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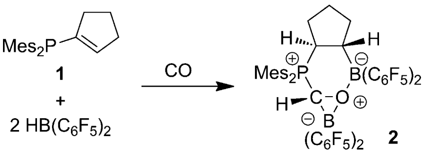
Activation of Small Molecules

Facile Carbon Monoxide Reduction at Intramolecular Frustrated Phosphane/Borane Lewis Pair Templates**

*Muhammad Sajid, Lisa-Maria Elmer, Christoph Rosorius, Constantin G. Daniliuc, Stefan Grimme, Gerald Kehr, and Gerhard Erker**

Finding novel pathways for the reduction of carbon oxides is important for the ongoing search for new systematic entries to hydrocarbon feedstocks. The CO to formyl conversion with readily available hydrides represents an important step along this way. Using boranes as the reducing reagents is desirable and potentially useful. Reactions of trialkylboranes with carbon monoxide are synthetically established. H. C. Brown had shown that R_3B systems readily react with CO at 100 to 125 °C at normal pressure to yield the respective tertiary alcohols after oxidative workup.[1] They modified this procedure to achieve the synthesis of ketones and aldehydes. In the latter case lithium aluminium hydride reagents were added.[1,2] However, carbon monoxide is surprisingly reluctant to be reduced with [B]H boranes.[3,4] Carbon monoxide is reported to react with B_2H_6 at 100 °C and 20 atm to give "borane carbonyl" [H_3B-CO], a gas (b.p. −64 °C) that dissociates at atmospheric pressure.[5,6]

We have now found that B−H borane reduction of carbon monoxide can be carried out with a suitable borane at a frustrated phosphane/borane Lewis pair (FLP)[7,8] template. We stirred a mixture of the bulky cyclopentenylphosphane **1** with the hydroboration reagent [$HB(C_6F_5)_2$][9] for about 15 minutes at RT and then subjected the resulting mixture to an atmosphere of carbon monoxide (2 bar). Workup after 12 h at RT eventually gave the reduction product **2** as a colorless solid in 63 % yield (see Scheme 1). Single crystals of **2** were obtained from dichloromethane/*n*-pentane. In the crystal compound **2** contains a "η^2-formyl" $B(C_6F_5)_2$ subunit that is bonded through the acyl carbon atom (C1) to the phosphorus atom and through the acyl oxygen atom (O1) to the boron center (B1) of the FLP framework (see Figure 1 and Table 1). The resulting six-membered heterocycle features a half-chair-like conformation. The annulated B,C,O heterocyclopropane subunit features typical element–element single bond lengths. Both the carbon (C1) and the boron (B2) atoms show pseudo-tetrahedral coordination geometries, whereas the onium-type oxygen atom exhibits a distorted trigonal planar coordination pattern (sum of bond angles at O1: 359.71°) The X-ray crystal structure analysis has revealed that the all-*trans*-diastereoisomer of **2** was obtained.



Scheme 1. Reaction of the cyclopentenylphosphane **1** with the hydroboration reagent [$HB(C_6F_5)_2$] and carbon monoxide.

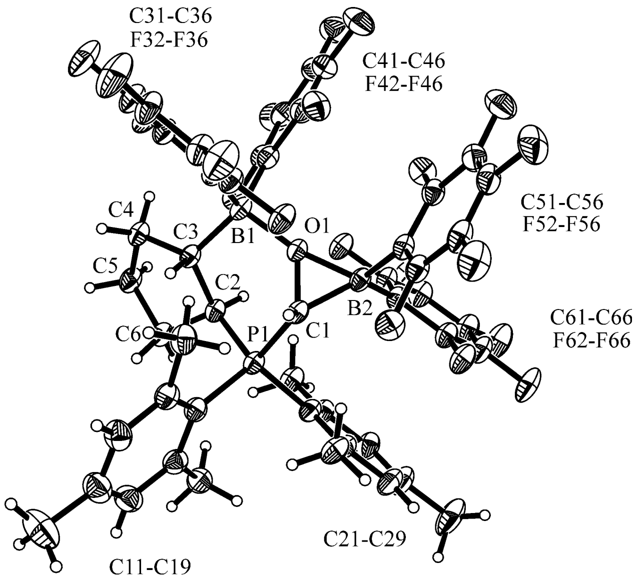


Figure 1. Molecular structure of compound **2**.[15]

Table 1: Selected structural data of the complexes **2**, **5**, and **7**.[a]

Compound	2	5	7
C1-O1	1.466(3)	1.487(3)	1.465(3)
C1-B2	1.588(4)	1.581(4)	1.588(4)
O1-B2	1.533(3)	1.588(4)	1.533(3)
C1-P1	1.828(3)	1.842(3)	1.827(3)
O1-B1	1.573(3)	1.635(4)	1.583(3)
ΣC^{POB}	296.79	302.10	296.15
ΣO^{CBB}	359.71	321.92	359.99

[a] Bond lengths in Å, angles in deg.

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[*] Dr. M. Sajid, L.-M. Elmer, C. Rosorius, Dr. C. G. Daniliuc, Dr. G. Kehr, Prof. Dr. G. Erker
Organisch-Chemisches Institut der Universität Münster
Corrensstraße 40, 48149 Münster (Germany)
E-mail: erker@uni-muenster.de

Prof. Dr. S. Grimme
Mulliken Center for Theoretical Chemistry
Institut für Physikalische und Theoretische Chemie
Universität Bonn, Beringstraße 4, 53115 Bonn (Germany)

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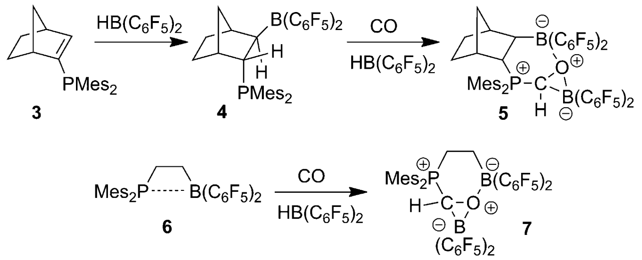
In solution compound **2** shows the $^{1}H/^{13}C$ NMR signals of the central -CHO- moiety at $\delta = 5.60$ ($^{2}J_{PH} = 17.6$ Hz) and $\delta = 56.1$ ppm ($^{1}J_{PC} \approx 60$ Hz), respectively. The ^{11}B NMR signals of compound **2** occur at $\delta = 7.7$ and -4.3 ppm and we have monitored the clearly separated *p*-F ^{19}F NMR signals of two pairs of diastereotopic C_6F_5 substituents at the two boron atoms. The ^{31}P NMR resonance of **2** was observed at $\delta = 36.7$ ppm (for further details see the Supporting Information).

The FLP **4**, in situ generated by treatment of the alkenylphosphane **3** with Piers' borane [$HB(C_6F_5)_2$] reacted similarly with CO and an additional molar equivalent of [$HB(C_6F_5)_2$] under mild conditions (RT, 12 h) to give the formyl derivative **5** that has been isolated as a colorless solid in about 80% yield (see Scheme 2). Compound **5** is characterized by ^{11}B NMR signals at $\delta = 8.4$ and $\delta = -1.3$ ppm, a ^{31}P NMR resonance at $\delta = 30.3$ ppm and the $^{1}H/^{13}C$ signals of the central -CHO- unit at $\delta = 5.14$ ($^{2}J_{PH} = 13.0$ Hz) and $\delta = 60.0$ ppm ($^{1}J_{PC} \approx 65$ Hz), respectively. Compound **5** was also characterized by an X-ray crystal structure analysis (see Figure 2 and Table 1 for some details). It showed that the stereoisomer was formed that had the formyl (C)-H hydrogen atom orientated towards the norbornane endo side. We note that in this geometrically constrained case the O1–B1 bond is rather long and the coordination geometry at O1 is markedly distorted from planarity.



Scheme 2. Reaction of the alkenylphosphane **3** with Piers' borane and CO.

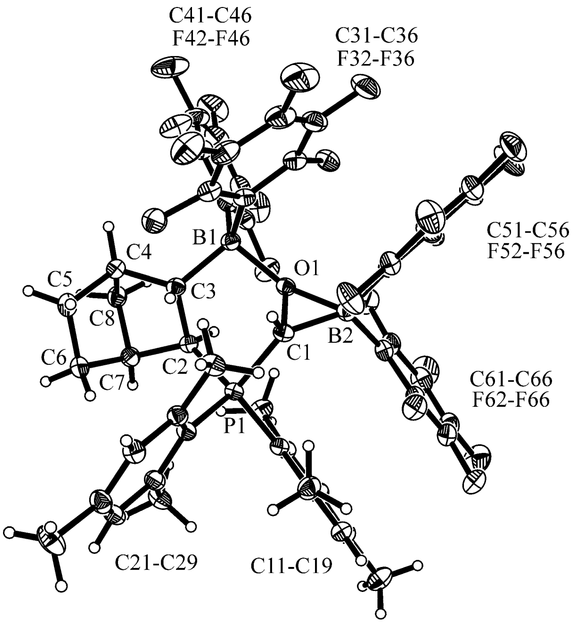


Figure 2. Molecular structure of compound **5**.[15]

The parent intramolecular ethylene-bridged FLP **6** features a weak internal P···B interaction.[10,11] Nevertheless, this system also reacts with the $CO/HB(C_6F_5)_2$ pair under our typical conditions to give the P,B,B-bonded CHO moiety (see Scheme 2). The respective product **7** was isolated in 82% yield [^{11}B NMR: $\delta = 5.8$, $\delta = -5.9$; ^{31}P NMR: $\delta = 31.7$; $^{1}H/^{13}C$ NMR: $\delta = 5.49$ ($^{2}J_{PH} = 19.7$ Hz), $\delta = 54.7$ ($^{1}J_{PC} = 63.8$ Hz)]. The X-ray crystal structure analysis features the characteristic heterocyclic framework with a typical C,O,B containing three-membered subunit (see Table 1 and Figure 3). Both the B1–O1 and B2–O1 bonds in **7** are rather short.

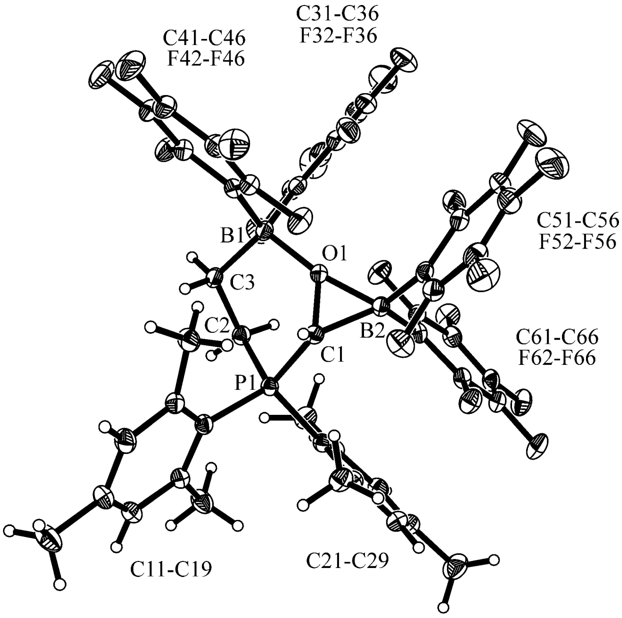
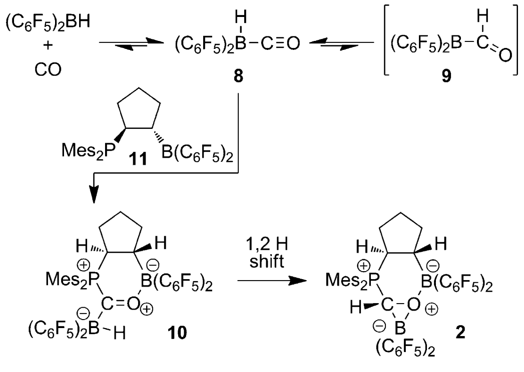


Figure 3. A view of the molecular structure of compound **7**.[15]

These reactions are taking place in rather complicated three-component systems that are not easy to analyze mechanistically because a manifold of potentially equilibrating active or dormant intermediates along the preferred pathway must principally be considered. However, it can probably be assumed that reduction of the carbon monoxide molecule by $HB(C_6F_5)_2$ at the FLP template plays an essential role. We investigated a plausible pathway taken in the reaction of the alleged FLP **11** with CO and $HB(C_6F_5)_2$ by a DFT analysis (PW6B95-D3//TPSS-D3 using def2-TZVP AO basis sets and including corrections to free enthalpies in toluene solution using the COSMO-RS model; for details see the Supporting Information).[12] It revealed that CO forms a thermodynamically favorable adduct (**8**) with Piers' borane. An allegedly competing formation of the corresponding $(C_6F_5)_2B$-CHO formyl system **9** is thermodynamically disfavored by about 13 kcal mol^{-1}. Therefore, this reaction probably avoids the intermediate **9.** It may react by $(C_6F_5)_2B(H)C{\equiv}O$ addition to the FLP **2**[13] to generate **10** (by an additional 6 kcal mol^{-1} exergonic). 1,2-Hydride shift from boron to carbon (about -17 kcal mol^{-1}) would then complete the favored CO reduction pathway to form the observed product **2** (see Scheme 3 and Figure 4).[14]



Scheme 3. Possible pathway taken in the reaction of the alleged FLP **11** with CO and $HB(C_6F_5)_2$.

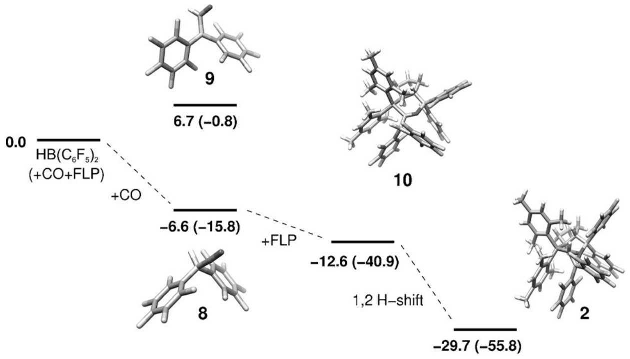


Figure 4. Reaction cascade of the formation of product **2** from FLP **11**, CO, and $HB(C_6F_5)_2$ calculated by DFT. The values given refer to free reaction enthalpies in toluene solution at 298 K (i.e., they include entropy as well as solvent effects) whereas the numbers in parentheses are pure electronic reaction energies in the gas phase.

The here described reactions of the intramolecular P/B FLPs with CO and $HB(C_6F_5)_2$ may be considered typical examples of efficient activation of a small molecule by a FLP. The direct formation of the formyl borane as CO reduction product is unfavorable. The involvement of the P/B FLP facilitates the reduction of CO both thermodynamically as well as kinetically. 1,2-Addition of the FLP to the borane carbonyl moiety may convert the inactive $R_2B(H){-}C{\equiv}O$ (**8**) unit to an activated intermediate **10** that may then undergo a 1,2-hydride shift to eventually form the thermodynamically stabilized product **2**.[14] We shall see whether this attractive FLP/CO activation route can be transferred to other hindered small molecule reduction reactions.

Experimental Section

General procedure: The phosphane **1** (150.0 mg, 0.45 mmol) and $HB(C_6F_5)_2$ (308.4 mg, 0.89 mmol) were weighted together, dissolved in CH_2Cl_2 (5.0 mL), and stirred at RT for 15 minutes. The resulting yellow solution was degassed by freeze-pump-thaw cycles, cooled to -78 °C, and CO gas was pressed (2.0 bar) over the solution. The reaction mixture was allowed to warm to RT and stirred for 12 h at RT. The solvent was evaporated under vacuum and the residue was washed with *n*-pentane (3 × 3 mL). The residue was dried under vacuum yielding compound **2** as a colorless solid (298.2 mg, 0.28 mmol, 63 % yield).

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[14] One can easily formulate alternative CO reduction pathways. A referee suggested potential carbon monoxide reduction at a preformed FLP – CO adduct as an alternative. We have found indications that both the FLPs **4** and **6** indeed form CO adducts, but both are thermally rather unstable and loose the CO molecule above −20 °C (M. Sajid, W. Dong, G. Kehr, G. Erker, unpublished).

[15] CCDC 916134 (**2**), CCDC 916135 (**5**), and CCDC 916136 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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