Borane Carbonyl Derivatives

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Formylborane Formation with Frustrated Lewis Pair Templates**

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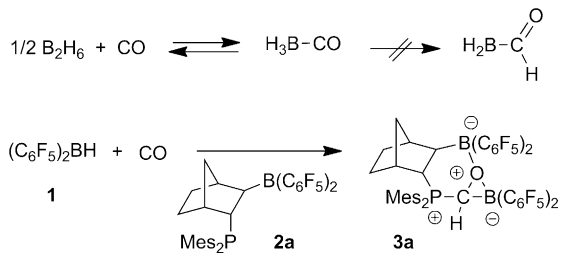
Abstract: *Boranes R_2BH react with carbon monoxide by forming the respective borane carbonyl compounds $R_2BH(CO)$. The formation of $(C_6F_5)_2BH(CO)$ derived from the Piers borane, $HB(C_6F_5)_2$, is a typical example. Subsequent CO-hydroboration does not take place, since the formation of the formylborane is usually endothermic. However, an "η^2-formylborane" was formed by CO-hydroboration with the Piers borane at vicinal phosphane/borane frustrated Lewis pair (FLP) templates. Subsequent treatment with pyridine liberated the intact formylborane from the FLP framework, and (pyridine)$(C_6F_5)_2B$–CHO was then isolated as a stable compound. This product underwent typical reactions of carbonyl compounds, such as Wittig olefination.*

Burg and Schlesinger had shown in 1937 that diborane (B_2H_6) reacted with carbon monoxide to give borane carbonyl (H_3BCO),[1] a low-boiling liquid that reversibly dissociated at a low CO partial pressure. Even under forcing conditions, borane carbonyl did not react further to give formylborane as a result of its unfavorable thermodynamics (Scheme 1).[2–7] In



Scheme 1. Reactions of BH boranes with carbon monoxide. Mes = mesityl (2,4,6-trimethylphenyl).

general, the carbonylation of free [B]–H-containing boranes seems not to lead to the formation of the respective borane carbaldehydes because of the endothermicity of this reaction.[2–7] We recently prepared a small series of annulated formylborane-like compounds[8] by the treatment of CO with $HB(C_6F_5)_2$ at frustrated Lewis pair (FLP) templates.[9–12] We have now carried out reactions of these FLP-stabilized formylborane derivatives with some remarkable outcomes.

We first treated compound **3a** with dihydrogen (60 bar). It reacted at room temperature to give the product **4**, which was isolated as a crystalline solid in 77% yield. X-ray crystal-structure analysis showed that the formyl group was reduced and its C–O linkage cleaved.[13] The structure contains a saturated seven-membered heterocycle that is annulated with the norbornane framework. The CO-derived methylene group was found to bridge a phosphonium and a borate unit [P1–C8 1.805(2) Å, C8–B2 1.637(4) Å, P1-C8-B2 119.4(2)°]. The former carbonyl oxygen atom had become protonated and was found to bridge the two borate units [B2–O1 1.554(4) Å, O1–B1 1.601(4) Å, B1-O1-B2 129.6(2)°]. The newly formed seven-membered ring adopted a typical cycloheptane-like boat conformation with the newly formed [B]-CH_2-[P] group at the tip [C8-B2-O1-B1 35.9(3)°, C8-P1-C2-C3 −40.5(2)°; Figure 1]. In solution, compound **4** showed ^{1}H/

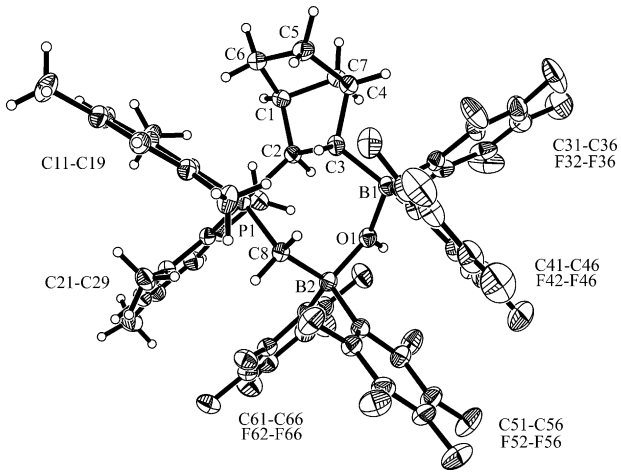


Figure 1. A view of the molecular structure of compound **4** (thermal ellipsoids are shown with 30% probability).[26]

^{13}C NMR signals for the [B]–CH_2–[P] methylene group at δ = 3.25, 2.75/19.2 ppm (^{31}P: δ = 33.2 ppm, ^{11}B: δ = 3.2 and 0.5 ppm). It showed ^{19}F NMR signals for the four diastereotopic C_6F_5 groups and an OH ^{1}H NMR resonance at δ = 5.78 ppm (for details, see the Supporting Information).

The B1–O1 bond in the starting material **3a** is very long.[8] Therefore, we assume (endothermic) equilibration of **3a** with its open form **5a**, which then serves as a reactive boron/oxygen FLP[14] to activate dihydrogen with formation of the intermediate **6a**. Intramolecular hydride attack would then readily open the adjacent three-membered ring to eventually yield the product **4** (Scheme 2).

This description of the reaction is supported by the reaction of the formylborane FLP adduct **3b** with pyridine derivatives. Compound **3b** was obtained analogously to **3a** by

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[+] X-ray crystal-structure analysis.

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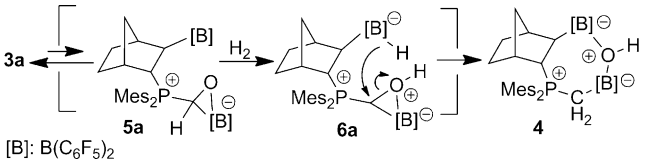
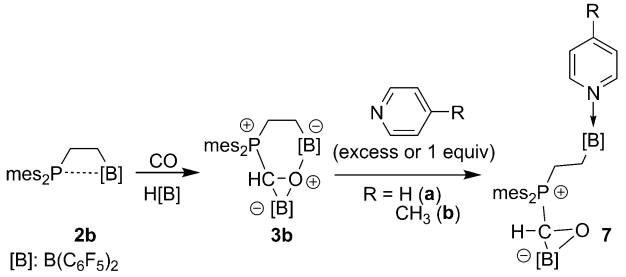


Scheme 2. Reaction of compound **3a** with dihydrogen.



Scheme 3. Reaction of compound **3b** with pyridines.

facile hydroboration of carbon monoxide with the Piers borane, $HB(C_6F_5)_2$,[15] at the FLP template **2b** (Scheme 3).[8] The treatment of **3b** with, for example, 4-methylpyridine in CH_2Cl_2 at room temperature instantly resulted in selective cleavage of the connecting B1–O1 bond to give the product of pyridine addition **7**, the open "η^2-formylborane" phosphane adduct. X-ray crystal-structure analysis of compound **7b** showed that the three-membered substructure was still intact (O1–C3 1.439(3) Å, O1–B2 1.465(4) Å, B2–C3 1.598(4) Å, P1–C3 1.789(3) Å; Figure 2 and Scheme 3) and that the

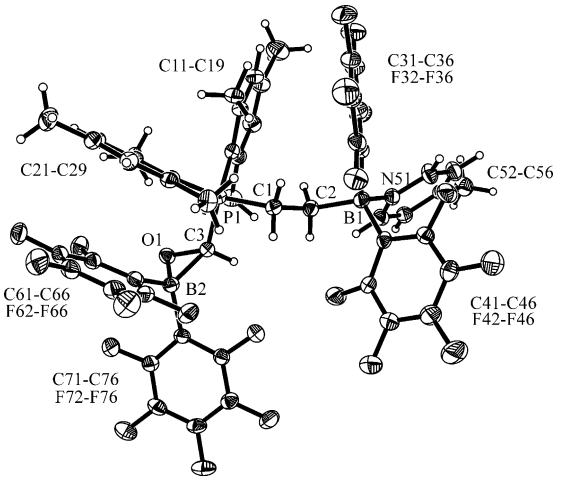
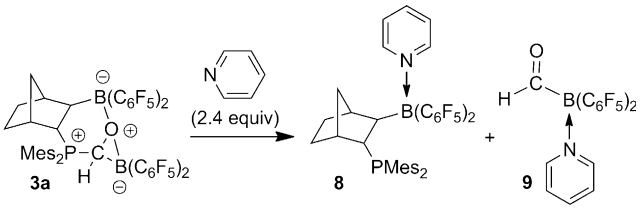


Figure 2. Molecular structure of compound **7b** (thermal ellipsoids are shown with 30% probability).[26]

methylpyridine donor was attached to the pendent borane functionality (B1–N51 1.638(4) Å).

This result prompted us to treat the FLP–CO/$HB(C_6F_5)_2$ reduction product **3a**[8] with excess pyridine. Compound **3a** reacted rapidly with pyridine (2.4 equiv) in CH_2Cl_2 to give the products **8** and **9**. Product **8** was characterized as the pyridine adduct of the free FLP **2a** (Scheme 4; for details, see the



Scheme 4. Liberation of a formylborane from compound **3a**.

Supporting Information). Compound **9** was isolated by crystallization and characterized by X-ray diffraction, C,H,N elemental analysis, and spectroscopy.

X-ray crystal-structure analysis showed that the unique formylborane $(C_6F_5)_2B–CHO$ had been liberated in this reaction and that we had isolated it as its pyridine adduct (Figure 3 and Scheme 4). The boron atom in compound **9** is tetracoordinated. It has bonded to it a pair of C_6F_5 groups

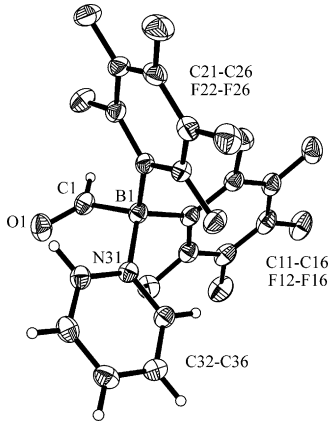
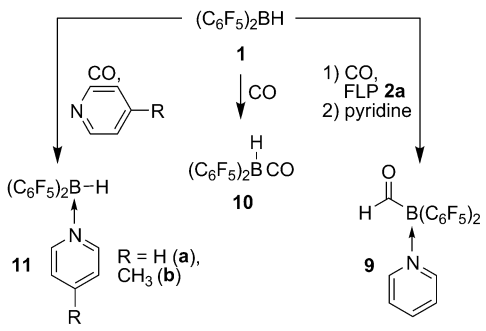


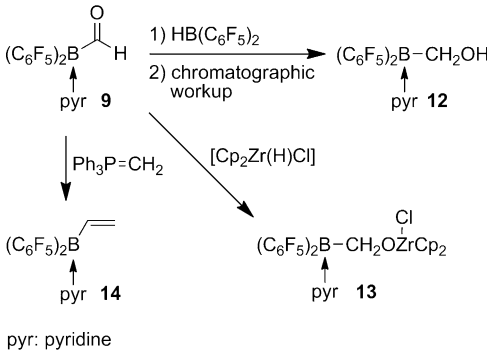
Figure 3. A projection of the molecular structure of the formylborane product **9** (thermal ellipsoids are shown with 30% probability).[26]

[B1–C11 1.646(3) Å, B1–C21 1.649(3) Å, C11-B1-C21 113.9(2)°], the pyridine donor ligand [B1–N31 1.610(3) Å], and the formyl group.[7,16] Compound **9** features a B1–C1 bond length of 1.649(3) Å, which is in the typical range for $B–C(sp^2)$ single bonds. The C1–O1 bond length [1.210(2) Å] is short, and the B1-C1-O1 angle is 126.3(2)°. In solution (CD_2Cl_2), compound **9** showed typical $^1H/^{13}C$ NMR aldehyde signals at $\delta = 11.24/233.1$ ppm. The ^{11}B NMR resonance occurred at $\delta = -5.1$ ppm, and we observed a single set of ^{19}F NMR signals for the pair of symmetry-equivalent C_6F_5 substituents with the expected chemical shift difference of $\Delta\delta(^{19}F_{m,p}) = 7.4$ ppm.

The proposed pathway of the favored FLP-assisted CO-reduction/hydroboration[8] was strongly supported by the outcome of two additional experiments. We exposed the Piers borane, $HB(C_6F_5)_2$, to carbon monoxide under carefully selected reaction conditions (for details, see the Supporting Information) and were indeed able to isolate the borane carbonyl $(C_6F_5)_2B(H)CO$ (**10**; Scheme 5). Compound **10** showed a ^{13}C NMR [B]–C≡O resonance at $\delta = 169.2$ ppm (223 K) and a ^{11}B NMR signal at $\delta = -30.6$ ppm (d, $^1J_{BH}$



Scheme 5. Formation and reactions of the borane carbonyl **10**.



Scheme 6. Some reactions of the formylborane **9**.

$\approx$95 Hz; 253 K).[17] Single crystals of compound **10** were obtained from a solution in CH_2Cl_2 under a CO atmosphere (2.5 bar) at −40 °C. X-ray crystal-structure analysis of compound **10** showed a tetracoordinated boron atom with a pseudotetrahedral geometry [sum of the C-B-C angles: 331.7°, B–C11 1.616(2) Å, B–C21 1.609(2) Å]. The linear [B]–C≡O unit [B1-C1-O1 174.7(2)°] showed a B1–C1 bond length of 1.601(2) Å. The carbonyl C1–O1 bond is short at 1.107(2) Å (Figure 4).[18]

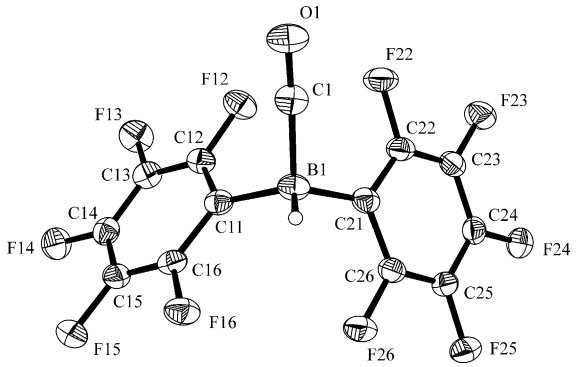


Figure 4. Molecular structure of the borane carbonyl **10** (thermal ellipsoids are shown with 30% probability).[26]

We also exposed the $HB(C_6F_5)_2$/CO mixture to 4-methylpyridine to check whether a direct pathway could be opened to the formylborane pyridine adduct **9** via an alleged $(C_6F_5)_2B$–CHO formylborane intermediate. However, only the corresponding $(C_6F_5)_2BH$(pyridine) adduct **11** was obtained. Compound **11b** (R = CH_3) was unequivocally identified by X-ray diffraction (for details, see the Supporting Information).

We carried out a few first experiments to characterize the chemical reactivity of the pyridine-stabilized formylborane **9**. It turned out that it behaved similarly to the way one would expect for a normal aldehyde. The treatment of **9** with $HB(C_6F_5)_2$ resulted in reduction of the formyl group. After chromatographic workup we obtained the corresponding boryl methanol product **12** [60% yield; ^{1}H NMR: δ = 3.97 (CH_2), 1.18 ppm (OH); ^{11}B NMR: δ = −1.7 ppm; Scheme 6; for details, see the Supporting Information]. The formyl group of compound **9** was also reduced by treatment with the Schwarz reagent [$(Cp_2Zr(H)Cl$] to give **13**. Finally, compound **9** was employed in a typical carbon–carbon bond-forming reaction of carbonyl compounds: Treatment of **9** with the phosphorous ylide $Ph_3P{=}CH_2$ gave the Wittig olefination product **14**, which was isolated in 66% yield after chromatographic workup [^{1}H NMR: δ = 6.84, 5.66, 4.97 (-CH=CH_2); ^{13}C NMR: δ = 145.8, 124.6 ppm (-CH=CH_2); ^{11}B NMR: δ = −2.1 ppm].

In summary, we were able to show that the unique borane carbaldehyde $(C_6F_5)_2B$–CHO (isolated as its pyridine-stabilized form **9**) can readily be obtained by reduction of carbon monoxide with the borane $HB(C_6F_5)_2$ at the intramolecular frustrated Lewis pair **2a**, followed by liberation from the template by treatment with pyridine. In this way, the thermodynamic restrictions of CO insertion into the boron–hydrogen bond[19–21] can be circumvented. This reaction sequence impressively demonstrates the potential of frustrated Lewis pairs in small-molecule binding and activation.[11,12,22–25] We are looking forward to investigating and developing the chemistry of borane carbaldehydes, now that such systems can be made in a convenient straightforward way.

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[26] CCDC 970103, 970104, 970105, 970106, and 970107 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

