



BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS
FACULTY OF CHEMICAL TECHNOLOGY AND BIOTECHNOLOGY
GEORGE OLAH DOCTORAL SCHOOL

Internal Catalytic Effect of Bulky Substituents

Thesis

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1. Introduction

It is well-known that the heavier group 14 elements like lead and tin tend to form divalent compounds. Therefore, the question immediately arises whether lighter elements of group 14, silicon and carbon, can also be stable in divalent structures.

I started my research in the group of Professor Tamás Veszprémi in 2007, when I was a second year undergraduate student, working in the field of low-valent silicon compounds. Studying the possible insertion reaction of small molecules to divalent silicon compounds provided the starting point of my thesis.

The core subject of my work is the first six-membered ring silylene, synthesized by Driess and coworkers in 2006. The electronic structure of the compound is very peculiar because there are formally 7 electrons in the center ring which cannot form a delocalized system. The reactivity of this molecule is also unique because it shows reactions which have been never observed for other silylenes such as reaction with white phosphorus. The most important point of my thesis is to understand this reactivity.

2. Literature overview

Even in the XIX. century, there were attempts to stabilize divalent carbon and silicon compounds, carbenes and silylenes, and „successful” synthesis had already been reported in 1835. Although, the first stable carbene beyond any doubt was synthesized by Arduengo and coworkers in 1991 (Figure 1, **5**).¹ As the next step carbenes with different backbones were tried to prepare. First the Wanzlick-type saturated 5-membered ring carbene was isolated (Scheme 4, **7**),² then acyclic carbene with only isopropyl bulky groups (**8**)³. The first non-diamino stabilized carbene was **9** with thiazole group⁴ and **10** was synthesized in 2006.⁵

¹ A. J. Arduengo III, R. L. Harlow, M. Kline: *J. Am. Chem. Soc.* 113, 361 (1991)

² A. J. Arduengo III, J. R. Goerlich, W. J. Marshall: *J. Am. Chem. Soc.* 117, 11027 (1995)

³ R. W. Alder, P. R. Allen, M. Murray, A. G. Orpen: *Angew. Chem.* 108, 1211 (1996)

⁴ A. J. Arduengo III, J. R. Goerlich: *Liebigs Ann.* 365 (1997)

⁵ V. Lavallo, Y. Canac, B. Donnadiou, W. W. Schoeller, G. Bertrand: *Science* 312, 722 (2006)

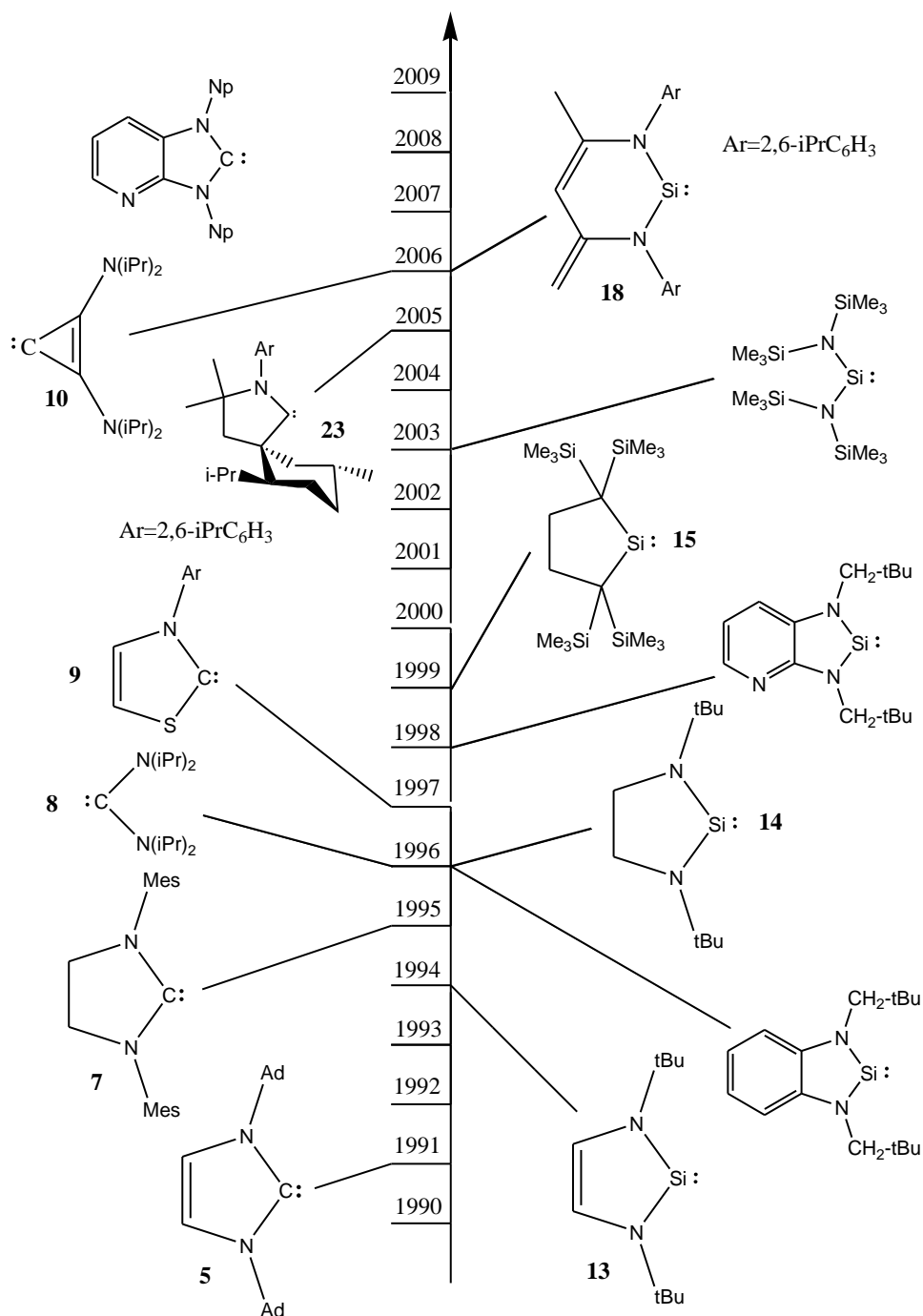


Figure 1. Important carbenes and silylenes in the order of their synthesis.

The quest for stable silylene was being occurred parallel with the development of carbenes. After the successful synthesis of **5** it immediately suggested an analog way to prepare the first stable silylene⁶ (**13**). Later, similarly to the carbenes several stable silylenes have been prepared.⁷ The Wanzlick-type cyclic silylene was synthesized by West and coworkers

⁶ M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler: *J. Am. Chem. Soc.* 116, 2691 (1994)

⁷ J. Heinicke, A. Oprea, M. K. Kindermann, T. Kárpáti, L. Nyulászi, T. Veszprémi: *Chem.-Eur. J.* 4, 541 (1998)

(**14**).⁸ The silylene with no carbene analog was reported in 1999 by Kira *et al.* (**15**).^{9,10,11} The peculiarity of the compound is that there is neither aromaticity nor π -donor nitrogen atoms, still, it is stable. In the beginning all carbenes and silylenes followed the path of Arduengo's work; they were 5-membered rings and N-substituted compounds. Theoretical study of our group suggested long time ago that other cyclic silylenes could also be stable,¹² however, this question was solved in 2006 by Driess and coworkers who synthesized the first six-membered ring silylene¹³ (Figure 2, **18**).

The structure of six-membered ring silylene is very interesting as it contains 7 electrons in the π -system of the ring. Although, it has aromatic resonance structure (**19**), calculations do not support aromaticity in the center ring suggesting that **18** is the leading resonance structure.¹⁴

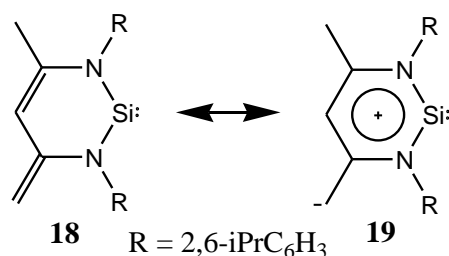


Figure 2. Resonance structures of the six-membered ring silylene.

Insertion (Figure 3) is one of the most important reaction of carbenes and silylenes to eliminate hypovalency when a single bond of the reactant molecule (Y-Z) cleavages and saturates the divalent center forming two new bonds (X-Y and X-Z). The simplest insertion reaction is the reaction with hydrogen molecule.¹⁵

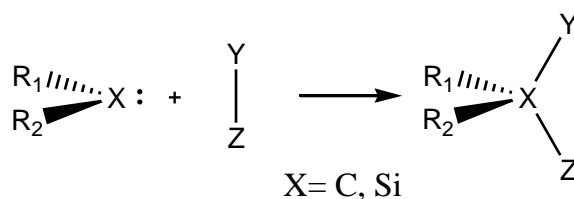


Figure 3. Insertion reaction of carbenes and silylenes.

⁸ R. West, M. Denk: *Pure Appl. Chem.* 68, 785 (1996)

⁹ S. Ishida, T. Iwamoto, C. Kabuto, M. Kira: *The 12th International Symposium on Organosilicon Chemistry, Sendai*, pp93 (1999)

¹⁰ M. Kira, S. Ishida, T. Iwamoto, C. Kabuto: *J. Am. Chem. Soc.* 121, 9722 (1999)

¹¹ M. Kira, S. Ishida, T. Iwamoto, M. Ichinohe, C. Kabuto, L. Ignatovich, H. Sakurai, *Chem. Lett.* 263 (1999)

¹² T. Veszprémi, L. Nyulászi, T. Kárpáti: *J. Phys. Chem.* 100, 6262 (1996)

¹³ M. Driess, S. Yao, M. Brym, C. van Wüllen, D. Lentz: *J. Am. Chem. Soc.* 128, 9628 (2006)

¹⁴ K. Nyíri, T. Veszprémi: *Organometallics*, 28, 5909 (2009)

¹⁵ G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller, G. Bertrand: *Science* 316, 439 (2007)

There are several papers in the literature which deal with some aspects of insertion reaction of silylenes. Insertion reaction has been observed with several simple molecules such as water^{16,17,18}, alcohol¹⁹, ammonia²⁰, hydrazine,²¹ or acetylene²². Besides, there are experimental results in the literature for several type of bonds for example Li-C²³, M-N^{24,25} (M = Li, Na, K), P-P²⁶, C-X^{27,28} vagy Si-X^{29,30} (X = Cl, Br, I).

The reactions that I have investigated is also connected to insertion reactions. The main goal of my research was to understand the peculiar reactivity of **18** especially to rationalize the experimental results of Driess and coworkers who reported about the reaction of white phosphorus and **18** (Figure 4).

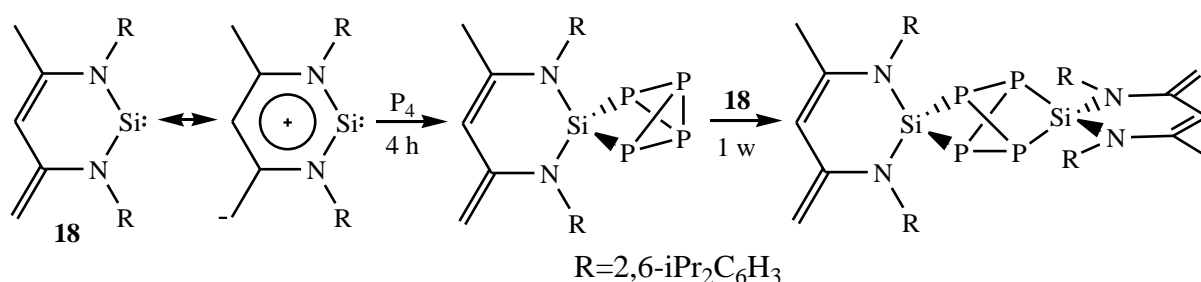


Figure 4. Insertion reaction of **18** and white phosphorus.

3. Applied methods

My research is theoretical thus I applied several quantum chemical programs such as Gaussian, Q-Chem or ACES II. I optimized most of the structures by using density functional theory (DFT) while for more accurate energy calculations I used DFT and post-HF methods as well. For benchmark study, I applied coupled cluster theory.

¹⁶ R. Becerra, J. P. Cannady, R. Walsh: *J. Phys. Chem. A*, 107, 11049 (2003)

¹⁷ S. Yao, M. Brym, C. van Wüllen, M. Driess: *Angew. Chem. Int. Ed.* 46, 4159 (2007)

¹⁸ U. N. Alexander, K. D. King, W. D. Lawrance: *J. Phys. Chem. A* 106, 973 (2002)

¹⁹ W. J. Leigh, S. S. Kostina, A. Bhattacharya, A. G. Moiseev: *Organometallics*, 29, 662 (2010)

²⁰ A. Jana, C. Schulzke, H. W. Roesky, J. Am. Chem. Soc. 131, 4600 (2009)

²¹ A. Jana, H. W. Roesky, C. Schulzke, P. P. Samuel: *Organometallics*, 28, 6574 (2009)

²² S. Yao, C. van Wüllen, X.-Y. Sun, M. Driess: *Angew. Chem. Int. Ed.* 47, 3250 (2008)

²³ X. Cai, B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. C. Slootweg: *J. Organomet. Chem.* 651, 150 (2002)

²⁴ B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. C. Slootweg: *Chem. Commun.* 1427 (2000)

²⁵ F. Antolini, B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. C. Slootweg: *Dalton Trans.* 3288 (2004)

²⁶ Y. Xiong, S. Yao, M. Brym, M. Driess: *Angew. Chem. Int. Ed.* 46, 4511 (2007)

²⁷ D. F. Moser, T. Bosse, J. Olson, J. L. Moser, I. A. Guzei, R. West: *J. Am. Chem. Soc.* 124, 4186 (2002)

²⁸ D. F. Moser, A. Naka, I. A. Guzei, T. Müller, R. West: *J. Am. Chem. Soc.* 127, 14730 (2005)

²⁹ S. Ishida, T. Iwamoto, C. Kabuto, M. Kira: *Chem. Lett.* 11, 1102 (2001)

³⁰ Y. Xiong, S. Yao, M. Driess: *Organometallics*, 28, 1927 (2009)

4. Results

4.1. Direct Insertion reaction of silylenes^{S1}

The difference between the transition state of carbenes and silylenes in the direct insertion mechanism was explained with the different occupancy of their vacant p-orbital. Based on the reaction of 7 silylenes and 8 small molecules (Figure 5) the reactivity order of silylenes was elucidated and the effect of thermodynamic stabilization factors was quantified. It was set up a relationship between the activation free energy barrier and the reaction free energy based on which one could estimate the activation energy barrier from the reaction free energy. It was proven that the reactivity of the silylene center in the six-membered ring silylene (**25**) and the five-membered silylene (**23**) is similar which contradicted the previous assumptions in the literature. Therefore, it was concluded that the direct insertion mechanism could not explain the experimental results of **18**.

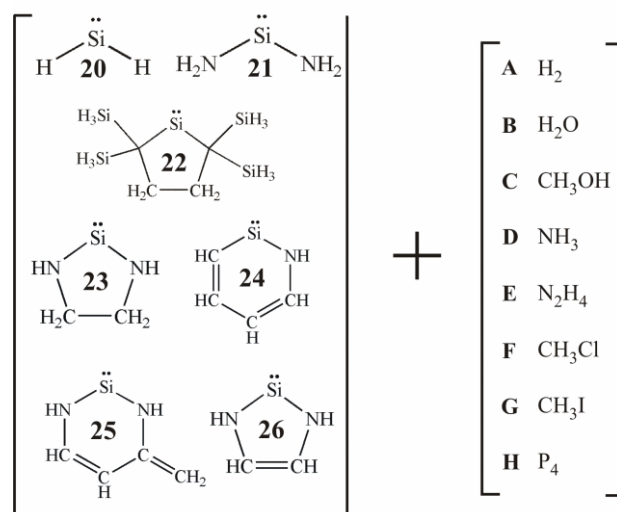


Figure 5. Investigated silylenes and small molecules in the direct insertion reaction scheme.

4.2. Special insertion reaction of the six-membered ring silylene^{S2}

18 possible special insertion mechanisms were explored in the reactions of **25** and small molecules. A central intermediate, formally an 1,4-addition intermediate, was found where all mechanisms intersected each other. Based on these, the previously suggested mechanism for the reaction of alkyl-, and silyl-halides was modified and an $\text{S}_{\text{N}}2$ -type mechanism was proposed. A generally available proton-transfer reactivity of the backbone of **25** was found which explained the observed experimental results in the reaction of **18** with water, hydrogen-

sulfide, ammonia, and hydrazine. These mechanisms also explained why other silylenes do not react similarly: the backbone of the previously known silylenes was different therefore these mechanisms could not proceed in those cases.

4. 3. The reaction of 18 with white phosphorus^{S3,S4}

Four possible reaction mechanisms were found and explored in the reaction of white phosphorus and **18**. A new mechanism with lower activation barrier than the previously proposed direct insertion mechanism was introduced in accordance with the nucleophile character of the molecules. The effect of the bulky ligands were also investigated and found that the bulky diisopropylphenyl ligand reduced the rate limiting activation barrier compared to the hydrogen substituted analog owing to favorable nonbonding interactions. This peculiar result was confirmed with different theoretical methods and provided the only explanation to this unique reaction because this bulky ligand had never been used for other silylenes.

4. 4. Substituent effect in the reaction of 7, 13, and 14 with white phosphorus^{S4}

The effect of different bulky substituents were investigated in case of three silylenes and concluded that the diisopropylphenyl ligand can accelerate the reaction of silylenes and P₄ in all cases through attractive nonbonding interactions. The previously commonly used t-butyl ligand, however, has larger activation barrier because of the steric hindrance which could explain the negative experiments with these compounds. Based on these results, a new silylene was proposed which could also react with white phosphorus. The potential reaction mechanisms were explored for the reaction of carbene (**7**) and white phosphorus as well and found that the same mechanism is more favorable than that for analog silylenes. I also found the peculiar effect of diisopropylphenyl ligand. This is in accordance with the experiments because carbenes that can react with white phosphorus all contained this bulky group.

4. 5. Catalytic effect of bulky substituents in Suzuki-reaction^{S5}

The reaction mechanism of Suzuki-reaction with carbene ligands was explored for the first time and found that the rate limiting step is the oxidative addition step (**TS2**). Mechanisms with different experimentally applied bulky substituents were investigated and found the reduction of the rate limiting activation barrier in case of 2,6-diisopropyl-4-tritylphenyl ligand (**27e**) compared to 2,6-diisopropylphenyl ligand in accordance with the kinetic meas-

urements. A favorable T-shape π -stacking interaction was revealed (Figure 6, **27e-TS2**) which was responsible for the reduction of the rate limiting activation barrier. It was also shown that the extremely bulky trityl-based ligand caused steric repulsion in the precursor boosting the formation of the active species and increasing the reaction rate. Based on these results, an enzyme-like lock-key model was introduced to explain the observed effects which provided a new concept for catalyst optimization.

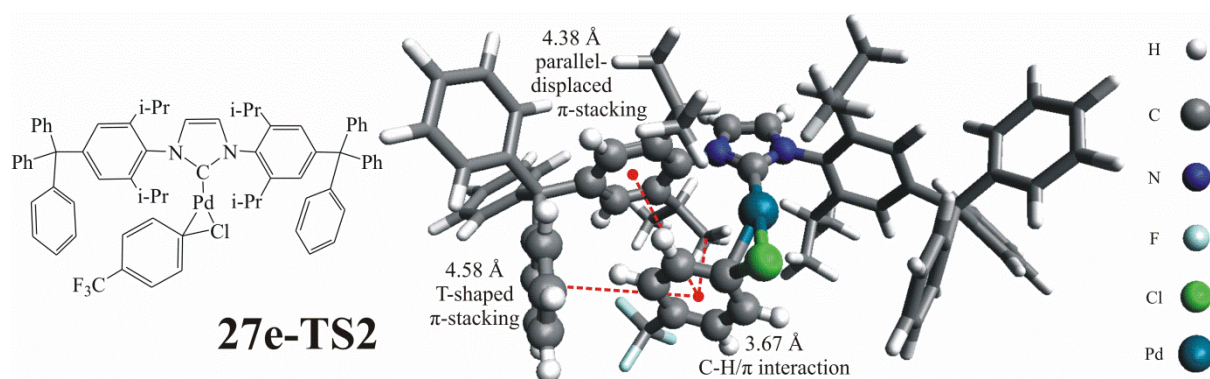


Figure 6. Transition state structure of **27e-TS2**. Dashed lines indicate favorable π - π and C-H/ π interaction.

5. Theses

1. Investigation of 56 direct insertion reaction revealed that the reactivity of the silicon center in five- and six-membered ring silylenes is similar in contrast to the previously assumed difference.^{S1}
2. The insertion reaction of six-membered ring silylene can proceed via an 1,4-addition reaction which explained the experimentally observed reactions.^{S2}
3. I explored a more favorable mechanism than the previously suggested direct insertion in the reaction of white phosphorus and six-membered ring silylene.^{S3}
4. I showed that the 2,6-diisopropylphenyl bulky group, which is usually applied to hinder chemical reactions, can accelerate the reaction of white phosphorus with carbenes and silylenes.^{S3,S4}

5. I proved that appropriately chosen bulky ligands can catalyze Suzuki-reaction and thus I introduced a new principle to optimize catalysts.^{S5}

6. Possible applications

The enzyme-like lock-key model that I have introduced to understand and design new catalysts can be applied in several fields to optimize and create new catalytic processes.

7. Publications

Publications included in this thesis

- [S1] K. Nyíri, T. Szilvási, T. Veszprémi: *The Mechanism and Energetics of Insertion Reactions of Silylenes*, Dalton Trans., 2010, 39, 9347. (IF: 3.647; C: 8)
- [S2] T. Szilvási, K. Nyíri, T. Veszprémi: *On the Unique Insertion Mechanisms of β -Diketiminato-Silylene*, Organometallics, 2011, 30, 5344. (IF: 3.963; C: 4)
- [S3] T. Szilvási, T. Veszprémi: *On the Mechanism of the Reaction of White Phosphorus With Silylenes*, Dalton Trans., 2011, 40, 7193. (IF: 3.838; C: 1)
- [S4] T. Szilvási, T. Veszprémi: *Why Do Carbenes and Silylenes Activate White Phosphorus Differently?*, Struc. Chem., 2015, 26, 1335. (IF: 1.837; C: 0)
- [S5] T. Szilvási, T. Veszprémi: *Internal Catalytic Effect of Bulky NHC Groups in Suzuki-Miyaura Cross-coupling Reaction*, ACS Catalysis, 2013, 3, 1984. (IF: 7.572; C: 10)

Publications not included in this thesis

- [S6] T. Szilvási, T. Veszprémi: *Molecular-tailoring: Reaction Path Control With Bulky Substituents*, Organometallics, 2012, 31, 3207. (IF: 4.145; C: 10)
- [S7] M. Vörös, T. Demjén, T. Szilvási, A. Gali: *Tuning the Optical Gap of Nanometer-size Diamond Cages by Sulfurization: A Time-Dependent Density Functional Study*, Phys. Rev. Lett., 2012, 108, 267401. (IF: 7.943; C: 17)
- [S8] K. Hansen, T. Szilvási, B. Blom, S. Inoue, J. Epping, M. Driess: *A Fragile Zwitterionic Phosphasilene as a Transfer Agent of the Elusive Parent Phosphinidene (:PH)*, J. Am. Chem. Soc., 2013, 135, 11795. (IF: 11.444; C: 20)
- [S9] T. Szilvási, T. Veszprémi: *Molecular-tailoring: Substituent Design for Hexagermabenzene*, Organometallics, 2013, 32, 4733. (IF: 4.253; C: 4)

- [S10] N. C. Breit, T. Szilvási, T. Suzuki, D. Gallego, S. Inoue: *From a Zwitterionic Phosphasilene to Base Stabilized Silyliumylidene-phosphide and Bis(silylene) Complexes*, J. Am. Chem. Soc., 2013, 135, 17958. (IF: 11.444; C: 17)
- [S11] P. Bagi, T. Kovács, T. Szilvási, P. Pongrácz, L. Kollár, L. Drahos, E. Fogassy, G. Keglevich: *Platinum(II) Complexes Incorporating Racemic and Optically Active 1-alkyl-3-phospholene P-ligands: Synthesis, Stereostructure, NMR Properties and Catalytic Activity*, J. Organomet. Chem., 2014, 751, 306. (IF: 2.173; C: 7)
- [S12] Z. Benedek, T. Szilvási, T. Veszprémi: *Molecular-tailoring: A Possible Synthetic Route to Hexasilabenzene*, Dalton Trans., 2014, 43, 1184. (IF: 4.197; C: 5)
- [S13] K. Hansen, T. Szilvási, B. Blom, E. Irran, M. Driess: *A Donor-stabilized Zwitterionic "Half-parent" Phosphasilene and Its Unusual Reactivity Towards Small Molecules*, Chem. Eur. J., 2014, 20, 1947. (IF: 5.731; C: 12)
- [S14] T. Szilvási, A. Gali: *Fluorine Modification of the Surface of Diamondoids: A Time-Dependent Density Functional Study*, J. Phys. Chem. C, 2014, 118, 4410. (IF: 4.772; C: 2)
- [S15] N. C. Breit, T. Szilvási, S. Inoue: *New Route to Access an Acyl-functionalized Phosphasilene and an Unprecedented Four-membered Si-P-C-O Heterocycle*, Chem. Eur. J., 2014, 20, 9312. (IF: 5.731; C: 5)
- [S16] P. Bagi, T. Szilvási, P. Pongrácz, L. Kollár, L. Drahos, G. Keglevich: *Platinum (II) Complexes Incorporating Racemic and Optically Active 1-Aryl-3-phospholene P-Ligands as Potential Catalysts in Hydroformylation*, Current Organic Chemistry, 2014, 18, 1529. (IF: 2.537; C: 2)
- [S17] S. U. Ahmad, T. Szilvási, S. Inoue: *A Facile Access to a Novel NHC-stabilized Silyliumylidene Ion and C–H Activation of Phenylacetylene*, Chem. Commun., 2014, 50, 12619. (IF: 6.834; C: 4)
- [S18] G. Tan, T. Szilvási, S. Inoue, B. Blom, M. Driess: *An Elusive Hydridoaluminum(I) Complex for Facile C–H and C–O Bond Activation of Ethers and Access to Its Isolable Hydridogallium(I) Analogue: Syntheses, Structures, and Theoretical Studies*, J. Am. Chem. Soc., 2014, 136, 9732. (IF: 12.113; C: 2)
- [S19] Y. Xiong, T. Szilvási, S. Yao, G. Tan, M. Driess: *Synthesis and Unexpected Reactivity of Gerymyliumylidene Hydride [$:\text{GeH}$] $^+$ Stabilized by a Bis(N-heterocyclic-carbene)borate Ligand*, J. Am. Chem. Soc., 2014, 136, 11300. (IF: 12.113; C: 6)
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- [S21] C. Eisenhut, T. Szilvási, N. C. Breit, S. Inoue: *Reaction of an N-Heterocyclic Carbene-*

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- [S23] S. Yao, N. Lindenmaier, Y. Xiong, S. Inoue, T. Szilvási, M. Adelhardt, J. Sutter, K. Meyer, M. Driess: *A Neutral Tetraphosphacyclobutadiene Ligand in Cobalt(I) Complexes*, Angew. Chem. Int. Ed., 2015, 54, 1250. (IF: 11.261[#]; C: 2)
- [S24] F. Ullah, T. Szilvási, T. Veszprémi, P. Jones, J. Heinicke: *Bis(N,N'-dineopentylbenzimidazoline-2-ylidene)molybdenumtricarbonyl – Synthesis and Investigation of the Bent Structure of the Coordinatively Unsaturated (np2bi)₂Mo(CO)₃ Complex*, J. Organomet. Chem., 2015, 783, 22. (IF: 2.173[#]; C: 0)
- [S25] R. Zitz, H. Arp, J. Hlina, M. Walewska, C. Marschner, T. Szilvási*, B. Blom, J. Baumgartner: *Open-Shell Lanthanide (+II) or (+III) Complexes Bearing σ -Silyl and Silylene Ligands: Synthesis, Structure and Bonding Analysis*, Inorg. Chem., 2015, 54, 3306. (IF: 4.762[#]; C: 1)
- [S26] S. Yao, T. Szilvási, N. Lindenmaier, Y. Xiong, S. Inoue, M. Adelhardt, J. Sutter, K. Meyer, M. Driess: *Facile Transformation of P₄ by an Iron(I) β -Diketiminato Complex to Yield Coordination Complexes with Bridging P₂²⁻ Ligands*, Chem. Commun., 2015, 51, 6153. (IF: 6.834[#]; C: 0)
- [S27] S. U. Ahmad, T. Szilvási, E. Irran, S. Inoue: *An NHC-Stabilized Silicon Analogue of Acylium Ion: Synthesis, Structure, Reactivity, and Theoretical Studies*, J. Am. Chem. Soc., 2015, 137, 5828. (IF: 12.113[#]; C: 0)
- [S28] Y. Xiong, S. Yao, T. Szilvási, M. Driess: *Facile Rearrangement of a Bis(N-heterocyclic carbene)borate Chelate Ligand and Access to [GeX]⁺ Complexes (X = H, Cl)*, Eur. J. Inorg. Chem., 2015, 2377. (IF: 2.942[#]; C: 0)
- [S29] N. C. Breit, T. Szilvási, S. Inoue: *Facile Rotation around a Silicon-Phosphorus Double Bond Enabled through Coordination to Tungsten*, Chem. Commun., 2015, 51, 11272. (IF: 6.834[#]; C: 1)
- [S30] R. Zitz, J. Hlina, K. Gatterer, C. Marschner, T. Szilvási*, J. Baumgartner: *Neutral “Cp-Free” Silyl-Lanthanide(II) Complexes: Synthesis, Structure, and Bonding Analysis*, Inorg. Chem., 2015, 54, 7065. (IF: 4.762[#]; C: 0)
- [S31] P. Bagi, K. Juhász, I. Timári, K. E. Kövér, M. Kállay, D. Mester, M. Kubinyi, T. Szilvási, P. Pongrácz, L. Kollár, K. Karaghiosoff, M. Czugler, L. Drahos, E. Fogassy, G. Keglevich: *The Resolution of 1-Isopropyl-3-Methyl-3-Phospholene-Oxide and Its Use as a*

Precursor for a P-ligand, J. Organomet. Chem., 2015, 10.1016/j.jorganchem.2015.08.013. (IF: 2.173[#]; C: 0)

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[S33] P. Bagi, K. Karaghiosoff, M. Czugler, D. Hessz, M. Kállay, M. Kubinyi, T. Szilvási, P. Pongrácz, L. Kollár, I. Timári, K. E. Kövér, L. Drahos, E. Fogassy, G. Keglevich: *Synthesis, Characterization and Application of Platinum(II) Complexes Incorporating Racemic and Optically Active 1-Phenyl-1,2,3,6-Tetrahydrophosphinine Ligand*, Heteroatom Chem., asap. (IF: 1.076[#]; C: 0)

[S34] A. Olasz, T. Szilvási*: *Quantifying Kinetic Stability of Reactive Species with Unburied Volume and Inverse Cone Angle*, submitted for publication.

[S35] C. Eisenhut, N. C. Breit, T. Szilvási, E. Irran, S. Inoue: *Comparative Study: the Reactivity of an NHC-Stabilized Silylene Monohydride towards a Ketone and CO₂*, submitted for publication.

[S36] D. Franz, T. Szilvási, E. Irran, S. Inoue: *A Monotopic Aluminum Telluride with an Al=Te Double Bond Stabilized by N-heterocyclic Carbenes*, Nature Commun. DOI: 10.1038/ncomms10037. (IF: 11.470[#]; C: 0)

[S37] K. Hansen, T. Szilvási, B. Blom, M. Driess: *A Persistent 1,2-Dihydrophosphasilene Adduct*, Angew. Chem. Int. Ed., asap. (IF: 11.261[#]; I: 0)

[S38] B. Blom, A. Said, T. Szilvási, P. W. Menezes, G. Tan, J. Baumgartner, M. Driess: *Alkaline-Earth Metal-Induced Liberation of Rare Allotropes of Elemental Silicon and Germanium From N-Heterocyclic Metallylenes*, Inorg. Chem., 2015, 54, 8840. (IF: 4.762[#]; C: 0)

[S39] B. Krámos, J. Oláh, T. Szilvási*: *Do Parameter-free Methods Outperform Empirically Tuned Analogs in Large Complex Systems?*, submitted for publication.

[#] previous year impact factor

Oral presentations

1. T. Szilvási, K. Nyíri, T. Veszprémi: *Szililének Inzertációs Reakcióinak Mechanizmusa*, KeMoMo–QSAR szimpózium, 2010, Szeged.

2. T. Szilvási, T. Veszprémi: *Molecular-tailoring: Internal Catalytic Effect of Bulky Substituents*, 16th International Symposium On Silicon Chemistry, 2011, Hamilton, Kanada.

3. T. Szilvási: *Szililének Inzertációs Reakciói*, Kémiai Előadói Napok, 2011, Szeged.
4. T. Szilvási: *Molecular-tailoring: Effect of Bulky Groups*, Young Scientist Award díjátadó, 2011, Düsseldorf, Németország.
5. T. Szilvási, T. Veszprémi: *Molecular-tailoring: Reaction Path Control With Bulky Substituents*, Oláh György Doktori Iskola IX. konferenciája, 2012, Budapest.
6. T. Szilvási, T. Veszprémi: *Nagy Térkitöltésű Karbén Ligandumok Katalitikus Hatása a Suzuki-reakcióban*, Kálmán Erika Doktori Konferencia, 2012, Mátraháza.
7. T. Szilvási, T. Veszprémi: *Nagy Térkitöltésű Karbén Ligandumok Katalitikus Hatása a Suzuki-reakcióban*, MTA Munkabizottsági ülés, 2012, Szeged.
8. T. Szilvási, T. Veszprémi: *Molekulaszabászat: Hexaszilabenzol, a Szilíciumkémia Szent Grálja*, KeMoMo–QSAR szimpózium, 2013, Szeged.
9. T. Szilvási, T. Veszprémi: *Molekulaszabászat: Hexaszilabenzol, a Szilíciumkémia Szent Grálja*, Superman szuperszámítógép konferencia, 2013, Budapest.
10. Z. Benedek, T. Szilvási: *Szililének Alkalmazhatósága Átmenetifém Katalitikus Reakciókban*, KeMoMo–QSAR szimpózium, 2014, Szeged.
11. Z. Benedek, T. Szilvási: *Can Low-valent Silicon Compounds Be Better Transition Metal Ligands Than Phosphines and NHC?*, 17th International Symposium On Silicon Chemistry, 2014, Berlin, Németország.
12. T. Szilvási: *Can Low-valent Silicon Compounds Be Better Transition Metal Ligands Than Phosphines and NHC?*, Central European Symposium on Theoretical Chemistry, 2014, Nagybörzsöny.
13. T. Szilvási: *Heavier Low-valent Group 14 Compounds: Alternatives for Carbenes and Phosphines as Transition Metal Ligands*, UniCat Colloquium, Technische Universität Berlin, 2014, Berlin, Németország.
14. T. Szilvási: *Homolytic activation of hydrogen with nonmetal compounds*, KeMoMo–QSAR szimpózium, 2015, Szeged.
15. T. Szilvási: *Olló-szerű (Pincer) ligandum stabilizált fősoportbeli elemek: régi-új katalitikus tulajdonságok*, MKE II. Nemzeti Konferencia, 2015, Hajdúszoboszló.

Poster presentations

1. K. Nyíri, T. Szilvási, T. Veszprémi: *The Mechanism of the Insertion Reactions of Silylenes*: Frontiers of Chemistry: From Molecules to Systems, 2010, Párizs.
2. T. Szilvási, T. Veszprémi: *On the Mechanism and Energetics of the Reaction of Carbenes*

and Silylenes With White Phosphorus: International Symposium On Silicon Chemistry, 2011, Hamilton, Kanada.

3. K. Nyíri, T. Szilvási, T. Veszprémi: Mechanisms of Insertion Reactions of Silylenes: International Symposium On Silicon Chemistry, 2011, Hamilton, Kanada.

4. T. Szilvási, T. Veszprémi: Activation of White Phosphorus by Heteroleptic Silylenes, 6th European Silicon Days, 2012, Lyon, Franciaország.

5. T. Szilvási, T. Veszprémi: Catalytic Effect of Internal Van Der Waals Interactions in Suzuki-Miyaura Cross-coupling Reaction, Toward the First-principles Description of Van Der Waals Interactions in Complex Materials, 2012, Lausanne, Svájc.

6. T. Szilvási, T. Veszprémi: Internal Catalytic Effect of Bulky NHC Groups in Suzuki-Miyaura Cross-coupling Reaction, Oláh György Doktori Iskola X. konferenciája, 2013, Budapest.

7. T. Szilvási, A. Gali: Fluorinated Diamondoids to Stabilize the Negatively Charged Nitrogen-vacancy Center in Diamond Nanoparticles, European Theoretical Spectroscopy Facility, Young Researchers' Meeting, 2013, Budapest.

8. T. Szilvási, T. Veszprémi: How to Synthesize Reactive Species: The Case of Hexasilabenzene, 9th European Conference on Computational Chemistry, 2013, Sopron.