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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 dimesitylneopentylsilene **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 $Me_2Si{=}CH–CH_2–{}^tBu$ [1], many transient neopentylsilenes $RR'Si{=}CH–CH_2–{}^tBu$ have been synthesized by Jones and Lee ($R = Me$, $R' = Ph$ [2]), Auner and coworkers ($R = R' = Cl$ [3]; $RR' = (CH_2)_3$ [4]; $R = R' = {}^tBuO$ [5]; $R = Cl$, $R' = CH{=}CH_2$ [6], $R = R' = {}^tBu$ [7]; $R = Me$, $R' = Cp(CO)_2Fe$ [8]; $R = R' = Ph$ [9]; $RR' = Me_3Si–N–CH_2–CH_2–N–SiMe_3$ [10]), Yoo *et al.* ($R = Cl$, $R' = Ph$ [11]) and by our group ($R = Me$, $R' = Mes$ [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].

We describe here the synthesis and the characterization of the silene analogue $Mes_2Si{=}CH–CH_2–{}^tBu$, 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

$$Cl_3SiH + 2MesMgBr \xrightarrow{THF} Mes_2Si(H)Cl \xrightarrow{H_2O/HF} \underset{\mathbf{2}}{Mes_2Si(H)F}$$

$$\mathbf{2} + HC{\equiv}CH \xrightarrow[benzene/70°C]{H_2PtCl_6} Mes_2Si(F)CH{=}CH_2 \quad \mathbf{1}$$

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.

$$\mathbf{1} + Li^tBu \rightarrow Mes_2Si(F)CH(Li)CH_2{}^tBu \xrightarrow[-LiF]{} \underset{\mathbf{3}}{Mes_2Si{=}CHCH_2{}^tBu}$$

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 −90%).

^1H NMR ($C_6D_6 + C_5$, 200.1 MHz): $\delta{}^tBu$ (not observed), 2.69 (d, 2H, $^3J_{H-H} = 9.8$ 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, $^3J_{H-H} = 9.8$ Hz, =CH), 7.25 (s, 2H, *m*-H, Mes), 7.31 (s, 2H, *m*-H, Mes′).

^{13}C NMR ($CDCl_3 + C_5$, 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}Bu), 32.15 (C, ^{t}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 ($CDCl_3 + C_5$, 39.8 MHz): δ + 77.6 ppm.

Mass spectrometry (EI, 70 eV): 350 (M^+, 17); 293 (M–^{t}Bu, 1); 266 (Mes_2Si, 18); 230 (M = MesH = Me, 5); 173 ($MesSiCHCH_2$–H, 51); 160 (MesSiCH, 100); 146 (MesSi–H, 44); 119 (Mes, 12); 57 (^{t}Bu, 6).

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

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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.

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