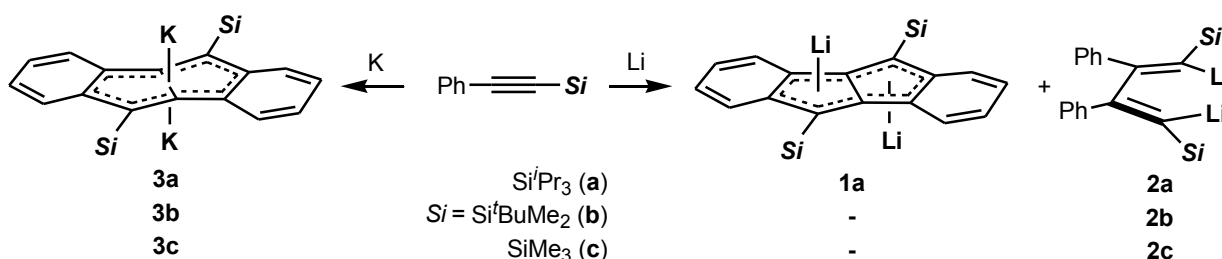


## Synthesis of Dibenzopentalenides by the Reduction of Phenylsilylacetylenes –from by chance to on purpose–

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The reduction of phenylacetylenes by lithium to afford 1,4-dilithio-1,3-butadienes have long been known since the first report in 1928<sup>[1]</sup> and the 1,4-dilithio-1,3-butadienes are now utilized as intermediates for the synthesis of a wide variety of  $\pi$ -conjugated compounds such as heteroles.<sup>[2]</sup> We also utilized 1,4-dilithio-1,3-butadienes for the synthesis of stannoles and plumboles, the dilithio derivatives of which possess considerable aromatic nature.<sup>[3]</sup> During the course of our studies on the synthesis of 1,4-dilithio-1,3-butadienes bearing bulky silyl groups at the 1,4-positions, we serendipitously found the formation of dilithium dibenzopentalenide **1a** as a minor product in the reduction of phenyl(triisopropylsilyl)acetylene with lithium, even though the expected 1,4-dilithio-1,3-butadiene **2a** was obtained as a major product.<sup>[4]</sup> In contrast, reduction of phenylacetylenes bearing silyl groups less bulky than a triisopropylsilyl group only afforded 1,4-dilithio-1,3-butadienes **2b-c**. However, using potassium as a reductant exclusively afforded dipotassium dibenzopentalenides **3**.<sup>[5]</sup> The synthesis of transition-metal complexes and polymers bearing dibenzopentalene units will also be demonstrated.<sup>[6]</sup>



- [1] (a) W. Schlenk, E. Bergmann, *Liebigs Ann. Chem.* **1928**, 463, 71.  
[2] (a) J. Dubac, A. Laporterie, G. Manuel, *Chem. Rev.* **1990**, 90, 215–263. (b) F. Mathey, *Chem. Rev.* **1988**, 88, 429–453.  
[3] (a) M. Saito, R. Haga, M. Yoshioka, K. Ishimura, S. Nagase, *Angew. Chem., Int. Ed.* **2005**, 44, 6553–6556. (b) M. Saito, T. Kuwabara, C. Kambayashi, M. Yoshioka, K. Ishimura, S. Nagase, *Chem. Lett.* **2010**, 39, 700–701. (c) M. Saito, M. Sakaguchi, T. Tajima, K. Ishimura, S. Nagase, M. Hada, *Science* **2010**, 328, 339–342. (d) M. Saito, M. Nakada, T. Kuwabara, M. Minoura, *Chem. Commun.* **2015**, 51, 4674–4676 (2015).  
[4] M. Saito, M. Nakamura, T. Tajima, M. Yoshioka, *Angew. Chem., Int. Ed.* **2007**, 46, 1504–1507.  
[5] T. Kuwabara, K. Ishimura, T. Sasamori, N. Tokitoh, M. Saito, *Chem. Eur. J.* **2014**, 20, 7571–7575.  
[6] (a) T. Kuwabara, N. Kurokawa, M. Saito, *ChemPlusChem* **2017**, 82, 1039–1042. (b) M. Saito, Y. Suda, S. Furukawa, T. Nakae, T. Kojima, H. Sakaguchi, *Chem. Lett.* **2017**, 46, 1099–1101.