**An Old Hat with New Feathers –  
Heteroldianions as Precursors for   
Unusual Silicon and Germanium Compounds**

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During the last years, we investigated the potential of heterole dianions **1** for the synthesis of low valent silicon and germanium compounds. Panel a) shows some recent examples including a dimeric Ti(III) complex **2** with an unprecedented Ti-Ge-Ge-Ti multi-center bond,[1] a borole complex of Ge(II) **4**[2]  and bicyclohexene-type tetrylenes **3**,[3-5] which are stabilized by homoconjugation with a remote C=C double bond. Although some of the here described compounds might safely be qualified as laboratory curiosities, their investigation allow deep insights into fundamental reactions in Chemistry.



Panel b) shows the simple Lewis acid base reaction between the nucleophilic germylene **3**(Ge) and B(C6F5)3 as a Lewis acid. We will provide evidence that this reaction proceeds via a single electron transfer (SET). [6] This unusual behavior is put into context with our recent investigation on Frustrated Radical Pairs that existent in equilibrium with silylium / phosphane Frustrated Lewis Pairs.[7]

[1] Z. Dong, O. Janka, J. Kösters, M. Schmidtmann, T. Müller „ *A Dimeric 1,5-Germole Dianion Bridged Titanium(III) Complex with a Multicenter Ti-Ge-Ge-Ti Bond*” Angew. Chem. Int. Ed. **2018**, 57, 8634-8638. [2] P. Tholen, Z. Dong, M. Schmidtmann, L. Albers „*A Neutral 5-Aminoborole Complex of Germanium(II)*“ Angew. Chem. Int. Ed. **2018**, 57, 13319-13324. [3] Z. Dong, C. R. W. Reinhold, M. Schmidtmann, T. Müller “***A Germylene Stabilized by Homoconjugation***“ Angew. Chem. Int. Ed. **2016**, 55, 15899-15904. [4] Z. Dong, C. R. W. Reinhold, M. Schmidtmann, T. Müller ***“A Stable Silylene with a σ2,π-Butadiene Ligand“***  J. Am. Chem. Soc. **2017**, 139, 7117-7123. [5] Z. Dong, K. Bedbur, M. Schmidtmann, T. Müller *„Hafnocene-based Bicyclo[2.1.1]hexane Germylenes – Formation, Reactivity and Structural Flexibility“* *J. Am. Chem. Soc*. **2018**, *140*, 3052. [6] Z. Dong, H. H. Cramer, M. Schmidtmann, L. A. Paul, I. Siewert, T. Müller „*Evidence for Single Electron Shift in a Lewis Acid Base Reaction*“ *J. Am. Chem. Soc*. **2018**, *140*, DOI: 10/1021/jacs8b09214. [7] A. Merk, H. Großekappenberg, M. Schmidtmann, M.-P. Luecke, C. Lorent, M. Driess, M. Oestreich, H. F. T. Klare, T. Müller “*Single-Electron Transfer Reactions in Frustrated and Conventional Silylium Ion /Phosphane Lewis Pairs*” *Angew. Chem. Int. Ed.* **2018**, *57* DOI: 10.1002/anie.201808922.