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Borylative cyclisation of diynes using BCl₃ and borocations†

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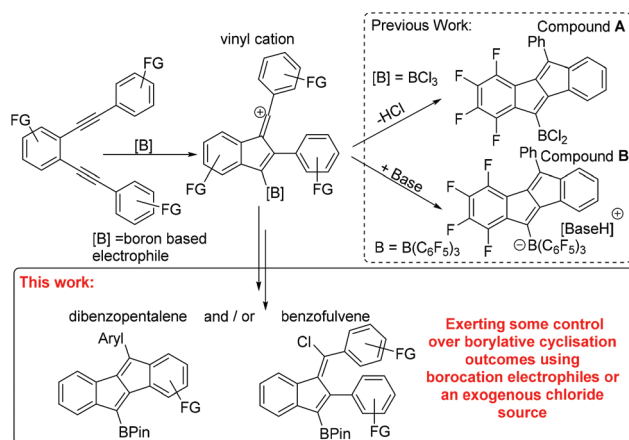
The borylative cyclisation of 1,2-dialkynyl benzenes with BCl₃ leads to dibenzopentalenes (via intramolecular S_EAr) or benzofulvenes (via chloride addition) depending on substituents, with stabilised vinyl cation intermediates (e.g. with a *p*-MeO-C₆H₄-group) favouring the latter. The use of borocations leads to more selective dibenzopentalene formation, while other diyne frameworks undergo intramolecular S_EAr selectively even with *p*-MeO groups.

The activation of a π nucleophile by a boron electrophile to induce cyclisation while forming C–Y (Y = C, N, S or O *etc.*) and C–B bonds concomitantly is an attractive method to make complex organoboranes. Termed borylative cyclisation, the catalyst-free version of this reaction^{1,2} requires sufficiently electrophilic boranes to proceed with pioneering work performed using B(C₆F₅)₃.³ While notable, borylative cyclisation with B(C₆F₅)₃ generally leads to [RB(C₆F₅)₃][–] containing products (though a carboboration step also occurs in some cases generating RB(C₆F₅)₂ containing cyclised products).⁴ The utility of the [RB(C₆F₅)₃][–] moiety is much less developed relative to RB(OR)₂ (for which there are a myriad of established functional group transformations)⁵ or RB(Aryl)₂ (e.g. as an acceptor for generating low LUMO energy conjugated materials).⁶ Therefore the use of alternative boron electrophiles for borylative cyclisation that form, or can be transformed readily into, RB(OR)₂ or RB(Aryl)₂ has become an area of significant activity. While we and others have utilised BCl₃,⁷ Blum and co-workers have exploited B-chloro-catecholborane (CatBCl) in borylative cyclisations,⁸ and a range of borylated systems now have been synthesised *via* borylative cyclisation methodologies.

In previous work of particular relevance to this study, Erker, Yamaguchi and co-workers used B(C₆F₅)₃, and in one example BCl₃, for the cyclisation of 1,2-dialkynyl benzenes to form dibenzopentalenes **A** and **B** (Scheme 1 inset top right).⁹ Due to our ongoing interest in low band gap boron containing polycyclic aromatic hydrocarbons,¹⁰ we were interested in extending BCl₃ induced cyclization to related diynes substituted with donor (e.g. –OMe) groups. During this study certain diynes were found to form alternative borylative cyclisation products, specifically chlorinated benzofulvenes (Scheme 1, bottom). Herein we present our results into the borylative cyclisation of a range of diynes along with the development of methods to control, to some extent, the product distribution principally by varying the electrophile from BCl₃ to a borocation.

Results and discussion

The borylative cyclisation of diyne **1a**, containing two *para*-methoxy groups (Fig. 1), was explored using BCl₃ in dichloro-



Scheme 1 Previous work on borylative cyclisation and bottom inset this work.

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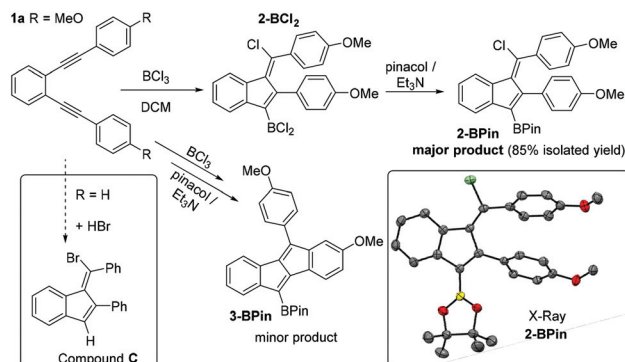


Fig. 1 The functionalisation of **1a** using BCl_3 and subsequent pinacol protection. Inset right, solid state structure of **2-BPin**, ellipsoids at the 50% probability level and hydrogens omitted for clarity. Inset left, previous work cyclising with HBr .

methane (DCM). While C–B bond formation occurred (as indicated by a $\delta_{11\text{B}} = 54$ ppm consistent with an RBCl_2 moiety) the major product was not the expected dibenzopentalene analogue of compound **A**. Addition of pinacol and Et_3N followed by isolation of the pinacol boronate ester derivative enabled identification of the major product as the benzofulvene, **2-BPin**, by single crystal X-ray diffraction (Fig. 1). This formulation was supported by mass and multinuclear NMR spectroscopy with **2-BPin** isolated in 85% yield as a single isomer. The solid state structure of **2-BPin** is unremarkable with both Ph groups and the Bpin moiety twisted out of the plane of the benzofulvene core to varying degrees to minimise steric interactions. Formation of related halogenated benzofulvenes, e.g. **C** (inset left Fig. 1), has been previously reported from the addition of HBr to *ortho*-bis(phenylethynyl)benzene, with alkyne protonation initiating the 5-*endo*-dig cyclisation.¹¹ In contrast to the use of HBr (or I_2),¹² using BCl_3 as the electrophile incorporates a nucleophilic C–B site in addition to an electrophilic C–X. The formation of **2-BCl₂** presumably arises from a zwitterionic vinyl cation intermediate (Scheme 1, top middle) being trapped by chloride instead of undergoing intramolecular $\text{S}_{\text{E}}\text{Ar}$. Analysis of the NMR spectra of **2-BCl₂** preparations prior to pinacol protection and for **2-BPin** prior to purification revealed a second minor cyclisation product assigned as the dibenzopentalenes **3-BCl₂** and **3-BPin** (the latter supported by GC-MS), respectively. The ratio of **2-BPin** : **3-BPin** in these mixtures from NMR spectroscopy and GC-MS is 17 : 1.

The borylative cyclisation of diyne **1b** using BCl_3 to form compound **A** has been previously reported.⁹ This transformation was explored again herein to determine if a borylated benzofulvene analogous to **2-BCl₂** was present at a low percentage using identical conditions to that for the formation of **2-BCl₂**. However, only compound **A** (and **4** post pinacol protection) was observed by multinuclear NMR spectroscopy under these conditions. Compound **4** was isolated in 92% yield and its formulation further confirmed by single crystal X-ray diffraction studies (Fig. 2, inset). The solid state metrics of **4** are

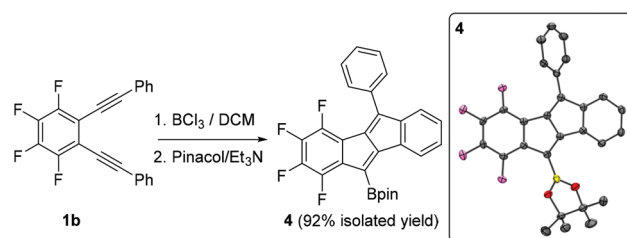


Fig. 2 Borylative cyclisation of **1b**. Inset right, the solid state structure of **4**, ellipsoids at 50% probability level and hydrogens omitted for clarity.

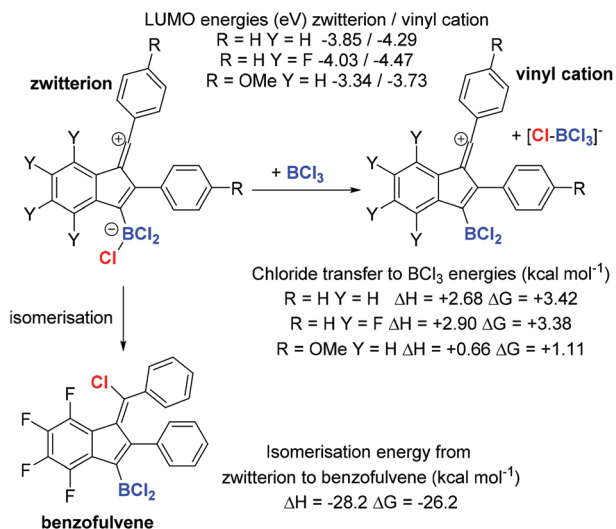
unremarkable with core C–C distances comparable to that reported for compound **B** (Scheme 1).

No intermediates were observed in the borylative cyclisation reactions starting from **1a** or **1b** and leaving **2-BCl₂** in the presence of excess BCl_3 for longer reaction times did not lead to any increase in the dibenzopentalene (disfavouring chloride abstraction from vinylC-Cl in **2-BCl₂** by BCl_3 generating the vinyl cation that subsequently undergoes $\text{S}_{\text{E}}\text{Ar}$). It should also be noted that the chloride present in the benzofulvene product is derived from BCl_3 as closely comparable outcomes were observed on replacing DCM with *o*-dichlorobenzene (*o*-DCB, which is a solvent more resistant to C–Cl heterolysis).

The disparate outcomes observed commencing from diynes **1a** and **1b** are clearly due to the substituent electronic effects. This is attributed predominantly to the ability of the *para* MeO group to stabilise vinyl cation intermediates (the methoxy group will also have a small deactivating effect for $\text{S}_{\text{E}}\text{Ar}$ due to the σ^+_{meta} value of +0.05). The reduced electrophilicity of the vinyl cation derived from **1a** will increase its lifetime in solution thereby enabling a reaction with a chloride source to proceed. In contrast, the vinyl cation derived from **1b** will be more electrophilic than that derived from **1a**, thus the $\text{S}_{\text{E}}\text{Ar}$ reaction will be more rapid (as found previously with related carbocations),¹³ outcompeting the chloride transfer reaction. DFT calculations at the M06-2X/6-311G(d,p) level with a polarisable continuum model (PCM) of DCM, revealed that the LUMO energies for the vinyl cations (which are dominated by $p\pi$ orbitals on the *sp* vinyl cation carbon and the adjacent aromatic ring in each case – see ESI†) vary significantly (Scheme 2). These energies will correlate with electrophilicity and the rates of reaction with π nucleophiles.¹³

Another factor that was considered in effecting the product outcome was the identity (and nucleophilicity) of the chloride donor that forms the benzofulvene. Isodesmic calculations revealed that in each case the vinyl cation (Scheme 2 top right), is more Lewis acidic towards chloride than BCl_3 , thus the zwitterionic vinyl cation (Scheme 2 top left) will be favoured in solution over $[\text{vinyl-cation}][\text{BCl}_4]$. Though it is notable that the vinyl cation derived from **1a** and BCl_3 have similar Lewis acidity towards chloride ($\Delta G = 1.11 \text{ kcal mol}^{-1}$) thus both $[\text{vinyl cation}][\text{BCl}_4]$ and the zwitterion should be present in solution as intermediates during this reaction. Furthermore, the chloride ion affinity (CIA) of the vinyl cation





Scheme 2 Calculations of the energy change in chloride transfer reactions (all at the M06-2x/6-311G(d,p)/PCM (DCM) level). In the vinyl cation the anion and cation were calculated at infinite distance.

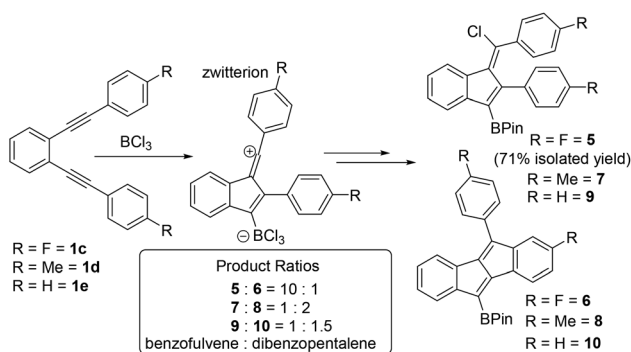
derived from **1a** is the lowest (of the three calculated), thus this zwitterion will be the better chloride donor and also have the highest concentration of $[BCl_4]^-$ in solution (due to the lowest ΔG). This factor coupled with the relative LUMO energies presumably explains why the benzofulvene is formed from **1a** but not **1b**. Finally, the formation of the benzofulvene from the zwitterion was found to be highly exergonic. This is consistent with the formation of the benzofulvene being irreversible under these conditions even in the presence of BCl_3 (hence there is no change in the benzofulvene/dibenzopentalene ratio from **1a** in the presence of excess BCl_3 over longer reaction times).

To probe substituent effects further and guided by these calculations three other diynes, **1c–1e** (Scheme 3), were synthesised and investigated. These were chosen to either stabilise vinyl cations to some extent or to be less Lewis acidic at boron relative to vinyl cations derived from **1b**. Compounds **1c** and **1d** have *para* F and Me substituents, respectively, while **1e** is the unsubstituted congener that was previously calculated and

shown to form benzofulvene **C** on reaction with HBr (Fig. 1). Notably, F and Me have distinct σ^+ values (Me $\sigma_{para}^+ = -0.31$ $\sigma_{meta}^+ = -0.10$, F $\sigma_{para}^+ = -0.07$ $\sigma_{meta}^+ = +0.35$), with both groups able to stabilise the vinyl cation to some extent (albeit less than MeO, $\sigma_{para}^+ = -0.78$), but Me is activating while F is deactivating, with respect to S_EAr in the *meta* position. In each case the diyne was combined with BCl_3 in DCM and after all starting diyne was consumed (by *in situ* NMR spectroscopy) the products were converted to the pinacol boronate esters which were analysed as crude mixtures to determine the ratio of dibenzopentalene:benzofulvene by NMR spectroscopy and GC-MS. This revealed that for fluoro substituted **1c** the benzofulvene **5** was the major product (*ca.* 90%). However, for **1d** and **1e** the dibenzopentalene products were the major products but were only formed in a slightly larger amount than the benzofulvene products. Combined these results indicate that deactivating the aromatic system towards S_EAr (e.g. using a *meta* fluorine relative to the site of S_EAr) is also an effective way to achieve preferential benzofulvene formation, more effective than vinyl cation stabilisation using a *p*-Me- C_6H_4 group in this case.

In previous work the frustrated Lewis pair (FLP) combination of $B(C_6F_5)_3/P(o\text{-tolyl})_3$ transformed **1e** selectively (97% isolated yield) to the dibenzopentalene analogue of compound **B**.⁹ The effect of using the FLP combination of $BCl_3/2,4,6\text{-tritylpyridine}$ (TBP) on product distribution was investigated as in weakly basic media the deprotonation of an arenium cation (a key step in dibenzopentalene formation) can become the rate determining step in S_EAr .¹⁴ Therefore the inclusion of TBP as a Brønsted base was hoped to favour dibenzopentalene formation. However, using BCl_3/TBP combinations led to comparable ratios of benzofulvene:dibenzopentalene starting from **1d** and **1e** as just using BCl_3 (>two equivalents of BCl_3 were used in these reactions as the by-product formed from S_EAr is $[TBPH][BCl_4]$, thus use of only one equiv. BCl_3 leads to incomplete consumption of the starting diyne).

With diynes **1d** and **1e** giving mixtures containing significant amounts of benzofulvene and dibenzopentalene products (which proved inseparable in our hands partly due to column chromatography leading to formation of protodeborylated products) alternative borylative cyclisation conditions were sought that would strongly favour formation of only one cyclised product. Considering a mechanism involving a vinyl cation intermediate two options were considered: (i) using boron electrophiles that form poorer chloride (or other anion) donors during the cyclisation process to favour dibenzopentalene formation. (ii) Increasing the concentration of chloride donor to favour benzofulvene formation, e.g. by adding $[BCl_4]^-$ salts. Borocations of the general formula $[Y_2B(amine)]^+$ were selected for the first approach. Initial attempts focused on using borocations containing catechol (Cat) substituents, with the chelating diol disfavouring anion transfer reactions. However, $[CatB(2\text{-DMAP})][AlCl_4]$ (2-DMAP = 2-(*N,N*-dimethylamino)-pyridine) led to no reaction with **1d** at room temperature or at 60 °C for 24 h. Other more electrophilic catechol based borocations,¹⁵



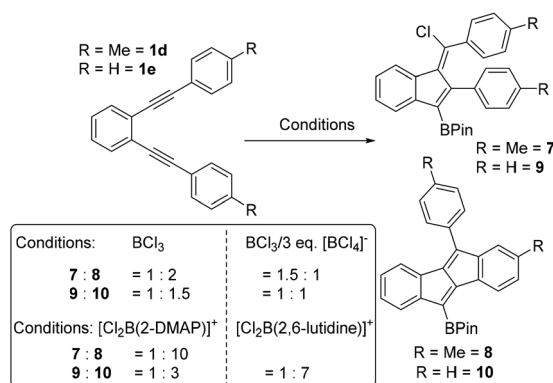
Scheme 3 Product ratios from the borylative cyclisation of **1c–1e**.



e.g. $[\text{CatB}(\text{NEt}_3)][\text{AlCl}_4]$, led to very slow reactions at room temperature, with heating furnishing multiple intractable products in our hands.

From previous work, dihalo-borocations are more electrophilic than catechol derivatives thus the boronium salt $[(2\text{-DMAP})\text{BCl}_2][\text{AlCl}_4]$,^{7b} and the borenium salt $[\text{Cl}_2\text{B}(2,6\text{-lutidine})][\text{AlCl}_4]$ ¹⁶ were investigated. In comparison to $[\text{BCl}_4]^-$ and $[\text{RBCl}_3]^-$ these borocations will form weaker chloride donors during cyclisation, as loss of chloride, *e.g.* from compounds with the general structure **D** (Fig. 3, right), would lead to dications, which will have a high chloride ion affinity (this is supported by the chloride ion affinity of the dication derived from **D** by loss of chloride (and where the amine is pyridine) being 23.8 kcal mol⁻¹ greater than that of BCl_3). Furthermore, the vinyl cation **D** (where the amine is pyridine) will also be more electrophilic than the comparable zwitterion (calculations support this with a LUMO energy of -4.13 eV significantly lower in energy than that for the comparable zwitterion, -3.85 eV). Finally, AlCl_3 is also a strong Lewis acid towards chloride, notably stronger than BCl_3 (by 25 kcal mol⁻¹),¹⁷ so $[\text{AlCl}_4]^-$ will also be a poor chloride donor.

Using the boronium salt $[\text{Cl}_2\text{B}(2\text{-DMAP})][\text{AlCl}_4]$ in the cyclisation of **1d** led to more selective formation of dibenzopentalene **8**, with a 1:10 ratio of **7**:**8** observed (by NMR spectroscopy and GC-MS). In contrast, the use of $[\text{Cl}_2\text{B}(2\text{-DMAP})][\text{AlCl}_4]$ in the cyclisation of **1e** led to a smaller change in the ratio of benzofulvene to dibenzopentalene (Scheme 4, inset for ratios). Therefore the borenium salt $[\text{Cl}_2\text{B}(2,6\text{-lutidine})][\text{AlCl}_4]$ was utilised as this will form an even poorer chloride donor (as 2,6-lutidine is a poorer nucleophile than 2-DMAP). Indeed using $[\text{Cl}_2\text{B}(2,6\text{-lutidine})][\text{AlCl}_4]$ the selectivity for the dibenzopentalene product **10** increased, with the ratio of **9**:**10** now 1:7. Thus it is possible to exert significant control over the product distribution in borylative cyclisation using borocations to increase the amount of dibenzopentalene products from **1d** and **1e**. However, attempts to use either of the $[\text{Cl}_2\text{B}(\text{amine})]^+$ borocations to initiate cyclisation of **1a** led to complex mixtures containing minimal dibenzopentalene, in part due to competitive ether cleavage, consistent with the reduced functional group tolerance of borocations relative to BCl_3 .^{7b,15}



Scheme 4 Change in product ratio on altering the boron electrophile or by the addition of an exogenous chloride source.

Attempts to increase the amount of benzofulvene product formed by addition of an exogenous chloride donor were partially successful. For example, while the borylative cyclisation of **1d** using BCl_3 in the presence of three equivalents of $[\text{NBu}_4][\text{BCl}_4]$ did lead to a change in the product ratio, the chlorinated benzofulvene **7**:dibenzopentalene **8** ratio was only 3:2. With diyne **1e** a small change also was observed with the ratio of **9**:**10** using BCl_3 /three equiv. of $[\text{NBu}_4][\text{BCl}_4]$ being 1:1. Compound **5** was formed more selectively (with no **6** observed by NMR spectroscopy) when cyclisation using BCl_3 was repeated in the presence of 3 equiv. $[\text{NBu}_4][\text{BCl}_4]$. However, attempts to form the benzofulvene derived from **1b** were unsuccessful using BCl_3 /3 equiv. $[\text{NBu}_4][\text{BCl}_4]$ with the dibenzopentalene product still formed in excellent conversion, presumably due to the intermediacy of a highly electrophilic vinyl cation that leads to rapid intramolecular $\text{S}_{\text{E}}\text{Ar}$. Thus increasing the chloride donor concentration using $[\text{BCl}_4]^-$ has only a modest effect on selectivity. The use of “better” halide donors (*i.e.* free halide as in previously reported systems using HBr or I_2)^{11,12} is not possible in this system as these would react with BCl_3 (to form $[\text{X-BCl}_3]^-$, X = halide). Furthermore, the use of weaker Lewis acids *e.g.* PhBCl_2 led to complex mixtures and significant amounts of unreacted diyne **1d** after 18 h. Therefore the ability to access other benzofulvenes is limited *via* this methodology to requiring substituents that strongly stabilise the vinyl cation or significantly disfavour $\text{S}_{\text{E}}\text{Ar}$.

With an understanding of substituent effects in hand for aryl substituted diynes, the heteroaromatic bis-thienyl derivative **1f**, was investigated next (Scheme 5). The 3-thienyl derivative was selected to preclude any $\text{S} \rightarrow \text{BCl}_3$ interactions directing reactivity and altering the reaction outcome.⁹ **1f** contains an electron rich thiophene heteroaromatic able to stabilise a vinyl cation to a greater extent (relative to benzene), however, the higher nucleophilicity of thiophene and its lower aromaticity (relative to benzene) will favour the $\text{S}_{\text{E}}\text{Ar}$ reaction. Indeed on addition of BCl_3 to **1f** the $\text{S}_{\text{E}}\text{Ar}$ product, **11**, was the major product with no benzofulvene product observed by NMR spectroscopy. Using other conditions discussed above

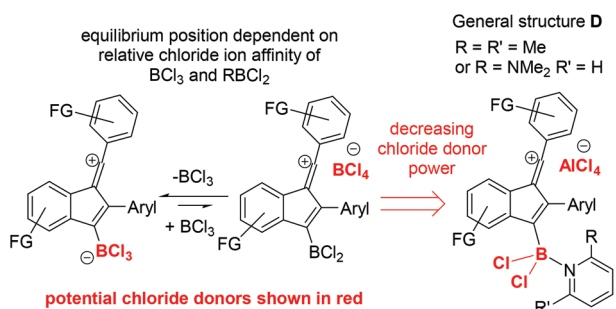
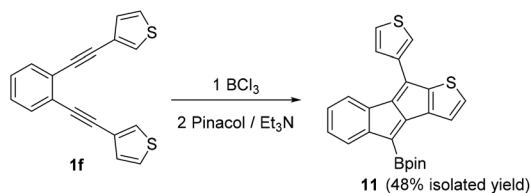


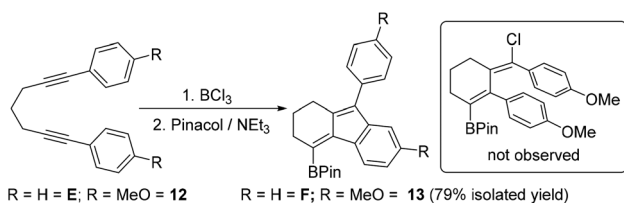
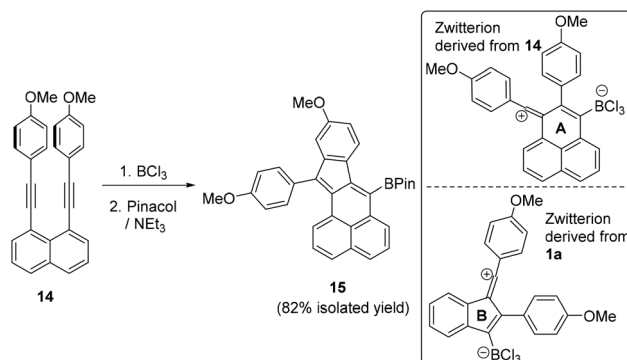
Fig. 3 Potential sources of chloride during the borylative cyclisation of diynes **1x** using different boron electrophiles.

Scheme 5 Borylative cyclisation of diyne **1f**.

led to no observation of a benzofulvene product by NMR spectroscopy and GC-MS.

Finally, other diynes were explored to determine if *p*-MeO-phenyl substituents would again lead to a chloro incorporated product (e.g. inset Scheme 6) by stabilising a vinyl cation intermediate during borylative cyclisation. Compound **E** had been previously shown to undergo cyclisation with BCl_3 readily and was isolated as compound **F** post protection.^{7b} Thus the *p*-MeO analogue, **12** was synthesised, however, this underwent cyclisation to give the product from intramolecular $\text{S}_{\text{E}}\text{Ar}$ exclusively, with **13** isolated in 79% yield. No difference in product distribution was observed on performing the cyclisation with BCl_3 in the presence of 3 equiv. of $[\text{NBu}_4][\text{BCl}_4]$.

Hypothesising that the absence of any vinyl chloride product derived from **12** maybe due to the flexibility in the partially saturated **12** leading to a low barrier for the intramolecular $\text{S}_{\text{E}}\text{Ar}$ step we investigated another fully Csp^2 based diyne substituted with *p*-MeO- C_6H_4 groups, **14**. However, addition of BCl_3 to this diyne also led exclusively to the $\text{S}_{\text{E}}\text{Ar}$ product, with no chloro-vinyl product observed, even when the reaction with BCl_3 was performed in the presence of 3 equiv. of $[\text{NBu}_4][\text{BCl}_4]$. Compound **15** can be isolated post pinacol protection in 82% yield and is analogous to the cyclisation product derived from **14** using I_2 as the electrophile.¹⁸ Again the BCl_3 route is complementary to I_2 induced cyclisation as the former installs a C-BPin nucleophilic moiety instead of an electrophilic C-I unit. We attribute the absence of any chlorine incorporated product in the borylative cyclisation of **14** with BCl_3 to a lower barrier to $\text{S}_{\text{E}}\text{Ar}$ due to the vinyl cation intermediate containing a six membered ring (ring A, inset Fig. 4) in contrast to a five membered ring in the vinyl cation derived from **1a** (ring B). The latter may result in a higher barrier for the intramolecular $\text{S}_{\text{E}}\text{Ar}$ step due to a less favourable geometry derived from the relative bond angles around rings A and B.

Scheme 6 Borylative cyclisation of **E** (previous work) and **12** (this work).Fig. 4 Borylative cyclisation of **14**. Inset right, the zwitterionic vinyl cations derived from **1a** and **14** on combination with BCl_3 .

Conclusions

In conclusion the product outcome from the borylative cyclisation of 1,2-dialkynylbenzenes with BCl_3 is highly dependent on substituents, with more strongly electrophilic vinyl cation intermediates favouring dibenzopentalene formation. In contrast, vinyl cations that are stabilised by donor groups (e.g. *p*-MeO- C_6H_4), or contain groups deactivating towards $\text{S}_{\text{E}}\text{Ar}$ lead to benzofulvene products. The product distribution can be controlled to some extent by variation in the boron electrophile and by addition of an exogenous chloride donor ($[\text{BCl}_4]^-$) that does not shut down borylative cyclisation by reaction with the electrophile. However, the reaction outcome divergence could not be extended to two other diynes substituted with *p*-MeO- C_6H_4 groups presumably due to lower barriers to the $\text{S}_{\text{E}}\text{Ar}$ reaction in these systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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