

Preliminary communication

METAL—SILICON BONDED COMPOUNDS

XV*. THE REACTIONS OF $(\text{LiSiMe}_3)_6$ AND $(\text{LiSiMe}_3)_2 \cdot (\text{TMEDA})_3$ WITH AROMATIC SUBSTRATES

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Summary

$(\text{LiSiMe}_3)_6$ (I) reacts with tetramethylethylenediamine (TMEDA) to yield the crystalline product $(\text{LiSiMe}_3)_2 \cdot (\text{TMEDA})_3$ (II). The reactions of I and II with simple aromatic and unsaturated compounds have been examined. I reacts with derivatives containing acidic protons including $\text{RC}\equiv\text{CH}$ and fluorene in a fashion similar to organolithium derivatives, yielding simple metalated products and Me_3SiH . II also reacts with these derivatives to give the metalated products but with benzene it yields trimethylphenylsilyl and LiH quantitatively. With toluene and other methylated benzenes II attacks the methyl substituent and LiH and the trimethylsilylmethyl-substituted benzene derivatives are produced. A possible mechanism for this reaction has been proposed.

As a result of the development of a convenient route to the $\text{Hg}(\text{SiR}_3)_2$ derivatives [1] and their subsequent conversion to unsolvated silyllithium compounds by the direct metal interchange indicated in equation 1 [2], it has become possible to investigate both the physical and chemical properties of alkylsilyllithium species under carefully controlled conditions.

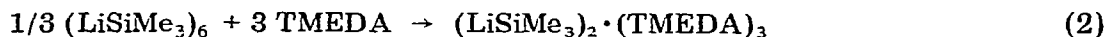


Our initial studies in this area have provided detailed information concerning reaction 1 [2a], and have established the structure of $(\text{LiSiMe}_3)_6$ by a single crystal X-ray diffraction determination [3]. We now report some preliminary studies on reactions of this species and of its tetramethylethylenediamine (TMEDA) complex, $(\text{LiSiMe}_3)_2 \cdot (\text{TMEDA})_3$, with acidic hydrocarbons and aromatic species.

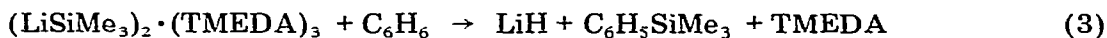
Solutions of the uncoordinated species, $(\text{LiSiMe}_3)_6$, in simple aromatic hydro-

carbons such as benzene, toluene, and the xylenes are stable for months at room temperature and show no detectable decomposition when maintained in toluene at 80°C for a week. With the compounds containing very acidic protons, the reactions of $(\text{LiSiMe}_3)_6$ are similar to those of $(\text{LiR})_n$, or of LiSiPh_3 as reported by Gilman* [3,5] and lead to formation of the corresponding organolithium derivative by metalation with liberation of the alkane or silane. Several of these reactions are summarized in Table 1.

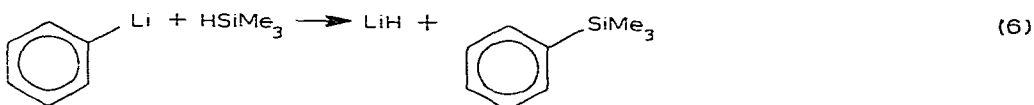
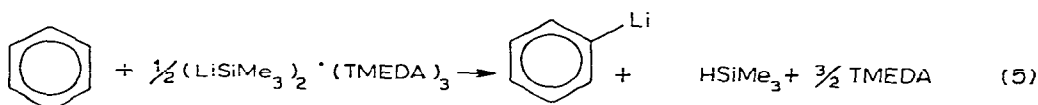
$(\text{LiSiMe}_3)_6$ reacts with basic molecules, ether, amines, and specifically N,N,N',N' -tetramethylethylenediamine, to yield stable complexes with enhanced reactivity. The addition of TMEDA proceeds as indicated in eq. 2 to give a new stable, crystalline complex, $[(\text{LiSiMe}_3)_2 \cdot (\text{TMEDA})_3]_n$, (n , not known) which has been characterized by NMR spectroscopy and elemental analysis.



This complex reacts with acidic hydrocarbons in a similar manner to the parent uncomplexed species and to organolithium derivatives, giving metalated products. However, a comparison between the reactions of $(\text{LiSiMe}_3)_2 \cdot (\text{TMEDA})_3$ and the related organolithium \cdot TMEDA complexes shows a dramatic change in reactivity toward less acidic aromatic compounds. The organolithium derivatives continue to yield metalated products [6]; in contrast, the silyllithium complex undergoes a new type of reaction, giving quantitative yields of LiH and silylated products as shown in eq. 3 and 4. Some additional reactions, along with reaction conditions, are indicated in Table 1.



The most probable pathway for the formation of the observed products initially seemed to be that described by eq. 5 and 6. However, we never were able to



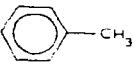

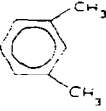
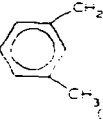
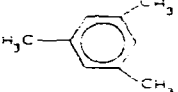
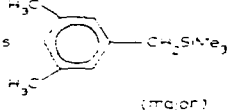
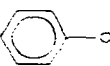
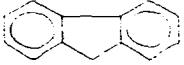
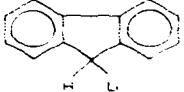
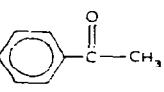
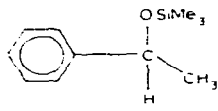
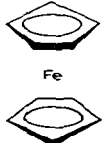


detect HSiMe_3 or LiPh . In addition, the known reaction indicated in eq. 6 is slow in ether** and limited studies in our laboratory showed that Me_3SiH was not readily attacked by LiPh under our reaction conditions. Furthermore, no Si_2Me_6 was found, indicating that an analogous coupling process between Me_3SiH and

*Gilman and his research group explored many reactions of silylmetallic derivatives over approximately 40 years. Much of the work pertinent to the present study has been reviewed [4].

**Several papers have appeared on the reaction between MR and R_3SiH . These suggest that the reaction proceeds slowly, if at all, under the conditions used in the present work [7].

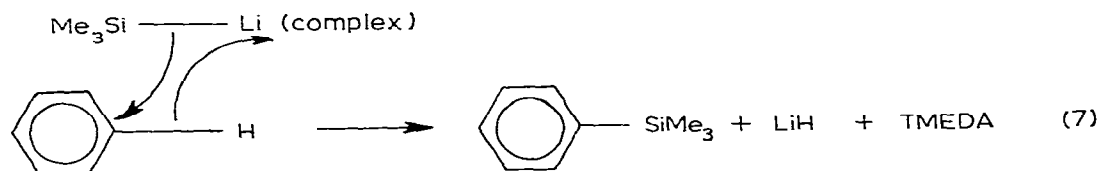
TABLE 1. REACTION CONDITIONS AND PRODUCTS FORMED FOR THE REACTIONS OF $(\text{LiSiMe}_3)_6$ (I) AND OF $(\text{LiSiMe}_3)_2(\text{TMEDA})_3$ (II) WITH VARIOUS ORGANIC SUBSTRATES

No.	Reactant	Substrate	Temp. ($^{\circ}\text{C}$)	Time	Products
1	II		55	4 days	 SiMe_3 + LiH + TMEDA (100%)
2	II		25	10 days	 CH_2SiMe_3 + LiH (100%)
3	II		25	2 days	 CH_2SiMe_3 - other products (major)
4	II		25	2 days	 CH_2SiMe_3 + other products (major)
5	I	 (a)	55	7 days	no reaction
6	I, II	$\text{Ph}-\text{C}\equiv\text{CH}$	25	1 min	$\text{Me}_3\text{SiH} + \text{LiC}\equiv\text{CPh}$
7	I, II		25	1 min	$\text{Me}_3\text{SiH} +$ 
8	I, II		25	5 min	
9	II		25	2 days	no reaction

^a Gilman and Trepka [9] reported that LiSiPh_3 cleaved anisole yielding Ph_3SiMe and PhOH (on work up) when the reaction in THF was allowed to proceed for 24 hours at 50°C . ^b The failure to react in this instance should be compared with the reaction of $n\text{-BuLi}$ ·pentaethylenetriamine (and other polyamine complexes) with ferrocene [e.g. 10].

$(\text{LiSiMe}_3) \cdot (\text{TMEDA})_3$ did not occur. Finally, no H_2 evolution was noted during any of the silylation reactions, eliminating the possibility that the known reaction between Me_3SiH and LiH had occurred [8].

All of these results caused us to rule out the initial metalation process and lead us to propose an attack by the SiMe_3 moiety on the benzene ring with a simultaneous elimination of LiH as indicated in eq. 7. This process occurs only



with the TMEDA-activated silyllithium and thus appears to involve a more polar Li-Si species. $(\text{LiSiMe}_3)_2 \cdot (\text{TMEDA})_3$ did not react with either anisole or ferrocene under conditions which lead to metalation by organolithium \cdot TMEDA complexes (See Table 1, Item 5), indicating additional differences between the reactivities of the silyl- and organolithium \cdot TMEDA complexes.

Experimental

$(\text{LiSiMe}_3)_6$ was prepared by the reaction of an excess of Li metal with $\text{Hg}(\text{SiMe}_3)_2$ [1] in cyclopentane as previously described [2]. The solvent was removed, yielding crystalline trimethylsilyllithium. This crystalline material was transferred in an argon-filled drybox to a reaction vessel which was closed off with a stopcock. The vessel then was removed from the drybox and attached to the vacuum system where cyclopentane solvent and excess TMEDA were added. On warming to room temperature, a white solid formed immediately. This was separated by filtration or, alternatively, by removal of solvent and excess TMEDA by vacuum distillation. The carbon and hydrogen analysis* of $(\text{Me}_3\text{SiLi})_2 \cdot (\text{TMEDA})_3$: Found: C, 56.50; H, 12.88. $\text{C}_{24}\text{H}_{66}\text{Li}_2\text{N}_6\text{Si}_2$ calcd.: C, 56.69; H, 12.99%. ^1H NMR (δ): s (9H) at 0.72 ppm, s (16H) at 2.12 ppm; ^{13}C NMR [^1H] gave lines at 55.7, 44.5 and 10.5 ppm relative to TMS. Reactions of $(\text{LiSiMe}_3)_6$ and $(\text{LiSiMe}_3)_2 \cdot (\text{TMEDA})_3$ with various substrates were carried out by placing a known quantity of the crystalline silyllithium or silyllithium \cdot TMEDA complex along with any other solid starting materials in a reaction vessel in the argon filled drybox. The reaction vessel was then removed from the drybox and attached to the vacuum system in which the liquid aromatic substrate was distilled into the reaction vessel and closed off by a stopcock (or sealed) and warmed to the reaction temperature and maintained at that temperature for the period indicated in Table 1. The silylated products were characterized by GC/MS and NMR analysis and were compared with authentic samples.

Acknowledgements

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References

- 1 a) T.F. Schaaf and J.P. Oliver, *J. Amer. Chem. Soc.*, **91** (1969) 4327; b) E. Hengge and N. Holtschmidt, *J. Organometal. Chem.*, **12** (1968) 5; c) N.S. Vyazankin, G.A. Razuvaev, E.N. Gladyshev and S.P. Korneva, *J. Organometal. Chem.*, **7** (1967) 353.
- 2 T.F. Schaaf, W. Butler, M.D. Glick and J.P. Oliver, *J. Amer. Chem. Soc.*, **96** (1974) 7593; W.H. Ilsley, T.F. Schaaf, M.D. Glick and J.P. Oliver, *J. Amer. Chem. Soc.*, **102** (1980) 3769.
- 3 H. Gilman and F.K. Cartledge, *J. Organometal. Chem.*, **3** (1965) 255.
- 4 H. Gilman and H.J.S. Winkler in H.H. Zeiss (Ed.), *Organometallic Chemistry*, ACS monograph No. 147, Reinhold, New York, NY, 1960, pp. 270–345.
- 5 B.J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon Press, Oxford, England, 1974.
- 6 R. West and P.C. Jones, *J. Amer. Chem. Soc.*, **90** (1968) 2656; also see A.J. Chalk and T.J. Hoogeboom, *J. Organometal. Chem.*, **11** (1968) 615; J. Klein, A. Medlik and A.Y. Meyer, *Tetrahedron*, **32** (1976) 51 and references therein.
- 7 H. Gilman and S.P. Massie, Jr., *J. Amer. Chem. Soc.*, **68** (1946) 1128; H. Gilman and M.W. Melvin, Jr., *J. Amer. Chem. Soc.*, **71** (1946) 4050; R.N. Meals, *J. Amer. Chem. Soc.*, **68** (1946) 1880.
- 8 R.J.P. Corriu and C. Guerin, *J. Chem. Soc. Chem. Commun.*, (1980) 168.
- 9 H. Gilman and W.J. Trepka, *J. Organometal. Chem.*, **1** (1963) 222.
- 10 M. Walczak, R. Mink, M.D. Rausch and G. Stucky, *J. Amer. Chem. Soc.*, **100** (1978) 6382; M.D. Rausch and D.J. Ciappenelli, *J. Organometal. Chem.*, **10** (1967) 127.