A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
International Edition
www.angewandte.org

Title: The [(NHC)B(H)C6F5]+ Cations and their [B](H)-CO Borane Carbonyls

Authors: Gerhard Erker, Chaohuang Chen, Jun Li, Constantin G. Daniliuc, Christian Mück-Lichtenfeld, and Gerald Kehr

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.202009353

Link to VoR: https://doi.org/10.1002/anie.202009353

WILEY-VCH

The $[(NHC)B(H)C_6F_5]^+$ Cations and their [B](H)-CO Borane Carbonyls

Chaohuang Chen,[a] Jun Li,[a] Constantin G. Daniliuc,[a] Christian Mück-Lichtenfeld,[a] Gerald Kehr,[a] and Gerhard Erker*[a]

Dedication ((optional))

[a] Dr. C. Chen, Dr. J. Li, Dr. C. G. Daniliuc, Dr. C. Mück-Lichtenfeld, Dr. G. Kehr, Prof. Dr. G. Erker
Organisch-Chemisches Institut
Westfälische Wilhelms-Universität Münster
Corrensstraße 40, 48149 Münster (Germany)
E-mail: erker@uni-muenster.de

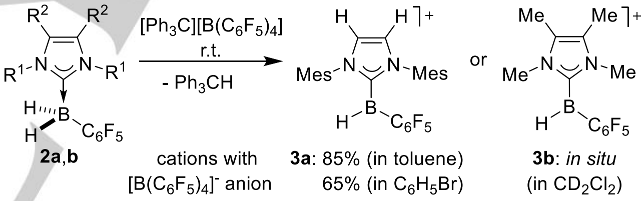
Supporting information for this article is given via a link at the end of the document.

Abstract: Hydride abstraction from the heterocyclic carbene borane adducts $(NHC)BH_2C_6F_5$ (NHC: IMes or IMe_4) gives the B–H containing $[(NHC)B(H)C_6F_5]^+$ borenium cations. They add carbon monoxide to give the respective $[(NHC)B(H)(C_6F_5)CO]^+$ boron carbonyl cations. Carbon nucleophiles add to the boron carbonyl to give [B](H) acyls. Hydride reduces the [B]CO cation to hydroxymethylborane derivatives.

Borocations show an interesting chemistry.[1] They are increasingly used as reactive boron containing reagents[2] and as active catalysts in organic synthesis.[3] Two types of B–H containing borocations were described, the tetracoordinated boronium ions[4] and the less frequently encountered B–H containing planar-tricoordinate borenium ions. The latter were often only spectroscopically characterized[5,6] or postulated as intermediates.[7] Alcarazo et al. described a rare example that was characterized by X-ray diffraction, namely the $[(carbodiphosphorane)BH_2]^+$ cation.[8] H. Wang had structurally characterized the $HSiEt_3$ adduct of an $[(NHC)(\sigma\text{-carboranyl})BH]^+$ cation recently.[9] We have now found a convenient entry to strongly electrophilic $[(NHC)B(H)C_6F_5]^+$ cations and have begun to develop their typical chemistry.[10] These compounds are of interest for studying CO reduction chemistry. The neutral B–H boranes usually do not reduce carbon monoxide unless catalyzed: they form borane carbonyls instead.[11,12] This posed the question whether our new $[(NHC)B(H)C_6F_5]^+$ B–H borenium cations would behave similarly or if these strongly electrophilic B–H cations would exhibit a different behavior toward the CO molecule.

We reacted each of the N-heterocyclic carbenes (NHCs) 1,3-dimesitylimidazol-2-ylidene (IMes, **1a**) and 1,3,4,5-tetramethylimidazol-2-ylidene (IMe_4, **1b**) with Lancaster's reagent $[H_2B(C_6F_5)SMe_2]$[13] and isolated the NHC-borane adducts in good yield [$(IMes)BH_2C_6F_5$ **2a**, 80%; $(IMe_4)BH_2C_6F_5$, **2b**, 72%]. Both were characterized spectroscopically [**2a**: ^{11}B NMR: δ -32.0 ($^1J_{BH}$ ~ 90 Hz); ^{13}C NMR: δ 170.1 ("carbene-C")] and by X-ray diffraction (see the Supporting Information for details including the depicted structures).

Hydride abstraction from $(IMes)BH_2C_6F_5$ (**2a**) with trityl tetrakis(pentafluorophenyl)borate gave the $[(IMes)B(H)C_6F_5][B(C_6F_5)_4]$ salt **3a** in good yield [^{11}B: δ 27.1, ^1H: δ 5.02 ([B]H) in C_6D_5Br; ^{11}B: δ 50.6, ^1H: δ 5.90 ([B]H) in CD_2Cl_2] (Scheme 1). The borenium salt **3a** was characterized by X-ray diffraction (Figure 1). The cation features a planar-tricoordinate borenium ion structure. The boron–C(NHC) and boron–C_6F_5 linkages are about equal in length. The bulky mesityl substituents are both rotated >70° from the central NHC plane, whereas the C_6F_5 plane is rotated a little less from the central B–NHC plane (ca. 40°). The $[(IMe_4)B(H)C_6F_5]^+$ borenium system **3b** was generated analogously. It was in situ characterized spectroscopically.



Scheme 1. Synthesis of B–H-containing borenium cations.

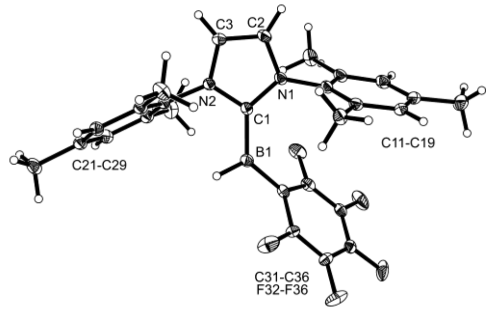
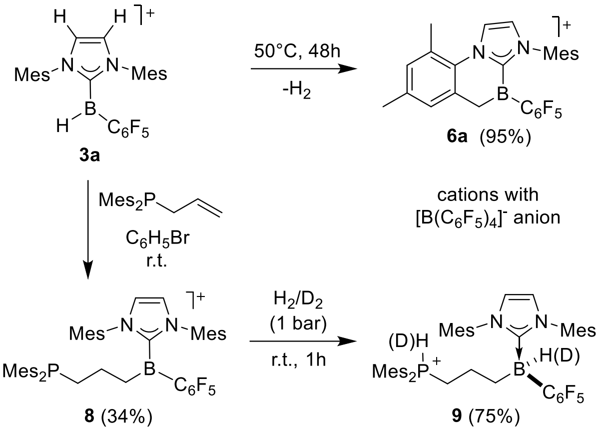


Figure 1. Molecular structure of compound **3a** (only the cation is depicted; thermal ellipsoids are set at 30% probability). Selected bond lengths (Å) and angles (°): C1–B1 1.559(3), B1–C31 1.557(8), C1–N1 1.362(3), C1–N2 1.356(3); N1–C1–N2 105.6(2), C1–B1–C31 128.3(8), C1–N2–C21–C22 -73.4(3), C2–N1–C11–C12 -71.8(3).

Both the compounds **3a** and **3b** are strong Lewis acids. The simplified Gutmann Beckett method[14] gave a shifting of the ^{31}P NMR signal of the triethylphosphane donor (TPO) upon coordination to **3a** of Δδ = +35.6 ppm (in CD_2Cl_2 solution; **3b**: +37.6 ppm), which renders them more Lewis acidic than

$B(C_6F_5)_3$ (Δδ = +26.7 or Piers' borane $HB(C_6F_5)_2$ (Δδ = +31.4 ppm).



Scheme 2. Reactions of the B–H borenium ion **3a**.

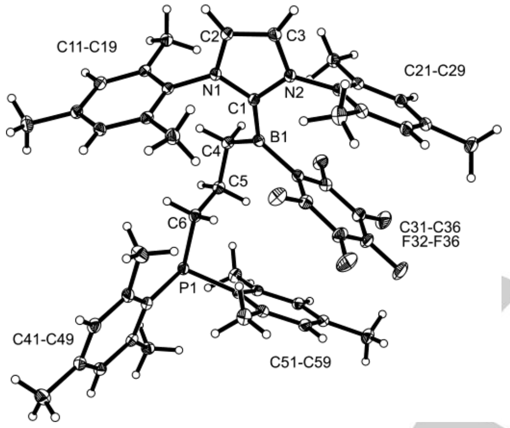


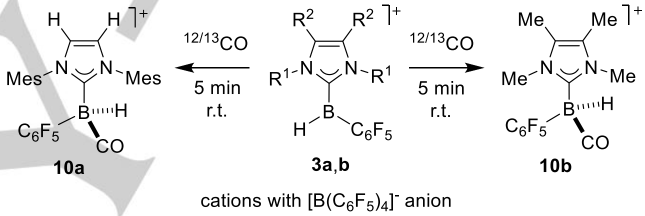
Figure 2. A view of the trimethylene-bridged FLP salt **8** (only the cation is depicted; thermal ellipsoids are set at 30% probability). Selected bond lengths (Å) and angles (°): B1–C1 1.579(4), B1–C4 1.559(4), P1–C6 1.852(2), $\Sigma B1^{CCC}$ = 359.8, $\Sigma P1^{CCC}$ = 319.3, P1–C6–C5–C4 178.3(2), C6–C5–C4–B1 61.2(3).

Both the $[(NHC)B(H)C_6F_5]^+$ cations each add one additional equivalent of the respective NHC to form the corresponding $[(NHC)_2B(H)C_6F_5]^+$ boronium salts (**4a**,**b**; with $[B(C_6F_5)_4]^-$ counter anion). Compound **3a** reacts slowly with CD_2Cl_2 (6h, r.t.) by hydride for chloride exchange. A donor stabilized derivative $[(NHC)B(xylyl\text{-}isocyanide)(Cl)C_6F_5]^+$ (**5a**) was isolated and characterized by X-ray diffraction. Compound **3a** is thermally labile. Keeping it for a prolonged period of time at 50 °C (48 h, in C_6H_5Br) resulted in a C–H activation reaction at one of the adjacent mesityl substituents with liberation of dihydrogen. The resulting C–H activation compound (**6a**) was isolated and characterized spectroscopically and by an X-ray crystal structure analysis (see the Supporting Information for details of the characterization of the compounds **4** to **6**).

Compound **3a** is an active hydroboration reagent. Its reaction with 4-phenyl-1-butene (r.t., 5 min in C_6H_5Br) generated the respective alkyl borenium compound. It was isolated as isonitrile (CN–Xyl) stabilized adduct (**7a**, isolated in 91% yield). It was characterized by X-ray diffraction (see the Supporting Information for details).

The cation of **3a** reacted rapidly at r.t. with allyl(dimesityl)phosphane to give the cationic frustrated P/B Lewis pair **8** [NMR in CD_2Cl_2: δ -22.6 (^{31}P), δ 70.3 (^{11}B)]. Together with the Δδ $^{19}F_{m,p}$ = 12.4 ppm chemical shift difference these data indicate Lewis acidic planar tricoordinate boron and, consequently, an open FLP structure of compound **8** in solution. The X-ray crystal structure analysis confirmed this (see Fig. 2).

The FLP **8** is an active metal-free hydrogen splitting reagent. Reaction with dihydrogen (1.0 bar, r.t., 1h) gave the $[PH/BH(IMes)][B(C_6F_5)_4]$ salt **9**, isolated in 75% yield. It was characterized by C,H,N elemental analysis, by NMR spectroscopy [PH: δ 7.14 (^1H), δ -12.3 (^{31}P), $^1J_{PH}$ = 467 Hz, BH: δ -22.8 ($^1J_{BH}$ = 82 Hz)] and by an X-ray crystal structure analysis (depicted in the Supporting Information). The reaction of the FLP **8** with dideuterium gave the respective product **9**-D_2. It showed the corresponding PD/BD resonances in the ^2H NMR spectrum. The high dihydrogen splitting reactivity of the cationic FLP **8** is remarkable since its $-B(C_6F_5)_2$ containing neutral "parent" trimethylene-linked P/B analogue shows no H_2-splitting activity due to a thermodynamic restriction.[15]



Scheme 3. Reaction of the borenium cations **3** with carbon monoxide.

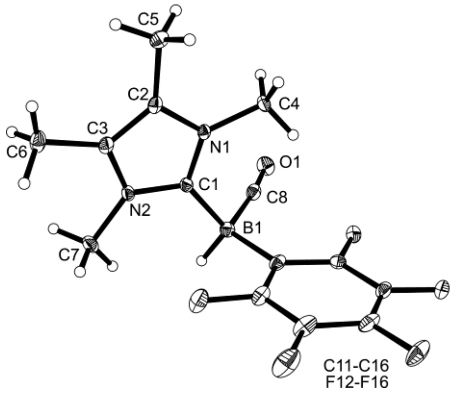


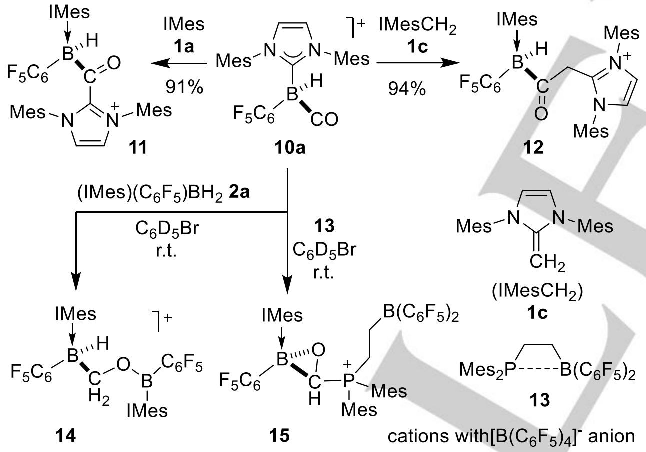
Figure 3. A view of the molecular structure of the boron-carbonyl **10b** (only the cation is shown; thermal ellipsoids are set at 30% probability). Selected bond lengths (Å) and angles (°): C1–N1 1.350(4), C1–N2 1.339(4), C1–B1 1.607(4), B1–C8 1.608(5), C8–O1 1.111(4), B1–C11 1.611(4), N1–C1–N2 106.1(2), C1–B1–C8 105.7(2), B1–C8–O1 173.3(3), C8–B1–C11 113.0(3), C8–B1–C1–N1 -57.6(4), C11–B1–C1–N1 65.9(4), C8–B1–C11–C16 -5.3(4).

Both the (NHC)borenium compounds **3a** and **3b** react rapidly with carbon monoxide (1 to 1.5 bar CO, 5 min at r.t.) to give the respective B–H containing borenium carbonyls **10a** and **10b**, respectively. Compound **10a** shows a ^{13}C NMR [B]–C≡O resonance at δ 165.6. The ^{11}B NMR resonance of the cationic unit was located at δ -29.2 [^1H NMR: $[B]^+(H)$ signal at δ 3.75].

10.1002/anie.202009353

The B–H borenium carbonyl salt **10a** was characterized by X-ray diffraction. The structure is depicted in the Supporting Information. The cation shows a pseudo tetrahedral structure. The sum of CCC angles at the boron atom amounts to $\Sigma B1^{CCC}$ = 332.0°. The B–C–O angle is slightly bent (169.3(3)°) and the CO bond is short (1.123(3) Å), actually slightly shorter than free CO. Compound **10a** shows a sharp IR C≡O band at $\tilde{\nu}$ = 2205 cm^{-1} (KBr).

The IMe_4 containing B–H borenium carbonyl **10b** was characterized spectroscopically from the in situ experiment [^1H NMR: δ 4.18 (BH), δ 3.70 (NMe), δ 2.25 (=CMe); ^{13}C NMR: δ 169.8 [B]–C≡O; ^{11}B NMR: δ -30]. The X-ray crystal structure analysis showed the structural framework of the parent borenium ion (**3b**) to which the CO molecule had added. The resulting new boron-carbon bond (B1–C8 1.608(5) Å) is in the same order of magnitude as the adjacent B1–C1 and B1–C11 linkages to the IMe_4 and the C_6F_5-substituents (Figure 3). The boron carbonyl unit is close to linear. The C–O bond of the boron-carbonyl unit is short. The coordination geometry at the boron atom is distorted tetrahedral ($\Sigma B1^{CCC}$ = 330.7°). The conformational orientation of the B–C≡O vector to the plane of the IMe_4 ligand is close to gauche, whereas it is oriented almost in plane with the adjacent C_6F_5 substituent. The borenium carbonyl **10b** shows a sharp IR CO-stretching band at $\tilde{\nu}$ = 2223 cm^{-1} (KBr). We also reacted the borenium salts **3a**,**b** with ^{13}C enriched carbon monoxide. As expected, the isotopologues ^{13}C-**10a**,**b** showed the IR-^{13}CO stretching band at $\tilde{\nu}$ = 2155 cm^{-1} and 2172 cm^{-1}, respectively.



Scheme 4. Reactions of the borenium carbonyl **10a**.

The CO ligands in the BH borenium carbonyls **10a**,**b** are apparently inert to intramolecular reduction by the adjacent B–H functionality. However, the carbonyl moiety at the positively charged borenium core is activated for external nucleophilic attack by the neutral carbon nucleophile IMes (**1a**) and its endiamine-type derivative $IMesCH_2$ (**1c**) (Scheme 4).

The N-heterocyclic carbene reacted rapidly with the borenium carbonyl **10a** (CD_2Cl_2, r.t., 2 min) to give the cationic acyl boron compound **11** [^{11}B NMR: δ -21.5 (br. d, $^1J_{BH}$ ~ 85 Hz), ^{13}C: δ 217.2 (C=O)]. The X-ray crystal structure of compound **11** is depicted in the Supporting Information.

The reaction of the borenium carbonyl salt **10a** with the $IMesCH_2$ reagent gave the substituted acetyl boron[16] cation system **12**, formed by nucleophilic endiamine attack at the B–C≡O carbon atom, in 94% yield. The X-ray crystal structure of compound **12** shows the presence of the newly formed IMes-substituted acetyl group attached at boron. The boron coordination geometry is distorted tetrahedral (Figure 4). In solution compound **12** shows the ^{13}C NMR acyl feature at δ 231.4 and the signals of the adjacent $–CH_2–$IMes unit at δ 41.0 (CH_2) and δ 161.9 (central IMes carbon), respectively. The $–CH_2–$ unit gives rise to an AB ^1H NMR pattern at δ 3.40, 3.14 ($^2J_{HH}$ = 17.6 Hz). The cation of compound **12** shows the ^{11}B NMR BH signal at δ -22.1 ($^1J_{BH}$ ~ 85 Hz).

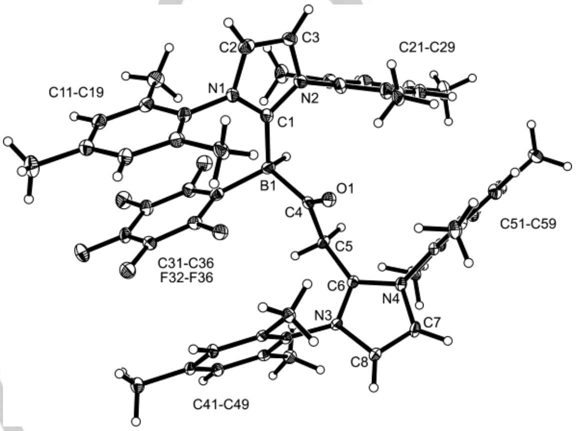
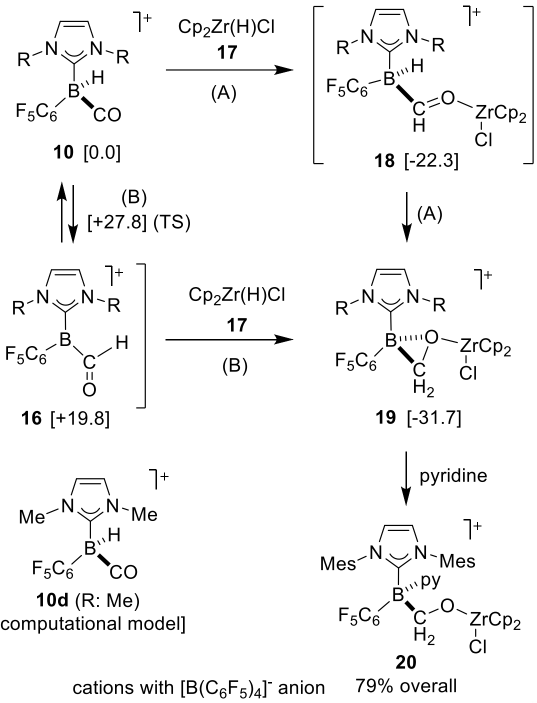


Figure 4. A view of the molecular structure of the substituted acetylboron cation part of compound **12** (only the cation is shown; thermal ellipsoids at 15% probability). Selected bond lengths (Å) and angles (°): C1–B1 1.627(10), B1–C4 1.627(9), C4–O1 1.223(7), C4–C5 1.542(8), C5–C6 1.490(7); $\Sigma B1^{CCC}$ 335.8, $\Sigma C4^{BCO}$ 359.9.

The reaction of **10a** with the (IMes)(C_6F_5)BH_2 borane **2a** (r.t. 24h in C_6D_5Br) gave a single product to which we tentatively assigned the composition of compound **14**. The cation shows ^{11}B NMR signals at δ 33.7 and -22.8, typical for the presence of three- and four-coordinated boron. It features the ^1H NMR signals of diastereotopic hydrogens of the newly formed $–CH_2–O$ unit (see Scheme 4). The reaction of **10a** with the ethylene-bridged FLP **13** made use of the B–H functionality. The reaction (r.t., 24h) gave a major product to which we propose the structure of **15** on the basis of the observed NMR spectra [^{11}B: δ 71.9 (–B(C_6F_5)$_2$), δ -13.8 (BC_6F_5); ^1H/^{13}C: δ 3.07 ($^2J_{PH}$ = 25.8 Hz)/49.2 ($^1J_{PC}$ ~ 58 Hz) (–CHO) in CD_2Cl_2].

The borenium carbonyl **10a** was reduced with Schwartz's reagent [$Cp_2Zr(H)Cl$] (**17**).[17] Treatment of **10a** with the zirconium hydride **17** (2 min, r.t., CD_2Cl_2) followed by trapping with pyridine gave the B–zirconoxymethyl product **20** (Scheme 5). The X-ray crystal structure analysis revealed that the boron bonded C≡O moiety of the starting material had become reduced to a $–CH_2–O–$ unit at boron. The $Zr(Cl)Cp_2$ moiety is found attached at its oxygen atom. The boron atom B1 of the cation has the newly formed $–CH_2–O[Zr]$, the C_6F_5 and –IMes group and a pyridine donor bonded to it in a distorted tetrahedral geometry.

We followed this reaction more closely in situ by NMR spectroscopy and found that the reaction of **10a** with the zirconium hydride initially gave the product **19a** (see Scheme 5). The ^1H NMR spectrum (CD_2Cl_2 at 233 K) showed the presence of a pair of diastereotopic Cp ligands at zirconium and a pair of diastereotopic methylene hydrogens adjacent to boron [^{11}B NMR: δ -9.5]. These data point to the presence of a three-membered BOC substructure with a marked boron-oxygen interaction.



Scheme 5. Reaction of the borenium carbonyl ion **10a** with Schwartz' reagent and DFT calculated Gibbs energies (in kcal mol^{-1}) of the reaction of the virtual model compound **10d** with Cp$_2$Zr(H)Cl [PW6B95-D3//TPSS-D3/def2-TZVP+(COSMO-RS) (CH$_2$Cl$_2$)].

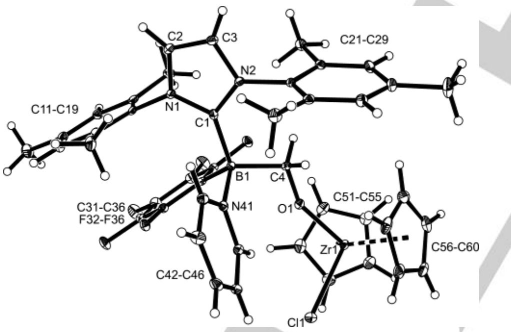


Figure 5. A view of the molecular structure of the cation part of compound **20** (thermal ellipsoids at 30% probability). Selected bond lengths (Å) and angles (°): C1–B1 1.659(4), B1–C4 1.641(3), C4–O1 1.417(3), O1–Zr1 1.944(2), B1–C4–O1 113.0(2), C4–O1–Zr1 150.6(2).

The reaction was analyzed by a DFT calculation[18] starting from the virtual model compound **10d**, featuring the IMe$_2$ ligand at boron. The calculation showed that the direct generation of the cationic formyl borane isomer **16d** from **10d** by an internal 1,2-hydride shift is a strongly endergonic reaction (by ca. +20 kcal mol^{-1}), and it has a high activation barrier. Therefore, we regard the direct involvement of the formyl borane **16** in reactions of the B–H borane carbonyl **10** as unlikely. In contrast, direct zirconium hydride addition to the borane-coordinated CO group to generate **18** is strongly exergonic (-22 kcal mol^{-1}) and then the subsequent 1,2-hydride shift to give **19** provides an additional thermodynamic driving force (by ca. -10 kcal mol^{-1}). Compound **19a** was then trapped with pyridine to give the isolated final product **20**.

The compounds **3a** and **3b** represent rare examples of [B]–H containing trivalent borenium ions. They were readily prepared from the (NHC)(C$_6$F$_5$)BH$_2$ precursors **2a,b** by hydride abstraction with trityl cation. They show the typical behaviour of electrophilic B–H species toward carbon monoxide. Similar to the chemistry of neutral B–H boranes, which form neutral B–H borane carbonyls,[11,12,19] both the compounds **3a** and **3b** reacted cleanly with carbon monoxide to form the respective cationic borenium carbonyls. The systems may superficially be reminiscent to many metal carbonyls, but the IR spectra indicate a fundamental difference: for both examples the C≡O stretching band is found at wavenumbers that are *higher* than free C≡O. This is a typical effect of CO coordination that is void of backbonding.[20-22] Consequently, the C≡O bond lengths in the [B]$^+$–carbonyls **10a** and **10b** are found slightly *below* the carbon-oxygen bond length in free CO (1.13 Å, although measured under different conditions[23]). We showed that compound **10a** contains a reactive carbonyl group. It reacts readily with nucleophiles. Addition of hydride from the Zr–H source even induces the utilization of the internal boron-hydride for the CO reduction to the –CH$_2$–O– group at boron. Aside from the ability of forming the interesting new cationic boron B(H)CO containing boron carbonyls, the [B]$^+$–H borenium systems may serve as reactive reagents for the synthesis of various interesting new [B]$^+$-containing systems.

Acknowledgements

C. C. and J. L. thank the Alexander von Humboldt foundation for postdoctoral fellowships.

Keywords: borocation • borenium • hydroboration • boron carbonyl • CO reduction

[1] For some reviews, see: a) P. Kölle, H. Nöth, *Chem. Rev*. **1985**, *85*, 399-418; b) W. E. Piers, S. C. Bourke, K. D. Conroy, *Angew. Chem*. **2005**, *117*, 5142-5163; *Angew. Chem. Int. Ed*. **2005**, *44*, 5016-5036; c) P. Eisenberger, C. M. Crudden, *Dalton Trans*. **2017**, *46*, 4874-4887; d) D. Franz, S. Inoue, *Chem. Eur. J*. **2019**, *25*, 2898-2926. For selected examples see: e) P. Eisenberger, B. P. Bestvater, E. C. Keske, C. M. Crudden, *Angew. Chem*. **2015**, *127*, 2497-2501; *Angew. Chem. Int. Ed*. **2015**, *54*, 2467-2471; f) L. C. Wilkins, J. R. Lawson, P. Wieneke, F. Rominger, A. S. K. Hashmi, M. M. Hansman, Rebecca L. Melen, *Chem. Eur. J*. **2016**, *22*, 14618-14624; g) J. E. Radcliffe, J. J. Dunsford, J. Cid, V. Fasano, M. J. Ingleson, *Organometallics*, **2017**, *36*, 4952-4960.

[2] T. S. De Vries, A. Prokofjevs, E. Vedejs, *Chem. Rev*. **2012**, *112*, 4246-4282.

[3] (a) J. M. Farrell, J. A. Hatnean, D. W. Stephan, *J. Am. Chem. Soc*. **2012**, *134*, 15728-15731; (b) P. Eisenberger, A. M. Bailey, C. M. Crudden, *J. Am. Chem. Soc.* **2012**, *134*, 17384-17387; c) E. J. Lawrence, T. J. Herrington, A. E. Ashley, G. G. Wildgoose, *Angew. Chem*. **2014**, *126*, 10080-10083; *Angew. Chem. Int. Ed*. **2014**, *53*, 9922-9925; (d) J. M. Ferrell, R. T. Posaratnanathan, D. W. Stephan, *Chem. Sci*. **2015**, *6*, 2010-2015; (e) K. L. Bamford, Z.-W. Qu, D. W. Stephan, *J. Am. Chem. Soc*. **2019**, *141*, 6180-6184; (f) B. Su, Y. Li, Z. H. Li, J.-L. Hou, H. Wang, *Organometallics*, **2020**, DOI: 10.1021/acs.organomet.0c00099; See also: (g) E. J. Corey, C. J. Helal,

Tetrahedron Lett. **1996**, *37*, 5675-5678; (h) E. J. Corey, T. Shibata, T. W. Lee, *J. Am. Chem. Soc*. **2002**, *124*, 3808-3809.

[4] See for example: K. C. Nainan, G. E. Ryschkewitsch, *J. Am. Chem. Soc*. **1969**, *91*, 330-336; and see also ref. (1).

[5] For rare X-ray structures of cyclic B–H borenium cations, see: (a) C. Bonnier, W. E. Piers, M. Parvez, T. S. Sorensen, *Chem. Commun*. **2008**, 4593-4595; (b) J. M. Farrell, D. W. Stephan, *Angew. Chem. Int. Ed*. **2015**, *127*, 5303-5306; *Angew. Chem. Int. Ed*. **2015**, *54*, 5214-5217; (c) K. Jaiswal, B. Prashanth, S Singh, *Chem. Eur. J*. **2016**, *22*, 11035-11041.

[6] (a) M. Devillard, R. Brousses, K. Miqueu, G. Bouhadir, D. A Bourissou, *Angew. Chem*. **2015**, *127*, 5814-5818; *Angew. Chem. Int. Ed*. **2015**, *54*, 5722-5726; (b) J. Lam, L. L. Cao, J. M. Farrell, D. W. Stephan, *Dalton Trans*. **2020**, 49, 1839-1846.

[7] For examples, see: (a) T. S. De Vries, A. Prokofjevs, J. N. Harvey, E. Vedejs, *J. Am. Chem. Soc*. **2009**, *131*, 14679-14687; (b) A. Prokofjevs, E. Vedejs, *J. Am. Chem. Soc*. **2011**, *133*, 20056-20059; (c) A. Prokofjevs, A. Boussonnière, L. Li, H. Bonin, E. Lacote, D. P. Curran, E. Vedejs, *J. Am. Chem. Soc*. **2012**, *134*, 12281-12288; (d) A. Prokofjevs, J. W. Kampf, A. Solovyev, D. P. Curran, E. Vedejs, *J. Am. Chem. Soc*. **2013**, *135*, 15686-15689; and see also ref. (2).

[8] B. Inés, M. Patil, J. Carreras, R. Goddard, W. Thiel, M. Alcarazo, *Angew. Chem*. **2011**, *123*, 8550-8553; *Angew. Chem. Int. Ed.* **2011**, *50*, 8400-8403.

[9] (a) Y. Liu, B. Su, W. Dong, Z. H. Li, H. Wang, *J. Am. Chem. Soc*. **2019**, *141*, 8358-8363. See also: (b) J. Zheng, Z. H. Li, H. Wang, *Chem. Sci.* **2018**, *9*, 1433-1438.

[10] For NHC adducts of main group element compounds see e.g., (a) S. Würtemberger-Pietsch, U. Radius, T. B. Marder, *Dalton Trans*. **2016**, *45*, 5880-5895; (b) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, *Chem. Rev*. **2018**, *118*, 9678-9842; (c) A. Doddo, M. Peters, M. Tamm, *Chem. Rev*. **2019**, *119*, 6994-7112.

[11] (a) A. B. Burg, H. I. Schlesinger, *J. Am. Chem. Soc*. **1937**, *59*, 780-787; (b) M. Sajid, G. Kehr, C. G. Daniliuc, G. Erker, *Angew. Chem*. **2014**, *126*, 1136-1139; *Angew. Chem. Int. Ed*. **2014**, *53*, 1118-1211

[12] For catalyzed borane CO reduction, see e.g.: (a) M. W. Rathke, H. C. Brown, *J. Am. Chem. Soc*. **1966**, *8*8, 2606-2607; (b) B. F. Spielvogel, A. T. Mcphail, J. A. Knight, C. G. Moreland, C. L. Gatchell, K. W. Morse, *Polyhedron* **1983**, *2*, 1345-1352.

[13] A.-M. Fuller, D. L. Hughes, S. J. Lancaster, C. M. White, *Organometallics* **2010**, *29*, 2194-2197.

[14] (a) M. A. Beckett, G. C. Strickland, J. R. Holland, K. S. Varma, *Polymer* **1996**, *37*, 4629-4631; see also: (b) V. Gutmann, *Coord. Chem. Rev.* **1976**, *18*, 225-255; (c) M. A. Beckett, D. S. Brassington, S. J. Coles, M. B. Hursthouse, *Inorg. Chem. Commun*. **2000**, *3*, 530-533.

[15] T. Özgün, K.-Y. Ye, C. G. Daniliuc, B. Wibbeling, L. Liu, S. Grimme, G. Kehr, G. Erker, *Chem.- Eur. J.* **2016**, *22*, 5988-5995.

[16] See for a comparison: (a) F. K. Scharnagel, S. K. Bose, T. Marder, *Org. Biomol. Chem.* **2017**, *15*, 1738-1753; (b) D. Wu, J. Taguchi, M. Tanriver, J. W. Bode, *Angew. Chem*. **2020**, 10.1002/ange.202005050, *Angew. Chem. Int. Ed*. **2020**, 10.1002/anie.202005050.

[17] (a) J. Schwartz, J. A. Labinger, *Angew. Chem.* **1976**, *88*, 402-409; *Angew. Chem. Int. Ed. Engl*. **1976**, *15*, 333-340; (b) S. L. Buchwald, S. J. LaMaire, R. B. Nielsen, B. T. Watson, S. M. King, *Tetrahedron Lett.* **1987**, *28*, 3895-3898.

[18] (a) A. Klamt, *J. Phys. Chem.* **1995**, *99*, 2224-2235; (b) Y. Zhao, D.G. Truhlar, *J. Phys. Chem. A* **2005**, *109*, 5656-5657; (c) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305; (d) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; (e) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.

[19] See for a comparison: (a) L. D. Curless, E. R. Clark, J. Cid, A. Del Grosso, M. J. Ingleson, *Chem. Comm*. **2015**, *51*, 10903-10906; (b) T. Heitkemper, C. P. Sindlinger, *Chem.- Eur. J.* **2020**, 10.1002/chem.202001916.

[20] See for a comparison: H. Jacobsen, H. Berke, S. Döring, G. Kehr, G. Erker, R. Fröhlich, O. Meyer, *Organometallics* **1999**, *18*, 1724-1735; and references cited therein.

[21] For borane carbonyls see e.g.: (a) J. C. Jeffery, N. C. Norman, J. A. J. Pardoe, P. L. Timms, *Chem. Commun*. **2000**, 2367-2367; (b) M. Finze, E. Bernhardt, A. Terheiden, M. Berkei, H. Willner, D. Christen, H. Oberhammer, F Aubke, *J. Am. Chem. Soc*. **2002**, *124*, 15385-15398; (c) A. Fukazawa, J. L. Dutton, C. Fan, L. G. Mercier, A. Y. Houghton, Q. Wu, W. E. Piers, M. Parvez, *Chem. Sci.* **2012**, *3*, 1814-1818; see also: (d) J. Jin, M. Zhou, *Dalton Trans*. **2018**, *47*, 17192-17197.

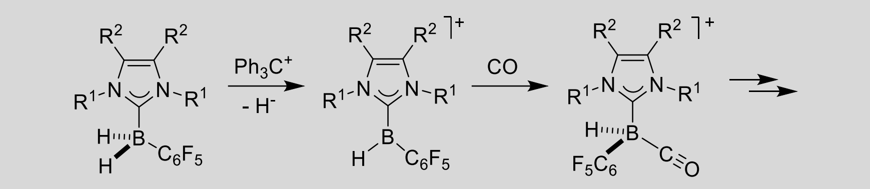
[22] For carbonyls of borylene, see e.g.: (a) F. Dahcheh, D. Martin, D. W. Stephan, G. Bertrand, *Angew. Chem*. **2014**, *126*, 13375-13379; *Angew. Chem. Int. Ed*. **2014**, *53*, 13159-13163; (b) H. Braunschweig, R. D. Dewhurst, F. Hupp, M. Nutz, K. Radacki, C. W. Tate, A. Vargas, Q. Ye, *Nature* **2015**, *522*, 327-330; (c) H. Wang, L. Wu, Z. Lin, Z. Xie, *J. Am. Chem. Soc*. **2017**, *139*, 13680-13683.

[23] O. R. Gilliam, C. M. Johnson, W. Gordy, *Phys. Rev*. **1950**, *78*, 140-144.

[24] CCDC 1977168 (**2a**), 1977169 (**2b**), 1977170 (**3a**), 1977171 (**4a**), 1977172 (**4b**), 1977173 (**5a**), 1977175 (**10a**/**10a'**), 1977176 (**10b**), 1977177 (**6a**), 1977178 (**7a**), 1977179 (**8**), 1977180 (**9**), 1992509 (**10a**), 1992510 (**11**), 1992511 (**12**), and 1992512 (**20**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Entry for the Table of Contents

Insert graphic for Table of Contents here.



The B–H containing $[(NHC)B(H)C_6F_5]^+$ borenium cations were obtained via hydride abstraction from the heterocyclic carbene borane adducts $(NHC)BH_2C_6F_5$. They cleanly add carbon monoxide to give the respective $[(NHC)B(H)(C_6F_5)CO]^+$ boron carbonyl cations. The activated C≡O can be attacked by carbon nucleophiles and reduced by external hydride.