Inspecting new cyclic diheterophospholane complexes as potential phosphanoxyl complex precursors

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In 2012, we had first speculated about the presence of phosphanoxyl complexes **I** in the decomposition of *P*-2,2,6,6-tetramethylpiperidinoxyl (TEMPO) substituted phosphane complexes **II**.[1] In the following years, we achieved to get further evidence for transient phosphanoxyl complexes **I** using *P*-TEMPO substituted complexes **II**, the latter being stable up to 60 °C.[2] First studies using a 1,3,2-diazaphospholane complex had revealed a significant decrease in thermal stability.[3] Therefore, a new study on synthesis and reactivity of diheterophospholane complexes **III** was launched.

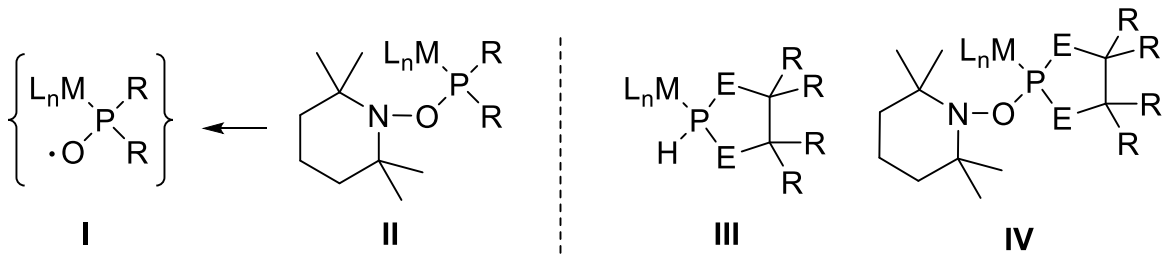

*Figure 1: Phosphanoxyl complex **I**, 2,2,6,6-Tetramethylpiperidinoxyl (TEMPO) substituted phosphan complex **II**, diheterophospholan complexes **III**, with E = O, R = Me, E = NR, R= H.*

Herein, a new multi-step synthetic protocol to access a family of diheterophospholane complexes **III** and their conversion into the *P*-TEMPO derivatives **IV** will be described.[4] The suitability of the latter to form transient phosphanoxyl complexes was experimentally and theoretically investigated, and the transient open-shell complexes were used to polymerize various common monomers.[4]

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[2] a) T. Heurich, Z.-W. Qu, S. Nozinovic, G. Schnakenburg, H. Matsuoka, S. Grimme, O. Schiemann, R. Streubel, *Chem. Eur. J.* **2016**, *22*, 10102 b) T. Heurich, V. Nesterov, G. Schnakenburg, Z.-W. Qu, S. Grimme, K. Hazin, D. P. Gates, M. Engeser, R. Streubel, *Angew. Chem. Int. Ed.* ***2016****, 55*, 14439 c) T. Heurich, Z.-W. Qu, G. Schnakenburg, Y. NejatyJahromy, O. Schiemann, S. Grimme, R. Streubel, *Organometallics* **2017**, *56*, 2877.

[3] T. Heurich, Z.-W. Qu, R. Kunzmann, G. Schnakenburg, M. Engeser, S. Nožinović, R. Streubel, *Chem. Eur. J.* **2018**, *24*, 6473-6478.

[4] P. C. Brehm, A. S. Müller-Feyen, G. Schnakenburg, R. Streubel, *unpublished results.*