Nitro-redox reactions at a frustrated borane/phosphate Lewis pair†

Guo-Qiang Chen, Gerald Kehr, Constantin G. Daniliuc‡ and Gerhard Erker*

The unsaturated 1,4-P/B-FLPs 6 reduced nitrobenzene to nitroso-benzene which was directly trapped by an allylboration reaction to give the seven-membered B–O–P compounds 9a and 9b. The FLP 6a reacted analogously with trans-β-nitrostyrene. The products were characterized by X-ray diffraction.

Frustrated Lewis pairs (FLPs) derived from combinations of main group element Lewis acids and bases undergo a great variety of reactions with essential small molecules. Many intra- as well as intermolecular FLPs are able to cleave dihydrogen under mild conditions. Consequently, they have served as the basis for the development of catalysts for metal-free hydrogenation of a variety of organic substrates. Frustrated Lewis pairs have been reported to cooperatively add to a variety of substrates, among them CO2, SO2 and N2O, and some intramolecular FLPs can even cooperatively add in a 1,1-fashion to carbon monoxide or nitric oxide. A number of new chemical reactions have been shown to take place at FLP frameworks, among them e.g. the [B]H reduction of CO or the phospha-Stork reaction. Surprisingly little is known about selective redox reactions at e.g. P/B FLPs; usually one observes oxidation of the phosphane component. We have now found an example that some organic nitro compounds react very specifically with an intramolecular P/B FLP system. In this study we first reacted the 1,4-P/B FLP 6a with nitrobenzene. In this case a sequence of allylboration/FLP addition was observed under our typical reaction conditions. The reaction was carried out by stirring compound 6a with nitrosobenzene (2 molar equiv.) for 1 day at r.t. in dichloromethane. Workup gave the product 8 as a white solid in 80% yield.

Single crystals for the X-ray crystal structure analysis were obtained from dichloromethane/pentane at −35 °C by the diffusion method. It shows the presence of a central eight-membered heterocyclic core that contains the boron and phosphorus atoms, the nitrosobenzene derived N–O units and two carbon atoms originating from the C4-bridge of the starting material 6a. The methyl substituent and the vinyl group that was generated during the initial allylboration reaction (see Scheme 2) are found attached at carbon atom C2. Nitrogen

Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, 48149 Münster, Germany. E-mail: erker@uni-muenster.de; Fax: +49-251-83 36503
†Electronic supplementary information (ESI) available: Experimental, analytical and structural details. CCDC 1450866–1450870. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00857g
‡X-Ray structure analysis.
atom N2 features a trigonal–pyramidal coordination geometry ($\sum N_2CCO = 328.6^\circ$), whereas N1 is almost trigonal planar ($\sum N_1COP = 353.0^\circ$). The phenyl substituents are pseudo-equatorially oriented at the distorted crown-shaped core (see Fig. 1). The –CH$_3$/–CH=CH$_2$ substituents at C2 were found in a 2 : 1 disordered.

In CD$_2$Cl$_2$ solution we found the NMR signals of a pair of diastereoisomers in a ca. 1 : 1 intensity ratio. These probably originate from the combination of the chiral center (C2) with some conformational chirality unit. This results in the observation of a total of 13 $^1$H NMR methyl signals (2 overlapping at 299 K) of the 2-CH$_3$ substituents and the mesityl groups at phosphorus. Likewise, we have observed a total of 8 $^3$P NMR resonances (253 K) and a pair of resolved $^{19}$F NMR resonances (253 K) and a pair of resolved $^{31}$P NMR signals (δ 49.46 and δ 49.52 at 299 K; for details see the ESI†).

This set the scene for the reactions of the 1,4-P/B FLPs with aryl and alkenyl nitro compounds. The reaction of the 1,4-P/B FLP 6a with nitrobenzene was carried out in dichloromethane (r.t., overnight). Workup gave compound 9a as a white solid in 90% yield. The X-ray crystal structure analysis (see Fig. 2) revealed that a redox reaction had taken place followed by an allylboration type reaction. The phosphane was oxidized and the resulting P===O unit coordinated to the boron Lewis acid. This was apparently followed by a subsequent allylboration reaction of the in situ generated nitrosobenzene product (see Scheme 3). This trapping reaction resulted in the typical substitution pattern at the boat-shaped core, namely the geminal pair of –CH$_3$ and –CH=CH$_2$ substituents at the ring carbon atom C2.

In solution (CD$_2$Cl$_2$) we observed again the NMR signals of a ca. 1 : 1 pair of diastereoisomers [$^{31}$P NMR: δ 62.1 and 61.8], probably resulting from the combination of the chirality center (C2) with a conformational chirality as it is often observed in sterically congested compounds derived from FLP chemistry. The reaction of the $^3$Bu substituted P/B FLP 6b with nitrosobenzene took a similar course. We isolated the P/B oxidation/nitrosobenzene allylboration product 9b in 80% yield. It showed similar structural and spectroscopic features (for details including the X-ray crystal structure analysis of compound 9b see the ESI†).

We reacted the 1,4-P/B FLP 6a (R = Mes) with trans-$\beta$-nitrostyrene in a 1 : 1 molar ratio (r.t., overnight, CH$_2$Cl$_2$). Workup in this case gave the product 10 in 91% yield (see Scheme 3). The reaction also took place by oxidation of the B===P pair concomitant with trapping of the resulting reduction product, the respective trans-$\beta$-nitrosobenzene by internal allylboration. In solution we observed the NMR signals of a pair of diastereoisomers in a ca. 2 : 1 molar ratio [$^{31}$P NMR: δ 62.39 (major) and 62.87 (minor)]. In the crystal we observed a boat-shaped seven-membered heterocyclic core with a bent B-O-P unit (see Fig. 3) and the trans-$\beta$-styril substituent attached at the ring nitrogen atom (N1) in a trigonal–pyramidal coordination geo-

---

**Fig. 1** Molecular structure of compound 8 (thermal ellipsoids are shown with 50% probability). Selected bond lengths (Å) and angles (°): P1–C1: 1.820(2), P1–N1: 1.675(2), B1–O1: 1.505(3), B1–O2: 1.473(3), C3–C4: 1.342(14), O1–B1–O2: 111.6(2), C1–P1–N1: 105.4(1), B1–O1–N1: 113.4(2), B1–O2–N2: 107.3(2), P1–N1–O1: 113.5(1), C2–N2–O2: 106.3(2).

**Fig. 2** Molecular structure of compound 9a (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (°): P1–C1: 1.802(5), P1–O1: 1.539(3), B1–O1: 1.524(6), B1–O2: 1.456(6), C3–C4: 1.308(7), O1–B1–O2: 110.0(4), C1–P1–O1: 109.3(2), B1–O1–P1: 124.2(3), B1–O2–N1: 111.1(3), C2–N1–O2: 104.8(3).

Notes and references


