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Organic derivatives of group 14 elements: general aspects of synthesis, modern trends, and application prospects

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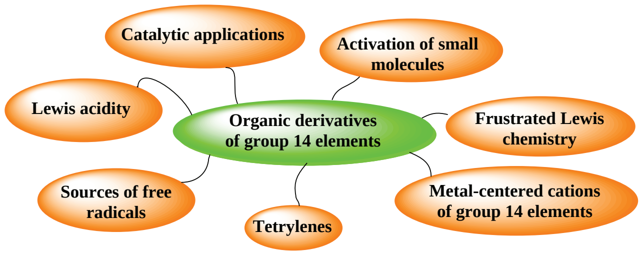
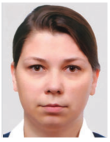
A general aspect of synthesis, modern trends and application prospects of organic derivatives of group 14 elements are briefly overviewed. This survey concerns actual research areas with pronounceable scientific sound such as Lewis acidity of catecholate silicon and germanium complexes, their ability to give free radicals and low valence 14 group derivatives. The main recent trends (published mainly within 2017–2022) in the chemistry of group 14 derivatives which are of paramount importance for the development of new catalytic systems, fluorescent marks, activation of small molecules and frustrated Lewis pair (FLP) chemistry are summarized.



Keywords: silicon, germanium, tin, complexes, organic derivatives, application prospects, Lewis acids.

1. Introduction

The development of synthetic approaches and methods for studying the structure of new compounds, including the development of knowledge on quantum chemical calculation methods, contributes to the systematic expansion of the range of organometallic compounds. Such derivatives of the elements of group 14 of the Periodic Table are no exception. The classical oxidative state of the elements of this group is +4, however, due to coordination with the donor atoms Z (Z = O, N, S, P), the coordination number of the central atom can be increased to five, six or even seven. The reactivity of such hypercoordinated complexes also increases, which opens



Elena N. Nikolaevskaya graduated from Lobachevsky State University of Nizhny Novgorod in 2012. She received her PhD degree in organoelement and organic chemistry in 2017 under the supervision of Professor Gleb A. Abakumov and Dr. Nikolay O. Druzhkov (Institute of Organometallic Chemistry of the Russian Academy of Sciences, Nizhny Novgorod). In 2017 she moved to N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences and obtained position of research scientist at the Laboratory of the Chemistry of Carbenes and Other Unstable Molecules. She specializes in organic and organometallic synthesis under rigorous air-free conditions. Her research interests include synthesis of redox-active compounds, organogermanium chemistry and NMR spectroscopy.

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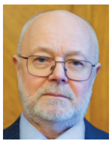


Mikhail P. Egorov[†] graduated from the Chemistry Department of Moscow State University in 1976. In 1980, he received his PhD degree. Since 1984, he has been working at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences (RAS). In 1992, he received his Dr. Sci. degree at this Institute. In 1997, Professor Egorov was elected Corresponding Member of the RAS and, in 2008, Full Member of the RAS. Currently, Academician Egorov is the head of the Laboratory of the Chemistry of Carbenes and Other Unstable Molecules, Director of the Institute and Academician-Secretary of the Division of Chemistry and Materials Sciences of the RAS. The subject of his research covers a number of sections of physical organic and organoelement chemistry, in particular the chemistry of elements of the carbon group. It includes the establishment of the mechanisms of thermal, photochemical and electrochemical reactions of both valence-unsaturated derivatives of group 14 elements (analogues of carbenes in the ground and excited states, element-centered radicals, ions, radical ions) and derivatives of tetravalent elements, direct spectroscopic identification of highly reactive short-lived intermediates of these reactions, the synthesis of stable representatives of a number of strained small silicon and germanium heterocycles, *etc*.

[†] The Editorial Board and Staff of the journal Mendeleev Communications take an opportunity to congratulate Academician M. P. Egorov on the occasion of his 70th birthday and wish him all the very best.

the way to new possible applications of these organic derivatives.

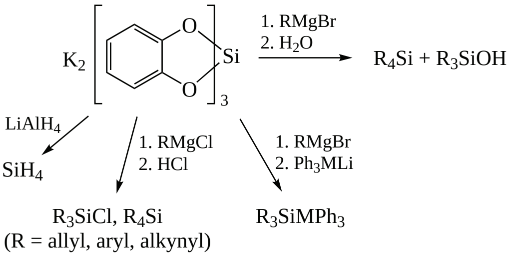
The coordination compounds of group 14 elements tirelessly attract the interest of researchers all over the world. This is evidenced by the fact that the large number of publications, annual reviews and surveys are devoted to separate aspects of the chemistry of five- and six-coordinated heavy group 14 elements (see, for example, reviews, monographs and books).[1–3] The attractiveness of this field is primarily based on the fundamental study of unique three-centre four-electron bonds (3c–4e), which are formed during hypercoordination.[4–9] Secondly, in recent years, hypercoordinated derivatives have increasingly been involved in the similarity of oxidative addition and reductive elimination reactions that are characteristic of transition metal complexes and not characteristic of p-block elements derivatives. This opens up broad prospects for the use of hypercoordinated group 14 compounds in catalytic reactions.[10–14]

This review is aimed at briefly discussing approaches to the synthesis of hypercoordinated derivatives of silicon, germanium and tin, modern trends and their application prospects in various fields of science and technology. It is not intended to fully cover the entire range of works on this topic, but only to focus the attention of researchers on the prospects for continuing research in this area.

2. Synthetic approaches to group 14 organic derivatives

2.1. Silicon

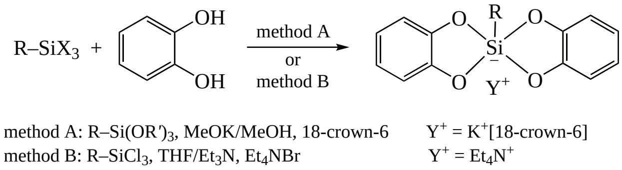
Pentacoordinate silicon complexes were formerly obtained[15–17] from cheap SiO_2 working on it with alkali in the presence of diols. However, further transformations of tris-catecholate silicon complexes are possible to start only with the help of very strong nucleophilic reagents (Scheme 1). More recently, it has been proposed to depolymerize silicon dioxide using one pot synthesis. It included the treatment of SiO_2 suspension in anhydrous THF with phenyllithium. The reaction was carried out in a Yang's NMR ampoule, so it is too early to speak with confidence about scaling the process.[18]



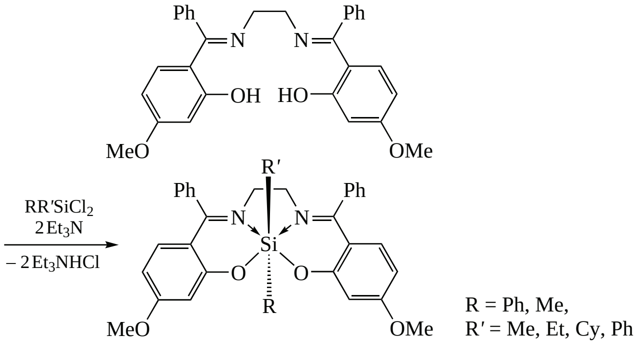
Scheme 1

It is far easier to synthesize such complexes from alkyl/aryl(trialkoxy)silanes or alkyl/arylsilanes working on them with diols/catechols (Scheme 2). At the moment, most silicon complexes are obtained using this method.[19] Greater part of silatranes,[20–23] metallocanes,[24] catecholates[25] and chelate silicon complexes[26,27] were obtained in analogous way.

Hexacoordinate silicon complexes based on salen ligands are also obtained *via* reaction illustrated in Scheme 3.



Scheme 2

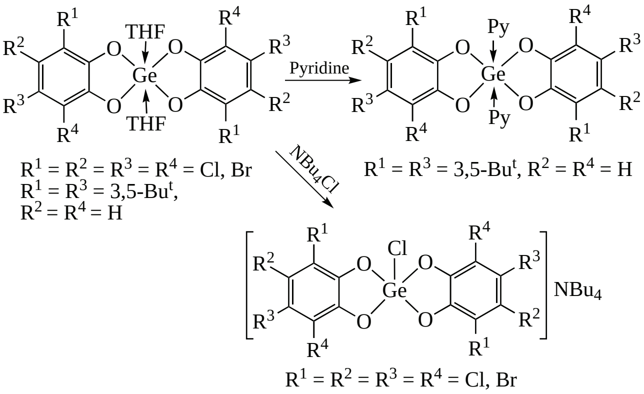


Scheme 3

2.2. Germanium

A chapter in the book, published in 2023 under the editorship of Lee, is devoted to obtaining highly coordinated germanium complexes.[28] The authors describe in detail the methods of synthesis of compounds with a Ge–C bond and deliberately cut off the discussion of the peculiarities of obtaining organogermanium derivatives without this bond. At the same time, the absence of this information gives a distorted understanding of the reactivity of hypercoordinated Ge derivatives. For a more complete understanding of the picture, this review includes examples of obtaining highly coordinated germanium complexes without Ge–C coupling, published after 2015.

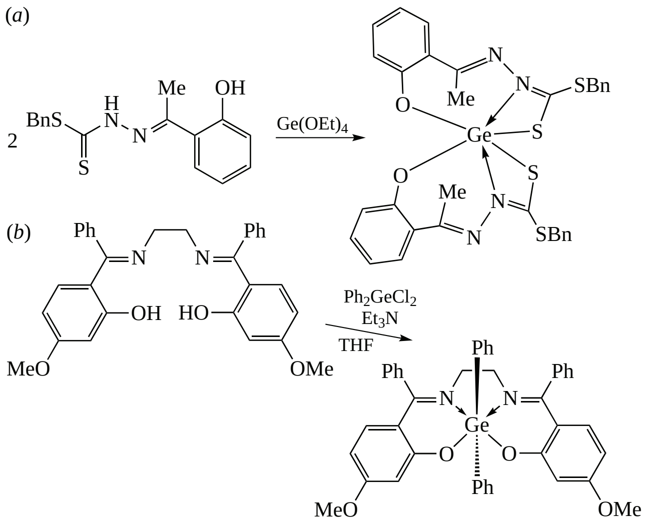
Due to the high Lewis acidity of Ge^{IV} site, it is possible to obtain the desired hypercoordinated compounds by coordinating donor molecules. Such ligand can contain different elements (carbon,[29,30] nitrogen,[31] oxygen,[32] sulfur,[33] phosphorus[34,35]). Donor ligands can easily enter the coordination sphere of germanium(IV) in its complexes. Thus, THF molecules weakly bound to the germanium(IV) atom in bis-catecholate complex can easily be replaced by pyridine molecules with high donor capacity, or even chloride anions (Scheme 4).[36]



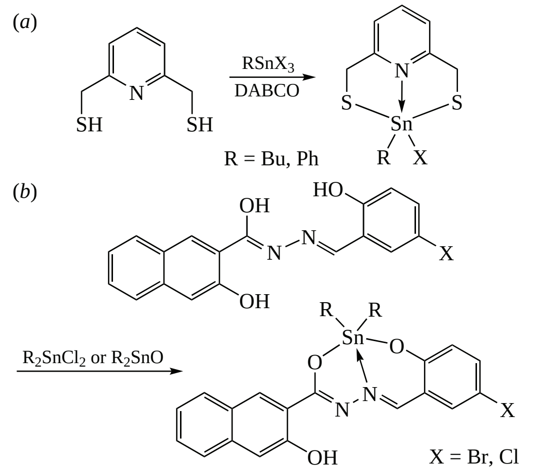
Scheme 4

In literature there are data on coordination compounds of ECl_4(NHC) (E = Ge, Sn) with N-heterocyclic carbenes (NHC). However, the stability of complexes of this type leaves much to be desired. Thus, the adduct $GeCl_4$(NHC) gradually dissociates into the original compounds. Thermal treatment of $GeCl_4$(NHC) entails the replacement of hydrogen atoms in NHC fragment with chlorine atoms and the formation of germanium(II) complexes with a chlorine-substituted carbene ligand.

By analogy with organic derivatives of hypercoordinated silicon, another widespread method of obtaining hypercoordinated germanium derivatives is the elimination of poorly soluble alkali metal halides or low-boiling alcohols by interaction of R_nGeCl_{4-n} or $R_nGe(OAlk)_{4-n}$ (R = Ph, Me, Et; Alk = Me, Et) with alcoholates, alkali metal phenolates or phenols/thiols. Thus, the production of sulfur-containing complexes of highly coordinated germanium can be carried out by the reaction of $Ge(OEt)_4$ with the



Scheme 5



method A: R_2SnCl_2, 2 Et_3N (R = Bu, Bz, *o*-ClBz, *p*-ClBz), toluene
method B: R_2SnO (R = Me, Ph, Cy), toluene, Dean–Stark apparatus

Scheme 6

corresponding phenol[33] (Scheme 5, part *a*). Hexacoordinated germanium complexes can also be obtained *via* reaction of the corresponding phenol with Ph_2GeCl_2 by elimination of Et_3NHCl (part *b*). A large number of organic derivatives have been obtained on the basis of germanium halides; they are atranes, tetrylenes.[37]

In all the methods described above, the halide or alkoxy germanium derivatives were the initial compounds for the production of germanium complexes. However, the development of methods and approaches to synthesis, as well as environmental safety requirements, are pushing researchers to less toxic starting compounds for the synthesis of useful derivatives. So, for the synthesis, for example, of germanium bis-catecholate complexes, non-toxic GeO_2 began to be used.[38-43] The limiting stage of this process is the dissolution of solid GeO_2 in water. This process was significantly accelerated using highly soluble germanium dioxide.[42] The reaction is quite universal and allows one, by changing the ratio of reagents and adding a weak base, to obtain germanium anionic complexes.[41,44,45]

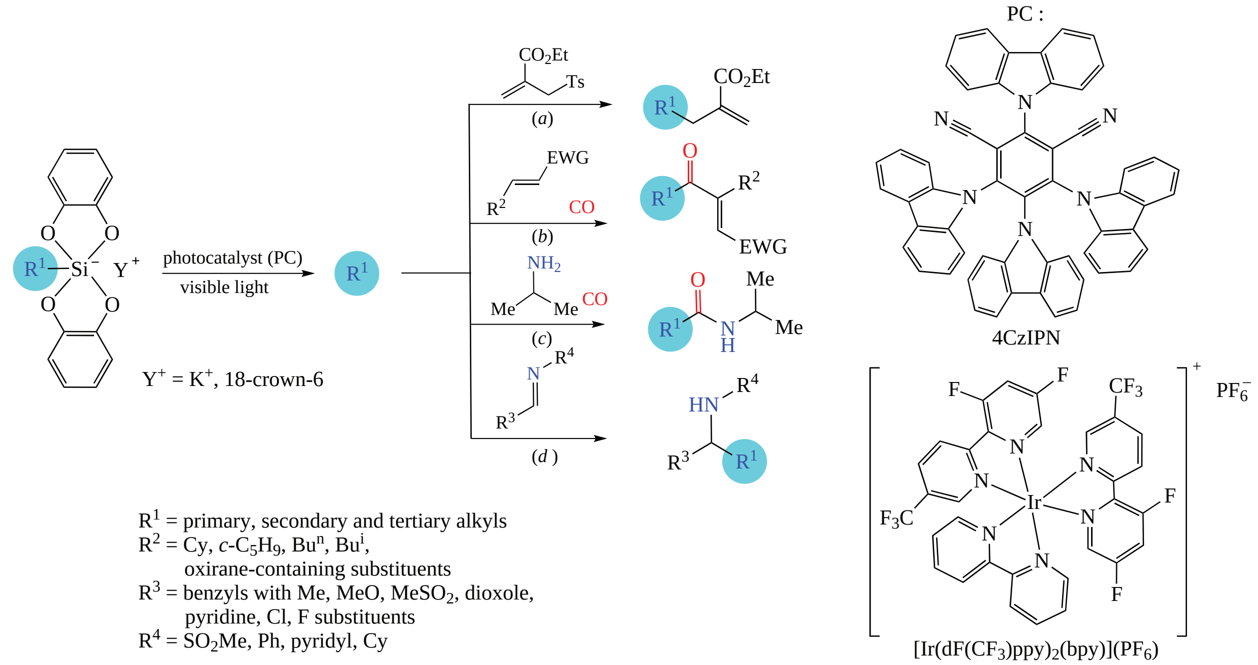
2.3. Tin

A detailed overview of the methods for obtaining hypercoordinated tin derivatives is described in the book.[46] By analogy with Si and Ge, hypercoordinated tin derivatives can be prepared by coordinating organic donor ligands to tin halides SnX_2 or SnX_4 (X = F, Cl, Br). Donor ligands can contain nitrogen[47–49] or sulfur[50] atoms. Using thiol[50] (Scheme 6, part *a*) or hydroxyl[51] (part *b*) functional-substituted ligands it is possible to obtain R_nSnXL (R = alkyl, aryl, X = halide, L = ligand). Similarly, various metallocanes,[52] catecholates[53]/iminoquinolate[54] and tetrylenes[37] are obtained from tin halides. Another convenient initial compound for production tin complexes is oxide R_2SnO. Thus, Sn^{IV} derivatives based on different hydrazides are synthesized by refluxing in toluene with a Dean–Stark apparatus to remove the water formed during the reaction (see Scheme 6, *b*).

3. Modern trends in reactivity of group 14 hypercoordinated derivatives

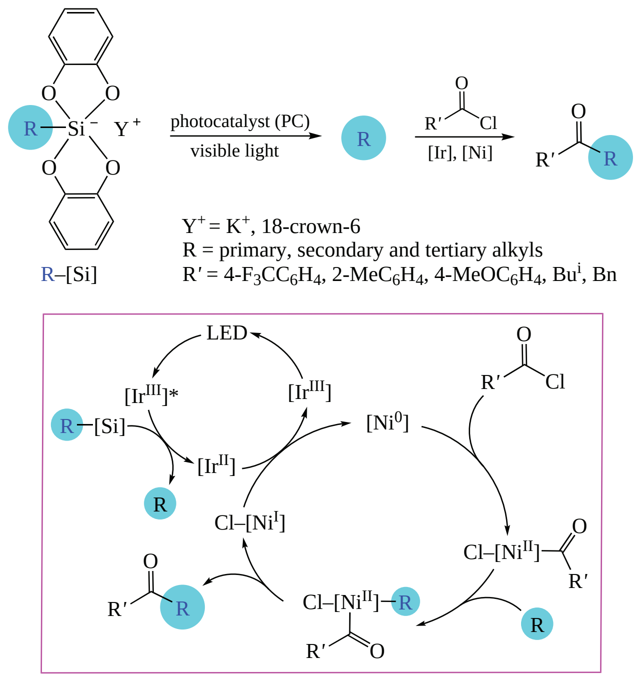
3.1. Organic silicon derivatives – sources of free radicals

The chemistry of five-coordinate silicon complexes with catecholate ligands produced an ‘explosion’ in this area. Over the past five years, a large number of high-quality publications have been published on this topic in top journals due to the fact that such derivatives are able to participate in catalytic reactions. Thus, irradiation of alkyl/aryl substituted biscatecholate silicon



R^1 = primary, secondary and tertiary alkyls
R^2 = Cy, *c*-C_5H_9, Bu^n, Bu^i,
oxirane-containing substituents
R^3 = benzyls with Me, MeO, $MeSO_2$, dioxole,
pyridine, Cl, F substituents
R^4 = SO_2Me, Ph, pyridyl, Cy

Scheme 7



Scheme 8

derivatives in the presence of a photocatalyst leads to one-electron oxidation and the formation of alkyl/aryl radicals.[55,56] Photooxidation of five-coordinate silicon derivatives becomes possible due to the fact that the oxidative potential of these derivatives lies in the range of 0.3–0.9 V.

Formed radicals enter into further reactions depending on the conditions. So, if unsaturated substrates are present in the reaction mixture, then the introduction of radicals to a double bond will take place (Scheme 7, part *a*).[57] When CO is also added to the mixture, it is possible to carbonylate the resulting radical particles and isolate the corresponding derivatives (see Scheme 7, part *b*).[58] In the presence of amines and CO, alkyl radicals are carbonylated and various aliphatic amines are formed (part *c*).[59] Imines[60] and hydrazones[61] also attach alkyl or aryl radicals and the addition is very selective (part *d*).

The process of photoinduced single-electron oxidation of alkyl/aryl silicates is combined with other catalysts. Thus, the tandem of nickel and iridium catalysts for silicates turned out to be promising for the isolation of various alkyl and aryl ketones[62] (Scheme 8). As a result, the complete process includes two cycles: photoinitiation and the transition of the iridium atom to the trivalent state, the ‘extra’ electron further provokes a one-electron reduction of the silicon complex, which leads to the release of radical particles. The iridium atom becomes divalent and its further catalytic oxidation is already carried out with the help of a nickel catalyst, which contributes to the return of the photoinitiator to its initial state.

Hexacoordinated silicon derivatives also can release radical particles under the UV irradiation (Scheme 9). For example, a phenyl substituent at a silicon atom in the salen complexes migrates to a double C=N bond after UV irradiation, which generally leads to a decrease in the coordination number of silicon to five.[27] The germanium salen analogue undergoes similar transformations, but the tin derivative is inert under these conditions.

3.2. Lewis acidity of group 14 hypercoordinated derivatives

Experimental and computational methods are used to assess Lewis acidity. Experimental methods, such as the Gutmann–Beckett[63] and the Childs’ method[64] use NMR spectroscopy to evaluate Lewis acidity. The Gutmann–Beckett method utilizes the $^{31}P\{^{1}H\}$ NMR shift of coordinated triethylphosphine oxide, while the Childs’ method uses the ^{1}H NMR shift of the proton on the β-carbon of coordinated crotonaldehyde. The Baumgartner and Caputo groups have utilized a dithienophosphole oxide as a probe to assess Lewis acidity of a species by evaluating changes in the fluorescence spectra between the uncomplexed and complexed Lewis acid.[65,66] Computationally, Fluoride Ion Affinity (FIA) calculations, where the enthalpy of the reaction of a Lewis acid with a fluoride anion is calculated, are commonly used to assess Lewis acidity.[67] Similarly, the analogous hydride,[68] chloride,[69] methide,[70] water,[71] and ammonia[72] affinities are also used to assess the Lewis acidity of a compound. The Global Electrophilicity Index (GEI) is a computational method in which the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) energies of a Lewis acid are used to evaluate its Lewis acid strength.[73]

3.2.1. Silicon compounds

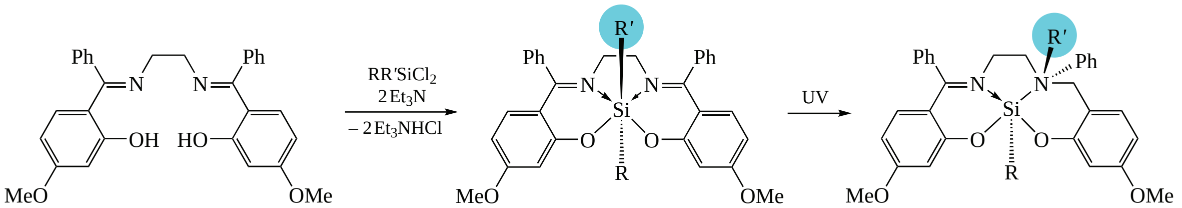
Over the past five years, there has been a significant increase in interest in studies of Lewis acidity of hypercoordinated silicon derivatives with catecholate ligands.[74] Almost all works on this topic have been published in high impact journals.[75–78]

Silicon biscatecholate $Si(Cat^{F})_2$ based on perfluorinated catechol[79] exhibits sufficiently strong acidic properties. So, $Si(Cat^{F})_2$ easily interacts with tris(dimethylamino)sulfonium difluoro(trimethyl)silicate, detaching F^- from difluoromethylsilicate anion (Scheme 10). Unlike $Si(Cat^{F})_2$, adduct $Si(Cat^{Cl})_2(MeCN)_2$ based on perchlorinated catechol shows superacid properties.[80] So, $Si(Cat^{Cl})_2(MeCN)_2$ detaches F^- (or Cl^-) from KF, tris(dimethylamino)sulfonium difluoro(trimethyl)silicate, tris(triphenylphosphino)iminium chloride ([PPN]Cl), trityl chloride $ClCPh_3$ or complex salts $[NEt_4][SbF_6]$ and $[PPh_4][SbF_6]$ forming corresponding pentacoordinate adducts (see Scheme 10).

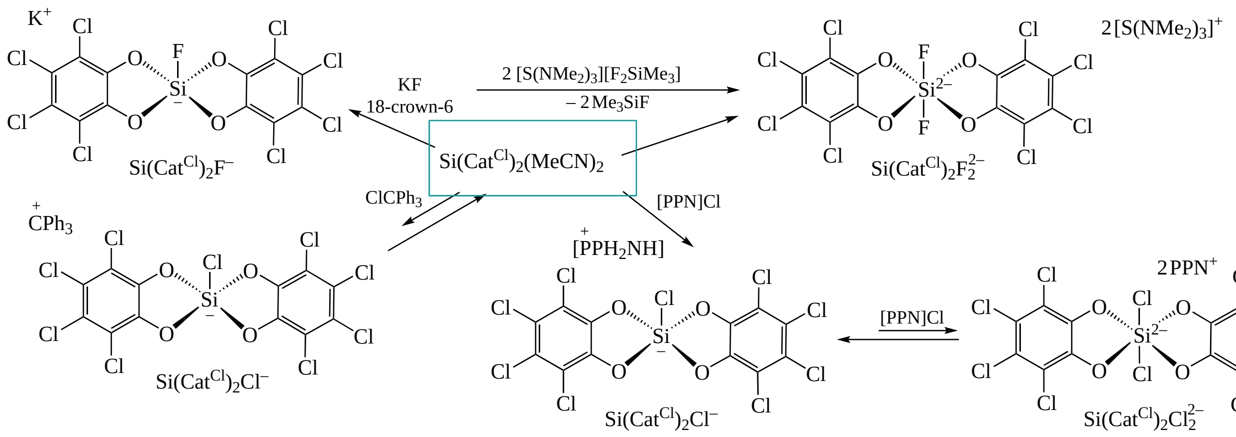
It is possible to replace coordinated MeCN in $Si(Cat^{X})_2(MeCN)_2$ by other donors (neutral DME, Et_2O or sulfolane, or Cl^-, $HC(O)O^-$, AcO^- and TfO^- anions[81]). Lewis acidity of adduct $Si(Cat^{CF_3})_2(sulfolane)_2$ is also high:[82] interaction of $Si(Cat^{CF_3})_2(sulfolane)_2$ with $[PPh_4][SbF_6]$ or $ClCPh_3$ leads to detaching F^- and Cl^- with formation of pentacoordinated silicon complexes $[PPh_4]^+[FSi(Cat^{CF_3})_2]^-$ and $[CPh_3]^+[ClSi(Cat^{CF_3})_2]^-$.

3.2.2. Germanium compounds

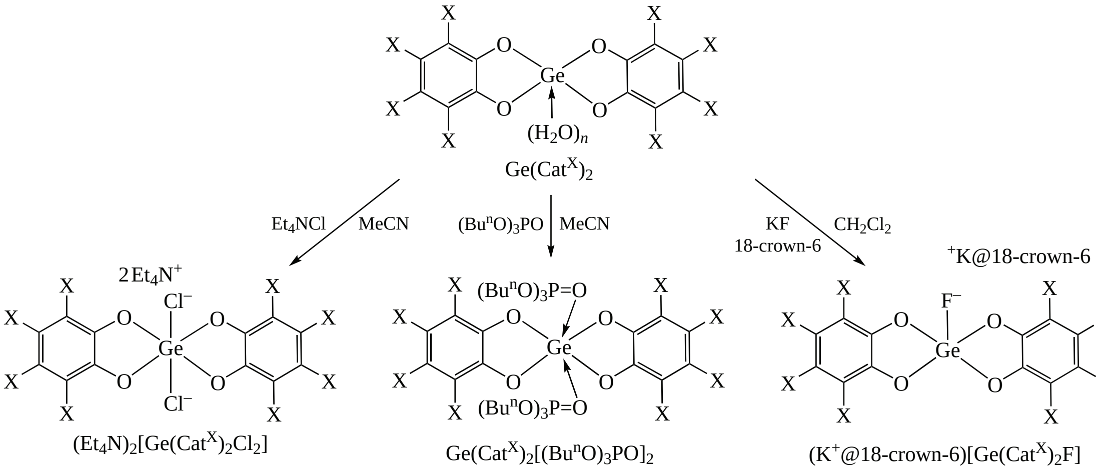
A variety of bis(catecholato)germanes[36,83,84] are excellent Lewis acids. So, derivatives $Ge(Cat^{X})_2$ are shown to attach Cl^- from Et_4NCl and F^- from KF (Scheme 11). Also, interaction of $Ge(Cat^{X})_2$ with $(Bu^{n}O)_3P{=}O$ leads to corresponding adducts



Scheme 9



Scheme 10



Scheme 11

Table 1 FIA and GEI values of $M(Cat^X)_2$ series (M = Si, Ge; Cat is catecholate, X is different substituents).[36]

Compound	FIA/kJ mol^{-1} [M = Ge]	FIA/kJ mol^{-1} [M = Si]	GEI/eV [M = Ge]
$M(3,5\text{-dtbc})_2$	433	–	1.20
$M(Cat)_2$	416	391	1.06
$M(Cat^F)_2$	502	490	2.10
$M(Cat^{Cl})_2$	508	507	1.92
$M(Cat^{Br})_2$	513	538	2.01
$M(3,5\text{-dtbc})_2(MeCN)$	429	–	1.45
$M(Cat)_2(MeCN)$	420	–	1.48
$M(Cat^F)_2(MeCN)$	484	–	2.16
$M(Cat^{Cl})_2(MeCN)$	492	–	2.17
$M(Cat^{Br})_2(MeCN)$	500	–	2.20
$M(Cat^{Br})_2(Et_2O)$	498	–	1.69
$M(Cat^{Br})_2(THF)$	494	–	1.68

$Ge(Cat^X)_2[(Bu^nO)_3P{=}O]_2$. Obtained experimentally, according to the Gutman–Becket method, the values of chemical shifts of signals of phosphorus atoms in $^{31}P\{^1H\}$ spectra of germanium catecholates $Ge(Cat^X)_2[(Bu^nO)_3P{=}O]_2$ (X = Cl, Br) are 84.0 and 85.7 ppm, respectively, which are slightly lower than those for silicon analogues with the same substituents (87.2 and 87.3 ppm). Calculated values of FIA and GEI are summarized in Table 1. The comparison shows that the derivative $M(Cat^{Br})_2$ based on perbrominated catechol has the highest affinity values for fluoride ions.

3.3. Tetrylene

One of the rapidly developing areas in the chemistry of organic compounds of group 14 elements can be called the chemistry of low-valent derivatives, the so-called tetrylenes (see recent reviews[85–88]). On the one hand, tetrylenes having an unshared electron pair can be sigma donors (Figure 1), and, on the other hand, due to the presence of a free p-orbital of the element, it is possible to coordinate various ligands (they may contain nitrogen,[89–91] phosphorus,[92,93] sulfur,[94] transition metals[95–97]). Moreover, these derivatives tend to be hypercoordinated, not only with third-party ligands or functional groups, but also with neighbouring tetrylene molecules.[87,88] The method of stabilization of such low-valent derivatives is based on the latter property. Coordination of the donor ligand on M^{II} leads to an increase in the thermodynamic stability of tetrylene.[98] And valence of element(II) allows such derivatives to react with a valence increasing. Thus, tetrylenes become real candidates to be catalysts in a wide variety of processes of oxidative addition[99] and reductive elimination,[100] and in combination with transition metals,[101] open new prospects for cooperative reactivity, examples of which are cleavage of bonds centered on metal or tetrylene, cycloaddition and metathesis.

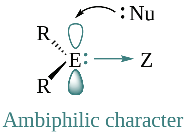
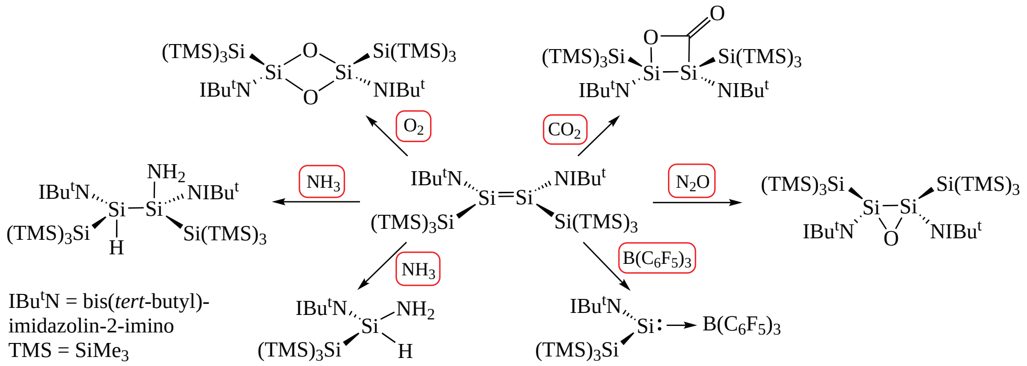


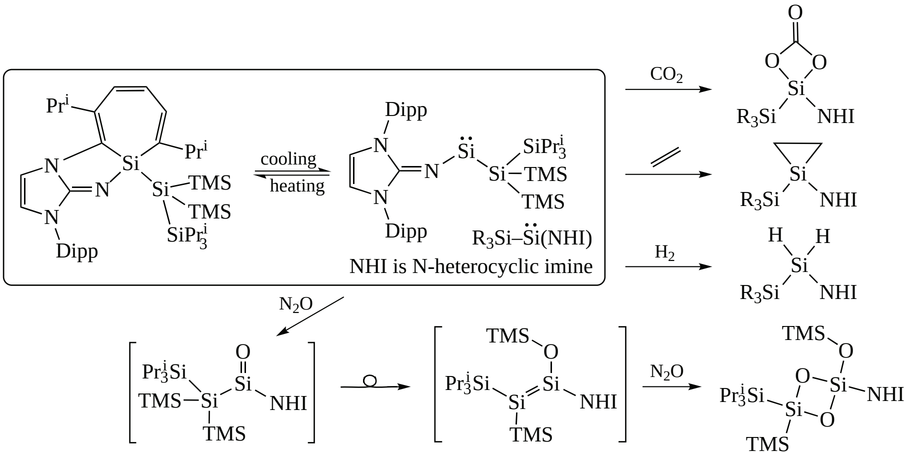
Figure 1 Structure of tetrylene molecule and reactivity modes.

Due to their structure, tetrylenes are very reactive species. They are able to activate small molecules,[102–107] integrate into organic and inorganic sigma bonds,[108,109] form donor–acceptor adducts, attach unsaturated substrates,[110] promote cycloaddition reactions, participate in redox processes,[111] coordinate with transition metals[112] (Scheme 12).



IBu^tN = bis(*tert*-butyl)-imidazolin-2-imino
TMS = $SiMe_3$

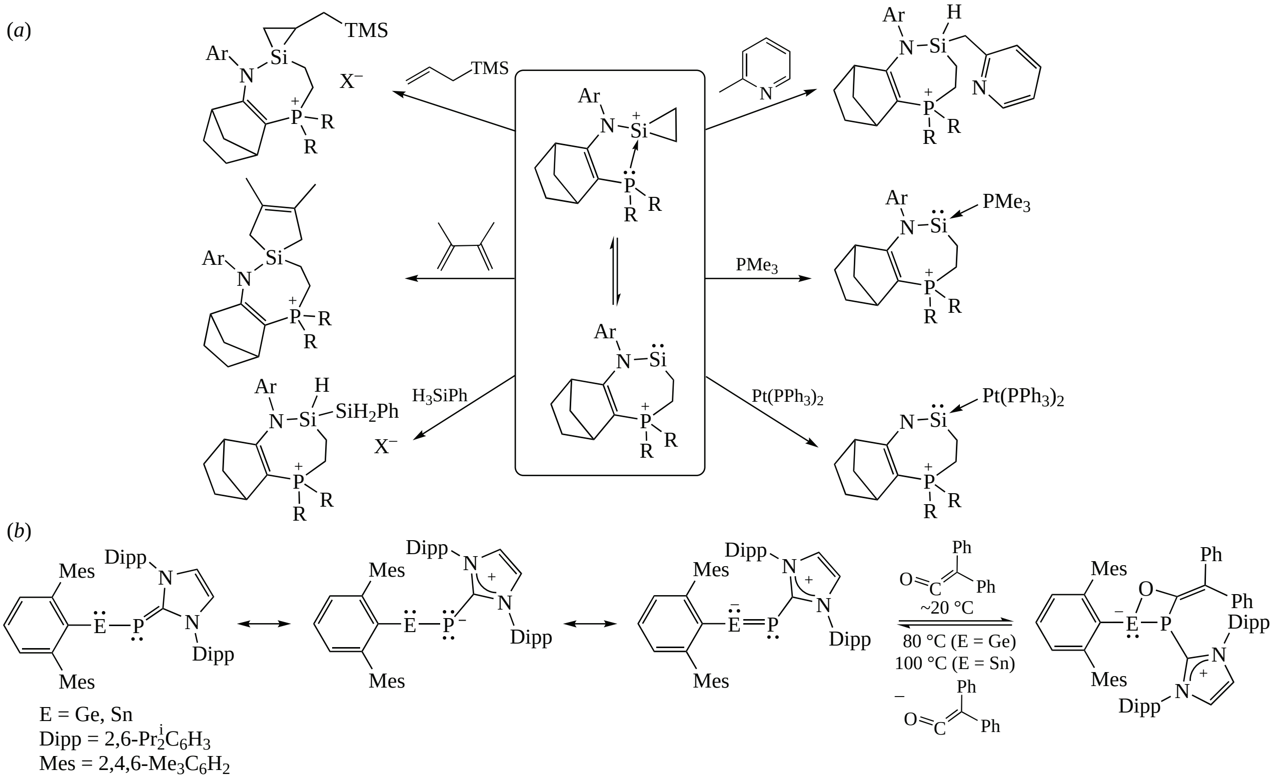
Scheme 12



Scheme 13

An example of reversible incorporation of a low-valent silicon derivative into an aryl ring[113] of the neighbouring substituent is shown in Scheme 13. When the temperature changes, the reversible introduction of Si^{II} into the aromatic diisopropylaniline ring occurs. Due to the presence of a reversible $Si^{II}–Si^{IV}$ transition, activation of small molecules (CO_2, H_2, N_2O, ethylene) is possible.

Phosphine-stabilized silacyclopropyl derivative[114] [Scheme 14(*a*)] is also capable of reversible intramolecular conversion. Low-valent Si^{II} derivative interacts with different substrates to give donor–acceptor adducts [with PMe_3 and $Pt(PPh_3)_2$] or insertion products (to C–H, Si–H, C=C–C=C and C=C bonds). Phosphine-stabilized germylene and stannylene[115] behave similarly by attaching unsaturated substrates. This



E = Ge, Sn
Dipp = 2,6-$Pr^i_2C_6H_3$
Mes = 2,4,6-$Me_3C_6H_2$

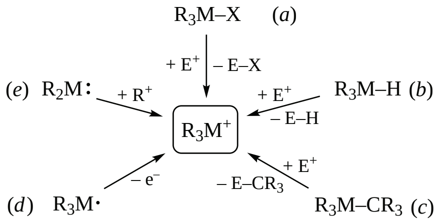
Scheme 14

behaviour of tetrylenes is actively used in catalysis [see Scheme 14(*b*)].

3.4. Metal-centered cations of group 14 elements

For a long time, metal-centered cations of group 14 elements remained the subject of research only by theoretical chemists. This was primarily due to the difficulties of stabilization and isolation of such cations because of high electrophilicity and oxophilicity. However, the situation changed when synthetic chemists ‘learned’ how to work with such reactive particles and began to stabilize the electron-deficient nature of such cations with the help of neutral or anionic donors whose electron density partially fills the vacant p-orbital of the element. After that, the development of this area was ‘explosive’. So, a lot of articles appeared[116–120] focused on stabilization of silylium cations with ethers, thioethers, bromine-substituted carboranes, chlorine-substituted arenes, SO$_2$, MeCN, ferrocene. Germylium cations, with an apparent analogy with silylium cations, are represented by a much smaller number of examples. This is primarily due to limitations in the initial germanium compounds, in the difficulties of analyzing the resulting derivatives by NMR spectroscopy due to the ‘invisibility’ of germanium. Nevertheless, progress does not stand still and several reviews on this topic have been published over the past five years.[121]

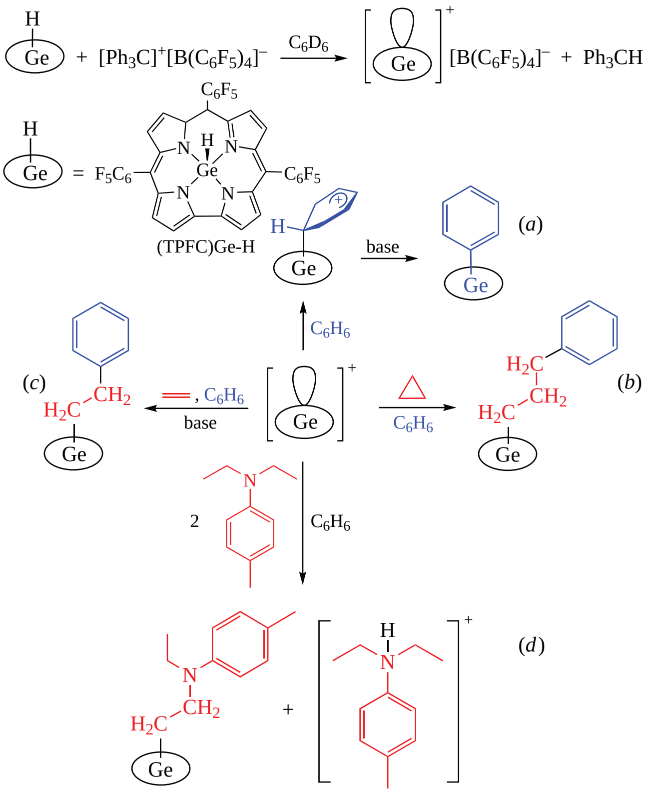
Quaternary silylium and germylium cations can be obtained from neutral tetracoordinated silanes/germanes *via* electrophilic activation and removal of one substituent. As a leaving group halide [F, Cl, Br, I, Scheme 15(*a*)], hydrogen (part *b*) and alkyl (part *c*) are used. The prominent electrophiles to be used in this area are [R$_3$C$^+$][WCA$^-$] (WCA = weakly coordinating anions such as ClO$_4^-$, $\mathrm{BAr^F_4}^-$, B(C$_6$F$_5$)$_4^-$, CHB$_{11}$H$_5$Br$_6^-$). The electrochemical method of generation [see Scheme 15(*d*)] and the interaction of low valent derivatives of elements with cationic particles (part *e*) are also used.



Scheme 15 Synthetic approaches to metal-centered cations.

The structure of the electron shell of an element in metal-centered cations (in particular, 6 valence electrons) explains their Lewis acidity, which makes them promising in catalysis. So, silyl cations[122] promote catalytic reduction of imines[123] and Diels–Alder reactions.[124] Furthermore, silyl cations in combination with phosphine ligands form adducts like frustrated Lewis acids and can activate CS$_2$,[125] CO$_2$, H$_2$.[126,127] The ability to activate molecular hydrogen is regulated by thermodynamic and steric factors. Thus, an increase in the proton affinity of a silylium cation and the steric hindrances of the phosphine ligand lead to an improvement in the properties of the Lewis pair silylium ion/phosphine.

By analogy with silylium cations, germylium cations [R$_3$Ge][B(C$_6$F$_5$)$_4$] form adducts with PR$_3$ which are promising in frustrated Lewis pair (FLP) chemistry.[128] A more sterically hindered cation [(TPFC)Ge]$^+$ [TPFC = 5,10,15-tris(pentafluorophenyl)corrole][129] exhibits electrophilic properties. For example, [(TPFC)Ge]$^+$ reacts with benzene with formation of (TPFC)Ge–C$_6$H$_5$ [Scheme 16(*a*)]. The key intermediate, σ-type germylium–benzene adduct, [(TPFC)Ge(η^1-C$_6$H$_6$)]$^+$ was isolated and characterized by X-ray diffraction. If ethylene or cyclopropane[130] are added to benzene solution of germylium cation [(TPFC)Ge]$^+$, insertion products, namely (TPFC)Ge–CH$_2$CH$_2$C$_6$H$_5$ and (TPFC)Ge–CH$_2$CH$_2$CH$_2$C$_6$H$_5$, respectively are formed [see Scheme 16, parts (*b*) and (*c*)]. Furthermore, cation [(TPFC)Ge]$^+$ is able to activate C–H and C–N bonds of tertiary amines[131] [part (*d*)]. The dissociation of C−H bonds occurs selectively at the β- and γ-positions in the tertiary amine, which differs from the well-studied action of transition metal complexes on α-protons of amines.



Scheme 16

3.5. Frustrated Lewis pairs based on group 14 elements

Since the discovery in 2006, ‘frustrated Lewis pairs’ (FLP) have continued to attract researchers around the world in the field of activation of small molecules.[132–135] FLP can be described as a combination of a Lewis acid and a Lewis base, which, due to steric obstacles, cannot form a dative bond in the classical manner, leading to an increase in reactivity (Figure 2).

Many FLPs are based on a combination of boron-containing Lewis acids and phosphorus-containing Lewis bases. However, due to acidic properties group 14 derivatives (Si,[127,136–138] Ge,[139] Sn[139,140–143]) are also used in FLP chemistry. Electron-deficient groups at the atom of an element (usually containing fluoride substituents) make this part of the molecule even more acidic and capable of ‘electron density contraction’ from the base (for example, phosphorus) part. In particular, silylium cations can manifest themselves as one of the FLP parts due to their high electrophilicity. However, there are difficulties in stabilizing the diffuse 3p Si orbital, which can be achieved by hyper- and π-conjugation.[144]

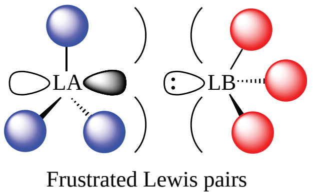
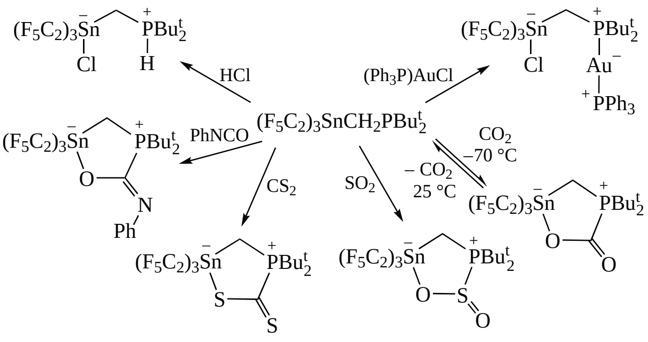


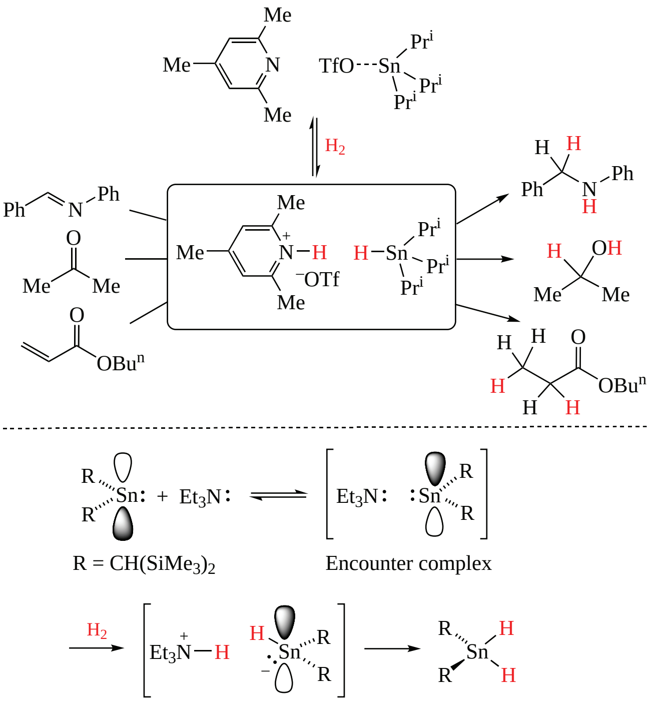
Figure 2 Schematic structure of frustrated Lewis pairs (LA = Lewis acid, LB = Lewis base).

Compounds $(C_2F_5)ECH_2PBu^t_2$ (E = Si,[145] Ge,[146] Sn[147]) show excellent FLP properties (Scheme 17). So, it easily attaches various substrates. Quite recently[148] it has been known about trifluoromethyl $CF_3CSiCH_2PBu^t_2$ and trichloromethyl $Cl_3CSiCH_2PBu^t_2$ derivatives displaying analogous properties.



Scheme 17

Another example of FLP based on group 14 elements is tin-containing compound $Pr^i_3Sn(OTf)$.[142] In combination with donor pyridine derivatives, $Pr^i_3Sn(OTf)$ attaches H_2 and transmits it to different functional groups (aldehydes, ketones, imines) and double C=C bonds (Scheme 18, over dashed line). Tin-containing tetrylene R_2Sn: [R = $CH(SiMe_3)_2$][143] in the presence of triethylamine also exhibits the properties of frustrated Lewis acids, activating hydrogen (see Scheme 18, below dashed line).



Scheme 18

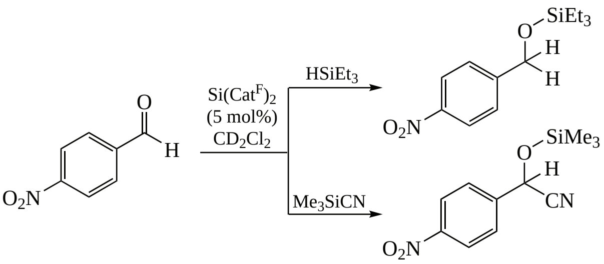
4. Application prospects

4.1. Silicon

The importance of organosilicon compounds in synthetic chemistry is difficult to overestimate, since there are many protecting groups with silicon used in synthesis. The catalytic activity of hypercoordinated silicon derivatives continues to be studied. Thus, complexes of five-coordinate silicon with diolate ligands have proven themselves well as a source of alkyl/aryl radicals,[55–61] which, in conjunction with a nickel catalyst, opens up ways to obtain practically useful compounds.[149]

The redox activity of the silicon complexes and, accordingly, their applicability as an oxidant in various processes are being actively studied. Thus, silicon trisdioxolene with perchlorocatechol is active in the model reaction of intramolecular oxidation and cyclization of 2-(4-methoxybenzyl)benzoic acid into the corresponding lactone (loading of the catalyst 5 mol%, or synthesized *in situ* from SiI_4 and the corresponding quinone).[150]

Due to the increased Lewis acidity, silicon bis-catecholate complexes have proven themselves well as catalysts. So, $Si(Cat^F)_2$ is active as a catalyst for hydrosilylation and cyanosilylation of aldehydes (Scheme 19).[79]

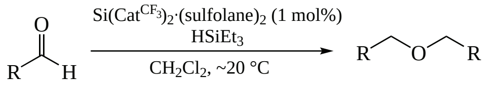


Scheme 19

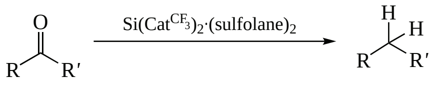
Owing to superacidity, hypercoordinated compound $Si(Cat^{CF_3})_2(sulfolane)_2$[82] [$Si(Cat^{CF_3})_2$ = bis(pertrifluoromethylcatecholato)silane] proved to be an effective catalyst for the formation of ether groups from aldehydes [Scheme 20(*a*)] (yields achieve 96% in the case of *p*-fluorobenzaldehyde), deoxygenation of carbonyl compounds [see Scheme 20, part (*b*)] in combination with reducing agent ($HSiEt_3$, $PhSiH_3$) (yields are more than good and range from 80% in the case of acetophenone and reach 99% in the case of benzophenone), deoxygenation of phosphine oxides [part (*c*)] (yields are 91% in case of $O{=}PPh_3$ and 96% in case of $O{=}PEt_3$) and metathesis of carbonyl olefins [part (*d*)].

Bis-catecholate silicon complex based on alizarin, bis(alizarinato)silane,[151] exhibits pronounced chromophore properties. Thus, due to the Lewis superacidity, this derivative accepts fluoride anions. Moreover, using optical methods it is possible to quantify how many fluoride anions bis(alizarinato)silane has attached. Thus, when interacting, for example, with

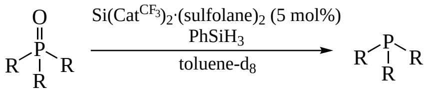
(*a*) Dialkyl ether formation



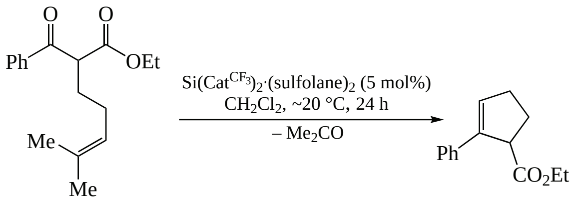
(*b*) Deoxygenation of carbonyls



(*c*) Deoxygenation of phosphine oxides



(*d*) Carbonyl olefin metathesis



Scheme 20

KF, one fluoride anion is sequentially attached first with the formation of a five-coordinate complex $K^+[FSi(Cat^{alizarin})_2]^-$, and then the second F^- is attached with the formation of a hexacoordination derivative $K_2[F_2Si(Cat^{alizarin})_2]^{2-}$. Moreover, the addition of both the first and the second F^- is fixed visually – absorption of $K^+[FSi(Cat^{alizarin})_2]^-$ is observed at $\lambda = 440$ nm, while the absorption of $K_2[F_2Si(Cat^{alizarin})_2]^{2-}$ occurs at $\lambda = 494$ nm.

The action of silicon sesquioxanes as indicators of the presence of fluoride ions[152] in solution is based on the same property. Encapsulation of the fluoride anion in the polymer structure of sesquioxane leads to formation of the corresponding adducts coloured differently from the initial sesquioxane (limit of fluoride anion detection is 1.61 ppb).

Silicon derivatives with coumarin fluorescing in various solvents are also known.[25] Moreover, the quantum yields of fluorescence strongly depend on the polarity of the solvent used. An increase in the polarity of the solvent leads to a bathochromic shift of the absorption and emission maxima.

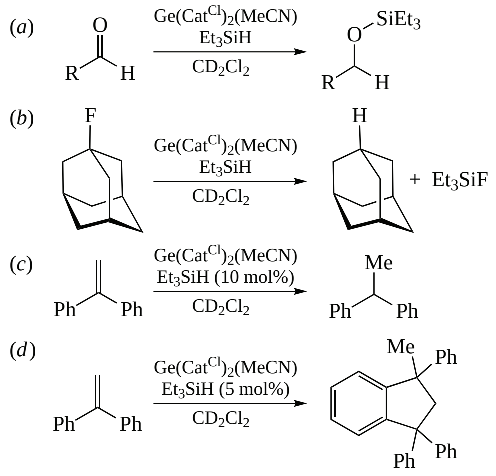
Hypercoordinated silicon derivatives, active under the action of UV radiation, are promising for the production of medicines.[60,61]

4.2. Germanium

The hydrosilylation of aldehydes, oligomerization of arylalkenes, hydroboration of phenylacetylene, and the Friedel–Crafts alkylation of diphenylamine were catalyzed by bis(catecholato)-germanes and demonstrated the versatility of the catalyst system. $Ge(cat^{Cl})_2(MeCN)_2$ displays the most efficient catalytic properties among the germanium catecholate catalysts.[36] So, $Ge(cat^{Cl})_2(MeCN)_2$ proved to be an effective catalyst for the hydrosilylation of aldehydes [yields achieve 97%, R = C_6H_4F, C_6H_4Me, Cy, Scheme 21(*a*)], defluorination of fluorine-substituted compounds [(part (*b*)] in combination with $HSiEt_3$ (yields are 97% in the case of fluoroadamantane), hydrogenation of 1,1-diphenylethylene with Et_3SiH [part (*c*), yields 93%]. In the case of a smaller amount of catalyst (5%), intramolecular alkylation of one of the phenyl rings occurs [see Scheme 21(*d*)].

Recently it has been reported on the possibility of catalysis by germanium complexes of the Friedel–Crafts reaction,[153] and, in general, the similarity of complexes of group 14 elements with transition metal complexes for oxidative addition and reductive elimination reactions, important cases of catalytic reactions.[154,155]

Another interesting class of germanium compounds in terms of application is poly-*trans*-[(2-carboxyethyl) germasesquioxane] (Ge-132; repagermanium).[156] Hydrolysate of Ge-132 [3-(trihydroxygermyl)propanoic acid (THGP)] exhibits various physiological effects, including anti-inflammatory properties, immunostimulating and anti-cancer effects.[157,158] Clinical studies have shown the safety of THGP and the applicability of Ge-132 as a dietary supplement to food and cosmetics.[159,160] The action of THG is based on binding the *cis*-diol structure of various catechols of the body and preventing their involvement in the production of, *e.g.*, melanin.[161–164]



Scheme 21

Another promising application of germanium complexes is their use against cancer cells.[165] So, hypercoordinated germanium(IV) complexes bearing acetylacetonato ligand $[Ge^{IV}(acac)_3]^+$ with different anions were explored as the anticancer reagents. The compounds display ~3-fold selectivity in cancer cells over normal epithelial cells. In addition to the promising anticancer activity, the compounds show high complex stability in biological media, induces G1 arrest, reactive oxygen stress (ROS) accumulation, and mitochondria membrane depolarization in cancer cells. Furthermore, the compounds induce significant apoptosis.

4.3. Tin

Organotin derivatives are most widely used in agrochemistry, industry and medical fields.[166] In addition, they are employed as stabilizers of polyvinyl chloride, as anticancer reagents,[167,168] antitumour drugs,[169] catalysts, and fungicides.[170]

Tin complexes with Schiff bases are often used as an antimicrobial agent. So for example, (*E*)-2-[(4-methoxybenzylidene)amino]benzenethiol adduct is effective against bacteria and fungi.[171] Hypercoordinated tin complexes with aromatic Schiff bases often exhibit fluorescent properties.[172] Compounds $[SnCl_3(L)]$ (HL = Schiff base) are active in DMSO ($\lambda_{max} = 492$–545 nm, fluorescence lifetime $\tau = 0.49$–1.76 ns).

The fluorescent properties of tin complexes can be applied in fluorescence bioimaging,[173] namely, highlighting of cells of a living organism for investigation using a confocal microscope. For instance, compounds **1**–**8** (Scheme 22) exhibit pronounced fluorescence at room temperature at $\lambda = 510$ nm, (quantum yield φ of fluorescence is 36–56%, fluorescence lifetime $\tau = 3.8$ ns) and are non-toxic to the body. Moreover, the use of Schiff bases with more than one hydroxy or nitro group capable of instantly reacting changes the acidity of the medium (see Scheme 22, compound **9**), which makes it possible to use such compounds for the detection of cancer cells.[174]

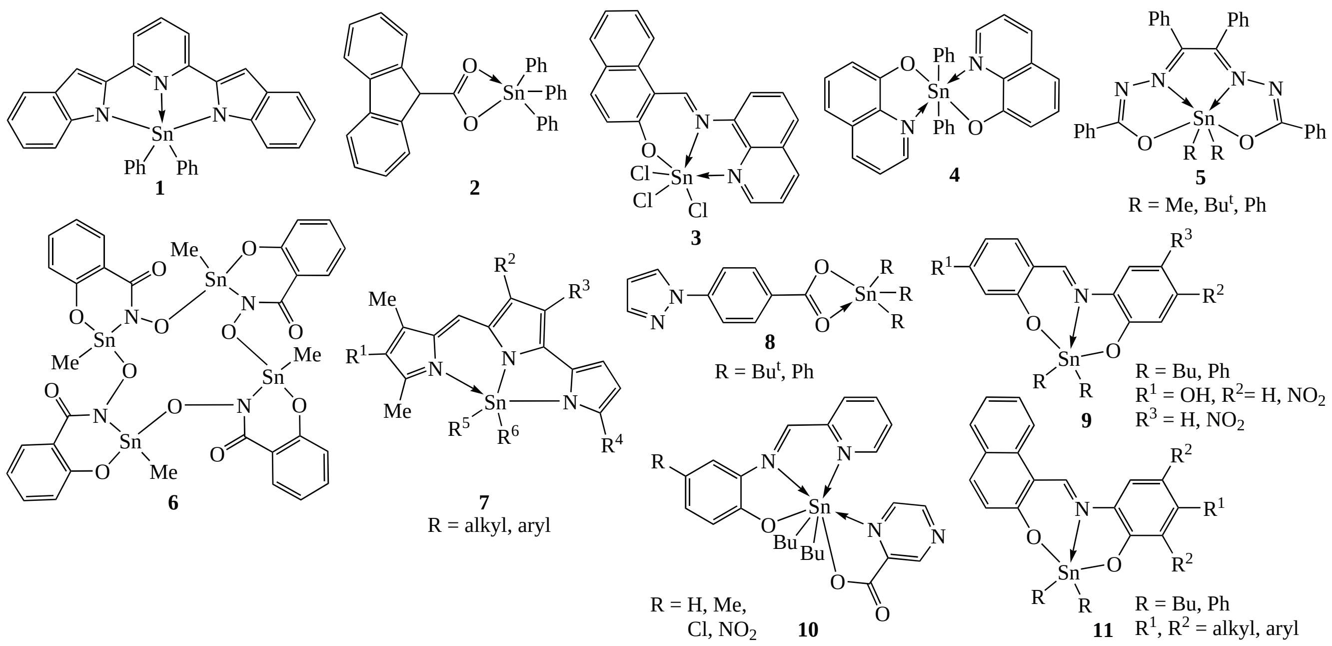
Another area of potential application of hypercoordinated tin complexes is their use as materials for optoelectronic devices.[175] Thus, tin complexes based on Schiff bases with carboxyl and alkyl substituents at the tin atom (see Scheme 22, compound **10**) have been manifested as organic semiconductors. The width of the forbidden zone is 1.88–1.98 eV for granules and 1.23–1.40 eV for thin films of these compounds obtained on poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate), or PEDOT:PSS. The best technical characteristics were shown by a material based on chlorine-substituted aminophenol.

The absorption of visible light waves (480–490 nm) by tin complexes **11** (see Scheme 22) makes it possible to use them as components for solar cells. The band gap for compounds **11** is 2.11–2.25 eV, which means that they also exhibit semiconductor properties. Also, type **11** compounds with butyl, cyclohexyl, phenyl and trimethylsilylmethyl groups at tin atoms are used as optoelectronic and photovoltaic materials.[176]

Porphyrin tin complexes exhibit electroluminescence delayed in time, which made it possible to use them as organic light-emitting diodes.[177]

5. Summary and outlook

In conclusion, in this focus article we briefly discussed methods for the synthesis of hypercoordinated organic derivatives of group 14 elements, and also paid attention to the main areas of



Scheme 22

research on the reactivity of such compounds. The prospects of using these compounds in various fields of science and technology were also described.

Due to the ability of group 14 elements to coordinate donor molecules and anions, prospects for their use in catalysis are opening. So, in this article, we paid more attention to the catecholate complexes of silicon and germanium that exhibit outstanding values of Lewis acidity, which became the starting point for publishing these results in high impact journals. The Friedel–Crafts reactions, hydrogenation and hydrocyanation of aldehydes, deoxygenation of ketones, metathesis reactions using alkylidene derivatives of group 14 (analogues of Fischer and Schrock carbenes[178,179]) are just some examples of the use of such derivatives as catalysts. Tetrylenes catalyze hydroelementation and cyanosilylation reactions no less efficiently.[180–187]

In addition, at this stage of the development of the field as a whole, it is difficult to imagine that earlier researchers did not know about the existence of silyl and germyl cations, low-valent tetrylenes and frustrated Lewis acids based on group 14 elements. With the development of methods for stabilizing such reactive particles, the researchers have stepped far ahead. Thus, activation of small molecules became possible, which previously proceeded only with the use of transition metal complexes. Hence, achievement of the ‘blue dream’ of all catalytic chemists, the use of complexes of non-transition metals in catalytic processes to produce practically useful compounds, ceases to be something unreal.

Taking into account all of the above, we are sincerely confident in the prospects of further research in this area and believe that there are still a lot of discoveries ahead.

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