

The Laboratory for Organic and Inorganic Chemistry

## Final Ph.D. Seminar

Monday, January 8<sup>th</sup> at 11:30 in the Seminar Room

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Apeloig Group

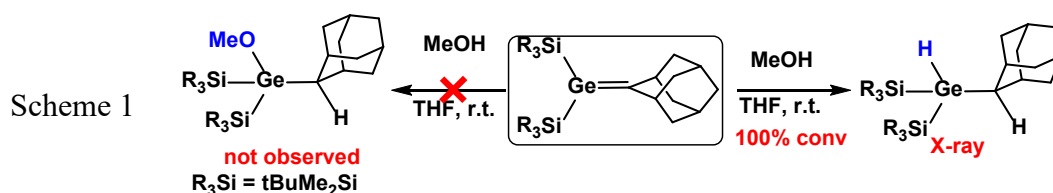
On the Topic of:

**Synthesis and reactivity of metallenes**  
 **$R_2E=CR'_2$  and metal substituted metallenes**  
 **$R(M)E=CR'_2$  (E = Ge, Sn; M=metal)**

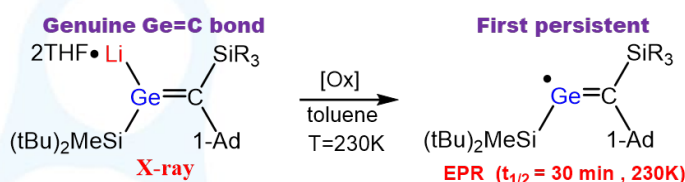
## Synthesis and reactivity of metallenes $R_2E=CR'_2$ and metal substituted metallenes $R(M)E=CR'_2$ (E = Ge, Sn; M=metal)

Metallenes,  $R_2E=CR'_2$ , and metal (M)-substituted metallenes,  $R(M)E=CR'_2$  (E = Si, Ge, Sn), are of synthetic interest since they can be used to incorporate E-C and E=C bonds into organic molecules, or for the synthesis of a variety of new E-based compounds. In my Master's degree, the new stable germene (t-BuMe<sub>2</sub>Si)<sub>2</sub>Ge=2-Ad, lacking resonance or heteroatom stabilization, was synthesized. The isoelectronic stannene (t-BuMe<sub>2</sub>Si)<sub>2</sub>Sn=2-Ad was found to be less stable, but was successfully trapped by Pt(0) complexes. While a variety of Group 14 metallenes were synthesized,<sup>1</sup> the only three silicon analogues of alkenyl anions, silenyl lithium  $R(Li)Si=CR'_2$ , were synthesized by our group.<sup>1</sup> Moreover, only two examples of germyl anions were reported,<sup>2</sup> while the tin analogues of alkenyl anion have not been yet synthesized.

The main goal of my Ph.D. research was to synthesize, isolate and characterize new  $R_2E=CR'_2$  and  $R(M)E=CR'_2$  (E = Ge, Sn) compounds, and to study their relative stability, reactivity, and properties. Having isostructural metallenes allows to compare experimentally systematically the reactivities for the entire series of "heavy" Group 14 compounds. For this purpose, alcohol addition to (t-BuMe<sub>2</sub>Si)<sub>2</sub>E=2-Ad (E = Si, Ge, Sn) was studied. Germene (E=Ge) showed a unique unexpected result, giving with methanol (and other alcohols) the H<sub>2</sub>-reduction product instead of the expected addition product (Scheme 1). The mechanism of this unusual reaction was studied by isotope labeling experiments, and computationally using DFT quantum chemical calculations.



I also synthesized the first two stable germyl lithiums,  $(R(Li)Ge=CR'_2)$ , via direct metalation of the corresponding acyl germanes, and characterized them by X-ray diffraction and NMR spectroscopy.<sup>3</sup> Some of their reactions were investigated. Oxidation of the germyl lithiums produces the first persistent germyl radicals  $(R-\bullet Ge=CR'_2)$ , which were characterized by EPR spectroscopy and DFT quantum chemical calculations (Scheme 2).<sup>3</sup>



Scheme 2

### References:

1. a) Zborovsky, L.; Dobrovetsky, R.; Botoshansky, M.; Bravo-Zhivotovskii, D.; Apeloig, Y., *J. Am. Chem. Soc.* **2012**, *134* (44), 18229-18232; b) Pinchuk, D.; Mathew, J.; Kaushansky, A.; Bravo-Zhivotovskii, D.; Apeloig, Y. *Angew. Chem. Inter. Ed.* **2016**, *55* (35), 10258-10262.
2. a) M. M. Siddiqui, S. Sinhababu, S. Dutta, S. Kundu, P. N. Ruth, A. Münch, R. Herbst-Irmer, D. Stalke, D. Koley, H. W. Roesky, *Angew. Chem. Int. Ed.* **2018**, *57*, 11776-11780; b) C. Gendy, J. Mikko Rautiainen, A. Mailman, H. M. Tuononen, *Chem. Eur. J.* **2021**, *27*, 14405-14409.
3. Y. Goldshtein, Y. Glagovsky, B. Tumanskii, N. Fridman, D. Bravo-Zhivotovskii, Y. Apeloig, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202452; *Angew. Chem.* **2022**, *134*, e202202452.

