Bis-[3]Ferrocenophanes with Central \( E=E'< \) Bonds (E, E’=P, SiH): Preparation, Properties, and Thermal Activation

Invited for this month’s cover picture are the groups of Professors Rudolf Pietschnig at the University of Kassel, Professor Dietrich Gudat at the University of Stuttgart and Professor László Nyulász at the Budapest University of Technology and Economics. The cover picture shows the thermally induced homolytic cleavage of the central P-P bond in a phosphorus–rich bis-ferrocenophane furnishing P-centered radicals (as evidenced by the computed spin-density highlighted in blue). The central P\( _{6} \) unit in the title compound is a structural analog of the connecting unit in Hittorf’s violet phosphorus, which links the orthogonally arranged tubular entities. A portrait of the German physicist Johann Wilhelm Hittorf is included. Read the full text of their Full Paper at 10.1002/open.201900182.

Who designed the cover?
The cover was designed by Dr. Zsolt Kelemen based on ideas of various co-authors.

What was the biggest challenge (on the way to the results presented in this paper)?
Once we discovered the homolytic cleavage of the central P-P bond, the temperature happened to be close to the limit of the temperature window of the EPR spectrometer available to our research consortium. It turned out to be quite a challenge to find a facility where VT-EPR spectra could be recorded at temperatures above 100 °C. Thanks to the participation of some of the authors in the EU-COST action Smart Inorganic Polymers (SIPs), we eventually found a partner within this network where EPR-measurements were possible even up to 250 °C.

What aspects of this project do you find most exciting?
The ease of cleavage of homonuclear bonds in these compounds is very exciting, and in particular the fact that, in contrast to our initial assumptions, phosphorus centered radicals with two phosphanyl substituents are sufficiently stable for detection while their amino substituted congeners are not. In addition, we are amazed by the structural parallels between our bisferrocenophanes and the bridging units in Hittorf’s violet phosphorus, which include even the bond length alternation pattern with the location of the shortest P-P bond in the center of the scaffold. Surprisingly enough, it is this shortest P-P bond in the molecule which acts as breaking point upon moderate heating.