

Synthesis of Trimethylsilyl Analogues of Dilithiomethane: a New Development in Polyolithium Chemistry

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The synthesis and preliminary characterization of bis(trimethylsilyl)dilithiomethane and (trimethylsilyl)dilithiomethane are reported.

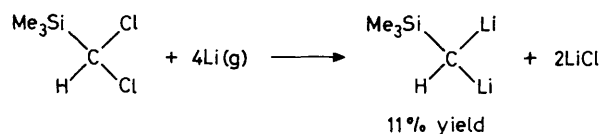
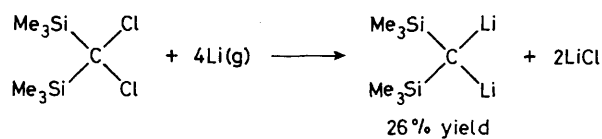
There is considerable current interest in the structure and reactivity of dilithiomethane.¹⁻⁶ We report here the synthesis of two new derivatives, bis(trimethylsilyl)dilithiomethane [(Me₃Si)₂CLi₂] and (trimethylsilyl)dilithiomethane (Me₃Si-CHLi₂), by the reaction of lithium vapour with bis(trimethylsilyl)dichloromethane [(Me₃Si)₂CCl₂] and (trimethylsilyl)dichloromethane (Me₃SiCHCl₂), respectively.

The syntheses were conducted in a Knudsen cell, lithium vapour synthesis apparatus.⁷ (Me₃Si)₂CCl₂ was prepared by a reported method.⁸ Commercially available Me₃SiCHCl₂ was freshly distilled and dried before use.

Lithium metal (*ca.* 2 g) was vaporized (10⁻⁴ Torr, oven temperature 700–720 °C) during three hours and allowed to react with (Me₃Si)₂CCl₂ (1.0 g). The products were collected on a liquid nitrogen-cooled cold-finger. The reactor was opened under argon and a blue-brown solid was removed from

the cold-finger. The products were carefully hydrolysed with D₂O in a vacuum line.

The products of hydrolysis were then extracted with diethyl ether and dried over magnesium sulphate. Removal of the solvent by distillation, followed by g.l.c. separation, gave the deuteriated compound, (Me₃Si)₂CD₂, in 26% yield based on (Me₃Si)₂CCl₂ consumed. The structure was confirmed by comparison of its g.l.c. retention time, ¹H n.m.r., i.r., and mass spectra with those of non-deuteriated (Me₃Si)₂CH₂. The deuteriation at the methylene position was indicated by ¹H n.m.r. and mass spectra. The ¹H n.m.r. spectrum in CCl₄ gave only a singlet at δ 0.09 and no significant peak for a methylene proton was observed. In the low resolution mass spectrum (70 eV), the base peak was observed at 147 (*M* – Me) instead of at 145 for the non-deuteriated (Me₃Si)₂CH₂.⁹ When flash-vaporization mass spectroscopy¹ was performed on the



lithiated product, only positive ions due to a dimer and monomer were observed. No higher polymers such as those observed for $(\text{CLi}_2\text{H}_2)_n$ were seen.

Similarly, the reaction of $\text{Me}_3\text{SiCHCl}_2$ with lithium, followed by deuteriolysis, gave deuteriated tetramethylsilane, $\text{Me}_3\text{SiCHD}_2$ (11%). The mass spectra of this compound showed a base peak at m/z 75 instead of 73 for non-deuteriated tetramethylsilane.⁹

Again, flash-vaporization mass spectroscopy showed positive ions due only to a dimer and the monomer of $\text{Me}_3\text{SiCHLi}_2$. Photoacoustic i.r. spectra showed bands at 2903, 1257, 1057, 849, and 691 cm^{-1} for $(\text{Me}_3\text{Si})_2\text{CLi}_2$ and 2903, 1253, 870, and 705 cm^{-1} for $\text{Me}_3\text{SiCHLi}_2$. In both preparations the only by-products (identified by high resolution mass spectroscopy) were lithiated methanes and silanes.

The very bulky trimethylsilyl groups in $(\text{Me}_3\text{Si})_2\text{CLi}_2$ and $\text{Me}_3\text{SiCHLi}_2$ were designed to prevent extensive polymerization such as we observed for other polyolithium compounds.^{1,2,10} The volatility of these new species should allow vaporization at low temperatures into matrices for vibrational studies. These are currently underway with Michl.¹¹ Further, the solubility of $(\text{Me}_3\text{Si})_2\text{CLi}_2$ and $\text{Me}_3\text{SiCHLi}_2$ in organic

solvents should facilitate detailed n.m.r. spectroscopic studies. Lithiated methanes are of considerable theoretical interest^{4,5} with respect to possible observation of planar carbon atom sites in gas phase monomers. Calculations¹² are underway to complement the experiments of Michl.

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