Synthesis and Lithiation of Ortho-Methylated Triphenylsilanes

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Abstract: The synthesis of tris(2,6-xylyl)silane (**1**) and its corresponding chloride (**2**) and fluoride (**3**) is described. Isopropyllithium was found to react with **2** and **3** to give benzosilacyclobutene **5** rather than isopropylsilane **4**. Lithiation of **2** yielded two products, the expected silane **1** as well as a novel and unexpected coupling product, **6**. The mechanism of this lithiation was investigated in detail and was shown to involve both intramolecular rearrangement of the initially formed silyllithium **7** to benzyllithium **8** as well as intermediate formation and reduction of **5**. In light of these unusual results, the lithiation of tris(*o*-tolyl)chlorosilane (**11**) was reexamined. Although this reaction proceeds by the conventional pathway, giving tris(*o*-tolyl)silyllithium (**14**) as the sole organometallic intermediate, the previously unreported hexakis(*o*-tolyl)disilane (**13**) was isolated for the first time.

As part of our continuing study of the dynamic stereochemistry of triarylsilanes and other propeller-like molecules, we attempted to prepare various derivatives of tris(2,6-xylyl)silane (**1**)[1] with substituents other than hydrogen attached to silicon. Although several synthetic approaches to such compounds are plausible, the most promising appeared to be alkylation of the corresponding silyllithium derivative of **1**.

Several reports have appeared in the literature concerning the formation and reactions of a variety of organosilylmetallic reagents; in these reports, triphenylsilyllithium has been exhaustively investigated.[2] This compound is formed from triphenylchlorosilane and lithium metal in tetrahydrofuran (THF). In the early stages of the reaction, hexaphenyldisilane forms by coupling and can be isolated.[3] Subsequent cleavage of the disilane with lithium again affords triphenylsilyllithium (eq 1).[3] Solutions of triphenylsilyllithium in THF are stable at room temperature; however, prolonged heating results in solvent cleavage.[4]

$$(C_6H_5)_3SiCl \xrightarrow[\text{THF}]{\text{Li}} (C_6H_5)_3SiLi \xrightarrow[\text{THF}]{(C_6H_5)_3SiCl} (C_6H_5)_3SiSi(C_6H_5)_3$$

$$(C_6H_5)_3SiSi(C_6H_5)_3 \xrightarrow[\text{THF}]{\text{Li}} 2(C_6H_5)_3SiLi \qquad (1)$$

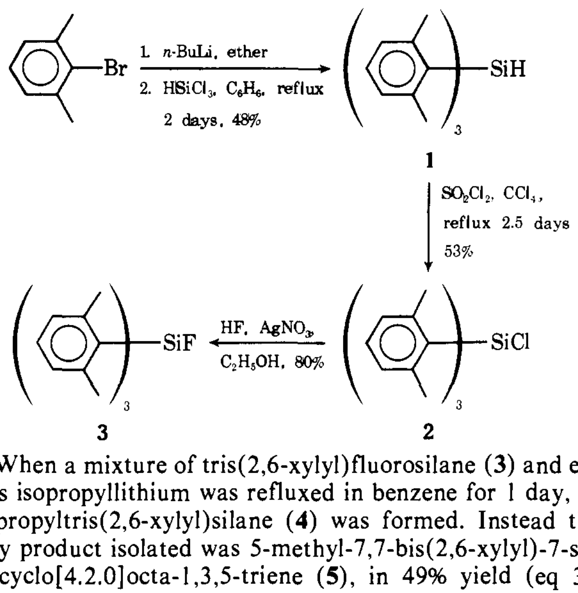
However, the only triply ortho-substituted triarylsilyllithium known is tris(*o*-tolyl)silyllithium, "an example of a highly hindered silylmetallic compound".[3] It also forms from the corresponding chlorosilane[5] and lithium in THF, but unlike the reaction giving triphenylsilyllithium, no hexakis(*o*-tolyl)disilane was found in this preparation (eq 2). Only tris(*o*-tolyl)silane was isolated after hydrolysis.[3]

$$(o\text{-tolyl})_3SiCl \xrightarrow[\text{THF}]{\text{Li}} (o\text{-tolyl})_3SiLi \not\xrightarrow[\text{THF}]{(o\text{-tolyl})_3SiCl} (o\text{-tolyl})_3SiSi(o\text{-tolyl})_3 \qquad (2)$$

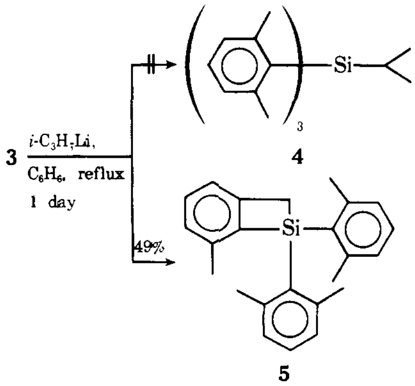
We are reporting below the detailed synthesis of some derivatives of tris(2,6-xylyl)silane (**1**) and the novel and unexpected results of the lithiation of tris(2,6-xylyl)chlorosilane (**2**).[1] These include the intramolecular rearrangement of tris(2,6-xylyl)silyllithium to a benzyllithium, formation of an unusual coupling product from this rearranged lithium compound, and the involvement of a benzosilacyclobutene in the overall lithiation sequence. We are also reporting a reinvestigation of the lithiation of tris(*o*-tolyl)chlorosilane, which in our hands resulted in the isolation of hexakis(*o*-tolyl)disilane.

Results and Discussion

Synthesis of Triarylsilanes. Tris(2,6-xylyl)silane and its halogen derivatives **2** and **3** were synthesized as shown below. The temperature dependent ^1H NMR spectra of these compounds were reported in earlier work.[1]



When a mixture of tris(2,6-xylyl)fluorosilane (**3**) and excess isopropyllithium was refluxed in benzene for 1 day, no isopropyltris(2,6-xylyl)silane (**4**) was formed. Instead the only product isolated was 5-methyl-7,7-bis(2,6-xylyl)-7-silabicyclo[4.2.0]octa-1,3,5-triene (**5**), in 49% yield (eq 3). The benzosilacyclobutene **5** was also formed from chlorosilane **2** and isopropyllithium in THF at room temperature, but the yield was only 30%. A small amount of **1** was also formed (12%), but again, no **4** could be found.

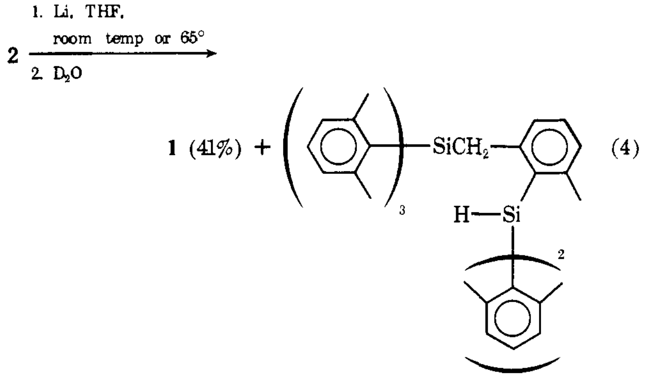


(3)

At ambient temperature, the 60-MHz ^1H NMR spectrum of **5** in C_6D_6 consists of three singlets (in addition to the aromatic resonances) at δ 2.25, 2.37, and 2.78 ppm. The normalized intensities[6] of these three resonances are 2.89 H, 11.72 H, and 1.78 H, respectively, while that of the aromatic protons is 9.62 H. Exact mass measurements and elemental analysis further support the assigned structure.

Although triphenylchlorosilane and triphenylfluorosilane react with several organolithium reagents to give tetrasubstituted silanes,[7] the failure of isopropyllithium to attack silicon in **2** and **3** can be explained on the basis of increased steric crowding around silicon by the six *o*-methyl groups. The formation of **5**, however, is unusual. Only three other silacyclobutenes have been prepared,[8] and none of these were synthesized by the above method, direct proton abstraction from a halosilane, followed by intramolecular cyclization. This method owes its success both to the inability of isopropyllithium to attack silicon in the sterically crowded substrates and to the acidity of the benzylic hydrogens of the adjacent *o*-methyl groups.

Lithiation and Subsequent Reactions of Tris(2,6-xylyl)-chlorosilane. Chlorosilane **2** and lithium in THF react at room temperature to give a red solution. When this solution was stirred either at room temperature or at 65° for 3 hr and hydrolyzed with D_2O, two products were obtained. One of the products, isolated in 41% yield, is tris(2,6-xylyl)silane (**1**), containing deuterium as shown below. The other is tris(2,6-xylyl)(2-bis(2,6-xylyl)silyl-3-methylbenzyl)silane (**6**), isolated in 42% yield (eq 4). Unlike the reaction of triphenylchlorosilane with lithium which gives hexaphenyldisilane (eq 1), no hexakis(2,6-xylyl)disilane was formed. The structure of **6** was first suggested by its ^1H NMR spectrum. At 60 MHz, and at ambient temperature in CS_2, it consists of four singlets at δ 1.92, 2.03, 3.00, and 5.78 ppm and an aromatic multiplet; the intensities[6] of these resonances are 33.89 (sum of the 1.92 and 2.03 resonances), 1.80 H, 0.91 H, and 17.41 H, respectively. Molecular weight determination, elemental analysis, and the mass spectrum verify the assigned structure. The silane **1** obtained in this experiment contains 0.38 atom of deuterium per molecule by mass spectrometry (see Experimental Section); its NMR spectrum reveals that about one-third of the deuterium is attached to silicon and that two-thirds is contained in the *o*-methyl groups.

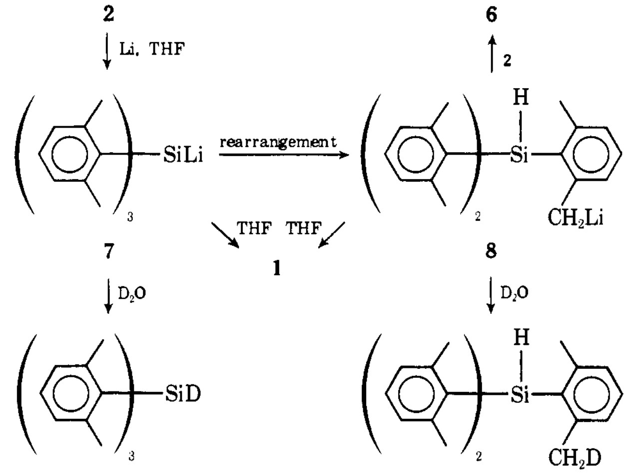


6 (42%)

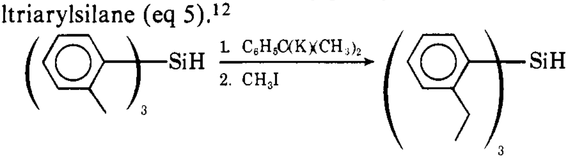
When a similar reaction mixture of **2** and lithium was treated with excess isopropyl chloride, refluxed briefly, and stirred at room temperature for 18 hr, again only **1** and **6** were isolated; no **4** was found. The analogous reaction of triphenylsilyllithium with isopropyl chloride gives isopropyltriphenylsilane in good yield.[2] The fluorosilane **3** underwent no reaction with lithium in refluxing THF, even after 30 hr, whereas triphenylfluorosilane and lithium in THF at room temperature afford triphenylsilyllithium in good yield.[9]

A mechanism to account for these observations is outlined in Scheme I. The key feature is the intramolecular rearrangement of the initially formed tris(2,6-xylyl)silyllithium (**7**) to the benzyllithium **8**. Coupling of **8** with chlorosilane **2** accounts for the formation of **6**, while hydrolysis of **7** and **8** with D_2O accounts for the observed pattern of deuterium incorporation in **1**. The incomplete incorporation of deuterium in **1** can be accounted for by competitive proton abstraction from THF by **7** and **8**. While triphenylsilyllithium cleaves this solvent,[4] **7** is probably too crowded to react similarly; deprotonation occurs instead. The failure of **7** to give **4** with isopropyl chloride can similarly be accounted for on the basis of steric arguments.

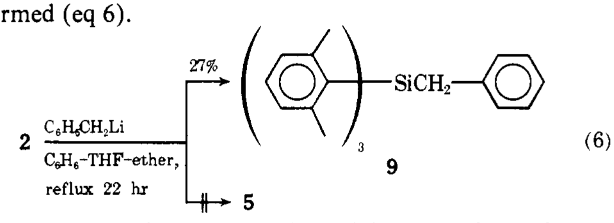
Scheme I



Despite the absence of precedent for the rearrangement of **7** to **8** in silicon chemistry, such an occurrence is reasonable if the benzyllithium is more stable than the isomeric silyllithium, as is likely on grounds both of resonance[10] and electronegativity considerations. This conclusion is supported by the observation that triphenylsilyllithium metallates toluene.[11] Furthermore, reaction of tris(*o*-tolyl)silane with α,α-dimethylbenzylpotassium, followed by reaction with methyl iodide, gives tris(2-ethylphenyl)silane and no methyltriarylsilane (eq 5).[12]



Although coupling of silyllithium **7** with **2** appears ruled out on steric grounds, reaction of **8** with **2** to give **6** is sterically feasible. Thus, **2** and benzyllithium react to give tris(2,6-xylyl)benzylsilane (**9**), in 27% yield. No silacyclobutene **5** is formed (eq 6).



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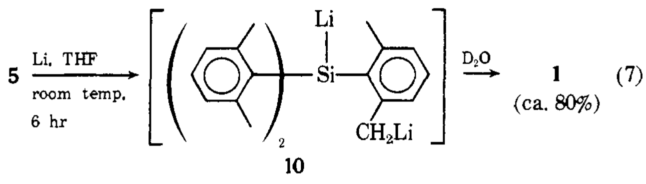
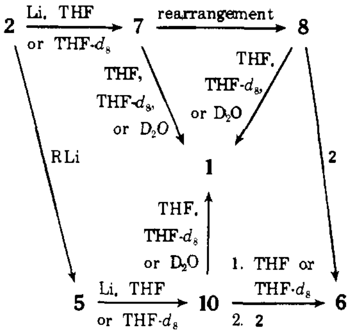
The observation that the silacyclobutene **5** forms from **2** and isopropyllithium suggests that it might also form from **2** and an organolithium during the lithiation of **2**. The intermediacy of **5** becomes plausible on the assumption that subsequent reduction with lithium of the bond between silicon and the benzylic carbon is facile.[13] This latter hypothesis was verified by reacting silacyclobutene **5** with lithium in THF at room temperature. When the reaction mixture was quenched with D_2O after 6 hr, silane **1** and unreacted **5** were the only products found, and the conversion was about 80% complete (eq 7). Presumably the doubly lithiated com-



10

Scheme II



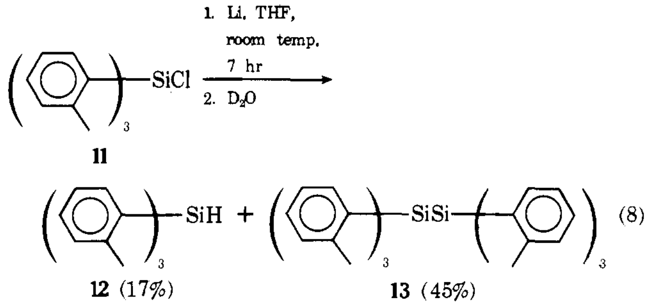
pound **10** forms during the reaction. The silane **1** obtained is only 24% monodeuterated, and no doubly labeled species is present (mass spectrum). NMR analysis suggests that about one-half of the deuterium is attached to silicon, and that the rest is in the *o*-methyl groups; however, the low overall deuterium incorporation weakens the precision of this analysis. This low incorporation may again arise from deprotonation of solvent by the intermediate (**10**).

Scheme II subsumes Scheme I and indicates how the silacyclobutene **5** might be involved as an intermediate in the lithiation of **2**. In order to determine whether **5** and **10** are in fact intermediates in the overall reaction, the lithiation of **2** was conducted in THF-d_8. With lithium in THF-d_8 (99% D) at room temperature for 6 hr, chlorosilane **2** again gave **1** and **6** after hydrolysis with D_2O. Furthermore, NMR and GLPC-mass spectral analysis of the reaction mixture revealed the presence of a small amount of **5**, confirming the above hypothesis. Analysis of the silane **1** showed that it consists of 23% d_0, 18% d_1, 48% d_2, and 11% d_3 species. The location of the deuterium, however, could not be determined precisely by NMR spectroscopy (see Experimental Section).

The formation of **1** containing two atoms of deuterium per molecule is in accord with the formation of significant quantities of **5** during the lithiation of **2**; its reduction product, **10**, either deprotonates the solvent or hydrolyzes in D_2O to give the observed d_2 species. The formation of monodeuterated silane is in accord with the alternative pathway shown in Schemes I and II operating simultaneously, i.e., direct lithiation of **2** to give **7** and subsequent rearrangement to **8**. Undeuterated **1** can be accounted for if **7** and/or **8** serve as the organolithium reagent in the conversion of **2** to **5**. We have no explanation for the formation of triply deuterated **1**.

Whether the coupling product **6** forms from **10** as well as **8** could not be accurately determined since its high molecular weight precluded precise determination of deuterium incorporation. As shown in Scheme II, formation of **6** from **10** in THF-d_8 requires the presence of deuterium attached to silicon. The NMR spectrum of **6** obtained in this experiment does contain the characteristic Si-H resonance (δ 5.78 ppm), suggesting that it arises at least in part from **8** and not from **10**. However, the possibility that **10** might rearrange in the same manner as silyllithium **7** cannot be excluded on the basis of the present observations. Consequently, the question of the precursor of **6** (**8** vs. **10**) remains open.

Lithiation and Subsequent Reactions of Tris(*o*-tolyl)chlorosilane. In light of the above results, the possibility that the lithiation of tris(*o*-tolyl)chlorosilane (eq 2) might be occurring in a similar but previously undetected fashion seemed likely and warranted a reinvestigation of the earlier report.[3] Reaction of tris(*o*-tolyl)chlorosilane (**11**)[5] with lithium in THF at room temperature for 7 hr gave, after hydrolysis with D_2O, tris(*o*-tolyl)silane (**12**) in 17% yield. Silane **12**, identified by comparison with an authentic sample,[5] contained deuterium. In contrast to the earlier report,[3] however, a second product was also observed during the lithiation, which proved to be the elusive hexakis(*o*-tolyl)disilane (**13**) (eq 8). The disilane was isolated in 45% yield, based on chlorosilane **11**, and its structure was assigned on the following basis. The 60-MHz ^1H NMR spectrum of **13** at ambient temperature in $CDCl_3$ contains only a singlet at δ 1.87 ppm (17.82 H) and an aromatic multiplet between δ 6.75 and 7.65 ppm (24.18 H). The mass spectrum of **13** exhibits a small parent ion at *m/e* 602; the base peak is at *m/e* 301 [tris(*o*-tolyl)silyl ion]. The fragmentation pattern below *m/e* 301 resembles that of tris(*o*-tolyl)silane (**12**) less 1 mass unit. Molecular weight determination, elemental analysis, and high melting point (296–299°) further support the structural assignment. The yield of disilane **13** increases to 74% when the reaction time is shortened to the previously reported[3] 3 hr.

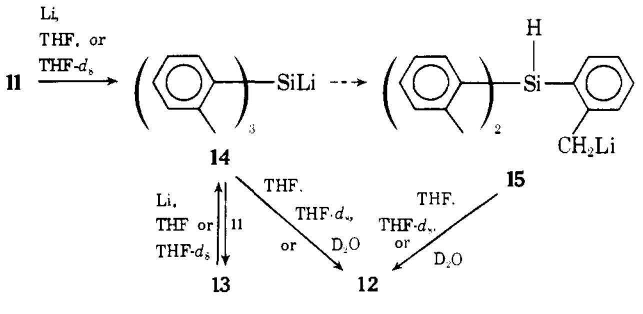


(8)

Analysis of the silane **12** obtained above revealed 0.43 atom of deuterium per molecule, with virtually all of the deuterium attached to silicon. Repeating the reaction in THF-d_8 and quenching with D_2O again afforded **12** and **13**; however, the silane consisted of only d_0 (73%) and d_1 (27%) species. Analysis again showed that essentially all the deuterium is attached to silicon. The disilane **13** contained no deuterium at all.

Reaction of **13** with lithium in THF-d_8 at room temperature for 6 hr gave, after hydrolysis with D_2O, **12** in 12% yield, along with unreacted disilane. The low conversion may be due to the limited solubility of **13** in THF-d_8. Analysis of **12** showed it to be 42% monodeuterated and 58% undeuterated, with at least 90% of the deuterium attached to silicon. The recovered disilane contained no deuterium.

Scheme III



The above results are summarized and ordered in Scheme III. The isolation of silane **12** with virtually all incorporated deuterium attached to silicon in each experiment, the failure to isolate any doubly deuterated **12** in the THF-d_8 experiment, and the isolation of **13** as the only other reaction product are all in accord with the hypothesis that tris(*o*-tolyl)silyllithium (**14**) is the sole organolithium species formed in the lithiation of **11**. The absence of doubly deuterated **12** from the THF-d_8 experiment eliminates a silacyclobutene as an intermediate, while the isolation of **12** with little, if any, deuterium in the *o*-methyl groups and the isolation of **13** rule out significant rearrangement of **14** to **15**. A possible explanation is that coupling of **14** with **11** to give **13** is facile and occurs rapidly as soon as **14** forms. Reduction of **13** with lithium affords 2 equiv of **14**, but only when the chlorosilane **11** has been consumed, does the silyllithium **14** have an appreciable lifetime. Even then no significant rearrangement to **15** occurs.

Conclusions

The essence of our findings resides in the contrasting behavior of tris(2,6-xylyl)chlorosilane and tris(*o*-tolyl)chlorosilane toward lithiation: whereas tris(2,6-xylyl)silyllithium (**7**) undergoes a facile intramolecular proton transfer to the isomeric benzyllithium **8**, tris(*o*-tolyl)silyllithium (**14**) does not. We propose the following rationalization of our results.

Both **7** and **14** should adopt propeller-like conformations in the ground state, and there are two possible sites which the *o*-methyl groups can occupy. One is proximal (methyl up, adjacent to the silicon-lithium bond), and the other is distal (methyl down, away from the silicon-lithium bond, and directed toward the base of the pyramid). Regardless of the mechanism responsible for exchanging these sites in **7**,[15] there will always be three proximal and three distal *o*-methyl groups; i.e., the molecule is conformationally homogeneous. Accordingly, if proton transfer occurs from one of the three proximal methyl groups to the nearby silicon-lithium bond, the inescapable propinquity of these groups in **7** establishes a high degree of probability for intramolecular transfer. In contrast, conformational alternatives exist for **14** which place the *o*-methyl groups in positions inaccessible for proton transfer. In particular, isomers may be envisaged for **14** in which three, two, one, or none of the *o*-methyl groups are proximal. To the extent that isomers of **14** are populated in which some or all of the methyl groups are distal, the failure of **14** to rearrange is accounted for since the requisite favorable spatial arrangement for proton transfer cannot be attained in these conformations.[16]

Experimental Section[20]

Tris(2,6-xylyl)silane (1). A 3-l., three-necked, round-bottomed flask fitted with a mechanical stirrer, reflux condenser, pressure-equalizing addition funnel, and nitrogen inlet was flamed under a nitrogen stream. 1-Bromo-2,6-dimethylbenzene[22] (185 g, 1.0 mol) was placed in the flask and dissolved in anhydrous ether (1 l.). The resulting solution was stirred and cooled to 0°, and *n*-butyllithium (1.0 mol of 1.9 *M* in hexane)[23] was added to it dropwise over a 2.5-hr period. The solution was warmed to room temperature for 1.5 hr and cooled to −78°. Trichlorosilane (10.2 ml, 13.55 g, 0.10 mol) was added, and the resulting mixture was stirred and allowed to warm to room temperature overnight. About 1200 ml of ether and hexane was distilled from the mixture and replaced by 850 ml of dry benzene. The mixture was refluxed and stirred for 49.5 hr and cooled to room temperature. Water (200 ml) and 5% HCl (200 ml) were added, and the layers were separated. The organic layer was washed with 250 ml of saturated $NaHCO_3$ and 3 × 200 ml of H_2O, dried ($MgSO_4$), and stripped (rotary evaporator followed by vacuum pump) to leave 81 g of yellow oil that slowly crystallized. Recrystallization from hexane (Norite) gave two crops which were combined and recrystallized from acetone to give 12.21 g (36%) of pure tris(2,6-xylyl)silane: mp 153.5–155.5°; NMR δ 2.10 (s, 17.96 H), 5.74 (s, 0.96 H), 6.73–7.25 (m, 9.08 H); mass spectrum *m/e* (rel intensity, %), 346 (P + 2, 2), 345 (P + 1, 11), 344 (P^+, 31), 343 (1), 239 (29), 238 (100), 223 (29), 146 (17), 133 (62), 132 (54). Concentration of the acetone mother liquor afforded a second crop, 1.62 g, 13.83 g total (40%). Another 2.89 g could be obtained from the hexane mother liquor, 16.72 g total (48%). Recrystallization of the first crop from acetone gave the analytical sample, mp 154–155.5°.

Anal. Calcd for $C_{24}H_{28}Si$: C, 83.66; H, 8.19; Si, 8.15. Found: C, 84.25; H, 8.45; Si, 7.80.

Tris(2,6-xylyl)chlorosilane (2). A solution of tris(2,6-xylyl)silane (**1**) (3.44 g, 0.01 mol) in CCl_4 and sulfuryl chloride (8.1 ml, 1.35 g, 0.1 mol) was refluxed for 60 hr, at which time the NMR spectrum of an aliquot showed the reaction to be complete. Removal of the solvent left 3.90 g of off-white crystals. Two recrystallizations from hexane gave 2.00 g (53%) of pure tris(2,6-xylyl)chlorosilane: mp 145–146.5°; NMR δ 2.18 (s, 17.93 H), 6.79–7.33 (m, 9.07 H); mass spectrum, exact mass 378.157623 (calcd, 378.157048), *m/e* (rel intensity, %) 378 (P, 7), 275 (10), 274 (43), 273 (31), 272 (100), 259 (12), 257 (33), 243 (metastable), 237 (11), 236 (15), 207 (42), 193 (19), 180 (12), 167 (84). Recrystallization from acetone followed by drying at 140° (0.1 mm) for 3 hr gave the analytical sample, mp 157–158°.

Anal. Calcd for $C_{24}H_{27}ClSi$: C, 76.06; H, 7.18; Cl, 9.35; Si, 7.41. Found: C, 76.10; H, 7.09; Cl, 10.01; Si, 6.92.

Tris(2,6-xylyl)fluorosilane (3). Tris(2,6-xylyl)chlorosilane (**2**) (1.00 g, 2.64 mmol) was dissolved in 75 ml of absolute ethanol (warming was necessary) in a 125-ml erlenmeyer flask containing a magnetic stirrer. Aqueous 48–51% HF (ca. 0.5 ml) was added, followed by a solution of $AgNO_3$ (500 mg, 2.94 mmol) in 1 ml of distilled water. The flask was stoppered and wrapped in aluminum foil, and the solution was stirred overnight. The mixture was filtered (Celite) and the cake washed well with benzene. The filtrate was stripped and the resulting residue taken up in hexane–benzene (3:1). Washing twice with 50 ml of H_2O, 50 ml of 5% $NaHCO_3$, and 50 ml of H_2O, drying ($MgSO_4$), and stripping afforded 0.90 g of pale yellow crystals. Recrystallization from hexane (two crops) gave 765 mg (80%) of pure tris(2,6-xylyl)fluorosilane: mp 152.5–154°; NMR δ 2.12 (d, ${}^5J_{HF}$ = 2.8 Hz, 18.03 H), 6.76–7.32 (m, 8.97 H); mass spectrum *m/e* (rel intensity, %) 363 (P + 1, 11), 362 (P^+, 35), 257 (28), 256 (100), 241 (29), 207 (14), 164 (12), 152 (10), 151 (60), 150 (17), 105 (10), 91 (10), 47 (10). Recrystallization from hexane gave the analytical sample, mp 153–154°.

Anal. Calcd for $C_{24}H_{27}FSi$: C, 79.51; H, 7.51; F, 5.24; Si, 7.75. Found: C, 79.35; H, 7.39; F, 4.95; Si, 7.55.

5-Methyl-7,7-bis(2,6-xylyl)-7-silabicyclo[4.2.0]octa-1,3,5-triene (5). A 25-ml, three-necked, round-bottomed flask fitted with a nitrogen inlet, reflux condenser, stopcock, stopper, and magnetic stirring bar was flame dried under a nitrogen stream. Tris(2,6-xylyl)fluorosilane (**3**) (432 mg, 1.19 mmol) was placed in the flask and dissolved in dry benzene (10 ml). Isopropyllithium (4.75 ml, 5.99 mmol of 1.26 *M* in pentane)[23] was added to the stirred solution in a single portion. The resulting yellow solution was stirred and refluxed for 28 hr. The solution was cooled and hydrolyzed with 5 ml of water. The layers were separated, and the aqueous layer was extracted once with 10 ml of ether. The combined organic layers were dried ($MgSO_4$) and stripped [rotary evaporation followed by a vacuum pump (0.1 mm)] to leave 603 mg of pale yellow solid. Recrystallization from absolute ethanol (Norite) gave two crops of impure product (348 mg total) which were combined and recrystallized from hexane to give 185 mg (45%) of pure 5-methyl-7,7-bis(2,6-xylyl)-7-silabicyclo[4.2.0]octa-1,3,5-triene, mp 180.5–182°. A second crop was obtained, 16 mg, 201 mg total (49%): NMR (C_6D_6) δ 2.25 (s, 2.89 H), 2.37 (s, 11.72 H), 2.78 (s, 1.78 H), 6.75–7.30 (m, 9.62 H); NMR (CS_2) δ 2.28 with shoulder at 2.26 (s, 14.70 H), 2.68 (s, 1.92 H), 6.72–7.33 (m, 9.38 H); mass spectrum, exact mass, 342.180084 (calcd, 342.180370), *m/e* (rel intensity, %) 343 (P + 1, 13), 342 (P^+, 37), 328 (19), 327 (54), 239 (20), 238 (18), 237 (50), 236 (57), 207 (22), 206 (26), 193 (10), 192 (16), 191 (11), 149 (15), 133 (15), 119 (17), 105 (18). Recrystallization of the first crop from hexane followed by drying at 80° (0.1 mm) for 3.5 hr gave the analytical sample, mp 182–182.5°.

Anal. Calcd for $C_{24}H_{26}Si$: C, 84.15; H, 7.65; Si, 8.20. Found: C, 84.16; H, 7.59; Si, 8.00.

Reaction of Tris(2,6-xylyl)chlorosilane (2) with Isopropyllithium in THF. A 25-ml, three-necked, round-bottomed flask fitted with a nitrogen inlet, stopcock, stopper, and magnetic stirrer was flame dried under a nitrogen stream. Tris(2,6-xylyl)chlorosilane (**2**) (201 mg, 0.53 mmol) was placed in the flask, and dry THF (5 ml) was added. Isopropyllithium (4.0 ml, 5.04 mmol, 1.26 *M* in pentane)[23] was added in two portions and the resulting solution stirred for 6.5 hr at room temperature. The mixture was hydrolyzed with water and diluted with ether, and the layers were separated. Drying ($MgSO_4$) and stripping left 445 mg of a pale yellow oil. The oil was chromatographed on 1.3 × 20 cm of silica gel (with phosphor added) packed in hexane using hexane as eluent. A forerun contained only hydrocarbon residues from the isopropyllithium. The first fraction to elute proved to be a mixture of silane **1**, 17 mg, chlorosilane **2**, 49 mg, and silacyclobutene **5**, 28 mg, as revealed by the NMR spectrum. A second fraction (13 mg) consisted entirely of silacyclobutene **5**. The total yield of silacyclobutene was 41 mg (22% or, corrected for unreacted chlorosilane, 30%). The yield of silane **1** was 9% or, corrected for unreacted chlorosilane, 12%.

Tris(2,6-xylyl)benzylsilane (9). A 25-ml, three-necked, round-bottomed flask fitted with a nitrogen inlet, reflux condenser, stopcock, stopper, and magnetic stirrer was flame dried under a nitrogen stream. Tris(2,6-xylyl)chlorosilane (**2**) (378.5 mg, 1.00 mmol) was placed in the flask and dissolved in dry benzene (5 ml). A solution (5 ml) of benzyllithium in THF-ether (2:1) prepared from 5 mmol of benzyl methyl ether[11] was added slowly to the stirred solution of chlorosilane. The resulting black mixture was stirred and refluxed for 22 hr. The mixture was cooled to room temperature and hydrolyzed with water (5 ml). After dilution with hexane, the layers were separated, and the aqueous layer was extracted once with hexane (10 ml). The combined organic layers were washed with water (10 ml), dried ($MgSO_4$) and stripped to leave 673 mg of yellow oil. Chromatography on 1.3 × 20 cm of silica gel (phosphor) in hexane using hexane and then 5% ether in hexane gave two fractions. The first was a mixture of the benzylsilane **9**, bibenzyl, and chlorosilane (by NMR spectroscopy). The second consisted entirely of benzylsilane. Each fraction was recrystallized from methanol to afford 51 mg, mp 118.5–122.5° and 68 mg, mp 130–132°, respectively, of benzylsilane (27% total). Although the melting point of the first fraction is low, no impurities could be detected by NMR or TLC: NMR δ 2.08 (s, 18.15 H), 3.06 (s, 1.95 H), 6.60–7.22 (m, 13.90 H); mass spectrum (15 eV), small parent ion at *m/e* 434, base peak, *m/e* 343 ($P - C_6H_5CH_2\cdot$). Both fractions were combined and recrystallized twice from methanol and dried at 80° (0.1 mm) for 3.5 hr to give the analytical sample, mp 131–132°.

Anal. Calcd for $C_{31}H_{34}Si$: C, 85.66; H, 7.88; Si, 6.46. Found: C, 85.28; H, 7.81; Si, 6.16.

An identical experiment using 1.0 mmol of tris(2,6-xylyl)fluorosilane (**3**) and 5 mmol of benzyllithium gave no benzylsilane **9** and only traces of silacyclobutene **5** on work-up. The only other substance found was starting material.

Reaction of Tris(2,6-xylyl)chlorosilane (2) with Lithium. (A) In THF. The following apparatus and procedure for preparing lithium metal for reaction are used in all subsequent reactions of this type.

A 25-ml, three-necked, round-bottomed flask fitted with a nitrogen inlet, stopcock, stopper, and magnetic stirrer was flame dried under a nitrogen stream. Lithium wire (3.25 mm, 13.9 mg, 2.0 mg-atoms) containing 1% sodium was placed in the flask and washed four times with 5-ml portions of dry pentane. Tris(2,6-xylyl)chlorosilane (**2**) (378.5 mg, 1.0 mmol) was placed in the flask, and dry THF (5 ml) was added. The lithium metal was split with a spatula to give clean surfaces. The mixture was stirred at room temperature; within 1 hr, it was cherry-red in color. After 3.25 hr, one-half of the solution was withdrawn and added to D_2O (ca. 1 ml). This mixture was diluted with ether, the layers were separated, and the organic layer was washed once with 5 ml of water. Drying ($MgSO_4$) and stripping afforded 186 mg of colorless oil, the NMR spectrum of which revealed the presence of tris(2,6-xylyl)silane (**1**) and tris(2,6-xylyl)(2-bis(2,6-xylyl)silyl-3-methylbenzyl)silane (**6**). The oil was chromatographed on 1.3 × 22 cm of silica gel (phosphor) in hexane. Elution with hexane afforded 100 mg of silane **1**. Elution with 10% ether in hexane gave 78 mg of the disilane **6**. A reflux condenser was fitted to the flask, and the remainder of the original reaction mixture was refluxed for 2.5 hr. Cooling and work-up as described above gave 40 mg of silane **1** and 66 mg of disilane **6**. The total yield of silane was 140 mg (41%) and of disilane, 144 mg (42%), both based on chlorosilane. The disilane from the room temperature run was recrystallized from hexane to give 52 mg of white prisms: mp 245–247°; NMR δ 1.92 and 2.03 (both s, 33.89 H total) 3.00 (broad s, 1.80 H), 5.78 (broad s, 0.91 H), 6.47–7.23 (m, 17.41 H); mass spectrum, parent ion between *m/e* 680 and 690 (requires 686, could not be determined accurately).

Two further recrystallizations from hexane gave the analytical sample, mp 247–247.5°.

Anal. Calcd for $C_{48}H_{54}Si_2$: C, 83.90; H, 7.92; Si, 8.17; mol wt, 687. Found: C, 83.44; H, 8.00; Si, 8.01; mol wt (osmometry in $CHCl_3$), 680.

The silane **1** was analyzed for deuterium content as follows. The mass spectrum was determined under conditions identical with those used for the undeuterated silane. The spectrum of deuterated material was analyzed according to the method of Biemann,[24] revealing that 62% of the sample was undeuterated, and that 38% of the sample contained one atom of deuterium per molecule. Accordingly, there are 27.62 protons per molecule on the average, and normalizing the integrated NMR spectrum (average of five integrations) to this value gives the following intensities: aromatic, 8.98 H; Si-H, 0.87 H; $Ar-CH_3$, 17.77 H; i.e., about one-third of the deuterium is attached to silicon, and two-thirds is in the *o*-methyl groups.

The above reaction was repeated in refluxing THF for 4.5 hr. Work-up of one-half of the mixture again afforded only silane **1** and disilane **6**. The remaining reaction mixture was treated with 3 equiv of isopropyl chloride, refluxed for 5 min, and stirred at room temperature for 18 hr. Subsequent work-up again gave only **1** and **6** and no isopropylsilane **4**.

When tris(2,6-xylyl)fluorosilane (**3**) was substituted for chlorosilane **2** in this experiment, no reaction occurred, even after 30 hr of refluxing in THF.

(B) **In THF-*d*$_8$.** The reaction described above was repeated using 201 mg (0.53 mmol) of tris(2,6-xylyl)chlorosilane (**2**), 3.5 mm (2.12 mg-atoms) of lithium wire, and THF-*d*$_8$ (1 ml). The reaction mixture was allowed to stir for 6.25 hr at room temperature. Addition of D_2O (ca. 1 ml) and work-up as described above gave 190 mg of a clear viscous oil. The NMR spectrum of the crude material revealed the presence of silane **1**, disilane **6**, silacyclobutene **5**, starting material, and other unidentifiable material. Chromatography on 21 × 1.3 cm of silica gel (phosphor) in hexane using hexane followed by 5% ether in hexane as eluents gave three fractions. Fraction 1 (71 mg) was silane **1**, silacyclobutene **5**, and impurity (δ 2.07, s, is the only characteristic). Fraction 2 (20 mg) was silane **1** and impurity, and fraction 3 (80 mg) was disilane **6** and other impurities (by NMR). Fraction 3 was rechromatographed on 19.5 × 1.3 cm of silica gel (phosphor) in hexane. Elution with 5% ether in hexane followed by recrystallization from hexane afforded 5 mg of disilane **6**, mp 237–240°.

Fractions 1 and 2 were combined and rechromatographed on 22 × 1.3 cm silica gel (phosphor) in hexane. The column was eluted with hexane and monitored by TLC (silica, hexane). A cut (28 mg) with the same R_f as the silane **1** was obtained, but its NMR spectrum showed the presence of traces of the silacyclobutene **5** and a significant amount of the impurity as well as the silane **1**. Attempts to crystallize the mixture from ethanol failed, as did an attempt to sublime the silane out of the mixture [125–130° (0.2 mm)]. The oil obtained on the cold finger as a result of this attempt was analyzed by NMR. A resonance at δ 5.74, corresponding to the Si-H proton in silane **1**, was present, but it could not be integrated accurately because of the presence of the unknown impurity.

The mixture was successfully analyzed by GLPC-mass spectrometry (220°, 6 ft × ⅛ in. 10% OV-1 on 120 mesh Chromosorb W). The presence of the silacyclobutene **5** was confirmed, and the deuterium content of the silane **1** could be determined. Analysis of the mass spectrum as described above (using an authentic standard run under these conditions) showed the silane to be 23% d_0, 18% d_1, 48% d_2, and 11% d_3.

Reaction of 5-Methyl-7,7-bis(2,6-xylyl)-7-silabicyclo[4.2.0]octa-1,3,5-triene (5) with Lithium. Lithium wire (1.50 mm, 6.45 mg, 0.93 mg-atom) was prepared for reaction as described above. 5-Methyl-7,7-bis(2,6-xylyl)-7-silabicyclo[4.2.0]octa-1,3,5-triene (**5**) (75 mg, 0.219 mmol) was placed in the flask, and dry THF (3 ml) was added. The resulting mixture was stirred for 6 hr at room temperature. D_2O (ca. 1 ml) was added, and the mixture was worked up as described above to give 71 mg of pale yellow oil. Analysis by NMR showed only silane **1** and starting material, and that about 80% conversion had occurred. Chromatography on 21 × 1.3 cm of silica gel (phosphor) in hexane using hexane as eluent gave two fractions. The first, containing only the silane, was stripped, and the crude material was recrystallized from ethanol. Mass spectral analysis as described above showed the silane to be 76% undeuterated and 24% monodeuterated. Normalizing the integrated NMR spectrum (average of three integrations) to 27.76 protons per molecule gave the following intensities: aromatics, 8.92 H; Si-H, 0.92 H; Ar-CH_3, 17.92 H. Thus, although it would appear that one-half of the deuterium is attached to silicon and the other half is in the *o*-methyl groups, the imprecision of the data weakens the force of this conclusion.

Reaction of Tris(*o*-tolyl)chlorosilane (11) with Lithium. Hexakis(*o*-tolyl)disilane. (A) In THF. Lithium wire (6.5 mm, 28 mg, 4.0 mg-atoms) was prepared for reaction as described above. Tris(*o*-tolyl)chlorosilane (**11**) (336.5 mg, 1.0 mmol)[5] was placed in the flask, and dry THF (5 ml) was added. The resulting mixture was stirred for 7 hr at room temperature. The brown solution was removed from the unreacted lithium and added to D_2O (ca. 1 ml). Work-up as described above afforded 335 mg of thick, colorless oil. NMR and TLC analysis suggested that some unreacted chlorosilane might be present. The crude mixture was dissolved in methanol-benzene and stirred with excess aqueous $AgNO_3$ for 2.5 hr at room temperature. The resulting black mixture was filtered (Celite) and the filtrate was stripped. The material thus obtained was taken up in ether and washed twice with 20 ml of dilute NH_4OH, once with 20 ml of water, dried ($MgSO_4$), and stripped. The mixture was chromatographed on 22 × 1.3 cm of silica gel (phosphor) packed in hexane. Elution with hexane followed by 10% ether in hexane gave two fractions.

The first fraction afforded 51 mg (17% based on chlorosilane) of tris(*o*-tolyl)silane (**12**).[5] Recrystallization from absolute ethanol gave two crops: first crop, 26 mg, mp 91.5-93° (lit.[5] mp 89-90°); second crop, 12 mg, mp 90-93°; total, 38 mg (12%). The structure of the silane was confirmed by comparison of its NMR spectrum with that of an authentic sample.[5] NMR found: δ 2.27 (s), 5.72 (s), 6.93-7.43 (m) [for an authentic sample: δ 2.27 (s, 8.90 H), 5.72 (s, 0.88 H), 6.93-7.44 (m, 12.22 H)]. Mass spectral analysis of the silane showed it to be 57% d_0 and 43% d_1. Normalizing the integrated NMR spectrum of the silane (average of five integrations) to 21.57 protons per molecule gave the following intensities: aromatics, 12.17 H; Si-H, 0.58 H; Ar-CH_3, 8.84 H. If the assumption is made that the aromatic rings contain no deuterium, the intensities of the remaining two resonances can be normalized to 9.57 protons with the following result: (aromatics, 12.00 H assumed); Si-H, 0.59 H; Ar-CH_3, 8.98 H. Thus virtually all of the deuterium is attached to silicon, and none is in the *o*-methyl groups.

The second chromatography fraction afforded 135 mg (45% based on chlorosilane) of a second product, pure by NMR, identified as hexakis(*o*-tolyl)disilane (**13**) as shown below. Recrystallization of the crude product from hexane afforded 56 mg of white crystals: mp 290-293° (uncorrected); NMR ($CDCl_3$) δ 1.87 (s, 17.82 H), 6.75-7.65 (m, 24.18 H); mass spectrum, weak parent ion at *m/e* 602, base peak at *m/e* 301 [tris(*o*-tolyl)silyl ion]; the fragmentation pattern below *m/e* 301 resembles that of tris(*o*-tolyl)silane, less 1 mass unit. Recrystallization from hexane gave the analytical sample, mp 296-299° (uncorrected).

Anal. Calcd for $C_{42}H_{42}Si_2$: C, 83.66; H, 7.02; Si, 9.32; mol wt, 603. Found: C, 83.16; H, 7.00; Si, 9.20; mol wt (osmometry in $CHCl_3$), 602.

The experiment was repeated using 673 mg (2.0 mmol) of **11**, 13 mm (56 mg, 8.0 mg-atoms) of lithium wire, and 10 ml of THF. The reaction was quenched after 3 hr with H_2O and worked up as described above (the $AgNO_3$ treatment proved unnecessary), and the yield of disilane **13** increased to 74% (after chromatography). The yield of silane **12** was 18%.

(B) **In THF-d_8.** The above reaction was repeated using 3.9 mm (16.8 mg, 2.4 mg-atoms) of lithium wire, 202 mg (0.60 mmol) of **11**, and THF-d_8 (1 ml). The reaction mixture was stirred for 6.25 hr at room temperature and hydrolyzed with D_2O (ca. 1 ml). Work-up as above afforded 214 mg of a clear, viscous oil. The NMR spectrum of the crude mixture showed the presence of silane **12**, disilane **13**, and an impurity [δ 2.15 (s)]. Chromatography on 21 × 1.3 cm of silica gel (phosphor) in hexane using hexane, then 5% ether in hexane as eluents, afforded three fractions.

The first fraction (79 mg), an oil, was homogeneous by TLC, but the NMR spectrum showed it to be a mixture of silane **12** and the impurity. As was the case with silane **1** from the THF-d_8 experiment above, the impurity could not be removed. The mixture was again analyzed by GLPC-mass spectroscopy (210°, 10% OV-1 column). The deuterium content of the silane was determined in the usual manner (using an authentic standard run under these conditions). The analysis showed the silane to be 73% d_0 and 27% d_1. The two resonances in the NMR spectrum of this mixture corresponding to the Si-H proton, and the *o*-methyl protons (δ 5.72 and 2.27, respectively) were integrated three times and normalized to 9.73 protons (assuming the aromatic rings to be unchanged in the experiment). The following intensities were obtained: Si-H, 0.56 H; Ar-CH_3, 9.17 H. Although the *o*-methyl intensity is high, again all the deuterium appears to be attached to silicon.

The second and third column chromatography fractions (120 mg) from above were combined and recrystallized from hexane to give hexakis(*o*-tolyl)disilane (**13**) (30 mg), mp 277-279° (uncorrected). NMR and mass spectral analysis (on the base peak, *m/e* 301, and its heavier isotopes) showed that no deuterium had been incorporated into the disilane.

Reaction of Hexakis(*o*-tolyl)disilane (13) with Lithium in THF-d_8. Lithium wire (2.6 mm, 11.1 mg, 1.6 mg-atoms) and hexakis(*o*-tolyl)disilane (**13**) (241 mg, 0.40 mmol) were placed in the usual apparatus, and THF-d_8 (4 g) was distilled from $LiAlH_4$ directly into the reaction flask. The resulting mixture (not all of the disilane dissolved) was stirred at room temperature for 6 hr. The yellow mixture was quenched with D_2O (ca. 1.5 ml) and diluted with ether-CH_2Cl_2, and the layers were separated. The organic layer was dried ($MgSO_4$) and stripped to leave 304 mg of white solid. The NMR spectrum of the crude material revealed the presence of tris(*o*-tolyl)silane (**12**) and unreacted disilane. Chromatography on 20 × 1.3 cm of silica gel (phosphor) in hexane using hexane, then 10% ether in hexane as eluents, afforded two fractions. The first gave **12** (30 mg, 12%) and the second the unreacted disilane (210 mg, 99% recovery corrected for the portion that reacted). The disilane was recrystallized from benzene-hexane to give 101 mg of white crystals, which, by mass spectrometry and NMR, contained no deuterium.

The silane was recrystallized from absolute ethanol to give 11 mg of white crystals. Mass spectral analysis showed the silane composition to be 58% d_0 and 42% d_1. Integration of the Si-H and Ar-CH_3 resonances of the NMR spectrum (average of three integrations) and normalization to 9.58 protons showed the Si-H intensity to be 0.62 H and the Ar-CH_3 intensity to be 8.96 H. Thus about 91% of the deuterium is attached to silicon. Analysis of the fragmentation pattern of the mass spectrum gave the same result.

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References and Notes

(1) R. J. Boettcher, D. Gust, and K. Mislow, *J. Am. Chem. Soc.*, **95**, 7157 (1973).

(2) H. Gilman and H. J. S. Winkler in "Organometallic Chemistry", H. Zeiss, Ed., Reinhold, New York, N.Y., 1960, pp 270-345, and references therein.

(3) M. V. George, D. J. Peterson, and H. Gilman, *J. Am. Chem. Soc.*, **82**, 403 (1960).

(4) D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **80**, 2677 (1958); A. G. Evans, M. L. Jones, and N. H. Rees, *J. Chem. Soc. B*, 894 (1969).

(5) H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950).

(6) Intensities of NMR resonances are not rounded to whole numbers but are normalized to the expected total number of protons.

(7) C. Eaborn and R. W. Bott in "Organometallic Compounds of the Group IV Elements", Vol. 1 (Part I), A. G. MacDiarmid, Ed., Marcel Dekker, New York, N.Y., 1968; H. Gilman and H. A. McNinch, *J. Org. Chem.*, **26**, 3723 (1961); H. Gilman, A. G. Brook, and L. S. Miller, *J. Am. Chem. Soc.*, **75**, 3757 (1953).

(8) (a) C. Eaborn, D. R. M. Walton, and M. Chan, *J. Organomet. Chem.*, 9, 251 (1967); (b) H. Gilman and W. H. Atwell, *J. Am. Chem. Soc.*, **87**, 2678 (1965); (c) ibid., **86**, 5589 (1964).

(9) G. Marr and D. E. Webster, *J. Organomet. Chem.*, **2**, 93 (1964).

(10) NMR studies have shown that, whereas trityllithium is highly dissociated, and its negative charge is delocalized, triphenylsilyllithium has a relatively covalent silicon–lithium bond. See R. H. Cox, E. G. Janzen, and W. B. Harrison, *J. Magn. Reson.*, 274 (1971).

(11) H. Gilman and G. L. Schwebke, *J. Org. Chem.*, **27**, 4259 (1962).

(12) R. A. Benkeser and F. J. Riel, *J. Am. Chem. Soc.*, **73**, 3472 (1951).

(13) Although none of the known benzosilacyclobutenes have been reduced by metals, nucleophilic cleavage of their rings results in rupture of the silicon–benzylic carbon bond.[8a,c] Reduction of 1,1,2-triphenyl-1-silacyclobutane with lithium gives polymeric material, probably via the initially formed 1,1,4-triphenyl-1,4-dilithio-1-silabutane.[14]

(14) H. Gilman and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 2687 (1964).

(15) D. Gust and K. Mislow, *J. Am. Chem. Soc.*, **95**, 1535 (1973).

(16) In the closely related case of tris(*o*-tolyl)phosphine, all three methyl groups are in proximal positions (i.e., pointing toward the apex of the phosphine pyramid), both in the crystal lattice[17] and in solution.[18] The same situation obtains for the corresponding oxide in the solid state.[17] However, in the crystal lattice, the corresponding sulfide[19] and selenide[17] have two proximal and one distal methyl groups, and tris(*m*-tolyl)phosphine sulfide has one proximal and two distal methyl groups.[19]

(17) R. A. Shaw, M. Woods, T. S. Cameron, and B. Dahlen, *Chem. Ind.* (*London*), 151 (1971); R. A. Shaw, M. Woods, W. Egan, and J. Jacobus, ibid., 532 (1973).

(18) E. J. Halpern and K. Mislow, *J. Am. Chem. Soc.*, **89**, 5224 (1967).

(19) T. S. Cameron, K. D. Howlett, R. A. Shaw, and M. Woods, *Phosphorus*, **3**, 71 (1973).

(20) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Tetrahydrofuran (THF) was dried over KOH and distilled from $LiAlH_4$ onto Linde type 4A molecular sieves. THF-d_8 (Stohler Isotope Chemicals, 99% D) was distilled either directly from $LiAlH_4$ into the reaction flask or onto 4A molecular sieves. Benzene was dried by refluxing over sodium and was distilled onto 4A molecular sieves. Dry solvents and reagents sensitive to air or moisture were transferred by syringe. The D_2O employed was 99.7% D. Unless specified otherwise, NMR spectra were recorded on a Varian A-60A spectrometer at ambient temperature (ca. 37°), refer to ca. 20% solutions in CS_2 containing tetramethylsilane (TMS) as internal reference, and are in parts per million from Me_4Si. Mass spectra were determined with an AEI MS-9 high-resolution mass spectrometer or a Du Pont 21-490 mass spectrometer[21] with an ionizing voltage of 70 eV. Fragmentation patterns include peaks with relative intensity $\geq 10\%$ of the base peak. Melting points were determined with a Thomas-Hoover apparatus and are corrected.

(21) Purchased with funds from NSF Chemistry Section Grant No. GP-32826.

(22) Prepared in 54–69% yield from 2,6-dimethylaniline and sodium nitrite in 48% HBr, followed by cuprous bromide or copper powder.

(23) Obtained from Alfa Inorganics, Beverly, Mass.

(24) K. Biemann, "Mass Spectrometry Organic Chemical Applications", McGraw-Hill, New York, N.Y., 1962, pp 204–250.

Empirical Force-Field Calculations on a Model System for Trimesityl Derivatives of Group IIIa, IVa, and Va Elements. Investigation of Stereoisomerization Pathways[1,2]

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Abstract: Stereoisomerization in the class of compounds $(Mes)_3Z$ (Mes = mesityl; Z = B, CH, N, etc.) has been investigated using the technique of empirical force-field calculations. The study was made feasible by employing a simplified model based on trimesitylmethane in which the only distinction among molecules in this class was the difference in the preferred length of the Z–Mes bond. Calculated energies for the idealized transition states point to the two-ring flip mechanism as the pathway of lowest energy over a wide range of structures. Calculated energies for this mechanism follow a trend which parallels experimental values. Activation energies are predicted for $(Mes)_3N$, $(Mes)_3SnH$, and $(Mes)_3Bi$ of 25–27, 5–7, and 3–5 kcal/mol, respectively. Results for the higher energy mechanisms are discussed in terms of structural changes accompanying the change in bond length to the central atom. The three-ring flip is found to be consistently higher in energy than the two-ring flip in the region of interest.

The intricacies of isomerism and isomerization in compounds containing three aromatic rings bonded to a common central atom, Z, have been the subject of continuing investigation in recent years in our[4] and other[5-11] laboratories. The interest in such triaryl compounds arises from the great variety of stereoisomerization pathways available to these systems.[12] In a previous paper,[4f] the stereochemistry of a simple representative, trimesitylmethane (**1**), was examined in detail utilizing the approach of full relaxation empirical force-field calculations. The present paper describes an extension of this earlier work to the general class of compounds $(Mes)_3Z$ (**2**, Mes = mesityl; Z = B, CH, N, etc.) and represents an effort to determine to what extent generalizations developed for **1** may be applied to other members of the series **2** and, by extension, to the class of triaryl compounds in general.

Specifically, for the members of series **2**, we will be concerned with the identification of the threshold mechanism[4e] of stereoisomerization and with the relative ordering of the activation energies for the nonthreshold mechanisms.[13]

The Model

The subject compounds of this study, **2**, were chosen because (1) they typify highly congested triaryl compounds, the chemistry of which is dominated by steric effects, and (2) while their high symmetry precludes[4e] a detailed laboratory investigation of mechanism, it simplifies the study by empirical force-field calculations.

The particular compounds of interest are all trimesityl derivatives of groups IIIa, IVa, and Va, *e.g.*, those with Z = B, CH, SiH, GeH, N, P, and As. A proper conformational analysis of these compounds by empirical force-field calculations would demand the specification of a large number of parameters for the interactions of each Z with the surrounding carbon and hydrogen atoms. Reliable parameters for such interactions as bond stretching, bond angle bending, torsion, and nonbonded potentials are scarce for most of these elements, and achieving such a parametrization would prove to be both risky and difficult.[16] Although it is conceivable that these constants might have been estimated by a lengthy parametrization process, we decided not to pursue this complex and arduous undertaking and instead cut the Gordian knot by adopting a starkly simplified model force field.

In this model, the entire class of compounds $(Mes)_3Z$ is represented by one member of that class, trimesitylmethane (**1**). This molecule was chosen because, being a hydrocarbon, its force-field parametrization is the most reliable available.[20] Each compound of series **2** is treated here as being identical with **1** except for the C–Mes bond length, which has been allowed to assume different values depending on the nature of the central atom. This model is founded