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Reductive Cleavage of the CO Molecule by a Reactive Vicinal Frustrated PH/BH Lewis Pair.

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Supporting Information Placeholder

ABSTRACT: A dimeric ethylene-bridged PH/BH system reduced carbon monoxide to the -CH₂-O- state. In the presence of $B(C_6F_5)_3$ the frustrated PH/BH Lewis pair reacted with carbon monoxide by reductive coupling of two CO molecules at the template. Removal of the $B(C_6F_5)_3$ borane with pyridine liberated one equiv. of carbon monoxide to give a cyclic five-membered P(=O)-CH₂-B compound, the product of reductive cleavage of carbon monoxide. It reacted as a borylated Horner $P(=O)CH_2B$ carbon nucleophile with carbon dioxide to give a bicyclic product by P-CH₂ attack on CO₂ combined with internal P=O to boron coordination.

Metal-free reduction of the carbon oxides has seen some major developments in the recent years. For carbon dioxide a considerable number of studies have been published involving the formation of all essential CO₂ reduction stages.¹ A much smaller number of reports on the selective reduction of carbon monoxide under metal-free conditions has been published.² This is to a considerable extent due to the observation that BH boranes do not reduce carbon monoxide unless catalyzed.³ Typically, B₂H₆ was reported to form borane carbonyl H₃B-CO when exposed to carbon monoxide, and HB(C₆F₅)₂ likewise forms Piers' borane carbonyl [(C₆F₅)₂B(H)CO].⁴ BH-reduction of CO has, however, been achieved by various combinations of reagents, most notably by the use of frustrated Lewis pairs (FLPs) and related systems. Several examples have achieved CO reduction in this way to the formyl stage and beyond.^{5,6}

The essential compound of our study is the new ethylene-bridged PH/BH FLP **3**. It was prepared by hydroboration of the aryl(vinyl)phosphane **1** with our recently reported (Fmes)BH₂·SMe₂ reagent (**2**).⁷ We isolated the PH/BH FLP as a doubly BH bridged dimer (**3**)₂ [δ -66.0 (¹*J*_{PH} ~ 225 Hz) (³¹P), δ 23.9 (¹¹B), δ 4.48, 3.03 (PH/BH)]. It was characterized by X-ray diffraction (Fig 1).

Compound (3)₂ reacted slowly with carbon monoxide (toluene, 110 °C ,12 h, 2 bar CO) to give the product 7 (yield: 95% isolated). The characterization by C, H elemental analysis, by X-ray diffraction (see the Supporting Information) and by NMR spectroscopy [δ 4.20/67.3 (-CH₂-O-), δ -66.5, -67.3 (³¹P), δ 77.3, 49.5 (¹¹B)] revealed that the CO molecule had been reduced to a bridging [B]-CH₂-O-[B] unit. We assume a reaction pathway that may initially involve P/B activation of CO⁸ to generate **5**, which was then opened by the reaction with the BH function of a second equivalent of the FLP **3** (Scheme 1). Under carefully controlled

reaction conditions we could observe compound 6 by NMR spectroscopy on the way to 7 (see the Supporting Information for details).





Figure 1. A view of the molecular structure of the PH/BH FLP dimer (3)₂ (thermal ellipsoids at 30 % probability). Selected bond lengths (Å) and angles (°): P1-C1 1.869(4), C1-C2 1.531(6), C2-B1 1.585(6), B1-B1* 1.828(9), C1-P1-C11 99.8(2), C2-B1-C31 124.2(3), P1-C1-C2-B1 179.9(3).¹⁴

In the presence of $B(C_6F_5)_3$ the carbonylation reaction took a different course. Treatment of the dimer (**3**)₂ with CO and $B(C_6F_5)_3$ (toluene, 2 bar CO, r.t., 12 h) gave an 85% yield of compound **8**. We assume that it is formed by the reaction of the in situ generated compound **5** (see Scheme 1) with the $(C_6F_5)_3B$ -CO borane carbonyl.⁹

Compound **8** was obtained as a mixture of two diastereoisomers in a ca. 4:1 ratio. The major isomer showed NMR resonances at δ

36.0 (³¹P, ¹*J*_{PH} = 462 Hz, ³*J*_{PH} = 45 Hz, ¹H: δ 6.89, 253 K), δ 10.5, -17.7 (¹¹B, 299 K), δ 5.17 (²*J*_{PH} = 3.8 Hz, 253K)/ 81.8([P]*CH*[B], 253 K) and δ 208.6 (¹³C, C=O, 253 K). The X-ray crystal structure analysis revealed the formation of a bicyclic framework featuring a *cis*-junction between the pair of five-membered rings through C3 and B1. The phosphorus atom bears a hydrogen and the bulky Mes* group. The bridgehead atoms C3 and B1 are each connected to oxygen atoms. The distal O1-C4-O2 unit is delocalized; it has the -B(C₆F₅)₃ moiety bonded to the central carbon atom (Fig 2.).

Scheme 2. Carbonylation of the FLP dimer $(3)_2$ in the presence of $B(C_6F_5)_3$.



Figure 2. A projection of the core framework of compound **8** (thermal ellipsoids at 30 % probability). Selected bond lengths (Å) and angles (°): B2-C4 1.643(4), C4-O1 1.315(3), C4-O2 1.269(3), B1-O2 1.582(3), B1-C3 1.676(4), C3-O1 1.476(3), C1-P1-C3 95.9(1), C3-O1-C4 110.7(2), O1-C4-O2 115.3(2), C4-O2-B1 114.3(2).¹⁴

Compound **8** reacts in an unusual way with pyridine. The reaction in a ca 1:1 molar ratio in CD_2Cl_2 at r.t. resulted in a ca. 95 % conversion to the $(C_6F_5)_3B$ -pyridine adduct **9** and the PO/B product **12**. A gas evolution was observed, and we identified the formation of carbon monoxide by *in situ* ¹³C NMR spectroscopy. Compound **12** was separated from the mixture by pentane extraction and obtained in 87% yield admixed with ca. 10% of the $B(C_6F_5)_3$ pyridine adduct **9**. According to X-ray diffraction the isolated crystalline material is probably the dimer **14** (see below); however, it dissociates to the monomer **12** upon bringing it back into solution. Compound **12** shows a ¹¹B NMR feature at δ 82.2 {[P]*CH*₂[B]: δ 58.7 (³¹P), δ 2.51, 2.23/39.1 (¹H/¹³C, ¹*J*_{PC} ~ 68 Hz)}. We note that compound **8** does not loose CO₂ upon treatment with pyridine but rather liberates CO, which seems to be the favored pathway for this system.

We reacted this PO/B compound 12 with $B(C_6F_5)_3$ for further characterization (1 h, r.t. in dichloromethane). Workup gave the $[P]=O-B(C_6F_5)_3$ adduct 13 in 95% yield [δ 81.3, -1.2 (¹¹B), δ 70.6 (³¹P), δ 2.60, 2.44 (¹H of [P]-CH₂-[B])]. The X-ray crystal structure analysis (Fig 3) confirmed the formation of the five-membered PO/B containing formed ring system bv the fragmentation/rearrangement reaction of 8 with pyridine. The central five-membered heterocycle has an envelope conformation with P1 serving as its tip. The phosphanoxide moiety has the $B(C_6F_5)_3$ Lewis acid bonded at oxygen.



Figure 3. Molecular structure of compound **13** (thermal ellipsoids shown at 30 %, only the Mes* ipso-C at P1 is shown for clarity) Selected bond lengths (Å) and angles (°): P1-O1 1.525(1), O1-B2 1.549(3), C1-P1-C3 94.8(9), $\sum B1^{CCC}$ 360.0.¹⁴

A possible rationalization of a pathway of the formation of compound **12** is shown in Scheme 2. The pyridine donor has obviously served to remove the $B(C_6F_5)_3$ unit from **8**. This resulted in cleavage of the oxygen to carbon linkage with proton transfer to form the bridging -CH₂- group, followed by PO bond formation by nucleophilic phosphane attack at the B-O- oxygen with liberation of CO. According to our DFT analysis (Scheme 4 below), the alleged heterobicyclo[2.1.1]hexane intermediate **11** is energetically within reach.¹⁰ It then undergoes ring-opening to form the observed product **12**.

Scheme 3. Formation of dimeric structures from 12 (with DFT calculated relative Gibbs energies in kcal mol⁻¹ [in benzene] method: PW6B95-D3//TPSS-D3/def2-TZVP).



Compound 12 formed two types of isolable dimers under different conditions. Crystallization from a heptane solution at -35 °C gave the dimer 14. The X-ray crystal structure analysis showed that it was formed by a pair of typical [P]=O-[B] contacts (Scheme 3, the structure is depicted in the Supporting Information). According to the DFT calculation the formation of the dimer 14 from 12 is slightly endergonic. This is in accordance with the observation that the dimer 14 dissociates to the monomer 12 upon dissolving it at r.t.

Keeping a solution of compound **12** in pentane solution at r.t. for 3 days led to the slow formation of a different dimer, namely

compound **16**. The X-ray crystal structure (Fig. 4) showed that two five-membered rings had become connected by a P-O-B linkage. One ring had retained its original heterocyclic structure, only the original P-CH₂-B unit had become converted to a delocalized P-CH-B P-ylide/borata-alkene like moiety.¹¹ The other five membered ring had undergone a rearrangement process. The external P=O phosphanoxide was converted to an internal P-O-B unit and its phosphorus atom bears a methyl substituent.



Figure 4. A view of the core framework of the dimer **16** (thermal ellipsoids is depicted at 30 %, for clarity only the ipso-carbon atoms of the aryl substituents are shown). Selected bond lengths (Å) and angles (°): P1-O1 1.566(1), P1-C1 1.830(2), P1-C3 1.726(2), B1-C2 1.597(3), B1-C3 1.459(3), O1-B2 1.510(2), B2-O2 1.569(2), O2-P2 1.562(1), P1-C3-B1 110.1(1), P1-O1-B2 138.7(1), B2-O2-P2 114.8(1).¹⁴

Compound **16** shows pairs each of ¹¹B (δ 50.1, 13.4) and ³¹P (δ 83.7, 77.8) NMR resonances (in CD₂Cl₂ solution). It shows ¹H/¹³C signals of the P-CH-B moiety at δ 3.67 (²J_{PH} = 13.1 Hz) and δ 82.5 (¹J_{PC} ~ 85 Hz) (see the Supporting Information for further details). The pathway of the formation of compound **16** apparently involves a single initial P=O coordination to the boron Lewis acid of a second molecule of **12**. The bridging P(O)-CH₂-B⁻ phosphanoxide/borate unit may then serve as a base to abstract a proton from the adjacent five-membered ring to generate the P-ylide/borata-alkene hybrid found in the product **16** (see Scheme 3).

In solution at 299 K only the monomer **12** was observed by NMR spectroscopy. However, in D_8 -toluene solution the ³¹P NMR signals of three new compounds appeared below ca. 223 K with increasing intensity. One could speculate that these might possibly be dimers (e.g. of type **14** and diastereoisomers of **15**) in a strongly temperature dependent equilibrium with **12** (see the Supporting Information for the depicted spectra).

Since the seminal work by L. Horner et al. is well known that the deprotonation of alkyl containing phosphanoxides and related compounds generates stabilized carbanions that show carbonyl olefination activity.¹² Our P-oxide system **12** might actually be looked at as a borylated analogue of such a "Horner $[R_2P(O)=CH_2]$ -" anion and, consequently, exhibit basic or nucleophilic properties at the P/B bridging CH₂ group. This showed up in the reaction of **12** with carbonyl and nitrile reagents.

Exposure of a solution of **12** in d_6 -benzene to CO₂ (2 bar, 60 °C, 2 h) gave the product **18a**, that was isolated in 88% yield after workup. The X-ray crystal structure analysis revealed that the CO₂ oxygen atom had become connected to boron, and the P-methylene carbon atom had formed a C-C bond with the CO₂ carbon to generate a heterobicyclo[3.2.1]octane framework (Fig. 5). It has an oxygen atom connecting the P and B heteroatoms and the ring carbon atom C4 is part of the C=O double bond.

The NMR spectrum of compound **18a** in CD₂Cl₂ solution shows the core heteroatom resonances at δ 70.0 (³¹P) and δ 8.3 (¹¹B), respectively. The ¹³C NMR methylene resonances occur at δ 14.0, 35.8 (¹J_{PC} ~ 65 Hz) and 37.7 (¹J_{PC} ~ 45 Hz). The ¹³C NMR carbonyl signal was located at δ 164.7 (²*J*_{PC} = 5.9 Hz) (for further details see the Supporting Information).

The P(O)-CH₂-B functionality of compound **12** underwent an analogous 1,2-addition to the CN group of the tosylcyanide reagent to give the bicyclic product **18b**. In this case the potent cyanation reagent Ts-CN¹³ added a second cyanide unit to the initially formed intermediate. Compound **18b** also features the internal P=O interaction with the adjacent boron Lewis acid. Compound **18b** was characterized by an X-ray crystal structure analysis (see the Supporting Information for details).

Scheme 4. Carbonyl addition reactions of compound 12 (with DFT calculated relative Gibbs energies in kcal mol⁻¹ [in dichloromethane] method: PW6B95-D3//TPSS-D3/def2-TZVP).



Figure 5. A view of the molecular structure of the CO_2 addition product **18a** (thermal ellipsoids shown at 30%, only the Mes* ipso-C at P1 is shown for clarity). Selected bond lengths (Å) and angles (°): P1-O1 1.565(1), O1-B1 1.538(2), B1-O2 1.517(2), O2-C4 1.311(2), C4-O3 1.213(2), C4-C3 1.533(2), C3-P1 1.823(2), P1-C1 1.808(2), C1-C2 1.554(2), C2-B1 1.637(3), P1-O1-B1 104.1(1), O2-C4-C3 119.6(2).¹⁴

Compound 12 reacted with benzaldehyde (CD₂Cl₂, 50 °C, 48 h). Crystallization from pentane at r.t. gave the product 18c in 85% yield admixed with ca. 10% of the pyridine-borane adduct 9. The X-ray crystal structure analysis of a recrystallized sample showed that the nucleophilic $P(=O)CH_2$ group had attacked the benzaldehyde carbon atom and the oxygen atom is found bonded to boron. In the crystal compound 18c shows a typical chair-like conformation of the seven-membered ring core with the bulky substituents oriented in pseudo-equatorial positions. The phenyl substituent and the Mes* group are 1,3-cis-oriented, the P=O vector is in a pseudo-axial position (see the Supporting Information for the depicted structure).

We conclude that the reaction of 3 with carbon monoxide results in the reductive cleavage of the CO molecule under metal-free conditions. The resulting product serves as a reactive borylated Horner-like ylidic system. It adds as a carbon nucleophile to carbon dioxide, to an aldehyde and to a nitrile functionality. Our DFT analysis shows that in solution compound **12** is the energetically preferred monomer in this system, but that its putative isomers, namely **11** and **17** are thermodynamically possibly within reach (see Scheme 4). So, it may be that the observed carbonyl reactions of **12** may constitute an intrinsic reactivity of this borylated Horner ylide analogue, or that alternatively the observed reactions were taking place via any of these isomeric systems. At present we cannot distinguish between these options. The observed reaction sequences indicate that the presence of the PH and BH functionalities at the internal P/B Lewis pair **3** serve to greatly advance the possibilities for small molecule activation at frustrated Lewis pairs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information contains details about the experimental work, the characterization of the new compounds and details about the DFT analysis. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>

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Notes

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The authors declare no competing financial interests.

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(14) CCDC 1996899 [(**3**)₂], 1996900 (7), 1996901 (**8**), 1996902 (**13**), 1996903 (**14**), 1996904 (**16**), 1996906 (**18a**), 2007813 (**18b**) and 1996905

(18c) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

