

Preliminary Communication

Organometallic alkenes: the first stable silene in the neopentyl series

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Abstract

The simple synthesis in nearly quantitative yield of dimesityl-neopentylsilene **3**, the first stable silene in the neopentyl series, was performed using *t*-butyllithium and dimesitylvinylfluorosilane. **3** was isolated by crystallization from pentane and characterized by ^{13}C (doubly bonded carbon at +110.4 ppm) and ^{29}Si (+77.6 ppm) NMR spectroscopy and analysis.

Key words: Silicon; Silene; Preparation

Of all the routes to silenes, the addition–elimination reaction between an organolithium compound and a vinylhalogenosilane is certainly one of the most suitable.

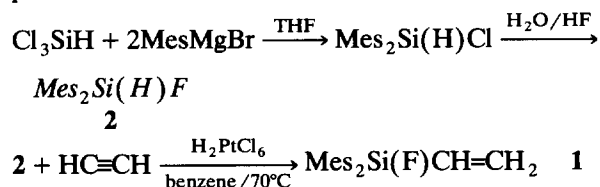
Since the first reaction described by Jones and Lim in 1977, with dimethylvinylchlorosilane and *t*-butyllithium, affording the unstable dimethylneopentylsilene $\text{Me}_2\text{Si}=\text{CH}-\text{CH}_2-{}^t\text{Bu}$ [1], many transient neopentylsilenes $\text{RR}'\text{Si}=\text{CH}-\text{CH}_2-{}^t\text{Bu}$ have been synthesized by Jones and Lee ($\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$ [2]), Auner and coworkers ($\text{R} = \text{R}' = \text{Cl}$ [3]; $\text{RR}' = (\text{CH}_2)_3$ [4]; $\text{R} = \text{R}' = {}^t\text{BuO}$ [5]; $\text{R} = \text{Cl}$, $\text{R}' = \text{CH}=\text{CH}_2$ [6], $\text{R} = \text{R}' = {}^t\text{Bu}$ [7]; $\text{R} = \text{Me}$, $\text{R}' = \text{Cp}(\text{CO})_2\text{Fe}$ [8]; $\text{R} = \text{R}' = \text{Ph}$ [9]; $\text{RR}' = \text{Me}_3\text{Si}-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{SiMe}_3$ [10]), Yoo *et al.* ($\text{R} = \text{Cl}$, $\text{R}' = \text{Ph}$ [11]) and by our group ($\text{R} = \text{Me}$, $\text{R}' = \text{Mes}$ [12]). Nevertheless, in spite of the use of uncreasingly bulkier substituents no stable neopentylsilene has yet been obtained. In contrast germanium chemistry we have recently stabilized such a structure by the introduction of two mesityl groups on the germanium atom [13].

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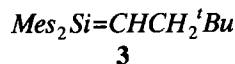
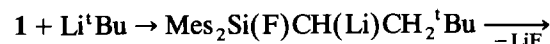
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We describe here the synthesis and the characterization of the silene analogue $\text{Mes}_2\text{Si}=\text{CH}-\text{CH}_2-{}^t\text{Bu}$, the first stable silene in the neopentyl series.

The precursor of the dimesitylneopentylsilene **3** was dimesitylvinylfluorosilane **1**, prepared from trichlorosilane via the dimesitylfluorosilane **2** by the following procedure



The addition of an equimolar amount of *t*-butyllithium (1.5 M in pentane) to **1** was performed at -78°C in pentane solution. The mixture was allowed to warm and after few minutes at room temperature lithium fluoride precipitated rapidly leading to **3** in nearly quantitative yield.



After removing the solvent in vacuo from the orange solution, yellow crystals of **3** were obtained by crystallization from pentane at -20°C (m.p.: 152°C , yield $\sim 90\%$).

^1H NMR ($\text{C}_6\text{D}_6 + \text{C}_5$, 200.1 MHz): δ ${}^t\text{Bu}$ (not observed), 2.69 (d, 2H, $^3J_{\text{H-H}} = 9.8$ Hz, CH_2), 2.74 (s, 3H, *p*-Me, Mes), 2.84 (s, 3H, *p*-Me, Mes'), 3.01 (s, 12H, *o*-Me, Mes, Mes'), 5.53 (t, $^3J_{\text{H-H}} = 9.8$ Hz, =CH), 7.25 (s, 2H, *m*-H, Mes), 7.31 (s, 2H, *m*-H, Mes').

^{13}C NMR ($\text{CDCl}_3 + \text{C}_5$, 50.3 MHz): δ 21.08 (*p*-Me, Mes), 22.13 (*p*-Me, Mes'), 23.98 (*o*-Me, Mes), 25.02 (*o*-Me, Mes'), 29.03 (Me, ${}^t\text{Bu}$), 32.15 (C, ${}^t\text{Bu}$), 44.53 (CH_2), 110.44 (=CH), 129.48 (*m*-C, Mes), 129.65 (*m*-C, Mes'), 136.60 (*ipso*-C, Mes), 136.90 (*ipso*-C, Mes'), 139.51 (*p*-C, Mes), 139.79 (*p*-C, Mes'), 144.28 (*o*-C, Mes), 144.34 (*o*-C, Mes').

^{29}Si NMR ($\text{CDCl}_3 + \text{C}_5$, 39.8 MHz): δ +77.6 ppm.

Mass spectrometry (EI, 70 eV): 350 (M^+ , 17); 293 ($\text{M}-{}^t\text{Bu}$, 1); 266 (Mes_2Si , 18); 230 ($\text{M} = \text{MesH} = \text{Me}$, 5); 173 ($\text{MesSiCHCH}_2-\text{H}$, 51); 160 (MesSiCH , 100); 146 ($\text{MesSi}-\text{H}$, 44); 119 (Mes, 12); 57 (${}^t\text{Bu}$, 6).

Anal. calc. for $\text{C}_{24}\text{H}_{34}\text{Si}$: C, 82.21; H, 9.77; Si, 8.09. Found: C, 82.47; H, 9.88%.

Although it is very stable, **3** has a high reactivity of which study is now in progress, mainly for comparison with dimesitylneopentylgermene. The use of this silene in organometallic and organic synthesis is also being investigated.

References

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