

Synthesis of π -Functional Molecules through 1,3-Dipolar Cycloaddition of Polycyclic Aromatic Azomethine Ylides and Silicon or Germanium Dipolarophiles

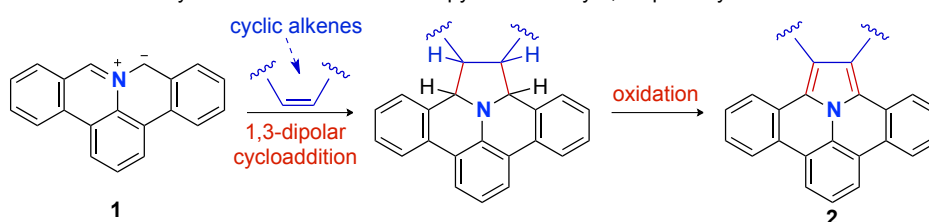
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Research Context and General Objectives

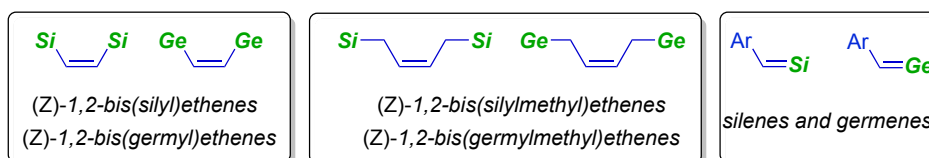
Incorporation of group 14 heteroatoms Si and Ge in π -conjugated molecules confers interesting electronic characteristics to the parent structure.¹ Inclusion of Si is increasingly frequent and this strategy has opened new perspectives for the design of functional materials. Conversely, less work has been focused on Ge congeners. It is important to underscore that the accessibility to such Si- and Ge-containing molecules relies heavily on the development of appropriate synthetic methodology for C–Si and C–Ge bond formation.

The Ito group has developed the use of polycyclic aromatic azomethine ylides (e.g. **1**) as versatile building blocks to prepare polycyclic aromatic hydrocarbons (PAHs) containing a fused pyrrole unit (e.g. **2**) through 1,3-dipolar cycloaddition / oxidation sequences. This strategy has been implemented with an array of (cyclic) alkenes to prepare original PAHs with diverse functionalities of interest for material chemistry.² Introduction of Si or Ge atoms to the fused pyrrole PAH frameworks should add novel functionalities such as emissive properties.³ To evaluate this prospect, the objective of our proposal is to develop Si- or Ge-containing dipolarophiles competent to be engaged with **1** in the 1,3-dipolar cycloaddition / oxidation sequence, and thereby access unprecedented Si- or Ge-containing PAHs. The originality of the work will be related to the development of innovative synthetic methodology and to the characterisation of new functional molecules.

Previous work : Synthesis of PAHs with fused pyrrole units by 1,3-dipolar cycloaddition / oxidation sequence

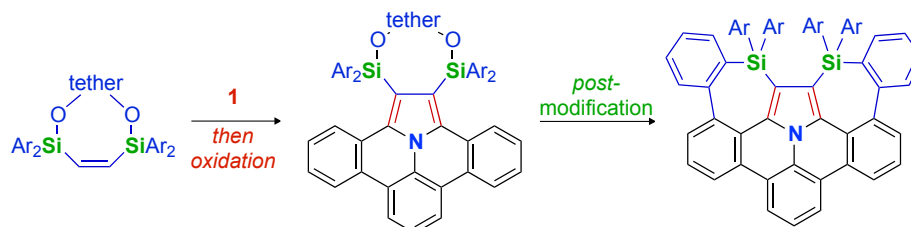


This proposal : Si or Ge-containing dipolarophiles for the 1,3-dipolar cycloaddition / oxidation sequence



Specific Research Objectives

Encouraged by literature precedents proving that disubstituted vinylsilanes are suitable partners for 1,3-cycloadditions with azomethine ylides,⁴ we will consider the performance of the related 1,2-bis(silyl)ethenes. Among the many possible options, cyclic



¹ a) K. Tamao, M. Uchida, T. Izumizawa, F. Furukawa, S. Yamaguchi, *J. Am. Chem. Soc.* **1996**, *118*, 11974. b) T. A. Su, H. Li, R. S. Klausen, N. T. Kim, M. Neupane, J. L. Leighton, M. L. Steigerwald, L. Venkataraman, C. Nuckolls, *Acc. Chem. Res.* **2017**, *50*, 1088. c) J. Ohshita, M. Sugino, Y. Ooyama, Y. Adachi, *Organometallics* **2019**, *38*, 1606.

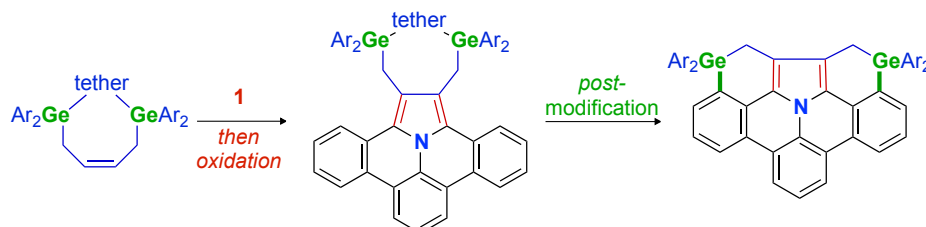
² Selected references: a) S. Ito, Y. Tokimaru, K. Nozaki, *Chem. Commun.* **2015**, *51*, 221. b) S. Ito, Y. Tokimaru, K. Nozaki, *Angew. Chem. Int. Ed.* **2015**, *54*, 7256. c) Y. Tokimaru, S. Ito, K. Nozaki, *Angew. Chem. Int. Ed.* **2017**, *56*, 15560. d) X. Zhang, M. R. Mackinnon, G. J. Bodwell, S. Ito, *Angew. Chem. Int. Ed.* **2022**, *61*, e202116585. e) W. Wang, F. Hanindita, Y. Tanaka, K. Ochiai, H. Sato, Y. Li, T. Yasuda, S. Ito, *Angew. Chem. Int. Ed.* **2023**, *62*, e202218176. f) Y. Hamamoto, K. Ochiai, Y. Li, E. Tapavicza, S. Ito, *Angew. Chem. Int. Ed.* **2024**, *63*, e202319022.

³ Y. Yabusaki, N. Ohshima, H. Kondo, T. Kusamoto, Y. Yamanoi, H. Nishihara, *Chem. Eur. J.* **2010**, *16*, 5581.

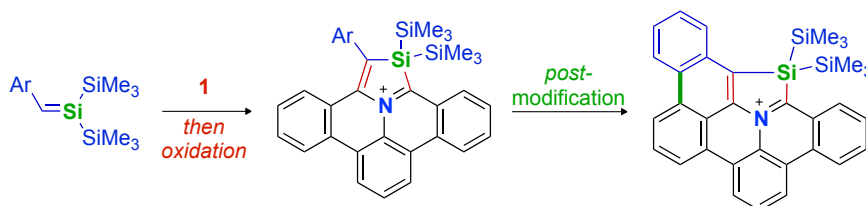
⁴ R. Chowdhury, A. K. Dubey, S. K. Ghosh, *J. Org. Chem.* **2019**, *84*, 2404.

structures having the two Si atoms linked by a dialkoxy tether are particularly attractive;⁵ the Z geometry of the double bond will reduce steric hindrance during the cycloaddition event and the alkoxy moiety will offer a handle for subsequent downstream elaboration. Following on this chemistry, analogous 1,2-bis(germyl)ethenes could be similarly considered (not shown in the scheme).

In a second related option, the 1,3-dipolar cycloaddition / oxidation sequence will be investigated for cyclic alkenes with Ge units (or Si units – not shown –) at the allylic position. A key point for this strategy is that it installs the Ge moiety (or Si moiety) in a manner that it should allow for the construction of additional rings by C–Ge (or C–Si) bond formation to the polycyclic aromatic pyrrole core.



The final and most challenging prospect will be to evaluate silenes or germenes as dipolarophiles. The 1,3-cycloaddition of tetrasubstituted germenes with azomethine ylides has been reported.⁶ Yet, with such substrate type, the substitution pattern of the cycloadduct would not allow for subsequent oxidation. Notwithstanding, these precedents give good indication that readily accessible trisubstituted silenes having trimethylsilyl groups at the silene silicon atom could be suitable cycloaddition partners.⁷ The performance of these reagents will thus be tested first. If successful, related trisubstituted germenes will be contemplated (not shown). For the latter however, synthetic methodology to access the reagents will have to be developed.



Consortium and International Cooperation

The proposal stems from the combination of the complementary expertise's of the two research groups. On the one hand, the ROCS group from Sorbonne Université has a recognised know-how in the field of synthetic methodology of organosilanes and organogermanes which will be essential to design and prepare the requisite Si and Ge dipolarophiles.⁸ On the other hand, the group of Prof. Ito has a longstanding interest in designing and preparing unprecedented PAHs with fused pyrrole structures.² This collaboration will offer a unique opportunity to evaluate the influence of incorporation of Si and Ge atoms to the pyrrole-based PAH core, with the outermost aim of finding molecules with original functionalities.

The project is associated to the Chemistry, Materials and Interfaces initiative. The experimental work will be carried out in both laboratories as the doctoral project (dual SU and NTU degree) includes a research stay in Singapore of 12 months.

Desired skills for PhD candidates: Training in organic and organometallic chemistry with an interest in methodology and physical organic chemistry.

⁵ P. Pawluć, B. Marciniak, B. Dudzic, G. Hreczycho, M. Kubicki, *Synthesis* **2006**, 3739.

⁶ S. E.-C. El Kettani, J. Escudié, C. Couret, H. Ranaivonjatovo, M. Lazraq, M. Soufiaoui, H. Gornitzka, G. Cretiu Nemes, *Chem. Commun.* **2003**, 1662. D. Gherag, H. Gornitzka, J. Escudié, S. Ladeira, *Inorg. Chem.* **2010**, *49*, 10497.

⁷ M. B. Berry, R. J. Griffiths, M. J. Sanganee, P. G. Steel, D. K. Whelligan, *Org. Biomol. Chem.* **2004**, *2*, 2381.

⁸ Selected references: a) E. Romain, C. Fopp, F. Chemla, F. Ferreira, O. Jackowski, M. Oestreich, A. Perez-Luna, *Angew. Chem. Int. Ed.* **2014**, *53*, 11333. b) E. Romain, K. de la Vega-Hernández, F. Guégan, J. S. García, C. Fopp, F. Chemla, F. Ferreira, H. Gerard, O. Jackowski, S. Halbert, M. Oestreich, A. Perez-Luna, *Adv. Synth. Catal.* **2021**, *363*, 2634. c) K. de la Vega-Hernández, E. Romain, A. Coffinet, K. Bijouard, G. Gontard, F. Chemla, F. Ferreira, O. Jackowski, A. Perez-Luna, *J. Am. Chem. Soc.* **2018**, *140*, 17632. d) S. Kassamba, A. Perez-Luna, F. Ferreira, M. Durandetti, *Chem. Commun.* **2022**, *58*, 3901.