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Chemistry of a geminal frustrated Lewis pair featuring electron withdrawing C_6F_5 substituents at both phosphorus and boron†

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Hydroboration of the electron poor phosphine (1-propenyl)-$P(C_6F_5)_2$ with Piers' borane $[HB(C_6F_5)_2]$ gave the geminal frustrated Lewis pair $(C_6F_5)_2P$–CH(Et)–$B(C_6F_5)_2$. It undergoes 1,2-addition reactions to an alkene and an alkyne and to the C═N bond of an isocyanate. With mesityl azide it undergoes a 1,3-addition reaction.

Frustrated Lewis pair (FLP) chemistry is developing rapidly.[1] Various combinations of bulky Lewis acids and bases have led to non-quenched "antagonistic" pairs,[2] that often feature remarkable reactivities and reaction modes with various small molecules. The ethylene-linked Mes_2P–CH_2–CH_2–$B(C_6F_5)_2$ system (**1**) is one of the most reactive and versatile intramolecular frustrated Lewis pairs.[3] Due to the steric bulk of its substituents it features only a weak interaction between the phosphorus Lewis base and the boron Lewis acid.[3a] The system **1** rapidly splits dihydrogen at ambient conditions and reacts with various unsaturated substrates, sometimes in remarkable ways (*e.g.* with phenyl azide or with phenyl isocyanate to yield **2** or **3**, respectively, see Chart 1).[4]

Introducing steric bulk has been a common way to protect Lewis pairs from mutual annihilation by stable adduct formation between its components.[5] Attaching electron-withdrawing C_6F_5 substituents also at the Lewis base component of the pair might be an attractive alternative to induce FLP behavior electronically. The resulting decreased Lewis basicity would undoubtedly diminish the self-quenching ability of the Lewis pair, but it remained to be shown whether a sufficient residual Lewis base reactivity would remain to still observe FLP chemical behavior. We have prepared such an electronically modified intramolecular frustrated P/B Lewis pair system and observed a remarkable new FLP addition chemistry.

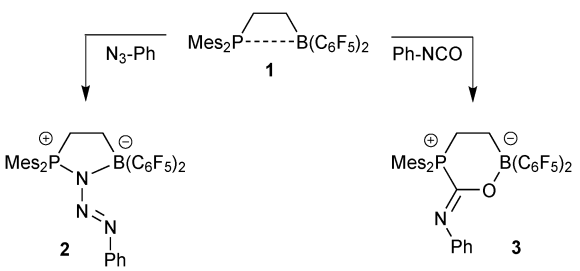
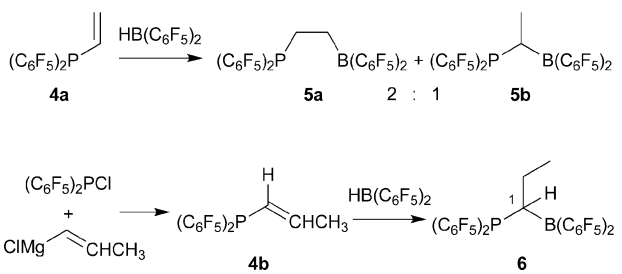


Chart 1

We prepared vinyl$P(C_6F_5)_2$ (**4a**) from $(C_6F_5)_2PCl$[6] and vinylmagnesium chloride. Subsequent hydroboration with Piers' borane $HB(C_6F_5)_2$[7] went smoothly. However, the H–[B] addition was not regioselective and we obtained the "Markovnikov" (**5b**) and "anti-Markovnikov" products (**5a**) in a *ca.* 1 : 2 ratio (see Scheme 1, for details see the ESI†). We figured that introduction of an electron-donating β-alkyl substituent should then favour the formation of the "Markovnikov product". Therefore, we reacted $(C_6F_5)_2PCl$ with 1-propenylmagnesium chloride to give a mixture of the propenyl$P(C_6F_5)_2$ products *E*- and *Z*-**4b**. Their hydroboration with $HB(C_6F_5)_2$ proceeded rapidly by regioselective "Markovnikov addition" to generate the geminal P/B Lewis pair **6** (see Scheme 1).

The hydrolysis-sensitive compound **6** was not isolated as a pure solid but freshly generated *in situ* for the respective trapping experiments. However, the geminal frustrated Lewis pair was unequivocally characterized spectroscopically. It shows the typical NMR signals of a tricoordinated boron atom [^{11}B NMR: δ 71; ^{19}F NMR: δ −128.7 (4F, *o*), −144.6 (2F, *p*) and −159.7 (4F, *m*-C_6F_5) ($\Delta\delta_{m,p}$ = 15.1)]. Due to the chiral center [^{1}H NMR: δ 4.40 (1-H)] the C_6F_5 substituents at the adjacent prochiral phosphorus atom [^{31}P NMR: δ −40.8] are diastereotopic [*e.g.* ^{19}F NMR: δ −147.8/−148.5 (*p*-C_6F_5)] (for further details see the ESI†).

Frustrated Lewis pairs add to isocyanates. Usually P/B addition to the reactive carbonyl function is observed



Scheme 1

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‡ X-ray structure analyses.

(see *e.g.* Chart 1).[4,8] The geminal P/B Lewis pair **6** also adds readily to *p*-tolyl isocyanate, but here 1,2-P/B attachment to the imine functionality is observed instead.[9] The product **7** was isolated in close to 80% yield. Single crystals for the X-ray crystal structure analysis were obtained from dichloromethane at −30 °C (see Fig. 1). It shows the formation of the five-membered heterocyclic structure of compound **7** with bond lengths P1–C01 1.889(4) Å, B1–N1 1.580(5) Å and C01–O1 1.212(5) Å. Boron and phosphorus are bridged by the propylidene unit (B1–C1 1.683(6) Å, P1–C1 1.790(4) Å, angle B1–C1–P1 102.5(2)°) originating from the FLP reagent **6**. In solution the ^{13}C NMR resonance of the carbonyl carbon of the addition product **7** was found as a broad doublet at δ 158.9 ($^{1}J_{PC} \sim 105$ Hz). The ^{19}F NMR spectrum (188 K) shows 16 signals for the diastereotopic pairs of C_6F_5 substituents at phosphorus and boron (for details see the ESI†). The IR (C═O) band of compound **7** was found at 1700 cm^{-1}.

The frustrated Lewis pair **6** reacts with 1-pentyne to regioselectively give the five-membered addition product **8** [^{31}P NMR: δ 29.8, ^{11}B NMR: δ −8.6]. It shows the ^{1}H NMR signals of the newly introduced *n*-propyl substituent. The 1-H NMR signal (δ 8.33) shows a typical large $^{3}J_{PH}$ coupling constant of *ca.* 68 Hz.[10] Similarly, the FLP **6** adds cleanly to ethylene[11] to yield the five-membered P/B heterocycle **9** [^{31}P NMR: δ 37.5, ^{11}B NMR: δ −8.7). The diastereotopic methylene ^{1}H NMR signals of the ethylene bridge occur at δ 3.38 (m)/2.91 (m) (PCH_2) and 2.05 ($^{3}J_{PH}$ = 42 Hz)/1.40 (m) (BCH_2), respectively. The diastereotopic ^{1}H NMR resonances of the CH_2 group of the ethyl substituent were found at δ 1.75 ($^{3}J_{PH}$ = 33 Hz) and 1.23 (m). Both the compounds **8** and **9** show typical ^{19}F NMR sets of signals of their pairs of diastereotopic C_6F_5 groups at both boron and phosphorus (for details see the ESI†) (Scheme 2).

Eventually, we reacted the FLP **6** with mesityl azide. Again a rapid addition reaction occurred and we isolated the product **10** in 50% yield. The X-ray crystal structure analysis revealed 1,3-addition of the frustrated P/B Lewis pair to the 1,3-dipolar reagent (Fig. 2; Scheme 3).[12] In the product **10** the strongly Lewis acidic borane was found attached at the nitrogen atom bearing the bulky aryl substituent. Inside the six-membered heterocycle compound **10** exhibits bond lengths B1–N3 1.615(3) Å, N3–N2 1.306(3) Å, N2–N1 1.304(3) Å and

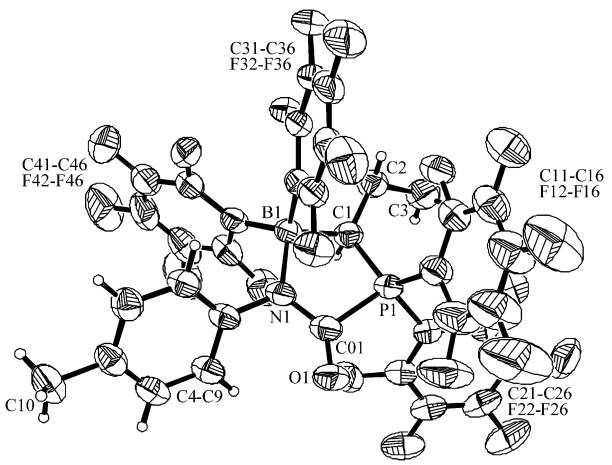
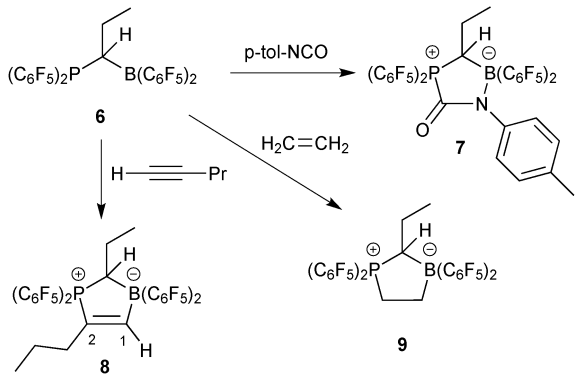


Fig. 1 Molecular structure of compound **7**.



Scheme 2

N1–P1 1.666(2) Å (bond angles: B1–C1–P1 107.6(2)°, C1–B1–N3 108.3(2)°, C1–P1–N1 108.17(11)°; dihedral angles: B1–N3–N2–N1 3.6(4)°, N3–N2–N1–P1 −9.6(3)°). The observed N–N–N bond delocalization indicates a participation of the phosphinimine resonance structure for the structural description of compound **10**. In solution compound **10** shows a NMR signal of a tetracoordinated boron center [^{11}B NMR: δ −9.3] and a broad ^{31}P NMR resonance at δ 4.0.[13] The presence of the bridging chirality center (C1) renders the pairs of C_6F_5 substituents at both boron and phosphorus diastereotopic.

We exposed the P/B system **6** to dihydrogen at various conditions but could not observe the respective splitting reaction.[5a] Nevertheless, the addition reactions described in this communication have shown that the electronically modified

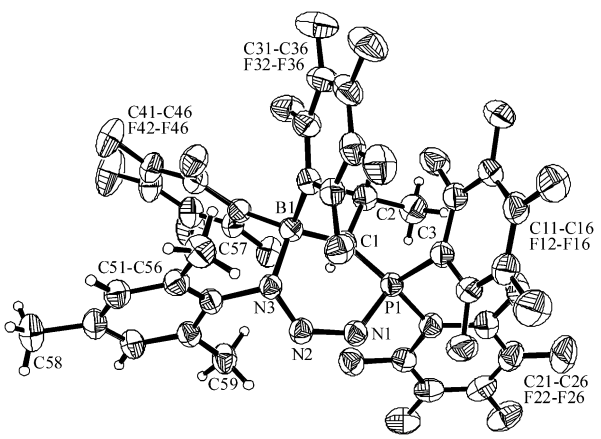
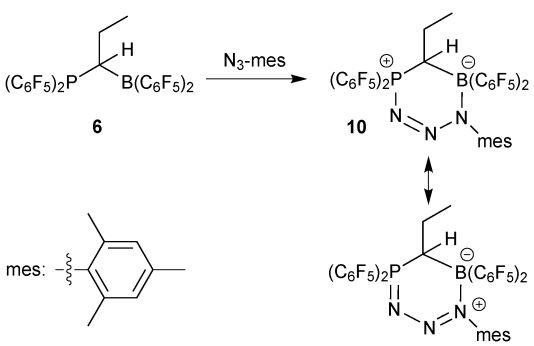


Fig. 2 Molecular structure of compound **10**.



Scheme 3

P/B system **6** shows pronounced frustrated Lewis pair reactivity despite the small spatial separation of its Lewis acid and base components in their geminal arrangement at its hydrocarbon backbone.[14] The electronically modified FLP showed some marked differences in the P/B addition reactions in detail such as a preferred addition to the C═N bond of the isocyanate as opposed to the usual C═O addition or the preferred 1,3-addition to an azide in contrast to the usual FLP 1,1- or 1,2-addition reactions to the N_3–R reagents.[4,15] This behavior indicates that electronic modification in addition to steric bulk is likely to become a powerful tool in the further development of frustrated Lewis pair construction and their characteristic chemistry.

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