$$Ar_2IX + 2PhC\equiv CH \longrightarrow 2PhC\equiv CAr$$

Ar = Ph (85 %), p-MeC_6H_4 (77 %), m-$NO_2C_6H_4$ (85%)
X = HSO_4, CF_3COO, BF_4

ambient temperature for 1.5 h, and then it was extracted with ether. The ethereal extracts were washed with water and dried over Na_2SO_4. After removal of the solvent and recrystallization from MeOH, *m*-nitrotolan (0.189 g, 85 %) was obtained.

The present work was supported by the International Science Foundation (Projects No. M 44000 and No. MPC000) and by the Russian Foundation for Basic Research (project No. 94-03-09770).

References

1. K. Sonogashira, Y. Tohada, and N. Nagihara, *Tetrahedron Lett.*, 1975, **50**, 4467.
2. N. A. Bumagin, A. B. Ponomarev, and I. P. Beletskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1561 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 1433 (Engl. Transl.)].
3. E. V. Luzikova, N. A. Bumagin, and I. P. Beletskaya, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 616 [*Russ. Chem. Bull.*, 1993, **42**, 585 (Engl. Transl.)].

Received December 28, 1994

The first example of metallation of an organogermanium hydride with an alkali metal under mild conditions: synthesis of 2,3,4,5-tetraphenyl-1,1-bis(trimethylsilyl)-1-germa-2,4-cyclopentadiene

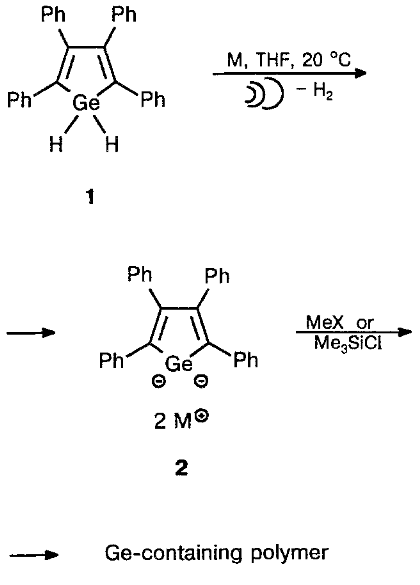
V. Ya. Lee, K. S. Nosov, M. P. Egorov, and O. M. Nefedov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

Germanium-centered anions of the R_3Ge^- type are important intermediates in the synthesis of compounds containing germanium-element bonds. However, the set of convenient methods for generating them is quite limited.[1] In particular, metallation of the $RGeH_3$ hydrides under the action of alkali metals to form $RGeH_2M$ (M = Li, Na)[2] requires the use of liquid ammonia and ethylamine as solvents. It cannot be excluded that the amides of alkali metals and not the metals themselves are the metallating agents under these conditions.

We found that 2,3,4,5-tetraphenyl-1-germa-2,4-cyclopentadiene (**1**) is metallated under the action of lithium or sodium (THF, 20 °C).

The evolution of hydrogen was observed in the course of the reaction. The signal of H—Ge disappeared completely in the ^1H NMR spectrum (δ 5.44) (in THF-d_8). The cherry-red solution obtained was diamagnetic and, evidently, it contained dianion **2**. However, attempts of its alkylation with MeCl or MeI or silylation with Me_3SiCl were unsuccessful. In all of these cases, only formation of germanium-containing polymers was observed. According the GLC-MS data, $Me_3SiSiMe_3$, *i.e.*,



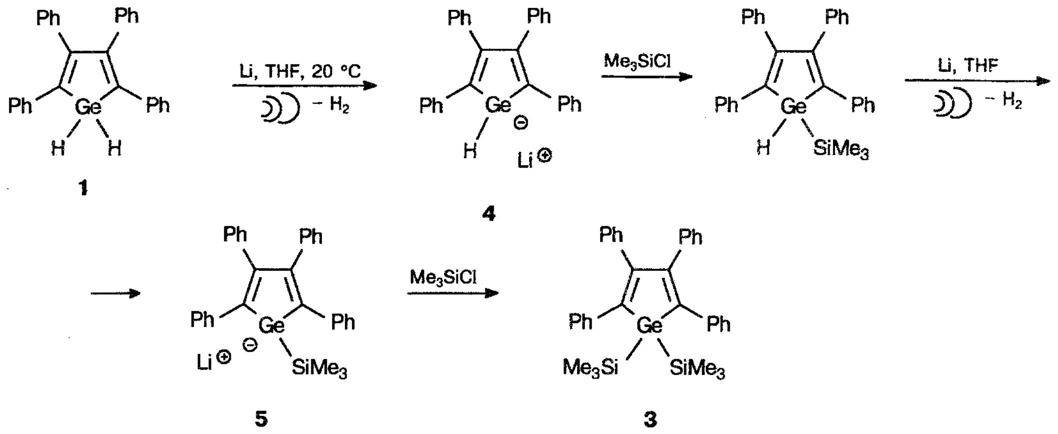
1

2

M = Li, Na

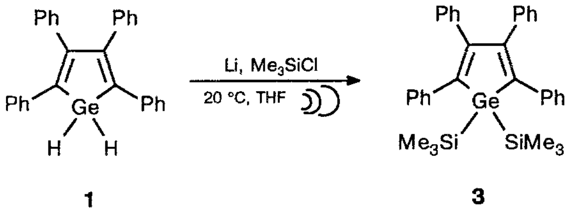
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 790—791, April, 1995.

Scheme 1



the product of the reduction of Me_3SiCl was found among the products of the reaction of **2** with Me_3SiCl. Therefore, one can assume that dianion **2** is a highly active reducing agent, for which redox processes proceed faster than nucleophilic substitution.

At the same time, metallation of **1** under the action of lithium in the presence of a scavenger of monogermyl-anions, *viz.*, trimethylchlorosilane, gave 2,3,4,5-tetraphenyl-1,1-bis(trimethylsilyl)-1-germa-2,4-cyclopentadiene (**3**) in high yield.



According to the literature data,[3] lithium does not react with Me_3SiCl under the conditions used, thus one can assume that the reaction proceeds as a discrete process, involving the intermediate formation of monogermyl anions (**4** and **5**) (Scheme 1).

Lithium (0.01 g, 1.4 mmol) was added to a solution of **1** (0.1 g, 0.23 mmol) obtained according to Ref. 4 and Me_3SiCl (0.24 mL, 0.2 g, 1.84 mmol) in anhydrous THF (3 mL) under Ar. The reaction mixture was placed in an ultrasonic bath and was sonicated for 10 min until lithium was completely dissolved, and then the mixture was stirred at 20 °C for 12 h. During this time, the solution turned yellow from deep red. THF was removed *in vacuo*, and the residue was extracted with benzene and filtered off. Benzene was removed, and the solid was recrystallized from hexane. Compound **3** (0.11 g, 83 %), m.p. 114—115 °C (*cf.* Ref. 4: m.p. 114 °C). ^1H NMR (200 MHz, C_6D_6, δ): 0.20 (s, 18 H, $\underline{Me_3}Si$); 6.90 (m, 20 H, Ph). Mass spectrum (70 eV, *m/z*): 576 $[M]^+$.

This work was supported by the Russian Foundation for Basic Research (Project No. 93-03-5452) and the International Science Foundation (Project No. MHL 000).

References

1. M. Lesbre, P. Mazerolles, and J. Satge, *The Organic Compounds of Germanium*, John Wiley&Sons, New York, 1971.
2. S. N. Glarum and C. A. Kraus, *J. Am. Chem. Soc.*, 1950, **72**, 5398.
3. D. A. Armitage, in *Comprehensive Organometallic Chemistry*, Ed. G. Wilkinson, 1982, **2**, 100
4. P. Jutzi and A. Karl, *J. Organomet. Chem.*, 1981, **215**, 19.

Received February 8, 1995