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

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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.**

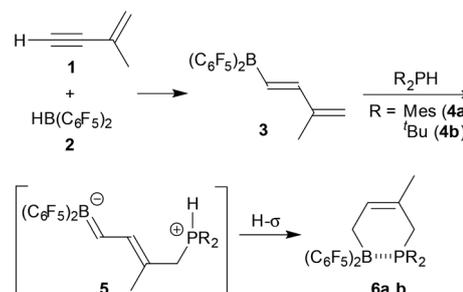
Frustrated Lewis pairs (FLPs) derived from combinations of main group element Lewis acids and bases undergo a great variety of reactions with essential small molecules.¹ Many intra- as well as intermolecular FLPs are able to cleave dihydrogen under mild conditions. Consequently, they have served as the basis for the development of catalysts for metal-free hydrogenation of a variety of organic substrates.² 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.^{3,4} 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 phospho-Stork reaction.^{5,6} 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 the course of this reaction type the phosphane was oxidized to the phosphinoyl, as expected, but the resulting organic nitroso compound was then selectively trapped and incorporated into the resulting FLP framework. Some examples of these transformations will be presented and discussed in this account.

We had shown that the C₄-linked frustrated P/B Lewis pairs (FLPs) **6** were readily formed by the uncatalyzed hydrophosphination of the strongly electrophilic boryl-diene **3** with sec-

ondary phosphanes R₂PH [R = mesityl (**4a**), *tert*-butyl (**4b**)] (see Scheme 1).⁷ The reaction was assumed to proceed *via* the stabilized borata-alkene intermediates **5**.^{7,8} The P/B FLPs **6** are multifunctional systems. They may show typical FLP reactions^{1–3} (the system **6a** served as a metal-free catalyst for the slow hydrogenation of an enamine) and they contain an active allylboration functionality⁹ which has been employed in respective C–C bond forming reactions and we have found sequential combinations of both reactivity types in some cases.¹⁰

In this study we first reacted the 1,4-P/B FLP **6a** with nitrosobenzene. In this case a sequence of allylboration⁹/FLP addition¹⁰ 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.

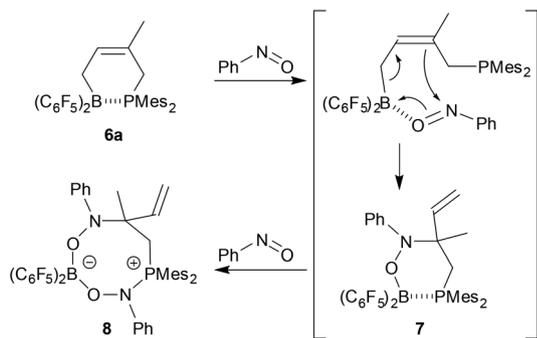
Single crystals for the X-ray crystal structure analysis were obtained from dichloromethane/pentane at –35 °C by the diffusion method. It shows the presence of a central eight-membered heterocyclic core that contains the boron and phosphorus atoms, the nitrosobenzene derived N–O units and two carbon 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



Scheme 1

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† 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.





Scheme 2

atom N2 features a trigonal-pyramidal coordination geometry ($\sum N2^{CCO} = 328.6^\circ$), whereas N1 is almost trigonal planar ($\sum N1^{COP} = 353.0^\circ$). The phenyl substituents are pseudo-equatorially oriented at the distorted crown-shaped core (see Fig. 1). The $-\text{CH}_3/-\text{CH}=\text{CH}_2$ substituents at C2 were found *ca.* 2 : 1 disordered.

In CD_2Cl_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 ^1H 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 *o*- C_6F_5 and 4 *p*- C_6F_5 ^{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

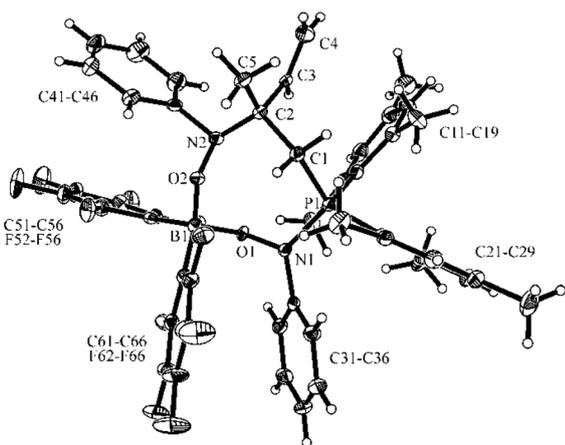


Fig. 1 Molecular structure of compound **8** (thermal ellipsoids are shown with 50% probability). Selected bond lengths (Å) and angles ($^\circ$): P1–C1: 1.820(2), P1–N1: 1.675(2), B1–O1: 1.505(3), B1–O2: 1.473(3), C3–C4: 1.342(14), O1–B1–O2: 111.6(2), C1–P1–N1: 105.4(1), B1–O1–N1: 113.4(2), B1–O2–N2: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

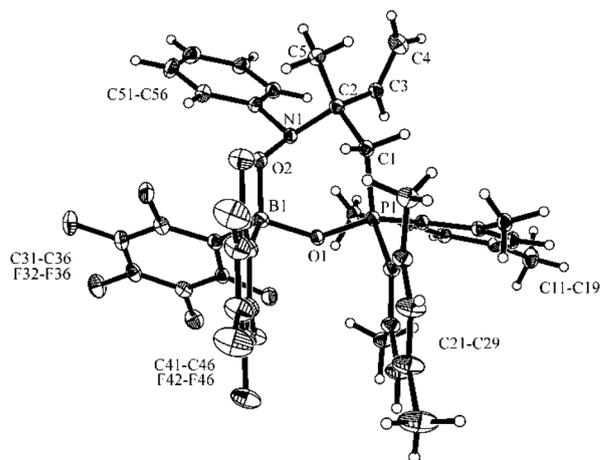


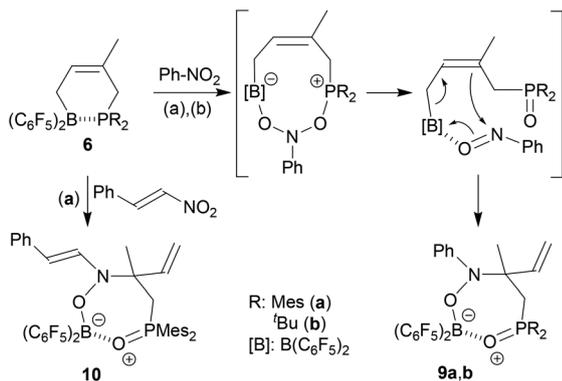
Fig. 2 Molecular structure of compound **9a** (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles ($^\circ$): P1–C1: 1.802(5), P1–O1: 1.539(3), B1–O1: 1.524(6), B1–O2: 1.456(6), C3–C4: 1.308(7), O1–B1–O2: 110.0(4), C1–P1–O1: 109.3(2), B1–O1–P1: 124.2(3), B1–O2–N1: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

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).¹¹ This trapping reaction resulted in the typical substitution pattern at the boat-shaped core,¹² namely the geminal pair of $-\text{CH}_3$ and $-\text{CH}=\text{CH}_2$ substituents at the ring carbon atom C2.

In solution (CD_2Cl_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 ^tBu substituted P/B FLP **6b** with nitrobenzene 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*- β -nitrostyrene in a 1 : 1 molar ratio (r.t., overnight, CH_2Cl_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*- β -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 62.89 (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*- β -styryl substituent attached at the ring nitrogen atom (N1) in a trigonal-pyramidal coordination geo-





Scheme 3

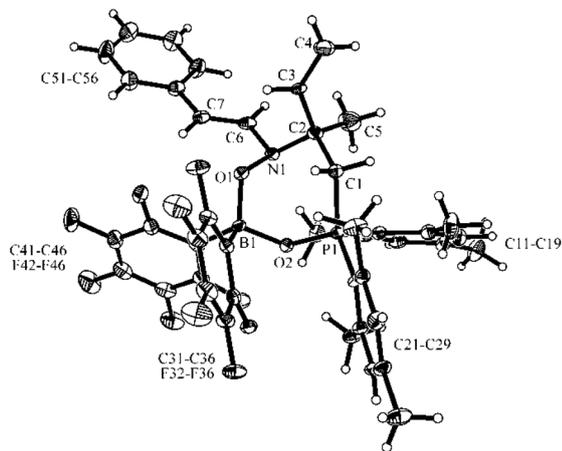


Fig. 3 A projection of the molecular structure of compound 10 (thermal ellipsoids are shown with 50% probability). Selected bond lengths (Å) and angles (°): P1–C1: 1.821(3), P1–O2: 1.545(2), B1–O1: 1.473(4), B1–O2: 1.518(4), C3–C4: 1.310(14), C6–C7: 1.329(5), O1–B1–O2: 109.5(2), C1–P1–O2: 108.4(1), B1–O2–P1: 126.0(2), B1–O1–N1: 113.1(2), C2–N1–O1: 106.9(2), $\sum \text{N1}^{\text{CCO}}$: 332.2(6).

metry. Again, the $-\text{CH}_3/-\text{CH}=\text{CH}_2$ substituent pair was found disordered at carbon atom C2 (1 : 1).

Frustrated Lewis pairs have been shown to bind or activate a variety of small molecules.^{1–3} Their typical action has even led to the discovery of a number of unprecedented reactions that can take place at some FLP frameworks.^{5,6} Among the manifold of FLP reactions, redox reactions are still quite rare and probably underrepresented.¹³ Our present study has shown that a reaction sequence involving redox transformation of organic nitro compounds can selectively be effected at suitable multifunctional 1,4-P/B FLP systems used here, which are able to scavenge the nitroso product¹⁴ component of our redox reaction sequence selectively. We hope that these findings may stimulate an increasing interest in oxidation reactions at frustrated Lewis pair frameworks.¹⁵

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