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 aminolithium 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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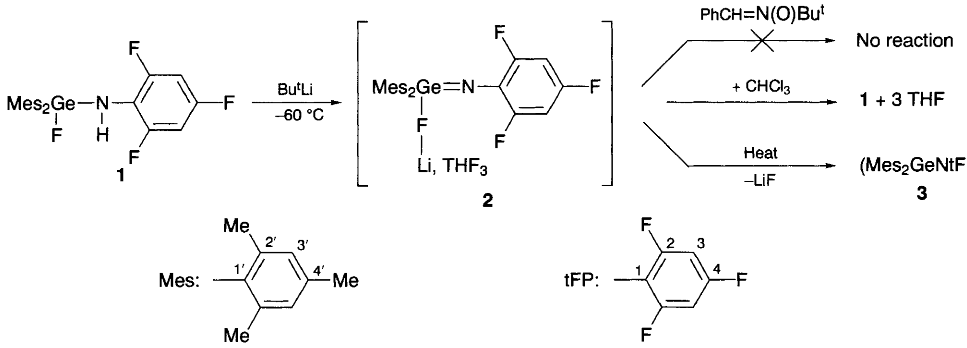
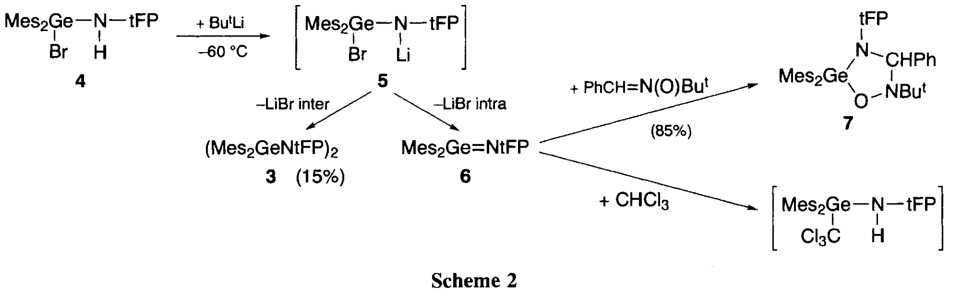


Scheme 1



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 BuᵗLi 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 ^{1}H 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, $^{5}J_{HF}$ 1.6 Hz, 12 H, *o*-CH_3), 3.95 (s, 1 H, N*H*), 6.58 (t, $^{3}J_{HF}$ 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, $^{1}J_{CF}$ 243 Hz, C2), 153.37 (dm, $^{1}J_{CF}$ 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, $^{3}J_{HF}$ 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, $^{3}J_{HF}$ 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, $^{2}J_{CF}$ 28 Hz, $^{4}J_{CF}$ 3.5 Hz, C3), 121.66 (m, C1), 157.93 (dt, $^{1}J_{CF}$ 244 Hz, $^{3}J_{CF}$ 15 Hz, C4), 161.57 (ddd, $^{1}J_{CF}$ 240 Hz, $^{3}J_{CF}$ 24 Hz, $^{3}J_{CF}$ 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, $^{3}J_{HF}$ 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, $^{3}J_{HF}$ 8.5 Hz, 1 F, *p*-F), −48.60 (d, $^{3}J_{HF}$ 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, $^{3}J_{HF}$ 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, $^{3}J_{HF}$ 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, $^{3}J_{HF}$ 7.5 Hz, 2 F, *o*-F), −44.30 (t, $^{3}J_{HF}$ 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, $^{3}J_{HF}$ 8.3 Hz, 2 F, *o*-F), −47.43 (t, $^{3}J_{HF}$ 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, $^{3}J_{HF}$ 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, $^{1}J_{CF}$ 252 Hz, C2), 99.93 (td, $^{2}J_{CF}$ 26 Hz, $^{4}J_{CF}$ 4 Hz, C3), 159.23 (dm, $^{1}J_{CF}$ 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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