Cooperative reaction chemistry derived from a borata-diene framework†

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The bifunctional frustrated BH/C0/B hydridoborate nucleophile/borane Lewis acid pair 6 is prepared starting from the borata-diene 3 by a sequence of sequential protonation/hydride attachment, followed by hydroboration with Piers’ borane [HB(C6F5)2]. The trans-1,2-bifunctional system 6 reduced carbon monoxide eventually to the aldehyde product 10.

Borohydrides are important reducing reagents. However, some of these systems show rather low hydride nucleophilicities, especially when additional strongly electron-withdrawing substituents are attached at the boron center.1 Lewis acid assistance is often helpful or even essential.2 We have now prepared a bifunctional −B(C6F5)2H/C0/B(C6F5)2 frustrated pair showed a high reaction potential, e.g. for the stoichiometric conversion of carbon monoxide.3 The preparation of the active hydridoborate/borane pair and some first reactions are described in this account.

Borata-alkenes represent mesomeric structures of α-boryl carbanions4 and consequently they can be prepared by deprotonation of the boranes with a suitable base.5 This reaction is, however, in most cases problematic since the majority of conventional bases would preferentially add to the boron Lewis acid site rather than deprotonate in the α-position. Therefore, a rather limited number of borata-alkenes were prepared in this straightforward way, isolated and amply characterized. The few structurally characterized examples show a pronounced B–C double bond character with boron–carbon bond lengths around 1.44 Å.6

We recently reported a base-free synthetic entry to the zwitterionic borata-diene compound 3 (see Scheme 1):7,8 hydroboration9 of the P-enyne 1 with Piers’ borane [HB(C6F5)2] generated the geminal P/B Lewis pair 2 that underwent rapid intramolecular ring-closure to 3.7 Compound 3 served as the starting material for the construction of a reactive borohydridoborate/borane pair. Treatment of 3 with triflic acid resulted in the protonation of the incipient carbanion site in the α-position to boron and attachment of the corresponding triflate anion to the boron atom.10 The resulting Brønsted acid addition product 4 was isolated in 67% yield. Its X-ray crystal structure analysis confirmed that a selective 1,2-addition of HOSO2CF3 had occurred across the B–C double bond. Compound 4 contains a sp3-hybridized carbon atom C1 in the ring and has the adjacent C2–C3 double bond intact. The triflate anion is found to be attached at the boron atom B1 (for structural details and the spectroscopic characterization of compound 4 see the ESI†).

We then exchanged the OTf group at boron for hydride. This was effected by treatment of compound 4 with excess chlorodimethylsilane (30 min, 60 °C, dichloromethane).10 The borohydride...
resonances of its pair of homotopic C₆F₅ groups with a typical 1.34 ppm (3d [HB(C₆F₅)₂] to give Compound 5.

The newly attached B(C₆F₅)₂ group shows a ¹¹B NMR resonance at 65.1 ppm) typical of a planar-tricoordinated boron Lewis acid. The ¹H NMR spectrum showed the C₃–CH₃ doublet at 2.12 ppm and a pair of broad ¹¹B NMR resonances at 9.4 and 5.5 ppm, respectively. It shows the typical ¹H NMR spectrum at δ = 2.12 ppm and a pair of broad ¹¹B NMR resonances at δ = 6.5 Hz and the three 1,2-cis-3-trans CH resonances at δ = 4.44 (C₁–H), 2.78 (C₂–H) and 3.11 ppm (C₃–H) (C₄H₂; δ = 3.17 and 2.35 ppm). The structure of compound 7 was confirmed by X-ray diffraction. It shows a cis-1,2-arrangement of the H-bridged −B(C₆F₅)₂[μH] B(C₆F₅)₂-unit at the ring carbon atoms C₁ and C₂ (see Fig. 3). The methyl group at C₃ is cis-oriented to the C₂–B₂ vector. Both the boron atoms feature markedly distorted tetrahedral coordination geometries (ΣB₁CCC = 346.9°, ΣB₂CCC = 345.8°).

Compound 7 represents just an example of a rather conventional hydride bridged B–H–B type compound. In contrast, compound 6 is remarkable in that it contains an unquenched pair of an active borohydride nucleophile and a strongly Lewis acidic boryl electrophile attached at adjacent carbon atoms at the central five-membered heterocyclic core structure. It is due to these specific structural features of the phosphoniacyclopentane framework that these two units are very effectively hindered from annihilating their typical reactivities by “neutralizing” bridging µ-hydride formation. In a way this situation may be regarded as a
new form of a frustrated Lewis pair (FLP), hereby having a pair of a hydride nucleophile and a borane Lewis acid being effectively hindered from mutual quenching by the specific nature of the framework that they are attached to. This opens the chance to find cooperative reaction with added substrates.

Reaction of the bifunctional compound 6 with benzaldehyde (r.t., 1 h) gave the reduction product 9 (isolated in 77% yield after crystallization from pentane) (see Scheme 2). The X-ray crystal structure analysis showed that hydride had been added to the carbonyl carbon atom to form the [B]-benzyl alcoholate product. The alcoholate oxygen is rather symmetrically bonded to both boron atoms. The oxygen atom shows a trigonal planar coordination geometry ($\angle \text{P} \text{O} \text{C} = 356.9^\circ$). The boryl substituents are found to be trans-1,2-attached at the ring carbon atoms C1 and C3 (see the ESI† for structural details and the spectroscopic characterization of compound 9).

Both isomers 6 and 7 were exposed to carbon monoxide. While the conventional hydride-bridged cis-isomer 7 was inert toward CO under our typical reaction conditions, BH /B FLP 6 reduced carbon monoxide under mild reaction conditions (r.t., 30 min). After a short reaction time, workup gave product 10 in 63% yield (see Scheme 3). The product was characterized by C,H elemental analysis, by NMR spectroscopy and X-ray diffraction (see Fig. 4).

The X-ray crystal structure analysis (single crystals were obtained from dichloromethane/pentane) showed that CO had become reduced at the BH /B framework of 6 and coupled with a –CF$_3$ group to give a pentafluorobenzaldehyde moiety. However, this reduction product is bonded in a special manner to the framework of 6: the newly introduced oxygen atom is found to bridge between the pair of boron atoms and the aldehyde carbon atom (which is derived from the CO molecule) is bonded to boron atom B1. So the C 6F5–CHO unit is found Z2-bonded to B1 and $\kappa$O-bonded to B2. This situation generates a rather special stereochemical situation by introducing a pair of new chirality centers, namely at the former CO carbon atom (C6) and its adjacent boron atom (B1). Together with the three carbon chiral centers of the framework (C1, C2, C3) this makes a total of five stereogenic centers present in compound 10. Three of these (at the framework) are determined in their relative stereochemistry by the starting material 6 (which was formed as a single diastereomer), but in principle the pair of newly introduced stereocenters could have led to the formation of 10 as a mixture of four diastereomers. However, we find only a single diastereomer of 10 being formed in the carbonylation reaction of 6. It is characterized...
by a syn-arrangement of the C6 group to the C5-methyl substituent and an exo-orientation of the C6-pentafluorophenyl substituent.

In solution (CD2Cl2), we have observed the 1H/13C NMR signals of the CO derived –CH–Ar group at δ 4.29 ppm/δ 60.8 ppm. Compound 10 shows the 31P NMR resonances of four different C6F3 substituents (for details see the ESIF) and we have recorded the heteronuclear magnetic resonances of the pair of boron atoms (11B: δ 4.2 and −3.5 ppm) and the phosphorus atom (31P; δ 38.9 ppm).

It has long been known that boranes can form carbonyl adducts upon exposure to CO. The borane carbonyl H2B–CO14 and Piers’ borane carbonyl (C6F5)2HB–CO15 are typical examples. Therefore, we were led to assume a reaction pathway for the formation of compound 10 that involved the reactive borane carbonyl intermediate 11. Subsequent reduction by the adjacent borohydride reagent to the formyl stage followed by nucleophilic hydride attack from the adjacent hydridoborate.

Notes and references

1 Z. M. Heiden and A. P. Latham, Organometallics, 2015, 34, 1818.
10 See for comparison: (a) J. Yu, G. Kehr, C. G. Daniliu, C. Bannwarth, S. Grimm and G. Erker, Organometallics, 2015, 33, 5783; See also: (b) G. C. Welch, R. R. San Juan, J. D. Masuda and D. W. Stephan, Science, 2006, 314, 1124–1126.