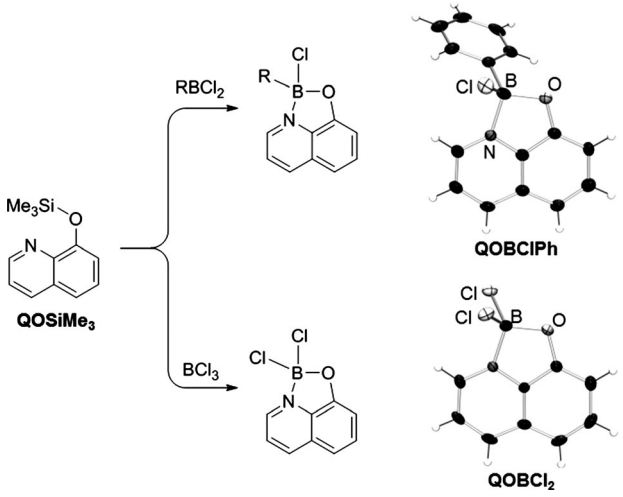



**Scheme 2.** Reactions of alkynes with borocation electrophiles, groups in bold indicate those that have been added to the alkyne. a) Reactions of alkynes with $[PhBCl(2\text{-}DMAP)]^+$ resulted exclusively in 1,2-haloboration with no phenyl migration. b) For $QOBR^+$ the anionic halide donor is replaced with a chelating aryloxy donor enabling carboboration.

## Results and Discussion

To overcome the greater reactivity of the boron–halogen bond, and favour hydrocarbyl migration, a modified borenium reagent was envisioned. In such a system, replacement of halide with an aryloxy group, as part of a chelating ligand, should focus the migratory reactivity of the borenium onto the remaining non chelated anionic donor, R. The quinolato ligand derived from 8-hydroxyquinoline (QOH) fulfils these requirements, furthermore, there is extensive literature precedence for the chelation of QO to boron.[12]

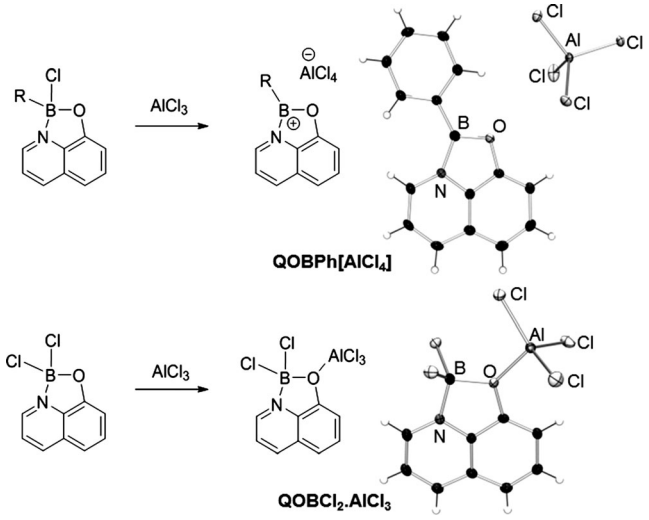
The 4-coordinate quinolato-chloroborane precursors are afforded by mixing the chloroborane with **QOSiMe$_3$** (Scheme 3), followed by washing with pentane to remove any unreacted




**Scheme 3.** Synthesis of **QOBCl$_2$** and **QOBClR** from $QOSiMe_3$ and a haloborane. R = Phenyl (**QOBPhCl**) and (5-hexyl)thienyl (**QOBThCl**). Single-crystal X-ray structures are shown for: **QOBClPh** and **QOBCl$_2$**, thermal ellipsoids at the 50% probability level.

$BCl_3/RBCl_2$ and/or **QOSiMe$_3$**. The final step en route to borenium formation is abstraction of the chloride ligand with aluminium trichloride concomitantly forming the tetrachloroaluminate counterion (Scheme 4). In previous studies this anion has been shown to be both stable and weakly coordinating towards highly electrophilic borenium centres unlike other classic weakly coordinating anions (WCA).[13] However, a feature of the quinolato architecture is the presence, even when coordinated to boron, of a mildly Lewis basic site at oxygen that complicates the reactivity with $AlCl_3$.

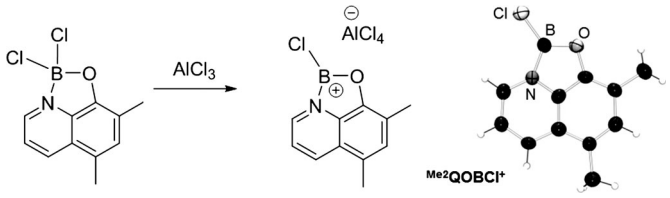
In the case of **QOBCl$_2$**, the normally potent halide abstraction agent is observed to bind to oxygen in preference to chloride and thus generates the neutral aluminium adduct, **QOBCl$_2$·AlCl$_3$**. No other products are observed and heating only




**Scheme 4.** Synthesis of **QOBR$^+$** and **QOBCl$_2$·AlCl$_3$**. R = Phenyl (**QOBPh$^+$-[AlCl$_4$]**) and (5-hexyl)thienyl (**QOBTh$^+$**). Single-crystal X-ray structures are shown for: **QOBPh[AlCl$_4$]** and **QOBCl$_2$·AlCl$_3$**. Thermal ellipsoids are at the 50% probability level.

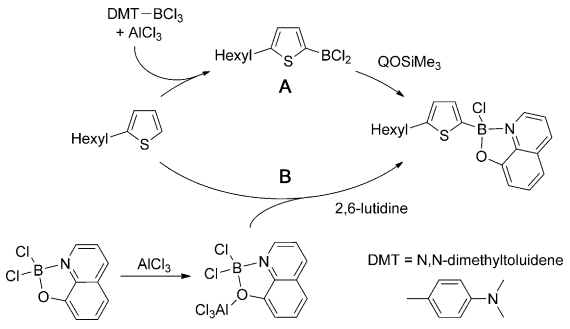
 

produces $QOAlCl_2$ and $BCl_3$. The binding of Lewis acids at the weakly nucleophilic oxygen site in related catecholboranes and pinacolboranes, termed B–O activation, has been repeatedly proposed,[14] but only crystallographically confirmed once before.[13a] The reactivity of **QOBCl$_2$** towards $AlCl_3$ contrasts with that observed for the related amine adducts of *B*-chlorocatecholborane, in which $AlCl_3$ abstracts halide selectively with no propensity for $AlCl_3$ coordination at oxygen observed.[15] However, it is notable that these catechol(amine)–borenium systems have all been synthesised with amines possessing significant bulk, something that will reduce chloride ion affinity at the boron centre.[16] In contrast, **QOBCl$^+$** possesses minimal steric bulk around the boron electrophile, thus the chloride ion affinity will remain high. Notably, even a relatively small increase in steric bulk around oxygen switches the observed reactivity from oxo adduct formation to generating a borenium. Installation of a methyl group at the 7-position of the QO backbone in **$^{Me_2}$QOBCl$_2$** provides sufficient steric shielding around the aryloxy group to allow formation of the desired borenium rather than the simple adduct (Scheme 5).




**Scheme 5.** Synthesis and single-crystal X-ray structure of **$^{Me_2}$QOBCl$^+$** (anion not shown for clarity, thermal ellipsoids at the 50% probability level).

As well as displaying an unexpected coordination to $AlCl_3$, **QOBCl$_2$** also displays notable reactivity applicable to the formation of **QOBClTh**, a key compound for subsequent carboboration studies. **QOBClTh** may be prepared by either of two routes (Scheme 6). The route using dimethyl-*para*-toluidene (DMT)/$BCl_3$/$AlCl_3$ (**A**) has been reported previously[17] and is the higher yielding of the two. However, it is notable that route **B** proceeds at all. This presumably indicates that, while not formally a borenium, the $AlCl_3$ adduct of **QOBCl$_2$** retains some borenium-like character and is capable of electrophilic aromatic substitution. This may be due to a small equilibrium concentration of **QOBCl$^+$**, afforded by dissociation of $AlCl_3$ followed by chloride abstraction, which we have not observed. Alternatively, it may be that co-ordination of $AlCl_3$ sufficiently weakens the B–O bond that the aryloxy donor is able to dissociate from boron during $S_EAr$. This is consistent with the elongation observed for the B–O bond (0.103 Å) on coordination of $AlCl_3$ to **QOBCl$_2$** to give **QOBCl$_2$·AlCl$_3$**. Both outcomes, and an alumination/transmetallation to $QOBCl_2$ sequence as previously proposed,[17] would enable the observed borylation in the presence of a base (2,6-lutidine).




**Scheme 6.** Synthesis of **QOBClTh**.

In contrast to the unexpected reactivity of **QOBCl$_2$** with $AlCl_3$, the *B*,*B*-chloroaryl systems, **QOBClR**, behaved as desired, yielding boreniums on exposure to $AlCl_3$. This difference in reactivity is likely due to significant influences of both steric and electronic effects. The aryl groups are both more sterically demanding than chloride thus would likely destabilise an aryloxy-bound $AlCl_3$ adduct. In addition to this, both phenyl and, to a greater extent, 5-hexylthienyl are significantly more π-electron-donating than chloride (see the section below on X-ray crystallography). This can also be expected to favour borenium cation formation due to stabilisation of the newly formed borocation, through π-donation. This disparity in reactivity persists in the solution phase as judged by $^{11}B$ and $^{27}Al$ NMR spectroscopy (Table 1). Both **QOBPh$^+$AlCl$_4^-$** and **$^{Me}$QOBCl$^+$AlCl$_4^-$** display $^{27}Al$ NMR resonances consistent with a $AlCl_4^-$ counterion and $^{11}B$ NMR resonances consistent with a three-coordinate borenium. In contrast, the $^{27}Al$ NMR resonance of **QOBCl$_2$·AlCl$_3$** is significantly broader than expected, indicating an aluminium environment less symmetrical than $AlCl_4^-$, consistent with an oxo-bound $AlCl_3$. The $^{11}B$ NMR spectrum also shows a single peak both at higher field and sharper than expected, close to the resonance associated with **QOBCl$_2$** and indicative of a four-coordinate neutral borane.

**Table 1.** NMR data for **QOBCl$_2$·AlCl$_3$**, **$^{Me_2}$QOBCl$^+$**, **QOBPh$^+$** and **Lut:BCl$_2^+$**.

| Compound | $^{11}B$[a] | fwhm[b] | $^{27}Al$[c] | fwhm[b] |
|---|---|---|---|---|
| **QOBCl$_2$·AlCl$_3$** | 11.8[d] | 86 | 102.0 | ca. 600 |
| **$^{Me_2}$QOBCl$^+$** | 29.4 | 182 | 102.9 | 15 |
| **QOBPh$^+$** | 26.0 | 381 | 103.1 | 10 |
| Lut:BCl$_2^+$[e] | 46.9 | 126 | 103.3 | 10 |

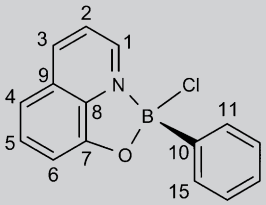
[a] 128.36 MHz. [b] Peak width in Hz. [c] 104.25 MHz. [d] Compare: $^{11}B$ NMR of **QOBCl$_2$** is 10.8 ppm. [e] Lut:$BCl_2$ $AlCl_4^-$, a borenium system exhibiting no close cation—$AlCl_4^-$ contacts in the solid state due to the steric demands of 2,6-lutidine[18]

## X-ray crystallography

The solid state structures of **QOBCl$_2$**, **QOBClPh**, **QOBPh$^+$** and **$^{Me_2}$QOBCl$^+$** are shown in Schemes 3–5. It is convenient to consider these four compounds as two pairs of structures, each related conceptually as a borane before and after chloride abstraction (Table 2). Unfortunately, direct comparison of **$^{Me_2}$QOBCl$_2$** with **$^{Me_2}$QOBCl$^+$** is not possible, as sufficiently high quality crystals of **$^{Me_2}$QOBCl$_2$** were not able to be grown. How-

**Table 2.** Selected bond metrics for **QOBCl$_2$** and **$^{Me_2}$QOBCl$^+$**, **QOBClPh** and **QOBPh$^+$**.




| Metric[a] | QOBCl$_2$ | $^{Me_2}$QOBCl$^+$[b] | QOBPhCl | QOBPh$^+$ |
|---|---|---|---|---|
| C(1)–N | 1.328(3) | 1.373(6) | 1.326(4) | 1.341(2) |
| C(7)–O | 1.363(3) | 1.395(5) | 1.346(4) | 1.387(2) |
| C(10)/Cl–B[c] | 1.849(3)[d] | 1.712(6) | 1.595(5) | 1.533(3) |
| N–B | 1.585(3) | 1.497(6) | 1.608(4) | 1.521(2) |
| O–B | 1.462(3) | 1.373(6) | 1.480(5) | 1.378(2) |
| C(8)-N-B | 106.35(17) | 104.8(4) | 133.6(3) | 136.60(16) |
| C(7)-O-B | 109.53(17) | 107.3(4) | 110.6(3) | 108.91(14) |
| N-B-O | 102.25(18) | 108.5(4) | 100.4(3) | 106.56(16) |
| C(11)-C(10)-B | - | - | 120.0(3) | 125.27(17) |

[a] Atom numbering for all compounds described follows the scheme shown at the top of the table for **QOBClPh**. [b] Bond lengths are given in Ångstroms, and angles in degrees. [c] C(10) for **QOBClPh** and **QOBPh$^+$** else Cl. [d] Mean average of the two B–Cl bonds present in **QOBCl$_2$**.

ever, structural data for the closely related **QOBCl$_2$** was able to be collected and allows for meaningful examination.

### *Comparison of QOBClPh with QOBPh$^+$*

The most significant changes associated with chloride abstraction are unsurprisingly focussed close to the boron centre. The three remaining ligands exhibit reductions in bond lengths to boron of 0.045, 0.074 and 0.086 Å for B–C(10), B–N and B–O, respectively. The strengthening of the boron–oxygen bond in the borenium species is accompanied by corresponding lengthening of the C(7)–O bond, by 0.028 Å. The boron core also dominates changes in bond angles upon chloride abstraction. Most significantly the C(1)-N-B and C(11)-C(10)-B angles increase by 3.0 and 5.3° respectively; this is accompanied by a reduction in the C(15)-C(10)-B angle of 5.2°. The overall effect of these changes is to draw the boron closer into the hydroxyquinoline ligand. This is accompanied by a significant tilting of the phenyl ring away from C(1)–H position to relieve the steric clash, whilst still allowing the whole molecule to remain coplanar. The presence of this tilting suggests some degree of π-conjugation between the phenyl π-system and the formally empty p-orbital on boron in **QOBPh$^+$** that favours the coplanar structure over the sterically favoured orientation in which the phenyl is twisted orthogonal to the QO plane.

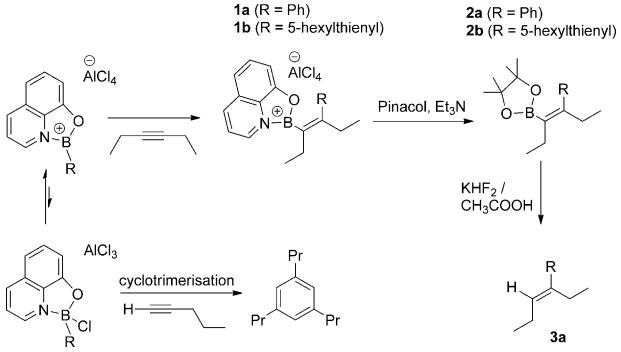
### *Comparison of QOBCl$_2$ with $^{Me_2}$QOBCl$^+$*

The structural changes for **QOBCl$_2$** and **$^{Me_2}$QOBCl$^+$** are broadly similar to those of the phenyl case. The three remaining ligands exhibit reductions in bond lengths to boron of 0.142, 0.088 and 0.089 Å for B–Cl, B–N and B–O, respectively. The shortening of the boron chlorine bond is notable for being more than three times greater than the shortening of the analogous B–C bond in **QOBPh$^+$**; this apparent anomaly is likely due to the differing steric demands of the chloride versus the phenyl ligand. The strengthening of the boron oxygen bond in the **$^{Me_2}$QOBCl$^+$** is again accompanied by corresponding lengthening of the C(7)–O(1) bond, this time by 0.032 Å. The boron core also dominates changes in bond angles upon chloride abstraction. However, the chloride ligand is significantly less sterically demanding than phenyl and these changes in bond angles are associated with the boron centre moving closer to hydroxyquinoline ligand rather than any tilting as observed in the phenyl case.

It is also worthwhile taking note of the packing structures of these compounds and their intermolecular interactions. Both borenium species possess a highly electrophilic boron centre, which can be expected to interact strongly with its nearby environment. In the case of **QOBPh$^+$**, the most significant interaction is that between symmetry related C(10)–B(1) bonds, which pair up in a head-to-tail fashion in the solid state (C(10)···B(1)* distance 3.382(3) Å, compare ΣVdW radii = 3.62 Å). In the case of **$^{Me_2}$QOBCl$^+$** the intermolecular bonding to the borenium involves interaction of the B(1) atom with two symmetry related $AlCl_4^-$ ions, above and below the plane of the cation (B(1)···Cl(3)/Cl(5)* distances of 3.265(6) and 3.288(6) respectively), consistent with a low degree of sterics around the boron centre.[13d]

### Reactivity with alkynes

Initial studies of these *B*-aryl-quinolatoborenium species focused on their reactivity with terminal alkynes. However, such substrates are not compatible with these systems due to the presence of aluminium based Lewis acids in the reaction, which are known to catalyse the rapid cyclotrimerisation of terminal alkynes (Scheme 7).[19] This remained problematic in both dichloromethane (DCM) and 1,2-dichlorobenzene (*o*-DCB) solvents, despite efforts to ensure exact stoichiometry was used in forming the borenium and indeed even when excess of **QOBRCl** precursor or crystallised borenium salts were used. The presence of aluminium Lewis acids is therefore probable and presumably originates from reversible halide transfer between the tetrachloroaluminate and **QOBR$^+$** as a result of the




**Scheme 7.** Competing processes observed for QOBR$^+$ with internal and terminal alkynes. R = phenyl (**1a**) and (5-hexyl)thienyl (**1b**).

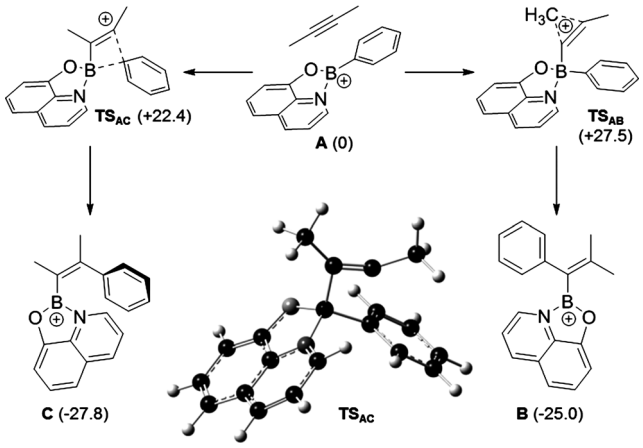
 

lack of steric protection afforded by the quinolato ligand. This is consistent with a range of other catechol and dichloro borenium cations partnered with $[AlCl_4]^-$, but ligated with bulkier amines leading to no trimerisation of terminal alkynes.[11] Attempts to synthesise $QOBR^+$ with weakly coordinating borate anions (e.g., tetra-(3,5-dichlorophenyl)borate) were complicated by anion decomposition, also indicating a lack of steric protection around the electrophilic boron centre.[13] Consequently, the reactivity of **QOBR$^+$** with internal alkynes, which are less susceptible to this cyclotrimerisation, was examined instead. Both **QOBPh$^+$** and **QOBTh$^+$** react with 3-hexyne to give the corresponding *syn*-1,2-carboborated products **1a** and **1b**, with no intermediates or other carboborated products observed at any point during the reaction by $^1$H NMR spectroscopy (Scheme 7). The products can be readily esterified and isolated as the more stable pinacolato esters **2a** and **2b**. The *syn*-1,2-addition was confirmed for **2a** by comparison with spectra recorded from authentic samples.[20] To further confirm assignment, **2a** was also exposed to acetic acid and $KHF_2$ to give protodeborylated **3a**. The $^1$H NMR spectrum of this compound displays a clear triplet at 5.66 ppm ($^3J_{HH} = 7.2$ Hz), corresponding to the vinyl proton coupling with the neighbouring methylene protons. Such a triplet agrees with literature values[20] and is only consistent with a 1,2-phenylborated structure and not the alternative 1,1-carboborated isomers.

Of the two borenium species, it is notable that **QOBTh$^+$** reacts far more rapidly than **QOBPh$^+$**, the former capable of reaction at room temperature, whereas the latter requires heating to 60 °C. The significant difference in reactivity of these two borenium species may be attributed to the more electron-rich (5-hexyl)thienyl group, which will have a higher migratory aptitude than phenyl, therefore is better able to interact with the carbon-centred cation in the vinyl cation intermediate. Thus not only reaction outcome (1,1 versus 1,2-carboboration), but also rate of reaction is controlled by the relative migratory aptitude. Recently, Curran et al., reported that reacting TMS-substituted alkynes with B–H-containing borenium cations resulted in 1,1-hydroboration due to the high migratory aptitude of TMS.[21] However, attempts to observe any 1,1-carboboration using internal alkynes containing the superior (relative to ethyl in 3-hexyne) migrating groups benzyl and trimethylsilyl repeatedly gave complex intractable mixtures on reaction with both **QOBPh$^+$** and **QOBTh$^+$**.

## Computational results

In order to gain a greater insight in to the reactivity of the quinolato(aryl)borenium systems, the reactivity with internal alkynes was examined in silico. Calculations were performed at the M06-2X level of theory using the 6-311(d,p) basis set with DCM solvent simulated using a PCM model. These conditions were chosen based on benchmark calculations performed previously.[16] In order to reduce the computational complexity of these systems, the alkyne examined was simplified from 3-hexyne to the less conformationally flexible 2-butyne. Calculations were also limited to the cationic component, excluding the $AlCl_4^-$ counterion. The results from these studies are summarised in Scheme 8, which depicts the calculated structures and energies of the initial van der Waals complex 2-butyne/$QOBPh^+$ (**A**), the products from 1,1- (**B**) and *syn*-1,2-phenylboration (**C**). Transition state geometries (**TS$_{AX}$**) were located for both reactions. These were confirmed by frequency analysis, both exhibiting a single imaginary frequency dominated by bond deformations associated with group migration. Two minima of similar energy were found for the structure of the product of 1,2-carboboration. These two isomers differ in terms of the orientation of the QO ring, the structure with the pyridyl ring eclipsed with phenyl being the more stable by 3.3 kcal mol$^{-1}$.




**Scheme 8.** Calculated relative energies (kcal mol$^{-1}$) of starting materials (**A**), transition states (**TS**) and products (**B** and **C**) of the reaction of **QOBPh$^+$** with 2-butyne. The structure of the key transition state en route to the *syn*-1,2-phenylborated product, **TS$_{AC}$**, is also shown.

Both the 1,1- (**A**→**B**) and 1,2-carboboration (**A**→**C**) reactions are predicted to be exothermic, with the 1,2-carboborated products being marginally more stable (−24.5 and −27.8 kcal mol$^{-1}$, respectively, relative to the van der Waals complex). The transition states for the two reactions involve migration of a methyl or phenyl (**TS$_{AB}$** = +27.5 and **TS$_{AC}$** = +22.4 kcal mol$^{-1}$). It is most notable that there is a significant difference in the energies of these two transition states, with the **TS$_{AC}$** being 5.1 kcal mol$^{-1}$ lower in energy. This is again consistent with the observation that only the *syn*-1,2-phenylborated product is formed from this reaction. The greater migratory aptitude of Ph relative to Me, must contribute significantly to the 5.1 kcal mol$^{-1}$ calculated difference in transition state energies and thus the overall 1,2-carboboration reaction outcome observed experimentally.

To probe the effect of migratory aptitude further the calculated transition state energies for the carboboration of 2-butyne with the hypothetical borenium cation $QOBMe^+$ was examined. The transition state for 1,2-carboboration involves methyl migration from boron to carbon and is significantly higher at 29.6 kcal mol$^{-1}$ (relative to the van der Waals complex of $QOBMe^+$/2-butyne). Furthermore, the transition state of 1,1-carboboration for $QOBMe^+$/2-butyne is now lower in energy at 28.4 kcal mol$^{-1}$. The inversion of relative transition state energies for 1,1- versus 1,2-carboboration and the 7.2 kcal mol$^{-1}$

higher barrier for 1,2-carboboration of 2-butyne with $QOBMe^+$ relative to $QOBPh^+$ is consistent with relative migratory aptitude dominating barriers to migration and thus the overall reaction outcome in alkyne carboborations.

## Conclusion

New quinolatoborenium salts have been prepared by reaction of quinolatoboronchlorides with $AlCl_3$. This reaction with $AlCl_3$ is complicated by the presence of two Lewis basic sites on the borenium precursor capable of binding to $AlCl_3$ (the chloride and aryloxy groups). The success of this halide abstraction in forming the desired borenium is strongly affected by sterics and π-donor capacity of the groups remaining on boron. Once formed the arylquinolatoborenium systems react with a terminal alkyne to give the product derived from cyclotrimerisation. In contrast they react with 3-hexyne to give products derived from *syn*-1,2-carboboration rather than the more widespread 1,1-carboboration. The rate of 1,2-carboboration is found by experiment (thienyl > phenyl) and calculations (phenyl > methyl) to be strongly dependant on the migratory aptitude of the hydrocarbyl group. The observation of 1,2-carboboration as the only mode of carboboration is in contrast to the 1,1-carboboration observed to date with $RB(C_6F_5)_2$ and $BEt_3$. This disparity can be attributed to the relatively greater migratory aptitude of phenyl and thienyl versus $C_6F_5$ or 1° alkyl and indicates that more 1,2-carboborations will be accessible provided sufficiently electrophilic arylboranes can be accessed.

## Experimental Section

**General synthesis of R-QOBXCl (R = 5,7-dimethyl, H; X = Cl, Ph, $^{HEX}$Th) exemplified by that of $QOBCl_2$: $QOSiMe_3$** (200 mg, 0.92 mmol, 1 equiv) was added dropwise to a stirred solution of $BCl_3$ (1 M in DCM, 0.92 mL, 0.92 mmol, 1 equiv) in DCM (1 mL) at room temperature (slight exotherm), this immediately afforded a yellow solution, Stirring was continued for 1 h to ensure complete reaction, the volatiles were then removed under vacuum and the resulting yellow solid washed with pentane to yield the desired product. This could be recrystallised from a solution of the sample in DCM layered with pentane. Yield: 200 mg, 97%; $^1$H NMR ($[D_2]$-DCM): $\delta = 8.88$ (br d, $J = 5.2$ Hz, 1H), 8.71 (dd, $J_{HH} = 8.3$, 0.8 Hz, 1H), 7.92 (dd, $J_{HH} = 8.2$, 5.2 Hz (coupling to broad resonance at 8.88, 1H), 7.76 (dd, $J_{HH} = 8.6$, 7.6 Hz, 1H), 7.53 (d, $J_{HH} = 8.6$ Hz, 1H), 7.27 ppm (d, $J_{HH} = 7.6$ Hz, 1H); $^{11}B\{^1H\}$ NMR ($[D_2]$-DCM): $\delta = 10.8$ ppm; $^{13}C\{^1H\}$ NMR ($[D_2]$-DCM): $\delta = 153.88$, 142.58, 141.06, 133.32, 128.24, 124.53, 116.22, 112.04 ppm (C-9 peak not observed); elemental analysis calcd (%) for $C_9H_6BCl_2NO$: C 47.86, H 2.68, N 6.20; found C 47.86, H 2.70, N 6.16.

**General reaction of R-QOBXCl (R = 5,7-dimethyl, H; X = Cl, Ph, $^{HEX}$Th) with $AlCl_3$ exemplified by that resulting in $^{Me_2}QOBCl^+$ $AlCl_4^-$: $^{Me_2}QOBCl_2$** (51 mg, 0.2 mmol) and $AlCl_3$ (27 mmg, 0.2 mmol) were added to a J. Young's ampoule and dissolved in dichloromethane (1 mL), the mixture was stirred for 15 min to ensure complete reaction of the sparingly soluble $AlCl_3$. The volatiles were then removed under vacuum and the residual solid washed with pentane (3 × 2 mL) to yield the desired crude product. This could be purified by crystallisation from a solution of the sample in DCM layered with pentane. Isolated crystallised yield: 30.5 mg, 39%; $^1$H NMR ($CH_2Cl_2/[D_6]$-DMSO capillary): $\delta = 9.37$ (d, $J_{HH} = 8.1$ Hz, 1H), 9.26 (d, $J_{HH} = 5.6$ Hz, 1H), 8.33 (dd, $J_{HH} = 8.0$, 5.8 Hz 1H), 7.66 (s, 1H), 2.85 (s, 3H), 2.72 ppm (s, 3H); $^{11}B\{^1H\}$ NMR ($CH_2Cl_2/[D_6]$-DMSO capillary): $\delta = 29.5$ ppm; $^{13}C\{^1H\}$ NMR ($CH_2Cl_2/[D_6]$-DMSO capillary): $\delta = 149.25$, 144.04, 143.35, 135.54, 135.26, 134.65, 134.22, 126.38, 124.59, 17.31, 15.96 ppm; $^{27}$Al NMR ($CH_2Cl_2/[D_6]$-DMSO): $\delta = 102.7$; MS: *m/z*: 246.1 $[M+H]^+$.

**General reaction of $QOBR^+$ $AlCl_4^-$ (R = Ph, $^{HEX}$Th) with 3-hexyne exemplified by that of $QOBTh^+$ $AlCl_4^-$: QOBThCl** (150 mg, 0.42 mmol) and $AlCl_3$ (53 mg, 0.4 mmol, 0.95 equiv) were added to a J. Young's ampoule and dissolved in DCM. This mixture was stirred at room temperature for 15 min to ensure complete reaction of the sparingly soluble $AlCl_3$. 3-Hexyne (47 μL, 0.42 mmol) was then added to the solution and the reaction stirred at room temperature for 3 days. The resulting red/brown suspension was cooled to 0 °C and layered with triethylamine (450 μL, 3.36 mmol, > 8 equiv), through which was added pinacol (100 mg, 0.84 mmol, 2 equiv). This mixture was then stirred vigorously for 5 min at 0 °C (slight exotherm) and then allowed to warm to room temperature. The volatiles were removed under vacuum and the resulting solid extracted with pentane and filtered through a short plug of cotton wool. The volatiles were evaporated under vacuum to yield an oily residue from which the desired product, **2b**, could be isolated by silica column chromatography (base treated silica, eluent pentane:DCM 95:5).

**2b (Bpin(Et) = (Et)Th)**: Isolated yield: 39 mg, 28%; $^1$H NMR ($CDCl_3$ 400 MHz): $\delta = 6.69$ (d, $J_{HH} = 3.3$ Hz, 1H; Th), 6.56 (d, $J_{HH} = 3.3$ Hz, 1H; Th), 2.75 (t, $J_{HH} = 7.4$ Hz, 2H; $CH_2$-Th), 2.40 (q, $J_{HH} = 7.3$ Hz, 2H), 2.26 (q, $J_{HH} = 7.6$ Hz, 2H), 1.62 (quin, $J_{HH} = 7.4$ Hz, 2H), 1.4–1.2 (m, 6H), 1.17 (s, 12H), 1.05 (t, $J_{HH} = 7.6$ Hz, 3H), 0.97 (d, $J_{HH} = 7.3$ Hz, 3H), 0.89 ppm (t, $J_{HH} = 6.8$ Hz, 3H); $^{11}B\{^1H\}$ NMR ($CDCl_3$ 400 MHz): $\delta = 31.4$ ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$ 400 MHz): $\delta = 144.93$, 144.69, 144.10, (vinyl-B peak not observed due to quadrupolar broadening), 125.30, 123.16, 83.09, 31.72, 31.58, 30.19, 28.68, 27.18, 24.67, 24.42, 22.58, 14.34, 14.07, 13.35 ppm; MS: *m/z*: 399.3 $[M+Na]^+$, 377.4 $[M+H]^+$, 251.1 $[M-Bpin+2H]^+$; HRMS calcd for $C_{22}H_{38}BO_2S$: 377.2686; found: 377.2680.

CCDC 1002906 (**$^{Me_2}$QOBCl[$AlCl_4$]**) and 1002907 (**$QOBCl_2$**), CCDC 1002908 (**$QOBCl_2 \cdot AlCl_3$**), 1002909 (**QOBPh[$AlCl_4$]**) and 1002910 (**QOBClPh**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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