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Tri-insertion with dearomatization of terminal arylalkynes using a carborane based frustrated Lewis pair template†

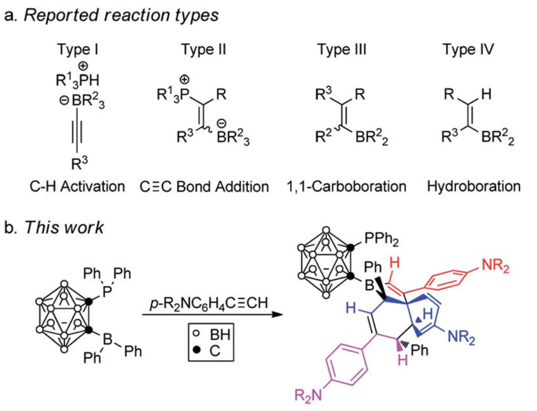
Jian Zhang and Zuowei Xie *

Intramolecular vicinal Frustrated Lewis Pairs (FLPs) have played a significant role in the activation of small molecules, and their stabilities and reactivities are found to strongly depend on the nature of the bridging units. This work reports a new carborane based FLP, 1-PPh$_2$-2-BPh$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**2**), which reacts with an equimolar amount of *p*-R$_2$NC$_6$H$_4$C≡CH (R = Me, Et, Ph) at room temperature to give C≡C triple bond addition products 1,2-[PPh$_2$C(R$_2$NC$_6$H$_4$)=CHBPh$_2$]-1,2-C$_2$B$_{10}$H$_{10}$ (**3**) in high yields. Compounds **3** react further with two equiv. of *p*-R$_2$NC$_6$H$_4$C≡CH (R = Me, Et) at 60–70 °C to give unprecedented stereoselective tri-insertion products, 3,3*a*,6,6*a*-tetrahydronaphtho[1,8*a*-*b*]borole tricycles (**4**), in which one of the aryl rings from arylacetylene moieties has been dearomatized with the formation of four stereocenters including one quaternary carbon center. It is noted that the phosphine unit functions as a catalyst during the reactions. After trapping and structural characterization of a key intermediate, a reaction mechanism is proposed, involving sequential alkyne insertion and 1,2-boryl migration.

Introduction

Frustrated Lewis Pairs (FLPs), in which Lewis acid/base adducts are not formed due to steric hindrance, can activate a variety of small molecules.[1] After the first example of H_2 activation by FLPs,[2] this concept has been widely used and FLPs showed reactivity toward a series of unsaturated compounds such as alkenes and alkynes,[3,4] carbonyl compounds,[4,5] carbon oxides,[6,7] nitrogen oxides,[8] SO_2,[7,9] *etc.* Among these, reactions of FLPs with alkynes were widely studied, which could be broadly classified into four types of reaction: C–H bond activation (type I),[3c] C≡C bond addition (type II),[3b–d] 1,1-carboboration (type III)[10] and 1,2-hydroboration (type IV)[4b,11] (Scheme 1a). For type I and II reactions, FLPs became part of the final products, whereas only a Lewis acid was incorporated in the final products in type III and IV reactions.

In the aforementioned developments, intramolecular vicinal FLPs have played an important role, and their stabilities and reactivities were found to strongly depend on the nature of the bridging units.[12–14] For example, the saturated **FLP1** has been one of the most active metal-free dihydrogen activators,[12] whereas the unsaturated otherwise closely related **FLP2** is almost inactive towards dihydrogen splitting (Scheme 2).[13] In contrast, the cyclohexadiene-derived **FLP3** and aromatic phenylene bridged **FLP4** are very active FLPs despite the presence of a pair of C(sp^2) centers in their vicinal bridges.[14] As a three-dimensional analog of benzene, *o*-carborane has two adjacent six-coordinate carbons with a C–C distance of *ca* 1.67 Å.[15] Such a 3D bridging system differs significantly from **FLP1-4** in terms of the bridging C–C distances, the hybridization and geometry of two bridging carbons and the bulkiness of the backbone, which offers an excellent model compound for comparison with



Scheme 1 Reaction types of alkynes with FLP templates: (a) reported reaction types, (b) tri-insertion reaction described in this work.

Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China. E-mail: zxie@cuhk.edu.hk

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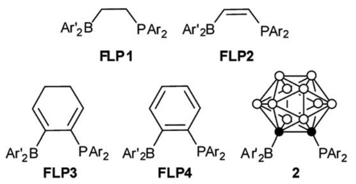


Scheme 2 Intramolecular vicinal frustrated Lewis pairs.

the 2D system. The results showed that a carborane based FLP,[16] 1-PPh_2-2-BPh_2-1,2-$C_2B_{10}H_{10}$ (**2**), reacted with *p*-$R_2NC_6H_4C{\equiv}CH$ to afford unprecedented stereoselective tri-insertion products, 3,3*a*,6,6*a*-tetrahydronaphtho[1,8*a*-*b*]borole tricycles (**4**) accompanied by the dearomatization of one of the aryl rings from arylacetylene moieties (Scheme 1b). Such properties had not been observed in FLP chemistry before.[1,17] These new results are reported in this article.

Results and discussion

The FLP 1-PPh_2-2-BPh_2-1,2-$C_2B_{10}H_{10}$ (**2**) was conveniently synthesized by treatment of 1-PPh_2-1,2-$C_2B_{10}H_{11}$ (**1**) with 1 equiv. of *n*-BuLi, followed by reaction with an equimolar amount of Ph_2BCl in toluene. The ^{11}B chemical shift of the *B*Ph_2 group was observed at 15.5 ppm. The ^{31}P chemical shift of the *P*Ph_2 unit appeared at 27.9 ppm, which was slightly downfield-shifted compared to that of 26.0 ppm in **1**. The P···B distance of 2.113(3) Å in **2** as determined by single-crystal X-ray analyses (Fig. S1 in the ESI†) is somewhat shorter than that of 2.203(6) Å in **FLP4**, and 2.182(3) Å in **FLP3** (Scheme 2).[14]

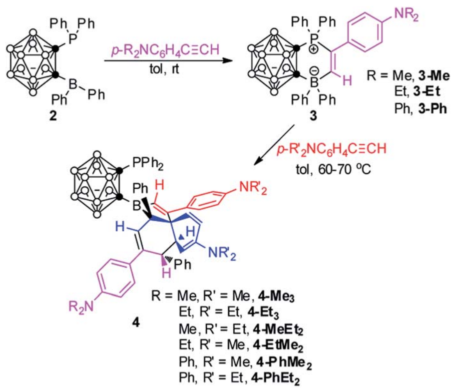
Compound **2** exhibited weak FLP properties and did not split H_2 under various reaction conditions (2 bar H_2, toluene, 2 days, and T = RT to 100 °C) as indicated by ^{31}P NMR spectra. However, it reacted readily with an equimolar amount of *p*-$R_2NC_6H_4C{\equiv}CH$ in toluene at room temperature to afford C≡C bond addition products 1,2-[$Ph_2PC(R_2NC_6H_4){=}C(H)BPh_2$]-1,2-$C_2B_{10}H_{10}$ [R = Me (**3-Me**), Et (**3-Et**), Ph (**3-Ph**)] in 85–94% isolated yields (Scheme 3).

These compounds were characterized using various spectroscopic data as well as HRMS. The ^{11}B chemical shift of the four-coordinate boron was observed at about −11 ppm, and the phosphorus signal appeared at *ca.* 12 ppm in the ^{31}P NMR spectra. The olefinic proton signal was observed at about 9.3 ppm, and the corresponding olefinic carbons appeared at about 191 ppm. The molecular structures of **3-Me** and **3-Ph** were further confirmed by single-crystal X-ray diffraction studies. Fig. 1 shows the representative structure of **3-Me**. It clearly indicates that the terminal alkyne carbon (C41) is bonded to B(13) due to the polarization of the C≡C bond. The C(41)–C(42) bond distance of 1.338(3) Å falls in the range of 1.32 to 1.39 Å normally observed for C=C double bonds.[3b,c,4b,d,10,11a,c,d]

Compounds **3-Me** and **3-Et** reacted slowly with 2 equiv. of *p*-$R_2NC_6H_4C{\equiv}CH$ (R = Me, Et) in toluene at 70 °C to give unprecedented tri-insertion products **4-Me$_3$** and **4-Et$_3$** in 60% and 50% isolated yields, respectively (Scheme 3).

The molecular structures of both **4-Me$_3$** and **4-Et$_3$** were confirmed by single-crystal X-ray analyses. Fig. 2 shows the representative structure of **4-Me$_3$**. The B(13)···P distances of 3.303(5) Å in **4-Me$_3$** and 3.305(4) Å in **4-Et$_3$** are significantly longer than that of 2.113(3) Å in **2**. Both P and B(13) atoms are three-coordinate, yet the coordination environment of the B(13) atom in **4** is completely different from that observed in **2**. The sum of bond angles around the B(13) atom is 359.4° in **4-Me$_3$** and 359.8° in **4-Et$_3$**, indicating that both B(13) atoms adopt a trigonal planar geometry. It is unambiguously confirmed that the insertion of three arylacetylenes into the FLP template **2** with the migration of the phenyl groups from the boron to two different carbons afforded 3,3*a*,6,6*a*-tetrahydronaphtho[1,8*a*-*b*] borole tricycles **4**, leading to the construction of four stereocenters including one quaternary carbon. To the best of our knowledge, this type of transformation has not been observed before in FLP chemistry.

To gain some insight into the reaction path, crossover experiments were performed. Treatment of **3-Me** with an excess amount of *p*-$Et_2NC_6H_4C{\equiv}CH$ in toluene at 70 °C gave the tri-insertion product **4-MeEt$_2$** in 51% isolated yield. In the same manner, the corresponding tri-insertion compounds **4-EtMe$_2$**, **4-PhMe$_2$** and **4-PhEt$_2$** were prepared in 51%, 81% and 77% isolated yields, respectively (Scheme 3).



Scheme 3 Insertion of terminal alkynes into the FLP template.

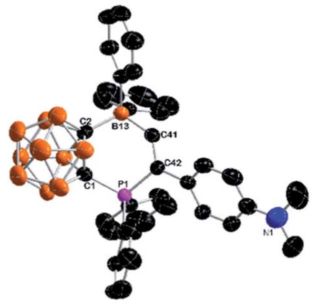


Fig. 1 Molecular structure of **3-Me**. All H atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Key bond distances (Å) and angles (°): B(13)–C(41) 1.632(4), B(13)–C(2) 1.691(4), C(41)–C(42) 1.338(3), P(1)–C(42) 1.787(3), P(1)–C(1) 1.844(3), C(1)–C(2) 1.690(4), C(2)–B(13)–C(41) 108.7(2), B(13)–C(41)–C(42) 133.9(2), C(41)–C(42)–P(1) 116.9(2), and C(42)–P(1)–C(1) 107.2(1).

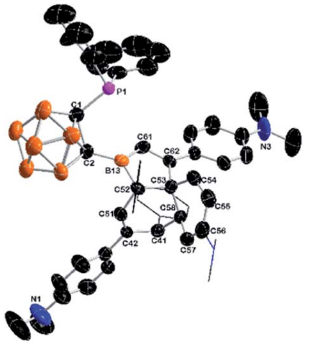


Fig. 2 Molecular structure of **4-Me**$_3$. All H atoms are omitted, two phenyls and one Me_2N group are shown in the wireframe format for clarity; thermal ellipsoids are drawn at the 50% probability level. Key bond distances (Å) and angles (°): B(13)–C(61) 1.495(6), B(13)–C(52) 1.586(6), B(13)–C(2) 1.618(6), C(61)–B(13)–C(52) 108.0(4), C(61)–B(13)–C(2) 125.1(4), and C(52)–B(13)–C(2) 126.3(4).

Their NMR spectra shared the same features as those of **4-Me**$_3$ and **4-Et**$_3$, indicating that these compounds should have similar molecular skeletons. Subsequently, the molecular structures of **4-EtMe**$_2$ and **4-PhEt**$_2$ were unambiguously determined by single-crystal X-ray analyses. The representative structure of **4-EtMe**$_2$ is shown in Fig. 3. These crossover experimental results suggested that the insertion of arylacetylene into **2** to form **3** was an irreversible reaction, otherwise, the homo-triinsertion product **4-Me**$_3$ or **4-Et**$_3$ would be isolated.

Another question then arises as to how the alkyne reacts with **3**. After careful analyses of the molecular structures of **4**, we speculated that the Ph group of the BPh_2 unit in **3** may migrate to vinyl carbon, followed by a rearrangement to regenerate a new FLP template for the reaction with alkynes. Each migration of Ph from the B center would accompany an alkyne insertion, leading to the formation of the final product **4**. However, many attempts to isolate the intermediates were not successful. We thought that a newly generated FLP species might be trapped by formaldehyde $(CH_2O)_n$.[4,5] Accordingly, treatment of **3-Ph** with an excess amount of $(CH_2O)_n$ in C_6D_6 at 40 °C for 7 d afforded 1,2-$\{Ph_2PCH_2OB(Ph)[C(C_6H_4NPh_2){=}CHPh]\}$-1,2-$C_2B_{10}H_{10}$ (**5-Ph**) as colorless crystals in 38% isolated yield (Scheme 4).

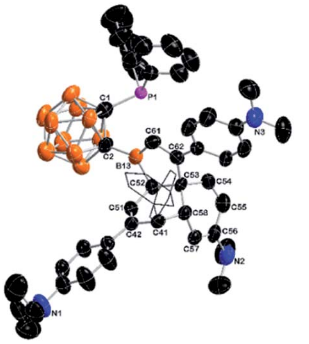
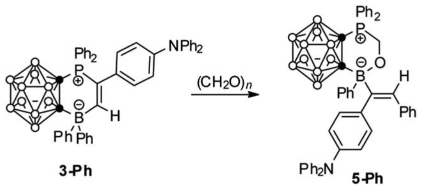


Fig. 3 Molecular structure of **4-EtMe**$_2$. All H atoms are omitted, and two phenyl groups are shown in the wireframe format for clarity; thermal ellipsoids are drawn at the 50% probability level. Key bond distances (Å) and angles (°): B(13)–C(61) 1.513(5), B(13)–C(52) 1.603(6), B(13)–C(2) 1.609(6), C(61)–B(13)–C(52) 106.4(3), C(61)–B(13)–C(2) 125.5(4), and C(52)–B(13)–C(2) 127.7(3).

The proton chemical shifts of the CH_2O unit were observed as two doublet of doublets at 5.06 and 4.84 ppm, and its ^{13}C signal appeared at 61.2 ppm. The ^{31}P resonance was observed at 3.7 ppm, while the exo-B signal was overlapped with cage B atoms in the ^{11}B NMR spectrum. The molecular structure of **5-Ph** was unambiguously confirmed by single-crystal X-ray analyses (Fig. 4). The C(41)–C(42) distance of 1.326(5) Å suggests that it is a typical C=C double bond, confirming that the borate and phenyl groups are in *trans*-positions in **5-Ph.**

On the basis of the aforementioned results and literature work,[3d,10,18,19] a plausible reaction mechanism is proposed for the formation of **4** (Scheme 5). 1,2-Migration of the phenyl group from the borate gives a phosphonium ylide **A1**. Another 1,2-boryl migration affords an intermediate **A2**, in which the boryl and Ph are in *trans*-positions due to steric reasons. **A2** can be trapped by formaldehyde to form **5** (Scheme 4). **A2** is a newly formed FLP template which is similar to that of **2**. A second equiv. of alkyne addition yields **B1**, an analogue of **3**. Similar 1,2-migration processes (from **3** to **A1** to **A2**) repeat to generate **B2** and **B3**. Electrocyclic ring closure of **B3** gives a dearomatized intermediate **B4** with the construction of two stereocenters in which two hydrogen atoms are *trans* to each other. **B4** is again a newly generated FLP. A third equiv. of alkyne addition to **B4**, followed by rearrangement constructs stereoselectively a quaternary carbon center, giving a dearomatized intermediate **C1**. 1,2-Migration of the phenyl group from the borate affords



Scheme 4 Reaction of **3-Ph** with formaldehyde.

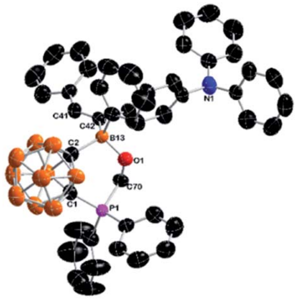
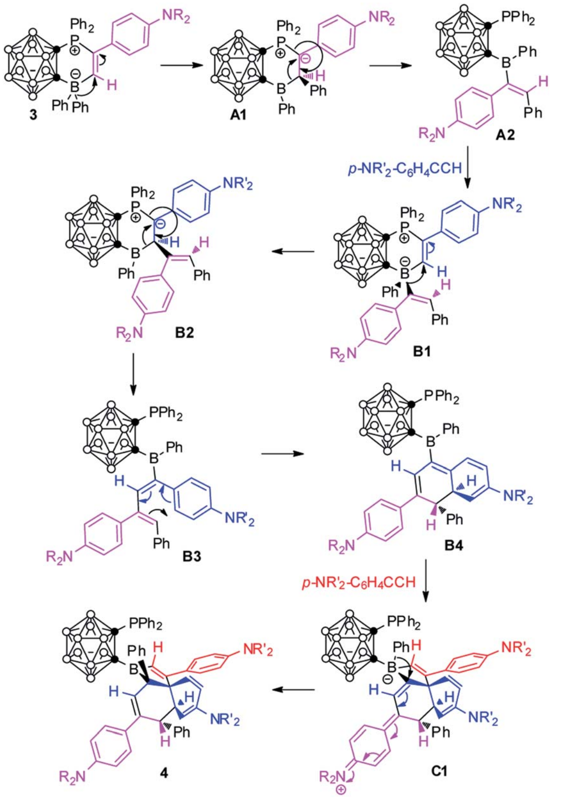


Fig. 4 Molecular structure of **5-Ph**. All H atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Key bond distances (Å) and angles (°): P(1)–C(70) 1.817(4), P(1)–C(1) 1.844(4), B(13)–O(1) 1.487(5), B(13)–C(2) 1.732(5), B(13)–C(42) 1.637(6), C(41)–C(42) 1.326(5), C(70)–O(1) 1.389(5), C(70)–P(1)–C(1) 102.9(2), and O(1)–B(13)–C(2) 106.7(3).



Scheme 5 Proposed mechanism for the formation of **4**.

the final product **4** with the generation of the fourth stereocenter.

Conclusions

In summary, a new FLP 1-PPh$_2$-2-BPh$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (**2**) having a carborane backbone was prepared and structurally characterized. Though it did not split H$_2$, it reacted with p-R$_2$NC$_6$H$_4$C≡CH to give typical C≡C bond insertion products **3**. In the presence of an excess amount of p-R$_2$NC$_6$H$_4$C≡CH, unprecedented tri-insertion products **4** were isolated. The structural analyses confirmed that four stereocenters including one quaternary carbon had been created in a single process. After trapping and structural characterization of a key intermediate, a plausible mechanism was proposed, which involves sequential alkyne addition and 1,2-migration. These new properties enrich the chemistry of FLPs.

The results of this work indicate that the chemical properties of intramolecular vicinal FLPs (Scheme 2) are not only dependent on the P⋯B distance, the hybridization of the vicinal carbons, and electronic properties of the backbone, but also the steric hindrance of the bridging unit. As FLPs can be easily incorporated into an *o*-carborane cage,[20] a new class of FLPs with various substituents would be accessible for the development of new FLP reactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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