reported when we have completed additional chemical and physical measurements with a variety of mono-, di-, tri-, and tetradentate ligands.

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Lithiation of Trimethylsilyl Compounds

Sir:

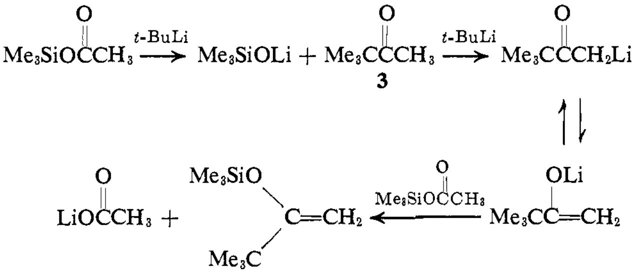
Lithiation of tetramethylsilane by *n*-butyllithium in the presence of N,N,N′,N′-tetramethylethylenediamine (TMEDA)[1] has recently been reported by Peterson.[2] In work contemporaneous with Peterson's, we have observed lithiation of methyl groups in various organosilanes, with and without potentiating catalysts such as TMEDA.[3] Silylmethyl protons appear to be distinctly more acidic than methyl protons in hydrocarbons. Probably silicon, like phosphorus,[4] stabilizes the partial negative charge on attached CR_2Li groups by means of dative π bonding from carbon into low-energy unfilled orbitals of the Si atom.

We now find that certain methylsilyl compounds can be metalated in the methyl group by *t*-butyllithium even when the silicon bears substituents highly reactive toward nucleophilic displacement. For example, trimethylchlorosilane undergoes lithiation by *t*-butyllithium at −78° in tetrahydrofuran, to give 33% $Me_3SiCH_2SiMe_2Cl$[5] (**1**) after work-up.

$$t\text{-BuLi} + Me_3SiCl \xrightarrow[\text{THF}]{-78°} LiCH_2SiMe_2Cl \xrightarrow{Me_3SiCl} \underset{\mathbf{1},\ 33\%}{Me_3SiCH_2SiMe_2Cl}$$

A substantial amount of the coupling product of **1** with *t*-butyllithium, $Me_3SiCH_2SiMe_2$-*t*-Bu,[6] is also produced (Table I). Trimethylchlorosilane is also lithiated rapidly and exothermically by the *t*-butyllithium–TMEDA complex in pentane at room temperature. Under these conditions the metalation of tetramethylsilane requires several days, showing that the protons in Me_3SiCl are significantly more acidic than those in Me_4Si. Steric hindrance to coupling appears to be vital for lithiation of trimethylchlorosilane, for with *n*-butyllithium, either with or without TMEDA, trimethylchlorosilane gives exclusively the coupling product *n*-butyltrimethylsilane.[7]

Other electronegative substituents on silicon lead to variable and often unexpected results upon treatment with *t*-butyllithium–TMEDA (Table I). Trimethylfluorosilane gives exclusively the coupling product *t*-butyltrimethylsilane. The latter is also the principal product with methoxytrimethylsilane, along with a minor amount of the metalation product $Me_3SiCH_2SiMe_2OMe$.[8] However, *ethoxytrimethylsilane gives virtually exclusive lithiation* to yield ultimately $Me_3SiCH_2SiMe_2OEt$,[6] only a trace of coupling being observed. Thus the slight increase in steric requirement from the methoxy to the ethoxy compound changes the nature of the reaction completely. Acetoxytrimethylsilane yields 3,3-dimethyl-2-trimethylsiloxy-1-butene[6] (**2**) in a rapid reaction. The formation of this unsaturated product can be accounted for by the following reaction sequence.



Compound **2** is also formed when a pentane solution of *t*-butyllithium is added to an excess of *t*-butyl methyl ketone (**3**) and trimethylchlorosilane.

Hexamethydisiloxane and *t*-butyllithium give, after aqueous work-up, the unexpected silanol, $Me_3SiCH_2SiMe_2OH$, as the only significant product along with unchanged starting material. The reactions leading to formation of the silanol are not clear, but lithiation

Table I. Reactions

Silane (*M*)	*t*-BuLi,[a] *M*	TMEDA, *M*	Temp, °C	Reacn time	Products (% yield)[e]
Me_3SiCl (0.36)[b]	0.12	0.00	−78	2 hr	$Me_3SiCH_2SiMe_2Cl$ (33); Me_3SiCMe_3 (25); $Me_3SiCH_2SiMe_2$-*t*-Bu (10)
Me_3SiCl (0.2)	0.05	0.012	15–30	<1 min	$Me_3SiCH_2SiMe_2Cl$ (20); Me_3SiCMe_3 (20); $Me_3SiCH_2SiMe_2CMe_3$ (40)
Me_4Si (0.12)	0.1	0.025	25	4 days	$(Me_3Si)_2CH_2$[c] (40)
$(Me_3Si)_2O$ (0.22)	0.1	0.025	25	11 days	$Me_3SiCH_2Me_2SiOH$[d] (30)
$Me_3SiOCH_2CH_3$ (0.07)	0.03	0.008	25	2 days	$Me_3SiCH_2SiMe_2OEt$ (50)
Me_3SiOMe (0.2)	0.05	0.012	25	6 hr	Me_3SiCMe_3 (40); $Me_3SiCH_2SiMe_2OMe$ (15)
Me_3SiF (0.2)	0.05	0.012	15–30	<1 min	Me_3SiCMe_3 (85)
$Me_3SiOC(O)CH_3$ (0.2)	0.05	0.012	15–30	<1 min	$Me_3SiO(Me_3C)C{=}CH_2$ (65)

[a] The solution of *t*-BuLi (1.3 *M*, Foote Mineral) in pentane was added to a solution of the silane and TMEDA. [b] Equal volumes of THF and pentane used as solvent. [c] After derivatization with trimethylchlorosilane. [d] After aqueous work-up. [e] Yields are based on products obtained by distillation after removal of LiCl by filtration.

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(6) All new compounds reported here gave satisfactory analyses for C, H, and Si, and nmr spectra consistent with the assigned structure.

(7) Trimethylchlorosilane is frequently employed as a derivatizing agent for active organometallic compounds. It is evident from our results that unexpected metalation products may be found with sterically hindered bases. *Cf.* also R. P. Bush, N. C. Lloyd, and C. A. Pearce, *Chem. Commun.*, 1271 (1967).

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must be involved at some stage. One reasonable pathway is[9]

$$(Me_3Si)_2O \xrightarrow{t\text{-BuLi}} LiCH_2SiMe_2OSiMe_3 \xrightarrow{} $$
$$Me_3SiCH_2SiMe_2OLi \xrightarrow{H_2O} Me_3SiCH_2SiMe_2OH$$

Reactions of *t*-butyllithium with other alkylsilyl compounds are under investigation.

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(9) This sequence would involve a 1,3-anionic rearrangement of silicon from carbon to oxygen. Such rearrangements are unknown but find precedent in the rapid anionic rearrangements of silicon–nitrogen compounds which have recently been described[10] and in the C → O rearrangements of organosilyl groups studied by Brook and his coworkers.[11]

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Some Aspects of the Molecular Dynamics of Methyl-Substituted Cyclopentadiene Compounds of Silicon and Tin

Sir:

The recent appearance of several examples of stereochemically nonrigid σ-cyclopentadienyl complexes[1-6] has resulted in apparently contradictory explanations of their behavior. We feel it important to restate the fundamental concepts involved and also report some of our preliminary work on this subject.

Muetterties[7] has already pointed out the importance of considering molecular dynamics in inorganic systems. With regard to stereochemically nonrigid ring systems, we wish to emphasize that (1) the so-called "static" or (low temperature) limiting structure need not refer to the molecules locked in a given configuration, (2) rearrangement continues to occur even though individual nonequivalent environments can be identified by some appropriate technique, and (3) nonequivalent environments can be observed only when the lifetime of the molecule in one configuration is long by comparison with the time scale of the measurement. Thus, stereochemically nonrigid cyclopentadienyl groups give rise to σ-bonded ir (10^{-13} sec) spectra but equivalent proton nmr (10^{-1} to 10^{-9} sec) signals. Moreover, these two observations place limits on the lifetime of the molecule in a given configuration. In several cases,[1,2] by going to lower temperatures, the intramolecular exchange could be slowed down sufficiently to observe the nmr spectra of the individual configurations.

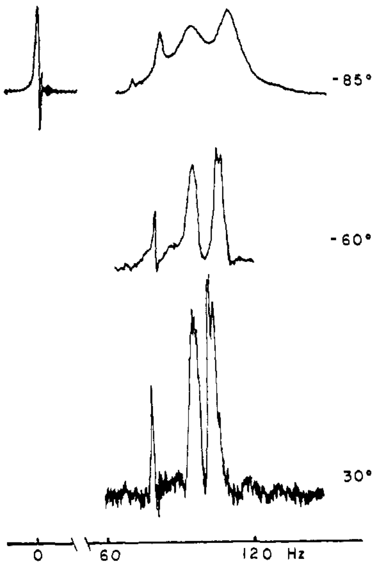

Figure 1. Proton nmr spectra of the ring protons of $(CH_3)_3SnC_5H_4CH_3$ showing broadening at temperatures below −60°. Note that the benzene resonance (as internal reference) remains sharp at this temperature. The peak at 80 Hz is due to the cyclopentadienyl resonance of $(CH_3)_3SnC_5H_5$. (Resonances are given in Hz upfield from benzene.)

The assertion by Fritz[2,4] (adopted by others[3]) that substitution of a methyl group onto the cyclopentadienyl ring causes the compound to assume a static configuration is neither verified by the following analysis nor by our experimental observations. The characteristic 2:2:3 pattern observed in the nmr for the methylcyclopentadienyl moiety in $Sn(C_5H_4CH_3)_4$, and heretofore assumed to be due to a static structure with the metal atom bonded to the unique carbon, is in fact *precisely* the pattern expected for a dynamic σ-methylcyclopentadiene group. To test this hypothesis, we have reinvestigated the temperature-dependent nmr spectrum of $Sn(C_5H_4CH_3)_4$ as well as other members of the general class of compounds $(CH_3)_nM(C_5H_5)_{4-n}$ and $(CH_3)_nM(C_5H_4CH_3)_{4-n}$ where M = Si, Ge, Sn and $n = 0, 1, 2, 3$. On cooling $Sn(C_5H_4CH_3)_4$ to −80°, a noticeable broadening of the resonances was observed. With $(CH_3)_3SnC_5H_4CH_3$ we obtained at −85° the spectrum in Figure 1. Significant broadening of the ring proton resonances has occurred, clearly showing the expected dynamic behavior. Similarly, the cyclopentadienyl resonance in $(CH_3)_3SnC_5H_5$ showed broadening at this temperature.

We found it more convenient to study $(CH_3)_3SiC_5H_4CH_3$ because, as expected, the entire range from "static" to dynamic behavior could be readily observed. The nmr spectra from −4 to +135° are given in Figure 2. From the changes in the τ 3 to 7 region it is clear that some rearrangement process is taking place although the complexity of the signals prevents a detailed analysis at present. At temperatures below +8°, the signal τ 8.0 due to the ring methyl group becomes an apparent triplet. Proton spin-decoupling measurements were carried out at −50°. Irradiation at 257 and 236 Hz downfield from the ring methyl resonance caused partial collapse of the signal at τ 8.0, but at no single frequency did irradiation produce a singlet for the ring methyl

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