

Borane Carbonyl Derivatives

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(C₆F₅)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 crystalstructure 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]-CH₂-[P] group at the tip [C8-B2-O1-B1 35.9(3)°, C8-P1-C2-C3 $-40.5(2)^{\circ}$; Figure 1]. In solution, compound 4 showed ¹H/



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

¹³C NMR signals for the [B]–CH₂–[P] methylene group at δ = 3.25, 2.75/19.2 ppm (³¹P: δ =33.2 ppm, ¹¹B: δ =3.2 and 0.5 ppm). It showed ¹⁹F NMR signals for the four diastereotopic C₆F₅ groups and an OH ¹H 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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^{[&}lt;sup>+</sup>] X-ray crystal-structure analysis.

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Scheme 2. Reaction of compound 3 a with dihydrogen.



Scheme 3. Reaction of compound 3 b with pyridines.

facile hydroboration of carbon monoxide with the Piers borane, HB(C₆F₅)₂,^[15] at the FLP template **2b** (Scheme 3).^[8] The treatment of **3b** with, for example, 4-methylpyridine in CH₂Cl₂ 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 CH₂Cl₂ 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 3 a.

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(sp²) 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 (CD₂Cl₂), compound **9** showed typical ¹H/¹³C NMR aldehyde signals at $\delta = 11.24/233.1$ ppm. The ¹¹B NMR resonance occurred at $\delta = -5.1$ ppm, and we observed a single set of ¹⁹F NMR signals for the pair of symmetry-equivalent C₆F₅ 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 COreduction/hydroboration^[8] was strongly supported by the outcome of two additional experiments. We exposed the Piers borane, HB(C₆F₅)₂, to carbon monoxide under carefully selected reaction conditions (for details, see the Supporting Information) and were indeed able to isolate the borane carbonyl (C₆F₅)₂B(H)CO (**10**; Scheme 5). Compound **10** showed a ¹³C NMR [B]–C=O resonance at $\delta = 169.2$ ppm (223 K) and a ¹¹B NMR signal at $\delta = -30.6$ ppm (d, ¹J_{BH}



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

≈ 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(C₆F₅)₂/CO mixture to 4-methylpyridine to check whether a direct pathway could be opened to the formylborane pyridine adduct **9** via an alleged (C₆F₅)₂B-CHO formylborane intermediate. However, only the corresponding (C₆F₅)₂BH(pyridine) adduct **11** was obtained. Compound **11b** (R = CH₃) 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(C₆F₅)₂ resulted in reduction of the formyl group. After chromatographic workup we obtained the corresponding boryl methanol product **12** [60 % yield; ¹H NMR: δ = 3.97 (CH₂), 1.18 ppm (OH); ¹¹B 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



Scheme 6. Some reactions of the formylborane 9.

Schwarz reagent [(Cp₂Zr(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 Ph₃P=CH₂ gave the Wittig olefination product **14**, which was isolated in 66% yield after chromatographic workup [¹H NMR: $\delta = 6.84$, 5.66, 4.97 (-CH=CH₂); ¹³C NMR: $\delta = 145.8$, 124.6 ppm (-CH=CH₂); ¹¹B NMR: $\delta = -2.1$ 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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