INVESTIGATION OF INTERACTIONS IN LEWIS PAIRS BETWEEN PHOSPHINES AND BORANES BY ANALYZING CRYSTAL STRUCTURES FROM CAMBRIDGE STRUCTURAL DATABASE

Milan M. Milovanović, Jelena M. Andrić, Vesna B. Medaković, Jean-Pierre Djukic and Snežana D. Zarić
**S1. The crystal structures of experimental and evaluated FLPs**

The representation of crystal structures of both, experimental (Figures S2 – S11) and evaluated FLPs (Figures S12 – S21) are given to illustrate considered structures.

**Figure S1** Crystal structure SEZKAL (Ekkert et al., 2013). P: orange; B: pink; F: yellow; C: gray; H: white. This structure corresponds to the experimental FLP.
Figure S2  Crystal structure FUWKUF (Liedtke et al., 2014). P: orange; B: pink; F: yellow; Si: light green; Cl: green; C: gray; H: white. This structure corresponds to the experimental FLP.

Figure S3  Crystal structure SEZJUE (Ekkert et al., 2013). P: orange; B: pink; F: yellow; C: gray; H: white. This structure corresponds to the experimental FLP.
**Figure S4** Crystal structure **ODUJUU** (Takeuchi et al., 2013). P: orange; B: pink; F: yellow; Si: light green; O: red; C: gray; H: white. This structure corresponds to the experimental FLP.

**Figure S5** Crystal structure **FAPGIO** (Caputo et al., 2013) P: orange; B: pink; F: yellow; O: red; C: gray; H: white. This structure corresponds to the experimental FLP.
Figure S6  Crystal structure FAPGEK (Caputo et al., 2013). P: orange; B: pink; F: yellow; O: red; C: gray; H: white. This structure corresponds to the experimental FLP.

Figure S7  Crystal structure OSUZEI (Heiden et al., 2011). P: orange; B: pink; F: yellow; C: gray; H: white. This structure corresponds to the experimental FLP.
Figure S8  Crystal structure OLAJOB (Ullrich et al., 2010). P: orange; B: pink; F: yellow; C: gray; H: white. This structure corresponds to the experimental FLP.

Figure S9  Crystal structure OLAJUH (Ullrich et al., 2010). P: orange; B: pink; F: yellow; C: gray; H: white. This structure corresponds to the experimental FLP.
Figure S10 Crystal structure MIKDER (Barry et al., 2013). P: orange; B: pink; F: yellow; the nitrogen atoms - blue, C: gray; H: white. This structure corresponds to the experimental FLP.

Figure S11 Crystal structure FUWLEQ (Liedtke et al., 2014). P: orange; B: pink; F: yellow; Si: light green; the sulfur brown, C: gray; H: white. This structure corresponds to the evaluated FLP.
Figure S12 Crystal structure BIRXAD (Yu et al., 2013). P: orange; B: pink; F: yellow; C: gray; H: white. This structure corresponds to the evaluated FLP.

Figure S13 Crystal structure XUPZAK (Geier & Stephan, 2010). P: orange; B: pink; F: yellow; Si: light green; C: gray; H: white. This structure corresponds to the evaluated FLP.
Figure S14 Crystal structure EWETAC (Ekkert et al., 2011). P: orange; B: pink; F: yellow; C: gray; H: white. This structure corresponds to the evaluated FLP.

Figure S15 Crystal structure MIKCUG (Barry et al., 2013). P: orange; B: pink; F: yellow; N: blue; C: gray; H: white. This structure corresponds to the evaluated FLP.
Figure S16 Crystal structure ROVLAR (Moquist et al., 2015). P: orange; B: pink; F: yellow; C: gray; H: white. This structure corresponds to the evaluated FLP.

Figure S17 Crystal structure YORPAX (Spies et al., 2009). P: orange; B: pink; F: yellow; C: gray; H: white. This structure corresponds to the evaluated FLP.
Figure S18  Crystal structure **EWESUV** (Ekkert et al., 2011). P: orange; B: pink; F: yellow; C: gray; H: white. This structure corresponds to the evaluated FLP.

Figure S19  Crystal structure **TACHAI** (Chapman et al., 2010). P: orange; B: pink; F: yellow; O: red; C: gray; H: white. This structure corresponds to the evaluated FLP.
Figure S20 Crystal structure SIGVUB01 (Beckmann et al., 2013). P: orange; B: pink; C: gray; H: white. This structure corresponds to the evaluated FLP.

S2. Analysis of the data from CSD for FLPs

The separated distributions of the studied geometrical parameters ($\phi$, $d_{B-P}$, $r$, $R$ (Figure 1)) of both, experimental and evaluated FLPs are given to show similarity in the distribution and to confirm the reliability of the way of choosing the evaluated FLPs.

Figure S21 The distribution of the dihedral angle $\phi$ (Figure 1) of the interacting molecules in the contacts in the FLPs set. The notation experimental FLPs represents the structures for which there is experimental evidence in the literature that they belong to the class of frustrated Lewis pairs. The notation evaluated FLPs represents the structures for which there is no experimental evidence in the
literature that they belong to the class of frustrated Lewis pairs, but they are structurally very similar to the documented ones.

**Figure S22** The distribution of the distance between phosphorus and boron atoms $d_{\text{B-P}}$ (Figure 1) of the interacting molecules in the FLPs set. The notation experimental FLPs represents the structures for which there is experimental evidence in the literature that they belong to the class of frustrated Lewis pairs. The notation evaluated FLPs represents the structures for which there is no experimental evidence in the literature that they belong to the class of frustrated Lewis pairs, but they are structurally very similar to the documented ones.

**Figure S23** The distribution of the offset distance $r$ (Figure 1) of the interacting molecules in the FLPs set. The notation experimental FLPs represents the structures for which there is experimental evidence in the literature that they belong to the class of frustrated Lewis pairs. The notation evaluated FLPs represents the structures for which there is no experimental evidence in the literature that they belong to the class of frustrated Lewis pairs, but they are structurally very similar to the documented ones.
Figure S24 The distribution of the normal distance $R$ (Figure 1) of the interacting molecules in the FLPs set. The notation experimental FLPs represents the structures for which there is experimental evidence in the literature that they belong to the class of frustrated Lewis pairs. The notation evaluated FLPs represents the structures for which there is no experimental evidence in the literature that they belong to the class of frustrated Lewis pairs, but they are structurally very similar to the documented ones.