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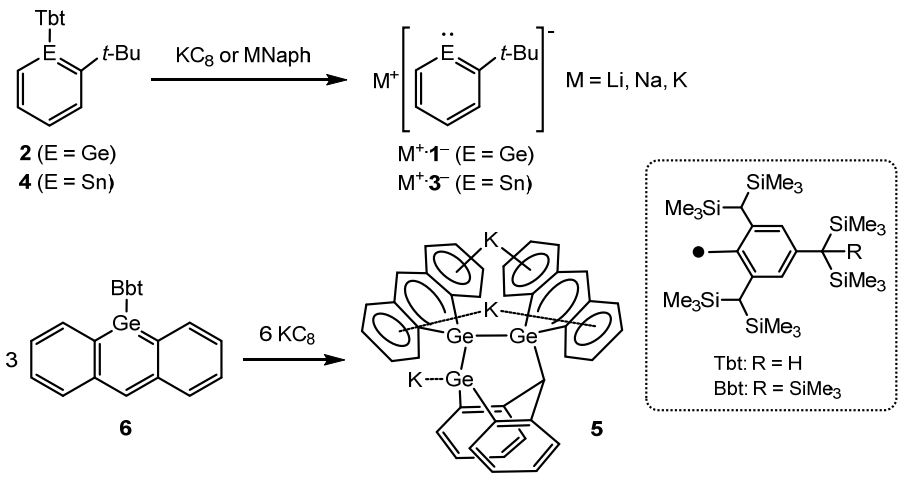
Synthesis and Properties of Heavier Group 14 Element Analogues of Aryl Anions

Shiori Fujimori,[1] Yoshiyuki Mizuhata[1,2] and Norihiro Tokitoh*[,1,2]
[1]*Institute for Chemical Research, Kyoto University,*
[2]*Integrated Research Consortium on Chemical Sciences (IRCCS),*
Gokasho, Uji, Kyoto 611-0011, JAPAN
tokitoh@boc.kuicr.kyoto-u.ac.jp, http://oec.kuicr.kyoto-u.ac.jp/~tokitohlab/tokitoh/index_e.html

We have recently reported the synthesis and isolation of 2-*tert*-butylgermabenzenylpotassium ($K^+\cdot\mathbf{1}^-$), the first example of heavy phenyl anion, *i.e.*, a germanium analogue of phenylpotassium, by the reaction of 1-Tbt-2-*tert*-butylgermabenzene **2** with KC_8.[1] Spectroscopic and X-ray crystallographic analysis together with theoretical calculations revealed that $K^+\cdot\mathbf{1}^-$ exhibits not only aromatic character due to the C_5Ge system but also germylene character due to the delocalization of negative charge on the five ring carbon atoms.[1] $Li^+\cdot\mathbf{1}^-$ and $Na^+\cdot\mathbf{1}^-$ were also synthesized from **2** to elucidate the effect of the counter ion on the properties of germabenzenyl anion and $Na^+\cdot\mathbf{1}^-$ was fully characterized by NMR spectroscopy and X-ray diffraction analysis.[2]

These results are of great interest from the viewpoints of not only the synthesis and characterization of new germabenzenyl anions but also systematic comparison for heavy arylmetals having different alkali metals, because such an approach is very scarce even in the chemistry of carbon analogues.



Furthermore, stannabezenylpotassium $K^+\cdot\mathbf{3}^-$ was also synthesized starting from the corresponding stannabenzene **4**. In the case of Bbt-substituted 9-germaanthracene **6**, the reaction with KC_8 resulted in the formation of a unique trimer **5** of the initially formed germaanthracenylpotassium.

References:

(1) Y. Mizuhata, S. Fujimori, T. Sasamori, N. Tokitoh, *Angew. Chem., Int. Ed.* **2017**, *56*, 4588.
(2) S. Fujimori, Y. Mizuhata, N. Tokitoh, *Chem. Lett.* **2018**, *37*, 708–710.