

Preparation and lithiation of tris(*o*-tolyl dimethylsilyl) methane

Abdulrahman I. Almansour *

Department of Chemistry, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

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Abstract

The compound (*o*-MeC₆H₄Me₂Si)₃CH has been prepared and shown to be metallated slowly by MeLi in refluxing THF to give the lithium reagent (*o*-MeC₆H₄Me₂Si)₃CLi. This reacts with MeI to give (*o*-MeC₆H₄Me₂Si)₃CMe, but not with Me₂SiHCl nor with a range of other organosilicon halides.

Keywords: Silicon; Hindered (bulky) ligands

1. Introduction

Several novel aspects of organosilicon chemistry have been revealed by studies of compounds in which the bulky ligand (Me₃Si)₃C (often known as the 'trisyl' group and denoted by Tsi), or to a lesser extent the related ligand (PhMe₂Si)₃C (frequently denoted by Tpsi), is attached to a potentially reactive silicon centre [1–5]. Owing to the very great hindrance provided by the bulky Tsi ligand, reactions expected for such derivatives were either much slower or forced to take a completely different course. For example, the silicon iodide TsiSiMe₂I has a half-life at 50°C in MeOH of about 13 d [2] and the treatment of TsiSiPh₂I with, for example, silver salts AgX (X = OAc, ONO₂, OSO₂CF₃, etc.) affords the rearranged products (Me₃Si)₂C(SiMe₂-X)(SiPh₂Me) [3] which are formed via bridged silicocationic intermediates. Studies of compounds possessing the closely related Tpsi ligand indicated that steric hindrance by that ligand is not necessarily greater than that by the Tsi ligand [4,6,7]. In order to make available an even more bulky ligand, we have prepared the compound (*o*-MeC₆H₄Me₂Si)₃CH and shown that it can be metallated to give the reagent (*o*-MeC₆H₄Me₂Si)₃CLi, which unfortunately fails to react with a range of simple organosilicon halides.

2. Results and discussion

In a procedure analogous to that now used to make (Me₃Si)₃CH and (PhMe₂Si)₃CH [8], involving the reaction between BuLi, CHBr₃ and *o*-MeC₆H₄SiMe₂Cl in THF initially at -78°C, we prepared tris(*o*-tolyl dimethylsilyl)methane in satisfactory yield (65%).

Metallation of (*o*-MeC₆H₄Me₂Si)₃CH by MeLi in THF was shown to be much slower than that of (PhMe₂Si)₃CH. Under conditions that result in virtually quantitative lithiation of (PhMe₂Si)₃CH [4], treatment of (*o*-MeC₆H₄Me₂Si)₃CH with an equimolar amount of MeLi in refluxing THF for 6 h and subsequent treatment with D₂O gave (*o*-MeC₆H₄Me₂Si)₃CH and (*o*-MeC₆H₄Me₂Si)₃CD in a 4:1 ratio, indicating that lithiation was only ca. 20% complete.

In another experiment, a mixture of (*o*-MeC₆H₄Me₂-Si)₃CH and an equimolar amount of MeLi in THF was stirred under reflux for 6 h, after which a sample of the mixture was withdrawn and treated with excess MeI. The product was shown by ¹H NMR spectroscopy to be a 23:77 mixture of (*o*-MeC₆H₄Me₂Si)₃CMe and (*o*-MeC₆H₄Me₂Si)₃CH, indicating that lithiation was ca. 23% complete. At appropriate intervals further additions of MeLi were made and further samples withdrawn for analysis, with the results shown in Table 1. These indicate that (*o*-MeC₆H₄Me₂Si)₃CLi can be produced in good yield (96%) after addition of a total of 2.5 mol equiv. of MeLi and 48 h stirring under reflux. The fact that a 96% yield was obtained after refluxing for 48 h in THF shows that the reagent is remarkably stable. The

* Corresponding author.

Table 1

Reaction of (*o*-MeC₆H₄Me₂Si)₃CH (8.8 mmol) with MeLi in refluxing THF, showing the ratio (*o*-MeC₆H₄Me₂Si)₃CMe/(*o*-MeC₆H₄Me₂Si)₃CH (*R*) at various times after treatment of a sample of the reaction mixture with MeI

Time (h)	MeLi added (mmol)	<i>R</i>
0	9	–
6	4.5	23:77
24	4.5	51:49
36	4.5	65:35
48	–	96:4

product (*o*-MeC₆H₄Me₂Si)₃CMe was isolated, and its ¹H NMR spectrum left no doubt that metallation had taken place at the central carbon atom and not at an *o*-Me group.

We had hoped that the lithium reagent (*o*-MeC₆H₄Me₂Si)₃CLi could be used to attach the bulky ligand (*o*-MeC₆H₄Me₂Si)₃C to a functional silicon centre but the (*o*-MeC₆H₄Me₂Si)₃CH was recovered unchanged after refluxing with Me₂SiHCl, MeSiHCl₂, SiCl₄ or Et₂SiF₂ for 24 h. The (*o*-MeC₆H₄Me₂Si)₃CLi is apparently substantially less reactive than both (PhMe₂Si)₃CLi [4,9] and (¹PrMe₂Si)₃CLi [10], which react with both Me₂SiHCl and SiCl₄ under relatively mild conditions.

3. Experimental details

The ¹H NMR spectra were recorded at 100 MHz for solutions in CDCl₃. Mass spectra were recorded at 70 eV under electron impact. Tetrahydrofuran (THF) was refluxed with Na wire and benzophenone until a deep purple colour appeared, and was distilled from the mixture as required immediately before use. Tribromomethane was shaken several times with water to remove EtOH (present as a stabilizer), dried over CaCl₂ and distilled under reduced pressure. The *o*-MeC₆H₄SiMe₂Cl was prepared by a published method [11].

3.1. Preparation of (*o*-MeC₆H₄SiMe₂)₃CH

A 2.5 M solution of BuLi in hexane (180 cm³, 0.45 mol of BuLi), cooled to –78°C, was added dropwise under nitrogen to a vigorously stirred solution of CHBr₃ (11 cm³, 0.13 mol) and *o*-MeC₆H₄SiMe₂Cl (72 g, 0.39 mol) in anhydrous THF (150 cm³) and maintained at –78°C. When addition was complete, the stirred mixture was allowed to warm overnight to room temperature and 10% aqueous hydrochloric acid was added cautiously with stirring and cooling. The organic layer was separated, washed with water, dried (MgSO₄) and filtered. Removal of the solvent left an oil, and to this excess MeOH was added. The mixture was then kept in the freezer for 2 d, during which tris(*o*-tolylidimethylsilyl)methane separated as a white solid (39 g, 65%), m.p.

114°C. Analysis: Found. C, 73.1; H, 8.7%. Calc. for C₂₈H₄₀Si₃: C, 73.0; H, 8.7%. ¹H NMR δ: 0.3 (18H, s, SiMe₂); 0.74 (1H, s, CH); 2.2 (9H, s, *o*-Me); 7.0–7.5 (12H, m, C₆H₄) ppm. MS, *m/z*: 445 (100%, M – Me); 353 (45); 281 (27); 205 (30); 149 (83); 121 (28).

3.2. Metallation of (*o*-MeC₆H₄SiMe₂)₃CH

(a) A 1.6 M solution of MeLi (2.2 mmol, prepared from MeBr) in Et₂O (1.4 cm³) was added to a solution of (*o*-MeC₆H₄Me₂Si)₃CH (1.0 g, 2.2 mmol) in THF (10 cm³) under dry nitrogen. The Et₂O was distilled out and the remaining solution was refluxed for 6 h and then cooled to room temperature. A solution of D₂O (0.056 g, 2.8 mmol) in THF (5 cm³) was added dropwise cautiously with stirring and cooling. The mixture was subsequently stirred at room temperature for 1 h and then an excess of aqueous NH₄Cl added. Ether extraction followed by washing, drying (MgSO₄) and evaporation of the extract gave a solid which was shown from its mass spectrum to consist of (*o*-MeC₆H₄Me₂Si)₃CH and (*o*-MeC₆H₄Me₂Si)₃CD in an 80:20 ratio.

(b) The amounts of 1.6 M solution of MeLi in Et₂O shown in Table 1 were added at intervals under nitrogen to a solution of (*o*-MeC₆H₄Me₂Si)₃CH (4.0 g, 8.8 mmol) in THF (20 cm³). After each addition the Et₂O was distilled out and the solution refluxed for the time shown. A sample was then withdrawn and added to an excess of MeI, the mixture kept at room temperature for 1 h then treated with excess aqueous NH₄Cl. Ether extraction, followed by washing, drying (MgSO₄) and evaporation of the extract gave a solid which was analyzed by ¹H NMR spectroscopy to determine the ratio of (*o*-MeC₆H₄Me₂Si)₃CH to (*o*-MeC₆H₄Me₂Si)₃CMe. The results are listed in Table 1.

3.3. Preparation of (*o*-MeC₆H₄Me₂Si)₃CMe

As described above, to a solution of (*o*-MeC₆H₄Me₂Si)₃CH (4.0 g, 8.8 mmol) in THF (20 cm³) under nitrogen were added at intervals appropriate amounts of a 1.6 M solution of MeLi in Et₂O (initially 9 mmol; after 6 h, 4.5 mmol; after 24 h, 4.5 mmol; and after 36 h, 4.5 mmol). After each addition the Et₂O was distilled out and the mixture refluxed until the next addition. After the final addition, refluxing was continued for 12 h making a total reflux time of 48 h. The mixture was subsequently cooled to room temperature, a solution containing excess MeI in THF (10 cm³) added dropwise, and the mixture stirred at room temperature for 1 h. Aqueous NH₄Cl was added dropwise cautiously with stirring, and this was followed by ether extraction and washing, drying (MgSO₄) and evaporation of the extract, to leave a solid which was recrystallized from MeOH to give methyl[tris(*o*-tolylidimethylsilyl)]methane (3.9 g, 95%), m.p. 183°C. Analysis: Found: C, 73.5; H, 8.9%. Calc. for C₂₉H₄₂Si₃: C, 73.4; H, 8.9%. ¹H NMR

δ : 0.17 (18H, s, SiMe₂); 1.89 (3H, s, CMe); 2.41 (9H, s, *o*-Me); 7.0–7.5 (12H, m, C₆H₄) ppm. MS *m/z*: 459 (12%, M – Me); 369 (10); 295 (22); 234 (29); 149 (100); and 121 (13).

3.4. Attempted reactions of (*o*-MeC₆H₄Me₂Si)₃CLi with various organosilicon halides

A solution of Me₂SiHCl (2.5 g, 27 mmol) in THF (5 cm³) was added dropwise to a solution of (*o*-MeC₆H₄Me₂Si)₃CLi prepared from (*o*-MeC₆H₄Me₂-Si)₃CH (4.0 g, 8.8 mmol) in THF (20 cm³) as described above. The mixture was stirred under reflux for 24 h, cooled to room temperature, then worked-up in the usual manner to give a solid which was shown by its ¹H NMR spectrum to be exclusively (*o*-MeC₆H₄-Me₂Si)₃CH. The same result was obtained when the following halides were used: Me₃SiCl, Me₂SiCl₂, MeSiHCl₂, SiCl₄ and Et₂SiF₂.

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