Identifying Suitable Strategies for Silole Synthesis

Biography
Alexander Pöcheim obtained his M.Sc. from Graz University of Technology in 2018. Currently he is pursuing his Ph.D. studies under the supervision of Dr. Judith Baumgartner and Prof. Christoph Marschner, focusing on the use of anionic silicon compounds as ligands for early transition and rare earth metals.

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Abstract
We are currently working in the field of group 4 metalloles with a main focus on siloles. Siloles are higher congeners of cyclopentadiene, which have an astoundingly narrow HOMO–LUMO gap. For this reason, we are interested in their electronic properties and their use as ligands for early transition and rare earth metals. In this case study I utilize Science of Synthesis Online to search the literature for strategies toward silole synthesis and to reduce the various options to a small number of most suitable pathways. (Scheme 1)

Discussion
Since the very first synthesis of a silole some 60 years ago by Braye et al., various synthetic strategies have been developed. The small HOMO–LUMO gap, fluorescent behavior, and the ability to engage in aggregation induced emission make siloles of special interest not only for optoelectronic devices, but also as ligands. Therefore, we used Science of Synthesis Online to search the available synthetic strategies for the most suited to our research.

Noteworthy is that Science of Synthesis Online has a distinct 18-page chapter on the subclass of siloles written by J. Kobayashi and T. Kawashima in 2014. This chapter was found by clicking on “Explore Contents” and subsequently following the subclasses “Organometallics”, “Silicon Compounds and As, Sb, Bi Compounds (Group 15)”, “Silicon Compounds” and “Siloles”. In this chapter the different synthetic approaches are sorted from a retrosynthetic point of view, based upon which bonds of the silole ring are formed. A careful review reduces our synthetic options to two, applying the criteria of having no siloles in condensed ring systems and the required possibility to introduce silyl substituents in 2- and 5-positions (Scheme 2). Path I is an endo–endo reductive intramolecular cyclization of a dialkynylsilane with lithium naphthalenide and subsequent treatment of the in situ generated 2,5-dilithiosilole with halosilanes.

This method offers a rich scope of different substituents in 1,2,5-positions, but critically depends on aryl substituents in positions 3 and 4. Yields of this method are typically very good with more than 80%. In a complementary route, path II offers manifold substitution possibilities for the 2-, 3-, 4-,and 5-positions, but is rather limited with respect to substituents on the central ring silicon atom (Scheme 2). The transmetallation step from the zirconacyclopentadiene requires silanes with high electrophilicity and low steric demand. Even in the case of tetrabromosilane the yield of 28% under harsh conditions is rather low.
Conclusion
Science of Synthesis Online is helpful on manifold different substructure related synthetic strategies. In the case of siloles, a dedicated chapter on this topic exists, providing an overview about the most common and synthetically reliable strategies. The additional option to search for structures and/or topics complemented the literature search well. Overall the focus on the experimental aspects of chemistry is very handy. The procedures, yields, and comparisons of solvents as well as the cross-referenced literature are easily obtainable from the text. In conclusion Science of Synthesis is an enrichment for a chemist’s everyday life.