Carbon Monoxide Bond Cleavage Mediated by an Intramolecular Frustrated Lewis Pair: Access to New B/N Heterocycles via Selective Incorporation of Single Carbon Atoms

Journal:	*ChemComm*
Manuscript ID	CC-COM-10-2021-005673.R1
Article Type:	Communication

Journal Name

COMMUNICATION

Carbon Monoxide Bond Cleavage Mediated by an Intramolecular Frustrated Lewis Pair: Access to New B/N Heterocycles via Selective Incorporation of Single Carbon Atoms

Chamila P. Manankandayalage, Daniel K. Unruh and Clemens Krempner*

**Utilizing an intramolecular frustrated Lewis pair (FLP) decorated with a strongly donating guanidino moiety enabled the formation of a thermally remarkably stable FLP-CO adduct, which at 120°C underwent CO migration to form an acyl borane. Both compounds underwent rapid CO cleavage in the presence of strong electrophiles leading to the selective formation of a range of new 1,2- and 1,3-benzazaboroles in good yields under mild conditions.**

The deoxygenation of carbon monoxide (i.e. C≡O cleavage) is a challenging chemical transformation of high relevance owing to its involvement in the generation of hydrocarbon products through Fischer-Tropsch chemistry.[1] To provide a better mechanistic understanding, significant efforts have recently been made toward the isolation and characterization of potential intermediates.[2] Particularly main group element hydrides and anions, as well as low-valent main group systems proved to be surprisingly effective in reductively coupling CO to C-C bonded species,[3-9] while only in rare cases has the deoxygenation of CO been accomplished (Scheme 1).[10,11] For example, Stephan's group reported the cleavage of CO (from syngas) utilizing the frustrated Lewis pair (FLP) $B(C_6F_5)_3/P(tBu)_3$.[11a] Erker and co-workers disclosed the reaction of an intramolecular FLP with CO and $HB(C_6F_5)_2$ to give a bora-oxirane species, which underwent CO bond cleavage upon exposure to H_2.[11b] Much less is known regarding carbon monoxide deoxygenation as a synthetic strategy to selectively and predictably incorporate single carbon atoms into organic molecules. Only Hillmann in his seminal work and later Brown have successfully employed CO as a C-1 synthon in the synthesis of a range of aliphatic carbinols from trialkylboranes (Scheme 2).[12] Notably, these reactions were proposed to proceed via insertion of CO into the B-C bond to

intermediately form acyl boranes, but their involvement could not be verified experimentally.[13]
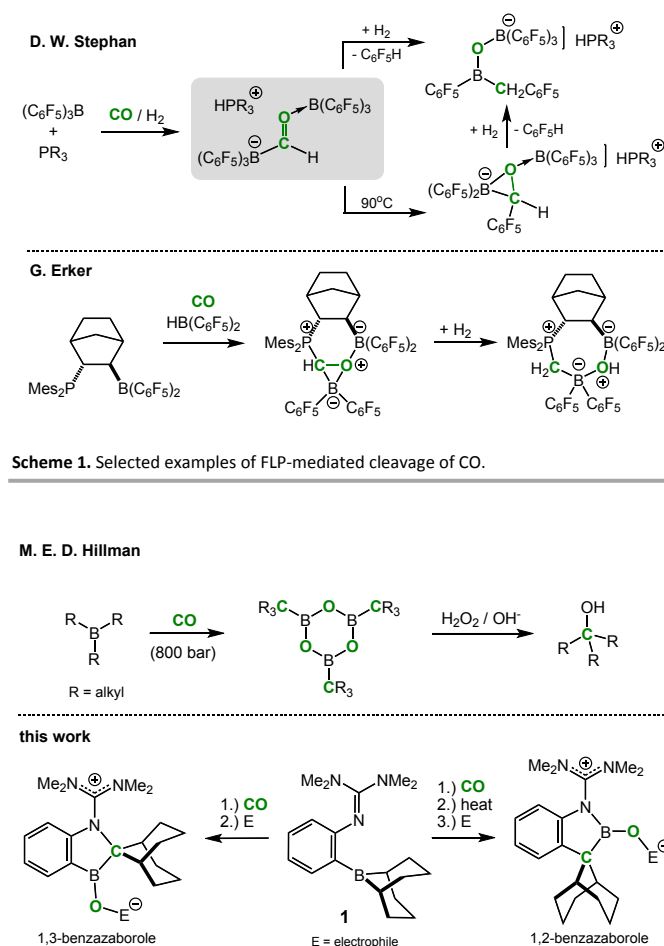
Scheme 1. Selected examples of FLP-mediated cleavage of CO.

Scheme 2. Selective incorporation of single carbon atoms through carbon monoxide bond cleavage.

We recently introduced intramolecular FLP **1** (Scheme 2) decorated with a highly basic and strongly donating guanidino unit, which

a. *Department of Chemistry and Biochemistry, Texas Tech University, Memorial Dr. & Boston, Lubbock, TX, 79409, USA. Fax: 806-742-1289; Tel: 806-834-3507; E-mail: clemens.krempner@ttu.edu*
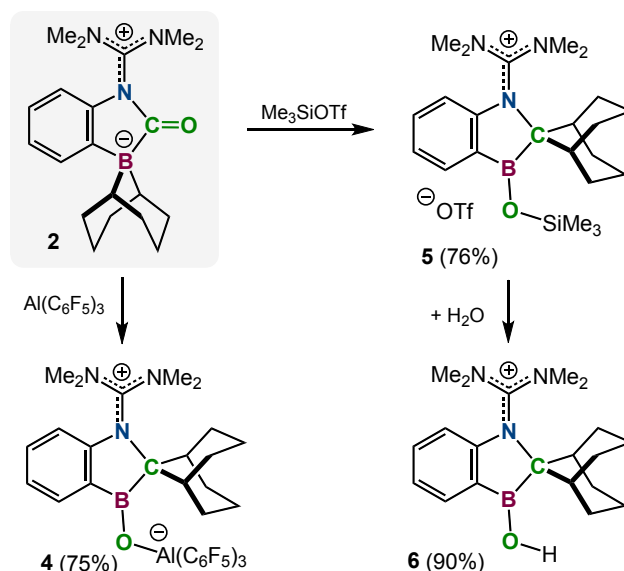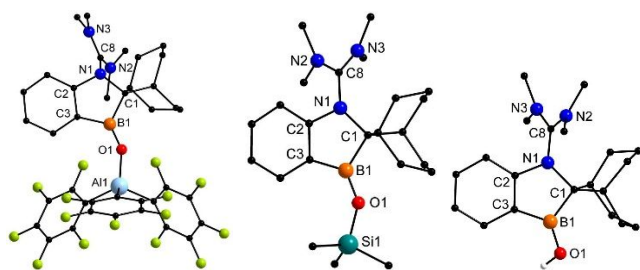
mediated the activation of E-H bonds in NH_3, $HC\equiv CH$, and H_2.[14] We envisioned that strong donation of the FLP to CO could substantially weaken the $C\equiv O$ bond thereby facilitating its full cleavage. Herein, we will demonstrate that interactions of **1** with CO and electrophiles will not only result in facile cleavage of the $C\equiv O$ bond, this approach also enables the regioselective incorporation of single carbons to produce a range of new 1,2- and 1,3-benzazaboroles under mild conditions.[15]

Upon exposure of CO to a hexane solution of **1**, a crystalline material precipitated, which was identified as FLP-CO adduct **2** (85%) (Figure 1). Its ^{11}B NMR spectrum displays a signal at -15 ppm confirming a tetra-coordinated boron centre. The ^{13}C NMR spectrum exhibits a signal at 209.1 ppm, and the IR spectrum shows absorption at 1708 cm^{-1}, consistent with the presence of a C=O group in the molecule. The X-ray data confirmed the formation of a five-membered ring with B1-C1 and C1-N1 distances of 1.639 and 1.501 Å, resp. The most striking feature is the C1-O1 bond length of 1.212 Å, which is one of the longest for FLP-CO adducts reported [16] and consistent with our hypothesis that the interaction of CO with a strong donor and a weak acceptor can substantially weaken the $C\equiv O$ bond. Notable is the thermal behaviour of **2**. It does not release CO up to 80°C even after heating overnight in C_6D_6. Most FLP-CO adducts are only stable at low temperatures. However, at ca. 120°C, the solution turned yellow with simultaneous formation of yellow crystals. The isolated crystals were identified by NMR and IR spectroscopy as acyl borane **3** (50% yield). Its connectivity was further supported by SC-XRD (Figure 1); the C=O bond [C1-O1, 1.237 Å] of **3** was found to be somewhat longer than that of **2**. Note that isolable acyl boranes derived from reactions of CO with organo boranes have not been reported in the literature.[17]
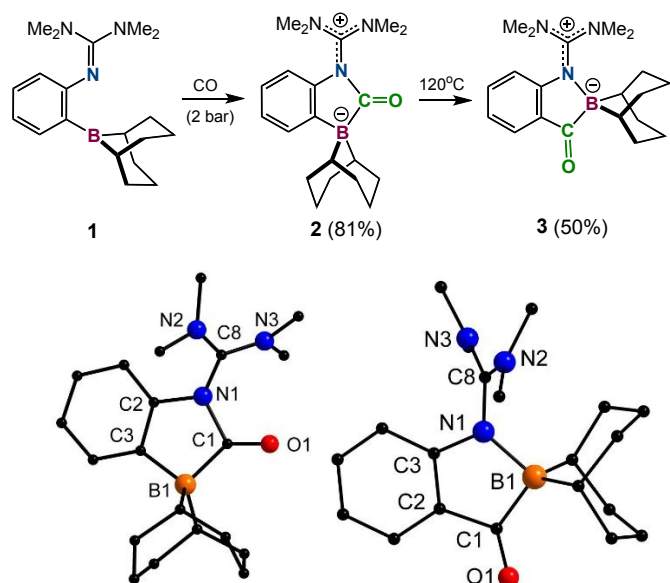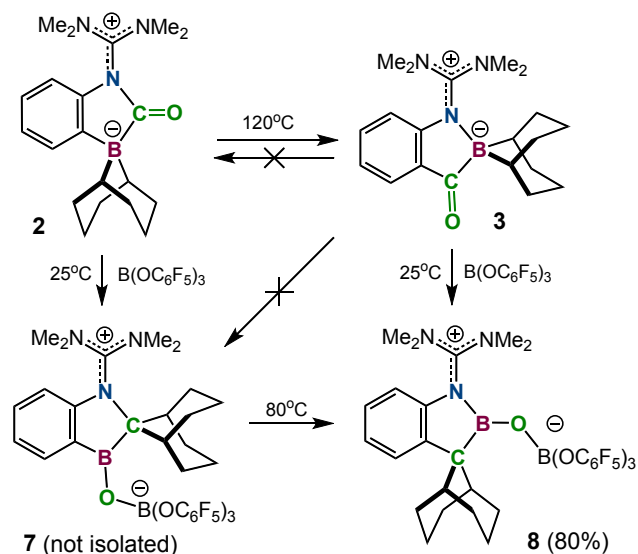
Envisioning the carbonyl oxygen of FLP-CO adduct **2** to be sufficiently Lewis basic, reactions with various electrophiles were investigated (Scheme 3). While treatment of **2** with BPh_3 did not lead to any Lewis acid-base interaction, interactions with $B(C_6F_5)_3$ gave mixtures of products. Gratifyingly, the reaction of **2** with $Al(C_6F_5)_3$ resulted in a single product, which by NMR spectroscopy and SC-XRD was identified as 1,3-benzazaborole **4** (75% yield). The ^{11}B NMR spectrum showed a broad signal at 43 ppm typical for a trigonal planar boron environment. The ^{13}C NMR spectrum of **4** revealed a new signal at 70.1 ppm attributable to an aliphatic quaternary carbon, while the carbon signal of the CO carbon found in **2** at 209 ppm had disappeared. The X-ray data confirmed the connectivity of the 1,3-azaborole ring structure with exocyclic B-O-Al and bicyclo[3.3.1]non-9-ylidene moieties being the most notable structural features. The formation of **4** formation is the result of a two-fold alkyl migration from the BBN framework to CO, by which the CO triple bond is cleaved. The reaction of **2** with Me_3SiOTf proceeded similarly in generating 3-trimethylsiloxy-1,3-benzaazaborole **5** in 76% yield.[18] Compound **5** is hydrolytically sensitive and smoothly converts in "wet" benzene or toluene to borinic acid **6** in yields of 90%. Since Me_3SiOTf does not react with FLP **1**, borinic acid **6** can also be synthesized in one pot from the reaction of **1** with Me_3SiOTf and CO. Subsequent hydrolysis with "wet" benzene affords **6** in overall yields of 85%. The ^{13}C NMR spectra of **5** and **6** show features similar to **4** with the quaternary borole ring carbons of the bicyclo[3.3.1]non-9-ylidene moiety appearing at 72.6 (**5**) and 70.2 (**6**) ppm. The ^{1}H NMR spectrum of **6** in DMSO-D_6 exhibits a signal at 11 ppm attributable to an OH group, which is further supported by a broad absorption at ~3213 cm^{-1} (solid) in the IR spectrum. The X-ray data of **4-6** (Figure 2) show structural similarities with elongated N1-C1 (1.53-1.55 Å) and B1-C1 (ca. 1.63 Å) distances. The exocyclic B1-O1 bonds of **5** [1.344 Å] and **6** [1.349 Å] are relatively short but longer than that of **4** with 1.322 Å.

Figure 1. Formation and solid-state structures of **2** (left) and **3** (right). All H atoms are omitted for clarity. Selected bond lengths [Å]: **2**, C1-O1 1.212(2), N1-C8 1.367(2), N2-C8 1.338(2), N3-C8 1.330(2), N1-C2 1.427(2), N1-C1 1.501(2), C1-B1 1.639(2), C3-B1 1.624(2); **3**, C1-O1 1.237(3), N1-C8 1.365(4), N2-C8 1.338(4), N3-C8 1.342(4), N1-B1 1.665(4), C1-B1 1.617(4).

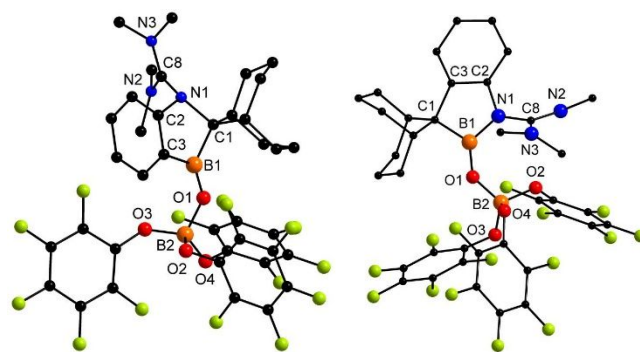**Scheme 3.** Reactions of **2** with electrophiles.

COMMUNICATION

Figure 2. Solid-state structures of **4** (left), **5** (centre) and **6** (right). Triflate anions of **5** and **6** and all H atoms except for OH of **6** are omitted for clarity. Selected bond lengths [Å] and angles [°]: **4**, Al1-O1 1.739(1), O1-B1 1.322(2), N1-C8 1.383(2), N1-C1 1.530(2), N2-C8 1.331(2), N3-C8 1.335(2), C1-B1 1.627(2), B1-O1-Al1 151.3(1); **5**, Si1-O1 1.656(1), O1-B1 1.344(2), N1-C1 1.536(2), N1-C8 1.394(2), N2-C8 1.326(2), N3-C8 1.337(2), C1-B1 1.632(3), B1-O1-Si1 145.4(1); **6**, O1-B1 1.349(4), N1-C8 1.378(3), N1-C1 1.550(3), N2-C8 1.345(4), N3-C8 1.338(4), C1-B1 1.626(4).

Figure 3. Solid-state structures of **7** (left) and **8** (right). All H atoms are omitted for clarity. Selected bond lengths [Å]: **7**, O1-B1 1.332(2), O1-B2 1.455(2), N1-C8 1.385(2), N2-C8 1.336(2), N3-C8 1.334(2), C1-B1 1.616(2), N1-C1 1.534(2); **8**, N1-B1 1.478(2), O1-B1 1.329(2), O1-B2 1.446(2), C1-B1 1.613(2), N1-C8 1.380(2), N2-C8 1.336(2), N3-C8 1.328(2).

Since our aforementioned attempts with $B(C_6F_5)_3$ as Lewis acid were unsuccessful, $B(OC_6F_5)_3$, its more oxophilic congener, was reacted with **2** in C_6D_6 (Scheme 4). The reaction proceeded smoothly at 25°C with formation of 1,3-benzaazaborole **7** as the major product (Figure 3). NMR spectroscopic analysis of the reaction revealed the presence of a by-product, which upon heating for ca. 2 hours at 80°C became the sole product. Characterization by NMR spectroscopy and SC-XRD (Figure 3) confirmed the formation of 1,2-benzaazaborole **8**, the isomer of **7**. While both isomers showed similar ^1H and ^{13}B NMR spectroscopic features, the ^{13}C NMR spectra revealed marked chemical shift differences for the quaternary carbons with 68.7 (**7**) and 38.5 (**8**) ppm. Note that the 1,3-boroles **4** and **5** did not undergo isomerization to the respective 1,2-boroles at 80°C. Puzzled by the unexpected formation of isomer **8**, we wondered whether acyl borane **3** would also undergo skeletal rearrangements in the presence of strong Lewis acids. In fact, treatment of $B(OC_6F_5)_3$ with **3** at 25°C in C_6D_6 proceeded smoothly in quantitatively generating **8** in solution. Note that the isomer 1,3-benzaazaborole **7** was not detected throughout the reaction suggesting the conversion of acyl borane **3** to **8** not to proceed via **7**.
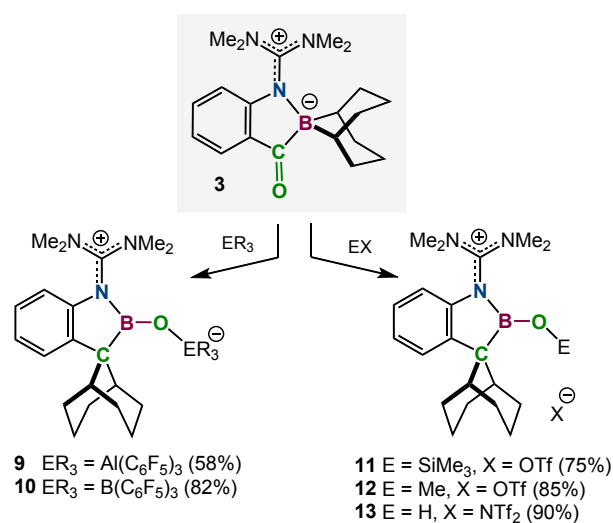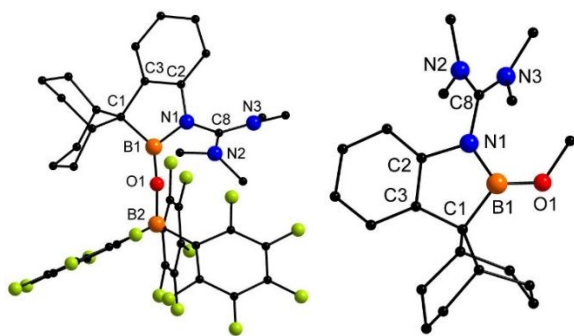
The ability of **3** to undergo CO bond cleavage, prompted us to investigate interactions with other electrophiles (Scheme 5). $B(C_6F_5)_3$ and $Al(C_6F_5)_3$ reacted smoothly with **3** at 25°C to generate 1,2-benzazaboroles **9** and **10**, resp. Also Me_3SiOTf, MeOTf, and $HNTf_2$, upon reacting with **3**, resp., at 25°C caused the CO moiety to be cleaved smoothly providing the 1,2-benzazaboroles **11**-**13** in good yields. ^{13}C NMR spectroscopic analysis of the isolated 1,2-benzazaboroles **9-13** revealed singlets of the quaternary azaborole ring carbons ranging from 38-42 ppm, similar to what was found for **8** ($\delta = 38.5$ ppm). A broad singlet in the ^1H NMR spectrum at 7.76 ppm and broad absorption in the IR spectrum at 3303 cm^{-1} confirmed the presence of an OH group in **13**. The SC-XRD data of **8**, **10,** and **12** (Figures 3 and 4) confirmed the connectivity of the 1,2-benzazaborole structures and revealed full cleavage of CO with the formation of two new C-C bonds. The central boron atoms adopt trigonal planar geometries, and the most notable bond parameters are the relatively short B1−O1 bond lengths for **8** [1.329 Å] and **10** [1.316 Å], which are relatively close to reported distances for Lewis acid stabilized B=O double bonds ranging from 1.29-1.33 Å.[19]

Scheme 4. Reactions of **2** and **3** with $B(OC_6F_5)_3$.

9 $ER_3 = Al(C_6F_5)_3$ (58%)
10 $ER_3 = B(C_6F_5)_3$ (82%)

11 E = $SiMe_3$, X = OTf (75%)
12 E = Me, X = OTf (85%)
13 E = H, X = NTf_2 (90%)

Scheme 5. Reaction of **3** with electrophiles.

Figure 4. Solid-state structures of **10** (left) and **12** (right). All H atoms are omitted for clarity. Selected bond lengths [Å]: **10**, N1-B1 1.510(2), O1-B1 1.316(2), O1-B2 1.478(2), C1-B1 1.622(2), N1-C8 1.370(2), N2-C8 1.333(2), N3-C8 1.340(2); **12**, O1-C21 1.436(3), O1-B1 1.349(3), N1-C8 1.398(3), N1-B1 1.441(3), N2-C8 1.327(3), N3-C8 1.327(2), C1-B1 1.614(3).

In summary, we report the facile cleavage of the carbon monoxide triple bond mediated by an intramolecular FLP featuring a strongly donating guanidino unit. This FLP system is capable of strongly binding to CO to form a remarkably stable FLP-CO adduct, which at 120°C isomerizes via CO migration to an acyl borane. Both compounds, FLP-CO adduct and acyl borane smoothly react with strong organic and organometallic electrophiles to selectively form a range of new 1,2-and 1,3-benzazaborole salts in excellent yields. Given that carbon monoxide is an inexpensive and readily available C-1 source, CO bond cleavage offers an alternative and promising approach toward the targeted design of organic and organometallic molecules and materials as highlighted by the one-pot synthesis of borinic acid **6**.[20] We are currently working to extend the scope of this new transformation to B/N heterocycles with other substituents at boron and nitrogen.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1   R. B. Anderson, H. Kölbel and M. Ralek, The Fischer–Tropsch Synthesis; Academic Press Inc.: New York, 1984; p 301.
2   R. Y. Kong and M. R. Crimmin, *Dalton Trans.*, 2020, **49**, 16587.
3   a) A. V. Protchenko, P. Vasko, D.C.H. Do, J. Hicks, M.A. Fuentes, C. Jones and S. Aldridge, *Angew. Chem. Int. Ed.* 2019, **58**, 1808-1812; b) M. D. Anker, M. S. Hill, J. P. Lowe and M. F. Mahon, *Angew. Chem. Int. Ed.* 2015, **54**, 10009-10011; c) W. Lu, H. Hu, Y. Li, R. Ganguly and R. Kinjo, *J. Am. Chem. Soc.* 2016, **138**, 6650-6661.
4   a) K. Yuvaraj, I. Douair, A. Paparo, L. Maron and C. Jones, *J. Am. Chem. Soc.* 2019, **141**, 8764-8768; b) K. Yuvaraj, I. Douair, D. D. L. Jones, L. Maron and C. Jones, *Chem. Sci.* 2020, **11**, 3516-3522.
5   X. Wang, Z. Zhu, Y. Peng, H. Lei, J. C. Fettinger and P. P. Power, *J. Am. Chem. Soc.* 2009, **131**, 6912–6913.
6   A. Heilmann, J. Hicks, P. Vasko, J. M. Goicoechea and S. Aldridge, *Angew. Chem. Int. Ed.* 2020, **59**, 4897-4901.
7   a) H. Braunschweig, T. Dellermann, R. D. Dewhurst, W. C. Ewing, K. Hammond, J. O. C. Jimenez-Halla, T. Kramer, I. Krummenacher, J. Mies, A. K. Phukan and A. Vargas, *Nature Chem.* 2013, **5**, 1025-1028; b) R. Y. Kong and M. R. Crimmin, *J. Am. Chem. Soc.* 2018, **140**, 13614-1361; c) B. Wang, G. Luo, M. Nishiura, Y. Luo and Z. Hou, *J. Am. Chem. Soc.* 2017, **139**, 16967-16973; d) A. Phanopoulos, S. Pal, T. Kawakami and K. Nozaki, *J. Am. Chem. Soc.* 2020, **142**, 14064-14068.
8   M. Xu, Z.-W. Qu, S. Grimme and D. W. Stephan, *J. Am. Chem. Soc.* 2021, **143**, 634-638.
9   L. D. Curless, E. R. Clark, J. Cid, A. Del Grosso and M. J. Ingleson, *Chem. Commun.* 2015, **51**, 10903-10906.
10 a) M. Majumdar, I. Omlor, C. B. Yildiz, A. Azizoglu, V. Huch and D. Scheschkewitz, *Angew. Chem., Int. Ed.* 2015, **54**, 8746-8750; b) Y. Wang, A. Kostenko, T. J. Hadlington, M.-P. Luecke, S. Yao and M. Driess, *J. Am. Chem. Soc.* 2019, **141**, 626-634; c) Y. Xiong, S. Yao, T. Szilvasi, A. Ruzicka and M. Driess, *Chem. Commun.* 2020, **56**, 747-750.
11 a) R. Dobrovetsky and D. W. Stephan, *J. Am. Chem. Soc.* 2013, **135**, 4974-4977; b) M. Sajid, G. Kehr, C. G. Daniliuc and G. Erker, *Angew. Chem. Int. Ed.* 2014, 53, 1118-1121; c) M. Devillard, B. de Bruin, M. A. Siegler and J. I. van der Vlugt, *Chem. Eur. J.* 2017, 23, 13628-13632; d) Q. Sun, C. G. Daniliuc, C. Mück-Lichtenfeld, K. Bergander, G. Kehr and G. Erker, *J. Am. Chem. Soc.* 2020, **142**, 17260-17264.
12 a) M. E. D. Hillman, *J. Am. Chem. Soc.* 1962, **84**, 4715-4720; b) H. C. Brown and M. W. Rathke, *J. Am. Chem. Soc.* 1967, **89**, 2737-2738.
13 H. C. Brown, *Acc. Chem. Res.* 1969, **2**, 65-72.
14 C. Manankandayalage, D. K. Unruh and C. Krempner, *Chem. Eur. J.* 2021, **27**, 6263-6273.
15 For selected examples of aza- and benzazaboroles: a) W. Lu, Y. Li, R. Ganguly and R. Kinjo, *J. Am. Chem. Soc.* 2017, **139**, 5047-5050; b) J. Li, C. G. Daniliuc, K. K. Kartha, G. Fernandez, G. Kehr and G. Erker, *J. Am. Chem. Soc.* 2021, **143**, 2059-2067; c) S. Kuwano, Y. Hosaka and T. Arai, *Chem. Eur. J.* 2019, **25**, 12920-12923.
16 For intramolecular FLP-CO adducts: a) M. A. Dureen and D. W. Stephan, *J. Am. Chem. Soc.* 2010, **132**, 13559-13568; b) A. Ramos, A. Antiñolo, F. Carrillo-Hermosilla, R. Fernández-Galán, M. del Pilar Montero-Rama, E. Villaseñor, A. Rodríguez-Diéguez and D. García-Vivó, *Dalton Trans.* 2017, **46**, 10281-10299; c) M. Sajid, A. Lawzer, W. Dong, C. Rosorius, W. Sander, B. Schirmer, S. Grimme, C. G. Daniliuc, G. Kehr and G. Erker, *J. Am. Chem. Soc.* 2013, **135**, 18567-18574; d) A. R. Cabrera, R. S. Rojas, M. Valderrama, P. Plüss, H. Berke, C. G. Daniliuc, G. Kehr and G. Erker, *Dalton Trans.* 2015, **44**, 19606-19614; e) L.-M. Elmer, G. Kehr, C. G. Daniliuc, M. Siedow, H. Eckert, M. Tesch, A. Studer, K. Williams, T. H. Warren and G. Erker, *Chem. Eur. J.* 2017, **23**, 6056-6068; f) A. Ueno, X. Tao, C. G. Daniliuc, G. Kehr and G. Erker, *Organometallics* 2018, **37**, 2665-2668.
17 For reviews on acyl boranes: a) F. K. Scharnagl, S. K. Bose and T. B. Marder, *Org. Biomol. Chem.* 2017, **15**, 1738-17523; b) D. Wu, J. Taguchi, M. Tanriver and J. W. Bode, *Angew. Chem.* 2020, **132**, 16993-170043.
18 Reactions of FLP-CO adduct **2** with MeOTf and HNTf$_2$, resp., resulted in loss of CO (see SI).
19 Y. K. Loh, K. Porteous, M. Á. Fuentes, D. C. H. Do, J. Hicks and S. Aldridge, *J. Am. Chem. Soc.* 2019, **141**, 8073-8077.
20 For applications of borinic acids: a) E. Dimitrijevića and M. S. Taylor, *Chem. Sci.* 2013, **4**, 3298-3303; b) E. Dimitrijevića and M. S. Taylor, *ACS Catal.* 2013, **3**, 945-962; c) K. Zhao, S. Yang, Q. Gong, L. Duan and Z. Gu, *Angew. Chem.* 2021, **133**, 5852-5857.