Si–H Bond Activation

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Radical Activation of Si–H Bonds by Organozinc and Silylzinc Reagents: Synthesis of Geminal Dizinciosilanes and Zinciolithiosilanes**

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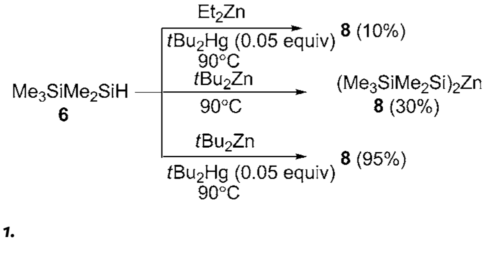
Dedicated to Professor Akira Sekiguchi on the occasion of his 60th birthday

Organozinc compounds are very useful reagents in synthesis, and in analogy to organomagnesium and organolithium compounds are used mainly as nucleophiles.[1a–c] Some reports are also available for silylzinc compounds.[1d–g] At the same time, as Zn and Hg are both Group 12 elements, organozinc compounds are expected also to exhibit some of the characteristic reactions of organomercury compounds. For example, organomercury and silylmercury compounds undergo radical reactions both thermally and photochemically and activate Si–H bonds, leading to silylmercury compounds.[2–4] Such compounds are also excellent precursors for the preparation of silyl anions by transmetalation.[2a,3,4a] The possibility to replace in these reactions the highly toxic organomercury compounds by the less toxic organozinc compounds is attractive. The radical chemistry of organozinc compounds, initiated by dioxygen, is a vigorously developing field of organic chemistry with many applications in synthesis.[5] In contrast, to the best of our knowledge, there are no reports on radical reactions of silylzinc compounds.

Activation of Si–H bonds is a very useful reaction synthetically and therefore it is intensively studied, both in academia and in industry.[6–8] There are two common strategies for Si–H bond activation: by radical initiators [7] and by transition-metal catalysts.[8] Silylzinc reagents became recently popular synthons in organic chemistry owing to their selective and mild nucleophilic nature.[1d–g,9] Therefore, a single-pot reaction leading to zinciosilanes by activation of Si–H bonds has a great synthetic potential. Furthermore, in analogy to the synthesis of bismercuriosilanes,[2b,3a,b] activation of dihydridosilanes by diorganozinc or disilylzinc compounds can lead, in a single-step reaction, to new geminal dizinciosilanes. These interesting dimetallic reagents are potentially very attractive reagents, in a similar fashion to geminal dizinciomethanes, their organic analogues.[10]

Herein, we present the first examples of radical activation of a Si–H bond in R_3SiH ($R = Me_3Si$, Me_3SiMe_2Si) and Me_3SiMe_2SiH by R'_2Zn ($R' = t$Bu, Et) and by $(tBuMe_2Si)_2Zn$ (**1**) (for experimental details see Supporting Information). Using this reaction we synthesized the silylenoid-type compound $[Cl(tBuMe_2Si)_2Si]_2Zn$ (**2**), which upon lithiation yields the zinc-bridged bis(silyllithium) $[(thf)_2Li(tBuMe_2Si)_2Si]_2Zn$ (**3**), the first known compound with lithium and zinc bonded to the same Group 14 atom. We have also synthesized and fully characterized the novel tetrametallic bis(zinciosilyllithium)silane $[(thf)_3Li(tBuMe_2Si)_2SiZn]_2Si(SiMe_2tBu)_2$ (**4**).

The reactions of Et_2Zn, which is commercially available, and of tBu_2Zn with $tBuMe_2SiH$ (**5**), Me_3SiMe_2SiH (**6**), and $(Me_3Si)_3SiH$ (**7**) were first studied. The reaction of Et_2Zn or of tBu_2Zn with **5** was disappointing; **5** remained unchanged after 3 h at 90 °C, even in the presence of azobisisobutyronitrile (AIBN) or tBu_2Hg as radical initiators. However, this situation changes upon silyl substitution of the silane. Thus, reaction of Me_3SiMe_2SiH (**6**) with tBu_2Zn for 3 h at 90 °C yielded $(Me_3SiMe_2Si)_2Zn$ (**8**) in 30 % yield. When a minute amount of tBu_2Hg, a radical initiator, was added the yield of **8** increased to 95 %. In contrast, **6** was recovered unreacted after reaction with neat Et_2Zn and yielded only 10 % of **8** in the presence of tBu_2Hg at 90 °C for 3 h (Scheme 1).



Scheme 1.

With the branched silane $(Me_3Si)_3SiH$ (**7**), zincation of the Si–H bond was much smoother. Reaction of **7** with neat Et_2Zn at 60 °C for 20 min produces $[(Me_3Si)_3Si]_2Zn$ (**9**) in 30 % yield. In the presence of 0.03 equivalents of AIBN or tBu_2Hg as radical initiators, the yield of **9** increased to 90 %. Reaction of **7** with tBu_2Zn under the same conditions gave **9** in 70 %

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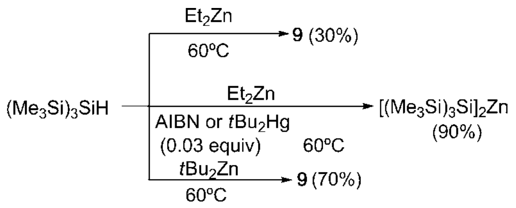


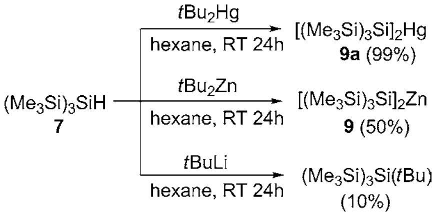
Scheme 2.

yield, even without addition of AIBN (Scheme 2). Previously, **9** was obtained by the less-convenient reaction of $(Me_3Si)_3SiLi$ with $ZnCl_2$.[11] As both **7** and Et_2Zn are commercially available, **9** becomes now an easily accessible reagent.

Our attempts to carry out the above reactions in the presence of dry dioxygen, which is effective in initiating radical reactions with dialkyl zinc,[5] failed, resulting in complex product mixtures with no traces of the desired silylzinc compounds. The different reaction course in the presence of dioxygen is probably due to the extremely high affinity of intermediate silyl radicals to oxygen, thus terminating the radical chain-propagation step. Thus, for a controlled activation of Si–H bonds, oxygen must be excluded.

The differences in the yields between the reactions of tBu_2Zn and Et_2Zn with $(Me_3Si)_3SiH$ (**7**) versus Me_3SiMe_2SiH (**6**) versus $tBuMe_2SiH$ (**5**) probably result from the fact that tBu_2Zn decomposes faster than Et_2Zn[12] to yield $tBu^{\bullet}$ radicals, which initiate the radical chain activation of the Si–H bond. Similarly, tBu_2Hg is less thermally stable than Et_2Hg.[4a] Furthermore, the ease of hydrogen abstraction follows the order **7** > **6** > **5**, reflecting the thermodynamic stability order of the corresponding silyl radicals, which become more stable the higher the number of silyl substituents.[2a,d,7]

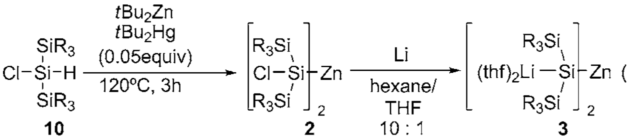
To study the effect of the metal on the metalation reaction, $(Me_3Si)_3SiH$ was reacted in hexane with tBu_2Hg, tBu_2Zn, and $tBuLi$ at room temperature for 24 h. With tBu_2Hg, $[(Me_3Si)_3Si]_2Hg$ (**9a**) was obtained in 99 % yield. With tBu_2Zn, the corresponding disilylzinc **9** was obtained in 50 % yield. In contrast, with $tBuLi$, **7** remained mostly unreacted, and only 10 % of $(Me_3Si)_3Si(tBu)$ was obtained (Scheme 3).[13]



Scheme 3.

The above experiments and in particular the higher yields obtained in the presence of AIBN or tBu_2Hg (Scheme 2) suggest that in analogy to R_2Hg,[2b,3a,b] R_2Zn reacts with silanes by a radical mechanism.

Encouraged by these results, we aimed to prepare functionalized zinciosilanes. Reaction of chlorosilane $Cl(tBuMe_2Si)_2SiH$ (**10**)[14] with tBu_2Zn for 3 h at 120 °C in the presence of 0.05 equivalent of tBu_2Hg yields the desired product $[Cl(tBuMe_2Si)_2Si]_2Zn$ (**2**) in 65 % yield [Eq. (1)].



(1)

$R_3Si = tBuMe_2Si$

Compound **2** can be classified as a silylenoid that is geminally substituted at silicon by an electronegative chlorine atom and an electropositive zinc atom. Lithiation of **2** with excess metallic lithium in a 10:1 hexane/THF mixture at room temperature for 4 h yields the zinc bridged bis(silyllithium) (**3**) in 60 % yield. Compound **3** was isolated by crystallization from hexane at room temperature, and its structure, as determined by X-ray crystallography, is shown in Figure 1.[15]

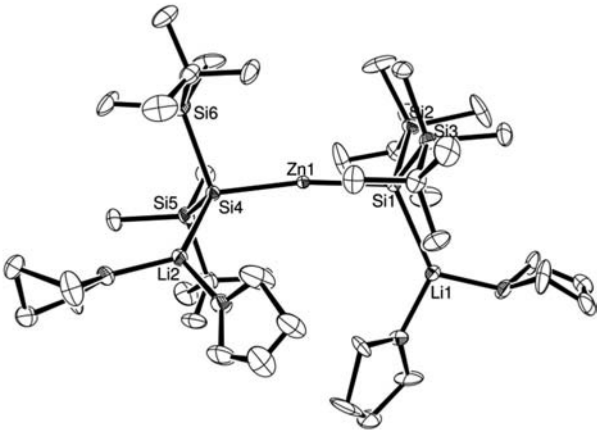
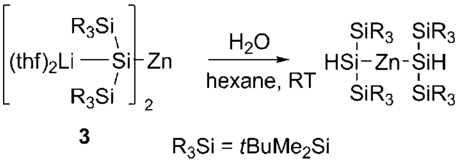


Figure 1. ORTEP of the molecular structure of compound **3**. Ellipsoids are set at 10 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [°], and dihedral angles [°]: Si1–Zn1 2.3620(15), Si4–Zn1 2.3620(15), Si1–Li1 2.531(9), Si4–Li2 2.531(9), Si1–Si2 2.336(2), Si1–Si3 2.341(2), Si4–Si5 2.336(2), Si4–Si6 2.341(2); Si1-Zn1-Si4 170.89(7), Zn1-Si1-Li1 116.0(2), Zn1-Si4-Li2 116.0(2), Li1-Si1-Si4-Li2 54.56(3), Si6-Si4-Si1-Li1-178.16(2), Si6-Si4-Si1-Si2 −50.88(5).

Compound **3** is the first isolated molecule with zinc and lithium atoms bonded to the same Group 14 atom: either silicon, carbon, or germanium. Attempts to synthesize compounds having the Li-C-Zn connectivity failed as these compounds spontaneously yield four-membered $(CZn)_2$ rings.[16] Compound **3** is the second isolated geminal dimetallosilane having two different metals (the first is a mercury analogue of **3**[2b]).

The X-ray structure of **3** reveals that the zinc atom in **3** is not solvated, whereas the lithium atoms are each solvated by two THF molecules. The Si1-Zn1-Si4 angle of 170.9° is slightly distored from the ideal 180° angle previously reported for disilylzinc.[17a] The bulky silyl substituents and the $(thf)_2Li$ groups are nearly staggered in respect to the Si1–Si4 axis. The Si–Zn bond lengths in **3** (2.362 Å) are similar to previously reported Si–Zn bond lengths (2.356–2.399 Å[11,17]). The Si–Li bond lengths (2.531 Å) are similar to *r*(Si–Li) in the analogous mercury-bridged bis(silyllithium) (2.53 Å[18]).

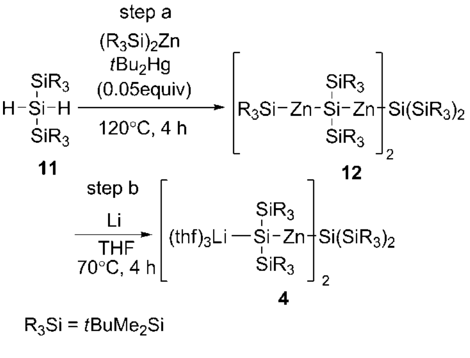
The ^{29}Si NMR chemical shift of the anionic silicon atoms (Si1 and Si4) in **3** of −192 ppm is shifted upfield by 80 ppm from that of $Hg[Si(SiR_3)_2Li]_2$.[18] This is consistent with the lower electronegativity of zinc compared with mercury (1.65 vs. 2[19]) and may indicate a higher nucleophilicity of Si1 and Si4 atoms in **3** compared with those in $Hg[Si(SiR_3)_2Li]_2$. Preliminary studies show that the Si–Zn bonds of **3** can be retained while the Si–Li bonds react. For example, hydrolysis of **3** leads to protonation of the Si–Li bonds while the Si–Zn bonds are retained [Eq. (2)]. In contrast, under similar conditions, $(tBuMe_2Si)_2Zn$ is hydrolyzed to $tBuMe_2SiH$.



(2)

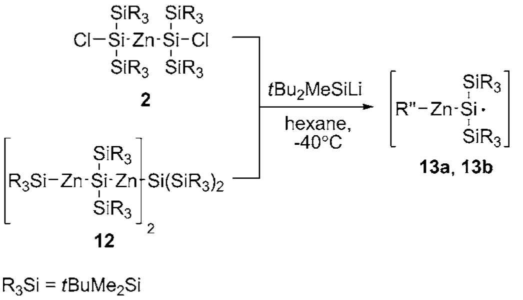
Attempting to synthesize a geminal bis(zinciosilane), $(tBuMe_2Si)_2SiH_2$ (**11**) was reacted with tBu_2Zn in the presence of 0.05 equivalent of tBu_2Hg. After 4 h at 120 °C an air-sensitive material that was insoluble in hydrocarbon solvents was obtained, but owing to its low solubility we were unable to characterize the reaction products.

In contrast, reaction of **11** with $(tBuMe_2Si)_2Zn$ (**1**) with 0.05 equivalents of tBu_2Hg in hexane produced the tetrazinciosilane **12** after 4 h at 120 °C in 60 % yield [Eq. (3), step a]. This reaction is analogous to the synthesis of silylmercury oligomers, obtained in the reaction between **11** and $(tBuMe_2Si)_2Hg$.[3a] The formation of **12** supports a radical mechanism for this reaction, similarly to that of the analogous silylmercury compounds.[20]



(3)

The fact that all the reactions presented above are induced by radical initiators strongly suggests that these reactions involve zinc-substituted silyl radicals. Attempts to observe such radicals by conducting the reactions within the EPR probe were unsuccessful, which may reflect the short lifetimes and thus low concentrations of the intermediate radicals. However, we could show that zincio-substituted silyl radicals are viable species. Thus, in reactions of **2** or of **12** with $tBu_2MeSiLi$ in hexane at about −40 °C, persistent $R''Zn(tBuMe_2Si)_2Si^{\bullet}$ radicals (**13a** and **13b**) were observed (Scheme 4).[21] Radicals **13a** and **13b** were characterized by the relatively small hyperfine coupling constant with the $^{29}Si_{\alpha}$ nuclei (25.3 G and 31.1 G, respectively), which is typical for α-metal-substituted silyl radicals.[3b,22] **13a** and **13b** differ in their R″ substituents, which were not yet determined.



Scheme 4.

Unfortunately, attempts to crystallize **12** failed. However, lithiation of **12** with dispersed lithium in THF for 4 h at 70 °C yields bis(zinciosilyllithium)silane **4** in 70 % yield [Eq. (3), step b]. Compound **4** was crystallized from hexane and the X-ray molecular structure is shown in Figure 2.[23] The formation of compound **4** supports the formula proposed for **12**.

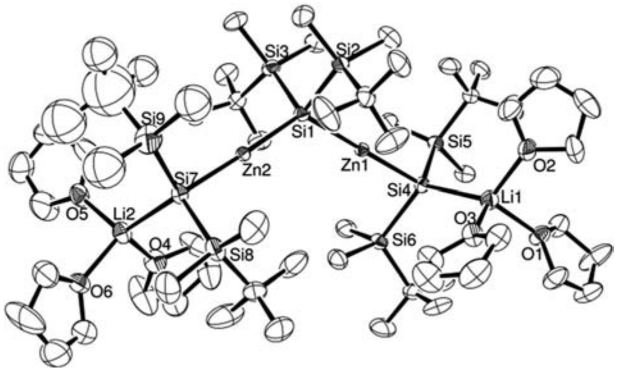


Figure 2. ORTEP of the molecular structure of compound **4**. Ellipsoids are set at 20 % probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [°], and dihedral angles [°]: Si1–Zn1 2.411(2), Si4–Zn1 2.367(19), Si1–Zn2 2.403(2), Si7–Zn2 2.355(2), Si4–Li1 2.737(12), Si7–Li2 2.731(12), Si1–Si2 2.348(3), Si1–Si3 2.348(3), Si7–Si8 2.336(3); Zn1-Si1-Zn2 123.66(6), Si7-Si9 2.322(4), Si4-Si5 2.357(3), Si4-Si6 2.355(3), Si1-Zn1-Si4 174.87(6), Si1-Zn2-Si7 175.51(6), Zn1-Si4-Li1 109.1(3), Zn2-Si7-Li2 115.7(3), Li2-Si7-Si4-Li1 −144.81(3), Si9-Si7-Si4-Si5 −75.99(4), Li1-Si4-Si1-Si7 −86.02(3), Li1-Si4-Zn1-Si1 −6.98(6), Li1-Si4-Si7-Li2 −144.81(2).

Compound **4** is the first characterized tetrametallosilane chain, and it has both a geminal dizinciosilyl unit and two heterozinciolithiosilyl fragments. Thus, **4** contains four active metallic sites composed of two different metals, which can act as nucleophilic sites or as radical precursor sites.

The zinc atoms in **4** are not solvated, similar to **3**, but each of the lithium atoms in **4** is solvated by three THF molecules (only two THF per Li in **3**). The two lithium atoms are located on opposite sides of the Si4-Si1-Si7 plane. The average Si−Zn bond length in **4** (2.384 Å) is slightly longer than *r*(Si−Zn) in **3** (2.362 Å). The Si−Li bond lengths in **4** are in the range of *r*(Si−Li) distances (2.64–2.77 Å[24]) in other THF-solvated lithiosilanes.

In conclusion, we have demonstrated that Si−H bonds can be activated by organozinc and silylzinc compounds in the presence of minute amounts of radical initiators, such as *t*Bu$_2$Hg or AIBN, yielding zinciosilanes in good yields in a single-pot reaction. Furthermore, activation of dihydridosilanes leads in a single-pot reaction to geminal dizinciosilanes. We also synthesized the novel zincio-bridged disilyllithiums **3** and **4**, which have three and four metal–silicon bonds, respectively. We continue to study the scope of the approach presented herein for the synthesis of other novel zinciosilane reagents, as well as to explore the chemistry and the synthetic versatility of these novel reagents.

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[15] Crystallographic data for **3**: C$_{40}$H$_{92}$Li$_2$O$_4$Si$_6$Zn, $M_r = 884.96$, monoclinic, space group *C*2/*c*, $a = 14.929(3)$, $b = 19.260(4)$, $c = 20.536(4)$ Å, $\beta = 102.43(3)°$, $V = 5766(2)$ Å^3, $Z = 4$, Nonius Kappa CCD, Mo$_{K\alpha}$ radiation (0.71073 Å), 240 K, $2\Theta_{max} = 25°$, $R = 0.0636$ $(I > 2\sigma I)$, w$R2 = 0.1561$ $(I > 2\sigma I)$, $Rw = 0.1421$ (all data), GOF = 0.862. Further crystallographic data of **3** is given in the Supporting Information. CCDC 858766 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[21] The EPR spectra of radicals **13a** and **13b** is given in the Supporting Information.

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[23] Crystallographic data for **4**: $C_{60}H_{138}Li_2O_6Si_9Zn_2$, $M_r = 1353.13$, triclinic, space group $P\bar{1}$, $a = 14.515(3)$, $b = 16.915(3)$, $c = 19.109(4)$ Å, $\alpha = 69.30(2)$, $\beta = 72.12(2)$, $\gamma = 83.58(2)°$, $V = 4176.8(14)$ Å^3, $Z = 2$, Nonius appa CCD, $Mo_{K\alpha}$ radiation (0.71073 Å), 240 K, $2\Theta_{max} = 25°$, $R = 0.0766$ ($I > 2\sigma I$), $wR2 = 0.1925$ ($I > 2\sigma I$), $Rw = 0.1540$ (all data), GOF = 1.004. CCDC 858767 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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