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Determination of the Solution Acidity of Tris(trimethylsilyl)silane

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The acidity of (Me$_3$Si)$_3$SiH was determined in diethyl ether solution by reactions of (Me$_3$Si)$_3$SiLi·3THF with a series of C−H acids. (Me$_3$Si)$_3$SiH and 9-phenylxanthyllithium (pK = 28.7) form in diethyl ether solution an equilibrium mixture in which the [silane]/[silyl anion] ratio is 12:7, corresponding to a pK value for (Me$_3$Si)$_3$SiH of 29.4.

Introduction

Knowledge about the acidity of carbon acids[1] is fundamental to the understanding of a variety of structure−reactivity relationships in organic chemistry.[2] It also has practical consequences as it reflects the stabilities of carbanions, key intermediates utilized in a multitude of synthetic transformations of organic molecules.[2] While much effort has been devoted to determining the thermodynamic[3] and the kinetic[4] acidities of carbon acids, relatively little is known about the acidities of hydrides of the other group 14 elements, silicon, germanium, tin, and lead.[5]

Silyl anions are important reagents in synthesis,[6] and they are probably involved in the formation and the degradation of polysilanes.[7] Of contemporary interest is the branched "hypersilyl" anion, (Me$_3$Si)$_3$Si$^-$, which was first prepared in situ,[8] and later its lithium salt was isolated and characterized as a stable complex with tetrahydrofuran (THF),[9a,b] with 1,2-dimethoxyethane (DME)[9c] and with lithium diphospholide,[9d] as well as the noncomplexed dimer.[9e] The large steric requirements,[10] the interesting electronic properties,[11] and the solubility of its derivatives in organic solvents have made (Me$_3$Si)$_3$Si a popular ligand in main-group[12] and transition-metal chemistry.[13] We have used this anion to prepare novel stable silenes[14] and have recently synthesized the longer homologues (Me$_3$SiMe$_2$Si)$_3$SiLi.[6k] Information on the acidities of silanes, especially of "hypersilyl" hydrides, is therefore of practical importance, as well as of fundamental interest. Naturally, the determination of the acidity of a silane yields also the basicity of the conjugate base, i.e., of its corresponding silyl anion. In this paper we determine the acidity of tris(trimethylsilyl)silane in solution.

Several studies of the acidity of organosilanes have been reported, but these are almost entirely gas-phase measurements.[15] We summarize the results of these studies in Table 1. The acidity of SiH$_4$ was determined to be 372 ± 2 kcal/mol, much higher than that of methane (416 kcal/mol, Table 1). A methyl substituent destabilizes the silyl anion (i.e., reduces the acidity of the silane) by ca. 6−11 kcal/mol (ΔH_{acid}(MeSiH$_3$) =

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Table 1. Gas-Phase Acidity of Silanes

compound	C−H	Si−H DePuy[15a]	Si−H Brauman[15b,c]
CH_4	416.6		
SiH_4		371 ± 2	372.8 ± 2
$MeSiH_3$	388 ± 3	383 ± 3	378.3 ± 2
Me_2SiH_2	391 ± 3	383 ± 3	380 ± 2
Me_3SiH	391 ± 3	383 ± 3	382.8 ± 2
Me_4Si	387 ± 3		
$PhSiH_3$		370 ± 3	370.7 ± 2
$HMe_2SiSiMe_2H$			366 ± 3
$(Me_3Si)_2SiH_2$			352 ± 6
$(Me_3Si)_3SiH$			346 ± 3[a]

[a] An acidity value for $(Me_3Si)_3SiH$ of 350.8 ± 2.8 kcal/mol was recommended by NIST[16] based on reevaluation of the data in ref 15c.

383 ± 3,[15a] 378 ± 2[15b]). Phenyl substitution has a small effect on the silane acidity ($\Delta H_{acid}(PhSiH_3) = 370 \pm 3$,[15a] 371 ± 2[15b]). On the other hand, a trimethylsilyl substituent stabilizes the silyl anion by 6−14 kcal/mol, and the gas-phase acidity of $(Me_3Si)_3SiH$ is ca. 26 kcal/mol higher than that of H_4Si.[15c]

The first (and up to now the only) determination of the acidity of a silane in solution, i.e., that of triphenylsilane, was reported during the course of this study (see below).[17] In this paper we present quantitative measurements of the acidity in solution of a branched polysilane, namely, $(Me_3Si)_3SiH$, allowing the quantification of the stabilization effect in solution of the three α-trimethylsilyl substituents. To the best of our knowledge, this is the first determination of the acidity of a polysilane in solution.

Results and Discussion

Ion pair acidity is defined in terms of equilibrium 1, in which AH is an acid and In^- is a suitable proton acceptor, generally an indicator of known relative acidity.

$$\mathrm{AH} + \mathrm{In}^{\ominus} \overset{K_{ip}}{\rightleftharpoons} \mathrm{AH{\cdot}In}^{-} \overset{K_{diss}}{\rightleftharpoons} \mathrm{A}^{\ominus} + \mathrm{InH} \qquad (1)$$

The product $K_{ip}K_{diss}$ is the ionic equilibrium constant K_a that corresponds to the pK_a value for AH. In the case where the K_{diss} values of the A^- and In^- are about the same, for example either Li^+ solvent-separated ion pairs (SSIP) or Cs^+ contact ion pairs (CIP) of delocalazed carbanions,[18] the classic method for the determination of the equilibrium acidities of carbanions is via reactions of the type shown in eq 2.[1] The acid R^1H is allowed to equilibrate with R^2M, where M is an alkali metal. When R^1H is a much weaker acid than R^2H, the position of the equilibrium is far to the left, and conversely when the inverse acidity order prevails. When the acidities of R^1H and R^2H are comparable, the relative acidities of R^1H and R^2H are given directly by the ratio of the equilibrium concentrations of R^1H and R^2H ($[R^1H]/[R^2H]$), which is usually determined spectroscopically, e.g., by NMR or UV techniques.[1]

$$\mathrm{R^1H} + \mathrm{R^2M} \overset{K}{\rightleftharpoons} \mathrm{R^1M} + \mathrm{R^2H} \qquad (2)$$

However, when the dissociation constants of the R^1M and R^2M ion pairs (K_{diss}) are different, the difference in the pK_a values of acids R^1H and R^2H (ΔpK_a) should be evaluated from eqs 3.[19]

$$-\log \Delta K_a = -\log K - \log[K_{diss}(R^1M)/K_{diss}(R^2M)] \qquad (3)$$

a. Determination of the Acidity of $(Me_3Si)_3SiH$ (1). It is known that silyl anions metalate weak carbon acids,[20] but formation of the silyl anions in organic solvent by direct deprotonation of silanes by carbanions or amides of alkali metals has not been observed, except for the metalation of triethylsilane by potassium hydrides in dimethoxyethane (DME) or hexamethylphosphoramide (HMPA).[21] Our attempts to abstract a proton from $(Me_3Si)_3SiH$ (**1**) with n-BuLi, MeLi, and Ph_3CLi in THF were not successful. Instead complete decomposition of **1** was observed. Also in diethyl ether the reaction of **1** with n-BuLi and MeLi leads to complete decomposition of **1**. In contrast, the less nucleophilic Ph_3CLi (solvated by THF) reacts in Et_2O with an equimolar amount of $(Me_3Si)_3SiH$ to give triphenylmethane. However, the reaction is not clean; in addition to Ph_3CH, a polymer (which results from the decomposition of THF) as well as some unchanged **1** are also observed. However, a slight change in the reaction conditions leads to a clean metalation of $(Me_3Si)_3SiH$. Thus, Ph_3CLi (solvated by two diethyl ether molecules, i.e., $Ph_3CLi{\cdot}2Et_2O$[22]) reacts with **1** in diethyl ether to give quantitatively the corresponding silyllithium compound and Ph_3CH (eq 4). To our best knowledge, this is the first example of a clean direct proton abstraction from a silane by a carbanion. Since the known number of synthetic methods for the preparation of silyl anions is quite limited,[6] this reaction presents an interesting new method for the preparation of silyl anions. The synthetic utility of this reaction is now being examined, and it will be discussed in more detail elsewhere.

$$\mathrm{Ph_3CLi{\cdot}2Et_2O} + \mathrm{(Me_3Si)_3SiH}\ (\mathbf{1}) \xrightarrow{Et_2O} \mathrm{Ph_3CH} + \mathrm{(Me_3Si)_3SiLi} \qquad (4)$$

From the experiment shown in eq 4 it is clear that in diethyl ether **1** is a stronger acid than Ph_3CH (pK_a = 31.3 in THF solution[23]). To evaluate quantitatively the acidity of $(Me_3Si)_3SiH$ (**1**), we have first reacted $(Me_3Si)_3SiLi{\cdot}3THF$ in toluene (or diethyl ether) with several carbon acids RH (eq 5) shown in Table 2, spanning the pK range of 22.9−31.3. The reactions were followed by ^1H NMR, by monitoring the absorptions of the Si−H,

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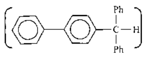
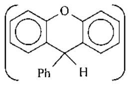
Table 2. Percentage of Metalation of Carbon Acids in Equilibration with$(Me_3Si)_3SiLi\cdot 3THF$

Carbon acid	pK[a]	Solvent	Percentage of silane (%)[b]
Fluorene	22.9	toluene	>99
Aniline	27.0	toluene	>99
p-Biphenyldiphenylmethane	30.7	toluene	<0.5
			
p-Biphenyldiphenylmethane	30.7	diethyl ether	0
Triphenylmethane	31.3	toluene	0
9-Phenylxanthene	28.7	diethyl ether	~ 60
			

[a] The p*K* values refer to Streitwieser's ion pair acidity scale determined in THF.[23] [b] Percentage of $(Me_3Si)_3SiH$ in the reaction mixture (eq 2) as determined by ^1H NMR from the concentration ratio of the [silane]/[silyllithium].

C−H, and the Me groups of the $(Me_3Si)_3Si$ unit (details are given below). In all cases clean reactions with only minor decomposition of the reagents or products were observed.

$$RH + (Me_3Si)_3SiLi\cdot 3THF \xrightarrow{\text{toluene}} RLi + (Me_3Si)_3SiH \quad (5)$$

The results in Table 2 suggest that in toluene **1** is a weaker acid than fluorene (pK = 22.90[23]) and aniline (pK = 27.0[23]) because the equilibrium of eq 5 lies entirely to the right. On the other hand $(Me_3Si)_3SiH$ is a stronger acid than triphenylmethane (pK = 31.26[23]) and *p*-biphenyldiphenylmethane (pK = 30.07[23]). These experiments place the acidity of **1** in the range of pK = 27.0−30.1. 9-Phenylxantyllithium (pK = 28.7[23]) reacts with 0.7 equiv[24] of **1** in diethyl ether to give after 2 days a 7:12 ratio between $(Me_3Si)_3SiLi$ and **1**. This ratio was determined by ^1H NMR from the integration ratio of the absorptions at 0.24 ppm (related to the 27 methyl protons of **1**) and at 0.57 ppm (related to the 27 methyl protons of $(Me_3Si)_3SiLi$). *From this experiment the pK difference between* $(Me_3Si)_3SiH$ *and 9-phenylxantyllithium (pK = 28.7 in THF*[23]*) in diethyl ether is determined to be 0.7 pK units*. Assuming that in eq 3 $K_{diss}((Me_3Si)_3SiLi) = K_{diss}$(9-phenylxantyllithium), the pK_a value of **1** would be 29.4. However, as explained above, this assumption must be tested.

Is the pK of $(Me_3Si)_3SiH$ *determined here relevant also to other solvents or to counterions other than lithium?* It is well known that most carbanions with alkalimetal counterions exist in solution either as contact (or "tight") ion pairs (CIP) or as solvent-separated ion pairs (SSIP).[25] Only very stable anions are "free", i.e., fully dissociated. The relative proportions of these species are functions of the substrate, gegenion, solvent, and temperature.[1,25] Previous studies have suggested that in THF the cesium salts of extensively delocalized carbanions exist as contact ion pairs.[26] This is the primary reason that the Streitwieser acidity scale[26] is given for the cesium compounds rather than for the lithium compounds, as the latter tend to form complex mixtures of CIP and SSIP. While we were aware of these facts, we had to carry out the measurements with the silyllithium rather than for the silylcesium because the silylcesium compound is very difficult to prepare and crystallize.[9e] For the same reason $(Me_3Si)_3SiLi$ is the reagent used in most applications.[6,12−14] Shatenshtein et al., who measured the redistribution equilibrium occurring between CH acids and organolithium or organocesium compounds in dimethoxyethane,[23,27] found that cesium salts are usually more stable (i.e., less basic) than the lithium analogues by 0.2−1.0 pK units.[27,28] More recently, Streitwieser et al. measured equilibrium constants for the dissociation in THF solution of the lithium and cesium salts of 11 hydrocarbons.[29] These dissociation constants were than used to determine the relative free ion acidities of the corresponding hydrocarbons in THF. The pK values of the hydrocarbons were found to be 0.1−0.5 units lower (i.e., more acidic) when measured using the alkyllithium compounds than for the corresponding alkylcesium compounds.[29] In general a close correspondence was found between the lithium and cesium acidity scales and the free ion acidities in THF.[29] The correspondence between the two acidity scales results from the similar dissociation constants of delocalized organolithium compounds, which exist in THF as SSIP, and of the corresponding organocesium compounds, which exist in THF as CIP.[29] However, this cannot be regarded to be a general rule. For example, in case of enolate salts the dissociation constants of the cesium CIP salts and of the lithium CIP salts are substantially different (by 5−6 pK units).[30]

Since $(Me_3Si)_3SiLi\cdot 3THF$ exists both in THF and diethyl ether solutions as CIP[6] while 9-phenylxantyllithium exists in THF solution as SSIP[29] and in diethyl ether solution probably as CIP, the ΔpK of these two anions in THF and in diethyl ether could be significantly different.

From the available literature data we conclude that the pK of $(Me_3Si)_3SiH$ determined in this work as being 29.4 in Et_2O could be slightly different in other solvents. It should be pointed out again that the pK values determined here are not pK_a values. To determine accurately the acidity of **1** on any of the available ion pair acidity scales for hydrocarbons in THF,[26−29] it is necessary to measure the equilibrium dissociation constant (K_{diss}) of $(Me_3Si)_3SiLi$, for example, by conductivity or NMR measurements. We hope to carry out these measurements in the future.

b. Comparison of the Acidity of $(Me_3Si)_3SiH$ with Other Acids. The Substituent Effect of the Me_3Si Group. In the case that the pK values of **1** will not differ

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[24] Since 9-phenylxanthyllithium is very sensitive to air and **1** must be kept extremely dry after distillation from $(Me_3Si)_3SiLi\cdot 3THF$ (see Experimental Section), we found that it is more convenient to use an approximate amount of **1** and to establish its relative amount in the reaction mixture by ^1H NMR.

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[28] However 9-phenylxanthyllithium and 9-phenylxanthylcesium have equal stability.[27]

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dramatically in THF from that in diethyl ether we can conclude that $(Me_3Si)_3SiH$ (pK = 29.4) is a significantly stronger acid than the corresponding carbon analogue $(Me_3Si)_3CH$ (pK = 36.8[31]). Consequently, $(Me_3Si)_3SiLi$ is a significantly weaker base than $(Me_3Si)_3CLi$. This result correlates well with previous gas-phase and theoretical studies.[15c] This suggests that silicon accommodates a negative charge much more effectively than carbon, despite its lower electronegativity (C 2.5, Si 1.7),[32a] probably because of its higher polarizability, allowing a better dispersion of the negative charge.[32a] In contrast, Ph_3SiH (pK = 35.1[17]) is a weaker acid than Ph_3CH (pK = 31.3[23]), because in Ph_3Si^- conjugation with the phenyl substituents is not effective[32] in contrast to the carbanion which is strongly stabilized by charge delocalization to the phenyl rings. Previous gas-phase studies[15a,b] also showed that a phenyl substituent has essentially no effect on the acidity of silyl anions, i.e., $\Delta H_{acid}(SiH_4) = 372 \pm 2$ kcal/mol, compared to $\Delta H_{acid}(PhSiH_3) = 371 \pm 2$.[15b]

In solution **1** is more acidic than Ph_3SiH by 5.7 pK units,[33] and thus on the average each trimethylsilyl group stabilizes the silyl anion by 1.5−2 pK units more than a phenyl group (or than a hydrogen, see comparison above between H_4Si and $PhSiH_3$). For carbon the situation is reversed: each phenyl group stabilizes a carbanion by 1.6 pK units better than a Me_3Si group.[23,31] Streitwieser and co-workers have found that the intrinsic stabilization of carbanions by a trimethylsilyl group (relative to H) is 2−3 pK units, and that the stabilization is higher by ca. 0.3 pK units in the free carbanion than in the organometalic ion pairs.[31] In the gas phase a Me_3Si group stabilizes a carbanion by 20 kcal/mol,[15a] while a silyl anion is stabilized by only 14 kcal/mol.[15c] Thus, both in the gas-phase and in solution carbanions are stabilized by a silyl group significantly better than a silyl anion.

To evaluate more systematically the effect of silyl substitution on the stability of silyl anions, we have performed quantum mechanical density functional calculations,[34] at the B3LYP/6-31+G(d) level of theory.[35,36] The structures of all calculated species (neutral and anionic) were determined to be minima on the potential energy surface (all calculated frequencies are real), and they are reported in the Supporting Information. The calculated (at the B3LYP/6-31+G(d) level corrected for unscaled zero-point energy differences (ZPVE)) gas-phase acidities of H_4Si, Me_3SiH, and $(Me_3Si)_3SiH$ are 369.9, 383.5, and 354.8 kcal/mol, respectively.[37,38]

The calculations show that α-Me_3Si substituents strongly stabilize silyl anions. Thus, the $(Me_3Si)_3Si^-$ anion is more stable than H_3Si^- by 15.1 kcal/mol (eq 6), and it is 28.7 kcal/mol more stable than Me_3Si^-. This result is in reasonable agreement with the experimental difference of 22.0 ± 4 kcal/mol in the gas-phase acidity of $(Me_3Si)_3SiH$ vs H_4Si.[39] The stabilization of the silyllithium compound by a trimethylsilyl group (ΔE(eq 7) = 2.8 kcal/mol[40]) is much smaller than in the silyl anion (ΔE(eq 6) = 15.1 kcal/mol).[41] According to eq 8, $(Me_3Si)_3C^-$ is more basic than the $(Me_3Si)_3Si^-$ anion by 5.7 kcal/mol.[37] This value is lower than the experimentally measured difference between the pK_a value of $(Me_3Si)_3CH$ (36.8)[30] and the pK value of $(Me_3Si)_3SiH$ (29.4), which corresponds to an energy difference (at 298 K) of eq 8 of 10.1 kcal/mol. This larger difference may reflect a more efficient solvation of the silyl anion.

$$(Me_3Si)_3Si^- + H_4Si \rightarrow H_3Si^- + (Me_3Si)_3SiH \quad (6)$$

$$(Me_3Si)_3Si{-}Li + H_4Si \rightarrow H_3SiLi + (Me_3Si)_3SiH \quad (7)$$

$$(Me_3Si)_3Si^- + (Me_3Si)_3CH \rightarrow (Me_3Si)_3C^- + (Me_3Si)_3SiH \quad (8)$$

In the future, we plan to determine the solution thermodynamic and kinetic acidity of other organosilanes as well as of metallanes of other group 14 elements.

Experimental Section

Standard Schlenk techniques were used for all syntheses and all sample manipulations. NMR spectra were recorded at room temperature in C_6D_6 solutions using a Bruker EM-200 or Bruker-400 instrument. For ^{13}C NMR measurements the

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[33] Note that the pK values of **1** and Ph_3SiH were determined in Et_2O and THF, respectively, and the above comparison is valid only if the dissociation constants of the corresponding lithium salts to the free ions are the same or similar.

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[36] All calculations used the GAUSSIAN 98 series of programs. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

[37] The reliability of the B3LYP/6-31+G(d) + ZPVE level of theory for calculating the acidity of silanes was tested by calculating the acidity of H_4Si at several state of the art levels of theory. The following results were obtained: G2 (372.4 kcal/mol), G3 (371.7 kcal/mol), B3LYP/6-311++G(2df,p)//B3LYP/6-31+G(d) + ZPVE (371.2 kcal/mol), CCSD(T)/6-311++G(2df,p)/B3LYP/6-31+G(d) + ZPVE (373.2 kcal/mol), CCSD(T)/AUG-CC-PVTZ//B3LYP/6-31+G(d) + ZPVE (370.8 kcal/mol). The deviation of the B3LYP/6-31+G(d) + ZPVE value of 369.9 kcal/mol from the results obtained at higher levels of theory as well as from experiment (372.8 ± 2 kcal/mol) is smaller than 3 kcal/mol, confirming the reliability of the B3LYP/6-31+G(d) results for calculating the acidity of other silanes. Also the experimental acidity of Me_3SiH (382.8 ± 2 kcal/mol)[15b] is close to the B3LYP/6-31+G(d) + ZPVE calculated value of 383.5 kcal/mol.

[38] The ΔH^{298} values are different by only ∼0.2 kcal/mol from the reported ΔE values.

[39] This value is based on an acidity value for $(Me_3Si)_3SiH$ of 350.8 ± 2.8 kcal/mol recommended by NIST (based on reevaluation of the data in ref 15c).[16]

[40] To make comparisons possible, we use in eq 7 the energy of H_3SiLi in a pyramidal conformation (HSiLi angle = 115.9°) which is a local minimum, although a lower energy structure of H_3SiLi exists.

[41] The calculated energies for eqs 6−8 where the Me_3Si groups are substituted by H_3Si groups are 28.6, 9.2, and 12.1 kcal/mol, respectively.

POWGATE (proton decoupling with NOE) program was used. For ^{29}Si NMR the INEPTRD program was used.

$(Me_3Si)_3SiH$ (**1**): **1** was prepared by hydrolysis of $(Me_3Si)_3SiLi{\cdot}3THF$, which was synthesized according to ref 8. ^{1}H NMR (C_6H_6): δ 0.24 (s, 27H, Si(Si*Me*$_3$)$_3$), 2.50 (s,1H, *H*Si(SiMe$_3$)$_3$). ^{13}C NMR (C_6H_6): δ 1.9 (Si(Si*Me*$_3$)$_3$). ^{29}Si NMR (C_6H_6): δ −119.5 (*Si*(SiMe$_3$)$_3$), −8.3 (Si(*Si*Me$_3$)$_3$.

p*K* Measurements. *p*-Biphenyldiphenylmethane and 9-phenylxanthene were prepared according to procedures reported previously.[42] The other carbon acids that we used are commercial. The various RLi were prepared by reaction of the corresponding carbon acids with n-BuLi, and they were crystallized from diethyl ether. In all cases crystalline RLi were used. Silane **1**, which has to be extremely dry in order to be suitable for the acidity measurements, was dried by distilling it under vacuum from a mixture of **1** and $(Me_3Si)_3SiLi{\cdot}3THF$.

A typical procedure for measuring the pK_a value of **1** is as follows: 0.6 g (2.4 mmol) of dry **1** in 50 mL of dry diethyl ether was added under vacuum at 0 °C into a Schlenk flask containing the red crystals of the desired RLi (3.3 mmol).[24] The reaction mixture was allowed to reach room temperature and was stirred for an additional 48 h. The progress of the reaction was followed by ^{1}H and ^{13}C NMR spectroscopy.

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Supporting Information Available: Absolute energies, enthalpies, zero-point vibrational energies, and optimized structures of all calculated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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