

# Stoichiometric Metal-Free Reduction of CO in Syn-Gas

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**S** Supporting Information

**ABSTRACT:** Reaction of a 2:1 mixture of  $B(C_6F_5)_3$  and  $tBu_3P$  with syn-gas results in the stoichiometric reduction of CO to give a formyl derivative which reacts further via an epoxy-borate intermediate to capture CO, affording a heterocyclic alkoxyborate. Heating the reaction prompts reaction with  $H_2$  to give a borane-oxy-borate derivative, the product of C–O bond cleavage.

Fischer–Tropsch (FT) catalysis effects the transformation of carbon monoxide and hydrogen to mixtures of liquid hydrocarbon fuels.<sup>1,2</sup> The processes used commercially employ heterogeneous metal-based catalysts and requires elevated temperature (150–320 °C) and pressures of syn-gas (CO/ $H_2$ ). The mechanism of FT catalysis involves a number of reactions including  $H_2$  activation, reduction of CO to formyl, subsequent reductive steps as well as C–O bond cleavage reactions. While a number of these reactions have been modeled in stoichiometric transformations of metal clusters, we had an interest in the potential of metal-free systems for CO reduction.

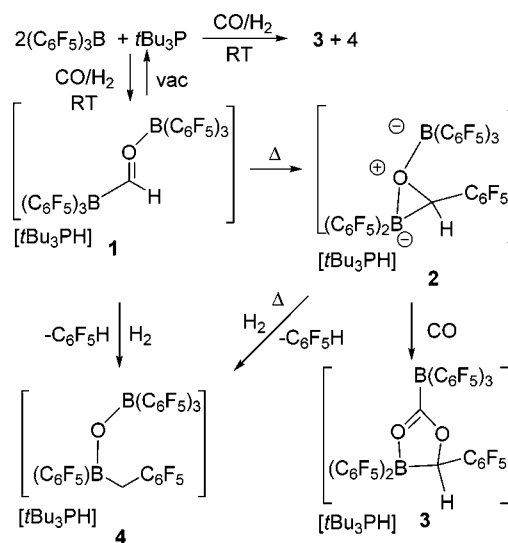
While the reactivity of transition-metal species with the individual components of syn-gas (i.e., CO and  $H_2$ ) is well established, the corresponding reactivity of main-group species has been rather limited. Organolithium and Grignard reagents are known to react with CO to produce metal acyls,<sup>3–6</sup> and CO is also known to insert into B–B,<sup>7</sup> and Al–C,<sup>8–10</sup> Ga–C,<sup>11</sup> and Ge–C<sup>12</sup> bonds. CAAC carbenes and silylenes react with CO to give ketenes and silyl ketenes,<sup>13–16</sup> whereas N-heterocyclic carbenes do not react with CO.<sup>17</sup> Donor–acceptor adducts of CO for the Al and Ga Lewis acids have been observed in matrix isolation studies, while the adducts  $R_3B(CO)$  [ $R = H$ ,<sup>18</sup> F,  $CF_3$ ,  $C_6F_5$ ,  $BX_2$  ( $X = Cl, F$ )]<sup>19</sup> have been isolated in some cases and are suggested as transient intermediates in alkyl transfer reactions en route to aldehydes, ketones, and alcohols.<sup>20,21</sup> Furthermore, boron–CO adducts undergo nucleophilic attack by amines<sup>22</sup> or phosphines, affording zwitterionic species of the form  $R_3B(CO)-ER'_3$  ( $E = N, P$ ;  $R = CF_3$ ;  $R' = Me$ ).<sup>23</sup>

Main group systems that react with  $H_2$  are not common. Ge–Ge single and multiple bonds<sup>24</sup> as well as CAAC-carbenes have been shown to react stoichiometrically with  $H_2$ .<sup>25</sup> Frustrated Lewis pairs (FLPs), combinations of bulky Lewis acids and bases have also been shown to activate  $H_2$ <sup>26–30</sup> and are effective in the catalytic hydrogenations of a variety of organic<sup>31–36</sup> and aromatic substrates.<sup>37,38</sup> In a very recent report, Erker et al. described the reactions of intermolecular FLPs with CO and  $(C_6F_5)_2BH$  yielding an epoxy-borate species.<sup>39</sup> In this report, we exploit the ability of FLPs to activate syn-gas showing that  $H_2$  and CO with  $B(C_6F_5)_3$  and

$tBu_3P$  result in a sequence of stoichiometric reactions affording the metal-free reduction of CO and ultimate C–O bond cleavage.

A solution of  $B(C_6F_5)_3$  and  $tBu_3P$  in 2:1 ratio was pressurized with  $^{13}CO/H_2$  mixture (4 atm, syn-gas). This results in the formation of a new product **1** in near quantitative isolated yield. The  $^{13}C$  NMR spectrum of **1** shows a resonance at 249.3 ppm attributable to the incorporation of C=O. The coupling to boron is evident from the  $J(^{13}C-B) = 52$  Hz. This boron atom gives rise to a  $^{11}B$  chemical shift of –13.7 ppm, while a second boron resonance is seen at 2.9 ppm as a broad singlet.  $^1H$  NMR data show a doublet at 10.6 ppm with  $J(^{13}C-H) = 151$  Hz. The  $^{19}F$  NMR shows two sets of signals corresponding to two different types of  $C_6F_5$  rings. Collectively, these data are consistent with the formulation of **1** as the formyl-borate derivative  $[tBu_3PH][B(C_6F_5)_3BCHO(C_6F_5)_3]$  (Scheme 1).

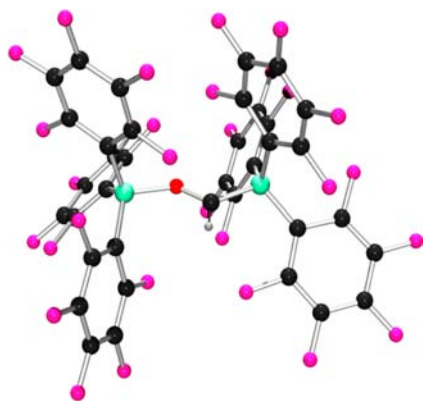
**Scheme 1.** Products from Reactions of  $tBu_3P/B(C_6F_5)_3$  with Syn-Gas



Recrystallization of **1** from  $CH_2Cl_2$ :hexane solution afforded crystals for X-ray crystallography which allowed this formulation to be confirmed (Figure 1). The C–O bond length in **1** of 1.248 Å is typical for carbonyl derivatives, while the B–O bond length of 1.577 Å is in the range seen for other carbonyl derivatives coordinated to boron.<sup>40</sup> Nonetheless, compound **1** is the first isolated and structurally characterized formyl-borate species.

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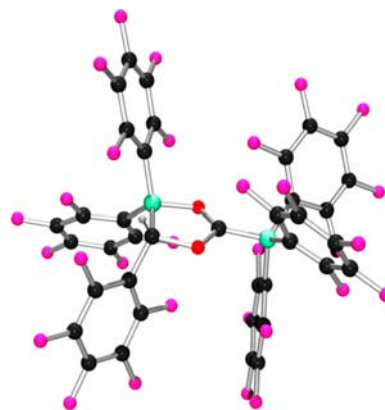
**Figure 1.** POV-ray depiction of the anion of **1**. (B: yellow-green; O: red; F: pale-pink; P: orange; H: white; C: black).

The formation of **1** clearly involves two steps, the activation of  $H_2$  and subsequent insertion of CO into the B–H bond. The activation of  $H_2$  by  $B(C_6F_5)_3$  and  $tBu_3P$  to give  $[tBu_3PH][HB(C_6F_5)_3]$  is well established.<sup>27</sup> It is noteworthy that independent reaction of  $[tBu_3PH][HB(C_6F_5)_3]$  with  $^{13}CO$  alone does not proceed, however **1** is formed upon addition of another equivalent of  $B(C_6F_5)_3$ . This suggests that the transient activation of CO is necessary in order to facilitate attack by the hydrido-borate anion. In this regard it is noteworthy that although the species  $(F_3C)_3B(CO)^{41-43}$  and  $(X_2B)_3BCO$  ( $X = F, Cl$ )<sup>44</sup> have been characterized, coordination of CO to  $B(C_6F_5)_3$  has not been observed but has been suggested by computational data.<sup>45</sup>

Compound **1** is stable in the solid state, however under vacuum overnight it loses CO and reverts to a mixture of borane and hydrido-borate. This back-reaction is analogous to retrohydroborations described by Piers et al.<sup>46</sup> Heating **1** to 90 °C for 2 h results in the near quantitative formation of the new species, **2**.  $^{19}F$ ,  $^{11}B$ , and  $^{13}C$  NMR data are consistent with the migration of the  $C_6F_5$  group from boron to the carbonyl carbon atom, thus inferring **2** is an epoxy-borate anion. Despite repeated attempts, crystals of **2** suitable for crystallographic study were not obtained. Nonetheless, this formulation is similar to the epoxy-borate prepared by the Erker group<sup>39</sup> in the reaction of  $(C_6F_5)_2BH$  and CO. It is also reminiscent of a Sc/B epoxide described by Piers et al.<sup>47</sup> The observed intramolecular migration of  $C_6F_5$  group to formyl-fragment of **1** in the formation of **2** is also consistent with the calculations at B3LYP-(6-311 d,p) level of theory<sup>48</sup> that reveal that the HOMO and LUMO of **1** are almost completely concentrated on the  $C_6F_5$  ring of the  $(C_6F_5)_3BCH=O$  moiety and the  $C=O$  fragment, respectively. It is also noteworthy that the C–B–C angles between the formyl group and the fluoro-arene rings of **1** are 112.4(1)°, 108.7(1)°, and 97.5(1)°, suggesting the latter are poised for migration.

Allowing a solution of **1** to stand under syn-gas overnight resulted in the transformation to a mixture of two new species **3** and **4** in an approximate ratio of 2:3. The former species **3** can be independently synthesized in 95% yield by treatment of **1** with CO for 16 h (Scheme 1). The product **3** gives rise to the  $^{13}C$  NMR diagnostic signals at 76.6 and 210.1 ppm.  $^{11}B$  NMR resonances are observed as a doublet at –17.2 ppm with  $J(^{13}C-B) = 61.5$  Hz and a broader signal at 4.0 ppm. Using  $^{13}CO$  initially, a doublet appears in the  $^1H$  NMR spectrum at 6.6 ppm ( $J(^{13}C-H) = 150$  Hz), while the  $^{19}F$  NMR spectrum reveals 11 distinct signals, 3 of which are attributed to a  $B(C_6F_5)_3$

fragment, and another 3 attributable to a C-bound  $C_6F_5$  unit. The remaining five signals are attributable to diastereotopic fluoro-arene ring of  $B(C_6F_5)_2$  moiety adjacent a chiral center, where the *o*- and *m*-fluorine environments are inequivalent. On the basis of these spectroscopic data, the structure of **3** remained ambiguous. Fortunately, X-ray quality crystals of **3** were obtained, and the structural data affirmed the formulation of **3** as  $[tBu_3PH][(C_6F_5)_2BCH(C_6F_5)O_2CB(C_6F_5)_3]$  (Figure 2). In this case, the anion is a five-membered BCOCO-ring in



**Figure 2.** POV-ray depiction of the anion of **3**. (B: yellow-green; O: red; F: pale-pink; P: orange; H: white; C: black).

which the C–O distances about the  $CO_2$  fragment are 1.309(4) and 1.262(4) Å. The oxygen atom associated with the latter bond is bound to a  $B(C_6F_5)_2$  fragment at a distance of 1.565(4) Å, while the carbon of this fragment is bound to an exocyclic  $B(C_6F_5)_3$  unit. The remaining C–O bond within the five-membered ring is 1.508(4) Å. A  $CH(C_6F_5)$  links this oxygen atom to the  $B(C_6F_5)_2$  fragment. The formation of **3** from **1** is thought to proceed via initial  $C_6F_5$  transfer from a  $B(C_6F_5)_3$  to the formyl-carbon atom generating **2** and subsequent reaction with CO to give **3**.

The nature of the second product derived from **1** under syn-gas, **4**, was also probed. Compound **4** was also obtained via heating compound **1** or **2** with  $H_2$  at 70 °C for 6 h and was isolated in 95% yield (Scheme 1). The  $^{11}B\{^1H\}$  NMR spectrum of **4** showed resonances at 41.0 and –4.0 ppm, while the  $^{19}F\{^1H\}$  NMR spectrum showed signals consistent with a  $B(C_6F_5)_3$  fragment as well as B and C bound  $C_6F_5$  groups and signals attributable to the formation of  $C_6F_5H$ . Among the  $^1H$  NMR signals was a signal at 2.54 ppm. Preparing  $^{13}C$  from  $^{13}CO$  revealed that this resonance as a doublet with 120.6 Hz coupling to  $^{13}C$ . In addition, the  $^1H$  and  $^{31}P$  NMR data were also consistent with the presence of the  $[tBu_3PH]$  cation. These spectroscopic data suggested the formulation of **4** as the phosphonium borane-oxy-borate salt  $[tBu_3PH][(C_6F_5)CH_2B(C_6F_5)OB(C_6F_5)_3]$ , and this was confirmed by X-ray crystallography (Figure 3).

The reactivity of the epoxy-borate **2** is akin to that of intramolecular FLPs developed by Erker and co-workers.<sup>30,49-51</sup> It is reasonable to suggest that ring strain generates an equilibrium involving the “open” form and the concerted action of the borane Lewis acid and the basic oxygen would account for both the capture of CO and the activation of  $H_2$  affording **3** and **4**, respectively (Scheme 2). It is noteworthy that similarly strained boron-amidates have been shown to capture a variety of substrates including CO.<sup>52</sup> In the case of  $H_2$

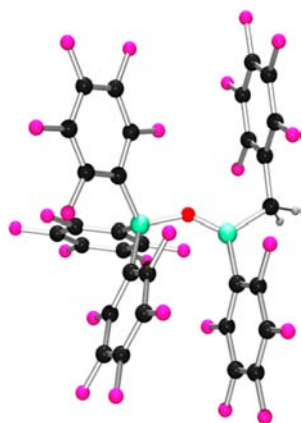
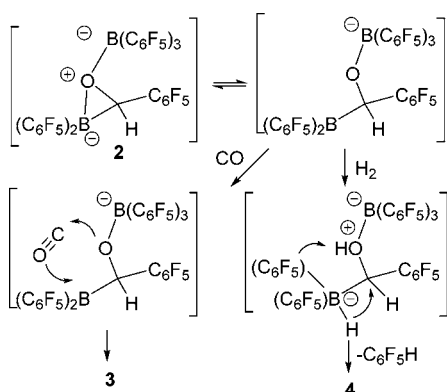


Figure 3. POV-ray depiction of 4. (B, yellow; O, red; F, purple; P, orange; H, white; C, black).

**Scheme 2. FLP Activations of CO and H<sub>2</sub> by 2 (Cations not shown)**



activation, heterolytic cleavage of H<sub>2</sub> would give rise to a transient borohydride and protonated oxygen. Migration of the hydride from boron to carbon would account for the resulting CH<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>) fragment in 4, while protonation of a C<sub>6</sub>F<sub>5</sub> would afford C<sub>6</sub>F<sub>5</sub>H. Similar loss of C<sub>6</sub>F<sub>5</sub>H has been effected by hydrogenation of some intramolecular amino-boranes.<sup>53</sup>

The above reactions demonstrate metal-free activation of syn-gas and confirm the generation of formyl and alkoxy intermediates and ultimately effecting C–O bond cleavage. These reaction products provide interesting homogeneous, main-group parallels to key steps in metal-catalyzed FT chemistry. We are continuing to probe the reactivity of FLPs in metal free reductions and catalysis.

**■ ASSOCIATED CONTENT**

**📄 Supporting Information**

Experimental details and crystallographic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**Notes**

The authors declare no competing financial interest.

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