RUSSIAN-FRENCH WORKSHOP ON

HYPER- AND HYPOCOORDINATED COMPOUNDS

OF THE GROUP 14 ELEMENTS

PROGRAM and
BOOK OF ABSTRACTS

28-30 AUGUST 2017
MOSCOW, RUSSIA
Monday, 28 Aug.

9:00-10:00 Institute main hall – Registration;
Institute dining room – Breakfast.

Conference-hall

10:00-10:15 – Workshop opening:
Mikhail EGOROV, Workshop chair, ZIOC RAS
Viacheslav JOUIKOV, Workshop chair, Université Rennes 1
Alexis MICHEL, Counsellor for Science and Technology of the French Embassy in Russia

Chairman – Mikhail EGOROV

10:15-11:00 – Antoine BACEIREDO, Toulouse, Université Paul Sabatier, France,
Stable silylenes: new perspectives in catalysis
11:00-11:45 – Vladimir LEE, University of Tsukuba, Japan,
Pyramidanes

11:45-12:00 – Coffee break
Chairman – Antoine BACEIREDO

12:00-12:45 – Christoph MARSCHNER, Graz University of Technology, Austria
Oligosilylanyl groups attached to hypo- and hyper-coordinated silicon, germanium, tin and lead atoms
12:45-13:00 – Ekaterina BELLAN, Toulouse, Université Paul Sabatier, France
Donor-stabilized 1,3-disila-2,4-diazacyclobutadiene with short nonbonded Si···Si distance: synthesis, computational study and reactivity
13:00-13:30 – Visit of Zelinsky Institute of Organic Chemistry

13:30-14:30 - Lunch

Library

Chairman – Tsuyoshi KATO

14:30-15:15 – Mikhail Egorov, ZIOC RAS, Russia,
Complexity in prototype reactions of carbene analogs
15:15-15:30 – Maxim CHEGEREV, Razuvaev Institute of Organometallic Chemistry, Russia, *Heavier carbene analogues bearing redox-active o-aminophenols*

Chairman – Klaus JURKSCHAT

15:30-16:15 – Herbert ROESKY, University of Goettingen, Germany, *Compounds of silicon and phosphorus with low coordinate elements*

16:15-16:30 – Evgeniya SAVERINA, ZIOC RAS, Sechenov Medical University, Russia, *Green approach to preparation of germanium*

16:30-16:45 – Coffee break

*Red Corner (Professors Club)*

Chairman – Mikhail EGOROV

16:45-18:00 – Round table on the new axes of the group 14 chemistry and their Franco-Germano-Russian international perspectives

16:45 – Visit to the vista point of the Academy of Sciences Presidium on Moscow River.

**Tuesday, 29 Aug.**

9:00-10:00 Dining room – Breakfast

*Library*

Chairman – Christoph MARSCHNER

10:00-10:45 – Viatcheslav JOUIKOV, Université Rennes 1, France, *Electron transfer in hypo- and hypercoordinated group 14 compounds at the electrochemical glance*

10:45-11:00 – Evgeniya DORONINA, Favorsky Irkutsk Institute of Chemistry, Russia, *Molecular design of photochromic systems with a hypervalent silicon atom*

Chairman – Viatcheslav JOUIKOV

11:00-11:45 – Tsuyoshi KATO, Toulouse, Université Paul Sabatier, France, *Cyclic (amino)(bora-ylide)silylene with a remarkably strong donating character*

11:45-12:00 – Antonina VISHTORSKAYA, ZIOC RAS, Sechenov Medical University, Russia, *Assessing Ge-132 as an antioxidant*
12:00-12:15 – Coffee break

Chairman – Jörg WAGLER

12:15-13:00 – Klaus JURKSCHAT, Technische Universität Dortmund, Germany, Donor group-containing ferrocenes and their tin derivatives

13:00-13:15 – Sergey BOGANOV, ZIOC RAS, Russia, Matrix isolation studies of complexation of SiCl₂ with weak Lewis bases

13:15-14:15 – Lunch

Red Corner (Professors Club)

13:45-15:15 – Round table with the French participants on organizational and administrative issues

15:00-21:00 – Barbecue party

Wednesday, 30 Aug.

9:00-10:00 Dining room – Breakfast

Library

Chairman – Herbert ROESKY

10:00-10:45 – Jörg WAGLER, Technische Universität Bergakademie Freiberg, Germany, Pyridine-2-thiolate and related ligands as chelators in group 14 complexes and bridges in group 14 – transition metal heterobinuclear complexes

10:45-11:00 – Yuri BAUKOV, Pirogov Medical University, Russia, Anionic, neutral, cationic, and zwitterionic chelates of hypercoordinated silicon, containing the derivatives of 2-acylaminopyridines and 2-hydroxy and 2-amino acids as ligands

Chairman – Viatcheslav JOUIKOV

11:00-11:45 – Andrey MENDKOVICH, ZIOC RAS, Russia, Dissociative electron transfer. Beyond the ECE

11:45-12:00 – Jonas HOFFMANN, Université Rennes 1, University of Bremen, France-Germany, Studies on stannoles and their polymers concerning their application for organic electronics

12:00-12:15 – Coffee break

Chairman – Evgenia DORONINA
12:15-13:00 – Rudolf PIETSCHNIG, University of Kassel, Germany, 
**Stereochemically constrained bisphosphano tetrylenes**

13:00-13:15 – Denis KARGIN, University of Kassel, Germany,  
**Approaches towards stereochemically constrained bisphosphano silylenes**

13:15-14:30 – Lunch

Chairman – Rudolf PIETSCHNIG

14:30-15:15 – Valery SIDORKIN, Favorsky Irkutsk Institute of Chemistry, Russia,  
**On the nature of bonding in the low-valent silicon compounds \( L_2Si \)**

15:15-15:30 – Alexander KORNEV, Razuvaev Institute of Organometallic Chemistry, Russia,  
**Structural variability of \( R_2C \) adducts of 3a,6a-diaza-1,4-diphosphapentalene: interplay between \( P\rightarrow CR_2 \) and \( N\rightarrow P \) bonding**

Chairman – Andrey MENDKOVICH

15:30-16:15 – Kirill ZAITSEV, Lomonosov Moscow State University, Russia,  
**Derivatives of group 14 elements based on polydentate ligands: tetrylenes and catenated compounds**

15:45-16:00 – Olga GAPURENKO, Rostov-on-Don Southern Federal University, Russia,  
**Silicon and germanium sandwich compounds**

16:00-16:30 – Workshop closing, Mikhail EGOROV, Viatcheslav JOUKOV

17:00 – Excursion
STABLE SILYLENES: NEW PERSPECTIVES IN CATALYSIS

Antoine BACEIREDO and Tsuyoshi KATO

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Oxidative addition and reductive elimination are exceedingly important processes in organometallic chemistry and, particularly, in catalysis. Very recently we have reported that phosphine-stabilized silylenes 1 display a unique ability to reversibly react with alkenes and E-H σ-bonds demonstrating that these silicon(II) complexes can behave like transition-metal complexes [1].

\[ \text{PR}_2\text{SiNAr}_X : \leftrightarrow \text{R'PR}_2\text{SiNAr}_X \]

In contrast, the original sila-cyclopropylidene 2, readily obtained by reaction of 1(H) with diphenyl acetylene, does not present a silylene-like reactivity, but it appears to be a robust and versatile ligand for transition metals [2]. Of special interest, the corresponding η¹-silacyclopropylidene-Pt⁰ complex, is an efficient catalyst for the hydrosilylation reaction of alkenes [3]. In the same vein, we have very recently prepared a new family of heterocyclic silylenes featuring two different π-donating substituents such an amino group as well as a more electropositive and stronger carbon-based π-donating phosphonium ylide function. Ligand 3 presents a high thermal stability and an unusual nucleophilic character as strong as that of NHC ligands [4].

\[ \text{Ar-N} \text{Si} \text{Ph-H} \text{PR}_2 \]

\[ \text{Ar-N} \text{Si}\text{NiPr}_2\text{Ar} \]

References
ANIONIC, NEUTRAL, CATIONIC, AND ZWITTERIONIC CHELATES OF HYPERCOORDINATED SILICON, CONTAINING THE DERIVATIVES OF 2-ACYLAMINOPYRIDINES AND 2-HYDROXY AND 2-AMINO ACIDS AS LIGANDS

Yuri BAUKOV,¹ Natalia KALASHNIKOVA,¹ Sergey BYLIKIN,² Alexey NIKOLIN,¹ Evgeniya KRAMAROVA,¹ S. V. VOROBYEV,¹ Aleksander SHIPOV,¹ Aleksander KORLYUKOV,³ Dmitry ARKHIPOV³ and Vadim NEGREBETSKY¹

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Hypercoordinate silicon chelates are known for their chemical and biological activity, structural diversity and stereodynamic behaviour in solutions [1]. In this work, we report the synthesis and structures of new ionic and neutral Si complexes with fragments of 2-hydroxyacids, 2-aminoacids, benzoxazinones and 2-acylaminopyridines.

The following complexes are discussed: a) anionic hexacoordinate mixed trischelates 1 (C₆H₁₁)₂NH₂⁺[LCH₂SiOCR₂C(O)O]₂⁻ (R = H, Me, Ph; LCH₂ = lactamomethyl or similar heterocyclic ligand); b) neutral C,N-monochelates (2), containing fragments of 2-acylaminopyridines; the first neutral pentacoordinate chelate with a dipeptide fragment, Ts-Gly-(S)-Pro-N(Me)CH₂SiMe₂F (3); c) O-chelate difluorides 4 R₃R₂NCH(R₁)C(O)N(CH₂SiMe₂F)₂ (R₁ = H, Me; R₂ = (CH₂)₃; R₃ = Ms, Ts) with one penta- and one tetracoordinate silicon atoms; d) cationic pentacoordinate C,O- and O,O-bischelates 5 [LCH₂Si(Me)[OCH(R)C(O)NMe₂]]⁺X⁻ (LCH₂ = lactamomethyl or similar heterocyclic ligand; R = H, Me, Ph; X = Br, OTf); and e) pentacoordinate zwitterionic complexes (6) based on 2-amino- and 2-hydroxyacids.

The structures of reported compounds were confirmed by an X-ray diffraction study and multinuclear (¹H, ¹³C, ¹⁹F, ²⁹Si and CP/MAS ²⁹Si) NMR spectroscopy.

Acknowledgement. This work was supported by the RFBR (Project Nos. 16-33-60168, 16-33-00956, 16-03-00957, 17-03-01211)

References
DONOR-STABILIZED 1,3-DISILA-2,4-DIAZACYCLOBUTADIENE WITH SHORT NONBONDED Si···Si DISTANCE: SYNTHESIS, COMPUTATIONAL STUDY AND REACTIVITY

Ekaterina BELLAN, David GAU, Raphaël NOUGUÉ, Nathalie SAFFON-MERCERON, Antoine BACEIREDO, Abel DE CÓZAR, Fernando P. COSSÍO, Daisuke HASHIZUME and Tsuyoshi KATO

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3 Materials Characterization Support Unit RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan

Here we report the synthesis of 1,3-disila-2,4-diazacyclobutadiene (2a and 2b) by the reaction of the phosphine-stabilized chlorosilylene 1 with sodium azide. The reaction proceeds by the dimerization of transient silanitrile 4 formed after decomposition of azide 3 by the nitrogen evolution (Scheme 1) [1].

![Scheme 1](image)

It is noteworthy that compound 2 presents an exceptionally short nonbonded Si···Si distance (2.23 Å) comparable with Si=Si double bond distances (2.15–2.23 Å). Accordingly to experimental X-ray electron density distribution analysis and theoretical investigations there is no bond between the two silicon atoms, and that the unusual geometry of 2 can be explained by a significant Coulombic repulsion between the two negatively charged ring nitrogen atoms.

The reactivity of 1 towards different substrates will be also discussed.

References
Silylenes, derivatives of divalent silicon, represent an important class of silicon containing compounds. On the basis of numerous investigations, it has been concluded that due to their unoccupied p orbitals, labile silylenes are prone to act as Lewis acids and capable to form complexes with different Lewis bases. Complexation with relatively strong Lewis bases (amines, phosphines, ethers) was found to decrease their reactivity and, therefore, increase their selectivity [1]. Formation of intermediate complexes between a silylene and a reactant explains effective negative activation energies revealed for many reactions of labile silylenes [2]. Despite wide acceptance of the capability of labile silylenes to complexation, almost all spectroscopically detected silylene complexes represent those with silylene centers coordinated by atoms of the Group 15 or 16 elements. Observations of silylene complexes with weaker organic Lewis bases such as halogenoalkanes are restricted to several reports only [3, 4], whereas those with unsaturated hydrocarbons have not been observed spectroscopically till now.

Using matrix FTIR spectroscopy, we succeeded in detection of donor-acceptor complexes between dichlorosilylene, SiCl₂, one of the simplest labile silylenes, and a series of weak Lewis bases such as allyl halides, Hal = Cl, Br, HCl, buta-1,3-diene and acetylene. On the basis of obtained experimental data and quantum chemical calculations, structural features, including conformational isomerism, and stabilities of the complexes were analyzed. Photochemical transformations of the complexes were examined. Possible directions of their thermal transformations were investigated theoretically.

Acknowledgement. This work was supported by the Russian Science Foundation (Project No. 14-13-01456).

References
HEAVIER CARBENE ANALOGUES BEARING REDOX-ACTIVE o-AMINOPHENOLS

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At present many stable silylenes, germylenes, stannylenes and plumbylenes derived from different heterocycles have been prepared. Interest in these compounds arises from their electronic structures, chemical properties and their ability to act in catalytically active metal complexes as N-heterocyclic carbenes. The variation of heteroatoms in the chelating fragment of various metallocenes provides a useful means for tuning their reactivity. Replacement of nitrogen atoms in the metallocycle with O-atoms leads to the formation of chelate O,N-(o-amidophenolate) and O,O-(catecholate) complexes. Moreover, as mentioned above, N,N, O,N and O,O - ligands are potentially redox-active, which significantly expands their scope of reactivity. Redox ligands can be used as reservoirs of electrons for bond-making and bond-breaking reactions. They also can support multi-electron transformations required to promote atom- and group-transfer reactions. The ability of o-iminoquinones to exist in three different redox states provides the foundation for their rich coordination chemistry. In particular, these species have proven to be very convenient objects for EPR investigations.

LA - Lewis acid; LB - Lewis base

Scheme 1.

Acknowledgement. We are grateful to the Russian Science Foundation (grant 17-13-01428) for financial support of this work.
In the literature, there are known examples of promising in practical terms photochromic systems, based on the silicon-containing azobenzenes, for which the light-induced $E \Leftrightarrow Z$ isomerization (rotation around the double N=N bond) is accompanied by a decrease in the coordination number of the silicon atom from 6 to 5 or from 5 to 4 [see, for example, refs. 1, 2]. We have performed an \textit{ab initio} and DFT design of the neutral hemi-indigo silicon-containing photochromic systems. They are characterized by a photoinduced transition from the $E$- to $Z$-isomer through rotating around the double C=C bond with the 5\textrightarrow4 recoordination of Si (Scheme 1).

The $E$-form is the first example of a structure in which the seven-membered cycle is closed by an extremely short ($\sim$1.8-1.9 Å) polar-covalent (AIM) dative O→Si bond. There is a tendency towards increasing the difference in the electron-orbital structure as well as in the optical properties of the $E$- and $Z$-isomers upon the strengthening of the O→Si contact.

\textit{References}

Trends in the reactivity of heavy carbene analogs were traced on a quantative basis. Their reactivity decreases on going from silylenes to stannylenes. All these species are reactive with respect to the same reagent types, react with them at comparable rates, and the mechanisms of these reactions are much the same.

In all types of reactions the unsubstituted \( \text{EH}_2 \) species are more reactive than \( \text{EMe}_2 \) ones. A large branching of the overall reaction channels occurs on going from silylenes to the heavier carbene analogs. Therefore in some reactions the expected end products are reactive intermediates.

In many cases the reactions of carbene analogs are not simple and often involve several steps. Typically the first step of the reaction is the formation of pre-reaction complex between the carbene analog and the reagent where the carbene analog acts as a Lewis acid. Due to the reversibility of this electrophilic step, in many cases a negative activation energy for the overall reaction is observed.
The DFT calculations predict stable non-classical sandwich structures with hypercoordinated silicon and germanium centers and boron rings.

Since the central atom contains four valence electrons and $\pi$-orbitals of boron rings have no electrons, the stable silicon/germanium sandwiches must bear a positive 4+ charge (due to the 8 electron counting rule) that ought to be compensated by either four counter-ions or four bridging hydrogen atoms. Thus, to stabilize a silicon sandwich with $(BH)_n$ boron rings, the latter must be used as the $(HB)_nH_2$ species.

Figure 1. The geometric characteristics of sandwich structures calculated by the DFT/M062X/6-311++G(3df,3p) method.

Acknowledgement. This work was supported by the Russian Ministry of Education and Science for Research (Project Part, project 4.844.2017/4.6).
Inorganic/organic materials based on heavier group 14 elements exhibit a small optical band gap and improve charge transport properties. Polymeric stannoles recently gained interest in the field of optoelectronic materials. So far, a copolymer with thiophene was reported by our group which was obtained by a cross-coupling route using the stannole and a dinucleophilic thiophene. [1]

We established a method that leads to homopolymers which consist of the thiophene-flanked stannole as repeating unit by using electropolymerization and oxidative polymerization. The properties of the resulting polymers were investigated and can be compared to the polymer which was synthesized by using a cross-coupling method.

Further we investigated intensively the thermal stability and absorption/fluorescence properties of these compounds to determine the ability for using these unique polymers for optoelectronical applications.

Acknowledgements. JH acknowledges funding for a Short Term Scientific Mission from the COST action COST 1302: ‘European Network on Smart Inorganic Polymers’. This research has been supported by the Institutional Strategy of the University of Bremen, funded by the German Excellence Initiative.

References.
Electron transfer (ET) from/to organic derivatives of the 14 group elements, especially when they are in less common low- and high-coordinated states, provides a versatile activation ranging from electrophilic to radical and nucleophilic. Moreover, ET often plays an important role in the intermediate formation of such states in the redox processes of initially four-coordinated derivatives.

Hypercoordination in the 14 group allows expanding the concept of polyelectron polycentric hyperbonds beyond the known, e.g. as in metallatranes, bonding 3c-4e systems [1]. Electrochemical aspects of di- and bis-metallatranes, new 4c-6e and 5c-6e hyperbonded systems, will be considered using voltammetry, real-time UV-Vis and EPR-spectroelectrochemistry.

One-electron uptake not only makes possible the formation of the hexa-coordinated complexes of halosilanes and halogermanes with non-innocent N-heteroaromatic ligands [2], but it also opens interesting perspectives of generating ligand-stabilized silyl (germyl) radicals characterized by EPR spectroscopy as the spin-adducts with α-phenyl-N-t-butyl nitron [3]. These radicals can react with appropriate molecular partners or to add to the conducting underlying macro support [4] thus allowing efficient silyl or germyl functionalization of the latter.

While isolated E=E double bonds of carbon are not electrochemically reducible, those with heavier elements (E = Si, Ge, Sn) show a quite easy electron uptake upon the reduction and an amazingly easy electron release under electrochemical oxidation. Contrary to earlier reports [5], most of these processes – both in reduction and in oxidation - were found to be reversible or quasi-reversible indicating that no bonds are being broken in such redox transformations. Further ET in both directions is also often possible in such cases, leading to the corresponding di-ionic species, mostly in the reversible way. Several examples of reversible formation of persistent anion radicals and cation radicals of dimetallenes will be considered.

Acknowledgement. The financial support of this work from Rennes Metropôle is gratefully acknowledged.

References
DONOR GROUP-CONTAINING FERROCENES AND THEIR TIN DERIVATIVES

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In continuation of our long-year interest in phosphorus-containing ligands and their main group element derivatives [1-5] the syntheses, structures, and reactivity of a variety of donor group-substituted ferrocene derivatives such as 1 - 8 is presented.

![Chemical structures](image)

Figure 1. Collection of donor group-containing ferrocene derivatives 1 – 8.

These compounds can easily be lithiated and subsequently transferred into the corresponding organotin derivatives. The compounds 5 and 6 show an interesting behaviour as chelate ligands towards tin halides. Compounds of types 3 and 7 are novel pincer-type pro-ligands, and 8 shows a unique behaviour in metalation reactions.

References
Phosphorus bridged [n]ferrocenophanes (with n accounting the number of atoms tethering both cyclopentadienylrings) are attractive molecules for various purposes such as asymmetric catalysis [1] or metal containing polymers [2-3]. The discovery of reactive, transient, low-valent silicon compounds occurred almost half a century ago, but isolation of more stable Si(II) derivatives like the N-heterocyclic derivative in 1994 by West and Denk [4] attracted more attention to this interesting field.

We are investigating the combination of bisphosphano based tetrylenes with the rich chemistry of ferrocene. In contrast to having nitrogen adjacent to the low valent group 14 element, electronic stabilization using phosphorus is limited but at the same time stereocenters are introduced and the control of stereochemistry lies within our focus. We already obtained a variety of suitable precursors for reduction processes or dehydrohalogenation I, exhibiting selective stereochemistry [5]. Currently we are aiming for free, phosphorus based tetrylenes incorporating silicon II, tin and germanium atoms inbetween two phosphorus atoms.

Acknowledgement. We gratefully acknowledge financial support by the following programs and institutions: Deutsche Forschungsgemeinschaft and ERA Chemistry (PI 353/8-1; PI 353/9-1), EU COST action CM1302 “SIPs”.

References
The importance of phosphonium ylides I in organic synthesis is obvious. Due to the highly polarized P=C bond toward the carbon atom, they present a strongly $\sigma$- and $\pi$-donating carbon centre, which allows to use them in various fields as Wittig reagents, transition metal ligands as well as strongly $\pi$-donating substituents to stabilize electron deficient species. Other phosphonium ylides featuring a different anionic site, with different properties, and therefore different applications, are also well known.

Very recently we have described the synthesis of the lightest homologue in the series, the phosphonium bora-ylide II stabilized by the coordination of an NHC ligand [1]. This ylide featuring an electropositive boron as the anionic site shows an exceptionally strong electron-donating character. Indeed, the new N-heterocyclic silylene (NHSi) III substituted by a bora-ylide fragment presents a remarkably high stability and a strong electron-donating character toward transition metals, which is much stronger than that of related NHSi stabilized by a classical phosphonium-ylide substituent [2].

Acknowledgement. This work was supported by CNRS and the European Research Council (ERC Starting grant agreement no. 306658) and the université de Toulouse (IDEX-SANDCOMPLEX)

References
STRUCTURAL VARIABILITY OF $R_2C$ ADDUCTS of 3a,6a-DIAZA-1,4-DIPHOSPHAPENTALENE: INTERPLAY BETWEEN $P \rightarrow CR_2$ AND $N \rightarrow P$ BONDING

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Aromatic (10π e) 3a,6a-diaza-1,4-diphosphapentalene (DDP) [1] may be represented as a compound containing either formally divalent (A) or monovalent (B) phosphorus. Formula C reflects its high polarizability. “Adducts” of DDP with carbenes $R_2C$ have different structure (D or E) depending on the nature of $R$ groups. Electron delocalizing $R_2C$-groups promote formation of zwitterionic structure of the type D containing covalent bond $N - P$ and $P - C$ bond of tautomeric type. Other $R_2C$ groups (not capable to delocalization of negative charge) such as $\text{Ph}_2C$, $\text{Cl}_2C$, $\text{Me}_2C$ provide the compounds of the type E containing only van-der Waals contacts $N - P$ and double $P = C$ bond.

Heavier analogues of carbens ($\text{Cl}_2\text{Si}$, $\text{Cl}_2\text{Ge}$, $\text{Cl}_2\text{Sn}$) show coordination to phosphorus of the type D, revealing pyramidal configuration of the IV main group elements. The $N \cdots P$ bond distances in DDP ligand in these cases vary only slightly (1.76 – 1.79 Å). We succeeded in fixing and separating some of adducts and explored their crystal structure and chemical properties.

Acknowledgement. This work was supported by the Russian Science Foundation (grant no. 14-13-01015-P).

References
PYRAMIDANES

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Pyramidanes, the compounds with a square-pyramidal shape, represent a novel highly challenging class of polyhedral clusters featuring an "invertedly" tetrahedral apical atom.

Although comprehensively approached on theoretical grounds, neither pyramidane itself nor its derivatives were synthetically accessible, and only very recently their first isolable representatives were described. In this presentation, we report on a series of the first group 14 element pyramidanes E'[E₄(SiR₃)₄] (E = C, Si, Ge; E' = Ge, Sn, Pb; R₃Si = SiMe₃, SiMe₂Bu₂) 1 with the C₄/Si₄/Ge₄-bases and Ge/Sn/Pb-apexes, their synthesis, structural features, and particular bonding situations (Figure 1) [1].

Hybrid pyramidanes with the group 14 elements at the base and group 15 (or group 13) element at the apex of the square-pyramid will be also presented, and their non-classical structures will be discussed [2].

Figure 1. Group 14 element pyramidanes.

Acknowledgement. This work was financially supported by the JSPS KAKENHI Grant (No. JP15K05413) from the Ministry of Education, Science, Sports, and Culture of Japan.

References
Using oligosilanyl anion chemistry we have set out to utilize bulky oligosilanyl groups in the chemistry of hypo- and hypercoordinated heavy group 14 compounds. Cyclic oligosilylated germylenes, stannylene and plumbylenes were found to form easily upon reactions of 1,4-oligosilanediides with $EX_2$ ($E = \text{Ge, Sn, Pb}; X = \text{Cl, Br}$). Despite the chemical similarity of Ge, Sn and Pb all obtained compounds dimerized to different structures (Scheme 1) [1].

![Scheme 1. Dimerization behavior of cyclic disilylated tetrylenes](image)

We have also studied effects of oligosilanyl groups on hypercoordinated silicon compounds. While silatranes with comparatively electronegative substituents have received much interest, electropositive groups have been largely neglected. As electron donating groups diminish the Si-N interaction this is partly understandable. However, introduction of silyl groups still maintains N->Si donation. Changing the electron donating ability of the silyl groups allows tuning the Si-N interaction which can be recorded using XRD and NMR analysis (Scheme 2) [2].

![Scheme 2. Formation of oligosilylated silatranes and metalation of the silyl group](image)

Acknowledgement. This work was supported by the Austrian Science Fund (FWF) via projects P 22678 and P26417.

References
DISSOCIATIVE ELECTRON TRANSFER. BEYOND THE ECE

Andrey MENDKOVICH\(^1\) and Alexandre RUSAKOV\(^2\)

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The electrochemical reductive cleavage of the bonds in organic compounds starts as ECE process and results in formation of two anions, what enable one to anticipate the reaction of proton transfer and/or nucleophilic substitution between the species and initial compound. A complex of experimental (cyclic voltammetry, chronoamperometry, electrolysis) and theoretical methods (digital simulation, quantum chemical calculations) was employed to study the processes using as an example OH-acids electroreduction in aprotic solvents [1-3].

The results obtained unable us to develop a general scheme describing the reaction following the bond dissociation and reveal intrinsic and external factors affecting the selectivity of the process.

References

STEREOCHEMICALLY CONSTRAINED BISPHOSPHANO TETRYLENES

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[n]Ferrocenophanes with an n-atomic chain bridging the rings of a ferrocene unit are attractive synthetic targets owing to their potential in the synthesis of metal containing polymers [1, 2]. We are aiming at [3]ferrocenophanes with two terminal phosphorus atoms involved in the tethering unit in order to study the synthetic potential as a suitable scaffold for phosphano substituted tetrylenes [3]. The donor properties of the phosphane unit and the acceptor properties of the tetrylene unit give rise to either intramolecular or intermolecular mutual donor/acceptor complexes (cf. Figure below). Moreover, we expanded our scope to bridging units with E = B-R and P-R. Since the phosphorus atoms behave as stereocenters, a special focus will be set on their stereochemical alignment with the aim to achieve stereocontrol [4].

Acknowledgement. We gratefully acknowledge financial support by the following programs and institutions: Deutsche Forschungsgemeinschaft and ERA Chemistry (PI 353/8-1 PI 353/9-1), EU COST action CM1302 “SIPs”.

References
The recent developed chemistry of low coordinate or low valent silicon will be presented. In detail the selected preparation of low valent species Si, Si₂, Si₃, SiH₂, HSiSiH, MeSiSiMe, MeGeGeMe and a few isolated radicals will be reported. Compounds with low valent phosphorus are well known. However compounds with interconnected Si-P units with low valent elements are rarely investigated.

The reaction of the silylene PhC(N₆-Bu)₂Si(:)N(SiMe₃)₂ with elemental phosphorus yielded the acyclic silicon–phosphorus compound containing the Si–P–P–P–P–Si chain structure in good yield. Treatment of the bis-silylene [PhC(N₆-Bu)₂Si(:)]₂ with AdCP and P₄ gave the four-membered rings [PhC(N₆-Bu)₂Si(:)]₂ PCAd and [PhC(N₆-Bu)₂Si(:)]₂ –P₂, respectively.

The first stable heterocyclopentadienyl cation was prepared from [PhC(N₆-Bu)₂]Si(:)Cl and MeCP, while the reaction of [PhC(N₆-Bu)₂]Si(:)N(SiMe₃)₂ and AdCP gave the five-membered Si₂NCP ring under activation of a Si-Me bond.

Moreover, the cycloalkylamino carbene (cAAC) is able to stabilize the cAAC→SiCl₂→PR backbone with two lone pairs of electrons at the phosphorus atom. Finally a radical of composition cAACSiCl₂PPh₂ was isolated and structural characterized. The EPR spectrum was recorded.

Finally, the preparation and characterization of the first silylene-phosphinidene (2) will be reported.
GREEN APPROACH TO PREPARATION OF GERMANIUM

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Electrochemical deposition of metallic germanium is intensively studied, which is
directly related to its use in the production of high-speed electronics, fiber optics, IR-
components and detectors, as well as in photovoltaics and for development of perspective
anodic materials for lithium-ion batteries. The processes of preparing nano-powdered
metallic Ge requires non-aqueous media, in particular glycols, and uses GeCl4 as a starting
Ge-containing substrate. GeCl4 is a toxic, volatile and easily hydrolysable compound, which
complicates the conditions and renders the whole process environmentally hazardous. It is
to note that GeCl4 is usually obtained from GeO2. We investigated the possibility of
preparing metallic germanium in an alternative process, circumventing the use of GeCl4, by
cathodic electrodeposition from the salts of germanium with organic acids.

While studying electrochemical behavior of the derivatives of hyper-coordinated
germanium with organic acids, we found that germanium nanoparticles could be effectively
electrochemically deposited from the solution of germanium citrate in 1,2-propyleneglycol of
nutritive grade. Germanium citrate is highly stable, resistant to hydrolysis, completely non-
volatile and is easy to synthesize from GeO2 in aqueous solution of citric acid, which makes
the process very attractive and environmentally friendly. The electrolysis was carried out
under the simple conditions of galvanostatic mode; it does not require the cell separation
e.g. with a diaphragm and can be performed under the direct contact of the solution with the
atmosphere.

Thus, environmentally safe, simple and efficient method of electrochemical
deposition allows obtaining germanium nanoparticles from germanium dioxide using its
readily available derivatives with organic acids.

Acknowledgement. This work was supported by Grant RSF 17-73-20281.
A critical analysis has been performed on the available data on the structure of molecules $L_2Si$ (silylone vs. silaallene), where the ligands $L$ are different carbenes and silylenes [1]. In the literature the choice in favor of the silylone structure of $L_2Si$ is not indisputable. The degree of support for the discussed models of bonding in $L_2Si$ depends on the applied quantum-chemical methods ($\textit{ab initio}$ and DFT) and approaches (AIM, ELF, NBO etc.).

References
Organogermanium sesquioxide, 2-carboxyethylgermanium (commercial name Ge-132) of the formulae \([\text{GeO}_3\text{GeCH}_2\text{CH}_2\text{COOH}]_n\), is a germanium dietary complement widely used in medical practice because of its antioxidant activity.

In order to parallel the antioxidant and redox activity of Ge-132, it has been studied using cyclic voltammetry at a glassy carbon working electrode as well as by spectrophotometry and ESR spectroscopy monitoring its interaction with a stable free radical, 2,2-diphenyl-1-picrylhydrazyl (DPPH) in acetonitrile and methanol and their mixtures with water. Our results obtained using these standard and common for testing antioxidant activity methods distinctly show that Ge-132 can exhibit the antioxidant properties exclusively in the absence of water, because in aqueous solutions or even in those containing trace amounts of water, the Ge–O–Ge bond responsible for the capture of free radicals and hence for the very antioxidant activity is hydrolyzed to an inactive germatril form.

Thus, although Ge-132 is reputed as a water-soluble germanium preparation, it can act as an antioxidant solely in the lipid environment, which is important from the point of view of revealing the mechanism of its biological action.

Acknowledgement. This work was supported by Grant MK-755.2017.3.
Pyridine-2-thiolate (pyS\(^-\)) may serve as a chelating ligand in group 14 coordination chemistry, as has been shown for compounds such as Si(pyS)\(_4\) (I) [1] and related complexes [1, 2]. Methimazolide (mt\(^-\)) does not form chelates with silicon, e.g., in (II) [3], but both pyS\(^-\) and mt\(^-\) were shown capable of forming bridges between group 14 elements and transition metals, e.g., in ClSi(μ-mt)\(_4\)PdCl (III) [4, 5] and Cl\(_2\)Sn(μ-pyS)\(_2\)PdPPh\(_3\) (IV) [6]. Thus, these ambidentate ligands may also support the formation of hypercoordinate group 14 metalloid complexes by “luring” electron rich transition metal (TM) atoms into their coordination sphere. In both cases of bridging ligands, the soft S atom binds to the TM atom and the N atom to the main group metalloid. Our recent investigations address the syntheses of 2-pyridyloxy substituted silanes and the investigation of their related coordination chemistry, which should be different because of the exchange of the hard and soft donor sites in the 2-pyridyloxy-anion (pyO\(^-\)) with respect to pyS\(^-\) [7].

References
DERIVATIVES OF GROUP 14 ELEMENTS BASED ON POLYDENTATE LIGANDS: TETRYLENES AND CATENATED COMPOUNDS

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Synthesis and investigation of the low-valent derivatives of Group 14 elements (M=Si, Ge, Sn, Pb) represents an actual scientific task. In our works various polydentate ligands (N,N,N-, N,N,O-, O,N,O-types etc.) were used for obtaining the tetrylenes [1] (Figure 1). Furthermore, the tetrylenes obtained were used as ligands in metal (Pd, Mo, W) complexes [2].

![Figure 1. Structural types of the tetrylenes obtained.](image)

Compounds of Group 14 elements (E = Si, Ge, Sn) with element – element bonds due to the presence of σ-conjugation along the chain of E atoms acquire useful properties typical for unsaturated compounds (intense UV absorption, conductivity, electrochemical reaction, luminescence). The establishment of the dependence of these properties from the structure represents an actual scientific challenge. In this report the recent results obtained in our scientific group concerning the catenated derivatives based on polydentate ligands [3] are also presented.

Acknowledgement. This work was supported by R.S.F. (project № 14-13-01456).

References