and as a $Th_3P_4$ type sulfide.[6] Since La and Y have no 4f electrons, we many conclude that any large net change in measured susceptibility between reactants and products is due to a change in valence of ytterbium. The measured values are most meaningful for those ternary products in which the $Ln^{III}$ component is diamagnetic, in which case any residual paramagnetism should be ascribed to the presence of tripositive ytterbium, divalent ytterbium being also diamagnetic. The measurements indicate that in the $YbLa_2S_4$ product no $Yb^{III}$ is present, whereas the $YbY_2S_4$ preparation still contains about 16% $Yb^{III}$. For $YbPr_2S_4$ and $Yb^{II}$-$Yb^{III}{}_2S_4$, the total magnetic susceptibilities are accounted for by the two atoms of $Ln^{III}$ present in the compounds. For Ho, Er, and Tm the magnetic susceptibilities are too large to allow a meaningful comparison of the experimentally measured difference between 2 g.-atoms of $Ln^{III}$ and any additional susceptibility that may be present in the ternary compounds.

We consider the experimental evidence to have demonstrated that a series of compounds of nominal stoichiometry $YbLn_2S_4$ has been produced with the ytterbium existing almost entirely in the +2 oxidation state. Under the preparative conditions employed, the compounds crystallize either in the cubic $Th_3P_4$ structure or in the orthorhombic $Yb_3S_4$ structure with the transition occurring between the Ln components Ho and Er. Due to the regularity in the series of rare earth elements, we postulate that the $Th_3P_4$ structure would be obtained for all Ln species between La and Ho which would remain trivalent under the synthetic conditions. In this series yttrium can be considered as a rare earth metal with an effective ionic radius slightly larger than that of holmium. Since both the $Th_3P_4$ phase of single rare earth metal sulfides[6] and the $Yb_3S_4$ phase[3] are stable over a range of sulfur to metal compositions, we would expect the double sulfides with ytterbium to exhibit a variability also. The compounds synthesized may be considered to be single phase within the detectability of the X-ray powder diffraction technique employed.

Divalent ytterbium may be considered to behave chemically as an alkaline earth metal ion. In the case of the rock salt structured monosulfides, the lattice parameter of $Yb^{II}S$, 5.67 Å.,[3] is very close to that of CaS, 5.69 Å.[7] It is not surprising, therefore, that the series $YbLn_2S_4$ is similar to the series $CaLn_2S_4$.[8] In the latter series the change from the $Th_3P_4$ to the $Yb_3S_4$ structures occurs between the Ln components Dy and Y when sufficient CaS is added to $Ln_2S_3$ to reach the stoichiometry $CaLn_2S_4$, although the $Th_3P_4$ phase is still formed with the yttrium compound on using a deficiency of CaS. Any conclusion as to a "demonstrated" difference between the two series based on the different phase change-over positions should be tempered by the following observations: the stoichiometries of the $YbLn_2S_4$ compounds in the change-over region are only approximate; the $CaLn_2S_4$ series was prepared at 1200–1300° and it has been shown that the region of stability of the $Th_3P_4$ phase becomes larger with increasing temperature with respect to CaS content for the solid solution $CaS + Y_2S_4$[9]; and the $CaS + Ho_2S_3$ system has not been investigated.

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# Correspondence

## The Structure of Lithiomethyltrimethylsilane[1]

*Sir:*

In a recent report of the preparation of crystalline lithiomethyltrimethylsilane, Connolly and Urry[2] made the observation that the compound is monomeric in 2-methylpentane. There is no compelling reason to expect that this compound should behave differently from other alkyllithium compounds, which are associated in hydrocarbon solutions.[3–6] We have accordingly investigated some properties of lithiomethyltrimethylsilane with the aim of clarifying the issue.

Crystalline $LiCH_2Si(CH_3)_3$ was prepared by the reaction of chloromethyltrimethylsilane with lithium dispersion (1% Na content) in *n*-pentane at room temperature. The crystalline product is isolated from the filtered solution in good yield and purified by sublimation. The proton n.m.r. spectrum in benzene reveals two sharp resonances in the expected intensity ratio at values of 7.06 and 9.25 p.p.m. from benzene, in agreement with the previous report.[2]

The $^7Li$ nuclear magnetic resonance for the compound in hexane appears at a chemical shift of −1.74 p.p.m. (downfield) from aqueous lithium bromide as external standard.[7] This may be compared with −1.76 p.p.m. for *n*-butyllithium in the same solvent. The $^7Li$ chemical shifts of $LiCH_2Si(CH_3)_3$, $LiC_2H_5$, and LiC-

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(1) This research was supported by a grant from the National Science Foundation.

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(7) The authors are grateful to Dr. J. A. Ladd for assistance in obtaining $^7Li$ n.m.r. spectra.

$(CH_3)_3$ in benzene, relative to the aqueous LiBr external standard, are −1.36, −1.00, and −0.53 p.p.m., respectively.

The molecular weight of lithiomethyltrimethylsilane in benzene was determined by freezing point lowering.[6] The results are as follows, where $\bar{n}$ represents apparent degree of association.

| $m$ (as monomer) | $\bar{n}$ | $m$ (as monomer) | $\bar{n}$ |
|---|---|---|---|
| 0.0566 | 3.91 | 0.360 | 4.05 |
| 0.145 | 3.98 | 0.489 | 4.28 |

It is apparent that the compound is highly associated in benzene at about 6°, even to fairly low concentrations. There is some evidence in the data for a concentration dependence of $\bar{n}$, but the predominant species in solution is probably tetramer.

The discrepancy between these data and the result reported by Connolly and Urry might be due to a temperature difference; their isopiestic measurement was performed at room temperature.[8] The $^7$Li n.m.r. results reported above were obtained at room temperature, however, and the concordance of the $^7$Li chemical shifts for lithiomethyltrimethylsilane and *n*-butyllithium are an indication that the lithium atoms are in similar chemical environments.[9] It is our conclusion, therefore, that lithiomethyltrimethylsilane behaves normally, *i.e.*, that it forms electron-deficient polymeric species as do other alkyllithium compounds. At the same time, the steric effect of the trimethylsilyl group is evident, in that a tetramer rather than hexamer predominates in solution.

(8) Dr. G. Urry, private communication.

(9) Ebulliometric measurements also indicate a tetrameric association: R. H. Baney and R. J. Krager, *Inorg. Chem.*, **3**, 1657 (1964).

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## The Nature of Lithiomethyltrimethylsilane in Hydrocarbon Solvents

*Sir:*

Recently Connolly and Urry[1] reported that lithiomethyltrimethylsilane was monomeric in 2-methylpentane. Their finding is in contrast to those for other alkyllithium compounds, which are tetrameric or hexameric in benzene or *n*-hexane.[2–5] Since this apparently abnormal behavior might be explained by some unusual stabilization of the carbanion portion by ($d\pi$–$p\pi$) bonding with the adjacent silicon atom, thus reducing the tendency to associate, we undertook to re-examine these results.

TABLE I

| Benzene (b.p. 80°) | | | 2-Methylpentane (b.p. 60°) | | |
|---|---|---|---|---|---|
| Molality (as monomer) | Molality (measured) | App. deg. of assn. | Molality (as monomer) | Molality (measured) | App. deg. of assn. |
| 0.58 | 0.166 | 3.5 | 0.20 | 0.047 | 4.3 |
| 0.79 | 0.193 | 3.9 | 0.39 | 0.094 | 4.1 |
| 1.45 | 0.355 | 4.1 | 0.44 | 0.145 | 3.0 |
| 1.75 | 0.438 | 4.0 | 0.76 | 0.184 | 4.1 |
| 1.82 | 0.436 | 4.2 | 0.80 | 0.195 | 4.1 |
| 2.78 | 0.637 | 4.3 | 0.84 | 0.229 | 3.7 |
| | | Av. 4.0 | 0.87 | 0.210 | 4.1 |
| | | | 1.04 | 0.270 | 3.9 |
| | | | 1.10 | 0.291 | 3.8 |
| | | | 1.23 | 0.324 | 3.8 |
| | | | | | Av. 3.9 |

Crystalline lithiomethyltrimethylsilane was prepared by the reaction of chloromethyltrimethylsilane with lithium in 2-methylpentane under an argon atmosphere by a procedure similar to that of Connolly and Urry.[1] The compound was then isolated from solution and purified by vacuum sublimation.

The ultraviolet spectrum of a dilute isooctane solution of $LiCH_2Si(CH_3)_3$ examined on a Cary Model 14 recording spectrophotometer revealed no absorption maxima above 200 m$\mu$. This lack of any significant bathochromic shift suggests that there is no extensive delocalization of the electron pair on the carbanion.

The molecular weight of $LiCH_2Si(CH_3)_3$ was determined ebulliometrically in benzene and 2-methylpentane following the procedure of Weiner, Vogel and West.[2] Table I summarizes the results.

It is evident that lithiomethyltrimethylsilane is highly associated in both benzene and 2-methylpentane at their boiling points. Results by Hartwell and Brown on freezing-point lowering of benzene solutions confirm the tetrameric association.[6] The change in polarity in going from benzene to 2-methylpentane has little effect upon the degree of association. The apparent slight concentration dependence of the degree of association in benzene most likely is coincidental, since the same degree of association is observed at the boiling and freezing points of benzene. The trend, even if real, would not account for the results of Connolly and Urry[1] at 0.24 $m$ (as monomer) since extrapolation to infinite dilution gives a degree of association still considerably greater than three. Likewise, the apparent discrepancy cannot be explained by a temperature difference since the isopiestic measurements of Connolly and Urry[1] were made at room temperature, intermediate between the ebulliometric and cryoscopic measurements. It seems evident that if ($d\pi$–$p\pi$) bonding between the carbanion and silicon atom in lithiomethyltrimethylsilane does exist, it has little effect on the ultraviolet spectrum or on the degree of association in hydrocarbon solvents.

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