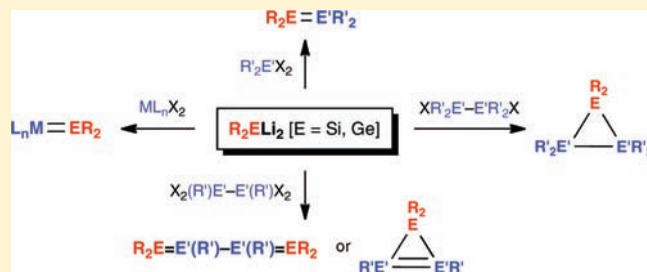# Novel Organometallic Reagents: Geminal Dianionic Derivatives of the Heavy Group 14 Elements

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ABSTRACT: This Forum review describes the most recent achievements in the novel prospective field of highly reactive main-group organometallics, namely, geminal dianionic derivatives of the heavy group 14 elements (Si, Ge, Sn). A brief historical introduction to the topic is followed by discussion of the current state of affairs in the field of stable derivatives and prospects for future efforts, highlighting our own synthetic approach and recent results. The most important experimental contributions, including synthesis of 1,1-dilithiosilane, -germane, and -stannane derivatives; dilithio(halo)silanes (lithiosilylenoids); metallole 1,1-dianions; and heavy analogues of the cyclobutadiene dianion derivatives, are presented, along with a discussion of the synthetic applications of the above-mentioned organometallic compounds.

1. INTRODUCTION

Highly nucleophilic carbanions are ubiquitous species in organic chemistry.[1] Without doubt, the best-known and synthetically most useful representatives of carbanionic derivatives are Grignard reagents $RMgX$[2] and organolithium reagents RLi,[3] of which the former have been known for more than a century (Victor Grignard, 1901), whereas the latter were discovered later (Wilhelm Schlenk, 1917). Although Grignard reagents are easier to prepare and handle, organolithium reagents, which are more sensitive and difficult to handle because of the greater ionicity of the $C-Li$ versus $C-Mg$ bond, are more reactive, becoming the reagents of choice, especially in cases when Grignard reagents fail to give the desired products. To date, the above-described metal salts of carbanions, both $RMgX$ and RLi, have become readily accessible (and, in many cases, commercially available) organometallic reagents that are widely used in preparative organic chemistry and thoroughly structurally studied from the viewpoint of such fundamentally important properties as basicity, stability, ion-pairing behavior, and aggregation states.

Geminal dianionic species, such as dilithiomethane R_2CLi_2 derivatives, bearing two negative charges on the same carbon, are even more challenging than their monoanionic organolithium congeners R_3CLi, because of their extreme reactivity. It is because of this reactivity that a great diversity of organic compounds is accessible through their use.[4] Although the landmark work by Ziegler and co-workers on the generation of the parent dilithiomethane CH_2Li_2 by the thermolysis of methyllithium CH_3Li was published as early as 1955,[5] systematic studies in the field of the synthetic application of dilithiomethane derivatives began only a couple of decades later. Such geminal dilithiomethane derivatives serve as indispensable reagents in single-step

multiple carbon—carbon bond formation through reaction of dilithiated nitriles, sulfonamides, sulfones, and phosphonates with a variety of electrophiles.[4b] In the course of investigations, the synthetic approaches for the dilithiomethane derivatives were significantly improved based on either the reduction of geminal dihalides [Ph_2CCl_2 with a large excess of ^tBuLi at low temperature,[6a] $(Me_3Si)_2CCl_2$ with lithium vapor[6b]] or the metalation of compounds containing acidic hydrogens (phenylacetonitrile $PhCH_2CN$ with ^nBuLi forming $PhCLi_2CN$,[7a] benzyl phenyl sulfone $PhSO_2CH_2Ph$ with ^nBuLi forming $PhSO_2CLi_2Ph$[7b,c]). Lagow and co-workers modified Ziegler's original method,[5] generating a variety of geminal dilithiomethane derivatives based on the thermolysis of monolithiated compounds.[8] Heavily overloaded with the two negative charges sitting on the same carbon, geminal dilithiomethane derivatives are intrinsically labile; therefore, those generated, for example, from a sulfone or nitrile, can be successfully formed only in the presence of a second group providing additional stabilization through either conjugative or hyperconjugative effects (for example, the Me_3Si group).[4b,9] From a structural viewpoint, an early study of X-ray powder diffraction data suggested a solid-state structure of CD_2Li_2,[10a,b] and more precise crystallographic data for the X-ray crystal structures of some geminal dilithiomethane derivatives were reported in the following years.[10c,d] As for the computational approach, several studies on the structure of the parent dilithiomethane were published in the 1970 and 1980s.[11] Thus, Schleyer and co-workers predicted that highly electropositive substituents (particularly lithium) can effectively stabilize the planar configuration at the central dianionic carbon of dilithiomethane

because of their π-accepting and σ-donating properties (RHF/6-31G*//RHF/STO-3G).[11a] Using the double-ζ plus polarization (DZ+P) basis set, Schaefer and co-workers further elaborated this conclusion by optimization of the four major electronic states of dilithiomethane (relative energies in kcal/mol): tetrahedral singlet (0.0), tetrahedral triplet (+2.1 kcal/mol), planar triplet (+3.9 kcal/mol), planar singlet (+8.3 kcal/mol) (CI/DZ+P).[11b] Although these calculations showed the tetrahedral singlet to be the ground state, other electronic states were found to be nearly degenerate, being within ca. 8 kcal/mol of the ground state. Further investigations revealed the predominantly ionic character of the C^-—Li^+ bond in the singlet CH_2Li_2 (RHF/6-31G**),[11c] and structures for the monomeric, dimeric, and even higher associates of CH_2Li_2 were proposed (RHF/4—31G//RHF/STO-3G).[11d] The results of the latest calculations on the methanediides $(CH_2M_2)_2$ (M = Li, Na, K, Rb, Cs) at the high MP2/def2-TZVPP level are in a good agreement with the earlier reports (vide supra), describing dilithiomethane (as well as its heavier alkali metal homologues) as the D_{2d} dimeric aggregates of two planar CH_2M_2 units, in which the central tetracoordinate carbon is planar.[11e]

The silyl anions (along with their germyl, stannyl, and plumbyl congeners) are also among the most fundamental species in heavy group 14 element chemistry, playing a key role analogous to that of carbanions in organic chemistry (vide supra).[12] Known since the early 1950s from the pioneering work of Gilman's group, such species were shown to participate in an overwhelming number of organometallic reactions. Given the well-documented extreme usefulness of monoanions centered on heavy group 14 elements, one can imagine the geminal dianionic derivatives (dilithiosilanes, dilithiogermanes, etc.) as the next synthetic challenge, even more attractive from the viewpoint of their unprecedented synthetic utility. The preparative approach to dilithiosilane derivatives was preceded by early calculations by Schleyer and co-workers,[13] who computationally addressed the structural issue. They found that the potential energy surfaces for the lowest singlet and triplet dilithio- and disodiosilanes, SiH_2Li_2 and SiH_2Na_2, are very flat, thus favoring the existence of a number of unusual structures. Similarly to the case of dilithiomethane, both dilithio- and disodiosilanes exhibited small energy differences between the planar and tetrahedral geometries for tetracoordinate silicon. The global minimum for SiH_2Li_2 was represented by the distorted structure featuring two lithiums unsymmetrically placed in the C_s symmetry plane orthogonal to the SiH_2 unit, whereas inverted tetrahedral and normal tetrahedral C_{2v} singlets were found to be 3.9 and 6.3 kcal/mol less stable (MP4SDTQ/6-31G**//HF/6-31G**).

Given the undeniable interest in geminal dianionic derivatives of the type R_2EM_2 (E = heavy group 14 element, M = alkali metal), our motivation to contribute to this field was driven by the intention to design a reasonable preparative-scale approach for such synthetically very attractive compounds, first dilithiosilanes, which were expected to be indispensible in the synthesis of novel unsaturated, cyclic, and polycyclic derivatives inaccessible by any other means (Scheme 1). Of particular importance were the highly challenging but as yet hardly available doubly bonded derivatives of both main-group (heavy analogues of alkenes) and d-block (heavy analogues of transition-metal carbene complexes) elements. Representative examples of the stable geminal dianionic derivatives are discussed below.

Scheme 1. Expected Synthetic Applications of the Geminal Dilithiosilane Derivatives
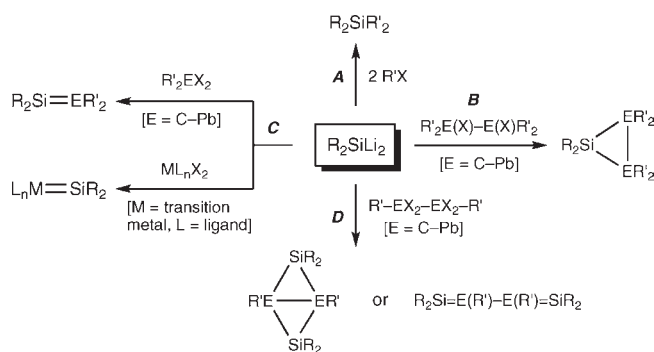
## 2. STABLE GEMINAL DIANIONIC DERIVATIVES OF THE HEAVY GROUP 14 ELEMENTS

2.1. 1,1-Dilithiosilane Derivatives. Our entering this field was preceded by two important experimental contributions. In the first, published in 1990, Lagow and co-workers claimed the generation of the first dilithiosilane derivative, $(Me_3Si)_2SiLi_2$, prepared by a modified Ziegler procedure based on the pyrolysis of $(Me_3Si)_3SiLi$ at 140—150 °C.[14] Although not isolable, $(Me_3Si)_2SiLi_2$ was identified by its quenching reactions with EtOD and MeI, as well as by flash vaporization mass spectrometry revealing the presence of both monomeric and dimeric forms of the dilithiosilane derivative. In the second, Tokitoh's group was able to generate the metastable diaryldilithiosilane derivative $Tbt(Dip)SiLi_2$ {Tbt = 2,4,6-[$(Me_3Si)_2CH$]$_3$—C_6H_2, Dip = 2,6-$^iPr_2$—C_6H_3} by the reduction of the corresponding dibromoprecursor $Tbt(Dip)SiBr_2$ with an excess of lithium naphthalenide in tetrahydrofuran (THF).[15] Stable below −78 °C (formation of 1,1-dilithiosilane was confirmed by trapping reactions), $Tbt(Dip)SiLi_2$ underwent unavoidable rearrangement at higher temperatures, involving intramolecular exchange between one of the lithium atoms and the methine proton of one of the ortho-$CH(SiMe_3)_2$ groups, finally leading to a monosilyllithium derivative. Thus, prior to our investigation, the isolation of room-temperature-stable, structurally identifiable 1,1-dilithiosilane (as well as its heavier group 14 element analogues) derivatives had not been achieved.

Given the above preliminary attempts to generate 1,1-dilithiosilane derivatives and taking into account their synthetic problems, we decided to design a new method by approaching the problem from a different angle. This method was based on the following considerations: (1) avoid the high-temperature Ziegler method applied by Lagow and co-workers, because isolation of the target product generated under such drastic conditions is highly problematic, and (2) use bulky silyl substituents at the dianionic silicon center, as they had previously proved to be very effective in the stabilization of the dilithiomethane derivative (vide supra).

In the course of our studies in the field of stable silirenes with bulky silyl substituents at the silicon atom, we unexpectedly found that compounds such as $cyclo$-[−$(R_3Si)_2Si$−$C(SiMe_3)$=$C(SiMe_3)$−] **1** (a, R_3Si = $^iPr_3Si$; b, $^tBu_2MeSi$) readily undergo reduction with lithium to form the first isolable dilithiosilane derivatives $(R_3Si)_2SiLi_2$ **2** (a, R_3Si = $^iPr_3Si$; b, $^tBu_2MeSi$) (Scheme 2).[16]

Although the formation of dilithiosilanes **2** can be viewed as the result of the formal reduction of the endocyclic Si—C bonds,

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dx.doi.org/10.1021/ic2006106 |*Inorg. Chem.* 2011, 50, 12303–12314

Scheme 2. Synthesis of the First Stable Dilithiosilane Derivatives 2

1 [a: $R_3Si = {^i}Pr_3Si$;
b: $R_3Si = {^t}Bu_2MeSi$]

2a,b [a: $R_3Si = {^i}Pr_3Si$;
b: $R_3Si = {^t}Bu_2MeSi$]
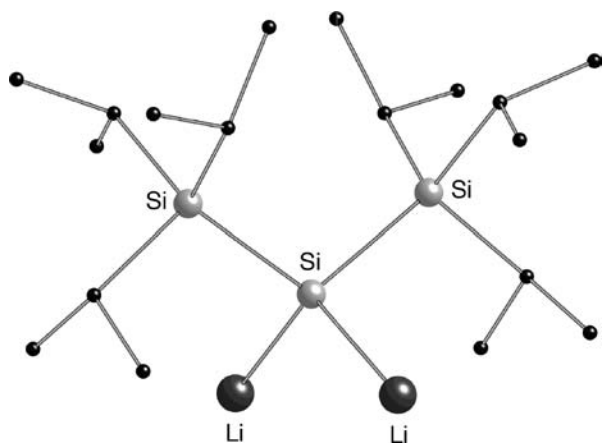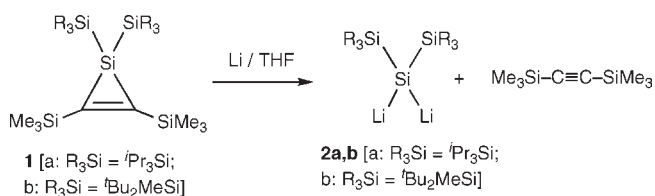
Figure 1. Crystal structure of the dilithiosilane derivative **2b**. (CrystalMaker view: four Li-coordinated THF molecules and H atoms are not shown.)

the mechanism for such unprecedented reductive "cycloreversion" of silirenes seems to be more complicated, apparently involving initial reduction of the C≡C bond facilitated by the silyl substitution at the sp^2 carbons lowering the lowest unoccupied molecular orbital (LUMO) energy level. X-ray diffraction analysis revealed a monomeric structure for $({^i}Pr_3Si)_2Si$-$[Li(THF)_2]_2$ **2a**, in which the two ${^i}Pr_3Si$ substituents and the two lithiums are bound to the central silicon (Figure 1). Although the Si—Si bond lengths of 2.335(2) and 2.337(2) Å were normal, the Si—Li distances of 2.549(7) and 2.55(1) Å were markedly shorter than those of the solvated monomeric silyllithiums (2.67–2.70 Å). In contrast to the theoretical predictions using parent models with readily movable hydrogen atoms,[13] the dianionic silicon in **2a** featured a normal tetrahedral configuration, which is quite reasonable given the high steric bulk of the silyl substituents and significant electrostatic repulsion between the two negative charges. The direct Si—Li bonding of **2a** in solution at 200 K, evidence of its existence as a contact-ion pair, was confirmed by the observation of the resonance of dianionic silicon as a quintet $[{^1}J(^{29}Si-^6Li) = 15.0$ Hz, coupling with two ^6Li nuclei with $I = 1]$ at −292.0 ppm. The chemical shift value for **2a** of −292.0 ppm is extraordinarily high-field-shifted compared with that of monoanionic $(Me_3Si)_3SiLi$ (−189.4 ppm), manifesting the greater electron population at the dianionic silicon in the former {the highest occupied molecular orbital (HOMO) of the $(Me_3Si)_2SiLi_2$ model is represented by the combination of the two σ_{Si-Li} orbitals holding negative charges [B3LYP/6-31G(d)]}.

Dilithiosilane derivative $({^t}Bu_3Si)_2SiLi_2$ **3**, featuring exceedingly bulky tri-*tert*-butylsilyl substituents, is available by a simple
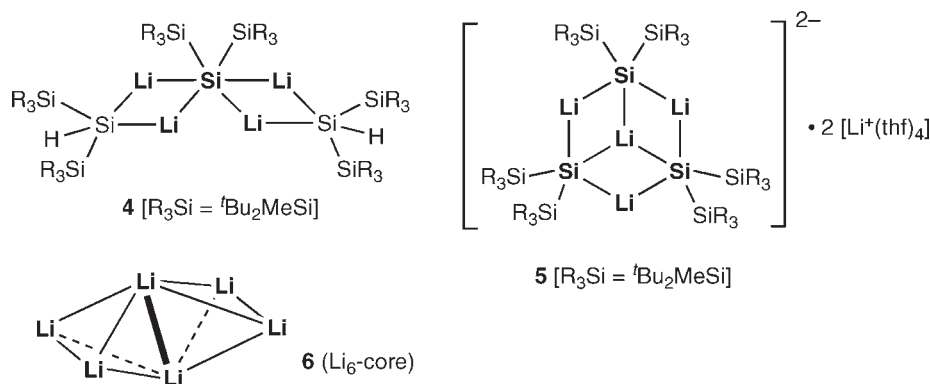
Scheme 3. Synthesis of Dilithiosilane Derivative 3
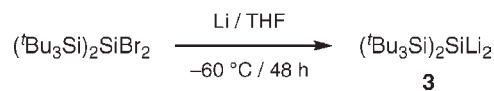
procedure involving a direct reductive dehalogenation of the $({^t}Bu_3Si)_2SiBr_2$ precursor with lithium (Scheme 3).[17] Low temperature and long reaction time are crucial for the successful formation of **3**, which otherwise undergoes intramolecular insertion of the intermediate silylenoid $({^t}Bu_3Si)_2SiLiBr$, giving the 1,2-disilacyclobutane derivative instead of **3**.

Dilithiosilanes **2a,b** were also alternatively prepared by the reduction of silylmercury derivatives with lithium by Apeloig and co-workers.[18] In the absence of a coordinating solvent, the dilithiosilane derivatives formed unusual aggregates and were isolated in a variety of structural modifications. Thus, unsolvated dilithiosilane $(R_3Si)_2SiLi_2$ **2b** ($R_3Si = SiMe^tBu_2$) was obtained as a coaggregate with two molecules of monolithiosilane $(R_3Si)_2HSiLi$ of the type $\{[(R_3Si)_2SiLi_2][(R_3Si)_2HSiLi]_2\}$ **4** (Scheme 4).[18a]

In the solid state, **4** features a hexacoordinate central silicon atom bonded to four lithiums with Si—Li distances of 2.613(8)–2.641(10) Å. In THF, however, the constitution of **4** is different, represented by a solvated silyllithium aggregate **5** of formally trimeric composition $[(R_3Si)_2SiLi_2]_3(THF)_8$ (Scheme 4).[18b] The anionic part of **5** consists of the $\{[(R_3Si)_2Si]_3Li_4\}^{2-}$ cluster with a star-like tetralithium core (the Si_3Li_3 hexagon is nearly planar, and the central lithium is pulled 0.4 Å above the mean plane of the hexagon), whereas the cationic part is represented by two lithium cations each solvated by four THF molecules. Unsolvated dilithiosilane $(R_3Si)_2SiLi_2$ **2a** ($R_3Si = Si^iPr_3$) was also isolated as a coaggregate with ${^t}BuLi$ of the type $\{[({^i}Pr_3Si)_2SiLi_2]_2[{^t}BuLi]_2\}$ **6**, featuring a central Li_6 core composed of two distorted tetrahedra sharing a common Li—Li edge (Scheme 4).[18c]

Using their signature approach based on transmetalation in nonsolvating media, Apeloig and co-workers very recently reported a novel dilithiosilane with the smallest silyl substituents, $(R_3Si)_2SiLi_2$ ($R_3Si = SiMe_2{^t}Bu$) **7**, prepared by the reduction of silyl mercury oligomers $R_3Si-[Hg-Si(SiR_3)_2]_n-Hg-SiR_3$ with lithium (Scheme 5).[18d] X-ray diffraction analysis of **7** revealed its rather complicated hexameric constitution $\{[(R_3Si)_2SiLi_2]_6-[Li_2O]_2\}$ in which the six $(R_3Si)_2SiLi_2$ units are coaggregated with the two Li_2O molecules. Transmetalation of **7** with Grignard reagent ${^t}BuMgCl\cdot(MgCl_2)_2$ resulted in the formation of the geminal dimagnesiosilane $[(R_3Si)_2SiMg(THF)_2]_2$ **8**, from which di(Grignard)silane $\{(R_3Si)_2Si[MgCl(THF)]_2\}_2$ **9** and dizinciosilane $(\{(R_3Si)_2Si(ZnCl)[ZnCl(THF)]\}_3[LiCl\cdot THF]$ **10** were prepared by reactions with ${^t}BuMgCl\cdot(MgCl_2)_2$ and $ZnCl_2$, respectively (Scheme 5).[18d] In accordance with the higher electronegativities of Mg and Zn compared to Li, the dianionic silicon centers in **8**–**10** were notably deshielded compared to that in **7**: −200 ppm (in **8**), −226 ppm (in **9**) and −184 ppm (in **10**) compared to −254 ppm (in **7**).

The same authors also reported an interesting geminal dianionic compound in which the central silicon is bound to the two different metals (lithium and mercury), $[(THF)_2Li({^i}Pr_3Si)_2Si-Hg-Si(Si^iPr_3)_2Li(THF)_2]$, available through the lithiation of the trimercury silyl precursor $[{^t}BuHg-({^i}Pr_3Si)_2Si-Hg-Si(Si^iPr_3)_2-Hg^tBu]$ in THF.[18e] The dianionic Si atoms, resonating

Scheme 4. Structural Modifications of the Dilithiosilane Derivatives: Aggregates 4−6[a]


4 [R₃Si = $^tBu_2MeSi$]

5 [R₃Si = $^tBu_2MeSi$]

6 (Li₆-core)

[a] In **6**, the central Li₆ core is surrounded on the four sides by two ($^iPr_3Si$)₂Si and two ^tBu fragments.

Scheme 5. Synthesis of Dilithiosilane 7, Dimagnesiosilane 8, Di(Grignard)silane 9, and Dizinciosilane 10

7

8

9

10
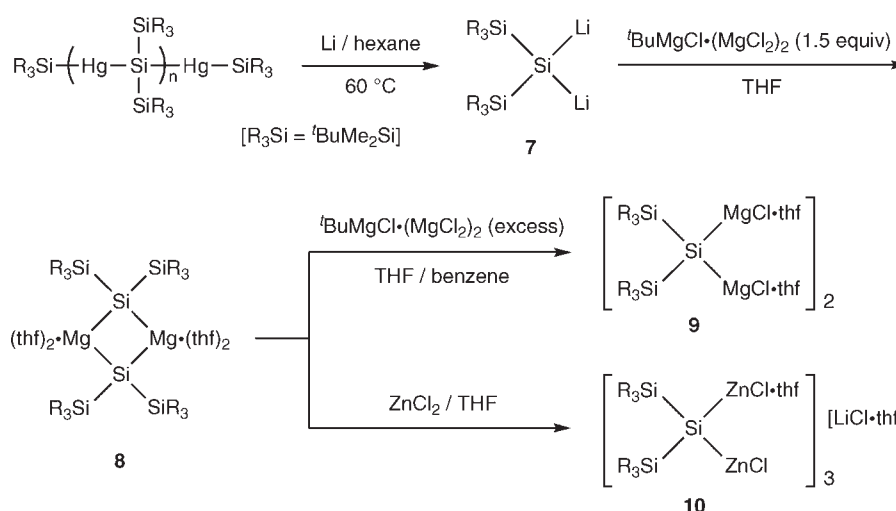
at −120 ppm, were further deshielded compared with those in 7−10 (vide supra).

2.2. 1,1-Dilithiogermane Derivatives. Taking advantage of the favorable $Ge^{\delta-}-H^{\delta+}$ bond polarization, generation of geminal 1,1-dilithiogermane derivatives of the type Ar_2GeM_2 (Ar = Ph, p-CH₃C₆H₄; M = Li, Na, K) by the metalation of the corresponding hydrides Ar_2GeH_2 with either alkali metals M or ^tBuLi was reported as early as the mid-1980s by Mochida's[19a] and Satgé's[19b−d] groups. Vyazankin and co-workers alternatively generated Et_2GeLi_2 by the reaction of (Me₃Si)Et₂GeLi with Me₃SiLi in HMPA.[19e] However, lacking stabilization by the thermodynamic and kinetic effects of appropriate substituents (vide supra), such Ar_2GeM_2 species were not isolable and were identified only by spectroscopic means and trapping reactions with water and methyl iodide.

To date, only a couple 1,1-dilithiogermane derivatives have been synthesized as isolable, room-temperature-stable, and fully characterizable compounds, (R₃Si)₂GeLi₂ **11** (a, R₃Si = $^iPr_3Si$; b, $^tBu_2MeSi$).[20] Isostructural with their silicon analogues (R₃Si)₂SiLi₂ **1**, dilithiogermanes **11** were similarly prepared by the reduction of the stable germirenes cyclo-[−(R₃Si)₂Ge−C(SiMe₃)=C-(SiMe₃)−] **12** (a, R₃Si = $^iPr_3Si$; b, $^tBu_2MeSi$) with lithium (Scheme 6).

Scheme 6. Synthesis of the First Stable Dilithiogermane Derivatives 12

11 [a: R₃Si = $^iPr_3Si$; b: R₃Si = $^tBu_2MeSi$]

12 [a: R₃Si = $^iPr_3Si$; b: R₃Si = $^tBu_2MeSi$]
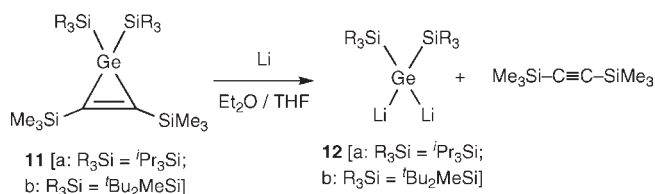
In contrast to monomeric dilithiosilane **2b**, the identically substituted dilithiogermane **12b** was aggregated in the solid state, representing a dimeric contact-ion pair, in which the two lithiums are shared by the two germaniums to form an almost regular Ge_2Li_2 rhombus (Figure 2).[20] The remaining two lithiums are each bound to a germanium center; therefore, in the overall dimeric structure, both germaniums are pentacoordinate and linked to three Li atoms.

Given the complicated (and sometimes poorly reproducible) procedure for the preparation of germirene precursors **11** (Scheme 6), we were interested in developing a novel experimental

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dx.doi.org/10.1021/ic2006106 |Inorg. Chem. 2011, 50, 12303−12314
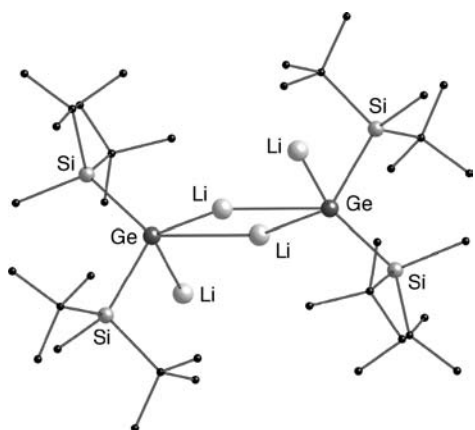
Figure 2. Crystal structure of the dimeric dilithiogermane derivative **12b**. (CrystalMaker view: four Li-coordinated THF molecules and H atoms are not shown.)

Scheme 7. Alternative and Improved Method for the Large-Scale Synthesis of Dilithiogermane 12b
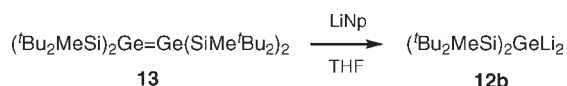

protocol for the synthetically very useful 1,1-dilithiogermane derivative **12b**: simpler, more straightforward, and higher in yield. This goal was finally achieved by the reduction of the readily available tetrakis(di-*tert*-butylmethylsilyl)digermene **13** with lithium naphthalenide, which allowed for the preparation of larger amounts of dilithiogermane **12b** in a shorter time (Scheme 7).[21]

Apart from the above-described isolable 1,1-dilithiogermanes **12**, there is also Tokitoh's diaryldilithiogermane derivative Tbt-(Dip)GeLi$_2$, which, similarly to its silicon analogue Tbt(Dip)SiLi$_2$,[15] was generated by the reduction of Tbt(Dip)GeBr$_2$ with an excess of lithium naphthalenide in THF and trapped with D$_2$O or MeOH.[22] The intramolecular lithium—methine proton exchange was observed in Tbt(Dip)GeLi$_2$ above −25 °C, whereas in its silicon analogue, Tbt(Dip)SiLi$_2$, this rearrangement occurred above −78 °C.

2.3. 1,1-Dilithiostannane Derivatives. The stabilization of the geminal dianionic species becomes more challenging descending group 14, and accordingly, geminal dilithiostannanes are still unknown as stable/isolable derivatives. An early report by Schumann and co-workers proposed the generation of Ph$_2$SnLi$_2$ by the reduction of Ph$_2$SnCl$_2$ with lithium in THF, which was subsequently trapped with sulfur to form the proposed Ph$_2$Sn-(SLi)$_2$; however, no direct NMR spectroscopic evidence for the formation of dianionic species was given.[23] This reaction was later monitored by NMR spectroscopy to assign ^{119}Sn NMR resonances of the proposed dianionic species Ph$_2$SnLi$_2$ [$\delta(^{119}$Sn$)$ = −103 ppm, $\Delta\delta$ (compared with the starting Ph$_2$SnCl$_2$) = −58 ppm].[24]

Following their previous reports on the metastable dilithiosilane Tbt(Dip)SiLi$_2$ and dilithiogermane Tbt(Dip)GeLi$_2$ derivatives, Tokitoh and co-workers generated Tbt(Dip)SnLi$_2$ and Tbt(Dip)SnK$_2$ by the reduction of the dibromide precursor Tbt(Dip)SnBr$_2$ with either lithium naphthalenide or potassium graphite.[25] Low-temperature generation of both dilithiostannane Tbt(Dip)SnLi$_2$ [$\delta(^{119}$Sn$)$ = −362.2 ppm at −80 °C]

Scheme 8. Resonance Forms of the Model Silylenoid 14′: F-Substituted Silyl Anion (Me$_3$Si)$_2$FSi$^-$ with a Me$_2$O-Solvated Li$^+$ Countercation (14′a) and (Me$_3$Si)$_2$Si: Silylene Fragment with a Me$_2$O-Solvated LiF Molecule (14′b)
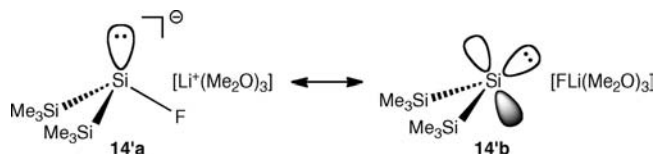

and dipotassiostannane Tbt(Dip)SnK$_2$ was confirmed by their trapping with DCl and MeI. Similarly to their lighter homologues (dilithiosilane and dilithiogermane), 1,1-dimetallastannane derivatives Tbt(Dip)SnM$_2$ (M = Li, K) are metastable, surviving only at temperatures below −25 °C (for M = Li) and −110 °C (for M = K).
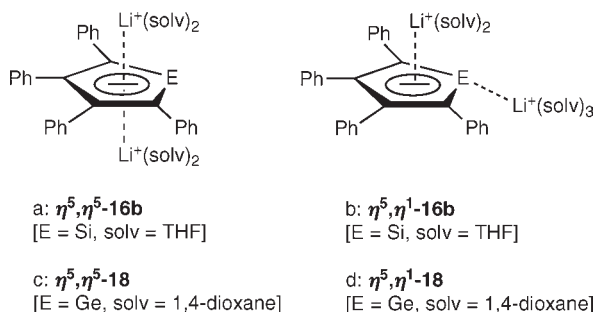
2.4. Lithiosilylenoids as Dilithio(halo)silanes. Monoanionic silylenoids R$_2$Si(X)M (X = halogen, M = metal), as the silicon analogues of ubiquitous carbenoids R$_2$C(X)Li in which the central silicon is tetracoordinate, bound to both halogen and alkali metal, chemically resemble free silylenes R$_2$Si:, which feature two-coordinate silicon centers. However, although silylenoids behave in many cases as the synthetic equivalents of silylenes, giving the same type of insertion and cycloaddition products characteristic of carbene analogues, they can also react as nucleophilic silyl anions, which reflects their ambiphilic nature. Some examples of silylenoids that are moderately stable at room temperature were reported by Lee and co-workers, including bromosilylenoid Br[(Me$_3$Si)$_3$C]Si(Br)Li,[26a−d] chlorosilylenoid Cl[(Me$_3$Si)$_3$C]Si(Cl)Li,[26b] and the mesitylsilylenoid—magnesium bromide complex Mes[(Me$_3$Si)$_3$C]Si(Br)Li·MgBr$_2$.[27] Apeloig and co-workers recently described the remarkably stable silylenoid (^{t}Bu$_2$MeSi)$_2$Si(F)[Li(THF)$_3$] **14**, prepared by the reaction of the bromofluorosilane (^{t}Bu$_2$MeSi)$_2$Si(F)Br with the silyllithium (^{t}Bu$_2$MeSi)$_3$SiLi in THF.[28] Interestingly, in its crystal structure, silylenoid **14** exhibits a tricoordinate (rather than the anticipated tetracoordinate) silicon center, featuring Si···F and Li···F interactions and lacking direct Si···Li bonding contacts. According to theoretical calculations on the model silylenoid **14′** [B3LYP/6-311+G(d)], it can be best described as a hybrid of the two resonance extremes, of which **14′a** is a major and **14′b** is a minor contributor (Scheme 8).

(Lithio)silylenoids Li[(Me$_3$Si)$_3$C]Si(X)Li (X = Cl, Br), which otherwise can be viewed as dilithio(halo)silanes (a particular case of dilithiosilanes in which one of the substituents is a halogen), were also recently claimed by the same group, being generated by the reductive dehalogenation of (Me$_3$Si)$_3$C—SiX$_3$ precursor with lithium naphthalenide (4 equiv).[29] Although reported as room-temperature-stable derivatives, dilithio(halo)silanes have eluded isolation as individual compounds, and accordingly, their structural identification has not yet been achieved. For example, the composition of Li[(Me$_3$Si)$_3$C]Si(X)Li was suggested based on the products of their trapping reactions and the high-field resonance of the central dianionic Si atoms observed at −106 ppm (for X = Br) and −110 ppm (for X = Cl) at −70 °C. Evidently, isolation, structural studies, and the search for more useful applications of such interesting species (for example, synthesis of functionalizable heavy alkene derivatives with a halogen atom at the doubly bonded Si atom) represent the next synthetic challenges in the field of stable dilithio(halo)silanes.

Scheme 9. Synthesis of the First 1-Sila- and 1-Germacyclo-pentadiene-1,1-diides 16 and 18

15 [E = Si]
17 [E = Ge]

16 [a: E = Si, M = Na;
b: E = Si, M = Li]
18 [E = Ge, M = Li]
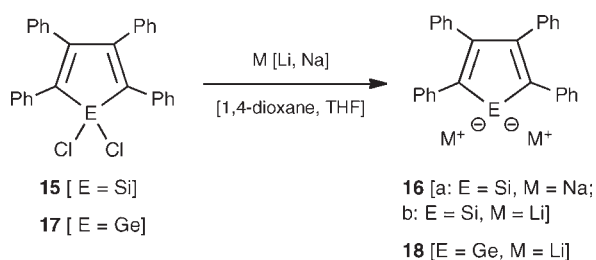
Scheme 10. Structural Modifications of Dilithiosilole and -Germole Derivatives 16b and 18[a]

a: η^5,η^5-**16b**
[E = Si, solv = THF]

b: η^5,η^1-**16b**
[E = Si, solv = THF]

c: η^5,η^5-**18**
[E = Ge, solv = 1,4-dioxane]

d: η^5,η^1-**18**
[E = Ge, solv = 1,4-dioxane]

[a] Experimental (a, c, d) and computational (a–d) results.

3. DIANIONIC DERIVATIVES OF THE 6π-ELECTRON SPECIES

3.1. Metallole 1,1-Dianions: Sila-, Germa-, Stanna-, and Plumbacyclopentadiene-1,1-diides. The heavy analogues of the cyclopentadiene dianion derivatives, that is, sila-, germa-, stanna-, and plumbacyclopentadiene-1,1-diides, have been known since the pioneering report by Joo and co-workers on the generation of the disodium salt of 2,3,4,5-tetraphenyl-1-silacy-clopentadiene-1,1-diide **15a** by the reduction of the 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene (1,1-dichlorosilole) precursor **14** with sodium in 1,4-dioxane (Scheme 9; E = Si, M = Na).[30]

The dilithium salt **16b** of the same 1-silacyclopentadiene-1,1-diide was subsequently prepared by the reduction of **15** with lithium in THF by Boudjouk and co-workers, who also discussed the potential cyclic aromatic π delocalization in **16b** based on its ^{13}C NMR data (Scheme 9; E = Si, M = Li).[31] The aromaticity of **16b** was further manifested in its peculiar structural features reported by West and co-workers: an essentially planar five-membered ring with nearly equal skeletal C—C bond lengths.[32] In contrast to computational studies at the MP2-(fc)/6-31+G*//MP2(fc)/6-31+G* level, which predicted the existence of both the symmetrical η^5-Li/η^5-Li "inverse-sandwich" structure (two Li ions above and below the ring plane: Scheme 10a without solvent molecules) and the unsymmetrical η^5-Li/η^1-Li configuration (one Li ion pentahap-tocoordinated to the five-membered ring and the other Li ion exclusively bound to the Si atom: Scheme 10b without solvent molecules) as minima on the potential energy surface, only the second structure was experimentally observed in **16b** (Scheme 10a).[32]

Scheme 11. Synthesis of Dilithium Salts of 1-Stannacyclopentadiene-1,1-diide 20 and 1-Plumbacyclopentadiene-1,1-diide 22

19 [E = Sn]
21 [E = Pb]

20 [E = Sn]
22 [E = Pb]
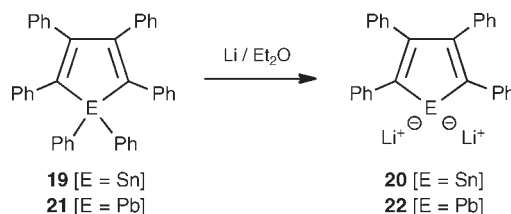
Both of the theoretically predicted germole dianion η^5,η^5 and η^5,η^1 structures (Scheme 10c,d without solvent molecules) were synthetically realized in the germanium version of **16b**, namely, the dilithium salt of the 1-germacyclopentadiene-1,1-diide **18** readily available by the reduction of 1,1-dichlorogermole **17** with lithium in THF (Scheme 9; E = Ge, M = Li).[33] The two structurally distinct forms, differing by the hapticity of coordination of one of the lithium ions, crystallized at different temperatures: the inverse-sandwich η^5,η^5 structure (Scheme 10c) at −20 °C, and the unsymmetrical η^5,η^1 structure (Scheme 10d) at room temperature. Similarly to its silicon analogue **16b**, germacyclopentadiene-1,1-diide **18** was classified as 6π-electron-aromatic based on the structural (equality of the cyclic C—C bond lengths) and energetic (aromatic stabilization energy of 13.0 kcal/mol calculated for the isodesmic reaction for the parent $H_4C_4Ge^{2-}$ dianion) criteria for aromaticity (B3LYP/6-311+G*).

Expanding the range of the heavy analogues of the cyclopentadiene-1,1-diide derivatives, 1-stannacyclopentadiene-1,1-diide **20** (the tin analogue of the above species) was prepared by the reduction of hexaphenyl-1-stannacyclopentadiene **19** with lithium (Scheme 11).[34]

In contrast to its silicon and germanium analogues **16b** and **18**, stannole dianion **20** exists in a single structural η^5,η^5 modification, although calculations revealed the presence of both η^5,η^5 and η^5,η^1 minimum structures. As in its lighter homologues (although to smaller degree), the aromatic π delocalization in stannacyclopentadiene-1,1-diide **20** was manifested by its structural (planar five-membered ring, equality of the skeletal C—C bonds) and magnetic {^{7}Li NMR resonance observed in a high field typical for aromatic lithium cyclopentadienides at −4.36 ppm; NICS(1) = −5.96 [B3LYP/TZDP for Sn and 6-31G(d) for C, H]} characteristics.

The lead analogue of **20**, 1-plumbacyclopentadienediide **22**, was prepared by the same procedure involving a reduction of hexaphenyl-1-plumbacyclopentadiene **21** with lithium (Scheme 11).[35] In its crystal structure, dianionic **22** revealed a distinct coordination mode for both lithiums: one of them was in direct η^5-bonding contact with the C_4Pb ring, also being solvated by a 1,2-dimethoxyethane (DME) molecule, whereas the other existed as a solvent-separated counterion solvated by three DME molecules. Similarly to the case of isostructural stannole dianion **20**, aromaticity of the plumbole dianion derivative **22** was deduced based on its geometric (planarity of the C_4Pb ring, equality of the cyclic C—C bonds) and magnetic {NICS(1) = −6.28 [B3LYP/ANO-RCC for Pb; 6-311G(2d) for Li, C, H; and 6-31G for C, H]} properties. However, in contrast to usual expectations, the plumbole ring-bound Li atom was not diagnostically shielded as in the case of other aromatic cyclopentadienide derivatives, being observed in the normal range for

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monohaptocoordinated lithiums at -1.11 ppm, which was explained by the rapid interchange between the η^5-bound and solvent-separated Li atoms in solution on the NMR time scale.

Apart from the above-described silole, germole, stannole, and plumbole dianions, several other dianionic heterocyclic systems, featuring sila-, germa-, and stannacyclopentadienediide fragments, have been described as exhibiting 6π-electron aromaticity to a greater or lesser extent. They include dipotassio-2,3,4,5-tetramethyl-1-silacyclopentadienediide,[36] dipotassio-2,3,4,5-tetramethyl-1-germacyclopentadienediide,[36b] dilithio-3-n-butyl-2-phenyl-1-silaindenediide,[37] disodio-3-n-butyl-2-phenyl-1-silaindenediide,[37] dipotassio-1-silafluorenediide,[38] dilithio-2,3,4,5-tetraethyl-1-germacyclopentadienediide (and its related dianionic trimer),[39,40] dilithio-2,3-diphenyl-1-germaindenediide,[41] disodio-2,3-diphenyl-1-germaindenediide,[41] dipotassio-9-germafluorenediide,[42] dilithio-3-n-butyl-2-phenyl-1-stannaindenediide,[43] and dipotassio-9-stannafluorenediide.[44]

The issue of aromaticity of the heavy analogues of the cyclopentadienediide derivatives was also computationally addressed by Schleyer and co-workers.[45] At high computational levels [MP2(fc)/6-31G*, RMP2(fc)/6-31+G**, and B3LYP/LanL2DZ, LanL2DZdp for Si, Ge, Sn, Pb, and 6-31+G*, 6-311++G** for C and H], they found appreciable aromaticity of the parent free dianions $H_4C_4E^{2-}$ (E = C–Pb), whereas aromaticity of their dilithium derivatives $(H_4C_4E)Li_2$ was even greater and remarkably constant for all derivatives regardless of the element E.

3.2. Heavy Analogues of the Cyclobutadiene Dianion Derivatives: Tetrasila-, Disiladigerma-, and Tetragermacyclobutadiene Dianions.

The 6π-electron cyclobutadiene dianion derivatives, in which the two negative charges are distributed within the four-membered ring, are isoelectronic with the cyclopentadienide ion species, although their stabilities are distinctly different.[46] If the singly charged cyclopentadienide ions greatly benefit from cyclic π delocalization and aromaticity, the delocalization in the doubly charged systems, such as cyclobutadiene dianions, results in the completely opposite destabilizing effect, caused by the unavoidable mixing of the two extra electrons resulting in a strong Coulomb repulsion. This unfavorable repulsive interaction outweighs the advantage of the π delocalization and aromatic stabilization, manifested in the pronounced trend of the cyclobutadiene dianion derivatives toward electron localization and separation and, as a result, to a remarkable departure of the four-membered ring from planarity. Moreover, in the planar delocalized cyclobutadiene dianion, four π electrons (of the total of six) are forced to occupy nonbonding orbitals, forming a pair of doubly degenerate HOMOs and giving rise to highly destabilizing repulsive 1,3-antibonding interactions. However, electropositive lithium counterions, directly bound to the cyclobutadiene dianion moiety, can significantly counteract the unfavorable Coulomb repulsion and mixing of the extra electrons, resulting in a greater extent of cyclic π delocalization and aromaticity: a hypothesis that was first proposed theoretically, with $[H_4C_4]^{2-}\cdot2Li^+$,[47] and then verified experimentally with $[(Me_3Si)_4C_4]^{2-}\cdot2Li^+$.[48] Although, strictly speaking, the above-described cyclobutadiene dianion derivatives are not geminal species because of the different alkali metal coordination mode, they are still dianionic (not many dianionic derivatives of the heavy group 14 elements have been reported to date[12k]) and very useful in organometallic syntheses; therefore, their heavy analogues, such as tetrasila- and tetragermacyclobutadiene dianions, are briefly discussed below.

Scheme 12. Synthesis of Dipotassium Derivatives of the Tetrasila-, Disiladigerma-, and Tetragermacyclobutadiene Dianions 24, 26, and 28
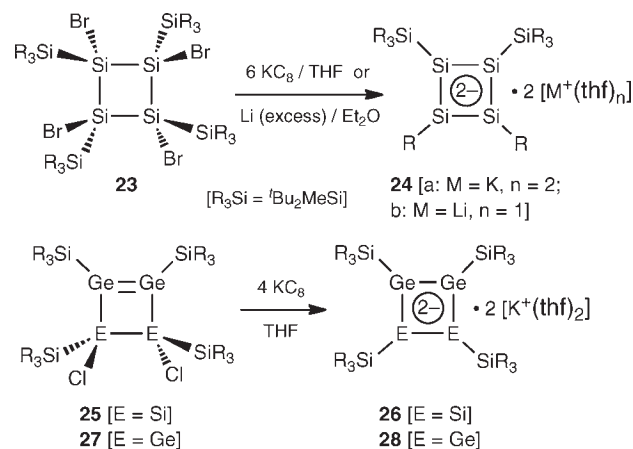
The tetrasila-, mixed disiladigerma-, and tetragermacyclobutadiene dianion dialkali metal derivatives 24, 26 and 28 were prepared by the reduction of either tetrabromocyclobutane 23 or dichlorocyclobutenes 25 and 27 (Scheme 12).[49]

All dipotassium derivatives 24, 26, and 28 are isostructural, featuring markedly folded four-membered rings (folding angles of $34°$ in 24a, $43°$ in 26, and $42°$ in 28) to which potassium ions, located above and below the ring, are η^2-bound at the 1,3 and 2,4 positions of the ring, instead of η^4 coordination indicative of a delocalized planar structure (the crystal structure of 24a is shown in Figure 3). The cyclic bonds in 24, 26, and 28 are not equal, with one shorter bond, one longer bond, and two bonds of intermediate lengths; therefore, the overall shape of the four-membered rings can be described as a folded trapeze. Accordingly, all skeletal atoms feature remarkably pyramidal geometry with the pyramidalization degree increasing as expected from silicon to germanium [sum of the bond angles around the skeletal atoms: $326/341°$ (in 24a, two types of differently pyramidalized skeletal silicons), $312(Ge)/339(Si)°$ (in 26), and $315/337°$ (in 28, two types of differently pyramidalized skeletal germaniums)]. Such structural deformations, both ring folding and pyramidalization of cyclic atoms, evidently originate from the high Coulomb repulsion between the two negative charges, resulting in electron localization that cannot be overcome by the influence of the spatially remote potassium ions. Thus, from the viewpoint of the structural requirements of aromaticity (ring planarity, cyclic bond equalization, tetrahaptocoordination of the potassium counterions), all heavy cyclobutadiene dianion derivatives 24, 26, and 28 are to be classified as nonaromatic compounds. This conclusion was further supported by magnetic property calculations at the B3LYP/6-31G(d) level: NICS(1) for all of the compounds was calculated to be positive, at $+6.1$ (for 24), $+4.3$ (for 26) and $+2.9$ (for 28), pointing to the absence of a diatropic ring current. However, the extent of π delocalization and cyclic aromaticity depends strongly on the degree of the cation–anion interaction: smaller cations can more closely approach the cyclobutadiene ring and, consequently, more effectively counteract the Coulomb repulsion to stabilize the system. For example, the dilithium derivative of the tetrasilacyclobutadiene dianion 24b, prepared by the reduction of 23 with Li in Et_2O (Scheme 12), exhibited the diagnostic η^4 coordination of both Li ions to the Si_4

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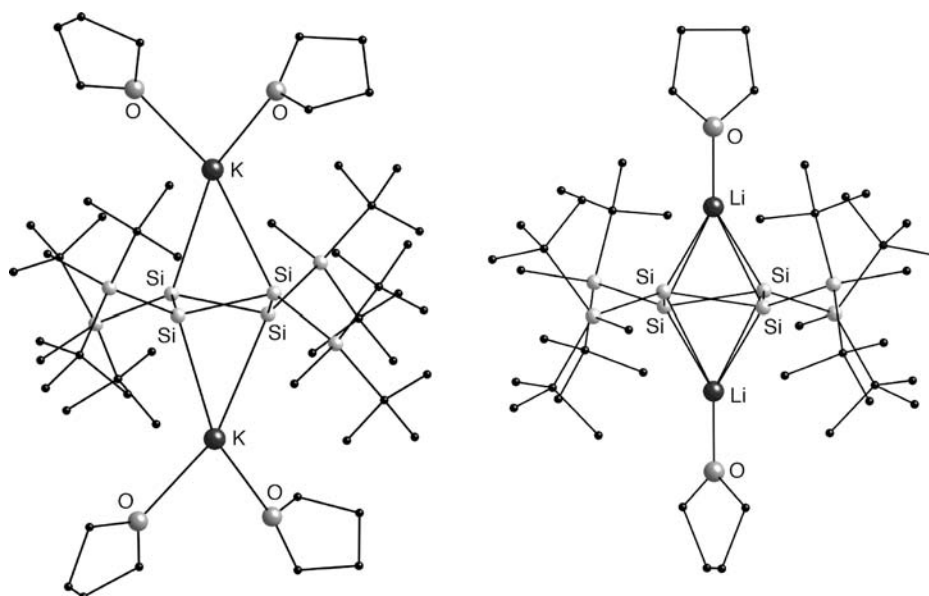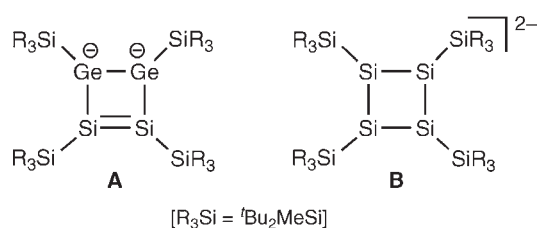dx.doi.org/10.1021/ic2006106 |*Inorg. Chem.* 2011, 50, 12303–12314

Figure 3. Crystal structures of **24a** (left) and **24b** (right). (CrystalMaker views: H atoms are not shown.)

Scheme 13. Major Resonance Contributions to the Overall Structure of Disiladigerma- and Tetrasilacyclobutadiene Dianion Derivatives 26 (Left) and 24a (Right)

ring (inverse-sandwich structure), which was markedly more planar than that in the dipotassium salt **24a** [folding angle, sum of the bond angles around the skeletal silicons: 34°, 326°/341° (in **24a**) versus 25°, 349° (in **24b**)] (Figure 3).[50]

The solution structures of the heavy cyclobutadiene dianion derivatives **24**, **26**, and **28** agree well with their solid-state structures. Thus, the skeletal Si atoms in heteronuclear **26** resonate in a low-field region at +113.7 ppm, diagnostic of the sp^2 silicons and pointing to the major contribution of a resonance form with a double bond between the Si atoms and the negative charges localized at the more electronegative Ge atoms (Scheme 13A). This agrees well with the general expectations based on the postulate that electronegativity difference favors electron localization.[49a,b]

In contrast, in the homonuclear tetrasilacyclobutadiene version **24a**, the resonances of the cyclic Si atoms were found at +17.0 ppm (that is, outside the range for doubly bonded Si atoms), thus pointing to a greater degree of cyclic π delocalization of negative charges in **24** (Scheme 13B).

Interestingly, the outcome of the reduction of precursor **25** depends on the nature of the metal used. Thus, when alkaline earth metals (Mg, Ca) were employed instead of alkali metals (Li, Na, K), the dianionic products featured different structures for the alkaline earth metal salts of disiladigermabicyclo[1.1.0]butane-2,4-diide derivatives **29** (M = Mg, n = 3; M = Ca, n = 4)

(Scheme 14).[51] The Mg, Ca, and Sr salts of the tetrasila- and disiladigermabicyclo[1.1.0]butane-2,4-diide derivatives **29** and **30** can alternatively be prepared by the transmetalation of the heavy cyclobutadiene dianions **24a** and **26** with MgBr$_2$, CaI$_2$, and SrI$_2$, respectively (Scheme 14).[51]

## 4. SYNTHETIC APPLICATIONS OF THE GEMINAL DIANIONIC DERIVATIVES OF THE HEAVY GROUP 14 ELEMENTS

Soon after their synthesis, readily available 1,1-dilithiosilanes R$_2$SiLi$_2$ and -germanes R$_2$GeLi$_2$ quickly became new organometallic reagents of paramount usefulness. Bearing two negative charges on the central atoms (Si or Ge), which one can describe as electron "extra-rich" centers, they were extremely, but nevertheless selectively, reactive toward a vast number of electrophiles. Our initial expectations (Scheme 1) were completely fulfilled: diverse acyclic, cyclic, polycyclic, and unsaturated compounds were made available in rather good yields. Of these, we were particularly interested in the development of reasonable routes to highly reactive and therefore synthetically very attractive organometallic compounds of two types: Si and Ge doubly bonded derivatives of the p-block (heavy analogues of alkenes) and d-block (heavy analogues of transition-metal carbene complexes) elements. Indeed, by reacting 1,1-dilithiosilanes **2a,b** and 1,1-dilithiogermane **12b** with the corresponding 1,1-dihalides, we were able to prepare a wide range of doubly bonded derivatives, including disilenes [(^{i}Pr$_3$Si)$_2$Si=SiMes$_2$,[16b] (^{i}Pr$_3$Si)$_2$Si=SiTip$_2$,[16b] (^{t}Bu$_2$MeSi)$_2$Si=SiMes$_2$,[16b] (^{t}Bu$_2$MeSi)$_2$Si=SiTip$_2$[16b]], silagermenes [(^{t}Bu$_2$MeSi)$_2$Si=GeMes$_2$,[16b] (^{t}Bu$_3$Si)$_2$Si=GeMes$_2$[52a]], silastannene [(^{t}Bu$_2$MeSi)$_2$Si=SnTip$_2$],[52b] germastannene [(^{t}Bu$_2$MeSi)$_2$Ge=SnTip$_2$],[52c] silaborene [(^{t}Bu$_2$MeSi)$_2$Si=BR (R = 2,2,6,6-tetramethylpiperidino)],[52d] phosphasilene (^{t}Bu$_2$MeSi)$_2$Si=PMes*,[52e] phosphagermene [(^{t}Bu$_2$MeSi)$_2$Ge=PMes*],[52e] tetrasilabuta-1,3-diene [(^{t}Bu$_2$MeSi)$_2$Si=Si(Mes)—Si(Mes)=Si(SiMe^{t}Bu$_2$)$_2$],[52f] and the Schrock-type hafnium—silylene complex [(η^5-C$_5$H$_4$Et)$_2$Hf(PMe$_3$)=Si(SiMe^{t}Bu$_2$)$_2$].[52g] Even more unusual compounds, such as anionic 1,3-disila-2-gallata-

Scheme 14. Synthesis of Alkaline Earth Metal Derivatives of Disiladigerma- and Tetrasilabicyclo[1.1.0]butane-2,4-diide Derivatives 29 and 30

25 [R$_3$Si = ^{t}Bu$_2$MeSi]

29 [E = Ge; M = Mg, Ca, Sr; n = 3 or 4]
30 [E = Si; M = Ca; n = 4]

24a [E = Si]
26 [E = Ge]
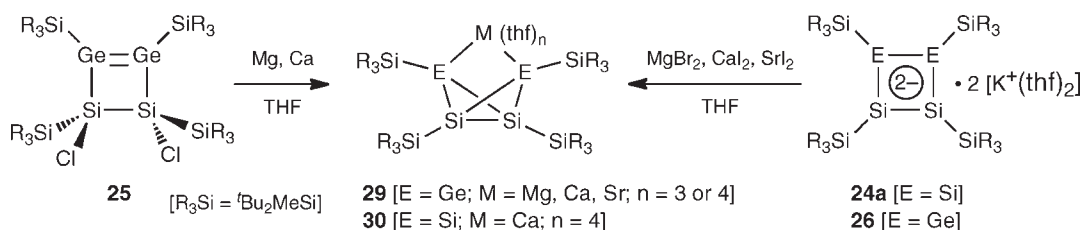
Scheme 15. Reaction of Metastable Dilithiostannane Derivatives Tbt(Dip)SnM$_2$ (M = Li, K), Giving a Rearrangement Product Instead of the Expected Stannacyclopropabenzene
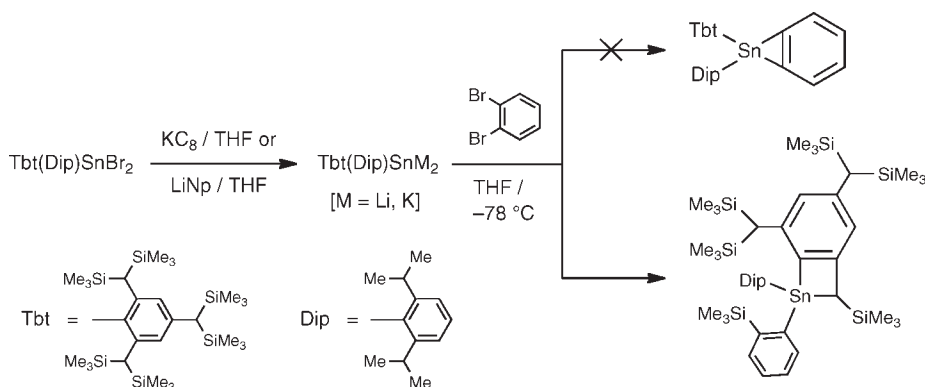
Scheme 16. Synthesis of Mo and W Silylene Complexes 31 (M = Mo, W)

30 [R$_3$Si = ^{t}Bu$_2$MeSi]

31
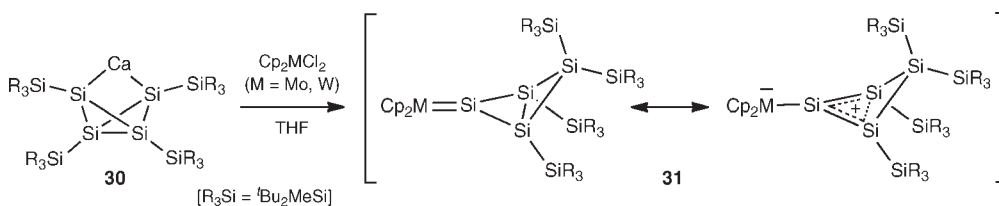
and -indataallenic derivatives [(^{t}Bu$_2$MeSi)$_2$Si•••M•••Si(SiMe-^{t}Bu$_2$)$_2$]$^-$·[Li$^+$(THF)$_4$] (M = Ga, In),[53a] anionic 1,3-digerma-2-gallata- and -indataallenic derivatives [(^{t}Bu$_2$MeSi)$_2$-Ge•••M•••Ge(SiMe^{t}Bu$_2$)$_2$]$^-$·[Li$^+$(THF)$_4$] (M = Ga, In),[53b] heavy cyclopropene analogues {trisilirene cyclo-[−(^{t}Bu$_2$MeSi)$_2$-Si−Si(Si^{t}Bu$_3$)=Si(Si^{t}Bu$_3$)−],[53c] trigermirene cyclo-[−(^{t}Bu$_2$MeSi)$_2$Ge−Ge(SiMe^{t}Bu$_2$)=Ge(SiMe^{t}Bu$_2$)−],[53d] and 1H-siladigermirene cyclo-[−(^{t}Bu$_2$MeSi)$_2$Si−Ge(SiMe^{t}Bu$_2$)=Ge(SiMe^{t}Bu$_2$)−]^{53d}}, and heterocyclic seven-membered ring [1,3,2]oxasilaborepane and [1,3,2]oxagermaborepane,[53e] were readily available using **2b** and **12b** as starting materials. For the coupling reactions of dilithiosilane or dilithiogermane derivatives (^{t}Bu$_2$MeSi)$_2$ELi$_2$ (E = Si, Ge) with the geminal dihalides R′EX$_2$ forming the above-described doubly bonded compounds, dichlorides R′ECl$_2$ proved to be the reagents of choice among other dihalides, and THF was found to be the best solvent. Typically, under such reaction conditions, the yields were quite reasonable, ranging from moderate (30−60%) to good (70−90%). However, sometimes, undesirable lithium−halogen

Scheme 17. Synthesis of the Pentasilatricyclo-[2.1.0.0^{2,5}]pentane Derivatives

30 [R$_3$Si = ^{t}Bu$_2$MeSi]
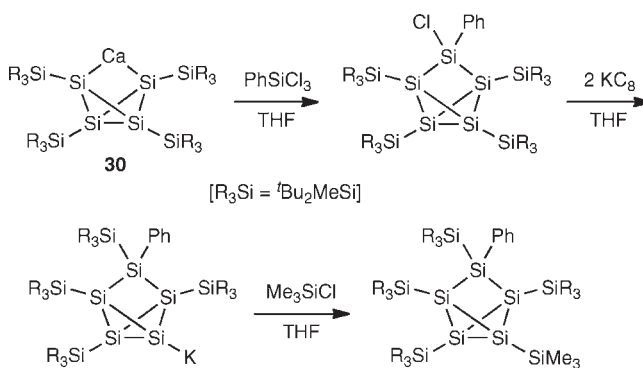
exchange was found to be a predominant pathway in THF, resulting in the generation of silylenoid/germylenoid species

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Scheme 18. Synthesis of the Hexasiladigermacubane Dianion Dipotassium Salt Derivative
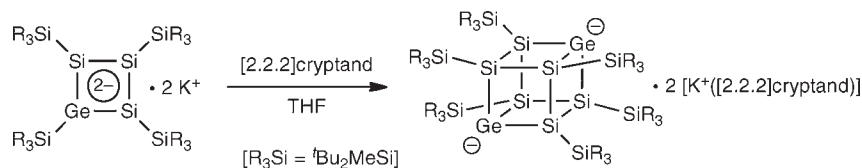
(^{t}Bu$_2$MeSi)$_2$E(X)Li, followed by α-elimination of LiX and oligomerization of the transient silylene/germylene (^{t}Bu$_2$-MeSi)$_2$E:. In such cases, nonpolar toluene was used as an effective substitute for polar THF.

The metastable geminal dilithiosilane Tbt(Dip)SiLi$_2$ and dilithiogermane Tbt(Dip)GeLi$_2$ derivatives reported by Tokitoh and co-workers were employed for the preparation of a series of bicyclic and tricyclic compounds, featuring annelated benzene rings, namely, silacyclopropabenzene,[54a,b] germacyclopropa-benzene,[54c] bis(silacyclopropa)benzene[54b,d] and bis(germacyclo-propa)benzene,[54e] prepared by the reaction of Tbt(Dip)SiLi$_2$ and Tbt(Dip)GeLi$_2$ with 1,2-dibromobenzene and 1,2,4,5-tetra-bromobenzene, respectively. Their tin analogue, Tbt(Dip)SnLi$_2$, however, failed to form the expected stannacyclopropabenzene, giving a rearrangement product instead (Scheme 15).[25]

Dilithio(halo)silanes (lithiosilylenoids), as was mentioned in section 2.4, still have not found synthetically useful applications. Nor have the metallole 1,1-dianions described in section 3.1; in contrast, metallole monoanions have been successfully used for the preparation of a variety of transition-metal complexes featuring sila- or germacyclopentadienyl ligands.

Highly reactive heavy analogues of the cyclobutadiene dianion, namely, tetrasila- and tetragermacyclobutadiene dianion derivatives **24a** and **28**, have also proved to be extremely useful organometallics with great synthetic potential, especially in the preparation of novel coordination compounds. Thus, starting from either **24a** or **28**, several transition-metal complexes featuring either tetrasila- or tetragermacyclobutadiene ligands are readily available, including the anionic dicarbonylcobalt complex [η^4-{(^{t}Bu$_2$MeSi)$_4$Si$_4$}]Co(CO)$_2$$^-$·[K$^+$(diglyme)$_2$(THF)],[55a] tricarbonyliron complex [η^4-{(^{t}Bu$_2$MeSi)$_4$Si$_4$}]Fe(CO)$_3$,[55b] tri-carbonylruthenium complex [η^4-{(^{t}Bu$_2$MeSi)$_4$Si$_4$}]Ru(CO)$_3$,[55c] sandwich cyclopentadienyl cobalt complexes [η^4-{(^{t}Bu$_2$MeSi)$_4$-Si$_3$E}]Co(η^5-C$_5$H$_5$) (E = Si, Ge),[55d] anionic cyclopentadienyl ruthenium complex [η^4-{(^{t}Bu$_2$MeSi)$_4$Si$_4$}]Ru(η^5-C$_5$Me$_5$)$^-$·[K$^+$(THF)$_2$],[55e] tricarbonyliron complex [η^4-{(^{t}Bu$_2$MeSi)$_4$-Ge$_4$}]Fe(CO)$_3$,[49c] and sandwich cyclopentadienyl cobalt complex [η^4-{(^{t}Bu$_2$MeSi)$_4$Ge$_4$}]Co(η^5-C$_5$H$_5$).[49c] Given the peculiar struc-tures and lack of other synthetic routes for these novel coordination compounds, the yields of 40−70% are more or less reasonable.

The calcium salt of the tetrasilabicyclo[1.1.0]butane-2,4-diide derivative **30** can also be used for the synthesis of base-free Mo and W bicyclic silylene complexes **31** stabilized by a homoaro-matic contribution (Scheme 16).[51b]

Apart from the preparation of coordination compounds, both heavy cyclobutadiene dianion and heavy bicyclo[1.1.0]butane-2,4-diide salts are very useful as the starting materials for poly-cyclic cages and clusters: pentasilatricyclo[2.1.0.0^{2,5}]pentanes (from **30**, Scheme 17),[56a] hexasiladigermacubane dianion dipo-tassium salt (from a trisilagermacyclobutadiene dianion deriva-tive, Scheme 18),[56b] and 1,2,5,6-tetrasilabenzobenzvalene (from **24a**, Scheme 19).[56c]

Scheme 19. Synthesis of the 1,2,5,6-Tetrasilabenzobenzva-lene Derivative
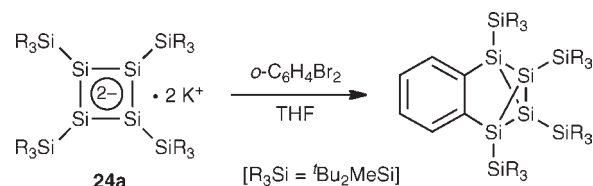
4. SUMMARY AND OUTLOOK

In the present overview, we have discussed the most recent achievements in the new field of geminal dianionic derivatives of the heavy group 14 elements. The syntheses, structures, and synthetic applications of the most important classes of these compounds, such as the derivatives of 1,1-dilithiosilanes, -ger-manes, and -stannanes; lithiosilylenoids; and heavy group 14 element analogues of the cyclopentadiene-1,1-diide and cyclo-butadiene dianion. As for future developments, the synthesis of the heaviest representatives, such as 1,1-dilithiostannanes and -plumbanes, is one of the most obvious prospective goals. Greater variations of the substituents R at the dianionic center E are also highly desirable; therefore, the development of new general synthetic strategies for the geminal dianionic derivatives R$_2$ELi$_2$ (E = Si−Pb) is one of the immediate tasks to be undertaken in this field. Solving this problem will definitely expand the scope of the synthetic applicability of R$_2$ELi$_2$, thus allowing easy access to a variety of unsaturated derivatives featuring doubly bonded heavy group 14 elements, the key precursors for a vast number of novel organometallics. The most promising utiliza-tion of the geminal dianionic compounds R$_2$ELi$_2$ is the preparation of heavy analogues of transition-metal carbene complexes of the type L$_n$M=ER$_2$ (M = transition metal), which can be further used in such commercially important reactions as alkene and alkyne metathesis processes. Investi-gations in this direction are among the top priorities for the organometallic chemists working in the field.

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■ ACKNOWLEDGMENT

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dx.doi.org/10.1021/ic2006106 |*Inorg. Chem.* 2011, 50, 12303–12314

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