



St Petersburg
University

**XII International Conference on Chemistry
for Young Scientists "MENDELEEV 2021"**

St Petersburg, Russia
September 6-10,
2021

ISBN 978-5-9651-1364-4

Book of abstracts contains theses of plenary, keynote, oral and poster presentations which were presented on **Mendeleev 2021**, the XII International Conference on Chemistry for Young Scientists. The Mendeleev 2021 Conference hold in Saint Petersburg (September 6–10, 2021).

Abstracts presented in the original edition

THE STABILIZATION OF ONLY HYDROGEN-SUBSTITUTED 13/14/15 GROUP ELEMENT CHAINS BY LEWIS ACIDS

Chernysheva A.M.,¹ Timoshkin A.Y.¹

¹Saint Petersburg State University, Saint Petersburg, Russia
Postgraduate
st040602@student.spbu.ru

The parent (bearing only hydrogen substituents) compounds of *p*-elements, representing isoelectronic homologues of alkanes and featuring the combination of elements of group 13/14/15 in one compound, are of high interest due to their potential use as single-source precursors for ternary materials, which can be used in small band gap optical devices [1]. Such parent compounds can also find application in construction of new inorganic polymers, which are highly desirable [2], as they represent the alternatives to the established organic-based polymers. So far, several Lewis acid and/or Lewis base stabilized parent compounds, containing binary combinations of group 13/15 and 14/15 elements, were synthesized [3]. In order to expand the element chain and obtain ternary parent group 13/14/15 element compounds, unknown up to now, the concept of donor-acceptor stabilization can be used.

In this report the results of computational study (B3LYP-D3/def2-TZVP level of theory) of complexes of $\text{PH}_2\text{BH}_2\text{E}'\text{H}_2$, $\text{PH}_2\text{E}'\text{H}_2\text{BH}_2$ and $\text{E}'\text{H}_2\text{PH}_2\text{BH}_2$ ($\text{E}' = \text{C, Si, Ge}$) with Lewis acids are presented. The donor-acceptor complexes in the most cases are not the stable ones: upon geometry optimization they convert to cyclic structures or substituent migration occurs. In case of $\text{LA} = \text{EX}_3$ ($\text{E} = \text{B, Al, Ga}$; $\text{X} = \text{F, Cl, Br, I}$), there is a strong tendency of one of the halogens to occupy bridging position or to migrate to the acceptor atom of the chain. Pentafluorophenyl-substituents of $\text{LA} = \text{E}(\text{C}_6\text{F}_5)_3$ ($\text{E} = \text{B, Al, Ga}$) in some cases reveal the same reactivity, becoming bridging or migrated. For $\text{LA} = \text{M}(\text{CO})_5$ ($\text{M} = \text{Cr, Mo, W}$) and $\text{Fe}(\text{CO})_4$, there are additional interactions between acceptor atom of the chain and carbonyl groups or the transition metal with formation of six- and four-membered cycles, respectively. In the cases of only donor-acceptor complex formation (without any other reactivity), the stability of complexes was evaluated by comparison of the equilibrium constants of this process and dimerization of free 13/14/15 chains. It is established that the stabilization by Lewis acid is possible only for $\text{PH}_2\text{CH}_2\text{BH}_2$. As a result, we propose complexes of $\text{PH}_2\text{CH}_2\text{BH}_2$ with GaF_3 , $\text{Cr}(\text{CO})_5$, $\text{Mo}(\text{CO})_5$, $\text{W}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4$ for further experimental investigation. For other chains additional stabilization by Lewis base is required.

References

- [1] R. Jia, T. Zhu, V. Bulovic, E. A. Fitzgerald, *J. Appl. Phys.* **2018**, *123*, 175101; b) T. Watkins, A. V. G. Chizmeshya, L. Jiang, D. J. Smith, R. T. Beeler, G. Grzybowski, C. D. Poweleit, J. Menendez, J. Kouvetakis, *J. Am. Chem. Soc.* **2011**, *133*, 16212-16218; c) A. G. Norman, J. M. Olson, J. F. Geisz, H. R. Moutinho, A. Mason, M. M. Al-Jassim, S. M. Vernon, *Appl. Phys. Lett.* **1999**, *74*, 1382.
- [2] I. Manners, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1602-1621.
- [3] a) U. Vogel, A. Y. Timoshkin, K.-C. Schwan, M. Bodensteiner, M. Scheer, *J. Organomet. Chem.* **2006**, *691*, 4556-4564; b) U. Vogel, P. Hoemensch, K.-C. Schwan, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2003**, *9*, 515-519; c) K.-C. Schwan, A. Y. Timoshkin, M. Zabel, M. Scheer, *Chem. Eur. J.* **2006**, *12*, 4900-4908; d) C. Marquardt, A. Adolf, A. Stauber, M. Bodensteiner, A. V. Virovets, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2013**, *19*, 11887-11891; e) C. Marquardt, O. Hegen, A. Vogel, A. Stauber, M. Bodensteiner, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2018**, *24*, 360-363; f) C. Marquardt, O. Hegen, M. Hautmann, G. Balázs, M. Bodensteiner, A. V. Virovets, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2015**, *127*, 13315-13318; g) U. Vogel, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2001**, *40*, 4409-4412. h) M.A.K. Weinhardt, A.S. Lisovenko, A.Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2019**, *59*, 5541-5545.

Acknowledgements. This work was supported by the joint grant of Russian Science Foundation and Deutsche Forschungsgemeinschaft (RSF project No 21-43-04404). The use of the equipment of the Resource Center "Computer Center SPbU" is gratefully acknowledged.