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1,1-Dilithiosilanes, 1,1-dilithiogermanes, 1,1-dilithiostannanes and related compounds: organometallic reagents of the new generation

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Novel main group element compounds, geminal dianionic derivatives of the heavier group 14 elements; namely, 1,1-dilithiosilanes, 1,1-dilithiogermanes and 1,1-dilithiostannanes (and closely related derivatives of the cyclopentadiene-1,1-diide and cyclobutadiene dianion), are the focus of the present review. The synthetic strategies for their preparation, structural features, and synthetic applications are discussed.

Introduction

Of the fundamental carbanions that are ubiquitous in organic chemistry, organomagnesium Grignard reagents RMgX (Victor Grignard, 1901)[1] and organolithium reagents RLi (Wilhelm Schlenk, 1917)[2] are undoubtedly of paramount importance, being by far the most popular and synthetically useful. Following their discovery, organolithium reagents were comprehensively studied in the 1930s with the crucial contribution by Ziegler, Wittig and Gilman, who found that organolithium reagents can in many cases (for example, in metalation) outperform Grignard reagents with increased reaction rates and higher product yields. Since then, organolithium reagents have remarkably surpassed Grignard reagents in synthetic usage.

More exotic geminal dilithio derivatives R_2CLi_2 featuring two negative charges at one carbon atom are extremely reactive, thus serving as indispensable reagents to access a great diversity of organic compounds, particularly multiply-bonded derivatives. The parent dilithiomethane CH_2Li_2 has been known since 1955 when it was introduced in the pioneering work of Ziegler on the thermolysis of methyllithium.[3] In due course, Lagow modified this method based on the thermolysis of monolithiated compounds to generate a number of 1,1-dilithiomethane derivatives.[4] Among other synthetic approaches for the latter compounds, one can mention the reduction of geminal dihalides [Ph_2CCl_2 with a large excess of Bu^tLi;[5(a)] $(Me_3Si)_2CCl_2$ with lithium vapour[5(b)]] or the metalation of acidic hydrogens ($PhCH_2CN$ with BuLi forming $PhCLi_2CN$;[6(a)] $PhSO_2CH_2Ph$ with BuLi forming $PhSO_2CLi_2Ph$[6(b),(c)]). Some of them were isolated and even characterized by X-ray diffraction analysis.[7]

Starting with silyl anions, known since the early 1950s from the pioneering work of Gilman, the anions based on the heavier group 14 elements are also key players in organometallic synthesis, behaving similarly to carbanions in organic chemistry.[8] As for the geminal dilithiosilane derivatives, their synthetic advances were preceded by early calculations of Schleyer, who found a number of unusual structures on the potential energy surface (PES) for the dilithio- and disodiosilanes, H_2SiLi_2 and H_2SiNa_2, with a small energy gap between the planar and tetrahedral forms for tetracoordinate silicon.[9]

Synthesis

1,1-Dilithiosilanes, 1,1-dilithiogermanes and 1,1-dilithiostannanes

From the synthetic side, Lagow was the first to claim the generation of the 1,1-dilithiosilane $(Me_3Si)_2SiLi_2$ employing Ziegler's original method, *i. e.* by the pyrolysis of $(Me_3Si)_3SiLi$ at 140–150 °C.[10] Unfortunately, the germinal dilithiosilane was not isolable, its formation being proven only by trapping with EtOD and MeI. Following this initial report, Tokitoh generated diaryldilithiosilane $Tbt(Dip)SiLi_2$ (Tbt = 2,4,6-$[(Me_3Si)_3CH]_3$-C_6H_2, Dip = 2,6-$Pr^i_2C_6H_3$) by the reduction of the corresponding precursor $Tbt(Dip)SiBr_2$ with lithium naphthalenide.[11] Compound $Tbt(Dip)SiLi_2$ was stable only below –78 °C, intramole-

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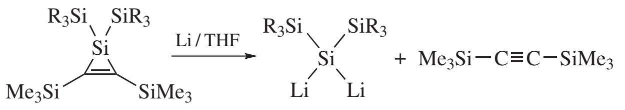
cularly rearranging at higher temperatures to a monosilyllithium derivative.

Finally, the first room temperature stable 1,1-dilithiosilanes $(R_3Si)_2SiLi_2$ **1a**,**b** were readily prepared by the reduction of silirenes **2** with lithium (Scheme 1).[12] The central silicon in **1a** was extraordinarily shielded appearing at –292 ppm (^{29}Si NMR) as a manifestation of the extreme electron population at the dianionic center, which also can be seen in its HOMO represented by the combination of the two σ_{Si-Li} orbitals holding negative charges [$(Me_3Si)_2SiLi_2$ model, B3LYP/6-31G(d) level].



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1a $R_3Si = Pr^i_3Si$

1b $R_3Si = Bu^t_2MeSi$

Scheme 1

X-ray diffraction analysis of **1a** revealed its monomeric structure with the tetrahedral dianionic silicon center (Figure 1).[12(a)] From its crystal structure, the surprising stability of the 1,1-dilithiosilane **1a** can be (at least, in part) attributed to the π-accepting effect of silyl substituents, that may lower the energy of the anionic silicon orbitals through the stabilizing $\sigma(Si_{central}–Li) \rightarrow \sigma^*(Si_{subst}–C)$ negative hyperconjugation.

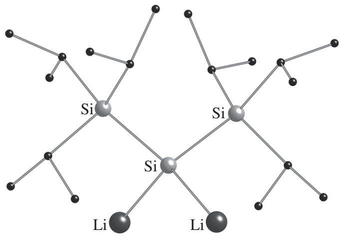


Figure 1 Crystal structure of the 1,1-dilithiosilane **1a** (CrystalMaker view: H atoms and four Li-coordinated THF molecules are not shown).

Alternatively, 1,1-dilithiosilane $(Bu^t_3Si)_2SiLi_2$ **1c** with the exceptionally bulky Bu^t_3Si groups can be simply prepared by a direct reductive dehalogenation of the dibromo precursor $(Bu^t_3Si)_2SiBr_2$ with lithium (Scheme 2).[13]

$$(Bu^t_3Si)_2SiBr_2 \xrightarrow[-60\,°C]{Li / THF} (Bu^t_3Si)_2SiLi_2$$

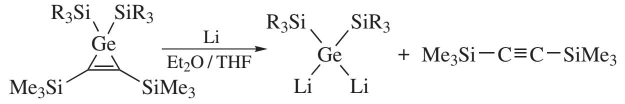
1c

Scheme 2

The above-described 1,1-dilithiosilanes **1a**,**b** were also available in a variety of structural modifications by the reduction of silylmercury derivatives with lithium.[14] Thus, in hexane **1b** was isolated as the nonsolvated co-aggregate with $(Bu^t_2MeSi)_2SiHLi$ of the type $\{[(Bu^t_2MeSi)_2SiLi_2][(Bu^t_2MeSi)_2SiHLi]_2\}$,[14(a)] whereas in THF a solvated silyllithium aggregate of formally trimeric composition $[(Bu^t_2MeSi)_2SiLi_2]_3(thf)_8$ was formed.[14(b)] Compound **1a** was also isolated as a co-aggregate with Bu^tLi of the type $\{[(Pr^i_3Si)_2SiLi_2]_2[Bu^tLi]_2\}$.[14(c)] 1,1-Dilithiosilane, with the smallest (to date) Bu^tMe_2Si substituents, showed in its crystalline form a complicated hexameric constitution $\{[(Bu^tMe_2Si)_2SiLi_2]_6[Li_2O]_2\}$,[14(d),(e)] which can be transmetalated with Grignard reagent $Bu^tMgCl\cdot(MgCl_2)_2$ to give the dimagnesiosilane $[(Bu^tMe_2Si)_2Mg(thf)_2]_2$. The latter compound can be further modified by reactions with either $Bu^tMgCl\cdot(MgCl_2)_2$ or $ZnCl_2$, forming ‘bis(Grignard)silane’ $\{(Bu^tMe_2Si)_2Si[MgCl(thf)]_2\}$ and dizinciosilane $\{(Bu^tMe_2Si)_2Si(ZnCl)[ZnCl(thf)]\}_3[LiCl(thf)]$.[14(d),(e)] An unusual geminal dianionic derivative $[(thf)_2Li(Pr^i_3Si)_2Si–Hg–Si(SiPr^i_3)_2Li(thf)_2]$, featuring a central silicon bound to the two different metals (lithium and mercury), was also available *via* the lithiation of the trimercury silyl precursor $[Bu^tHg–(Pr^i_3Si)_2Si–Hg–Si(SiPr^i_3)_2–HgBu^t]$ in THF.[14(f)]

As was the case of their silicon analogues, successful isolation of the first stable dilithiogermane derivatives was preceded by the report on the metastable diaryldilithiogermane $Tbt(Dip)GeLi_2$, which was generated by the reduction of $Tbt(Dip)GeBr_2$ with lithium naphthalenide.[15] Similar to its silicon counterpart $Tbt(Dip)SiLi_2$,[11] $Tbt(Dip)GeLi_2$ also underwent intramolecular rearrangement, albeit at higher temperatures: above –25 °C [for $Tbt(Dip)GeLi_2$] *vs*. –78 °C [for $Tbt(Dip)SiLi_2$].

As for the isolable representatives, up to date, only a couple of 1,1-dilithiogermane derivatives $(R_3Si)_2GeLi_2$ **3a**,**b** have been reported as room temperature stable compounds.[16] Like their silicon analogues **1a**,**b**, 1,1-dilithiogermanes **3a**,**b** were synthesized by the reduction of the stable germirenes with lithium (Scheme 3).



3a $R_3Si = Pr^i_3Si$

3b $R_3Si = Bu^t_2MeSi$

Scheme 3

In contrast to monomeric dilithiosilane **1b**, isostructural dilithiogermane **3b** aggregated in the solid state, as a dimeric contact-ion pair, in which the two lithiums are shared by the two anionic germaniums forming a Ge_2Li_2 rhombus (Figure 2).[16] The two remaining lithiums are each bound to a germanium atom, which makes both germaniums pentacoordinate and bound to three Li atoms.

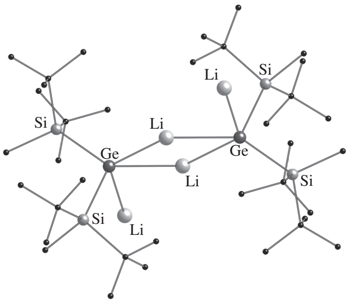


Figure 2 Crystal structure of the dimeric dilithiogermane **3b** (CrystalMaker view: H atoms and four Li-coordinated THF molecules are not shown).

Alternatively, the very synthetically useful dilithiogermane **3b** can be easily prepared in large scale by a simpler, more straightforward, higher yielding procedure, namely, by the reduction of tetrakis(di-*tert*-butylmethylsilyl)digermene with lithium naphthalenide (Scheme 4).[17]

$$(Bu^t_2MeSi)_2Ge{=}Ge(SiMeBu^t_2)_2 \xrightarrow[THF]{LiNp} (Bu^t_2MeSi)_2GeLi_2$$

3b

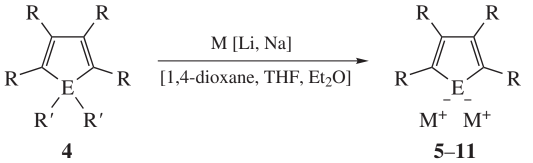
Scheme 4

Descending group 14, the stabilization of the geminal dianionic species becomes more and more challenging, therefore it comes as no surprise that 1,1-dilithiostannanes still eluded their experimental realization. The closest approach to such elusive compounds is based on the system that has already been proved effective in the generation of the isostructural 1,1-dilithiosilane Tbt(Dip)$SiLi_2$ and 1,1-dilithiogermane Tbt(Dip)$GeLi_2$, namely, reduction of the dibromostannane Tbt(Dip)$SnBr_2$ with lithium naphthalenide at –78 °C or with potassium graphite at –110 °C, affording 1,1-dilithiostannane Tbt(Dip)$SnLi_2$ and 1,1-dipotassiostannane Tbt(Dip)SnK_2, respectively.[18] Formation of Tbt(Dip)$SnLi_2$ (^{119}Sn NMR, δ –362.2 ppm at –80 °C) and 1,1-dipotassiostannane Tbt(Dip)SnK_2 was proven by their low-temperature trapping with DCl and MeI. Like their lighter homologues [Tbt(Dip)$SiLi_2$ and Tbt(Dip)$GeLi_2$], both Tbt(Dip)SnM_2 (M = Li, K) are metastable, surviving only at temperatures below –25 °C (for M = Li) and –110 °C (for M = K).

1,1,1-Trilithiostannane $ArSnLi_3$ has also been generated by the transmetalation of $ArSn(SiHMe_2)_3$ [Ar = 2,6-(2,4,6-$Pr^i_3C_6H_2)_2$-C_6H_3] precursor with excess MeLi in THF.[19] Although claimed to be a room temperature stable compound, $ArSnLi_3$ (^{119}Sn NMR in THF: –443 ppm) was not isolated, and its generation was supported by trapping with H_2O, D_2O, MeI and EtBr, forming the corresponding quenching products $ArSnH_3$, $ArSnD_3$, $ArSnMe_3$ and $ArSnEt_3$, respectively. Likewise, the tripotassium salt $ArSnK_3$ (^{119}Sn NMR in THF: –473 ppm) was also generated by treatment of $ArSn(SiHMe_2)_3$ with Bu^tOK in THF and trapped with MeI to give $ArSnMe_3$.[19]

Sila-, germa-, stanna- and plumbacyclopentadiene-1,1-diides

The very first representative of the title compounds, namely, the disodium salt of 2,3,4,5-tetraphenyl-1-silacyclopentadiene-1,1-diide, **5**-Na, was generated by the reductive dechlorination of the 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene precursor **4** with sodium in 1,4-dioxane (Scheme 5: E = Si, R = Ph, R′ = Cl, M = Na).[20]



Scheme 5

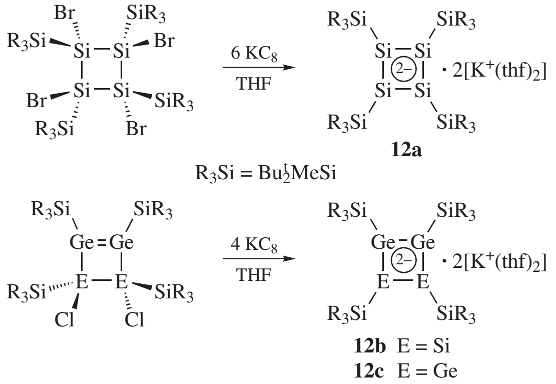
The dilithium salt of the same dianion **5**-Li, was similarly generated by the reduction of **4** with lithium in THF (see Scheme 5: E = Si, R = Ph, R′ = Cl, M = Li).[21(*a*)] Based on its spectroscopic (^{13}C NMR),[21(*a*)] structural (X-ray diffraction)[21(*b*)] and computational[21(*b*)] studies, dilithium salt **5**-Li was recognized as an aromatic 6π-electron species. Likewise, the dilithium salts of the germa-, stanna- and plumbacyclopentadiene-1,1-diides, **6** (E = Ge, R = Ph, R′ = Cl, M = Li),[22] **7** (E = Sn, R = R′ = Ph, M = Li),[23] **8** (E = Sn, R = Et, R′ = Ph, M = Li),[24] **9** (E = Sn, R^α = $SiMe_3$ and R^β = Ph, R′ = Ph, M = Li),[25] **10** (E = Sn, R^α = $SiMe_2Bu^t$ and R^β = Ph, R′ = Ph, M = Li),[25] **11** (E = Pb, R = R′ = Ph, M = Li),[26] respectively, were also classified as aromatic compounds (based on ^{7}Li NMR, X-ray diffraction and computational studies).

In addition to the above-discussed compounds, several other dianionic cyclic systems, featuring sila-, germa- and stannacyclopentadienediide fragments, were also reported as aromatic derivatives, including: dipotassio-2,3,4,5-tetramethyl-1-silacyclopentadienediide,[27] dipotassio-2,3,4,5-tetramethyl-1-germacyclopentadienediide,[27(*b*)] dilithio-3-butyl-2-phenyl-1-silaindenediide,[28] disodio-3-butyl-2-phenyl-1-silaindenediide,[28] dipotassio-1-silafluorenediide,[29] dilithio-2,3,4,5-tetraethyl-1-germacyclopentadienediide (and related dianionic trimer),[30,31] dilithio-2,3-diphenyl-1-germaindenediide,[32] disodio-2,3-diphenyl-1-germaindenediide,[32] dipotassio-1-germafluorenediide,[33] dilithio-3-butyl-2-phenyl-1-stannaindenediide,[34] and dipotassio-9-stannafluorenediide.[35]

Tetrasila- and tetragermacyclobutadiene dianions

Although, strictly speaking, tetrasila- and tetragermacyclobutadiene dianions do not belong to the class of geminal 1,1-lithio derivatives, they are closely related, therefore their chemistry will also be discussed below.

Tetrasila-, disiladigerma- and tetragermacyclobutadiene dianion dipotassium salts **12a–c** have been shown to be quantitatively available by the reductive dehalogenation of either tetrabromotetrasilacyclobutane or dichlorodisiladigermacyclobutene/dichlorotetragermacyclobutene with potassium graphite (Scheme 6).[36]



Scheme 6

All dianionic derivatives **12a–c** revealed folded four-membered rings (folding angles 34–43°), η^2-coordination of both potassium ions above and below the ring, non-equivalence of the skeletal bonds and remarkable pyramidalization at all skeletal atoms. All of these structural features originate from the strong Coulomb repulsion between the two negative charges, resulting in electron localization (Figure 3).[36]

Based on the geometric criterion of aromaticity (ring planarity, cyclic bond equalization, η^4-coordination of the potassium cations), heavy cyclobutadiene dianion derivatives **12a–c** are classified as nonaromatic compounds.[36] This conclusion is in line with the magnetic property calculations, which showed that the Nuclear Independent Chemical Shifts (NICS) for all dianionic derivatives are positive: NICS(1) = +6.1[36(*a*)] (for the tetrasilacyclobutadiene dianion), +4.3[36(*a*)] (for the disiladigermacyclobutadiene dianion) and +2.9[36(*b*)] (for the tetragermacyclobutadiene dianion), indicative of the absence of a diatropic ring current.

The alkali metal salts of heavy cyclobutadiene dianions **12a**,**b** can be readily converted into the alkaline earth metal salts **13a**,**b** by simple transmetalation with $MgBr_2$, CaI_2 and SrI_2 (Scheme 7).[37]

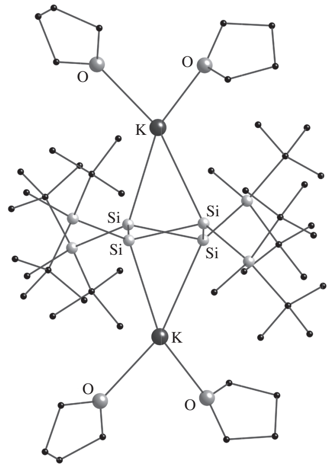
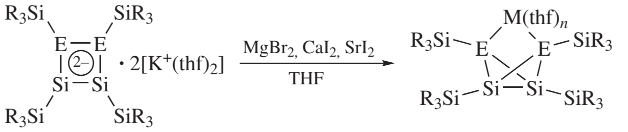


Figure 3 Crystal structure of the tetrasilacyclobutadiene dianion dipotassium salt **12a** (CrystalMaker view: H atoms are not shown).



12a E = Si
12b E = Ge

R$_3$Si = Bu$^t_2$MeSi

13a E = Si, M = Ca, n = 4
13b E = Ge, M = Mg/Ca/Sr, n = 3/4

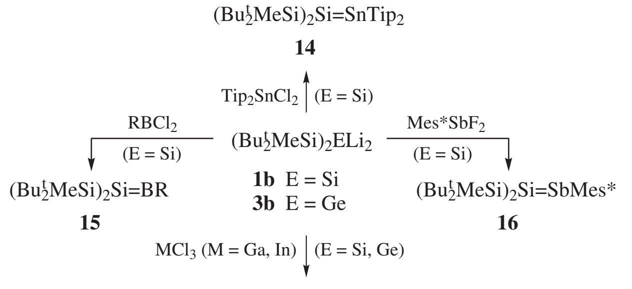
Scheme 7

Synthetic applications

1,1-Dilithiosilanes, -germanes and -stannanes

The most prominent synthetic feature of the geminal dilithio derivatives R$_2$ELi$_2$ (E = Si, Ge, Sn; R = alkyl, aryl, silyl groups) is their coupling with the appropriate electrophiles, either R′$_2$E′X$_2$ (E′ = main group element; R′ = alkyl, aryl, silyl group; X = halogen) or L$_n$MX$_2$ (M = transition metal; L = ligand; X = halogen), forming novel doubly-bonded derivatives R$_2$E=E′R′$_2$ and L$_n$M=ER$_2$, that are often inaccessible following other synthetic approaches.

Using this method, a variety of novel 'heavy' alkenes were synthesized, including disilenes [(Pr$^i_3$Si)$_2$Si=SiMes$_2$,[12(b)] (Pr$^i_3$Si)$_2$Si=SiTip$_2$,[12(b)] (Bu$^t_2$MeSi)$_2$Si=SiMes$_2$,[12(b)] (Bu$^t_2$MeSi)$_2$Si=SiTip$_2$)],[12(b)] silagermenes [(Bu$^t_2$MeSi)$_2$Si=GeMes$_2$,[12(b)] (Bu$^t_3$Si)$_2$Si=GeMes$_2$],[38(a)] germastannene [(Bu$^t_2$MeSi)$_2$Ge=SnTip$_2$],[38(b)] phosphasilene [(Bu$^t_2$MeSi)$_2$Si=PMes*],[38(c)] phosphagermene [(Bu$^t_2$MeSi)$_2$Ge=PMes*],[38(c)] arsasilene [(Bu$^t_2$MeSi)$_2$Si=AsMes*][38(d)] and tetrasilabuta-1,3-diene [(Bu$^t_2$MeSi)$_2$Si=Si(Mes)–Si(Mes)=Si(SiMeBu$^t_2$)$_2$].[38(e)] Indeed, using this reaction strategy, the following doubly-bonded derivatives were readily available, each representing the first example of a new class of organometallics: silastannene [(Bu$^t_2$MeSi)$_2$Si=SnTip$_2$ (Tip = 2,4,6-Pr$^i_3$-C$_6$H$_2$)] **14**,[38(f)] silaborene [(Bu$^t_2$MeSi)$_2$Si=BR (R = 2,2,6,6-tetramethylpiperidino)] **15**,[38(g)] stibasilene [(Bu$^t_2$MeSi)$_2$Si=SbMes* (Mes* = 2,4,6-Bu$^t_3$-C$_6$H$_2$)] **16**,[38(d)] anionic 1,3-disila-2-gallata- and -indataallenic derivatives [(Bu$^t_2$MeSi)$_2$Si$\overset{..}{-}$M$\overset{..}{-}$Si(SiMeBu$^t_2$)$_2$]$^+$·[Li$^+$(thf)$_4$]$^-$ (M = Ga, In) **17a**,[38(h)] and anionic 1,3-digerma-2-gallata- and -indataallenic derivatives [(Bu$^t_2$MeSi)$_2$Ge$\overset{..}{-}$M$\overset{..}{-}$Ge(SiMeBu$^t_2$)$_2$]$^+$·[Li$^+$(thf)$_4$]$^-$ (M = Ga, In) **17b**[38(i)] (Scheme 8).



(Bu$^t_2$MeSi)$_2$Si=SnTip$_2$
14

(Bu$^t_2$MeSi)$_2$ELi$_2$
1b E = Si
3b E = Ge

(Bu$^t_2$MeSi)$_2$Si=BR
15

(Bu$^t_2$MeSi)$_2$Si=SbMes*
16

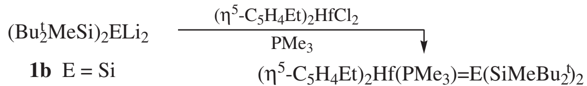
[(Bu$^t_2$MeSi)$_2$E$\overset{..}{-}$M$\overset{..}{-}$E(SiMeBu$^t_2$)$_2$]$^-$·[Li$^+$(thf)$_4$]

17a E = Si
17b E = Ge

Scheme 8

The reaction of 1,1-dilithiosilane **1b** and 1,1-dilithiogermane **3b** with the metallocene dihalides of the early transition metals opens access to the previously unknown 'heavy' carbene transition metal complexes of the Schrock type [(η^5-C$_5$H$_4$Et)$_2$Hf(PMe$_3$)=E(SiMeBu$^t_2$)$_2$] (E = Si, Ge) **18a**,**b** (Scheme 9).[39]

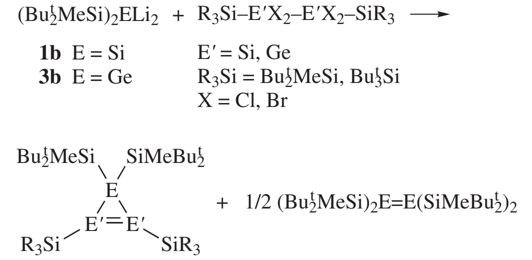
Moreover, cyclic compounds were also available by the reaction of the 1,1-dilithiosilane and 1,1-dilithiogermane with the 1,1,2,2-tetrahalodisilanes and -germanes: trisilirene **19a**,[40(a)] trigermirene **19b**,[40(b)] 1*H*-siladigermirene **19c**[40(b)] (Scheme 10), as well as the seven-membered ring compounds [1,3,2]oxasilaborepane **20a**[40(c)] and [1,3,2]oxagermaborepane **20b**[40(c)] (Scheme 11).



(Bu$^t_2$MeSi)$_2$ELi$_2$
1b E = Si
3b E = Ge

(η^5-C$_5$H$_4$Et)$_2$Hf(PMe$_3$)=E(SiMeBu$^t_2$)$_2$
18a E = Si
18b E = Ge

Scheme 9

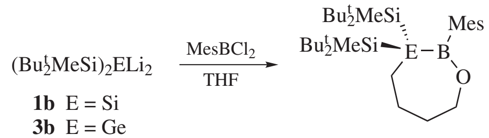


1b E = Si
3b E = Ge

E′ = Si, Ge
R$_3$Si = Bu$^t_2$MeSi, Bu$^t_3$Si
X = Cl, Br

19a E = E′ = Si, R$_3$Si = Bu$^t_3$Si
19b E = E′ = Ge, R$_3$Si = Bu$^t_2$MeSi
19c E = Si, E′ = Ge, R$_3$Si = Bu$^t_2$MeSi

Scheme 10



(Bu$^t_2$MeSi)$_2$ELi$_2$
1b E = Si
3b E = Ge

20a E = Si
20b E = Ge

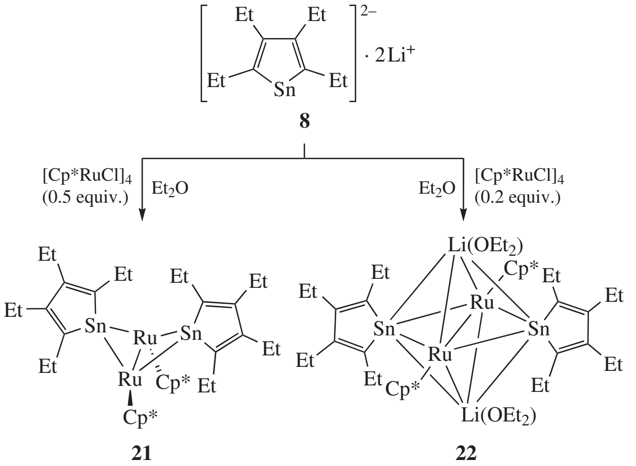
Scheme 11

Metastable dilithiosilane Tbt(Dip)SiLi$_2$[11] and dilithiogermane Tbt(Dip)GeLi$_2$[15] were used for a series of polycyclic compounds, featuring annelated benzene rings: silacyclopropabenzene,[41(a),(b)] germacyclopropabenzene,[15(a)] bis(silacyclopropa)benzene[41(b),(c)] and bis(germacyclopropa)benzene,[15(b)] prepared by the reaction of dilithio derivatives with 1,2-dibromobenzene and 1,2,4,5-tetrabromobenzene, respectively.

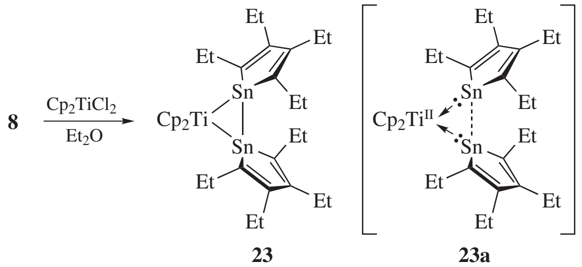
Sila-, germa-, stanna- and plumbacyclopentadiene-1,1-diides

In contrast to the monoanionic sila- and germacyclopentadienides that were used in the preparation of a variety of transition metal complexes featuring sila- or germacyclopentadienyl ligands, their dianionic counterparts, sila- and germacyclopentadiene-1,1-diides, have not exhibited, to date, the same utility in coordination chemistry. Only very recently, tin analogues of the title compounds, that is stannacyclopentadiene-1,1-diide derivatives were successfully employed as convenient precursors for novel transition metal complexes. 2,3,4,5-Tetraethyl-1-stannacyclopentadiene-1,1-diide **8** reacted with 0.5 equiv. of tetrameric [Cp*RuCl]$_4$ affording the bis(stannylene)-bridged dinuclear ruthenium complex **21**, which has a Ru$_2$Sn$_2$ butterfly-type core with the Ru atoms in the bridgehead and Sn atoms in the bridging positions (Scheme 12).[42] Interestingly, using only 0.2 equiv. of [Cp*RuCl]$_4$ led to the formation of the dianionic inverse-sandwich structure **22** with a flat Ru$_2$Sn$_2$-core, that can be considered as the doubly-reduced complex **21** (Scheme 12).[42]

Reaction of the same 2,3,4,5-tetraethyl-1-stannacyclopentadiene-1,1-diide **8** with the titanocene dichloride Cp$_2$TiCl$_2$ gave the titanium complex **23** featuring the three-membered TiSn$_2$ core (Scheme 13).[43] The ^{119}Sn resonance of **23** was observed at very low-field at +1333 ppm, diagnostic of the stannylene structures and pointing to an important contribution of the bis(stannylene) titanium complex resonance form **23a** (Scheme 13), although **23** can be alternatively viewed in a number of different ways, for example, as a Sn–Sn σ-complex or as a structure with a delocalized aromatic TiSn$_2$-core.

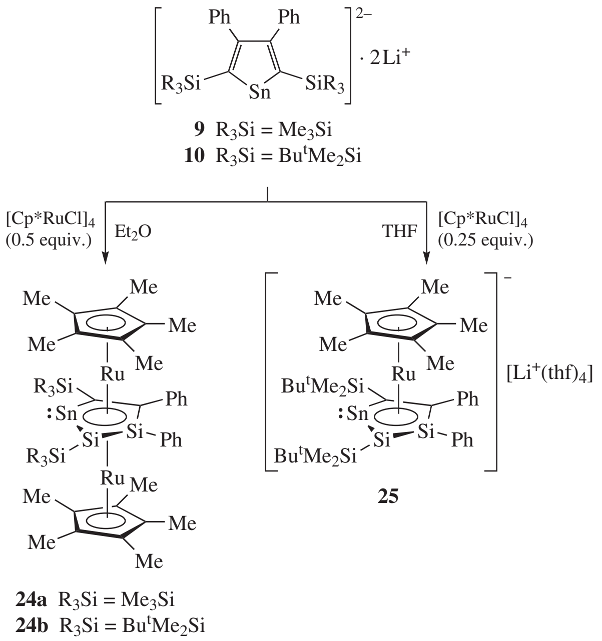


Scheme 12



Scheme 13

Note that the reaction of the tetrameric $[Cp^*RuCl]_4$ with the stannacyclopentadiene-1,1-diides featuring silyl substituents at the α-position to the Sn atom, **9** ($R_3Si = Me_3Si$) and **10** ($R_3Si = Bu^tMe_2Si$), resulted in the formation of different products, namely, triple- and double-decker ruthenocenes **24** and **25** (Scheme 14).[44]

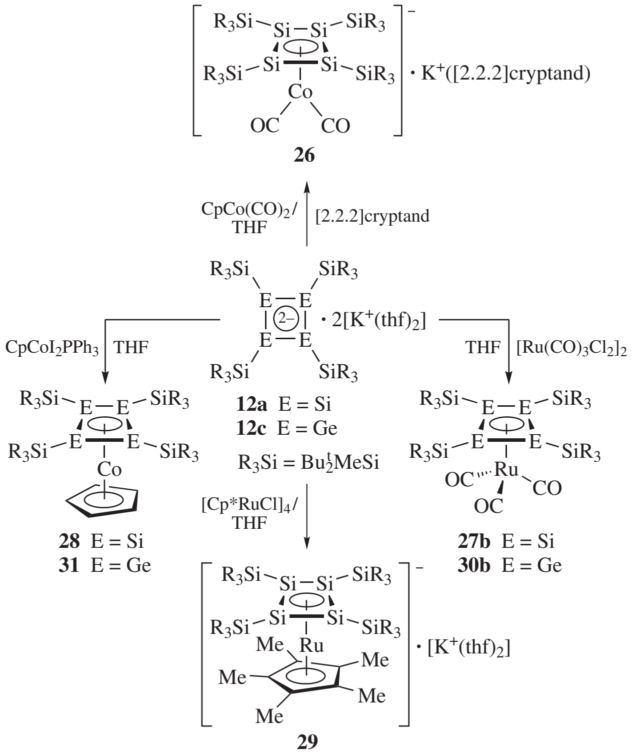


Scheme 14

Cyclic voltammetry studies of the triple-decker ruthenocene **24a** revealed that its central stannacyclopentadienyl ligand is a powerful π-electron donor in respect to the Ru fragment, even surpassing the strong π-donor character of the Cp* group.

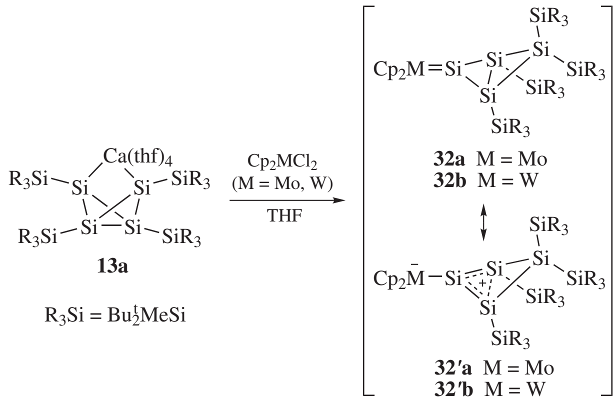
Tetrasila- and tetragermacyclobutadiene dianions

The heavy analogues of the cyclobutadiene dianion, namely, tetrasila- and tetragermacyclobutadiene dianion derivatives **12a**,**c**, have already been proven very useful in organometallic synthesis, especially in the preparation of novel coordination compounds. Thus, both **12a** and **12c** were indispensable in the synthesis of transition metal complexes featuring either tetrasila- or tetragermacyclobutadiene ligands, that were inaccessible by any other known synthetic route. They include the following complexes: anionic tetrasilacyclobutadiene dicarbonyl cobalt **26**,[45(a)] tetrasilacyclobutadiene tricarbonyl iron **27a**,[45(b)] tetrasilacyclobutadiene tricarbonyl ruthenium **27b**,[45(c)] sandwich tetrasilacyclobutadiene cyclopentadienyl cobalt **28**,[45(d)] anionic tetrasilacyclobutadiene pentamethylcyclopentadienyl ruthenium **29**,[45(e)] tetragermacyclobutadiene tricarbonyl iron **30a**,[36(b)] tetragermacyclobutadiene tricarbonyl ruthenium **30b**,[45(f)] and sandwich tetragermacyclobutadiene cyclopentadienyl cobalt **31**[36(b)] (Scheme 15).



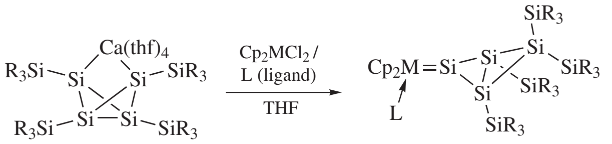
Scheme 15

Alkaline earth metal salts, bicyclo[1.1.0]butane-2,4-diides **13a**,**b**, are also useful in the preparation of novel transition metal complexes. Thus, the Ca-salt **13a** was successfully utilized as the



Scheme 16

precursor for the base-free group 6 metal (Mo, W) bicyclic silylene complexes **32a**,**b**, stabilized by a homoaromatic contribution **32′a**,**b** (Scheme 16),[37(*b*)] as well as the first Schrock-type silylene complexes of the group 4 metals (Ti, Zr, Hf) **33a–c** (Scheme 17).[46] The latter complexes **33a–c**, in particular, the titanium silylidene **33a**, readily undergo [2+2] cycloaddition with a variety of unsaturated compounds (alkynes, nitriles), opening the way for the development of the silicon version of metathesis as the novel route for the generation of Si–C bonds.[46]



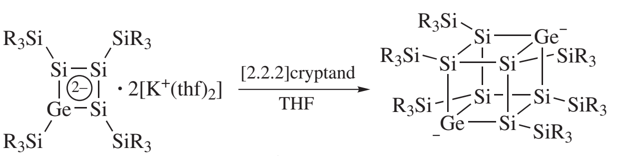
13a

33a M = Ti
33b M = Zr
33c M = Hf

$R_3Si = Bu^t_2MeSi$
M = Ti, Zr, Hf
L = thf, Me_3P, $(2,6\text{-}Me_2C_6H_3)NC$

Scheme 17

In addition to the transition metal complexes, the ‘heavy’ cyclobutadiene dianion derivatives provide ready access to a variety of organometallic cages and clusters, such as the hexasiladigermacubane dianion dipotassum salt **34**[47(*a*)] (Scheme 18), pentasilatricyclo[2.1.0.0^{2,5}]pentane **35**[47(*b*)] (as the valence isomer of the highly desirable but still elusive pentasilacyclopentadiene) (Scheme 19), and tetrasilabenzobenzvalene **36**[47(*c*)] (as the valence isomer of the tetrasilanaphthalene) (Scheme 20).

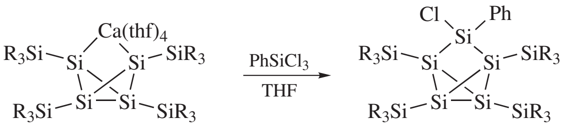


$R_3Si = Bu^t_2MeSi$

$\cdot\ 2\,[K^+([2.2.2]cryptand)]$

34

Scheme 18

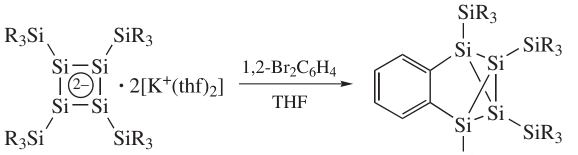


13a

35

$R_3Si = Bu^t_2MeSi$

Scheme 19

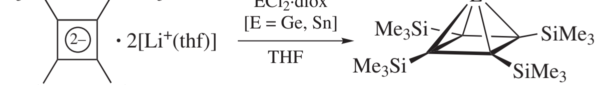


12a

$R_3Si = Bu^t_2MeSi$

36

Scheme 20



37

38a E = Ge
38b E = Sn

Scheme 21

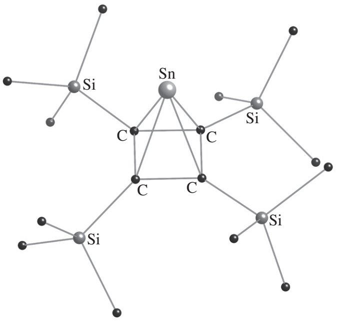


Figure 4 Crystal structure of the stannapyramidane **38b** (CrystalMaker view: H atoms are not shown).

Reaction of the carbon analogue of the cyclobutadiene dianion, namely, the dilithium salt of the tetrakis(trimethylsilyl)cyclobutadiene dianion **37**, with the dichlorogermylene and dichlorostannylene dioxane complexes, forms a novel class of polyhedral compounds, pyramidanes **38a**,**b** manifesting a non-classical bonding interaction mode between the C_4-base and the Ge/Sn apex of the square pyramid (Scheme 21, Figure 4).[48]

Conclusions

Geminal 1,1-dilithiosilanes, 1,1-dilithiogermanes, 1,1-dilithiostannanes and closely related compounds, such as heavy group 14 element analogues of the cyclopentadiene-1,1-diides and cyclobutadiene dianions, are indispensable in the synthesis of a diversity of the novel classes of compounds. They should therefore, undoubtedly, be classified as the organometallic reagents of the new generation. From the multiply-bonded derivatives to cyclic/polycyclic/cluster compounds to transition metal complexes: a broad range of synthetic applications is covered by the use of the title compounds. As for the prospective developments in the field, one can anticipate the future syntheses of the stable heaviest representatives, such as 1,1-dilithiostannane and 1,1-dilithioplumbane derivatives. The development of novel, simple and high-yielding general strategies for the synthesis of geminal dianionic derivatives R_2ELi_2 (R = alkyl, aryl, silyl; E = Si–Pb) is evidently a goal of paramount importance for synthetic chemists. Among the most promising practical applications of the dianionic derivatives of the type R_2ELi_2 is the synthesis of heavy analogues of transition metal carbene complexes $L_nM{=}ER_2$ (M = early transition metal, L = ligand), that have great potential for their use in such commercially important processes as alkene and alkyne metathesis. Certainly, studies in this direction are among the top priorities for the organometallic chemists working in the field.

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