Tackling the chemistry of 1,2-oxaphosphetanes via theoretical calculations

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In recent years, 1,2$\sigma^3\lambda^3$-oxaphosphetanes *κP*-metal carbonyl complexes (**I**, Figure 1) were successfully prepared through ring expansion of epoxides using Li/Cl phosphinidenoid complexes.[1] However, the mechanistic aspects of this reaction have never been investigated. On the other hand, free 1,2$\sigma^3\lambda^3$-oxaphosphetanes (**II**) could be accessed from their ligated counterparts using a decomplexation strategy, and first investigations towards *P*-oxidation were conducted.[2] More recently, new *C*-substituted derivatives of **II** were prepared and oxidation to the corresponding *P*-chalcogenides **III** (E = O, S, Se) was achieved,[3] thus entering the rather elusive area of 1,2$\sigma^4\lambda^5$-oxaphosphetanes.

Herein, the mechanism and regiochemical outcome of the formation of C^3- and C^4-phenyl substituted 1,2$\sigma^3\lambda^3$-oxaphosphetane *κP*-$Mo(CO)_5$ complexes by means of DFT calculations are presented using styrene oxide and a model Li/Cl phosphinidenoid complex as starting materials *in silico*. In addition, ring strain energies (RSEs), isomerization reactions leading to 1,2$\sigma^4\lambda^5$-chalcogenaphosphetane *P*-oxides (**IV**) or 1,3,2$\sigma^3\lambda^3$-oxachalcogenaphospholanes (**V**) were calculated, and the potential retro-[2+2] cycloaddition reactions of **III** analysed.

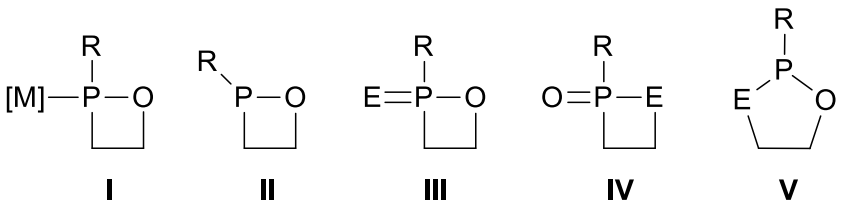

*Figure 1: 1,2$\sigma^3\lambda^3$-oxaphosphetane metal complexes (**I**), 1,2$\sigma^3\lambda^3$-oxaphosphetanes (**II**), 1,2$\sigma^4\lambda^5$-oxaphosphetanes (**III**), 1,2$\sigma^4\lambda^5$-chalcogenaphosphetanes (**IV**) and 1,3,2$\sigma^3\lambda^3$-oxachalcogenaphospholanes (**V**).*

[1] a) A. W. Kyri, V. Nesterov, G. Schnakenburg, R. Streubel, *Angew. Chem. Int. Ed.* **2014**, *53*, 10809–10812; b) A. W. Kyri, G. Schnakenburg, R. Streubel, *Organometallics,* **2016**, *35*, 563-568.

[2] A. W. Kyri, F. Gleim, A. García Alcaraz, G. Schnakenburg, A. Espinosa Ferao, R. Streubel, *Chem. Commun.* **2018**, *54*, 7123-7126.

[3] F. Gleim, G. Schnakenburg, A. García Alcaraz, A. Espinosa Ferao, R. Streubel, *unpublished results.*