Boron-mediated sequential alkyne insertion and C–C coupling reactions affording extended π-conjugated molecules

Yoshiaki Shoji[1], Naoki Tanaka[1], Sho Muranaka[1], Naoki Shigeno[1], Haruka Sugiyama[1], Kumiko Takenouchi[1], Fatin Hajjaj[1] & Takanori Fukushima[1]

C–C bond coupling reactions illustrate the wealth of organic transformations, which are usually mediated by organotransition metal complexes. Here, we show that a borafluorene with a B–Cl moiety can mediate sequential alkyne insertion (1,2-carboboration) and deborylation/Csp^2–Csp^2 coupling reactions, leading to aromatic molecules. The first step, which affords a borepin derivative, proceeds very efficiently between the borafluorene and various alkynes by simply mixing these two components. The second step is triggered by a one-electron oxidation of the borepin derivative, which results in the formation of a phenanthrene framework. When an excess amount of oxidant is used in the second step, the phenanthrene derivatives can be further transformed *in situ* to afford dibenzo[*g,p*]chrysene derivatives. The results presented herein will substantially expand the understanding of main group chemistry and provide a powerful synthetic tool for the construction of a wide variety of extended π-conjugated systems.

[1] Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. Correspondence and requests for materials should be addressed to T.F. (email: fukushima@res.titech.ac.jp).

Recently, several studies have demonstrated that main group compounds can exhibit remarkable reactivity, which is typical of transition metals[1]. Pioneering works include the multiple complexation of CO with boron[2], the reversible addition of ethylene to a distannyne[3], and the activation of H_2 with a carbene[4] and frustrated Lewis pairs[5,6] (Fig. 1a), all of which are characterized by the activation of small inert molecules with reactive main group centres. Meanwhile, in the context of organic transformations, many organotransition metal compounds allow the insertion of unsaturated compounds into their metal–carbon bonds, and some of the resulting complexes subsequently undergo elimination of the metal moiety to mediate cross-coupling reactions[7,8] (Fig. 1b). This sequence of reactions still sets the chemistry of transition metals apart from that of main group elements. Here, we show that a three-coordinate borane with a B–Cl moiety, embedded in a π-conjugated five-membered ring, undergoes a sequential reaction that involves an alkyne insertion (1,2-carboboration) and a subsequent oxidative deborylation/Csp^2–Csp^2 coupling (Fig. 1c), which enables the conversion of alkynes into the corresponding benzannulated and cyclodehydrogenated products with extended π-conjugated frameworks.

Boron with strong Lewis acidity and low electronegativity is known to mediate C–C coupling reactions. Examples include 1,1- and 1,2-carboborations[9–18], electrocyclizations[19] and carbonylations[20] of three-coordinate boranes, as well as the oxidative 1,2-migration of carbon substituents and the subsequent deborylation of four-coordinate borate anions[12,21,22] (Supplementary Fig. 1). However, it has never been expected that one-electron oxidations of three-coordinate boranes result in C–C coupling reactions (Fig. 1c). Such reactions may seem unlikely, as they would require the elimination of the boron moiety from the radical cation state of the parent boranes under concomitant generation of a low-valent cationic boron species, which usually represents a very high-energy state[23–25]. In fact, the boron-mediated Csp^2–Csp^2 coupling reaction reported herein (Figs 1c and 2a) was observed serendipitously during our attempts to synthesize boron-substituted acetylenes through the metathesis reaction of 9-chloro-9-borafluorene (1) and bis(trimethylsilyl)acetylene (Fig. 2b). In contrast to our initial expectations, this reaction yielded boron-containing seven-membered-ring compound 5 almost quantitatively (Fig. 2b and Supplementary Fig. 3). Since the addition reaction of 9-borabicyclo[3.3.1]nonane to bis(trimethylsilyl)acetylene has previously been reported to be initiated by a hydroboration (Supplementary Fig. 2)[26], we assumed that 5 was formed via the 1,2-carboboration of 1 and bis(trimethylsilyl)acetylene, followed by a 1,2-migration of the trimethylsilyl group. In that case, the 1,2-migration should be suppressed when bis(trimethylsilyl)acetylene is replaced with diphenylacetylene (2a). Indeed, when borafluorene 1 was treated with one equivalent of 2a, the 1,2-carboboration occurred and yielded 5-chloro-6,7-diphenyl-5H-dibenzo[b,d]borepin (3a) exclusively (Fig. 2a). However, to our surprise, 3a was immediately transformed into 9,10-diphenylphenanthrene (4a) on exposure to air. This absolutely unexpected observation prompted us to further explore the reactivity of these chloro-substituted borepins.

Results

Carboboration of diphenylacetylene with borafluorene.
The 1,2-carboboration between 1 and 2a in CH_2Cl_2 at 25 °C under an argon atmosphere yielded 3a almost quantitatively, even though the reaction required 4 days for completion. When performed in 1,2-dichloroethane (DCE) at 80 °C, the reaction was completed within 12 h, and detectable byproducts were not observed.

Thus, 3a was isolated in 87% yield, simply by recrystallization of the reaction mixture under argon (see Supplementary Methods). The structure of 3a was assigned unambiguously on the basis of ^{1}H, ^{13}C and ^{11}B NMR as well as infrared spectroscopy, atmospheric pressure chemical ionization time-of-flight mass spectrometry and single-crystal X-ray diffraction analysis (Supplementary Fig. 4). So far, only a limited number of examples of such catalyst-free 1,2-carboboration reactions of alkynes and related unsaturated compounds have been reported; mostly for diarylchloroboranes[9], boroles[10–15] and borenium ions (three-coordinate boron cations)[16,17]. Borafluorene 1 can thus be considered as a readily available 1,2-carboboration reagent for acetylenes. In contrast, diphenylchloroborane, which is an acyclic C–B(Cl)–C system, did not react with diphenylacetylene 2a, even in refluxing DCE. Hence, sterically less-hindered cyclic structures might facilitate the 1,2-carboboration with alkynes.

Oxidative deborylation/C–C coupling of borepins.
During the isolation of chloroborepin 3a, we noticed that 3a underwent a certain transformation on minimal contamination of the reaction mixture with air. The ^{1}H NMR analysis identified 9,10-diphenyl-phenanthrene (4a) as the resulting product. Furthermore, the exposure of a DCE solution of 3a at 25 °C to O_2 immediately led to its transformation into 4a, which could be isolated in 54% yield (Fig. 2a and Supplementary Table 3, entry 1). It seemed that the auto-oxidation induced the deborylation/C–C coupling of 3a into 4a, and therefore we further investigated the oxidation of 3a. Remarkably, under very mild conditions using organic one-electron oxidants such as iodine, tris(4-bromophenyl)ammoniumyl hexachloroantimonate $[(p\text{-}BrC_6H_4)_3N^{\bullet +}][SbCl_6^-]$, or 2-azaada-mantane-N-oxyl (AZADO), as well as $FeCl_3$ or MnO_2, 3a could be converted efficiently into 4a (Supplementary Table 3). The highest isolated yield of 4a (94%) was obtained when $FeCl_3$ or MnO_2 were used (Supplementary Table 3, entries 4 and 5). The oxidation reactions using $[(p\text{-}BrC_6H_4)_3N^{\bullet +}][SbCl_6^-]$ and $FeCl_3$ (Supplementary Table 3, entries 2 and 4) indicated that the conversion from 3a to 4a requires essentially only one equivalent of oxidant. The deborylation/C–C coupling reaction of 3a into 4a can also be achieved by electrochemical oxidation, which involves an electron transfer at an electrode surface. Cyclic voltammetry of 3a in o-dichlorobenzene (ODCB), which contained tetrabutylammonium hexafluorophosphate $[Bu_4N^+][PF_6^-]$ as the supporting electrolyte, showed an irreversible oxidation wave at 1.05 V (versus ferrocene/ferrocenium) during the first anodic scan (Supplementary Fig. 9). After the second cycle, the height of the oxidation wave of 3a markedly decreased and, instead, a reversible oxidation wave with a half wave potential of 1.18 V appeared, which perfectly matched the first oxidation potential of 4a under identical electrolysis conditions (Supplementary Fig. 10). The ^{1}H NMR analysis of a mixture of 3a and $[Bu_4N^+][PF_6^-]$ in ODCB-d_4 confirmed that the boron atom of 3a is free-from coordination by the supporting electrolyte used in the electrochemical measurements.

Similar to 3a, fully benzannulated chloroborepin 6 also underwent this deborylation/C–C coupling reaction (Fig. 2c). When 6 was treated with an equimolar amount of $FeCl_3$ at 25 °C, triphenylene was formed quantitatively (see Supplementary Methods). This result, together with those observed for 3a, clearly indicates that one-electron oxidation of the chloroborepins 3a and 6 results in the spontaneous release of their boron functionality to cause the Csp^2–Csp^2 coupling. When taking the material balance of the deborylation/C–C coupling reaction into account, a low-valent cationic boron species such as $[B\text{–}Cl]^{\bullet +}$ should thus be generated from the borepin radical cations 3a$^{\bullet +}$ and 6$^{\bullet +}$. At present, we presume that solvent molecules and/or
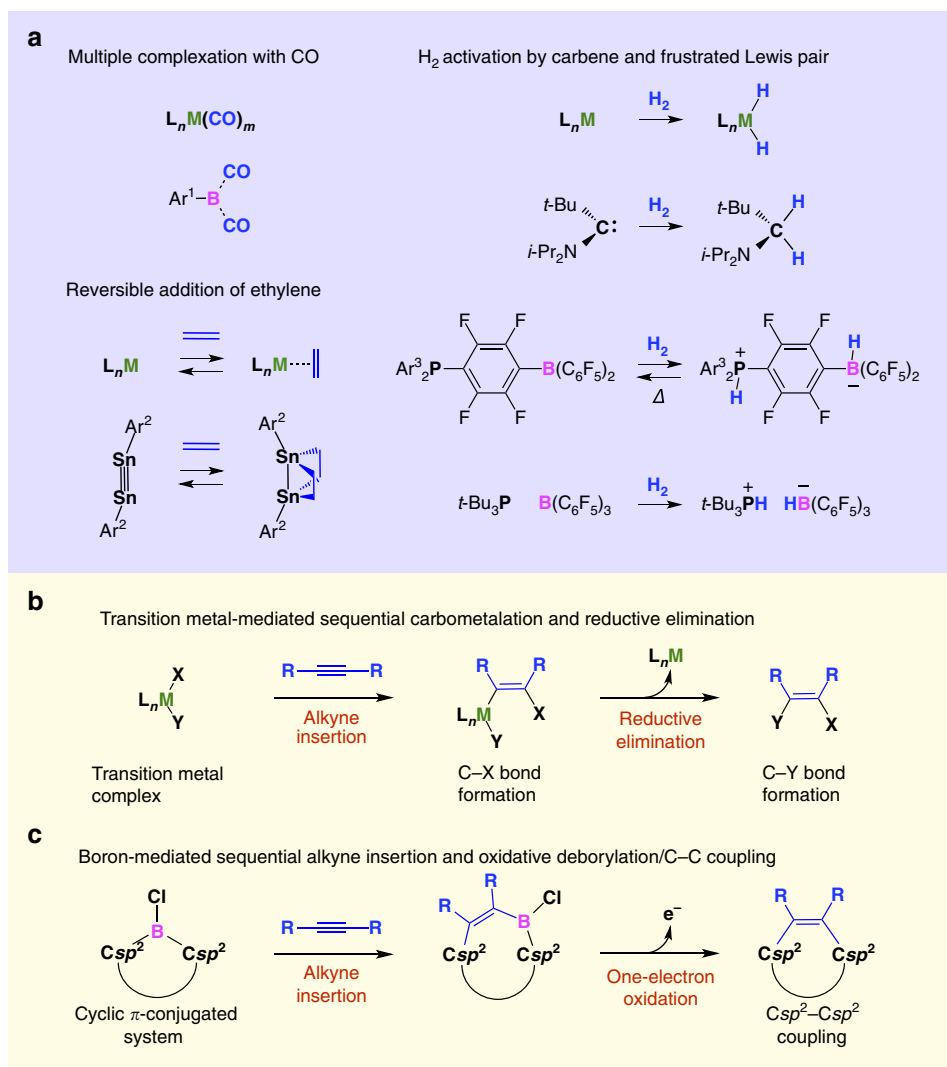
Figure 1 | Examples of transition metal-like reactivity of main group compounds and C-C coupling reactions mediated by boron and transition metals.
(**a**) Reported examples of transition metal-like reactivity of main group compounds. $Ar^1 = 2,6$-bis(2,4,6-triisopropylphenyl)phenyl; $Ar^2 = 2,6$-bis (2,6-triisopropylphenyl)phenyl; $Ar^3 = 2,4,6$-trimethylphenyl. (**b**) Sequential alkyne insertion and reductive elimination reactions mediated by organotransition metal complexes. (**c**) Sequential alkyne insertion (1,2-carboboration) and oxidative deborylation/Csp^2-Csp^2 coupling reaction from C-B(Cl)-C bonds embedded in cyclic π-conjugated systems. The first step, which affords a borepin derivative, proceeds very efficiently between the borafluorene and various alkynes by simply mixing the two components. The second step is triggered by a one-electron oxidation of the borepin derivative. This sequential reaction is chemoselective for alkynes and can be executed in a one-pot manner. L, ligand; M, transition metal; X and Y, non-metal elements.

anionic species from the oxidants could interact with the boron centre of the radical cations to assist the formal elimination of $[B–Cl]^{\bullet+}$. Despite numerous efforts, we have been unable to isolate any products arising from the eliminated boron moiety.

Substrate scope. So far, several reactive main group compounds have been reported to behave like transition metal compounds in the activation of small inert molecules[1–6]. The sequential 1,2-carboboration and oxidative deborylation/C–C coupling reactions between borafluorene **1** and alkynes are useful for the construction of a diverse range of aromatic systems (Table 1) in a one-pot procedure (see the 'Methods' section and Supplementary Methods). Typically, under an argon atmosphere, internal alkyne **2** was allowed to react with borafluorene **1** (1.1 equivalents) in DCE at 80 °C for 12 h, and then a nitromethane solution containing FeCl$_3$ (1.1 equivalents relative to **2**) was added to the

resulting mixture. The ^{1}H NMR analysis confirmed that the catalyst-free 1,2-carboboration using borafluorene **1** proceeded very efficiently for all internal alkynes used, and afforded the corresponding borepins in excellent yields (**3b–3j**: 83–99%; Table 1). After oxidation, 9,10-diarylphenanthrenes with 4-methyl and 4-methoxy groups were isolated in good yield (**4b**: 85%, **4c**: 82%; Table 1). Similarly, 9,10-diarylphenanthrenes with halogen functionalities were obtained in high yield (**4d**: 82%, **4e**: 80%; Table 1). The use of diarylacetylenes with strongly electron-withdrawing 4-trifluoromethyl or polar Lewis-basic 4-methoxycarbonyl groups resulted in lower isolated yields of the product (**4f**: 67%, **4g**: 48%; Table 1). Moreover, di(thiophene-1-yl)acetylene could be converted into 9,10-bis(thiophene-1-yl)phenanthrene (**4h**: 73%; Table 1). Interestingly, internal alkynes with aryl or alkyl substituents (**4i**: 64%; Table 1), and even with fully aliphatic substituents (**4j**: 71%; Table 1) were also susceptible to the sequential 1,2-carboboration and oxidative
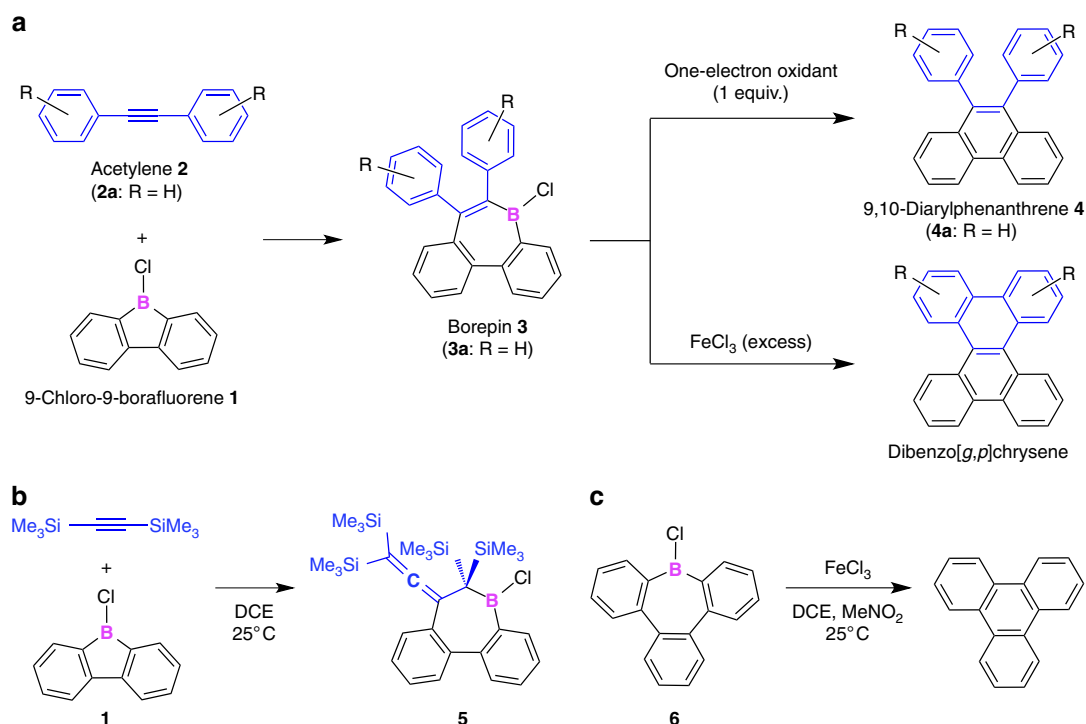
a

b

c

Figure 2 | Boron-mediated Csp^2–Csp^2 coupling reactions. (**a**) 1,2-Carboboration of diarylacetylene **2** with borafluorene **1**, followed by a deborylation/Csp^2–Csp^2 coupling reaction in the presence of an oxidant. (**b**) Reaction between bis(trimethylsilyl)acetylene and **1**. (**c**) Oxidative deborylation/Csp^2–Csp^2 coupling reaction of **6**.

Table 1 | Substrate scope of the one-pot reaction between 1 and various types of acetylenes.
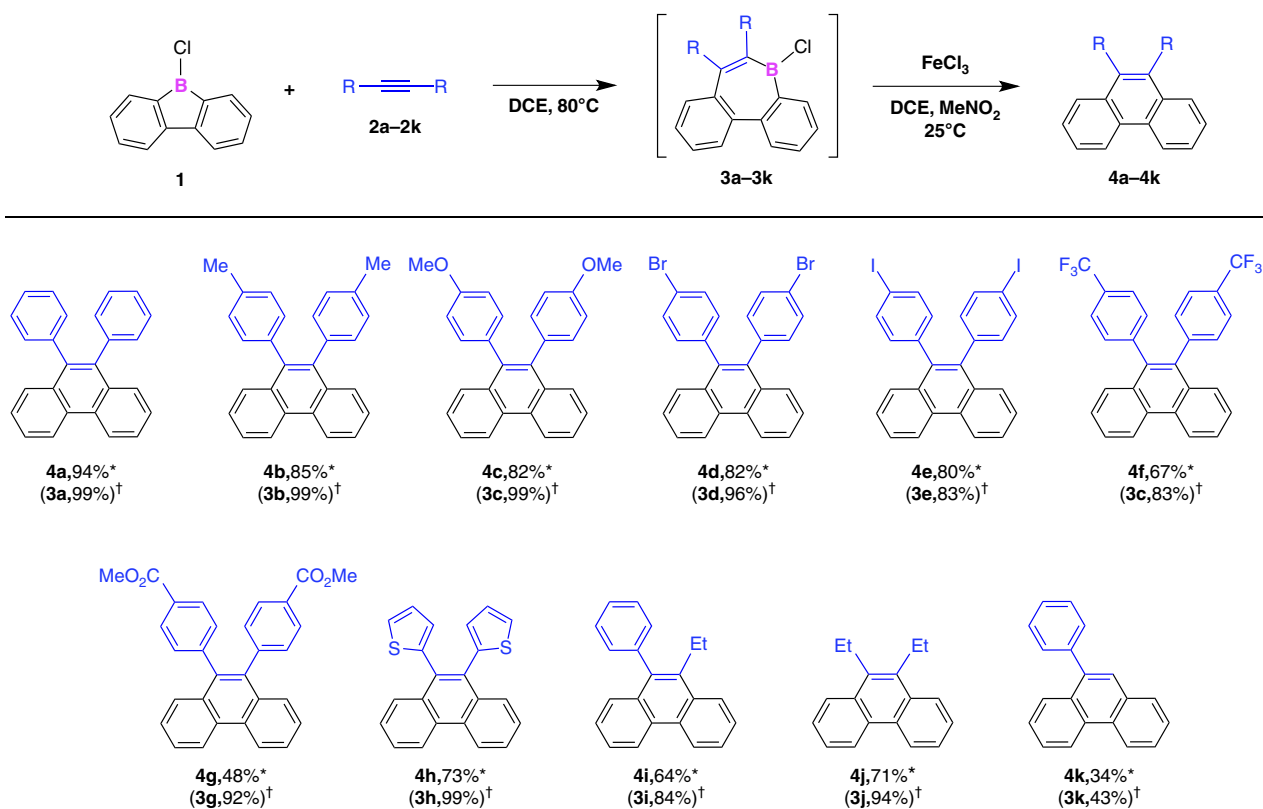
*Isolated yield.
†Yield determined by ^{1}H NMR spectroscopic analysis of the reaction mixture using hexamethylbenzene as the internal standard.

Table 2 | Benzannulated and cyclodehydrogenated products obtained from the one-pot reaction between 1 and various types of acetylenes.*
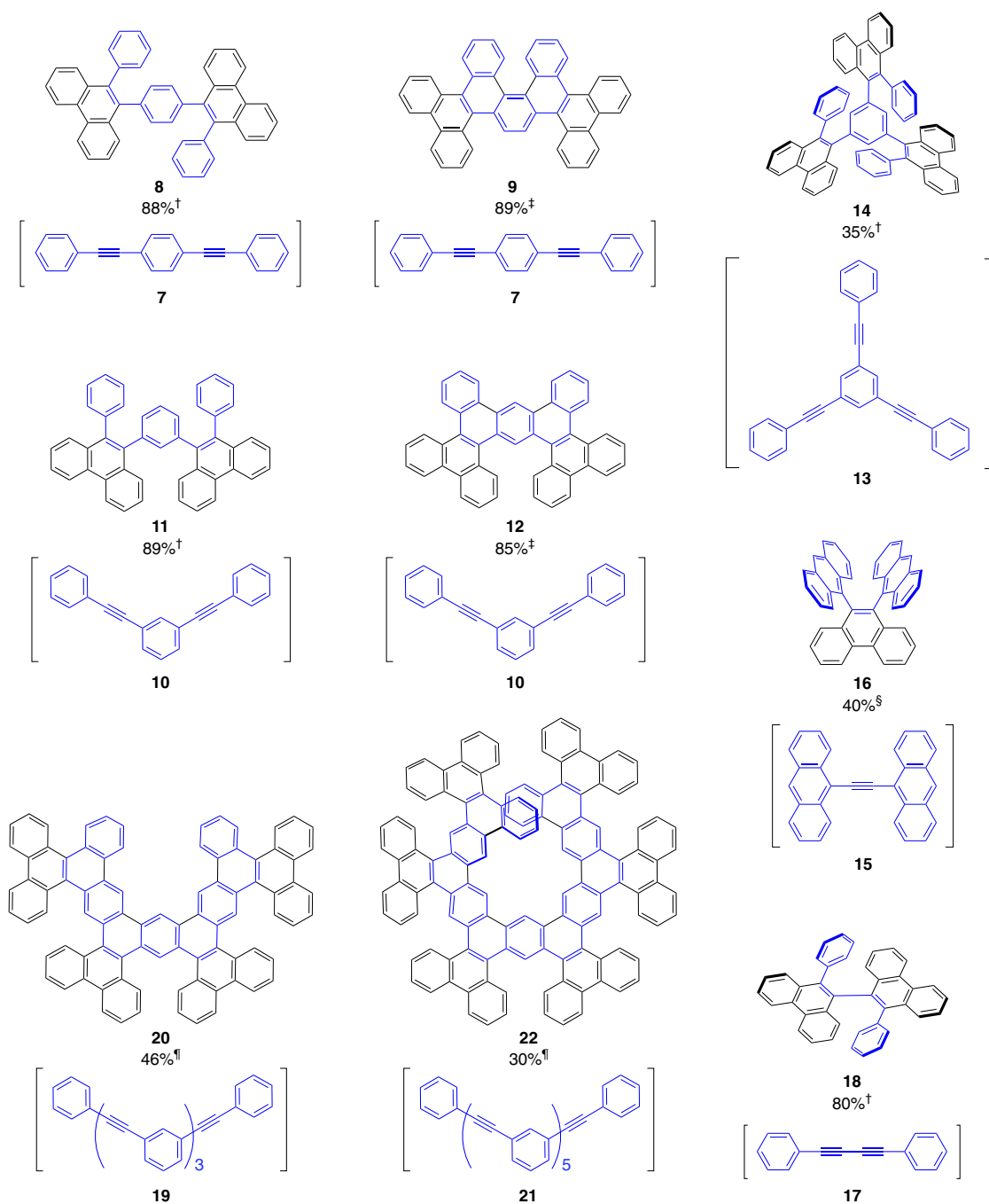
*Chemical structures of the corresponding acetylenes are shown in parentheses.
†1.1 equivalents of **1** and FeCl$_3$ per acetylene unit in the substrates were used.
‡1.1 and 15 equivalents of **1** and FeCl$_3$ per acetylene unit in the substrates were used, respectively.
§5.7 and 1.1 equivalents of **1** and AZADO per acetylene unit in the substrates were used, respectively.
¶1.1 and 11 equivalents of **1** and FeCl$_3$ per acetylene unit in the substrates were used.

deborylation/C–C coupling reactions with **1**. A terminal alkyne could also be converted into the corresponding phenanthrene derivative (**4k**), albeit in moderate yield (34%; Table 1). Notably, stilbene was unreactive in the presence of **1**, even in refluxing ODCB, indicating that the 1,2-carboboration is chemoselective for alkynes.

The one-pot, sequential 1,2-carboboration and oxidative deborylation/C–C coupling reactions are moreover applicable to substrates with multiple acetylene moieties (Table 2). For example, 1,4-bis(10-phenylphenanthren-9-yl)benzene (**8**) was obtained in 88% isolated yield from **1** and 1,4-bis(phenylethynyl)benzene (**7**) when 2.2 equivalents of FeCl$_3$ were used.

When a large excess of FeCl$_3$ (for example, 30 equivalents relative to **7**) was used, a Scholl-type cyclization[27] of as-formed **8** occurred simultaneously to generate hexabenzo[*a,c,f,j,m,o*] picene (**9**; 89%), which features a [5]helicene structure. Similarly, the treatment of a reaction mixture of **1** and 1,3-bis(phenylethynyl)benzene (**10**) with 2.2 or 30 equivalents of FeCl$_3$ furnished 1,3-bis(10-phenylphenanthren-9-yl)benzene (**11**) or tetrabenzo[*a,c,f,k*]phenanthro[9,10-*m*]tetraphene (**12**) in 89 and 85% yield, respectively. Remarkably, borafluorene **1** also reacts with sterically demanding internal alkynes, which then undergo the oxidative deborylation/C–C coupling. For example, 1,3,5-tris(phenylethynyl)benzene (**13**) was converted into 1,3,5-tris(10-phenylphenanthren-9-yl)benzene (**14**) in moderate yield (35%), and **16**, with two anthracene moieties in close proximity to each other, could be synthesized from 1,2-di(anthracen-9-yl)ethyne (**15**). The successful preparation of single crystals of **9**, **12** and **14** allowed the determination of their molecular structures by X-ray diffraction analysis (Supplementary Figs 5–7). Compounds **9** and **12**, containing multiple dibenzo[*g,p*]chrysene[28] moieties, adopt a highly twisted structure and feature a curved π-conjugated skeleton (Supplementary Figs 5 and 6). Using a procedure similar to that for bifunctional acetylenes, 1,4-diphenylbuta-1,3-diyne (**17**) could be benzannulated with **1** to afford 10,10′-diphenyl-9,9′-biphenanthrene (**18**)[29] in 80% isolated yield (Table 2). This product was obtained as a racemic mixture of *P*- and *M*-helical chiral enantiomers, which did not exhibit helix inversion at 25 °C, most likely on account of the intrinsic steric congestion. The enantiomers could therefore be separated using chiral high-performance liquid chromatography (Supplementary Fig. 11). The fact that even sterically demanding substrates such as **13**, **15** and **17** are easily transformed into the corresponding benzannulated products demonstrates the great potential and synthetic utility of the sequential 1,2-carboboration and oxidative deborylation/C–C coupling for the construction of extended π-conjugated systems with complex three-dimensional structures.

To further examine the versatility of the present benzannulation of acetylenes, we converted *meta*-phenylene ethynylene oligomers **19** and **21** into highly extended π-conjugated systems (Table 2). In this context, hexamer **21** is especially interesting, as it gives rise to a large helical molecule, which may potentially possess chiroptical properties. Oligomers **19** and **21** were successfully transformed into the desired products **20** and **22**, respectively, on reaction with **1** and subsequent oxidation with an excess of FeCl$_3$ (Table 2; see Supplementary Methods). Powder X-ray diffraction analysis of the isolated products revealed that **20** is crystalline, while **22** is amorphous. Compound **22** displayed very broad signals in the ^{1}H NMR spectrum (Supplementary Fig. 15), most likely due to rich conformational isomerism. Fourier-transform ion cyclotron resonance mass spectra clearly showed the ion peaks for **20** (calculated for C$_{86}$H$_{46}$ [M]$^+$: $m/z = 1,078.3594$; found: 1,078.3594) and **22** (calculated for C$_{126}$H$_{66}$ [M]$^+$: $m/z = 1,578.5159$; found: 1,578.5147; Supplementary Figs 14 and 17). Moreover, the single-crystal X-ray crystallographic analysis of **20** revealed an extended π-conjugated skeleton with a heavily twisted geometry (Supplementary Fig. 8).

Discussion

We have demonstrated an unprecedented reaction of organoboron compounds, which allows the facile transformation of acetylenes into non-planar, curved three-dimensional π-conjugated molecules. Such curved and/or twisted π-conjugated systems have recently received considerable attention, as they can exhibit dynamic structural changes[30–32],

chiroptical properties[33–35] and characteristic assembling behaviour, which may be beneficial for applications in organic electronics[28,36]. Besides the synthetic utility, the sequential nature of this protocol, featuring the insertion of an alkyne (1,2-carboboration) into a B–C bond, followed by an oxidative deborylation/C–C coupling reaction, sets it substantially apart from hitherto known reactions mediated by main group elements. Although the boron species released from the chloroborepin radical cations has not yet been identified, this unexpected reactivity will most likely spark new interest in the scientific community to promote further experimental and theoretical investigations in this area.

Methods

General. Air- and/or moisture-sensitive compounds were handled either in an argon-filled glove box or by applying standard Schlenk-line techniques. Anhydrous CH$_2$Cl$_2$ and hexane were dried by successive passage through an activated alumina column and a Q-5 column (Nikko Hansen & Co, Ltd). DCE, nitromethane (MeNO$_2$), ODCB, CDCl$_3$ and ODCB-d_4 were dried over CaH$_2$ and distilled immediately before use.

General procedure for the on-pot synthesis of phenanthrenes 4a–4k. Under argon, a dry DCE solution (2.0 ml) of a mixture of **1** (109 mg, 0.55 mmol) and the corresponding acetylene (0.50 mmol) was stirred for 12 h at 80 °C and then allowed to cool to 25 °C (note: at this stage, the yield of the corresponding borepin derivative (**3a**–**3k**) was calculated on the basis of the ^{1}H NMR spectroscopic analysis of the reaction mixture using hexamethylbenzene as the internal standard). After adding a dry MeNO$_2$ solution (1.0 ml) of FeCl$_3$ (81 mg, 0.50 mmol), the resulting mixture was stirred for 30 min at 25 °C and then poured into MeOH (150 ml). The precipitate thus formed was collected by filtration, dissolved in CH$_2$Cl$_2$, passed through a plug of Florisil, and evaporated to dryness under reduced pressure to afford the corresponding phenanthrene (**4a**–**4k**) (note: in some cases, an additional amount of the phenanthrene product could be isolated from the methanol filtrate by extraction with CH$_2$Cl$_2$, followed by SEC purification with CHCl$_3$ as the eluent).

Data availability. Crystal data of **3a**, **5**, **9**, **12**, **14** and **20** are available from the Cambridge Crystallographic Data Centre under reference numbers CCDC 1450400–1450405 via www.ccdc.cam.ac.uk/data_request/cif. For the analytical data of the compounds in this article including the NMR spectra, mass spectra, crystal data, a HPLC profile and cyclic voltammograms, see Supplementary Methods, Supplementary Figs 3–17 and Supplementary Tables 1–2. The authors declare that the other data supporting the findings of this study are available on request.

References

1. Power, P. P. Main-group elements as transition metals. *Nature* **463,** 171–177 (2010).
2. Braunschweig, H. *et al.* Multiple complexation of CO and related ligands to a main-group element. *Nature* **522,** 327–330 (2015).
3. Peng, Y., Ellis, B. D., Wang, X., Fettinger, J. C. & Power, P. P. Reversible reactions of ethylene with distannynes under ambient conditions. *Science* **325,** 1668–1670 (2009).
4. Frey, G. D., Lavallo, V., Donnadieu, B., Schoeller, W. W. & Bertrand, G. Facile splitting of hydrogen and ammonia by nucleophilic activation at a single carbon center. *Science* **316,** 439–441 (2007).
5. Welch, G. C., San Juan, R. R., Masuda, J. D. & Stephan, D. W. Reversible, metal-free hydrogen activation. *Science* **314,** 1124–1126 (2006).
6. Welch, G. C. & Stephan, D. W. Facile heterolytic cleavage of dihydrogen by phosphines and boranes. *J. Am. Chem. Soc.* **129,** 1880–1881 (2007).
7. Heck, R. F. *Organotransition Metal Chemistry* (Academic Press, 1974).
8. Tanaka, K. (ed.) *Transition-Metal-Mediated Aromatic Ring Construction* (John Wiley & Sons, Inc., 2013).
9. Lappert, M. F. & Prokai, B. Chloroboration and allied reactions of unsaturated compounds II. Haloboration and phenylboration of acetylenes; and the preparation of some alkynylboranes. *J. Organomet. Chem.* **1,** 384–400 (1964).
10. Braunschweig, H. & Kupfer, T. Recent developments in the chemistry of antiaromatic boroles. *Chem. Commun.* **47,** 10903–10914 (2011).
11. Eisch, J. J. & Galle, J. E. Rearrangements of organometallic compounds. XIII. Boraaromatic systems. IV. Synthesis of heptaphenylborepin via the thermal rearrangement of heptaphenyl-7-borabicyclo[2.2.1]heptadiene. *J. Am. Chem. Soc.* **97,** 4436–4437 (1975).
12. Eisch, J. J., Galle, J. E., Shafii, B. & Rheingold, A. L. Bora-aromatic systems. 12. Thermal generation and transformation of the borepin ring system: a paradigm of pericyclic processes. *Organometallics* **9,** 2342–2349 (1990).

13. Fan, C., Piers, W. E., Parvez, M. & McDonald, R. Divergent reactivity of perfluoropentaphenylborole with alkynes. *Organometallics* **29,** 5132–5139 (2010).

14. Huang, K., Couchman, S. A., Wilson, D. J. D., Dutton, J. L. & Martin, C. D. Reactions of imines, nitriles, and isocyanides with pentaphenylborole: coordination, ring expansion, C − H bond activation, and hydrogen migration reactions. *Inorg. Chem.* **54,** 8957–8968 (2015).

15. Huang, K. & Martin, C. D. Peculiar reactivity of isothiocyanates with pentaphenylborole. *Inorg. Chem.* **55,** 330–337 (2016).

16. Cade, I. A. & Ingleson, M. J. syn-1,2-Carboboration of alkynes with borenium cations. *Chem. Eur. J.* **20,** 12874–12880 (2014).

17. Devillard, M., Brousses, R., Miqueu, K., Bouhadir, G. & Bourissou, D. A stable but highly reactive phosphine-coordinated borenium: metal-free dihydrogen activation and alkyne 1,2-carboboration. *Angew. Chem. Int. Ed.* **54,** 5722–5726 (2015).

18. Kehr, G. & Erker, G. 1,1-Carboboration. *Chem. Commun.* **48,** 1839–1850 (2012).

19. Pelter, A. Tilden lecture. Carbon–carbon bond formation involving boron reagents. *Chem. Soc. Rev.* **11,** 191–225 (1982).

20. Brown, H. C. Organoborane-carbon monoxide reactions. A new versatile approach to the synthesis of carbon structures. *Acc. Chem. Res.* **2,** 65–72 (1969).

21. Bonet, A., Odachowski, M., Leonori, D., Essafi, S. & Aggarwal, V. K. Enantiospecific sp^2–sp^3 coupling of secondary and tertiary boronic esters. *Nat. Chem.* **6,** 584–589 (2014).

22. Sun, C.-L. & Shi, Z.-J. Transition-metal-free coupling reactions. *Chem. Rev.* **114,** 9219–9280 (2014).

23. Kölle, P. & Nöth, H. The chemistry of borinium and borenium ions. *Chem. Rev.* **85,** 399–418 (1985).

24. Piers, W. E., Bourke, S. C. & Conroy, K. D. Borinium, borenium, and boronium ions: synthesis, reactivity, and applications. *Angew. Chem. Int. Ed.* **44,** 5016–5036 (2005).

25. Shoji, Y., Tanaka, N., Mikami, K., Uchiyama, M. & Fukushima, T. A two-coordinate boron cation featuring C–B$^+$–C bonding. *Nat. Chem.* **6,** 498–503 (2014).

26. Wrackmeyer, B., Tok, O. L., Milius, W., Bhatti, M. H. & Ali, S. Hydroboration of bis(trimethylsilyl)ethyne. New aspects of hydroboration. *Z. Naturforsch.* **58b,** 133–138 (2002).

27. Grzybowski, M., Skonieczny, K., Butenschön, H. & Gryko, D. T. Comparison of oxidative aromatic coupling and the scholl reaction. *Angew. Chem. Int. Ed.* **53,** 9900–9930 (2013).

28. Ueda, Y., Tsuji, H., Tanaka, H. & Nakamura, E. Synthesis, crystal packing, and ambipolar carrier transport property of twisted dibenzo[g,p]chrysenes. *Chem. Asian J.* **9,** 1623–1628 (2014).

29. Matsumoto, A., Ilies, L. & Nakamura, E. Phenanthrene synthesis by iron-catalyzed [4 + 2] benzannulation between alkyne and biaryl or 2-alkenylphenyl Grignard reagent. *J. Am. Chem. Soc.* **133,** 6557–6559 (2011).

30. Rabideau, P. W. & Sygula, A. Buckybowls: polynuclear aromatic hydrocarbons related to the buckminsterfullerene surface. *Acc. Chem. Res.* **29,** 235–242 (1996).

31. Sakurai, H., Daiko, T. & Hirao, T. A synthesis of sumanene, a fullerene fragment. *Science* **301,** 1878 (2003).

32. Kawasumi, K. *et al.* A grossly warped nanographene and the consequences of multiple odd-membered-ring defects. *Nat. Chem.* **5,** 739–744 (2013).

33. Grimme, S., Harren, J., Sobanski, A. & Vogtle, F. Structure/chiroptics relationships of planar chiral and helical molecules. *Eur. J. Org. Chem.* 1491–1509 (1998).

34. Nakamura, K., Furumi, S., Takeuchi, M., Shibuya, T. & Tanaka, K. Enantioselective synthesis and enhanced circularly polarized luminescence of S-shaped double azahelicenes. *J. Am. Chem. Soc.* **136,** 5555–5558 (2014).

35. Suzuki, N. *et al.* Chiral graphene quantum dots. *ACS Nano* **10,** 1744–1755 (2016).

36. Wakamiya, A. *et al.* On-top π-stacking of quasiplanar molecules in hole-transporting materials: inducing anisotropic carrier mobility in amorphous films. *Angew. Chem. Int. Ed.* **53,** 5800–5804 (2014).

Acknowledgements

Author contributions

Y.S. and T.F. conceived and designed the study; Y.S., N.T., S.M., N.S., H.S., K.T. and F.H. performed the synthetic experiments; Y.S., N.T. and T.F. analysed the experimental data; Y.S. and T.F. co-wrote the paper.

Additional information