High-Coordinate Phosphasiliranes: Do they exist?

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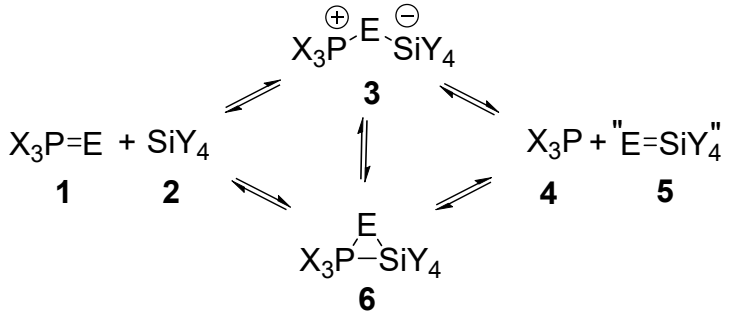
A fundamental discovery in *p*-block chemistry has been the development of FLPs (frustrated Lewis pairs).[1] Those derived from 1,3-zwitterionic species could form the corresponding three-membered ring isomers. These are systems composed of a Lewis acidic and basic centres that, generally, are not likely to form a stable adduct due to steric factors. Therefore, it could be envisaged that such systems could activate small molecules[2] through a synergistic action of both centres.

The following reactions have been studied: *a priori* stable $X_3P{=}E$ species react with coordinatively saturated (and stable) SiY_4 species to give dipolar species **3** with a hypervalent (pentacoordinate) silicon centre (Scheme 1), which could eventually form phosphasiliranes **6** bearing a hexacoordinate silicon and pentacoordinate phosphorus atom.[3] But both species **3** and **6** could also enable a E-group transfer giving rise to X_3P (**4**) and $E{=}SiY_4$ (**5**), finally.



Scheme 1: Studied interconversions (E = CH_2, SiH_2, NH, PH, O or S; X,Y = Me, NH_2, Tms, F, CF_3).

As it turned out, the choice of substituents is key to finding stable species in these interconversions (Scheme 1), *i.e.*, donors X at P and acceptors Y at Si should favour acyclic zwitterionic structures **3**. The opposite electronic nature of X and Y could eventually favour a cyclic structure **6** which would represent the first example of a three-membered heterocyclic ring with two hypercoordinate centres.[3]

[1] D. W. Stephan, *J. Am. Chem. Soc,* **2015**, *137*, 10018–10032.
[2] G. C.Welch. R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science*, **2006**, *314*, 1124–1126.
[3] A. Rey Planells, A. Espinosa Ferao, R. Streubel, *to be published.*