A Stable Germa-imine: *N*-2,4,6-Trifluorophenyldimesitylgerma-imine; Synthesis and Reactivity

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Stabilization of a germa-imine is achieved by the use of the electron-withdrawing 2,4,6-trifluorophenyl group on nitrogen.

Most stable germa-imines isolated have been stabilized by steric hindrance and/or by complexation of the germanium atom.[1–4] We recently isolated very stable germa-imines in which stabilization was achieved both by complexation of the metal and by electron-withdrawing effects on nitrogen.[5] If complexation of germanium prevents dimerization by decreasing the π character of the double bond of the germa-imine, we thought that electron-withdrawing effects on nitrogen might have the same result. Such a hypothesis is also supported by Ang and Lee's work on stabilization of low molecular mass germa-imines by highly electronegative groups.[6] This paper describes preliminary results in our attempts to stabilize a moderately hindered germa-imine, taking avantage of electron-withdrawing effects on the nitrogen atom.

Starting from *N*-dimesitylfluorogermyl 2,4,6-trifluoroaniline **1**, we found that elimination of lithium fluoride from the aminolithium derivative **2** in THF was difficult even at room temperature.† Under these conditions, the subsequent germa-imine could not be characterized by its specific addition reaction with nitrone, and upon heating we obtained cyclodigermazane **3** (Scheme 1).‡

Since similar results were obtained in the silicon series,[7,8] the fluoroaminolithium derivative **2** might be expected to have the same iminolithium structure (Scheme 1) as its silicon homologue.[7] When isolated from the THF solution, **2** treated with chloroform led to the starting material **1** and THF.

Starting from the more polarizable germylbromide **4** (Scheme 2), the corresponding lithium derivative slowly eliminates lithium bromide, and the expected germa-imine is clearly characterized by NMR spectroscopy and by its addition reactions with nitrone and chloroform (Scheme 2).§ In the presence of any of these specific reagents, the formation of cyclodigermazane **3** (Scheme 2) is observed in yields of less than 20%, and must probably occur mainly by intermolecular elimination of lithium fluoride, although dimerization of the germa-imine cannot be excluded. The cyclodigermazane **3** (formed either through Scheme 1 or 2) has been isolated and clearly characterized. It does not react either with nitrone or chloroform. The nitrone itself never reacts with any amino-lithium derivative such as **2**, Ph_2NLi or (tFP)N(H)Li.

The adduct of *N*-trifluorophenyl-dimesitylgerma-imine with chloroform, as already known for such compounds, leads to the corresponding *N*-dimesityl-chlorogermyl-2,4,6-trifluorophenyl $Mes_2Ge(Cl)$-N(H)(tFP), through α elimination of dichlorocarbene.[9]

The unambiguous characterization of *N*-2,4,6-trifluorophenyl-dimesitylgerma-imine clearly shows that electron-withdrawing substituants on nitrogen are sufficient to stabilize the monomeric germa-imine. We are now trying more powerful electron-withdrawing substituants on nitrogen in order to stabilise non-sterically hindered reactive synthons.

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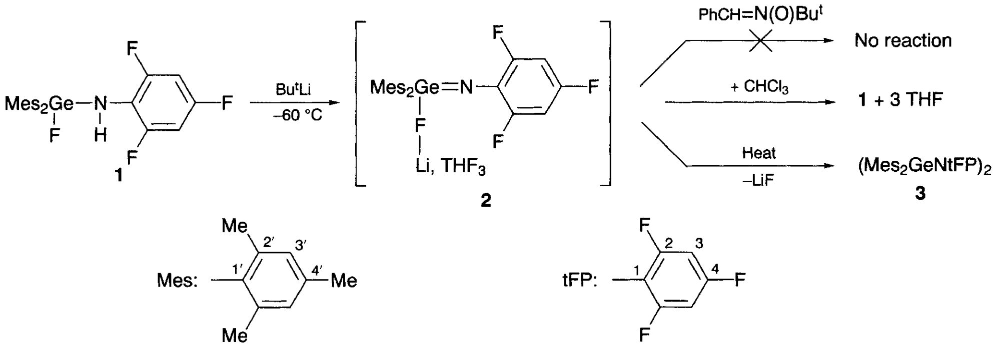
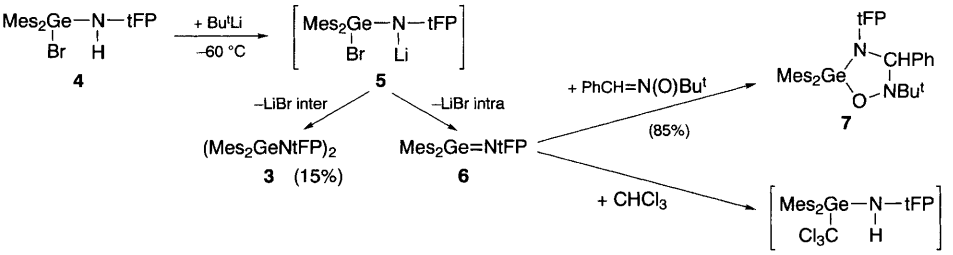


Scheme 1



Scheme 2

Footnotes

† *General procedure*: Reactions were done under nitrogen using standard Schlenk techniques. A typical procedure was as follows: to the halogermylamine (1 mmol) in 4 ml THF cooled at −78 °C, is added dropwise Bu^tLi 1.7 mol dm^{-3} in pentane (1 mmol). The reaction mixture was slowly warmed until disappearance of the starting material, then kept in the fridge for

further experiments. Progress of the reaction was followed by ${}^1H$ and ${}^{19}F$ NMR on samples syringed out.

‡ *Selected physical data* for **1**: *m*/*z* 477 ($M^{+\cdot}$); δ_H (80 MHz, $CDCl_3$, 25 °C, $SiMe_4$): 2.29 (s, 6 H, p-CH_3), 2.42 (d, ${}^5J_{HF}$ 1.6 Hz, 12 H, o-CH_3), 3.95 (s, 1 H, N*H*), 6.58 (t, ${}^3J_{HF}$ 8.5 Hz, 2 H, $C_6H_2F_3$), 6.87 (s, 4 H, $C_6H_2Me_3$); δ_C (50 MHz, $CDCl_3$, 25 °C) 21.18 (p-CH_3), 22.81 (o-CH_3), 100.01 (m, C3), 121.50 (m, C1), 153.00 (dm, ${}^1J_{CF}$ 243 Hz, C2), 153.37 (dm, ${}^1J_{CF}$ 243 Hz, C4), 129.60 (C3′), 131.21 (C1′), 140.80 (C4′), 143.50 (C2′), δ_F (75 MHz, $CDCl_3$, 25 °C, CF_3CO_2H) −80.06 (s1, 1 F, Ge*F*), −50.29 (m, 2 F, o-F), −48.52 (t, ${}^3J_{HF}$ 8.5 Hz, 1 F, p-F). **2**: δ_H (80 MHz, C_6D_6, 25 °C, $SiMe_4$) 2.07 (s, 6 H, p-CH_3), 2.65 (s, 12 H, o-CH_3), 6.72 (s, 4 H, $C_6H_2Me_3$); THF: 1.44 (m, 12 H, CH_2-C), 3.56 (m, 12 H, CH_2-O); δ_F (75 MHz, C_6D_6, 25 °C, CF_3CO_2H) −56.04 (s, 2 F, o-F), −62.73 (s, 1 F; p-F), −80.21 (s, 1 F, GeF).

3: *m*/*z* 912 ($M^{+\cdot}$); δ_H (80 MHz, $CDCl_3$, 25 °C, $SiMe_4$) 2.11 (s, 12 H, p-CH_3), 2.39 (s, 24 H; o-CH_3), 6.18 [t, ${}^3J_{HF}$ 8.8 Hz, 4 H, $C_6H_2F_3$], 6.55 (s, 8 H, $C_6H_2Me_3$); δ_C (50 MHz, $CDCl_3$, 25 °C) 20.93 (p-CH_3), 22.76 (o-CH_3), 99.41 (td, ${}^2J_{CF}$ 28 Hz, ${}^4J_{CF}$ 3.5 Hz, C3), 121.66 (m, C1), 157.93 (dt, ${}^1J_{CF}$ 244 Hz, ${}^3J_{CF}$ 15 Hz, C4), 161.57 (ddd, ${}^1J_{CF}$ 240 Hz, ${}^3J_{CF}$ 24 Hz, ${}^3J_{CF}$ 18 Hz, C2), 128.23 (C3′), 136.79 (C1′), 138.37 (C2′), 141.65 (C4′); δ_F (75 MHz, $CDCl_3$, 25 °C, CF_3CO_2H) −39.45 (m, 2 F, p-F), −33.48 (s1, 4 F. o-F).

4: *m*/*z* 537 ($M^{+\cdot}$); δ_H (80 MHz, $CDCl_3$, 25 °C, $SiMe_4$ 2.26 (s, 6 H, p-CH_3), 2.46 (s, 12 H, o-CH_3), 4.00 (s, 1 H, N*H*), 6.52 (t, ${}^3J_{HF}$ 8.8 Hz, 2 H, $C_6H_2F_3$), 6.83 (s, 4 H, $C_6H_2Me_3$); δ_C (50 MHz, $CDCl_3$, 25 °C, $SiMe_4$) 21.07 (p-CH_3), 23.59 (o-CH_3), 99.96 (m, C3), 130.07 (C3′), 133.42 (C4′), 140.45 (C1′), 143.05 (C2′), 153.92 (m, C4), 153.15 (m, C2); δ_F (75 MHz, $CDCl_3$, 25 °C, CF_3CO_2H) −46.99 (t, ${}^3J_{HF}$ 8.5 Hz, 1 F, p-F), −48.60 (d, ${}^3J_{HF}$ 8.8 Hz, 2 F, o-F).

5: δ_H (80 MHz, C_6D_6, 25 °C, $SiMe_4$) 2.10 (s, 6 H, p-CH_3), 2.75 (s, 12 H, o-CH_3), 6.30 (t, ${}^3J_{HF}$ 8.3 Hz, 2 H, $C_6H_2F_3$), 6.78 (s, 4 H, $C_6H_2Me_3$); δ_F (75 MHz, C_6D_6, 25 °C, CF_3CO_2H) −57.01 (s, 2 F; o-F), −61.75 (t, ${}^3J_{HF}$ 8.3 Hz, 1 F, p-F).

§ A pure sample of **5** when followed by ${}^{19}F$ NMR in C_6D_6 showed slow elimination of LiBr forming **6** and **3**. Recrystallisation in THF–pentane eliminated **3**. ${}^{19}F$ analysis in $CDCl_3$ of the resulting brown powder showed the characteristic signals of **6**: δ_F (75 MHz, $CDCl_3$, 25 °C, CF_3CO_2H) −43.71 (d, ${}^3J_{HF}$ 7.5 Hz, 2 F, o-F), −44.30 (t, ${}^3J_{HF}$ 7.5 Hz, 1 F, p-F); *m*/*z* 457 ($M^{+\cdot}$). Upon addition of $CHCl_3$, **6** was slowly converted into $Mes_2Ge(Cl)NHtFP$; δ_F (75 MHz, $CDCl_3$, 25 °C, CF_3CO_2H) −49.07 (d, ${}^3J_{HF}$ 8.3 Hz, 2 F, o-F), −47.43 (t, ${}^3J_{HF}$ 8.3 Hz, 1 F, p-F); *m*/*z* 493 ($M^{+\cdot}$) [through the formation of the transient adduct $Mes_2Ge(CCl_3)NHtFP$; *m*/*z* 556 ($M^{+\cdot}$)-F), while the remaining **5** instantaneously gave **4**. For another, similar sample of **6**, addition of *N*-*tert*-butylphenylnitrone, lead to the adduct **7** formed over 20 h at room temp. (80% yield).

7: *m*/*z* 634 ($M^{+\cdot}$); δ_H (80 MHz, C_6D_6, 25 °C, $SiMe_4$) 1.07 (s, 9 H, NBu^t 1.99 (s, 3 H, p-CH_3), 2.09 (s, 3 H, p-CH_3), 2.46 (s, 6 H, o-CH_3), 2.82 (s, 6 H, o-CH_3), 5.40 (s, 1 H, C*H*), 6.18 (t, ${}^3J_{HF}$ 8.9 Hz, 2 H, $C_6H_2F_3$), 6.60 (s, 2 H, $C_6H_2Me_3$), 6.77 (s, 2 H, $C_6H_2Me_3$), 7.01 (m, 3 H, C_6H_5), 7.51 (m, 2 H, C_6H_5); δ_C (50 MHz, $CDCl_3$, 25 °C, $SiMe_4$) 21.17 (p-CH_3), 22.86 (p-CH_3), 23.00 (o-CH_3), 28.42 (o-CH_3), 27.28 (CH_3 Bu^t), 59.26 (C, Bu^t), 120.77 (m, C1), 161.53 (dm, ${}^1J_{CF}$ 252 Hz, C2), 99.93 (td, ${}^2J_{CF}$ 26 Hz, ${}^4J_{CF}$ 4 Hz, C3), 159.23 (dm, ${}^1J_{CF}$ 252 Hz, C4), 133.22 (C1′), 142.67 (C2′), 142.93 (C2′), 128.54 (C3′), 128.78 (C3′), 139.17 (C4′), 139.40 (C4′), 83.43 (CH Ph), 128.40 (C1″), 127.50 (C2″), 129.18 (C3″), 127.98 (C4″); δ_F (75 MHz, C_6D_6, 25 °C, CF_3CO_2H) −37.78 (s, 1 F, p-F), −34.31 (s, 2 F, o-F); δ_F (75 MHz, $CDCl_3$, 25 °C, CF_3CO_2H) −38.57 (m, 1 F, p-F), −34.62 (s, 2 F, o-F).

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