View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1976. Downloaded by University of Michigan Library on 23/10/2014 18:19:37.

Preparation and Spectroscopic Studies of Some Reactions of Lithium Derivatives of Silanol, Disilylphosphine, and Related Compounds

By **Stephen Cradock, E. A. V. Ebsworth,* David W. H. Rankin,** and **W. John Savage,** Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Methyl-lithium reacts with $Y(SiH_3)_2$ (Y = O, S, or Se) or $Z(SiH_3)_3$ (Z = P or As) in diethyl ether to give $Li(YSiH_3)$ or $Li[Z(SiH_3)_2]$; these compounds have been characterised by i.r., Raman, and n.m.r. spectroscopy, and some of their reactions with halides have been studied. Trisilylamine does not react cleanly with LiMe to form an analogous compound. The n.m.r. spectra of solutions containing both $Li(YSiH_3)$ and $Y(SiH_3)_2$ show that exchange occurs that is rapid on the n.m.r. time scale unless Y = O. Silyl selenoacetate can be prepared from $Li(SeSiH_3)$ and MeCOCl, and the kinetic parameters for the intramolecular exchange in this species have been determined.

ALKALI-METAL derivatives of trimethylsilanol and of hexamethyldisilazane have proved to be of great importance as synthetic intermediates.[1] We have now prepared the lithium derivatives of silanol, silanethiol, silaneselenol, disilylphosphine, and disilylarsine, and have described their characterisation, together with a preliminary study of their potential value as synthetic intermediates. A preliminary account of this work has appeared.[2]

RESULTS AND DISCUSSION

Methyl-lithium reacted smoothly at low temperatures in diethyl ether with $Y(SiH_3)_2$ (Y = O, S, or Se) or $Z(SiH_3)_3$ (Z = P or As) to give $SiMeH_3$ in 80—90% of the amount required by equations (1) and (2). Since the

$$Y(SiH_3)_2 + LiMe \longrightarrow SiMeH_3 + Li(YSiH_3) \quad (1)$$

$$Z(SiH_3)_3 + LiMe \longrightarrow SiMeH_3 + Li[Z(SiH_3)_2] \quad (2)$$

LiMe was to some extent contaminated with lithium chloride, and since the solid residues could not be freed from diethyl ether even after prolonged pumping, the products were characterised by vibrational and n.m.r. spectroscopy and by their reactions with chlorotrimethylsilane. Although $N(SiH_3)_3$ reacted with LiMe with the evolution of methylsilane, we were unable to obtain any evidence for the formation of $Li[N(SiH_3)_2]$.

Vibrational Spectra.—The i.r. spectra of solid $Li(YSiH_3)$ and solid $Li[Z(SiH_3)_2]$, and the Raman spectra

[1] U. Wannagat, K. Behmel, and H. Buerger, *Ber.*, 1964, **97**, 2029.

[2] E. A. V. Ebsworth, H. Moretto, D. W. H. Rankin, and W. J. Savage, *Angew. Chem.*, 1973, **8**, 344.

View Article Online

Published on 01 January 1976. Downloaded by University of Michigan Library on 23/10/2014 18:19:37.

of these compounds as solids or in solution in diethyl ether, contained bands assigned to the expected modes of the SiH_3 groups. In addition, the Raman spectra of all the compounds except the oxygen derivative showed strong lines in the region associated with Si–Y or Si–Z stretching; these lines were polarised in the spectra of solutions, and correspond to peaks in the i.r. spectra. For Z = P, two Raman lines were resolved (assigned to ν_{sym} and ν_{asym}); for Z = As, the greater mass presumably prevents resolution with our instrument. In each case, ν(SiY) or ν(SiZ) was higher in frequency than all the analogous modes from $\nu(Si_2Y)$ or $\nu(Si_3Z)$ in the corresponding starting compound. For $Li(OSiH_3)$ we were not able to identify ν(SiY) with certainty. This compound gave poor-quality Raman spectra, and in the i.r. spectra there were bands at *ca.* 1 000 and *ca.* 850 cm^{-1} that could not be assigned to internal modes of SiH_3 groups. Without work with ^{17}O-labelled compounds we cannot be sure which of these represents ν(SiO). It is possible that one band is due to ν(LiO) and the other to ν(SiO). Observed frequencies and assignments are summarised in Table 1.

N.M.R. Spectra.—The ^1H n.m.r. spectra of $Li(YSiH_3)$ consisted in each case of a single central line. Only one ^{29}Si satellite was observed; the other was obscured by peaks due to residual diethyl ether; however, we were able to confirm by heteronuclear double resonance that the peaks observed were ^{29}Si satellites. The ^{29}Si spectra, obtained by INDOR methods, were all quartets, showing that each compound contains SiH_3 groups. For $Li(SeSiH_3)$, ^{77}Se satellites to the main peak were observed at 260 K; from these the ^{77}Se spectrum was also shown to be of quartet form, establishing the presence of one SiH_3 group bound to each selenium.

In the spectrum of $Li[P(SiH_3)_2]$, the main resonance consisted of a doublet due to coupling between ^1H and ^{31}P; because of peaks due to diethyl ether, we only observed one of the satellite doublets associated with H directly bound to ^{29}Si. This, however, showed a small additional quartet splitting on each line, due to $^4J(HH)$, which affects the spectrum because of the magnetic non-equivalence of protons bound to ^{28}Si and to ^{29}Si. The ^{31}P spectrum, obtained both directly and by INDOR methods, showed a heptet pattern, indicating coupling between phosphorus and six equivalent protons. Tickling experiments showed that $K(PH)$ and $K(^{29}SiP)$ were of opposite sign. In the ^{29}Si INDOR spectrum, the main pattern was a quartet. These observations established beyond doubt that the species contains two SiH_3 groups bound to P. The n.m.r. parameters are given in Table 2.

Although coupling between phosphorus and SiH

TABLE 1

Vibrational spectra (cm^{-1}) of $Li(YSiH_3)$ and $Li[Z(SiH_3)_2]$ (Y = O, S, or Se; Z = P or As)

	$Li(OSiH_3)$	$Li(SSiH_3)$			$Li(SeSiH_3)$		
	I.r.	I.r.	Raman [a]	Raman [b]	I.r.	Raman [a]	Raman [b]
ν(SiH)	2 100s	2 145s	2 165m	2 130m dp	2 140s	2 160m	2 118m, p
?ν(SiO)	1 000s, br						
$\delta(SiH_3)$	940s, br	935m, br	964m, br	945w, br, dp	945s (sh)	945m	940w, br, dp
			935m, sp		920vs	920m	
?	850m (sh)						
$\rho(SiH_3)$	730s, br	630m, sp	640w, br	655w, br, dp	600m	615m, br	624w, br, dp
ν(SiS/Se)		530m	545vs	565s, p	410m	418m, br	429vs, p
ν(LiY) or lattice mode	465m, br	n.o.	n.o.	n.o.	310m, br	n.o.	n.o.

	$Li[P(SiH_3)_2]$			$Li[As(SiH_3)_2]$	
	I.r.	Raman [a]	Raman [b]	Raman [a]	Raman [b]
ν(SiH)	2 085vs	2 105s	2 100s, p	2 110m	2 100m, p
	945 (sh)	950 (sh)	955sh, dp	950 (sh)	
$\delta(SiH_3)$	925 (sh)	935m	935br, dp	930w	930m, br, dp
	905s	905 (sh)	900w (sh), dp		
$\rho(SiH_3)$	600m	600w, br	n.o.	575w	580w, br, dp
$\nu(Si_2Z)$ asym	495m	485m	495m, dp	374vs	374vw, p
sym	460w	460s	470m, p		

Peaks were observed in the i.r. spectra due to residual OEt_2. n.o. = Not observed; w = weak, m = medium, s = strong, sh = shoulder, br = broad, p = polarised, and dp = depolarised.

[a] Solid. [b] Solution in OEt_2.

TABLE 2

Parameters from ^1H n.m.r. spectra of $Li(YSiH_3)$ and $Li[Z(SiH_3)_2]$

	τ	$\delta(^{29}Si)$ [a] (p.p.m.)	$\delta(^{31}P/^{77}Se)$ [b] (p.p.m.)	$^1J(^{29}SiH)$ (Hz)	$^2J(^{31}PH)$ (Hz)	$^4J(HH)$ (Hz)	$^3J(^{29}SiH)$ (Hz)
$Li(OSiH_3)$	5.25	−48		194			
$Li(SSiH_3)$	5.65	−58		200			
$Li(SeSiH_3)$	6.06	−71	−736	198	9 ± 2		
$Li[P(SiH_3)_2]$ [b]	6.02	−62	−406	184	15.5 ± 1	1 ± 0.2	7.5
$Li[As(SiH_3)_2]$	6.25	−75		194		0.9 ± 0.1	6

[a] Positive to high frequency of $SiMe_4$ (for ^{29}Si), 85% H_3PO_4 (for ^{31}P), or $SeMe_2$ (for ^{77}Se). [b] $^1J(PSi)$ + 256 Hz, relative to $^2J(PSiH)$, assumed positive (K. D. Crosbie and G. M. Sheldrick, *Mol. Phys.*, 1971, **20**, 317).

View Article Online

Published on 01 January 1976. Downloaded by University of Michigan Library on 23/10/2014 18:19:37.

protons was observed at room temperature in the spectrum of $Li[P(SiH_3)_2]$, the selenium satellites in the spectrum of $Li(SeSiH_3)$ collapsed at temperatures above 260 K. These observations imply that there is fast exchange of SiH_3 groups in solutions of $Li(SeSiH_3)$ at room temperature, and that any analogous exchange in solutions of $Li[P(SiH_3)_2]$ must be slow on the n.m.r. time scale. A series of experiments was undertaken to see whether such exchange occurred in solutions containing $Li(YSiH_3)$ and $Y(SiH_3)_2$ or $Li[Z(SiH_3)_2]$ and $Z(SiH_3)_3$. With Y = O, separate signals were observed for both species present at room temperature. For Y = S, a single main resonance was observed at room temperature and at 190 K. This is not surprising, since $Li(SSiH_3)$ and $S(SiH_3)_2$ have the same chemical shift. However, $^1J(^{29}SiH)$ is substantially different in the two species.[3] At room temperature, the main resonance showed a single ^{29}Si satellite, in a position corresponding to a weighted average value for J; at 190 K, two satellites were observed, corresponding to the two species present. With Y = Se, a single sharp resonance with a single sharp satellite was observed at all temperatures from 300 to 180 K; the coupling constant corresponded to an averaged value, and since no selenium satellites were observed it is clear that fast exchange was taking place even at the lowest temperature studied. Solutions containing $Li(OSiH_3)$ and $Se(SiH_3)_2$ at room temperature gave three resonances, corresponding to $Li(OSiH_3)$, $O(SiH_3)_2$, and the time-averaged peak for $Li(SeSiH_3)$ and $Se(SiH_3)_2$. A similar solution made up from $Li(SeSiH_3)$ and $O(SiH_3)_2$ gave a very similar spectrum. From the coupling constant associated with the peak due to $SeSiH_3$ groups, and from the integrated areas of the peaks associated with the two oxygen derivatives, we estimate that equilibrium (3) has been set up, with an equilibrium constant of *ca.* 80.

$$Li(OSiH_3) + Se(SiH_3)_2 \rightleftharpoons O(SiH_3)_2 + Li(SeSiH_3) \quad (3)$$

Exchange between selenium species is fast at room temperature, but between oxygen-containing species is slow under these conditions. Since almost identical spectra were obtained from starting materials of different compositions, we are satisfied that the data we give are for the system at equilibrium. When $Li(SSiH_3)$ was treated with $Se(SiH_3)_2$, or $Li(SeSiH_3)$ with $S(SiH_3)_2$, a single peak was observed at room temperature, but at 180 K this split into two; one peak is associated with $SSiH_3$ and the other with $SeSiH_3$ species. The n.m.r. parameters indicate that $Li(SeSiH_3)$ is the preferred product.

A solution of $Li[P(SiH_3)_2]$ containing a large excess of $P(SiH_3)_3$ gave an extremely broad phosphorus resonance at 300 K which split into two at 180 K.

Reactions.—With inorganic or organometallic halides. Few of the reactions we have studied led to the formation in high yield of the product we had hoped to obtain. Lithium siloxide proved particularly unsatisfactory as a reagent. Even with $SiMe_3Cl$, reaction in the presence of solvent gave SiH_4 and hexamethyldisiloxane, and we were only able to obtain 1,1,1-trimethyldisiloxane by working without solvent. In general, reactions of $Li(YSiH_3)$ with halides gave $Y(SiH_3)_2$ as the main or the only SiH-containing product. With lithium silyl sulphide, for example, reaction with $SiMe_nCl_{4-n}$ depended very much on n. When $n = 3$, reaction proceeded in high yield according to equation (4). With $n = 0$ or 1,

$$SiMe_3Cl + Li(SSiH_3) \longrightarrow Me_3SiSSiH_3 + LiCl \quad (4)$$

the only hydride product detected was disilyl sulphide. With $n = 2$, the reaction was more complicated. A lot of $S(SiH_3)_2$ was formed, but we believe that we were able to detect the presence of $SiMe_2(SSiH_3)_2$, which appears to lose $S(SiH_3)_2$ to form $(Me_2SiS)_2$. Treatment of $Li(SSiH_3)$ with $PBrF_2$, PF_3, $HgCl_2$, or $SnCl_2$ gave $S(SiH_3)_2$, at least initially, as the only hydride-containing product. Only with BCl_3 did we find any evidence for the formation of an intermediate. With bromopentacarbonylmanganese, we were a little surprised to find that $[Mn(CO)_5(SiH_3)]$ was formed in *ca.* 60% yield; the other product was intractable, and there was no reaction between $Li(SeSiH_3)$ and $[Mn_2(CO)_{10}]$. It seemed possible that the formation of $Y(SiH_3)_2$ in many of these reactions was due to the presence of the lithium derivatives in solution as aggregates. In an attempt to suppress the formation of disilyl selenide by breaking up any aggregates, we added trimethylamine to a solution of $Li(SeSiH_3)$; the n.m.r. parameters were not much affected, but the selenium satellites became sharp at room temperature. Treatment of the resulting solution with $SiMe_3Cl$ gave a white volatile solid which we formulate as the adduct $Me_3SiSeSiH_3{\cdot}NMe_3$, from which NMe_3 could be removed with BF_3 to give pure $Me_3SiSeSiH_3$. Because of the formation of the adduct[4] we did not pursue this method of modifying the reactivity of the lithium derivatives further.

We only investigated one reaction of $Li[P(SiH_3)_2]$. We wanted a method of preparing $PH(SiH_3)_2$; treatment of $Li[P(SiH_3)_2]$ with H_2S in the absence of solvent at low temperatures gave the required product in high yield.

With acetyl compounds. Acetyl chloride reacted with lithium siloxide, silyl sulphide, or selenide to give $MeC(O,Y)SiH_3$ in high yield [equation (5)]. Acetic

$$MeCOCl + Li(YSiH_3) \longrightarrow MeC(O,Y)SiH_3 \quad (5)$$

anhydride reacted with lithium siloxide to give disiloxane and lithium acetate; with lithium silyl selenide, a mixture of silyl acetate and silyl selenoacetate was formed, the proportion of silyl acetate in the mixture increasing with reaction time. The formation of these two products can be understood if the initial reaction is to give lithium acetate and silyl selenoacetate, which then react together to give silyl acetate and lithium selenoacetate [equations (6) and (7)]. Addition of silyl bromide

[3] E. A. V. Ebsworth and J. J. Turner, *J. Phys. Chem.*, 1963, **67**, 805.

[4] A. G. MacDiarmid, *Quart. Rev.*, 1956, **10**, 208.

View Article Online

Published on 01 January 1976. Downloaded by University of Michigan Library on 23/10/2014 18:19:37.

to the involatile residue gave more of a mixture of silyl acetate and silyl selenoacetate, which is consistent with

$$Li(SeSiH_3) + (MeCO)_2O \longrightarrow MeCO_2Li + MeC(O,Se)SiH_3 \quad (6)$$

$$MeCO_2Li + MeC(O,Se)SiH_3 \longrightarrow MeC(O,Se)Li + MeCO_2SiH_3 \quad (7)$$

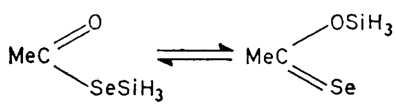
the presence in the residue of lithium acetate and lithium selenoacetate [equations (8) and (9) *]. We have

$$MeCO_2Li + SiBrH_3 \longrightarrow MeCO_2SiH_3 + LiBr \quad (8)$$

$$MeC(O,Se)Li + SiBrH_3 \longrightarrow MeC(O,Se)SiH_3 + LiBr \quad (9)$$

confirmed that lithium acetate reacts with silyl selenoacetate, forming silyl acetate [equation (7)]. Lithium silyl selenide reacted with acetic acid to give silyl acetate in high yield.

We investigated further the intramolecular exchange process described in an earlier paper [5] as taking place in silyl selenoacetate. The equilibrium constants in



different solvents are between 0.25 and 0.5; activation parameters were also determined (Table 3). In order to

TABLE 3

Parameters for the exchange: $MeCO{\cdot}SeSiH_3 \rightleftharpoons MeCSe{\cdot}OSiH_3$

	Solvent		
	$SiMe_4$	CCl_4–C_6H_6	OEt_2
(*a*) Thermodynamic			
K	0.26 ± 0.01	0.30 ± 0.01	0.45 ± 0.01
$\Delta G^{\ominus}$/kJ mol^{-1}	3.3 ± 0.1	3.0 ± 0.1	2.0 ± 0.1
$\Delta H^{\ominus}$/kJ mol^{-1}	*ca.* 0	0	0
$\Delta S^{\ominus}$/J K^{-1} mol^{-1}	−2.1	−1.9	−1.6
(*b*) Kinetic			
$E^{\ddagger}$/kJ mol^{-1}	48.9 ± 1	55 ± 2	67 ± 3
$\Delta G^{\ddagger}$/kJ mol^{-1}	60 ± 3	61 ± 5	60 ± 25
$\Delta H^{\ddagger}$/kJ mol^{-1}	45 ± 1	54 ± 1	66 ± 3
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	−48 ± 8	−22 ± 14	+30 ± 60

see how the system was affected by changing the substituents at the acetyl group we tried to prepare silyl selenotrifluoroacetate or silyl selenomonochloroacetate. Unfortunately, when trifluoroacetyl bromide was allowed to react with lithium silyl selenide, $Se(SiH_3)_2$ was the only silyl-containing product detected. The reaction between trifluoroacetic anhydride and $Li(SeSiH_3)$ was very complex; the proportion of volatile products was small, and nothing corresponded with what was expected for silyl selenotrifluoroacetate. Trifluoroacetic acid reacted cleanly with $Se(SiH_3)_2$ giving silyl trifluoroacetate. Chloroacetyl chloride and chloroacetyl bromide both reacted with $Li(SeSiH_3)$ to give $Se(SiH_3)_2$; again there was no evidence for the formation of the expected $ClCH_2C(O,Se)SiH_3$. It seems possible that with both CF_3COBr and $ClCH_2COBr$ the desired product may be formed initially, but that this reacts rapidly with any local excess of $Li(SeSiH_3)$ [equation (10)].

$$CF_3COBr + Li(SeSiH_3) \longrightarrow CF_3C(O,Se)SiH_3 \xrightarrow{Li(SeSiH_3)} CF_3C(O,Se)Li + Se(SiH_3)_2 \quad (10)$$

Conclusion.—Although lithium derivatives of $YH(SiH_3)$ or $ZH(SiH_3)_2$ can be prepared without difficulty, they are not very useful as synthetic intermediates in diethyl ether solution. Many halides react with $Li(YSiH_3)$ to give $Y(SiH_3)_2$ as the main silyl-containing product. This may be associated with the lability of the SiH_3 groups in these systems.

EXPERIMENTAL

Preparations.—The compounds $Y(SiH_3)_2$ or $Z(SiH_3)_3$ (Y = O, S, or Se; Z = P or As) react with LiMe in diethyl ether to give SiH_4, $SiMeH_3$, a trace amount of H_2, and $Li(YSiH_3)$ or $Li[Z(SiH_3)_2]$. The conditions giving minimum proportions of H_2 and SiH_4 and maximum proportions of $SiMeH_3$ among the most volatile products were the same for Y or Z: a reaction temperature of 210 K and a reaction time of 180 s. Typical experiments are summarised below.

Amount taken (mmol)		Amount evolved (mmol)		
Silyl compound	LiMe	SiH_4	$SiMeH_3$	% [a]
$O(SiH_3)_2$ 1.0	0.7	0.1	0.6	85
$S(SiH_3)_2$ 1.0	0.7	0.1	0.6	85
$Se(SiH_3)_2$ 1.0	0.7	0.1	0.6	85
$P(SiH_3)_3$ 0.7	0.5	0.05 [b]	0.45	90
$As(SiH_3)_3$ 0.7	0.5	0.1	0.40	80

[a] Based on equation (1). [b] 0.2 mmol of the silyl compound were recovered.

The products were obtained as white solids from which residual OEt_2 could not be removed by prolonged pumping. They were soluble in OEt_2 but not in benzene and were characterised spectroscopically and by reaction with $SiMe_3Cl$.

Treatment of $N(SiH_3)_3$ (0.7 mmol) with LiMe (0.5 mmol) (at 210 K) gave $SiMeH_3$ (0.45 mmol) and SiH_4 (0.05 mmol).

Attempts to Characterise $Li[N(SiH_3)_2]$.—A white solid, insoluble in diethyl ether, was precipitated. If the solvent was removed at 210 K after the initial reaction, a white solid was obtained; this also decomposed when it was warmed to room temperature, giving H_2 and SiH_4. Attempts to allow the initial product of the reaction to form derivatives with $SiMe_3Cl$ or with H_2S at 210 K were unsuccessful, the only products identified being H_2 and SiH_4. The n.m.r. spectrum of the initial product at 210 K after evolution of $SiMeH_3$ showed three peaks beside that due to solvent: a sharp weak one at τ 2.76, a very broad and weak one at τ 3.46, and a very broad and strong one at τ 4.96; the spectrum was unaltered if the trisilylamine used contained 90% ^{15}N, so that the broad lines were not associated with quadrupolar effects. When the solution was warmed to 250 K, the broad peaks became weaker and the sharp peak stronger; at 260 K, the peak at τ 2.76 (which we believe to be due to H_2) was strong and the broad peaks had almost disappeared.

Physical Properties.—The lithium compounds are all white solids which react rapidly with trace amounts of air and/or moisture. A sample of lithium silyl selenide (0.5

* The formula for silyl selenoacetate is written $MeC(O,Se)SiH_3$ because of the exchange described.

[5] S. Cradock, E. A. V. Ebsworth, and H. F. Jessep, *J.C.S. Dalton*, 1972, 964.

View Article Online

Published on 01 January 1976. Downloaded by University of Michigan Library on 23/10/2014 18:19:37.

mmol) was kept at room temperature (10 weeks) in OEt_2; a trace of SiH_4 had been formed, but no other compounds were detected either in the n.m.r. spectrum of the solution or when the tube was opened and the solvent removed. The solid residue was kept in the absence of solvent (3 months) at room temperature; no volatile material had been formed, and the residue on treatment with $SiMe_3Cl$ and OEt_2 gave silyl trimethylsilyl selenide (0.4 mmol).

Reactions of $SiMe_3Cl$.—(a) *With* $Li(OSiH_3)$. Lithium siloxide (0.2 mmol) was prepared as described above from $O(SiH_3)_2$ and as much solvent as possible was removed by prolonged pumping. Chlorotrimethylsilane (0.4 mmol) was allowed to react with the solid in the absence of solvent for a few minutes at room temperature. The i.r. and ^1H n.m.r. spectra (τ 5.29 and 9.84 in C_6H_6; intensity ratios 1 : 3; lit.[6] 5.39 and 9.92 in C_6H_{12}) showed that the product of the reaction was 1,1,1-trimethyldisiloxane. Attempts to prepare this compound from the same reagents in diethyl ether gave SiH_4 and $O(SiMe_3)_2$ with solid products.

(b) *With* $Li(SSiH_3)$. The compound $Li(SSiH_3)$ was prepared as described above from $S(SiH_3)_2$ (1 mmol) and LiMe (0.7 mmol). Solvent and excess of $S(SiH_3)_2$ were removed by prolonged pumping at room temperature. Fresh diethyl ether (*ca.* 2 cm^3) was added, in which the solid dissolved readily; $SiMe_3Cl$ (0.6 mmol) was added, and the reactants allowed to warm to room temperature. A white precipitate (presumably of LiCl) was rapidly formed. From the volatile products, $S(SiH_3)(SiMe_3)$ (0.5 mmol) was recovered by fractional distillation and identified spectroscopically.[5] A trace amount of $S(SiH_3)_2$ was also found.

(c) *With* $Li(SeSiH_3)$. The compound $Li(SeSiH_3)$, prepared as in (a) from $Se(SiH_3)_2$ (1.0 mmol) and LiMe (0.7 mmol), was allowed to react with $SiMe_3Cl$ in diethyl ether. Silyl trimethylsilyl selenide (0.5 mmol) was isolated from among the volatile products of the reaction and identified spectroscopically.[5] A trace amount of $Se(SiH_3)_2$ was also found, but this could not be separated from OEt_2.

Other Reactions of $Li(OSiH_3)$.—(a) *With* $SiClF_3$. Lithium siloxide (0.4 mmol) was allowed to react at 200 K with $SiClF_3$ (0.4 mmol) in diethyl ether; a white precipitate was formed rapidly. The volatile products consisted of $O(SiH_3)_2$ and $SiFH_3$ (*ca.* 0.05 mmol); $O(SiH_3)_2$ could not be separated from the solvent, but the absence of any other silyl compound was confirmed by i.r. and ^1H n.m.r. spectroscopy.

(b) *With* MeCOCl. Lithium siloxide (0.2 mmol) was allowed to react at 200 K with MeCOCl (0.3 mmol) in diethyl ether. The only product containing SiH_3 groups was identified spectroscopically as $O(SiH_3)_2$. No silyl acetate was formed.

(c) *With acetic anhydride.* Lithium siloxide (0.5 mmol) was allowed to react with acetic anhydride (0.5 mmol) in diethyl ether at 300 K. A white precipitate formed, and the volatile products were shown spectroscopically to consist of a mixture of $O(SiH_3)_2$ and solvent.

(d) *With* CY_2. There was no evidence of any reaction between lithium siloxide and either CO_2 or CS_2 in diethyl ether at 300 K over 5 d.

Other Reactions of $Li(SSiH_3)$.—(a) *With* MeI. Lithium silyl sulphide (0.2 mmol) was allowed to react with MeI (0.3 mmol) at room temperature in diethyl ether. The products were identified from their n.m.r. spectra as a mixture of methyl silyl sulphide [τ (Si*H*) 5.70 (lit.[7] 5.70); ^4J(H–H) 0.45 Hz (lit. 0.45 Hz)] with a small amount (*ca.* 10%) of $S(SiH_3)_2$.

(b) *With* $SiMe_2Cl_2$. Lithium silyl sulphide (0.4 mmol) was allowed to react with $SiMe_2Cl_2$ at 200 K in diethyl ether. Peaks were observed in the n.m.r. spectrum at τ 5.67 and 5.75, the former being initially the stronger; after the tube had been allowed to warm to 300 K for 2 h, the latter peak became the stronger. The volatile products consisted of an inseparable mixture of solvent and disilyl sulphide, together with a less-volatile fraction. The n.m.r. spectra of this fraction gave peaks at τ 5.76, 5.86 (v. weak), 9.46, and 9.54 in benzene, the first and last being of equal intensity. The mass spectrum showed a peak at *m/e* 179.992026 (calc. for $C_4H_{12}S_2Si_2$: 179.991898) so we assign the n.m.r. peak at τ 9.46 to tetramethylcyclodisiladithiane. The peaks at τ 5.76 and 9.54 are then assigned to $SiMe_2(SSiH_3)_2$. In a second experiment with initial component ratios of 1 : 1, the peak assigned to $(Me_2SiS)_2$ was relatively much more prominent among the products. Attempts to obtain the mass spectrum of $SiMe_2(SSiH_3)_2$ were unsuccessful.

(c) *With* $SiMeCl_3$. Lithium silyl sulphide (0.3 mmol) was allowed to react with $SiMeCl_3$ (0.1 mmol) at 200 K in diethyl ether. A white solid precipitated rapidly. The only silyl-containing product present in significant amounts was identified spectroscopically as $S(SiH_3)_2$.

(d) *With* $SiCl_4$. Lithium silyl sulphide (0.4 mmol) was allowed to react with $SiCl_4$ (0.1 mmol) in diethyl ether at 200 K. A white solid precipitated rapidly; the only silyl-containing product was identified as $S(SiH_3)_2$.

(e) *With* $PBrF_2$. Lithium silyl sulphide (0.2 mmol) was treated with $PBrF_2$ (0.2 mmol) in diethyl ether at 280 K. A very fast reaction gave a yellow solution and a white precipitate. Initially, the main reaction products consisted of $SiFH_3$ and $S(SiH_3)_2$, but after the tube had been allowed to stand at 250 K for a few minutes the amount of $SiFH_3$ increased and $S(SiH_3)_2$ disappeared. In a subsequent experiment, the ^{31}P n.m.r. spectrum of the products at room temperature showed that PF_3 had been formed, with small amounts of two other unidentified phosphorus-containing species. No evidence was obtained for the formation of difluorophosphino silyl sulphide.

(f) *With* PF_3. Lithium silyl sulphide (0.3 mmol) was allowed to react with PF_3 (0.3 mmol) at 200 K in diethyl ether. The solution turned pale yellow, but no precipitate was formed. The ^1H n.m.r. spectrum at this temperature showed that much $S(SiH_3)_2$ and a little $SiFH_3$ had been formed; after several hours at room temperature, $SiFH_3$ was the only silyl-containing product present.

(g) *With* $HgCl_2$. Lithium silyl sulphide (0.2 mmol) was allowed to react with $HgCl_2$ (0.1 mmol) in diethyl ether at 210 K. A black precipitate was formed rapidly. The ^1H n.m.r. spectrum recorded at this temperature showed that $S(SiH_3)_2$ was the main product, with a trace amount of $SiCl_2H_2$. There was no evidence for the formation of silylthiomercury compounds.

(h) *With* $SnCl_2$. Lithium silyl sulphide (0.2 mmol) was allowed to react with $SnCl_2$ in diethyl ether at 210 K. A white precipitate formed at once; the only silyl-containing product was identified spectroscopically as $S(SiH_3)_2$.

(i) *With* BCl_3. Lithium silyl sulphide (0.3 mmol) was treated with BCl_3 (0.1 mmol) in diethyl ether at 200 K. No reaction occurred. At 230 K, a white precipitate formed and the ^1H n.m.r. peak at τ 5.67 became substantially

[6] C. H. Van Dyke and A. G. MacDiarmid, *Inorg. Chem.*, 1964, **3**, 747.

[7] B. Sternbach and A. G. MacDiarmid, *J. Inorg. Nuclear Chem.*, 1961, **23**, 225.

View Article Online

Published on 01 January 1976. Downloaded by University of Michigan Library on 23/10/2014 18:19:37.

broader, while a new broad peak appeared at τ 4.74. At 260 K both peaks disappeared, and SiH_4 remained as the sole silyl-containing product.

(j) *With* MeCOCl. Lithium silyl sulphide (0.4 mmol) was allowed to react with MeCOCl (0.5 mmol) in OEt_2 at 210 K (300 s). A white precipitate formed and silyl thioacetate was found (identified spectroscopically) in *ca.* 80% yield, with trace amounts of $(MeCO)_2S$ and $S(SiH_3)_2$.

Other Reactions of $Li(SeSiH_3)$.—(a) *With* MeCOCl. Lithium silyl selenide (0.4 mmol) was allowed to react with MeCOCl (0.5 mmol) in diethyl ether at 210 K (5 min). A white precipitate formed, with a yellow solution. The volatile products consisted of a mixture of silyl selenoacetate [5] and *ca.* 10% $Se(SiH_3)_2$. Reactions under different conditions gave much larger proportions of $Se(SiH_3)_2$.

(b) *With* $(MeCO)_2O$. Lithium silyl selenide (0.4 mmol) was allowed to react with $(MeCO)_2O$ (0.4 mmol) in diethyl ether at room temperature (1 min). A rapid reaction led to the formation of a white precipitate. The volatile products consisted of a mixture of silyl selenoacetate and silyl acetate [8] in roughly equimolar proportions. When the reaction was allowed to proceed for 5 min, the proportion of $MeCO_2SiH_3$ in the volatile products was much higher. Treatment of the solid residue with excess of $SiBrH_3$ gave a similar mixture of acetyl silyl selenide and $MeCO_2SiH_3$.

(c) *With* $MeCO_2H$. Lithium silyl selenide (0.4 mmol) was allowed to react with $MeCO_2H$ (0.4 mmol) in diethyl ether at room temperature (5 min). A white precipitate formed at once; the only volatile product detected was $MeCO_2SiH_3$ (0.3 mmol).

(d) *With* CF_3CO_2H. Lithium silyl selenide (0.4 mmol) was allowed to react with CF_3CO_2H (0.4 mmol) in diethyl ether at room temperature (5 min). The only volatile product detected was silyl trifluoroacetate [8] (0.3 mmol).

(e) *With* CF_3COBr. Lithium silyl selenide (0.4 mmol) was allowed to react with CF_3COBr (0.5 mmol) in diethyl ether at 180 K (5 min). A white precipitate formed and the solution became red. The only volatile product was $Se(SiH_3)_2$ (0.2 mmol). Reactions using an excess of acid halide, or in dilute solution, gave only $Se(SiH_3)_2$ as volatile product.

(f) *With* $CH_2ClCOCl$. Lithium silyl selenide (0.4 mmol) was allowed to react with $CH_2ClCOCl$ (0.4 mmol) at 180 K (5 min); the only volatile product was $Se(SiH_3)_2$.

(g) *With* $[MnBr(CO)_5]$. Lithium silyl selenide (0.4 mmol) was allowed to react with $[MnBr(CO)_5]$ (0.4 mmol) in tetrahydrofuran (thf) (2 h). The main volatile product was pentacarbonylsilylmanganese [9] (0.23 mmol), with a trace amount of $[Mn(CO)_5H]$.

Lithium silyl selenide did not react with $[Mn_2(CO)_{10}]$.

(h) *With* NMe_3. A solution of lithium silyl selenide (0.2 mmol) and NMe_3 (2 mmol) in diethyl ether gave the ^1H n.m.r. spectrum expected for the two components, with unchanged parameters, except that ^{77}Se satellites were observed at room temperature, and the ^{77}Se chemical shift (−751 p.p.m.) was slightly different from its value for $Li(SeSiH_3)$ (−736 p.p.m.).

(i) *With* $SiMe_3Cl$ *and* NMe_3. Lithium silyl selenide (0.4 mmol) was allowed to react with $SiMe_3Cl$ (0.4 mmol) in the presence of NMe_3 (1.0 mmol) using diethyl ether as solvent. The volatile product consisted of NMe_3 and a volatile solid which was formulated as the adduct $Me_3SiSeSiH_3{\cdot}NMe_3$. Treatment of this adduct with a small excess of BF_3 gave a mixture of $SiH_3SeSiMe_3$ and BF_3 from which BF_3 was removed with diethyl ether, giving pure $SiH_3SeSiMe_3$ [50% yield based on $Li(SeSiH_3)$ taken].

Reaction of $Li[P(SiH_3)_2]$ *with* H_2S.—Lithium disilyl phosphide (0.3 mmol) was treated with H_2S (1 mmol) in diethyl ether; the products consisted of a mixture of $P(SiH_3)_3$, $PH(SiH_3)_2$, and $PH_2(SiH_3)$. A similar reaction in the absence of solvent at 180 K (10 min) gave disilylphosphine [10] (0.25 mmol, 80%) with trace amounts of $PH_2(SiH_3)$ and $S(SiH_3)_2$.

N.m.r. Spectra of Mixtures of Silyl Compounds with Silyl Anions.—(a) $Li(OSiH_3)$ *and* $O(SiH_3)_2$. A solution in diethyl ether of $Li(OSiH_3)$ (0.2 mmol) and $O(SiH_3)_2$ (0.2 mmol) gave two discrete signals at room temperature [τ 5.39, $^1J(^{29}SiH)$ 222 Hz, $O(SiH_3)_2$; 5.25, $^1J(^{29}SiH)$ 194 Hz, $Li(OSiH_3)$].

(b) $Li(SSiH_3)$ *and* $S(SiH_3)_2$. A solution in diethyl ether of $Li(SSiH_3)$ (0.4 mmol) and $S(SiH_3)_2$ (0.2 mmol) gave one sharp signal at 300 K [τ 5.65, $^1J(^{29}SiH)$ 211 Hz]. At 190 K the satellite split into two peaks of equal intensity [$^1J(^{29}SiH)$ 199 and 225 Hz], due respectively to $S(SiH_3)_2$ and $Li(SSiH_3)$.

(c) $Li(SeSiH_3)$ *and* $Se(SiH_3)_2$. A solution in diethyl ether of $Li(SeSiH_3)$ (0.2 mmol) and $Se(SiH_3)_2$ (0.2 mmol) gave a single sharp ^1H resonance [τ 5.97, $^1J(^{29}SiH)$ 216 Hz]. The spectrum was unchanged at 180 K. No satellites due to ^{77}Se were observed.

(d) $Li(OSiH_3)$ *and* $Se(SiH_3)_2$. A solution in diethyl ether of $Li(OSiH_3)$ (0.4 mmol) and $Se(SiH_3)_2$ (0.2 mmol) at 300 K gave resonances at τ 5.25 $Li(OSiH_3)$, 5.40 $O(SiH_3)_2$, and 6.05 $Se(SiH_3)_2$ and $Li(SeSiH_3)$. The heights of the first two peaks were in the ratio *ca.* 1 : 4; for the time-averaged peak at τ 6.05 $^1J(^{29}SiH)$ was 199 Hz, implying that the proportion of $Se(SiH_3)_2$ in the mixture was small. The spectrum was unchanged at 180 K.

(e) $Li(SeSiH_3)$ *and* $O(SiH_3)_2$. A similar solution containing $Li(SeSiH_3)$ (0.2 mmol) and $O(SiH_3)_2$ (0.4 mmol) gave peaks in the same positions. Integrations gave the ratio $O(SiH_3)_2 : Li(OSiH_3)$ as 9 : 1, and from $^1J(^{29}SiH)$ associated with the peaks due to SiH_3Se species (230 Hz) the ratio $Li(SeSiH_3) : Se(SiH_3)_2$ is 9 : 1. Hence for equilibrium (3), $K = 80$.

(f) $Li(SSiH_3)$ *and* $Se(SiH_3)_2$. A solution of $Li(SSiH_3)$ (0.2 mmol) and $Se(SiH_3)_2$ (0.2 mmol) in diethyl ether gave a single peak at room temperature [τ 5.83, $^1J(^{29}SiH)$ 216 Hz]. At 190 K the main peak and the satellites had both split into two [τ 5.70 and 6.08; $^1J(^{29}SiH)$ 224 and 192 Hz]. These peaks are assigned to $S(SiH_3)_2$ and $Li(SeSiH_3)$, respectively.

(g) $Li(SeSiH_3)$ *and* $S(SiH_3)_2$. A solution of $Li(SeSiH_3)$ (0.2 mmol) and $S(SiH_3)_2$ (0.2 mmol) in diethyl ether gave a spectrum identical to that described in (f) above.

(h) $Li[P(SiH_3)_2]$ *and* $P(SiH_3)_3$. A solution of $Li[P(SiH_3)_2]$ (0.2 mmol) and $P(SiH_3)_3$ (1.5 mmol) in diethyl ether gave a single broad peak in the ^1H n.m.r. spectrum (τ 6.05) at 300 and at 170 K. The ^{31}P spectrum of the same solution showed one very broad peak −382 p.p.m. relative to H_3PO_4 (high frequency shifts positive), linewidth 600 Hz at 300 K. At 200 K two peaks were observed, at −378 p.p.m. due to $P(SiH_3)_3$ and −411 p.p.m. due to $Li[P(SiH_3)_2]$. Both peaks were broad, and were unaffected by ^1H noise decoupling.

[8] E. A. V. Ebsworth and J. C. Thomson, *Spectrochim. Acta*, 1965, **21**, 2023.

[9] B. G. Aylett and J. M. Campbell, *J. Chem. Soc.* (*A*), 1969, 1916.

[10] S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, 1964, **3**, 1141.

View Article Online

Published on 01 January 1976. Downloaded by University of Michigan Library on 23/10/2014 18:19:37.

Kinetics of Intramolecular Exchange in $MeC(O,Se)SiH_3$.—Samples of acetyl silyl selenide [90% pure; impurities $Se(SiH_3)_2$ and $(CH_3CO)_2Se$] were prepared from MeCOCl and $Li(SeSiH_3)$, and their n.m.r. spectra were studied as a function of temperature in three different solvents: $SiMe_4$; benzene–carbon tetrachloride (1 : 1); OEt_2. The spectra showed the features described previously; the coalescence temperatures were reproducible from sample to sample indicating that the impurities did not affect the rate of exchange. Thermodynamic parameters were calculated assuming that the chemical shifts involved did not change with temperature; this assumption could be checked and was found to hold for the region of slow exchange (<260 K). Kinetic parameters were calculated using a computer program for lineshape analysis written by Nakagawa,[11] modified by Dr. R. K. Harris.[12] The results are given in Table 3. They have been averaged for the forward and reverse reactions.

Compounds were prepared by standard methods or obtained commercially; all were dried and purified before use, and were handled either in glass vacuum systems, fitted with greased or Sovirel taps, or in glove-boxes under dry nitrogen. Infrared spectra (200—4 000 cm^{-1}) were obtained using Perkin-Elmer 225 or 457 spectrometers, Raman spectra using a Cary 83 spectrometer with Ar laser excitation (488 nm), and n.m.r. spectra using a Varian Associates HA 100 spectrometer whose probe has been double-tuned [13] to accept a heterofrequency from a Schlumberger frequency synthesiser or (for ^{31}P spectra) a Varian Associates XL 100 FT spectrometer.

We thank the S.R.C. for a maintenance grant (to W. J. S.).

[5/2411 *Received*, 11*th December*, 1975]

[11] T. Nakagawa, *Bull. Chem. Soc. Japan*, 1966, **39**, 1006.
[12] Atlas Computer Laboratory, N.m.r. Program Library, Science Research Council, 1971.
[13] A. Charles and W. McFarlane, *Mol. Phys.*, 1968, **14**, 299.