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Mercury-Substituted Silyl Radical Intermediates in Formation and Fragmentation of Geminal Dimercury Silyl Compounds[†]

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The first known trimercury and cyclic tetramercury organosilicon compounds containing the $-(Hg{-}R_2Si{-}Hg)-$ fragment, $(t\text{-}BuHgSiR_2)_2Hg$ [R = i-Pr_3Si (**3a**), R = t-Bu_2MeSi (**3b**)] and $[(i\text{-}Pr_3Si)_2SiHg]_4$ (**6**), were synthesized and characterized. Reactions of the corresponding H_2SiR_2 silanes with t-Bu_2Hg yielded **3a** and **3b**. **6** was obtained from a hexane solution of **3a** that was stored at room temperature for 6 months. The molecular structures of **3a**, **3b**, and **6** were determined by X-ray analysis. Photolysis and thermolysis of **3** leads to formation of mercury-substituted silyl radicals (previously unknown). Their structure was confirmed by a detailed EPR study and by trapping with 2,2,6,6,-tetramethyl-1-piperidinyloxyl (TEMPO) radical. A radical mechanism for the formation of **3** was evidenced by the observation of EPR signals in the reaction mixture of Hg-substituted silyl radicals.

Introduction

Silylmercury compounds have been known since the 1960s[1] and recently gained renewed interest as precursors in the synthesis of silyllithium compounds[2] and in the generation of silyl radicals,[3] as shown in eq 1. Silyllithium compounds are prepared in high yields from silylmercury compounds by reaction with lithium metal (lithiation) in nonsolvating media, and this is the main synthetic method for the preparation of silyllithium aggregates.[4] Silylmercury compounds are excellent precursors for the selective generation of silyl radicals, and unlike in other methods (e.g., silanes[3]) there is no need to use initiators.[5] Moreover, with silyl mercury precursors only the Si−Hg bond is fragmented to produce the silyl radical, in contrast to polysilanes, where several fragmentation modes are possible.[6]

By analogy, geminal dimercury silicon compounds of the type $R'-(Hg{-}SiR_2{-}Hg)-R'$ may serve as precursors for the preparation of dilithium silicon compounds[7,8] as well as of the corresponding silylenes,[9] as shown in eq 2.

$$2\ R_3Si^{\bullet} \xleftarrow[-Hg]{h\nu} (R_3Si)_2Hg \xrightarrow[-Hg]{Li} 2\ R_3SiLi \qquad (1)$$

$$R_2Si\colon \xleftarrow[\substack{-\,2\,R'^{\bullet}\\ -\,2\,Hg}]{h\nu} R'{-}Hg{-}SiR_2{-}Hg{-}R' \xrightarrow[\substack{-2\,R'Li\\ -\,2\,Hg}]{Li} Li{-}SiR_2{-}Li \qquad (2)$$

Recently, we used geminal dimercury silicon compounds in the synthesis of the first known nonsolvated

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[†] This paper is dedicated to Professor Paul von Rague Schleyer, a great scientist, a mentor, and a friend, on the occasion of his 75th birthday.

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aggregated 1,1-dilithiosilane[10] and of the unique geminal dimetallic organosilicon compound $[(THF)_2{\cdot}Li(i\text{-}Pr_3Si)_2Si]_2Hg$, (**1a**)[11]—the first known geminal dimetallasilane having two different metals, Li and Hg, bonded to the same silicon atom.

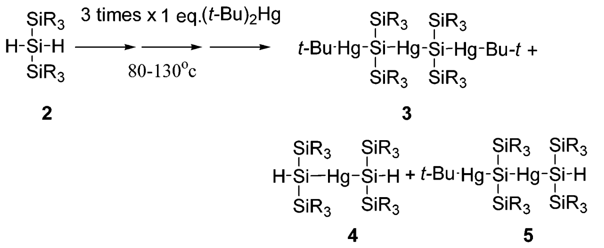
In this paper we report the generation from geminal silyl dimercury compounds of unprecedented species, Hg-substituted silyl radicals. We also report the synthesis and molecular structure of several new compounds having a geminal dimercury silyl fragment including trimercurysilyl and cyclic tetramercurysilyl derivatives.

Results and Discussion

Synthesis of Geminal Dimercury Silicon Compounds. West and co-workers reported the synthesis of silylmercury oligomers of the general formula $(-Hg-SiPhMe-)_n$ by reaction of $PhMeSiH_2$ with $t\text{-}Bu_2Hg$.[12] We have utilized the same type of reaction, using dihydridosilanes, R_2SiH_2, with increasing steric size of the R substituents, i.e., R = Me_3Si, Et_3Si, $i\text{-}Pr_3Si$, and $t\text{-}Bu_2MeSi$, aiming at avoiding the observed oligomerization.

Thermolysis of a mixture of $t\text{-}Bu_2Hg$ and either $(Me_3Si)_2SiH_2$ or $(Et_3Si)_2SiH_2$ in 2:1 equimolar ratio yielded complex product mixtures containing oligomeric silylmercury compounds (which were not isolated) as the major products.

On the other hand, thermolysis of $(i\text{-}Pr_3Si)_2SiH_2$ (**2a**) and 2 equiv of $t\text{-}Bu_2Hg$ produced a less complex product mixture from which we were able to isolate the first known silyl *tri*mercury compound **3a** in 30% yield. The modification of the reaction conditions (eq 3) allowed isolation of **3a** in 70% yield. Along with **3a**, the shorter silyl mercury hydrides **4a** and **5a** were also obtained, as was shown by NMR spectroscopy. Using the same procedure as for **3a** the analogous trimercury silyl compound **3b**, where R_3Si = $t\text{-}Bu_2MeSi$ (eq 3), was also synthesized and isolated. However, in this case the yield was only 30% and the shorter silyl mercury hydrides **4b** and **5b** were the major products. Both **3a** and **3b** were crystallized and their molecular structures were determined by X-ray crystallography as reported below.



$$H\text{-}Si(SiR_3)_2\text{-}H \xrightarrow[80\text{-}130^{\circ}C]{3 \times 1\ eq.\ (t\text{-}Bu)_2Hg} t\text{-}Bu\text{-}Hg\text{-}Si(SiR_3)_2\text{-}Hg\text{-}Si(SiR_3)_2\text{-}Hg\text{-}Bu\text{-}t + H\text{-}Si(SiR_3)_2\text{-}Hg\text{-}Si(SiR_3)_2\text{-}H + t\text{-}Bu\text{-}Hg\text{-}Si(SiR_3)_2\text{-}Hg\text{-}Si(SiR_3)_2\text{-}H \quad (3)$$

a, R_3Si = $i\text{-}Pr_3Si$; **b**, R_3Si = $t\text{-}Bu_2MeSi$

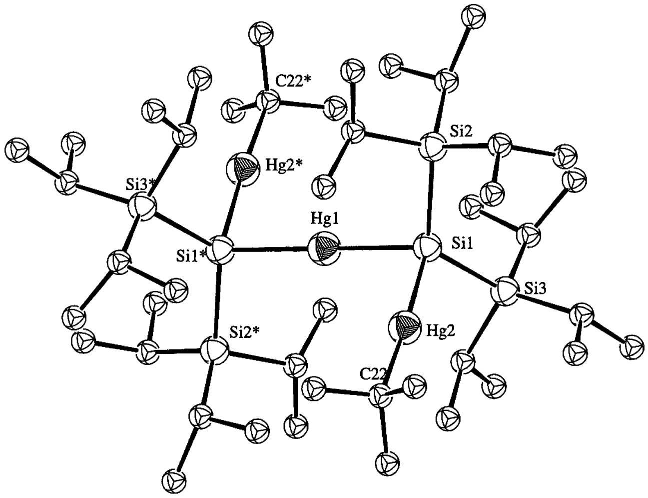
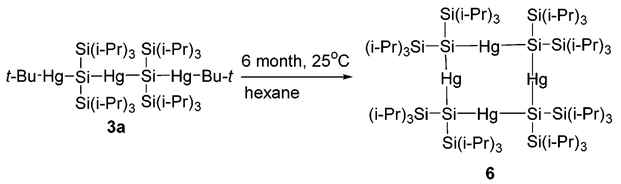


Figure 1. ORTEP drawing of **3a** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Hg1−Si1 2.47(3), Hg2−Si1 2.43(3), Hg2−C22 2.11(13), Si1−Si2 2.36(4), Si1−Si3 2.37(4). Selected bond angles (deg): Si1*−Hg1−Si1 180.0, C22−Hg2−Si1 177.3(4), Si2−Si1−Si3 126.64(17), Si2−Si1−Hg2 105.98(15), Si3−Si1−Hg1 107.94(13), Si2−Si1−Hg1 105.95(13), Hg2−Si1−Hg1 98.80(11) Selected torsion angles: (deg) Hg2*−Si1*−Si1−Hg2 180.0, Si2−Si1−Si1*−Si2* 180.0, Si2−Si1−Si1*−Si3* −41.9.

When **3a** is stored in hexane in the dark, it slowly decomposes, yielding **5a** as the major product (95% yield) and the novel cyclic tetramercury silane **6** in a 5% yield (eq 4). Red crystals of **6** suitable for X-ray crystallography precipitated from a hexane solution of **3a** that was stored at room temperature in the dark for 6 months. Only 30% of **3a** decomposed in this period of time.



$$t\text{-}Bu\text{-}Hg\text{-}Si(Si(i\text{-}Pr)_3)_2\text{-}Hg\text{-}Si(Si(i\text{-}Pr)_3)_2\text{-}Hg\text{-}Bu\text{-}t \xrightarrow[hexane]{6\ month,\ 25^{\circ}C} [\text{-}Si(Si(i\text{-}Pr)_3)_2\text{-}Hg\text{-}]_4 \quad (4)$$

Molecular Structures of 3a, 3b, and 6. **3a** was crystallized from a hexane solution, while **3b** was crystallized from ethanol, both yielding green crystals. The molecular structures of **3a**, **3b**, and **6** were determined by X-ray crystallography, and their ORTEP drawings are shown in Figures 1−3, respectively. The figure captions include some of the most important geometrical parameters for **3a**, **3b**, and **6**; Table 1 summarizes the crystallographic data collection and structural refinement information. Full details of the structures are reported in the Supporting Information.

The Si−Hg−Si moiety in silylmercury compounds of the type $[(R_3Si)_3Si]_2Hg$ is typically linear.[13] Also in the trimercurial **3a**, where R_3Si = $i\text{-}Pr_3Si$, the Si−Hg−Si fragment is linear, but in **3b**, where R_3Si = $t\text{-}Bu_2MeSi$, the SiHgSi bond angle is 172.4°. The C−Hg−Si bond angles in **3a** and **3b** of 177.3° and 177.5°, respectively, are both nearly linear. **3a** and **3b** are the first examples of compounds with a Si−Hg−C fragment whose molecular structures were determined. The Si−Hg, Si−Si, and C−Hg bonds lengths in **3b** are slightly elongated relative to those in **3a**, indicating increased steric repulsion between the substituents.

Surprisingly the Si−Si−Si bond angle is significantly larger in **3a** (126°) than in **3b** (116°). It might have been

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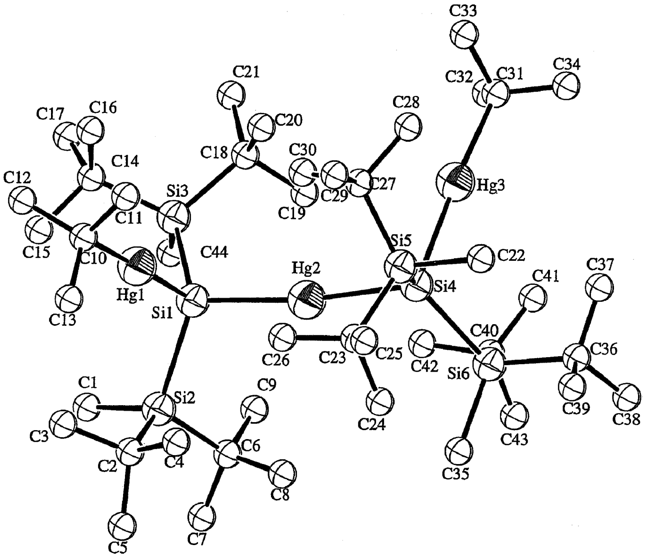

Figure 2. ORTEP drawing of **3b** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Hg2−Si1 2.49(3), Hg2−Si4 2.49(3), Hg1−C31 2.16(13), Hg3−Si4 2.46(4), Si4−Si5 2.38(4), Si4−Si6 2.39(5). Selected bond angles (deg): Si4−Hg2−Si1 172.37 (11), C10−Hg1−Si1 177.47(3), Si3−Si1−Si2 116.85(17), Si2−Si1−Hg1 109.18(16), Si3−Si1−Hg2 112.39(15), Si2−Si1−Hg2 110.85(15), Hg1−Si1−Hg2 98.84(11). Selected torsion angles (deg): Hg1−Si1−Si4−Hg3−103.6, Si2−Si1−Si4−Si6 32.1, Si2−Si1−Si4−Si5−105.9.

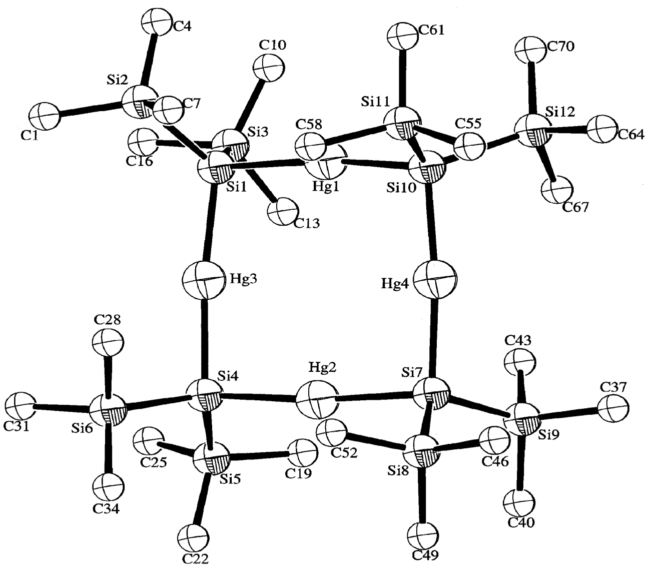

Figure 3. ORTEP drawing of the cyclic tetramercury silane **6** (hydrogen atoms and some of the carbon atoms are omitted for clarity). Selected bond lengths (Å): Hg1−Si1 2.55(10), Hg1−Si10 2.50(9), Hg2−Si4 2.50(10), Hg3−Si1 2.51(11), Hg3−Si4 2.54(11), Hg2−Si4 2.50(10) Si1−Si2 2.38(15), Si1−Si3 2.39(15), Si4−Si5 2.36(14), Si4−Si6 2.38(15). Selected bond angles (deg): Si1−Hg1−Si10 171.5(4), Si1−Hg3−Si4 173.1(3), Si4−Hg2−Si7 174.5(3), Hg1−Si1−Hg3 96.3(4), Hg3−Si4−Hg2 96.0(4), Si2−Si1−Si3 116.3(6), Si2−Si1−Hg3 120.9(6), Si3−Si1−Hg3 105.1(5), Si2−Si1−Hg1 101.4(4), Si3−Si1−Hg1 115.3(5). Selected torsion angles (deg): Hg1−Hg3−Hg2−Hg4 2.1, Si1−Si4−Si7−Si10 7.5, Hg1−Si1−Si4−Hg2−5.2.

expected that the bulkier substituents in **3b** would induce a larger Si−Si−Si bond angle. We believe that this apparent anomaly is due to the fact that the t-Bu$_2$MeSi groups can rotate to adopt a conformation in which the smaller methyl groups face each other, thus reducing the steric repulsion between the two large t-Bu$_2$MeSi groups. In contrast, the i-Pr$_3$Si groups, being nearly spherically symmetric, cannot reduce their mutual steric repulsion by rotation around the Si−Si bonds, and consequently the steric congestion in **3a** is alternatively relieved by the widening of the Si−Si−Si bond angles.

The cyclic structure of **6** resulted in a slight nonlinearity of the Si−Hg−Si moieties (bond angles in the range 170−175°) and in elongation of the Si−Hg bonds (average bond length 2.51 Å) compared to **3a** (2.47 Å) and **3b** (2.49 Å). The Si−Si bond lengths (average 2.38 Å) were not changed by cyclization and are similar to **3a**, which is also substituted by i-Pr$_3$Si groups.

Photolysis of 3a. Disilyl mercury compounds, $(R_3Si)_2Hg$, are usually colored, with colors ranging from green to yellow.[14] **3a** exhibits absorption maxima at 340 (6400) and 380 (2100) nm. We note that the presence of the $-Hg-R_2Si-Hg-$ fragment in **3a** has no significant influence on the wavelength of absorption maxima relative to other silylmercury compounds,[14] but it increases the extinction coefficients approximately by 1 order of magnitude.

Photolysis of **3a** in C_6D_6 (Scheme 1) resulted first in formation of the silyl mercury hydride **5a** and later of **4a** (according to NMR spectroscopy) both as intermediate products of the process. Thus, similarly to lithiation,[11] photolysis of **3a** proceeded via reaction of the external Si−Hg bonds. The photolytic cleavage of Si−Hg bonds is a convenient method for the generation of silyl radicals.[5,11] Thus, we propose that both **5a** and **4a** are formed in the reaction generated by the photolysis of Hg-substituted silyl and t-Bu[15] radicals (Scheme 1).

EPR Studies of Hg-Substituted Silyl Radical. To provide evidence of Hg-substituted silyl radical formation in the photolysis of both **3a** and **3b**, the reactions were monitored by EPR spectroscopy. EPR spectra of previously unknown silyl radicals with g-factors around 1.983 were observed after 10 s photolysis of **3b** (spectrum shown in Figure 4a) and **3a**.[16] The observed g-factor is significantly smaller (downfield-shifted) relative to all known silyl radicals, which are usually in the range 2.003−2.007.[3a] The spectra exhibiting the novel g-factor were tentatively assigned to a mercury-substituted silyl radical.

The assignment is supported by the observation of isotropic hyperfine interaction of the unpaired electron with magnetic isotope ^{199}Hg and ^{29}Si nuclei (intensity of the satellites lines corresponds to the natural abundances of the ^{199}Hg (16.8%) and ^{29}Si (4.7%) nuclei) and by a fact that the carbon analogue, ClHgH$_2$C$^{\bullet}$, has g-factor of 1.990,[17] also significantly downfield-shifted

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(15) The disproportionation of the t-Bu radical yielding isobutane and isobutene is faster than radical recombination. See: Kerr, J. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, p 1.

(16) Corresponding EPR spectrum presented in the Supporting Information.

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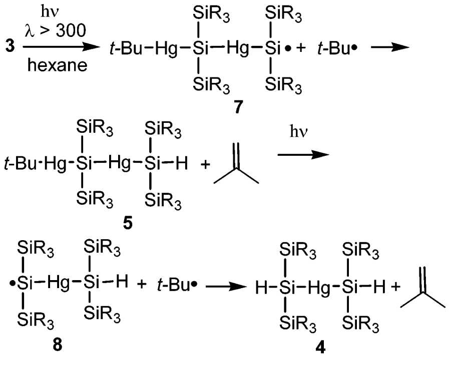
Table 1. Crystallographic Data Collection and Structural Refinement Information for Compounds 3a, 3b, 6, and 11

	3a	**3b**	**6**	**11**
empirical formula	$C_{22}H_{51}Hg_{1.5}Si_3$	C_{44} H_{102} Hg_3 Si_6	$C_{72}H_{168}Hg_4Si_{12}$	$C_{58}H_{120}HgN_2O_3Si_6$
fw	700.78	1401.57	2173.51	1262.69
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	*C*-2/*c*	$P\bar{1}$	$P\bar{1}$	*P*-21/*c*
temp (K)	230	293	210	293
a (Å)	19.2360(17)	12.074(2)	12.059(8)	11.341(3)
b (Å)	12.3510(13)	15.524(2)	15.141(9)	21.241(5)
c (Å)	25.4760(16)	16.676(3)	28.530(16)	15.609(5)
α (deg)	90.000	75.65(2)	76.479(30)	90.000(8)
β (deg)	101.182(5)	81.49(2)	83.037(30)	110.285(10)
γ (deg)	90.000	83.76(2)	68.299(30)	90.000(9)
vol ($Å^3$)	5937.8(9)	2986.4(9)	4702.3(5)	3526.91(17)
Z	8	2	2	2
R	0.0338	0.0599	0.0672	0.0474
GOF on F^2	0.573	0.802	0.967	0.963

Scheme 1. Proposed Mechanism for the Photolysis of Trimercurysily Compounds 3



a, R_3Si = *i*-Pr_3Si; **b**, R_3Si = *t*-Bu_2MeSi

compared to other alkyl radicals.[18] We assume that the large spin−orbital coupling of the mercury atom leads to the observed strong shift in the *g*-factors of Hg-substituted silyl and alkyl radicals.

According to the mechanism proposed for the photolysis of **3** (Scheme 1), the spectrum shown in Figure 4a was assigned to **7b** (g = 1.983; $a(\alpha\text{-}^{29}Si)$ = 56 G; $a(^{199}Hg)$ = 105.3 G). Upon continuous photolysis (15−20 min), the intensity of the signals assigned to **7b** decreased and a new silyl radical with *g*-factor 1.984[16] was observed. These new signals were assigned to Hg-substituted silyl radical **8b** (g = 1.984; $a(\alpha\text{-}^{29}Si)$ = 56 G; $a(^{199}Hg)$ = 104.9 G) (Scheme 1). In contrast to **3b**, the EPR spectrum of only a single Hg-substituted silyl radical was observed during the photolysis of **3a**.[16] This spectrum was assigned to **8a** (g = 1.983; $a(\alpha\text{-}^{29}Si)$ = 56 G; $a(^{199}Hg)$ = 101.5 G).

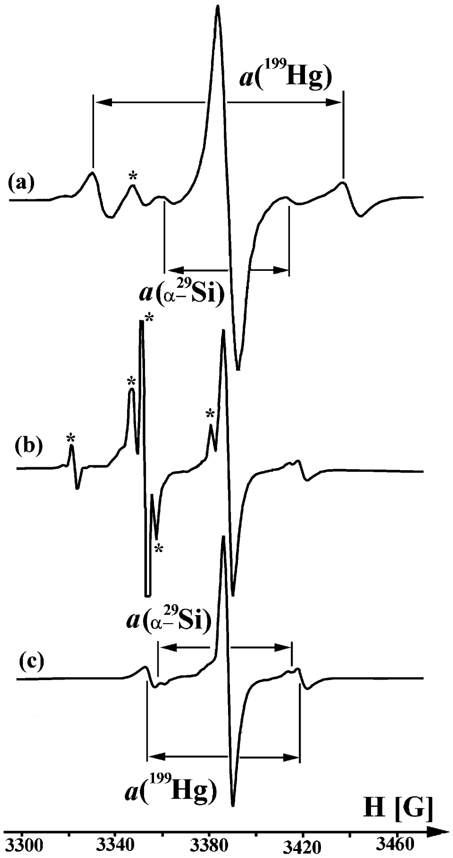
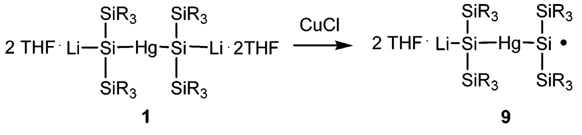


Figure 4. (a) EPR spectra of the Hg-substituted silyl radical, **7b**, observed during irradiation of a hexane solution of **3b** (Scheme 1) at 200 K (at microwave radiation power of 100 mW). (b) Experimental spectrum observed during oxidation of **1b** by CuCl (eq 5) at 240 K and at 5 mW microwave power, lines of unassigned hypersilyl radical marked by "*"; (c) EPR spectrum assigned to **9b** (g = 1.984; $a(\alpha\text{-}^{29}Si)$ = 56 G; $a(^{199}Hg)$ = 63.4 G) obtained by subtraction of the spectrum of the silyl radical marked by "*" from the experimental spectrum shown in (b).

To verify the EPR assignment of novel Hg-substituted silyl radicals, we used another reaction pathway for the generation of Hg-substituted silyl radicals. The oxidation reactions of compounds with Si−M bonds (M = alkali metal) were shown to be a convenient method for the generation of silyl radicals.[19] Thus, one-electron oxidation of **1** is expected, similarly to photolysis of **3**, to lead to the generation of the Hg-substituted silyl radicals (**9**, eq 5). Indeed EPR spectra of radicals with g = 1.984 were observed during oxidation of **1b** (spectrum shown in Figure 4c) and **1a**[16] by CuCl (eq 5).



(5)

a, R_3Si = *i*-Pr_3Si; **b**, R_3Si = *t*-Bu_2MeSi

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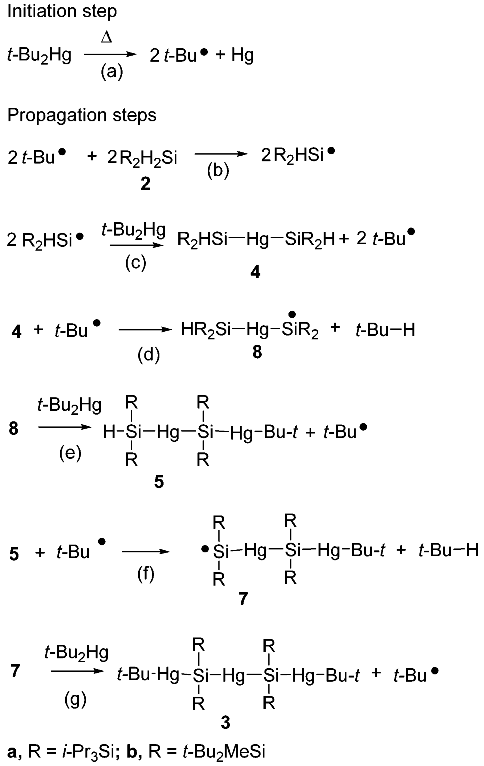
[19] (a) Kira, M.; Obata, T.; Kon, I.; Hashimoto, H.; Ichinohe, M.; Sakurai, H.; Kyushin, S.; Matsumoto, H. *Chem. Lett.* **1998**, *27*, 1097. (b) Sekiguchi, A.; Fukawa, T.; Nakamoto, M.; Lee V. Ya.; Ichinoche, M. *J. Am. Chem. Soc.* **2002**, *124*, 9865.

Scheme 2. Proposed Mechanism for the Formation of the Trimercury Silanes 2a and 2b



The appearance of EPR signals for Hg-substituted silyl radicals and the *t*-Bu radical[20] was observed[16] during the reaction that leads to the formation of **3a**, namely, thermolysis of a mixture of *t*-Bu_2Hg and dihydrosilane **2a** (eq 3). On the other hand, thermolysis of **3a** also generates Hg-substituted silyl radicals, as was observed by EPR spectroscopy.[16] Thus we propose that formation and degradation of silylmercury chains proceed via the radical intermediates, including Hg-substituted silyl radicals.

The proposed chain radical mechanism for the formation of trimercury silanes is summarized in Scheme 2. The initiation step is the thermolysis of *t*-Bu_2Hg, which leads to the formation of the *t*-Bu radical[21] (Scheme 2, step a). The propagation steps are (1) hydrogen abstraction by the *t*-Bu radical from the dihydridosilane **2** in the first reaction stage or from a mercury-substituted hydrosilanes of the $R'{-}Hg{-}(R_3Si)_2Si{-}H$ type as the silylmercury chain grows (Scheme 2, steps b, d, and f); (2) the reaction of a silyl or mercury-substituted silyl radical generated in a previous step, with compounds having a *t*-Bu−Hg bond, forming a new Hg−Si bond and regenerating the *t*-Bu radicals, which continue the chain reaction (Scheme 2, steps c, e, and g). These reactions (Scheme 2 steps c, e and g) could be explained in terms of a S_H2 mechanism that has been previously demonstrated for alkylmercury compounds.[22]

We suggest that chain growth terminates at the stage of the trimercury silanes due to reduced reactivity of the RHg-*t*-Bu and $RHgR'_2Si{-}H$ bonds as the steric congestion around these bonds increases when the silylmercury chain is elongated from **2** to **3**.

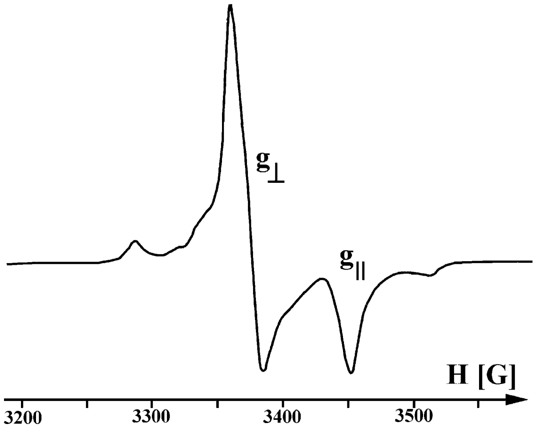


Figure 5. EPR spectrum of the Hg-substituted silyl radical, **7b**, recorded in frozen hexane solution at 130 K.

Spectroscopic Features of Mercury-Substituted Silyl Radicals Derived from the EPR Studies. We find that mercury substitution at the α-silicon results in fast relaxation of the paramagnetic species, and as a result, the absorption due to the mercury-substituted radicals is practically not saturated by microwave radiation (up to 200 mW). As a result, registration of EPR spectra using high microwave radiation power (100−200 mW) allowed increasing the intensity of the signal due to Hg-substituted silyl radicals relative to the signals of other radicals that are saturated under these conditions.

The EPR spectra of the $R'{-}Hg{-}(R_3Si)_2Si^{\bullet}$ radicals are characterized by the following features: (1) a downfield-shifted *g*-factor (compared to other silyl radicals) of 1.983−1.984; (2) interaction of the unpaired electron with both the ^{29}Si and the ^{199}Hg nuclei, as indicated by the measured coupling constants, $a(\alpha\text{-}^{29}Si)$ of 56 G and $a(^{199}Hg)$ of 63−105 G (satellites due to ^{201}Hg nucleus were not observed).

The magnitude of $a(\alpha\text{-}^{29}Si)$ of 56G is comparable to that measured in hypersilyl radicals.[3a] The magnitude of $a(^{199}Hg) = 63{-}105$ G indicates that only 0.5−0.8% of the spin density resides in a 6s-type orbital on the mercury. This is based on the fact that a full 6s-orbital spin results in $a(^{199}Hg)$ of ca. 12 000 G.[23] This huge *hfc* constant value indicates that even small changes in the distribution of the spin density are expected to lead to meaningful changes in $a(^{199}Hg)$.

Finally the $R'{-}Hg{-}R_2Si^{\bullet}$ radicals are characterized by the strong anisotropy of the *g*-factor, which results in two EPR signals in frozen solutions, belonging to radicals whose Si−Hg bonds are oriented parallel ($g_{\parallel}$) or perpendicular ($g_{\perp}$) to the applied magnetic field. For example, the EPR spectrum of the Hg-substituted silyl radical **7b** (Figure 4a) recorded in frozen hexane solution (130 K) (Figure 5) shows $g_{\perp} = 1.996$ and $g_{\parallel} = 1.952$. The observed anisotropy of the *g*-factor in frozen solutions indicates that Hg-substituted silyl radicals possess axial symmetry,[24] in agreement with their molecular structure.

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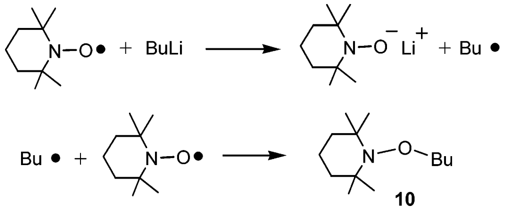
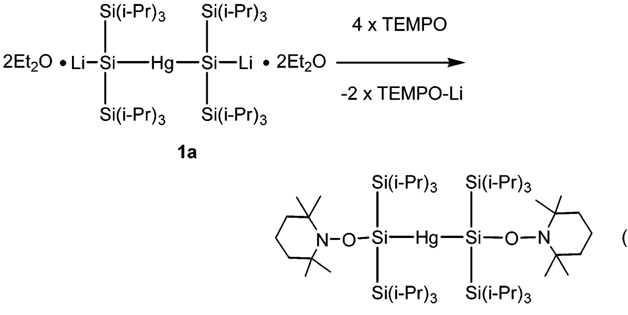
Scheme 3



10

Chemical Trapping of Hg-Substituted Silyl Radicals. Chemical trapping experiments provide additional evidence for the formation of Hg-substituted silyl radicals in the above-mentioned processes. It was recently demonstrated that the stable nitroxyl radical 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) is an efficient trapping agent for silyl radicals.[25] In addition it was shown that n-BuLi reacts with 2 molar equiv of TEMPO, to form the corresponding Bu-TEMPO adduct **10**. The proposed mechanism, which involves a single electron transfer followed by formation of the *n*-Bu radical and its trapping by TEMPO, is shown in Scheme 3.[26]

The dilithium silyl mercury compound **1a** reacts with 4 equiv of TEMPO to yield **11** in a 90% yield (eq 6). **11** was isolated from the reaction mixture by crystallization, and its molecular structure was determined by X-ray crystallography (see Supporting Information). As mentioned above, a Hg-substituted silyl radical was observed by EPR spectroscopy in the one-electron oxidation of **1**. Therefore, **11** can be regarded to be a trapping product of the Hg-substituted silyl radicals that were generated by a one-electron oxidation of the Si−Li bonds of **1a** by TEMPO.



1a

11

(6)

Conclusion

The first known trimercury silanes **3a** and **3b**, and cyclic tetramercury silane **6**, all containing a −Hg−R$_2$-Si−Hg− fragment, were synthesized, and their molecular structures were determined by X-ray analysis. These compounds are among the first known geminal silicon bimetallic compounds and were used in the generation of a novel type of a silyl radical carrying a mercury substituent. Their structure was confirmed by a detailed EPR study and by chemical trapping by TEMPO. The radical nature of the formation and fragmentation of the geminal dimercury silyl compounds was evidenced by the observation of Hg-substituted silyl radicals in these processes using EPR spectroscopy.

Experimental Part

All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture by standard Schlenk-type techniques. Dry oxygen-free solvents were employed. ^{1}H, ^{13}C, and ^{29}Si spectra were recorded using Bruker Avance 300 or Bruker Avance 500 instruments. Solid-state NMR spectra were recorded using a Chemagnetics/Varian CMX-Infinity 300 spectrometer. Mass spectroscopy (MS) data were obtained with a Finigan MAT TSQ 45 triple-stage quadrupole mass spectrometer. EPR spectra were recorded on a Bruker EMX-10/12 X-band (ν = 9.4 GHz) digital EPR spectrometer equipped with a Bruker N$_2$-temperature controller. Samples were irradiated with the focused and filtered (λ = 300 nm) light of a high-pressure mercury lamp (1 kW) (ARC lamp power supply model 69920) in the resonator of the EPR spectrometer. Absorption spectra were measured using a Hewlett-Packard 8452A diode array spectrophotometer.

Synthesis of [*t*-Bu-Hg-(*i*-Pr$_3$Si)$_2$Si]$_2$Hg (3a). A mixture of 10 g (29 mmol) of **2a**[27] and 9.1 g (29 mmol) of *t*-Bu$_2$Hg was heated under an argon atmosphere to 130 °C over a 4 h period, during which isobutene was evolved. Heating was discontinued when isobutene evolution ceased. The same procedure was repeated three times, after which the crude product was dissolved in hexane. **3a** (14.2 g, 10 mmol; 70% yield) was obtained after crystallization from hexane. ^{1}H NMR (C$_6$D$_6$): δ 1.52 (d, 36H, C**Me**$_2$). ^{13}C NMR (C$_6$D$_6$): δ 15.98 (Me$_2$**C**H), 20.91 (**Me**$_2$CH), 21.02 (**Me**$_2$CH), 31, 14.3 (CCH$_3$), 78.13 (CCH$_3$). ^{29}Si NMR (C$_6$D$_6$): δ −55.54 ((*i*-Pr$_3$Si)$_2$**Si**), 34.07 ((*i*-Pr$_3$**Si**)$_2$Si). ^{199}Hg NMR (C$_6$D$_6$): δ 38 (*t*-Bu**Hg**), 1087 (Si-**Hg**-Si). MS(CI): *m/e* 1402 (M$^+$).

Synthesis of [*t*-Bu-Hg-(*t*-Bu$_2$MeSi)$_2$Si]$_2$Hg (3b). A mixture of 9 g (26 mmol) of **2b**[27] and 8.2 g (26 mmol) of *t*-Bu$_2$Hg was heated under an argon atmosphere to 130 °C over a 4 h period, during which isobutene was evolved. Heating was discontinued when isobutene evolution ceased. The same procedure was repeated three times, yielding 5.6 g (9.4 mmol) of **3b** (30% yield) after crystallization from ethanol. ^{1}H NMR (hexane using C$_6$D$_6$ capillary): δ 0.23 (12H, s, *t*-Bu$_2$**Me**Si), 1.13 (72H, s, ***t*-Bu**$_2$MeSi), 1.52 (18H, s, ***t*-Bu**-Hg). ^{13}C NMR (hexane using C$_6$D$_6$ capillary): δ −1.22 (*t*-Bu$_2$**Me**Si), 30.88 (***t*-Bu**$_2$MeSi), 31.0; 78.9 (***t*-Bu**-Hg). ^{29}Si NMR (hexane using C$_6$D$_6$ capillary): δ 34.7 (*t*-Bu$_2$MeS**i**)$_2$Si; −80 (*t*-Bu$_2$MeSi)$_2$**Si**. MS-CI: *m/z* 1142 (M − HgBu-*t*); 887 (M − 2* HgBu-*t*).

Synthesis of [2THF·Li(*t*-Bu$_2$MeSi)$_2$Si]$_2$Hg (1b). A mixture of 2.5 g (1.8 mmol) of **3b** and 5 g of lithium metal (a large excess) in 50 mL of THF was stirred at rt for 2 h. The THF solution was separated from lithium metal and cooled to 0 °C, yielding a green precipitate. The product was purified by crystallization from THF to yield 1.5 g (60% yield) of **1b**. **1b** has poor solubility in common organic solvents. Solid-state ^{7}Li NMR: δ 2.5. Solid state ^{13}C NMR: δ −0.32; 0.59 (*t*-Bu$_2$**Me**Si); 31.3; 29.9; 27.2 (***t*-Bu**$_2$MeSi); 69.25; 68.1; 23.6 (**THF**). Solid state ^{29}Si NMR: δ 30.3; 33.4 (*t*-Bu$_2$Me**Si**)$_2$Si; −99 (*t*-Bu$_2$-MeSi)$_2$**Si**.

Synthesis of [(*i*-Pr$_3$Si)$_2$SiHg]$_4$ (6). **6** (0.2 g) precipitated as red crystals, suitable for X-ray crystallography, from a solution of 2.6 g of **3a** in 50 mL of hexane stored for 6 month in the dark at room temperature. **6** is insoluble in common organic solvents. Solid-state ^{29}Si NMR (in mineral oil): δ 31.1, 29.3 ((*i*-Pr$_3$**Si**)$_2$Si), −33.3 ((*i*-Pr$_3$Si)$_2$**Si**).

Trapping Experiment Yielding [(TEMPO)(*i*-Pr$_3$Si)$_2$-Si]$_2$Hg (11). A solution of 1.5 g (1.2 mol) of TEMPO in 10 mL of hexane was added slowly to a cold (−45 °C) toluene solution containing 0.8 g (5 mmol) of ether-solvated **1a**, which was

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[27] **2a** and **2b** were prepared by the procedure shown for **2b** in: Sekiguchi, A. Fukawa, T.; Nakamoto, M.; Lee, V. Ya.; Ichinohe M. *J Am. Chem. Soc.* **2002**, *124*, 9865. **6a** was already characterized: Gaspar, P.; Beatty, A.; Chen, T.; Haile, T.; Lei, D.; Winchester, W.; Braddock-Wilking, J.; Rath, N.; Klooster, W.; Koetzle, T.; Mason, S.; Albinati, A. *Organometallics* **1999**, *18*, 3921.

prepared similarly to the THF-solvated **1a**,[11] and the mixture was stirred for 10 min. The reaction yielded 0.5 g (90% yield) of **11** as yellow crystals, suitable for X-ray crystallography. Solid-state ^{13}C NMR: δ 21, 13.4 ($\boldsymbol{i}$**-Pr**$_3$Si), 62.6, 41; 37.2, 33.6, 18 (TEMPO), 60.5, 40.5, 35.3, 33.6, 20.0 (TEMPO). Solid-state ^{29}Si NMR: δ 14.4, 12.1, (i-Pr$_3$**Si**), 25.7, (i-Pr$_3$Si)$_2$**Si**. MS(CI): *m*/*e* 1058 (M − NC$_9$H$_{18}$); 1042 (M − TEMPO); 888 (M − 2TEMPO). Crystals were used for solid-state NMR analysis because the compound is not stable in hexane solution at temperatures above 0 °C.

Characterization of 4a. Characterization of **4a** was reported.[11]

Preparation of H($\boldsymbol{i}$-Pr$_3$Si)$_2$SiHg($\boldsymbol{i}$-Pr$_3$Si)$_2$SiHgBu-$\boldsymbol{t}$ (5a). A 0.7 g amount of **3a** in 60 mL of dry THF was added to 4 g of lithium metal. After 10 min at room temperature (without stirring) the solution was separated from the lithium metal. The THF was evaporated, and 0.2 g (30% yield) of green crystals of 2THF·Li(i-Pr$_3$Si)$_2$SiHg(i-Pr$_3$Si)$_2$SiHgBu-t was obtained by crystallization from hexane. ^{1}H NMR (C$_6$D$_6$): δ 3.48, 1.41 (THF) 1.41, 1.37 (i-Pr$_3$Si) 1.86 (t-Bu). ^{13}C NMR (C$_6$D$_6$): δ 21.6, 21.3, 21.2, 17.1 (i-Pr$_3$Si), 31.5, 16.5 (t-Bu), 68.3, 25.4 (THF). ^{29}Si NMR (C$_6$D$_6$): δ 33.5, 29.2 (i-Pr$_3$**Si**)$_2$Si; −39.8 (i-Pr$_3$Si)$_2$**Si**Hg$_2$, −120.9 (i-Pr$_3$Si)$_2$**Si**HgLi.

Degassed water (1 mL) was added to 0.1 g of 2THF·Li(i-Pr$_3$Si)$_2$SiHg(i-Pr$_3$Si)$_2$SiHgBu-t in 50 mL of hexane. The hexane fraction was separated and was dried over MgSO$_4$. After filtration and evaporation of the hexane solvent 0.08 g (80% yield) of **5a** was obtained. ^{1}H NMR (C$_6$D$_6$): δ 3.68, (H-Si) 1.26, 1.30 (i-Pr$_3$Si) 1.77 (t-Bu). ^{13}C NMR (C$_6$D$_6$): δ 20.9, 20.8, 20.59, 20.55, 17.2 (i-Pr$_3$Si), 31.1, 16.5 (t-Bu). ^{29}Si NMR (C$_6$D$_6$): δ 34.9, 23.6 (i-Pr$_3$**Si**)$_2$Si, −60.7 (i-Pr$_3$Si)$_2$**Si**Hg$_2$, −81.5 (i-Pr$_3$Si)$_2$**Si**HgH.

Characterization of 4b and 5b in Reaction Mixtures. **4b** and **5b** were characterized by ^{29}Si NMR, as they have ^{29}Si chemical shifts similar to **4a** and **5a**: **4b**: ^{29}Si NMR (hexane): δ 25.5 (t-Bu$_2$Me**Si**)$_2$Si; −69.3 ppm (t-Bu$_2$MeSi)$_2$**Si**. **5b**: ^{29}Si NMR (hexane): δ 35.9 (t-Bu$_2$Me**Si**)$_2$SiHg$_2$; −58.0 (t-Bu$_2$MeSi)$_2$**Si**Hg$_2$, 25.8 (t-Bu$_2$Me**Si**)$_2$SiHHg; −74.6 ppm (t-Bu$_2$MeSi)$_2$**Si**HHg.

General Procedure for the EPR Experiments. All measurements were performed using vacuum Pyrex NMR tubes equipped with Teflon stopcocks to keep the sample under vacuum.

Photolysis of 3. A hexane solution of **3** in an NMR tube was irradiated at room temperature by a Hg-lamp using a glass filter, which cuts off the UV radiation below λ of 300 nm. EPR spectra were recorded 10 s, 30 s, and 15 min after irradiation was started. Spectra were recorded without irradiation.

Oxidation of 1. A hexane solution of **1** in an NMR tube frozen in liquid nitrogen was opened under argon atmosphere, and an excess of CuCl was inserted. The sample was heated to 240 K, and EPR spectra were recorded 10 s after the reactants were mixed and heated.

Thermolysis of a Mixture of $\boldsymbol{t}$-Bu$_2$Hg and 2a. A mixture of 0.2 g of t-Bu$_2$Hg and 0.1 g of **2a** was heated within the EPR resonator cavity. The first EPR spectrum was taken after 30 s at 80 °C (EPR microwave radiation power 1 mW). After 10 min at 80 °C a second EPR spectrum was recorded (EPR microwave radiation power 200 mW).

Thermolysis of 3a. A mixture of 0.1 g of **3a** in mineral oil (Najol) was heated within the EPR resonator cavity to 190 °C, and the EPR spectrum was taken.

X-ray Crystallographic Studies of Compounds 3a, 3b, 6, and 11. Crystal data are presented in Table 1. Data were collected at low temperatures on a Nonius KappaCCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods by means of SHELXS-97[28] and refined with all data on F^2 by means of SHELXL-97.[29] All non-hydrogen atoms were refined anisotropically.

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Supporting Information Available: X-ray crystallographic data, in cif format, for **3a**, **3b**, **6**, and **11**. EPR spectra observed during photolysis and thermolysis of **3a**, oxidation of **1a**, and during the thermolysis of a mixture of t-Bu$_2$Hg and dihydrosilane **2a**. These materials are available free of charge via the Internet http://pubs.acs.org.

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(29) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; University of Göttingen, 1997.