

Supplementary Material Available: A listing of the observed and the final calculated structure factors (16 pages). Ordering information is given on any current masthead page.

References and Notes

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Diastereotopic Groups in Silyllithium and Germyllithium Compounds. Slow Inversion about Silicon and Germanium

Joseph B. Lambert*^{1a} and Migdalia Urdaneta-Pérez^{1b}

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received June 6, 1977

Abstract: Diisopropylphenylsilyllithium (**1**), dibenzylphenylsilyllithium (**2**), and diisopropylphenylgermyllithium (**3**) have been prepared by the reaction of lithium with the corresponding disilane or digermane. The methyls in the isopropyl groups of **1** and **3** are diastereotopic and anisochronous at room temperature in a wide range of solvents. The benzyl protons in **2** are accidentally isochronous even at 270 MHz. The isopropyl methyl groups remain anisochronous in both the silyl (**1**) and the germyl (**3**) systems as the temperature is raised to 185 °C in diglyme. Because the ⁷Li resonances of **1** and **3** are very similar to that of diisopropylphenylcarbonyllithium (**5**), the ionicities of the Si-Li and Ge-Li bonds cannot be greatly different from that of the C-Li bond. A lower limit to inversion about trivalent silicon and germanium can therefore be set at about 24 kcal/mol.

Barriers have been measured for pyramidal inversion about carbon, nitrogen, oxygen, phosphorus, sulfur, arsenic, and selenium.² In the group 4 series, formal trivalency (required for pyramidal inversion) is found in negatively charged species, such as carbanions. Such materials are prone to aggregation,³ although exchange out of the aggregate is probably fast on the NMR time scale.⁴ Bimolecular ligand exchange is possible within the aggregate, so that higher order processes other than unimolecular pyramidal inversion might bring about spectral equivalence.³ Before inversion can take place, it is necessary for the partially covalent bond between the metal and the central atom to break. Thus the process of inversion can involve up to three steps, exchange out of the aggregate, cleavage of the metal-X covalent bond, and pyramidal inversion.⁵ If spectral changes are observed that can be attributed to pyramidal inversion, further experiments would be necessary to specify which of these three steps is rate determining.

In the present paper, we are considering the inversion properties of silicon and germanium. By analogy with phosphines and arsines,² it is to be expected that pyramidal inversion about trivalent silicon and germanium is slow on the NMR time scale. The slowness of inversion, however, has never been demonstrated by experiment. Thus it is possible that, although unimolecular inversion is indeed slow, bimolecular exchange within an aggregate rapidly inverts Si and Ge configuration. The only information on the subject is an LCAO-MO-SCF

calculation on SiH₃⁻, which gave a barrier of 39.6 kcal/mol.⁶ This figure of course refers to a gas phase-like operation, so that the effects of aggregation are not considered.

The two most common methods for studying inversion barriers are temperature variation of the NMR spectrum and loss of optical activity.² Although in principle it is possible to follow the racemization or epimerization of a silyl or germyl anion, in practice these processes can also occur during the formation of the anion. If the inversion process were to be followed by quenching the anion, e.g., with CO₂, the quenching reaction must be stereospecific, its stereochemistry must be known, and the optical purity of the quenching product must be determinable. The dynamic NMR experiment suffers from none of these limitations, since in its usual form, it only requires the exchange of diastereotopic groups via the inversion process. In order to determine the configurational stability of silyl or germyl anions, we have chosen the DNMR method as the more likely to yield interpretable results.

For the silyl or germyl anion to have sufficient stability, it must be tertiary and possess at least one aromatic substituent. One or both of the remaining substituents must possess groups that are diastereotopic when atomic inversion is slow. Interconversion of these groups would serve as the monitor on the inversion process. The aromatic substituent also would lower the barrier slightly.² The systems diisopropylphenylsilyllithium, C₆H₅(*i*-Pr)₂SiLi (**1**), and dibenzylphenylsilyllithium, C₆H₅(C₆H₅CH₂)₂SiLi (**2**), possess these structural require-

ments. The methyls in the isopropyl groups and the methylene protons in the benzyl groups would be diastereotopic when inversion is slow. Either pyramidal inversion or exchange within the aggregate could cause these groups to become enantiotopic and hence equivalent on the NMR time scale. We have prepared these materials and the analogous diisopropylphenylgermyllithium, $C_6H_5(i-Pr)_2GeLi$ (**3**), and examined their NMR spectra. Diastereotopic groups due to slowly inverting silyl or germyl anions have not been reported previous to our work,⁷ although neutral tetracoordinate silicon is known to cause such spectral nonequivalence.⁸ We report herein the results of these experiments.

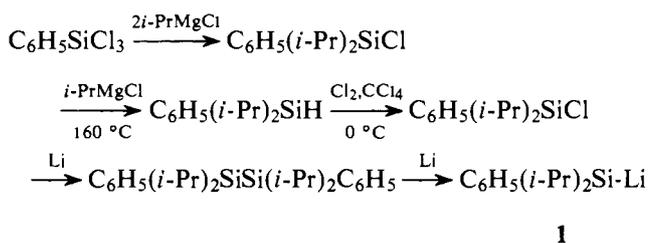
Results

Diisopropylphenylsilyllithium (**1**) was synthesized according to the procedure outlined in Scheme I. From the reaction of phenyltrichlorosilane with isopropylmagnesium chloride, only a mixture of the desired diisopropylphenylchlorosilane with other halides could be obtained. Under forced conditions, however, a disproportionation reaction occurred, and diisopropylphenylsilane could be isolated in pure form but in poor yield. This material could be converted via the chlorosilane and the disilane (isolated or in situ) to the silyllithium compound (**1**). Preparation of dibenzylphenylsilyllithium was somewhat more straightforward, since in this case dibenzylphenylchlorosilane could be isolated from the direct reaction of phenyltrichlorosilane with benzylmagnesium chloride. The corresponding disilane, however, could not be isolated but spontaneously cleaved under the reaction conditions to form the silyllithium compound (**2**). The disilane could be obtained by subsequent reaction of **2** with dibenzylphenylchlorosilane. This disilane in turn could be converted back to **2** by reaction with lithium. Reaction of the silyllithium compounds with H_2O or D_2O gave high yields of diisopropylphenylsilane and dibenzylphenylsilane, respectively, with deuterium in the appropriate position. Diisopropylphenylsilyllithium (**1**) was stable in tetrahydrofuran (THF) solutions for considerable periods of time, but dibenzylphenylsilyllithium (**2**) gave cleavage products, probably 4-(dibenzylphenylsilyl)butan-1-ol, after prolonged times at room temperature.

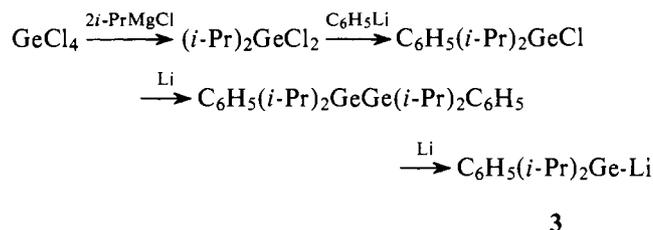
Diisopropylphenylgermyllithium (**3**) was prepared according to the procedure in Scheme II. Reaction of germanium tetrachloride with isopropylmagnesium chloride gave a mixture of isopropylchlorogermans. Reaction conditions (see Experimental Section) were used to optimize the yield of diisopropylchlorogermans. Reaction of this material (along with some triisopropylchlorogermane impurity) with phenylsilyllithium gave diisopropylphenylchlorogermane. Reaction with lithium gave the digermane, which spontaneously cleaved to give diisopropylphenylgermyllithium (**3**). Reaction of this material with diisopropylphenylchlorogermane gave isolable digermane, which again could be cleaved with lithium back to **3**. Hydrolysis of **3** in D_2O gave diisopropylphenylgermane with deuterium in the appropriate position.

The methyl groups in the isopropyl compounds are diastereotopic by symmetry for all members of the synthetic series of Scheme I (in the lithium compound, inversion about silicon must be slow for the methyls to be diastereotopic). At 270 MHz, diisopropylphenylchlorosilane, 1,1,2,2-tetraisopropyl-1,2-diphenyldisilane, diisopropylphenylsilane, and diisopropylphenylsilyllithium all exhibited two well-separated methyl doublets in the proton spectrum, as illustrated in Figure 1a (supplementary material) for diisopropylphenylchlorosilane. The splitting ranged from 0.07 ppm (the hydride) to 0.1 ppm (**1**). At 90 MHz the separation often was such that the two doublets overlapped to give a deceptive triplet. For the lithium reagent (**1**), the nonequivalence was observed in tetrahydrofuran, diglyme, glyme, hexamethylphosphoramide,

Scheme I



Scheme II



1,2-dimethoxyethane, benzene, and 1,4-dioxane.⁹ In diglyme, the nonequivalence was maintained up to 185 °C in a 0.3 M solution.

Although the benzyl protons are diastereotopic by symmetry, they were observed to be equivalent in all the systems (H, Li, SiR_3) except dibenzylphenylchlorosilane, in which a small splitting (1.2 Hz) was observed at 270 MHz. Such overlap was considered to be the result of accidental degeneracy, and it was for this reason that the benzyl system was not investigated in the germanium series.

Each member of the germanium series exhibited nonequivalent methyl doublets at 270 MHz (see Figure 1b in the supplementary material for the digermane), the splitting varying from 0.06 ppm (the digermane) to 0.1 ppm (**3**). The spectrum of the germlyllithium compound (**3**) (0.3 M in diglyme) did not lose the methyl nonequivalence up to 185 °C.

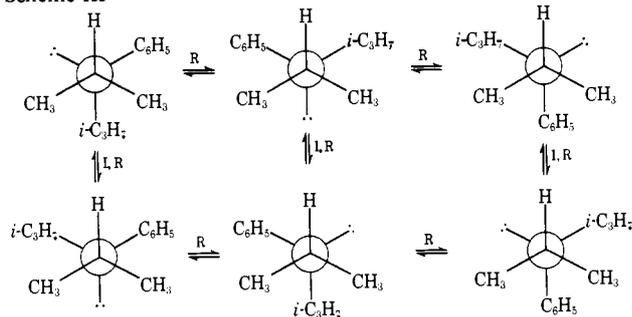
With the exclusion of air, the solutions of the silyl and germyl anions are brown. Exposure to air discharges the color but does not result in any rapid change in the NMR spectra. The observations suggest that free radicals of some sort might be present. Consequently, we examined the ESR spectra of the anion solutions. In 1,2-dimethoxyethane and in THF, diisopropylphenylsilyllithium (**1**) gave a simple quintet spectrum.¹⁰ Similar spectra were observed not only for dibenzylphenylsilyllithium (**2**) but also for triphenylsilyllithium. A common or similar paramagnetic material was suggested. Very little signal could be obtained for diisopropylphenylgermyllithium (**3**) even after ten passes. Comparison of these samples with the Varian standard gave the following spin concentrations: **1** (0.012%), **2** (0.00033%), **3** (0.000033%), triphenylsilyllithium (0.4%), and triphenylgermyllithium (too small to measure).

Discussion

Each of the silyl and germyl compounds (anion, chloride, hydride, disilane/digermane) examined in this study can exist in three distinct rotational isomers (see Scheme III for the anion). Rotation (R) around the various C–C, Si–C, and Ge–C bonds in these compounds is rapid on the NMR time scale at room temperature, since only one set of resonances is obtained for each functional group. No changes were observed in the spectrum of the chlorosilane or the chlorogermane as the temperature was lowered to –150 °C at 90 MHz, so the rotational barriers must be quite small.

For the silyl and germyl anions (**1–3**), inversional motion (I) is possible in addition to the rotational motion. The vertical

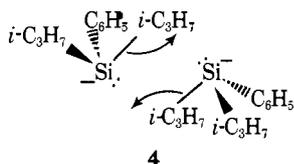
Scheme III



arrows in Scheme III indicate not only pyramidal atomic inversion, which alone would lead to an eclipsed structure, but also a 60° rotation (arbitrarily clockwise) to give the illustrated staggered structures. The methyl groups are nonequivalent in each of the rotamers, so that rotational interconversion alone does not lead to magnetic equivalence, except in the accidental event of peak overlap, which is apparently the case for the benzyl series. In order for the diastereotopic protons to become equivalent, both the inversion and rotation processes must be fast on the NMR time scale. Since rotation appears to be fast in all these compounds, the nonequivalence of the isopropyl methyl groups in the anions is evidence for slow inversion about silicon (1) and germanium (3), respectively.

The continued nonequivalence of the isopropyl methyl groups in 1 and 3 in diglyme (5%) at 185 °C places a lower limit on inversion about silicon and germanium. From the observed chemical shift differences and the temperatures, limits to these barriers can be calculated to be about 24 kcal/mol by standard procedures.² These measurements provide the first experimental information on silicon and germanium inversion barriers.

Because these organolithium compounds commonly exist as aggregates, we generated the silyl anion in a number of different solvents (HMPA, diglyme, THF, 1,2-DME, benzene, and 1,4-dioxane) with dielectric constants ranging from 2.2 to 37. The isopropyl methyl groups were nonequivalent in all of these solvents at room temperature. Our main concern was that a bimolecular exchange (4) could operate within the ag-



gregate and lead to spectral equivalence.⁴ Had a dynamic process been observed, we would have had to determine its molecularity. The nonequivalence of the isopropyl methyl protons indicates that such higher order processes, as well as unimolecular atomic inversion, are slow on the NMR time scale.

Up to this point in the Discussion, we have treated the organolithium reagents as if they were anions in solution. As we pointed out in the first paragraph, however, the Si-Li and Ge-Li bonds, like the C-Li, are partially covalent, and bond dissociation must occur before inversion can take place.⁵ It is convenient to describe these molecules as existing in an equilibrium between distinct ionic and covalent forms, $R-Li \rightleftharpoons R^{-}Li^{+}$, but we have no assurance that this model is completely accurate. As in carbonium ion chemistry, various types of ion pairs may exist. Under any circumstance, it is correct to say that the dissociation process by itself cannot render the diastereotopic protons equivalent.

In this context, two problems must be considered. First, the calculated barrier limit of 24 kcal/mol refers to the difference between the ground state in solution and the inversion transi-

tion state. If the ionic form is lower in energy, the limit refers to the actual inversion barrier. If the covalent form is lower in energy, the limit must be reduced by the energy difference between the inverting ionic and the noninverting covalent forms. Second, if the covalent form is lower in energy and if the barrier to conversion to the ionic form is large enough to be essentially unsurmountable, the observation of anisochronous nuclei in the silyllithium and germyllithium materials is strictly analogous to that in tetracoordinate, covalent forms described by others.⁷ The calculation of an inversion barrier is then irrelevant. The frequent observation of carbon inversion in carbon-lithium systems demands that the barrier to C-Li bond cleavage be surmountable, and various arguments suggest that bond cleavage is faster than inversion.^{3,4} If there is a fundamental difference between the C-Li and the Si-Li (Ge-Li) bonds, however, these problems may be significant in the silicon and germanium systems. We have examined this possibility from three points of view.

First, the observation of spectral nonequivalence in solvents of widely different dielectric properties is consistent with, though not proof of, anisochrony in both ionic and covalent forms.

Second, published crystal structures have demonstrated a close analogy between carbon-lithium and silicon-lithium bonding. In the crystal structure of hexameric trimethylsilyllithium (Me_3SiLi), the six lithium atoms form a highly puckered chair six-membered ring, and each silicon atom is bonded to three, not one, lithiums.¹¹ The silicons lie over the center of a triangular array of lithium atoms, with the average Si-Li distance 2.68 Å. The structure of hexameric cyclohexyllithium is quite analogous, with the C-Li distance 2.184 or 2.300 Å (the carbon is not quite symmetrically placed with respect to the three lithium atoms).¹² Exchange out of such aggregates appears to be faster than carbon inversion.⁴ Thus the barrier to C-Li dissociation must be lower than that to carbon inversion. Since the structures are so analogous, it is reasonable, though not certain, that the barrier to Si-Li (Ge-Li) dissociation is also lower than silicon (germanium) inversion.

Third, something can be said about the ionicity of the X-Li bond from the ⁷Li chemical shift. Covalent systems tend to have resonances downfield from aqueous lithium bromide, whereas ionic systems are upfield.¹³ Since bond anisotropies contribute to the chemical shift, we prepared the homologous series of diisopropylphenyl compounds, 1, 3, and 5,

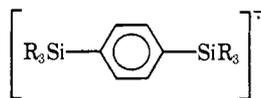
	X
1	Si
3	Ge
5	C

and examined their ⁷Li resonances.¹⁴ The organometallics were in tetrahydrofuran (about 0.3 M), and the resonance positions were compared to that of external saturated aqueous lithium chloride. Each sample exhibited only one relative sharp ($lw_{1/2} < 0.5$ Hz) peak. All the resonances were found to be downfield of the standard (LiCl), the carbon compound (5) by 0.07 ± 0.03 ppm, the silicon compound (1) by 0.25 ± 0.06 ppm, and the germanium compound (3) by 0.10 ± 0.03 ppm. The scale of ⁷Li resonances in ethyl ether runs from about 0.7 ppm above aqueous lithium bromide (allyllithium) to about 1.0 ppm below the standard (phenyllithium).¹³ Although our standard was the chloride, the chemical shift of 5 is quite similar to that reported for other tertiary compounds, such as *tert*-butyllithium.¹³ Irrespective of the difference in standards, it is of primary significance that the ⁷Li chemical shift differences between the carbon and the silicon or germanium systems are extremely small. The differences (0.18 ppm maximum) are considerably smaller than the observed range of carbon-lith-

ium systems (about 1.9 ppm). We conclude that the lithium atom in the silicon and germanium systems does not differ greatly in ionicity from that in the analogous carbon systems. These ionicities are about midrange on the scale for lithium-carbon systems.

These three lines of reasoning suggest strong resemblances between the C-Li and the Si-Li (Ge-Li) bonds. Since dissociation appears to be rapid in the carbon system, and since the ionic form cannot be greatly different in energy from the covalent form in the carbon system,^{3,4} we conclude that the observed anisochrony in the silyllithium and germyllithium systems is due to slow inversion rather than slow dissociation. We further conclude that the calculated barrier limit cannot be far from the appropriate limit for the difference between the ionic ground state and the inversion transition state.

We cannot identify with certainty the structure of the material that gives rise to the quintet ESR spectrum. The splitting pattern would seem to indicate that the electron resonance is split by four equivalent or nearly equivalent protons. A simple anion radical derived directly from **1-3** does not explain such a pattern. Furthermore, the observation of an identical spectrum from triphenylsilyllithium suggests that a more general explanation should be sought. Quintet patterns have been observed by others during the generation of anion radicals from triphenylsilyl hydride,¹⁵ dimethyldiphenylsilane, diethyldiphenylsilane, and triethylphenylsilane.¹⁶ The spectra were attributed to *p*-bis(silyl)benzenes of the type **6**. The quintet



6

splitting arises from interaction of the electron with the four aromatic protons. The splitting we observed (about 2 G) is very similar to that observed in these previous cases.^{15,16} Apparently a small amount of our substrates is reduced to the anion radicals **6**, but the measured percentages are too small to affect the NMR spectra.

In summary, we have observed that the diastereotopic isopropyl methyl groups in diisopropylphenylsilyllithium (**1**) and diisopropylphenylgermyllithium (**3**) remain nonequivalent up to 185 °C. This result requires that unimolecular atomic inversion about silicon (germanium) and higher order ligand exchange reactions within an aggregate must be slow on the NMR time scale. A lower limit of 24 kcal/mol can be set for these processes. The similar ⁷Li chemical shifts in the C (**5**), Si (**1**), and Ge (**3**) systems are consistent with similar X-Li ionicities.

Experimental Section

Commercial chemical reagents were used without further purification, with the exception of benzyl chloride, which was dried over P₂O₅ prior to use. All reactions involving Grignard reagents and chlorosilanes or -germanes were carried out under dry, oxygen-free N₂ and those of silyl- and germyllithium under an Ar atmosphere circulated over KOH, CaCl₂, and BTS catalyst. Anhydrous ethyl ether (Baker) was distilled from LiAlH₄. Tetrahydrofuran (THF, Matheson Coleman and Bell) was freed from peroxides and moisture before use by treatment with cuprous chloride, distillation, refluxing over Na for several hours, and finally distillation from LiAlH₄. It was stored under N₂. Hexamethylphosphoramide (HMPA) was stored for 1.5 days over Linde molecular sieves 13 X (pore size 10 Å) and then distilled under vacuum from BaO. Glyme and diglyme were stored over CaH₂ and then distilled from LiAlH₄. 1,4-Dioxane was stored over KOH and distilled from LiAlH₄. Benzene was stored over Na and distilled from previously cleaned Li dispersion. Pyridine was stored over KOH and then distilled from BaO. Boiling and melting points are uncorrected. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill., and by the Analytical Services Laboratory of the Chemistry Department of Northwestern University.

Infrared spectra were recorded on Beckman IR-9 and IR-12 spectrophotometers equipped with a flushed cell compartment. Electron spin resonance spectra were taken on a Varian E-4 spectrometer operating in the X-band mode and equipped with a temperature controller device and signal averager, through the facilities of the Materials Research Center of Northwestern University. Mass spectra were run at 70 eV in a Hewlett-Packard 5930 A mass spectrometer. Proton magnetic resonance spectra were recorded at 60 MHz on the R20-B Hitachi Perkin-Elmer spectrometer, at 90 MHz on the Bruker HFX-90, and at 270 MHz by Dr. H.-n. Sun on the Bruker HX-270 at the University of Chicago.

Diisopropylphenylsilane.¹⁷ In a 1-L three-necked round-bottom flask, equipped with a reflux condenser, a N₂ inlet, a mechanical stirrer, and a dropping funnel, was placed oven-dried Mg turnings (19 g, 0.8 g-atom, Mallinckrodt) covered with anhydrous ethyl ether (300 mL). To the stirred suspension was added slowly 2-chloropropane (64 g, 0.8 mol, Aldrich) in anhydrous ethyl ether (200 mL). After the addition was complete, reflux was continued for another 2 h. Phenyltrichlorosilane (66.2 g, 0.3 mol, Alfa) was then added to the Grignard solution dropwise, and stirring was continued overnight. The solvent was distilled off, and the temperature was raised to 160 °C slowly, while the strong evolution of a gas (propene) took place. Hydrolysis of the residue in the distillation flask was then performed by pouring the reaction mixture into a beaker containing 3 M HCl (300 mL), immersed in an ice-salt bath. The organic layer was separated, and the aqueous layer was extracted several times with ethyl ether. The combined organics were dried over Drierite and decanted, and the solvent was pumped off with the rotary evaporator. Vacuum distillation of the residue gave 12.5 g (18%) of a colorless liquid, diisopropylphenylsilane, bp 58–59 °C (0.5 mm) [lit.¹⁷ 74 °C (1.2 mm)]. Only one peak was observed on a 10% Carbowax 20M on Chromosorb P 60/80 VPC column: IR (film) 2040, 1400, 1120, 1000, 800, 740, 690 cm⁻¹; NMR (neat) δ 1.0 (m, 14 H, isopropyl), 3.9 (s, 1 H, SiH), 7.3 (m, 5 H, aromatic). Another 25 g of an oily, sticky material was collected at 80–100 °C (0.5 mm). An IR spectrum of this fraction showed a broad band at 3440 cm⁻¹, which corresponded well to the usual OH stretching frequency found in monomers and hydrogen-bonded silicon polymers,¹⁸ and also a strong band at 1060 cm⁻¹ due to Si-O-Si bonds.

Diisopropylphenylchlorosilane was prepared from the corresponding silane by hydrogen-halogen exchange.¹⁹ Chlorine gas (Matheson Gas Products) was bubbled through a solution of diisopropylphenylsilane (12.5 g, 0.064 mol) in dried CCl₄ (30 mL) for a period of 1.5 h. The reaction vessel was kept in an ice-salt bath. The excess Cl₂ trapped in the reaction flask was freed overnight. The solvent was then removed by distillation under N₂. The residual oil was distilled under vacuum to afford diisopropylphenylchlorosilane (10.8 g, 75%): bp 73–75 °C (0.05 mm); NMR (neat) δ 2.1 (m, 14 H, isopropyl), 7.6 (m, 5 H, aromatic); the mass spectrum showed the parent peak at *m/e* 226. Anal. Calcd for C₁₂H₁₉SiCl: C, 63.50; H, 8.44; Cl, 15.65. Found: C, 62.78; H, 8.50; Cl, 14.92.

1,1,2,2-Tetraisopropyl-1,2-diphenyldisilane. To a stirred suspension of finely cut Li wire (0.6 g, 0.09 g-atom) in dried THF (35 mL) was added freshly distilled diisopropylphenylchlorosilane (20 g, 0.09 mol) in THF (20 mL). Evolution of heat occurred during the addition period and persisted afterward for about 1 h. Stirring was continued for another 7 h, after which time hydrolysis of the reaction mixture was performed with 3 M HCl (30 mL). The organic layer was separated, the aqueous layer was washed with ethyl ether, and the combined extracts were dried over Drierite. The solution was decanted, the solvent removed, and the residual oil distilled under vacuum to afford diisopropylphenylsilanol (2.0 g, 0.01 mol), colorless liquid, bp 80 °C (0.05 mm), and 1,1,2,2-tetraisopropyl-1,2-diphenyldisilane (12 g, 0.031 mol, 74%), colorless liquid: bp 167 °C (0.05 mm); NMR (CCl₄) δ 1.2 (m, 28 H, isopropyl), 7.2 (m, 10 H, aromatic); the mass spectrum showed a parent peak at *m/e* 382. Anal. Calcd for C₁₄H₃₈Si₂: C, 75.31; H, 10.00. Found: C, 74.67; H, 10.13.

Diisopropylphenylsilyllithium (1). **Method A.** In a typical experiment a 0.3 M solution of diisopropylphenylsilyllithium in hydrocarbon or ether solvents was prepared with rapid stirring at room temperature under an Ar atmosphere from 250 mg of 1,1,2,2-tetraisopropyl-1,2-diphenyldisilane and an excess of finely cut Li wire in 1 mL of solvent. The yellow-brown color of the silyl solution developed in the reaction flask after 30–40 min. Stirring was continued for 3 h or even longer with the solvents benzene and 1,4-dioxane. The solution (0.3 mL) was then transferred under an Ar atmosphere into a purged

NMR tube by means of a gas-tight syringe. The concentration of the solutions was determined by titration against standardized HCl with phenolphthalein as indicator. The results were 3–5% higher than expected because of the formation of the oxide of the alkaline metal and of lithium hydride. Samples of the brown solutions of the silyl anion, with an overall concentration range between 0.1 and 1 M, in the solvents THF and 1,2-DME, were syringed at room temperature into a dried Ar-purged quartz capillary tube, which was then sealed for obtaining ESR spectra.

Method B. Under an Ar atmosphere, a solution of freshly distilled diisopropylphenylchlorosilane (7.0 g, 0.031 mol) in dried THF (20 mL) was added to a stirred suspension of previously cleaned, finely cut Li wire (0.22 g, 0.031 g-atom, Alfa, 1% Na). Heat was evolved during the addition, and salts (LiCl) separated out from the solution. After 2 h of stirring, more heat was given off in the reaction flask, and the yellowish-brown color of the corresponding silyllithium compound began to develop. More Li wire (0.2 g, 0.03 g-atom) was then introduced into the reaction flask, and stirring was continued for a further 4 h. The concentration of a clear aliquot of the silyllithium solution (0.934 M) was determined by acidimetric titration until no change was observed (8 h).

Diisopropylphenylsilane-d. Hydrolysis of the diisopropylphenylsilyllithium solution in tetrahydrofuran, prepared by method B, was performed by reaction with an equimolar amount of D₂O. The white solid that separated out from the solution (LiOD) was filtered, the organic layer was dried (Na₂SO₄), and the solvent was distilled off. Vacuum distillation of the residual oil afforded diisopropylphenylsilane-*d* (4.1 g, 0.021 mol, 70%): bp 76 °C (1.5 mm); IR 1590 cm⁻¹ (C–D); NMR (CCl₄) δ 1.1 (m, 14 H, isopropyl), 7.4 (m, 5 H, aromatic); the mass spectrum contained a parent peak at *m/e* 193. Anal. Calcd for C₁₂H₂₀Si: C, 74.90; H, 10.50. Found: C, 74.97; H, 10.41.

Dibenzylphenylchlorosilane was prepared following the procedure outlined in the literature for the synthesis of dimethylphenylchlorosilane.²⁰ Under a N₂ atmosphere, oven-dried Mg turnings (10 g, 0.41 g-atom, Mallinckrodt) in anhydrous ethyl ether (200 mL) were allowed to react with benzyl chloride (53 g, 0.41 mol, Aldrich) in anhydrous ethyl ether (50 mL). Addition of benzyl chloride was carried out at a rate to maintain a slow reflux. When it was completed, reflux was continued for an additional 2 h, until all of the Mg had been consumed. Phenyltrichlorosilane (84.7 g, 0.4 mol, Alfa) without solvent was then added in a dropwise manner to the Grignard reagent. Separation of the Mg salts was observed after about 4 mL of phenyltrichlorosilane had been added. A gentle reflux was maintained during the addition process, and when addition was completed, the reaction mixture was kept under reflux for a further 4 h. The solvent was distilled under N₂ with the temperature below 40 °C to avoid the reduction of the Si–Cl bond. The yellowish oil that remained in the distillation flask was taken up in hot benzene, and the suspension was filtered under N₂. The Mg salts were washed thoroughly with the same solvent. Distillation of the filtrate was performed under N₂ to afford benzene in the first place and then under vacuum to give 23.3 g of unreacted phenyltrichlorosilane, bp 30 °C (0.2 mm), which was identified by comparing its IR and NMR spectra with those of an authentic sample. The next fraction contained 30.9 g of a colorless liquid, benzylphenyldichlorosilane: bp 115 °C (0.2 mm); IR 590, 525 cm⁻¹ (Si–Cl stretch); NMR δ 2.6 (s, 2 H, CH₂), 8.2 (m, 10 H, aromatic). A third fraction afforded the desired product, dibenzylphenylchlorosilane (29.5 g, 22% based on benzyl chloride), a colorless, very dense liquid: bp 160 °C (0.2 mm); IR 1430, 1125, 705, 500 cm⁻¹; NMR (CCl₄) δ 1.8 (s, 4 H, CH₂), 7.4 (m, 15 H, aromatic); the mass spectrum had the parent peak at *m/e* 322. Anal. Calcd for C₂₀H₁₉SiCl: C, 74.39; H, 5.94; Cl, 10.98. Found: C, 74.43; H, 6.04; Cl, 10.40.

1,1,2,2-Tetrabenzyl-1,2-diphenyldisilane. Under an Ar atmosphere, dibenzylphenylchlorosilane (6.88 g, 0.021 mol) in dried THF (30 mL) was added to a stirred suspension of finely cut Li wire (0.5 g, 0.07 g-atom) in THF (10 mL). Once the evolution of heat of the reaction had ceased and the brown color of the corresponding silyllithium compound developed, stirring was continued for another 4 h. When all the LiCl had settled, the solution was syringed into another flask. A solution of freshly distilled dibenzylphenylchlorosilane (6.9 g, 0.021 mol) in THF (15 mL) was added dropwise to the silyllithium solution. Evolution of heat and disappearance of the brown color were observed during the addition. The reaction mixture was stirred for another 4 h and then hydrolyzed with dilute HCl. The organic layer was separated, the aqueous layer was washed with THF, and the combined

organics were dried over Drierite. The solvent was removed and the residual oil treated with a mixture of hexane–absolute alcohol (15 mL) to facilitate the separation of a very fine white powder, 1,1,2,2-tetrabenzyl-1,2-diphenyldisilane (1.6 g, 0.003 mol, 18%). The final product was recrystallized from absolute alcohol: mp 135 °C; NMR (C₆D₆) δ 2.2 (s, 8 H, CH₂), 6.85 (m, 30 H, aromatic); the mass spectrum had the parent peak at *m/e* 574. Anal. Calcd for C₄₀H₃₈Si₂: C, 83.57; H, 6.66. Found: C, 83.23; H, 6.74.

Dibenzylphenylsilyllithium (2). **Method A.** The procedure paralleled that for diisopropylphenylsilyllithium (1), except that 0.1 M solutions were prepared from 40 mg of the disilane. The yellow-brown color developed in 2–3 min.

Method B. Under an Ar atmosphere, freshly distilled dibenzylphenylchlorosilane (3.0 g, 0.009 mol) in THF was added in a dropwise manner to previously cleaned, finely cut Li wire (1.3 g, 0.19 g-atom, Alfa, 1% Na) in dried THF (10 mL). After 10 min of stirring some cloudiness and evolution of heat were noticeable in the reaction mixture. Then the yellow-brown color of the silyl anion developed in the reaction flask and almost abruptly changed to dark brown. Stirring was continued for a further 5 h. The excess Li and LiCl, which separated out from the solution, were filtered under Ar by passing the solution through glass wool in a separatory funnel. The solution was stored under an Ar atmosphere. The intensity of the color of the solution decreased after 2 days, but the brown color persisted after 2 months. The concentration of the solution as determined by acidimetric titration was 0.23 M.

Dibenzylphenylsilane-d. Dibenzylphenylsilyllithium (0.23 M) was prepared in THF by method B. The reaction was stopped after 1 h of stirring, and hydrolysis of the reaction mixture was performed by treatment with an equimolar amount of D₂O. The white solid (LiOD) that separated out from the solution was filtered, the organic layer dried (Na₂SO₄) and decanted, and the solvent distilled off. Vacuum distillation of the residual oil afforded dibenzylphenylsilane-*d* (2.3 g, 0.008 mol, 88%): bp 153 °C (0.05 mm); IR 1500 cm⁻¹ (C–D); NMR δ 2.2 (s, 4 H, CH₂), 6.85 (m, 15 H, aromatic); the mass spectrum had a parent peak at *m/e* 288. Anal. Calcd for C₂₀H₂₀Si: C, 83.26; H, 7.00. Found: C, 83.29; H, 6.88.

Diisopropylchlorogermane. This synthesis was patterned after several literature procedures.²¹ Under a N₂ atmosphere, 2-chloropropane (24.3 g, 0.31 mol, Aldrich) was added to oven-dried Mg turnings (7.5 g, 0.31 g-atom) in anhydrous ethyl ether (300 mL) in a dropwise manner to maintain a slow reflux. Refluxing was continued for 1 h after the addition was complete. The Grignard mixture was cooled to –78 °C, and pure GeCl₄ (25 g, 0.116 mol, Alfa) was added within 10 min with vigorous stirring. Separation of the Mg salts was noticeable immediately after the addition. The reaction flask was allowed to come to room temperature and was stirred for 3 h. The Mg salts were filtered under N₂, and the solvent was removed by rotary evaporation. The white solid that separated out from the residual oil was filtered under N₂ and recrystallized from a mixture of hexane–ethyl ether (20 mL) to give a compound of mp >230 °C, probably corresponding to the composition C₁₅H₃₅Ge₃Cl₃ (2.3 g, 0.043 mol, 3%); the mass spectrum had a parent peak multiplet at *m/e* 534–540 and fragmentation peaks at 193 (loss of –Ge(*i*-Pr)₂–Ge(*i*-Pr)Cl₂) and 351 (loss of –Ge(*i*-Pr)Cl₂). On this basis, the structure is tentatively assigned Cl(*i*-Pr)₂Ge–Ge(*i*-Pr)₂–Ge(*i*-Pr)Cl₂. The oily residue was then distilled under vacuum to afford a colorless liquid, isopropyltrichlorogermane (2.1 g, 0.009 mol, 7%): bp 25 °C (1 mm); NMR δ 1.25 (d, 6 H, CH₃), 2.1 (m, 1 H, CH); the mass spectrum had a parent peak multiplet at *m/e* 220–226. Anal. Calcd for C₃H₇GeCl₃: C, 16.23; H, 3.18. Found: C, 15.96; H, 3.72. The second distillation fraction corresponded to a mixture of mono- and dihalogermanes (12.7 g), bp 35 °C (1 mm). Its composition, as determined by the next reaction (with phenyllithium), was indicated to be the desired diisopropylchlorogermane (11 g, 41%) and triisopropylchlorogermane (1.5 g, 0.006 mol, 4%). This mixture could not be separated, although the undesired triisopropylchlorogermane was isolated in the next step. Its characterization nonetheless is given here: colorless liquid, bp 28 °C (0.05 mm); NMR (CCl₄) δ 1.3–2.05 (all protons); the mass spectrum had the parent peak multiplet at *m/e* 235–241. Anal. Calcd for C₉H₂₁GeCl: C, 45.55; H, 8.92; Cl, 14.94. Found: C, 45.27; H, 9.12; Cl, 15.43. A higher boiling third fraction was a colorless liquid, probably corresponding to the chemical composition C₁₂H₂₈Ge₃Cl₄ (4.4 g, 0.008 mol, 7%): bp 95 °C (0.02 mm); the mass spectrum had the parent peak multiplet at *m/e* 531–537 and fragmentation peaks at 190 (loss of –Ge(*i*-Pr)Cl–Ge(*i*-Pr)₂Cl) and at 340 (loss of –Ge(*i*-

Pr)₂Cl). Anal. Calcd for C₁₂H₂₈Ge₃Cl₄: C, 26.99; H, 5.28; Cl, 26.56. Found: C, 26.24; H, 5.39; Cl, 26.03. These results suggest that *i*-PrCl₂Ge-Ge-*i*-PrCl-Ge(*i*-Pr)₂Cl is a possible structure for the compound. In all runs there was always a 10–14% recovery of unreacted GeCl₄.

Diisopropylphenylchlorogermane. Under a N₂ atmosphere and with vigorous stirring, the freshly distilled above mixture of diisopropyl-dichlorogermane and triisopropylchlorogermane (31.75 g) in dried ethyl ether (150 mL) was reacted with phenyllithium (0.139 mol, 1.86 M in 70–30 benzene, Alfa). The separation of salts took place immediately after the aryllithium reagent had been syringed into the reaction flask at –78 °C. The reaction mixture was allowed to come to room temperature, and stirring was continued for another 3 h. The Li salts were filtered under N₂, the solvent was removed by rotary evaporation, and the residual yellowish oil was distilled under vacuum to afford as the first fraction unreacted triisopropylchlorogermane (4.5 g, 0.025 mol), bp 28 °C (0.05 mm). The characterization of this compound was presented in the previous preparation. The second fraction was the desired diisopropylphenylchlorogermane (19.3 g, 0.07 mol, 59% based on the amount of diisopropyl-dichlorogermane in the original mixture), a colorless liquid: bp 65 °C (0.02 mm); NMR (CCl₄) δ 1.2 (m, 12 H, CH₃), 1.65 (heptet, 2 H, CH), 7.4 (m, 5 H, aromatic); the mass spectrum had the parent peak multiplet at *m/e* 268–274. Anal. Calcd for C₁₂H₁₉GeCl: C, 53.12; H, 7.06; Cl, 13.07. Found: C, 53.81; H, 7.25; Cl, 13.03. A small amount of diisopropyl-diphenylgermane (0.8 g, 0.003 mol, 2%) was also obtained, bp 80 °C (0.02 mm). This compound solidifies at room temperature in the crystalline form: mp 23 °C; NMR (CCl₄) δ 1.1 (m, 14 H, isopropyl), 7.35 (m, 10 H, aromatic); the mass spectrum had the parent peak mass at *m/e* 310–316. Anal. Calcd for C₁₈H₂₄Ge: C, 69.07; H, 7.73. Found: C, 68.15; H, 7.82.

1,1,2,2-Tetraisopropyl-1,2-diphenyldigermane. Under an Ar atmosphere, freshly distilled diisopropylphenylchlorogermane (5.0 g, 0.018 mol) was added slowly to a rapidly stirred suspension of previously cleaned, finely cut Li wire (0.3 g, 0.045 g-atom, Alfa, 1% Na) in THF (35 mL). A slight evolution of heat was observed during the addition, and a yellowish color that later turned to dark yellow-brown developed in the reaction flask. The reaction mixture was stirred vigorously for 2 h. The excess Li was separated from the germyllithium solution by passing it through glass wool under an Ar atmosphere. Diisopropylphenylchlorogermane (4.5 g, 0.017 mol) in dried THF (10 mL) was then added slowly to the dark-colored solution. A rapid disappearance of the brown color, which was not accompanied by evolution of heat, took place immediately. Stirring was continued for a further 4 h. Hydrolysis of the reaction mixture was performed by slowly adding 3 M HCl (30 mL) to the reaction flask. The mixture was stirred for 30 min until no more evolution of heat was noticeable. The organic layer was separated and washed with ethyl ether. The combined extracts were dried overnight (Na₂SO₄). The organic layer was decanted, the solvents were removed under reduced pressure by rotary evaporation, and the residual yellowish oil was distilled under vacuum to afford as the first fraction diisopropylphenylgermanol (0.4 g, 0.002 mol, 4%), a colorless liquid: bp 90 °C (0.05 mm); IR 3390 cm⁻¹ (O–H); NMR (CCl₄) δ 1.2 (m, 15 H, OH and isopropyl), 7.3 (m, 5 H, aromatic); the mass spectrum had the parent peak multiplet at *m/e* 248–254. Anal. Calcd for C₁₂H₁₉GeOH: C, 56.99; H, 7.97. Found: C, 56.52; H, 7.23. The second fraction yielded 1,1,2,2-tetraisopropyl-1,2-diphenyldigermane (4.7 g, 0.001 mol, 57%), a very dense, colorless liquid: bp 165 °C (0.05 mm); NMR (CCl₄) δ 1.3 (m, 28 H, isopropyl), 7.3 (m, 10 H, aromatic); the mass spectrum had the parent peak multiplet at *m/e* 468–474. Anal. Calcd for C₂₄H₃₈Ge₂: C, 61.11; H, 8.12. Found: C, 61.07; H, 8.17.

Diisopropylphenylgermyllithium (3). Under an Ar atmosphere, 1,1,2,2-tetraisopropyl-1,2-diphenyldigermane (1.5 g, 0.0032 mol) was

rapidly stirred with previously washed, finely cut Li wire (0.1 g, 0.013 g-atom, Alfa, 1% Na) suspended in dried THF (20 mL) or another solvent. After 30 min, the brown color of the germyllithium compound could be observed. Stirring was continued for a further 2 h. The concentration of a filtered aliquot of the solution as determined by acid-metric titration was 0.29 M.

Diisopropylphenylgermane-d. The dark-colored solution of germyllithium prepared in the previous experiment was syringed into another flask under an Ar atmosphere and hydrolyzed by reaction with an equimolar amount of D₂O with stirring. A white solid (LiOD) separated from the solution. The mixture was filtered and dried (Na₂SO₄), and the solvent was removed by rotary evaporation. The residual yellowish oil was distilled under vacuum to afford a colorless liquid, diisopropylphenylgermane-*d* (1.13 g, 0.005 mol, 75% based on the initial amount of digermane): bp 38 °C (0.02 mm); IR 1440 cm⁻¹ (Ge–D); NMR (CCl₄) δ 1.1 (m, 14 H, isopropyl), 7.3 (m, 5 H, aromatic); the mass spectrum had the parent peak multiplet at *m/e* 235–241. Anal. Calcd for C₁₂H₂₀Ge: C, 60.83; H, 8.53. Found: C, 60.25; H, 8.64.

Supplementary Material Available: Figure 1, the proton spectra of diisopropylphenylchlorosilane and of 1,1,2,2-tetraisopropyl-1,2-diphenyldigermane (1 page). Ordering information is given on any current masthead page.

References and Notes

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