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Preparation of ($^iPrMe_2Si)_3CH$ and its use as a source of the bulky ligand ($^iPrMe_2Si)_3C$

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Abstract

The compound $(^iPrMe_2Si)_3CH$ has been made, and shown to be metallated slowly by MeLi in refluxing THF to give the lithium reagent $(^iPrMe_2Si)_3CLi$. That the latter can be used to attach the bulky ligand $(^iPrMe_2Si)_3C$ to a metalloid or metal centre was demonstrated by treating it with Me_2SiHCl to give a 77% yield of $(^iPrMe_2Si)_3CSiMe_2H$, which with iodine gave the iodide $(^iPrMe_2Si)_3CSiMe_2I$. Reactions of $(^iPrMe_2Si)_3CLi$ with Me_3SiCl and $SiCl_4$ likewise gave $(^iPrMe_2Si)_3CSiMe_3$ and $(^iPrMe_2Si)_3CSiCl_3$ in ca. 33% and 16% yields, respectively.

Keywords: Silicon; Steric hindrance; Bulky ligand

1. Introduction

Much novel chemistry has emerged from studies of compounds in which the bulky ligand $(Me_3Si)_3C$, or to a lesser extent the related ligand $(PhMe_2Si)_3C$, is attached to a metal or metalloid centre [1–4]. In order to make available an even more bulky ligand we have made the compound $(^iPrMe_2Si)_3CH$, **1**, and shown that it can be metallated to give the reagent $(^iPrMe_2Si)_3CLi$, which can be used to attach the ligand $(^iPrMe_2Si)_3C$ to a functional silicon centre.

2. Results and discussion

In a procedure analogous to that now used to make $(Me_3Si)_3CH$ and $(PhMe_2Si)_3CH$ [4], we made **1** by the reaction between BuLi, $CHBr_3$, and $^iPrMe_2SiCl$ in THF, initially at −78°C; it was obtained as an oil in 60% yield.

Lithiation of **1** by MeLi in THF proved to be much slower than that of $(Me_3Si)_3CH$. Thus when a mixture of **1** with an equimolar amount of MeLi in THF was refluxed (conditions that result in virtually quantitative lithiation of $(Me_3Si)_3CH$ within 6 h [5]), initially for 12 h, and after addition of a further equimolar amount of MeLi for a further 12 h, subsequent treatment with D_2O gave approximately a 1:1 mixture of $(^iPrMe_2Si)_3CH$ and $(^iPrMe_2Si)_3CD$, indicating that metallation had been only half complete. In another experiment, after reaction between $(^iPrMe_2Si)_3CH$ and an equimolar amount of MeLi in THF had been allowed to proceed for 6 h under reflux, a sample of the mixture was withdrawn and treated with an excess of Me_2SiHCl. The product was shown by ^1H NMR spectroscopy to be a 17:83 mixture of $(^iPrMe_2Si)_3CSiMe_2H$ and $(^iPrMe_2Si)_3CH$, indicating that lithiation was ca. 17% complete. At intervals further additions of MeLi were made and further samples withdrawn for analysis, with the results shown in Table 1. It can be seen that the extent of lithiation reached a maximum of 80% after addition of a total of 3 molar equivalents of MeLi and 48 h under reflux and then, after addition of another 0.5 equivalents of MeLi, remained roughly constant during a further 24 h under reflux. Evidently the rate of decomposition of the MeLi is comparable with that of metallation, and ultimately decomposition of $(^iPrMe_2Si)_3CLi$ seems to limit its yield under these conditions, though a better yield could perhaps be obtained by initial use of a large excess of MeLi.

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Table 1
Reaction of 12.7 mmol of **1** with MeLi in refluxing THF, showing at various times the ratio $(^iPrMe_2Si)_3CSiMe_2H$:$(^iPrMe_2Si)_3CH$, *R*, after treatment of a sample of the reaction mixture with Me_2SiHCl

Time (h)	MeLi (added/mmol)	*R*
0	12.7	
6		17:83
12	12.7	
24	6.3	50:50
36	6.3	
48	3.2	80:20
60	3.2	
70		78:22

In order to show that the $(^iPrMe_2Si)_3CLi$ could be used to attach the new bulky ligand to a functional metalloid centre, after a metallation of $(^iPrMe_2Si)_3CH$ involving several additions of MeLi and refluxing for a total of 48 h, addition of an excess of Me_2SiHCl gave, after work up, ca. an 80:20 mixture of $(^iPrMe_2Si)_3CSiMe_2H$ and $(^iPrMe_2Si)_3CH$. The latter was distilled out to leave reasonably pure $(^iPrMe_2Si)_3CSiMe_2H$ as a liquid. Treatment of the latter with iodine in CCl_4 then gave a good yield of the solid iodide, $(^iPrMe_2Si)_3CSiMe_2I$. (It is noteworthy that the chemical shift for the $SiMe_2I$ protons, δ 0.43, is significantly smaller for this iodide than for for $(Me_3Si)_3CSiMe_2I$, δ 1.03.) Reactions of $(^iPrMe_2Si)_3CLi$ with Me_3SiCl and $SiCl_4$ gave lower yields of $(^iPrMe_2Si)_3CSiMe_3$ (33%) and $(^iPrMe_2Si)_3CSiCl_3$ (13%), and only unchanged $(^iPrMe_2Si)_3CH$ was recovered from the reaction with Me_2SiCl_2. It seems that $(^iPrMe_2Si)_3CLi$ is somewhat less reactive than $(Me_3Si)_3CLi$, which reacts readily and quantitatively with Me_3SiCl and Me_2SiCl_2, but more reactive than $(PhMe_2Si)_3CLi$, which reacts with neither of these halides [6].

Although the relative difficulty of metallating $(^iPrMe_2Si)_3CH$ may tend to restrict the use of the ligand $(^iPrMe_2Si)_3C$, the extra bulk of the ligand could serve to bestow particularly unusual properties on compounds containing it.

3. Experimental details

3.1. Preparation of $(^iPrMe_2Si)_3CH$, 1

Tribromomethane was shaken several times with water to remove EtOH (present as a stabilizer), dried over $CaCl_2$, and distilled under reduced pressure. A 2.5 M solution of BuLi in hexane (240 cm^3, 0.60 mol of BuLi) cooled to -78°C was added dropwise under nitrogen to a vigorously stirred solution of $CHBr_3$ (15.8 cm^3, 0.18 mol) and $^iPrMe_2SiCl$ (75 g, 0.53 mol) in anhydrous THF (300 cm^3) kept at -78°C. When the addition was complete, the stirred mixture was allowed to warm overnight to room temperature and 10% aqueous hydrochloric acid was cautiously added with stirring and cooling. The organic layer was separated, washed with water, dried, and filtered. Volatile materials were distilled off under reduced pressure and the residue carefully distilled at 118–20°C at 2 mm Hg to give tri(isopropyldimethylsilyl)methane, **1**, as a colourless liquid (35 g, 60%). Anal. Found: C, 60.7; H, 12.65. Calc. for $C_{16}H_{40}Si_3$: C, 60.7; H 12.7%. δ(H) ($CDCl_3$) -0.31 (1H, s, CH), 0.095 (18H, s, $SiMe_2$), 0.96 (18H, s, *Me*$_2$CH). *m/z* 301 (10%, M − Me), 273 (100, M − Pr), 231 (45), 189 (30), 129 (25), 115 (15), 73 (45), 59 (20).

3.2. Metallation of 1

(a) A 1.4 M solution of MeLi in hexane in Et_2O (4.5 cm^3, 6.3 mmol) was added dropwise under nitrogen to a solution of **1** (2.0 g, 6.3 mmol) in anhydrous THF (10 cm^3), the Et_2O was distilled out, and the remaining solution was refluxed for 12 h. Further MeLi (6.3 mmol) was then added, the Et_2O distilled out as before, and the solution again refluxed for 12 h before being allowed to cool to room temperature. A solution of D_2O (0.30 g, 15 mmol) in THF (5 cm^3) was cautiously added with stirring and cooling. The mixture was stirred at room temperature for 1 h and an excess of aqueous NH_4Cl was then added, followed by Et_2O (50 cm^3). The organic layer was washed with water, dried ($MgSO_4$), and evaporated, to leave a liquid that was shown by its mass spectrum to contain $(^iPrMe_2Si)_3CH$ and $(^iPrMe_2Si)_3CD$ in ca. 50:50 ratio. As expected the 1H NMR spectrum was identical with that of $(^iPrMe_2Si)_3CH$ except that the integral of the signal from the CH proton was roughly halved.

(b) The amounts of a 1.4 M solution of MeLi in Et_2O shown in Table 1 were added at intervals under nitrogen to a solution of **1** (4.0 g, 12.7 mmol) in THF (20 cm^3); after each addition the Et_2O was distilled out, the solution refluxed for the time shown, a sample then withdrawn and added to an excess of Me_2SiHCl, and the mixture kept at room temperature for 1 h; the 1H NMR spectrum was then recorded to reveal the ratio of $(^iPrMe_2Si)_3CSiMe_2H$ to $(^iPrMe_2Si)_3CH$. The results are shown in Table 1.

3.3. Preparation of $(^iPrMe_2Si)_3CSiMe_2H$

As described above, to a solution of $(^iPrMe_2Si)_3CH$ (6.0 g, 19 mmol) in THF (30 cm^3) under nitrogen were added at intervals appropriate amounts of a 1.4 M solution of MeLi in Et_2O (19 mmol initially; 19 mmol after 12 h; 9.5 mmol after 24 h; and 9.5 mmol after 36 h). After each addition the Et_2O was distilled out and the mixture was refluxed until the next addition. After the final addition, refluxing was carried on for 12 h, making a total reflux time of 48 h. The mixture was subsequently cooled to room temperature, a solution of $\mathrm{Me_2SiHCl}$ (5.6 g, 60 mmol) in THF (10 $\mathrm{cm^3}$) added dropwise, and the mixture stirred at room temperature for 1 h. Volatile organosilicon compounds (residual $\mathrm{Me_2SiHCl}$ and formed $\mathrm{Me_3SiH}$) were distilled out, the solution was cooled, and aqueous $\mathrm{NH_4Cl}$ was cautiously added dropwise with stirring. Addition of ether, followed by separation, washing, drying, and evaporation of the organic layer left a liquid, which was shown by ^{1}H NMR spectroscopy to be an ca. 80:20 mixture of $({}^i\mathrm{PrMe_2Si})_3\mathrm{CSiMe_2H}$ and $({}^i\mathrm{PrMe_2Si})_3\mathrm{CH}$. The latter was distilled out under reduced pressure to leave, as a liquid, dimethyl[tri(isopropyldimethylsilyl)methyl]silane (5.5 g, 77%). δ(H) ($\mathrm{CDCl_3}$) 0.25 (18H, s, $\mathrm{SiMe_2}$), 0.40 (6H, d, $J = 1$ Hz, $\mathrm{Si}Me_2\mathrm{H}$), 1.04 (18H, d, $J = 2$ Hz, $Me_2\mathrm{CH}$), 4.40 (1H, m, SiH). m/z 331 (50%, M – Pr), 218 (5), 215 (10), 187 (25), 173 (15), 171 (10), 130 (10), 129 (25), 101 (10), 98 (10), 73 (100), 69 (20), 59 (40).

3.4. Preparation of $({}^iPrMe_2Si)_3CSiMe_2I$

A solution of $\mathrm{I_2}$ (11 mmol) in $\mathrm{CCl_4}$ (80 $\mathrm{cm^3}$) was added with stirring to a solution of $({}^i\mathrm{PrMe_2Si})_3\mathrm{CSiMe_2H}$ (2.0 g, 5.3 mmol) in $\mathrm{CCl_4}$ (20 $\mathrm{cm^3}$) containing $\mathrm{PhSiMe_3}$ (0.8 g, 5.3 mmol) to take up generated HI. (This may not be necessary.) The mixture was stirred for 72 h at room temperature, then shaken with aqueous $\mathrm{NaHSO_3}$ to remove residual iodine. The organic layer was separated, washed, and dried ($\mathrm{MgSO_4}$), and the solvent was then evaporated off under reduced pressure. The solid residue was recrystallized twice from EtOH to give $({}^i\mathrm{PrMe_2Si})_3\mathrm{CSiMe_2I}$ (1.9 g, 71%), as a white solid that sublimed at 300°C without melting. Anal. (Found: C, 43.5, H 8.8. Calc. for $\mathrm{C_{18}Si_4H_{45}I}$: C, 43.2; H, 9.0%. δ(H) ($\mathrm{CDCl_3}$) 0.35 (18H, s, $\mathrm{Si}Me_2^{i}\mathrm{Pr}$), 0.43 (6H, s, $\mathrm{SiMe_2I}$), 1.06 (18H, d, $J = 6$ Hz, $\mathrm{SiCH}Me_2$).

3.5. Reactions of $({}^iPrMe_2Si)_3CLi$ with Me_3SiCl, Me_2SiCl_2, and $SiCl_4$

(a) To a solution of $({}^i\mathrm{PrMe_2Si})_3\mathrm{CLi}$ in THF (10 $\mathrm{cm^3}$), prepared from $({}^i\mathrm{PrMe_2Si})_3\mathrm{CH}$ (19 mmol) as described above for the reaction with $\mathrm{Me_2SiHCl}$, was added dropwise with cooling, a solution of $\mathrm{Me_3SiCl}$ (60 mmol) in THF (10 $\mathrm{cm^3}$). The mixture was refluxed for 5 h then worked up as above to give a liquid that was shown by ^{1}H NMR spectroscopy and GLC-MS (2 m of 3% OV-17 at 230°C) to be a ca. 67:33 mixture of $({}^i\mathrm{PrMe_2Si})_3\mathrm{CH}$ and $({}^i\mathrm{PrMe_2Si})_3\mathrm{CSiMe_3}$. For the latter: δ(H) ($\mathrm{CDCl_3}$) 0.13 (9H, s, $\mathrm{SiMe_3}$), 0.15 (18H, s, $\mathrm{SiMe_2}$), 1.10 (18H, d, $J = \mathrm{CH}Me_2$). m/z 345 (60%, M – Pr), 271 (15), 215 (10), 187 (35), 129 (25), 101 (5), 73 (100) and 59 (35).

(b) When the procedure was repeated, but starting from $\mathrm{SiCl_4}$, a ca. 84:16 mixture of $({}^i\mathrm{PrMe_2Si})_3\mathrm{CH}$ and $({}^i\mathrm{PrMe_2Si})_3\mathrm{CSiCl_3}$ was obtained. For the latter: δ(H) ($\mathrm{CDCl_3}$) 0.19 (18H, s, $\mathrm{SiMe_2}$), 1.04 (18H, d, $J = 2$ Hz, $\mathrm{CH}Me_2$). m/z 405 (45%, M – Pr), 269 (55), 187 (35), 129 (25) 101 (5), 93 (10), 73 (100), 59 (45).

(c) When the procedure was repeated but starting from $\mathrm{Me_2SiCl_2}$, only unchanged $({}^i\mathrm{PrMe_2Si})_3\mathrm{CH}$ was present at the end.

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References

[1] P.D. Lickiss in A.R. Katritzky, O. Meth-Cohn and C.W. Rees (eds.), *Organic Functional Group Transformations*, Pergamon, Oxford, 1995, Vol. 6, Part II, Ch. 6.13.

[2] A.R. Bassindale and P.G. Taylor, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, New York, 1989, pp. 880–888.

[3] For some recent leading references see: C. Eaborn, K.L. Jones and P.D. Lickiss, *J. Organomet. Chem.*, *466* (1994) 35; C. Eaborn, P.B. Hitchcock, K. Izod, A.J. Jaggar and J.D. Smith, *Organometallics*, *13* (1994) 753; S.S. Al-Juaid, C. Eaborn, P.B. Hitchcock, K. Kundu, C.A. McGeary and J.D. Smith. *J. Organomet. Chem.*, *469* (1994) 129.

[4] S.S. Al-Juaid, C. Eaborn, A. Habtemariam, P.B. Hitchcock, J.D. Smith, K. Tavakkoli and A.D. Webb, *J. Organomet. Chem.*, *462* (1993) 45.

[5] Z.H. Aiube and C. Eaborn, *J. Organomet. Chem.*, *269* (1984) 217.

[6] C. Eaborn and A.I. Mansour, *J. Chem. Soc., Perkin Trans.*, *2* (1985) 729.