

GROUP 4 METAL SILYLIDENES AND GERMYLIDENES

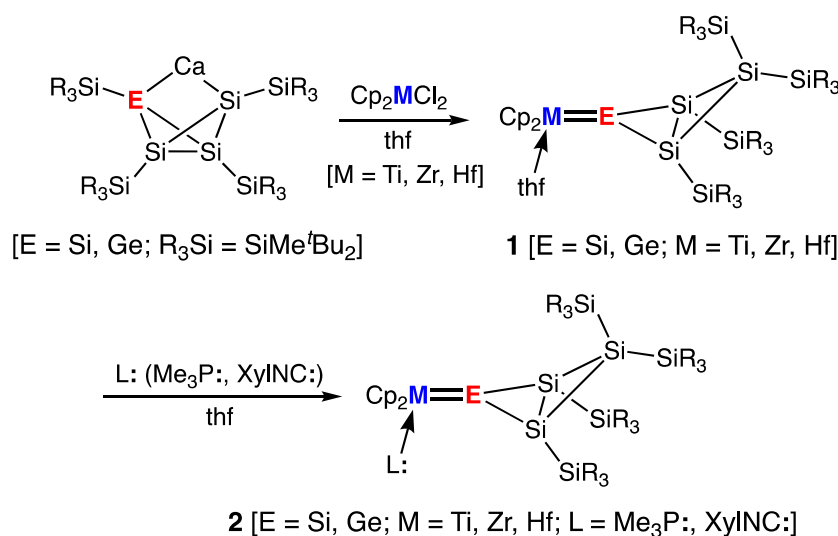
Vladimir Ya. Lee^a, Shinji Aoki^a, Taka Yokoyama^a, Ryo Sakai^a, Akira Sekiguchi^a,
Olga A. Gapurenko^b, and Ruslan M. Minyaev^b

^aUniversity of Tsukuba, Tsukuba 305-8571, Ibaraki, Japan

^bInstitute of Physical and Organic Chemistry, Southern Federal University, Rostov on
Don 344090, Russian Federation

Schrock carbene complexes (or Schrock alkylidenes) is an important class of coordination compounds which found a widespread application in alkene metathesis process. Likewise, silylene and germylene complexes of the Schrock-type (Schrock-type silylidenes and germylidenes) are of a paramount importance, from both fundamental and applied points of view. However, to date very few of them are synthesized, identified, and classified as Schrock-type complexes.

In this presentation, we report on the synthesis, structural characterization, assessment of the particular bonding nature, and specific reactivity of the group 4 metal silylidenes and germylidenes, **1** and **2**, readily available by the reaction of the calcium salt of bicyclo[1.1.0]butane-2,4-diide with group 4 metallocene dichlorides (Scheme) [1]. Based on their spectroscopic (NMR, UV), structural (X-ray crystallography), and reactivity data, both **1** and **2** are classified as Schrock-type silylidenes and germylidenes {Cp₂M(L)=E[Si₃(SiMe^tBu₂)₄]} (M = Ti, Zr, Hf; L = thf, Me₃P:, XylNC:; E = Si, Ge), and this conclusion was finally proved by our DFT computations.



Scheme. Synthesis of the group 4 metal silylidenes and germylidenes **1** and **2**.

[1] (a) Lee, V. Ya.; Aoki, S.; Yokoyama, T.; Horiguchi, S.; Sekiguchi, A.; Gornitzka, H.; Guo, J.-D.; Nagase, S. *J. Am. Chem. Soc.* **2013**, *135*, 2987; (b) Lee, V. Ya.; Horiguchi, S.; Gapurenko, O. A.; Minyaev, R. M.; Minkin, V. I. Gornitzka, H.; Sekiguchi, A. *Eur. J. Inorg. Chem.* **2019**, 4224; (c) Lee, V. Ya.; Sakai, R.; Takanashi, K.; Gapurenko, O. A.; Minyaev, R. M.; Gornitzka, H.; Sekiguchi, A. *Angew. Chem. Int. Ed.* **2021**, *60*, 3951.