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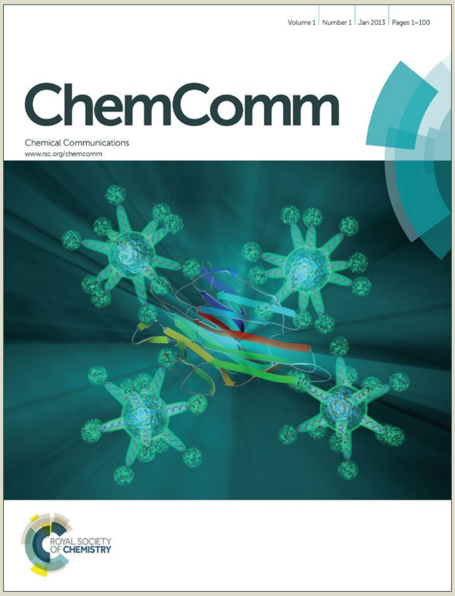

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Synthesis and Fluxional Behaviour of Novel Chloroborole Dimers †

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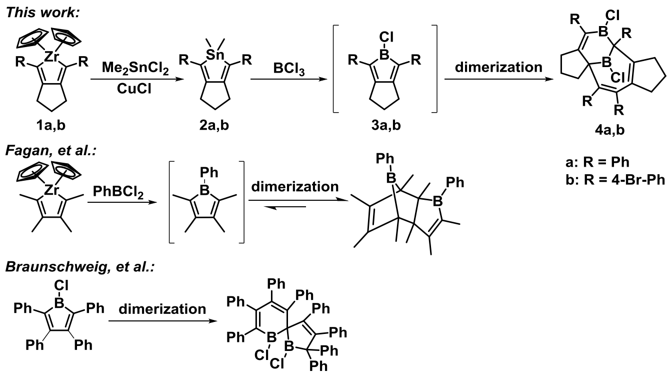
The (*B*-Cl)-chloroboroles 2-chloro-1,3-di(4-R-phenyl)-2,4,5,6-tetrahydrocyclopenta[*c*]borole (R = H, Br) undergo a novel dimerization process in CH_2Cl_2 solution. The resulting unsymmetric dimers are highly fluxional in solution via reversible enantiomerization through an intermediate with mirror symmetry. DFT calculations suggest an unusual dimerisation mechanism and provide insight into the dynamics of the dimers.

Organoboron compounds are widely studied as optical and optoelectronic materials, anion sensors and reagents for chemical synthesis.[1-3] Among various boron-containing systems, boroles,[4] *i.e.* boracyclopentadienes comprising a 4π-electron BC_4 ring, have attracted increasing attention because of their antiaromaticity, photophysical and redox properties and also their various reactivities.[5–10] For example, boroles can be readily reduced to their radical-anions due to the electron-poor nature of the BC_4 ring,[5c,d,f,g] they form adducts with Lewis bases due to their Lewis acidity,[5b,e,f,h,6c] they can activate H–H[6d] and Si–H[5i] bonds, and they react with azides to generate 1,2-azaborinines.[5h] Another typical reaction of boroles is the [4π+2π] Diels–Alder reaction, which includes not only the cycloaddition of the borole diene system to alkenes[10e] and alkynes,[6b,8a,10c,d] but also the dimerisation of the BC_4 ring. Such dimerisation was initially studied on sterically less encumbered boroles, *i.e.* 1-Ph-2,3,4,5-Me_4BC_4 (Scheme 1)[10e] and 1-(iPr)$_2$NBC$_4$H$_4$,[10j] and the addition reaction was found to occur easily between the diene system and the C=C bond of another borole molecule. However, the facile dimerisation led to failure in the isolation of monomeric boroles.[10e] Recently, the Braunschweig group reported the dimerisation of 1-Cl- and 1-Br-2,3,4,5-Ph_4BC_4.[5d,j] Although these monomeric boroles can be isolated, possibly due to the kinetic stabilization by more bulky phenyl substituents, they still undergo dimerization at *ca.* 40 to 55 °C to generate diboron-containing species with a spiro structure (Scheme 1). The mechanism of the dimerization was proposed to include an addition reaction between the diene system of one zwitterionic form of the borole and the B=C bond in another molecule with the same form, and subsequent phenyl migrations and B–C bond rearrangements.[5d] The chloro-substituted dimer was later found to react with dilithio-1,2,3,4-tetraphenylbuta-1,3-diene to generate a carborane cluster.[5k] Though dimerization represents a drawback for the isolation of boroles, especially those with less bulky substituents, it is useful for generating novel diboron-containing systems. However, to the best of our knowledge, studies of the dimerisation of boroles are limited to the above mentioned examples.

Whilst developing pentaaryl and triarylboroles with a 2,4,6-tris(trifluoromethyl)phenyl group on the boron atom with greatly enhanced air stability for applications in optoelectronic devices,[11] we attempted the synthesis of potentially versatile precursors 2-chloro-1,3-di(4-R-phenyl)-2,4,5,6-tetrahydrocyclopenta[*c*]borole (R = H (**3a**), Br (**3b**)) via a boron–tin exchange reaction. However, we found that these chloroboroles undergo a novel dimerisation process to generate unusual dimers (Scheme 1), which also display an interesting dynamic process in solution.



Scheme 1 Syntheses of novel chloroborole dimers **4a**,**b** and known borole dimers.

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The reaction of zirconoles **1a,b** with Me_2SnCl_2 in the presence of CuCl in THF at 80 °C gave the stannoles **2a,b** in very good yields, which have been fully characterized by multi-nuclear NMR spectroscopy, mass spectrometry and elemental analysis (Scheme 1 and ESI). Addition of BCl_3 (heptane solution) to a CH_2Cl_2 solution of **2a,b** at –78 °C led to a rapid colour change from light green to dark brown/purple, indicating the generation of chloroboroles **3a,b** (Scheme 1).[11] However, increasing the temperature for workup resulted in the fading of the deep colour, suggesting further reaction. Unfortunately, we were not able to isolate **3a,b** even at low temperature, and the NMR spectra obtained at -78 °C were uninformative. A very light coloured solution was obtained when the reaction mixture was stirred at r.t. for 2 h, and the major product of the crude mixture observed by NMR spectroscopy was successfully crystallised as large block-shaped crystals.

Crystallographic analysis confirmed that compounds**4a** and 4b, isolated in 74 and 57% yields, respectively, are actually dimers of **3a** and **3b**, respectively (Fig. 1). The core skeletons of **4a** and **4b** are the same, unaffected by the presence or absence of the bromine atoms on the phenyl substituents. The boron atoms in both dimers exhibit a trigonal planar geometry with the sum of the three angles around the boron atom being 360°. The C1–C2, C7–C26 and C25–C21 bond lengths are typical of C=C bonds, whilst C2–C6, C6–C7, C26–C25, C21–C20, B1–C1, B1–C20, B2–C6 and B2–C20 are clearly single bonds. It is notable that the core skeletons of both dimers feature a six-membered diboron-containing (B1 and B2) ring and a seven-membered single boron-containing (B2) ring, which is quite different from those of dimerized $PhBC_4Me_4$ and $ClBC_4Ph_4$ (Scheme 1). This result clearly indicates the strong influence of the substituents at the 3,4-positions of the BC_4 ring on the dimer structures.

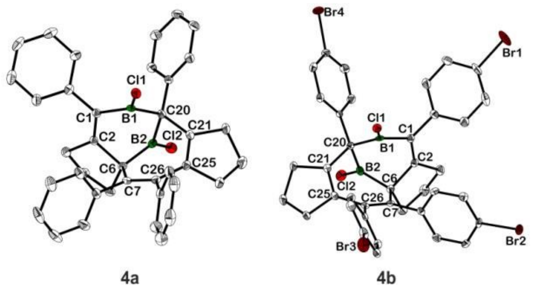

Fig. 1 Molecular structures of **4a** and **4b** from X-ray diffraction. Hydrogen atoms, as well as the second molecule and the CH_2Cl_2 solvent molecule in the asymmetric unit of **4a** are omitted for clarity. Thermal ellipsoids correspond to 50% probability at 100 K. Selected bond lengths (Å) for **4a** (values for the second molecule in [ ]): C1–C2 1.348(2) [1.350(2)], C2–C6 1.558(2) [1.558(2)], C6–C7 1.534(2) [1.531(2)], C7–C26 1.349(2) [1.350(2)], C26–C25 1.470(2) [1.472(2)], C25–C21 1.358(2) [1.359(2)], C21–C20 1.497(2) [1.501(2)], B1–C1 1.546(2) [1.551(2)], B1–C20 1.577(2) [1.579(2)], B1-Cl1 1.7734(18),[1.7713(18)], B2–C6 1.591(2) [1.587(2)], B2–C20 1.571(2) [1.566(2)], B2.Cl2 1.7836(18) [1.7837(19)]; for **4b**: C1–C2 1.346(4), C2–C6 1.559(4), C6–C7 1.537(4), C7–C26 1.346(4), C26–C25 1.471(4), C25–C21 1.359(4), C21–C20 1.489(4), B1–C1 1.553(4), B1–C20 1.583(4), B1-Cl1 1.761(3), B2–C6 1.595(4), B2–C20 1.568(4), B2-Cl2 1.785(3).

To understand the mechanism of the dimerization, DFT calculations (M06-2X/(6-31G* on C,H,B/6-311+G* on Cl)) were carried out based on the prior formation of **3a**. The calculations reveal an energetically very favourable pathway for the dimerization (Fig. 2). Two molecules of chloroborole firstly form a van der Waals complex (**A**) which then undergoes a [2σ+2π] addition between a C–B σ bond and a C=C double bond to give the addition intermediate **B**. From **B**, a stepwise 1,5-boryl shift gives the final dimer product **4a**. A concerted pathway for the reaction of **B** to **4a** corresponding to a formal [2σ+4π] addition seems possible. However, we failed to locate such a transition state after many attempts. For the [2σ+2π] addition, TS_{A-B} is the rate-determining transition state. The overall free energy barrier is calculated to be 14.2 kcal/mol, corresponding to the energy difference between **A** and TS_{A-B}. The reaction free energy for the dimerization is 20.2 kcal/mol.

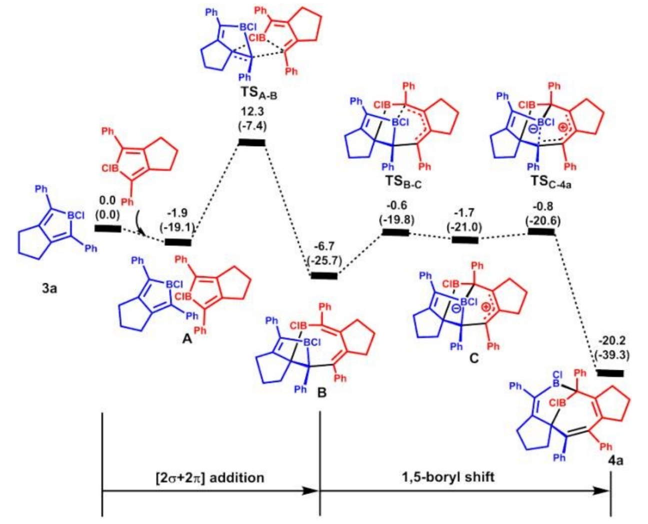

Fig. 2 Energy profile calculated for the formation of chloroborole dimer **4a** along the most favourable pathway. Relative free energies and electronic energies (in parentheses) are given in kcal/mol.

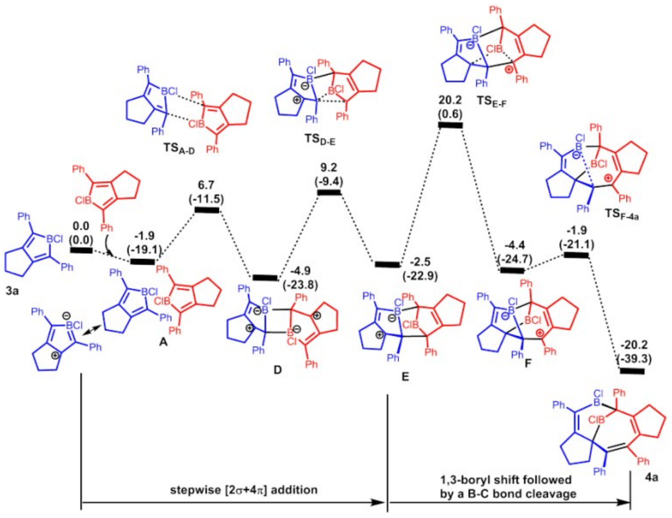

Fig. 3 Energy profile calculated for the formation of chloroborole dimer **4a** along a less favourable pathway. Relative free energies and electronic energies (in parentheses) are given in kcal/mol.

Another possible pathway via a [2σ+4π] addition was also calculated. As shown in Fig. 3, in this pathway the van der Waals complex **A** undergoes a stepwise addition to give the intermediate **E**. Interestingly, the stepwise [2σ+4π] addition starts with a simple [2σ+2σ] addition followed by a 1,2-alkyl shift. From **E**, a 1,3-boryl shift occurs to give **F**, which then undergoes B–C bond cleavage to give the final product **4a**. The overall free energy barrier for this pathway is 25.1 kcal/mol, significantly higher than the pathway shown in Fig. 2. Therefore, the possibility of the dimerization taking place via this pathway can be ruled out.

We also investigated the pathway for a [2π+4π] Diels-Alder addition that is known to be responsible for the dimerization of sterically less encumbered boroles.[10e] As shown in Fig. 4, from the van der Waals complex **A**, the Diels-Alder addition occurs via an asynchronous concerted mechanism. The barrier for this pathway is 19.6 kcal/mol, which is higher than that for the most favourable pathway shown in Fig. 2, suggesting that the formation of **4a** and **4b** are unlikely to be related to the Diels-Alder addition pathway.

Fig. 5 shows plots of the HOMO and LUMO calculated for chloroborole **3a**. The HOMO corresponds to an out-of-phase combination of the two C=C π bonding orbitals in the BC_4 ring. In the LUMO, the boron p_π orbital makes the major contribution. The orbital interactions involved in the dimerization process are expected to occur between the HOMO of one chloroborole molecule and the LUMO of the other chloroborole molecule. **TS$_{A-B}$** (Fig. 2), **TS$_{A-D}$** (Fig. 3) and **TS$_{A-G}$** (Fig. 4) correspond to [2σ+2π], [2σ+2σ] and [2π+4π] addition transition states, respectively. Among the three transition states, the [2π+4π] **TS$_{A-G}$** one is the highest in energy. This is because, in the LUMO, the p_π contributions from the two boron-bonded carbon atoms are small.

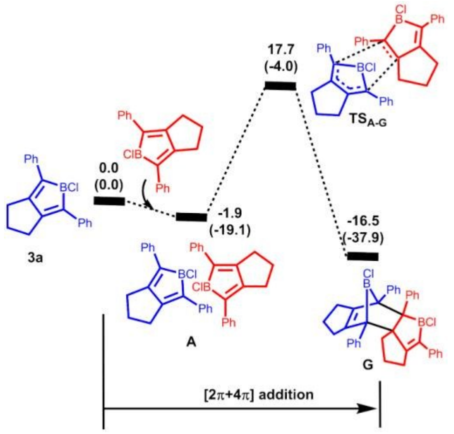

Fig. 4 Energy profile calculated for the formation of the Diels-Alder dimer. Relative free energies and electronic energies (in parentheses) are given in kcal/mol.

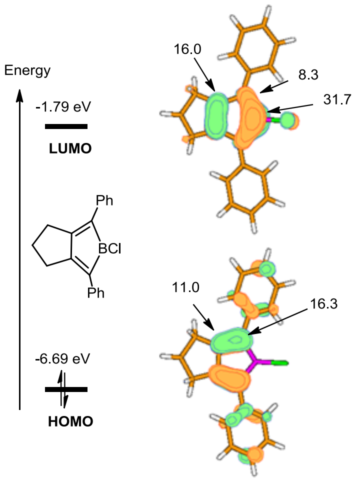

Fig. 5 The HOMO and LUMO calculated for chloroborole **3a** with percentage contributions of the p_π atomic orbitals.

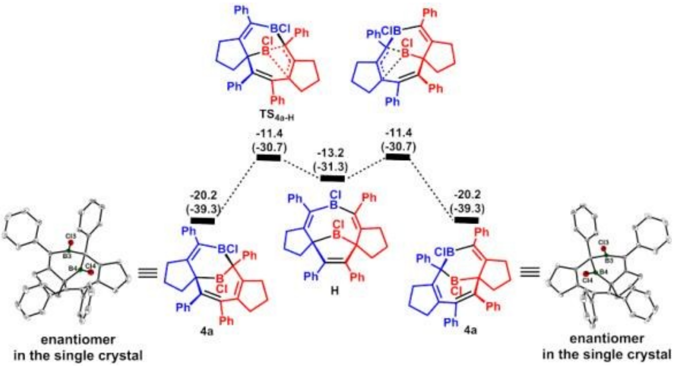

Fig. 6 One pair of two non-symmetry equivalent pairs of enantiomers in the single crystal of **4a**, and the energy profile for the interconversion between the enantiomers. Relative free energies and electronic energies (in parentheses) are given in kcal/mol.

Interestingly, the ^1H and ^{13}C NMR spectra of dimers **4a,b** are much simpler than expected from the unsymmetric solid-state structures. For **4b**, only four doublets (4:4:4:4) and four multiplets (4:4:2:2) can be observed for the aromatic and aliphatic hydrogen atoms, respectively, in the ^1H NMR spectrum. In addition, only eight sharp peaks plus two weak and broad peaks in the aromatic region and three sharp peaks in the aliphatic region can be observed in the $^{13}C\{^1H\}$ NMR spectrum. Dimer **4a** shows the same characteristics in its ^1H and $^{13}C\{^1H\}$ NMR spectra, except that the aromatic region of the ^1H NMR spectrum is more complex due to the substitution of hydrogen for bromine at the *para* position of the phenyl substituents in this compound. The simple and similar spectra of **4a** and **4b** suggest that a facile, low-energy dynamic process occurs for both dimers in solution.[12] Low temperature (–90 °C) ^1H and $^{13}C\{^1H\}$ NMR measurements have been attempted on dimer **4b** to freeze out the dynamic process. Although broadening and splitting of some signals was observed (Figs. S19 and S20), the dynamic process could not be fully frozen out, further indicating a low energy barrier for the process. Careful examination of the crystal structures disclosed the existence of two non-symmetry equivalent pairs of enantiomers with quite similar structures in the single crystal of **4a** and two enantiomers in the single crystal of **4b** (Figs. 6, S3 and S4). Reversible interconversion between two enantiomers is observed as a rapid dynamic process in solution considering the features of the NMR spectra. The interconversion makes the two phenyl/bromophenyl groups attached to the boron-bonded carbon atoms, as well as the other two phenyl/bromophenyl groups, indistinguishable on the NMR time scale due to the apparent mirror symmetry generated by the fluxionality. This explains the observation of only four doublets (4:4:4:4) for the aromatic hydrogens of **4b** in the ^1H NMR spectrum and only eight sharp peaks (from phenyl groups) in the aromatic region of the $^{13}C\{^1H\}$ NMR spectra of these dimers. Similarly, the two $–(CH_2)_3–$ groups also appear to be equivalent due to the dynamic process, resulting in the three observed carbon signals in the aliphatic region of the $^{13}C\{^1H\}$ NMR spectra of **4a,b**. Theoretical calculations suggest that the reversible enantiomerisation can easily occur through a symmetric intermediate (**H** in Fig. 6) formed by 1,3-boryl migration, as such a process has a small free energy barrier of only 8.8 kcal/mol (Fig. 6). The ^{11}B NMR spectrum of each dimer shows two peaks at *ca.* 64 and 35 ppm, consistent with the existence of two inequivalent boron atoms with quite different chemical environments maintained throughout the dynamic process.

In summary, 2-chloro-1,3-di(4-R-phenyl)-2,4,5,6-tetrahydrocyclopenta[*c*]borole (R = H (**3a**), Br (**3b**)) undergo dimerization to generate a novel borole-dimer skeleton with an unsymmetric structure. Theoretical studies suggest that the dimerisation occurs through an unusual [2σ+2π] addition and subsequent 1,5-boryl shift, which is quite different from previously reported borole dimerisations related to [4π+2π] Diels–Alder reactions. The isolated and structurally characterised dimers show an interesting dynamic process in solution, which corresponds to the reversible interconversion between their enantiomers, as suggested by NMR studies and theoretical calculations. This study not only discloses a new pathway for borole dimerization, but will benefit the further development of diboron systems and exploration of their various reactivities.

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