

**Reviewers' Comments:**

Reviewer #1: Stephan et al. have reported a new reactivity mechanism for FLPs, that is, one -electron transfer (SET) process. FLPs were first reacted each other to form radical pairs and then reacted with other molecules, leading to a homolytic cleavage rather than previously well studied heterolytic cleavage. The SET mechanism has been identified by a series of well-designed reactions. The new radical mechanism will be an alternative way to understand reactivity of FLP systems. The manuscript is very suitable for publication in Chem.

Reviewer #2: Stephan and coworkers report an interesting mechanistic study of the reactivity of frustrated Lewis pairs derived from the combination of R<sub>3</sub>P (R = tBu and Mes<sub>3</sub>) and E(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (E = B and Al) with small molecules. It has been suggested that while tBu<sub>3</sub>P/E(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> react through a classical two-electron process involving a transient encounter complex, Mes<sub>3</sub>P/ E(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> proceed via a single electron transfer mechanism. To support these hypotheses, a series of control experiments have been carried and EPR and NMR analyses of some of the intermediates have been performed.

The manuscript is well presented and contains very useful data that will be of great importance not only to people working on FLP chemistry but to physical organic chemists as well.

However, I feel that some extra mechanistic experiments should be performed to fully support the mechanism suggested by the authors. I will therefore wait for authors responses to my concerns before accepting this nice study.

Because chloranile is known to be a good electron acceptor, it is possible that it forms a charge transfer complex when combined with Mes<sub>3</sub>P. Complexes of this type have UV-Vis spectra similar to that given in the supporting information and assigned to be of the phosphorus radical cation. For instance, please see: (Tetrahedron Letters, 1994, 35, 8577-8580; Spectrochimica Acta Part A 57 (2001) 223-229...). The intermediates 5-8 can also be formed if the reaction proceeds through a CTC between chloranile and Mes<sub>3</sub>P. It would therefore be interesting to perform electrochemical investigations to rule out this mechanistic scenario.

Minor points:

The seminal work by Kochi as well as Fukuzumi on the formation of CTC complexes with quinones and related structures should be quoted.

Many references must be cited in the introduction. Specifically, the authors should quote monographs and reviews when talking about importance of reaction mechanisms (for example: Dougherty, D. A.; Anslyn, E. V. Modern Physical Organic Chemistry; University Science: Sausalito, CA, 2006, etc...

Reviewer #3: Comments enter in this field will be shared with the author; your identity will remain anonymous.

I think that this report by Stephan et al is an important paper that should by all means be published in

Chem. They showed in a very clever experimental approach that the tBu<sub>3</sub>P/E(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> frustrated Lewis pairs (E=B or Al) reacted with tetrachloro-p-benzoquinone in a conventional way giving the 1,6-phosphane/borane addition product 1 or 2. With Ph<sub>3</sub>SnH these systems also reacted in a conventional way giving the hydride transfer products (3 and 4, respectively). It is the reaction mode of the corresponding (mesityl)<sub>3</sub>P/E(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> frustrated pairs that makes this paper so special: the authors could convincingly show that in this case a different pathway is favored, initiated by SET (single electron transfer) to give the respective radical cation/radical anion pairs. With 0.5 molar equiv. of the p-quinone these form the dianionic bis-Lewis acid to carbonyl oxygen adducts with the mes<sub>3</sub>P-radical cation (2 equiv.) serving as counter ions. Trapping of the salts 5 or 6 with Ph<sub>3</sub>SnH then gave the respective mes<sub>3</sub>PH<sup>+</sup> cation containing products; trapping with another half equiv. of the quinone gave the P/B adducts 8 or 9. In addition, some of the radical ions were identified by X-band epr spectroscopy and many of the products were structurally secured by X-ray diffraction. There are only a few minor amendments or corrections being called for. On the first page of the Results and Discussion section, 2nd paragraph, the sentence -Regardless... should be rephrased ..treatment of these toluene dissolved frustrated Lewis pair mixtures...In Figure 2 probably the wrong structure has been inserted at the upper right corner: depicted is the structure of the mes<sub>3</sub>P adduct 9 instead of the tBu<sub>3</sub>P compound 1. Aside from these very minor issues I consider this as a seminal paper that should find the interest of the general chemical public addressed by this Journal. I strongly recommend publication of this paper in Chem.