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Preliminary communication

Synthesis, reactivity and crystal structure of trimesitylgermylamine, Mes_3GeNH_2

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Abstract

Trimesitylgermylamine, Mes_3GeNH_2, prepared in high yield by the coupling of Mes_3GeCl (Mes = 2,4,6-$Me_3C_6H_2$) with $NaNH_2$ or $LiNH_2$, has been fully characterized by ^1H and ^{13}C NMR, IR and mass spectrometry. It is a rare example of a stable primary germylamine, melting at 166°C, which is only slowly cleaved by H_2O, CH_3OH, HCl or phenol, indicating that the central Ge atom is protected from attack by the mesityl groups. Unlike other germylamines, Mes_3GeNH_2 reacts with ^tBuCOCl to give the *N*-substituted amide, $Mes_3GeNHCO^tBu$, rather than Mes_3GeCl. Preliminary X-ray crystallographic analyses reveal that the Ge atom has approximate tetrahedral coordination with an average Ge–C bond length of 1.978(3) Å and a Ge–N bond length of 1.854(3) Å, and crowding around the Ge atom so that it is shielded from attack by approaching reactants.

Only two primary germylamines have so far been described, R_3GeNH_2 where R = Ph [1] and ^iPr [2,3], and these are not stable. For smaller substituents such compounds undergo spontaneous deamination into the corresponding secondary amines [4,5] (eq. 1).

$$2\,R_3GeNH_2 \longrightarrow (R_3Ge)_2NH + NH_3 \qquad (1)$$

We have synthesized Mes_3GeNH_2 in order to study the influence of steric effects upon the stability and reactivity of primary germylamines. Our preliminary results are outlined below, including the X-ray crystal structure of the primary organogermylamine.

We have found that trimesitylgermylamine can be prepared easily in high yield (84%) by the reaction of sodium or lithium amide with trimesitylchlorogermane (eqs. 2 and 3), a classical route for Ge–N bond formation [4,5].

$$Mes_3GeCl + NaNH_2 \xrightarrow[Et_2O,\ 20°C]{NH_3\ liq.} Mes_3GeNH_2 + NaCl \qquad (2)$$

$$Mes_3GeCl + LiNH_2 \xrightarrow{THF,\ 20°C} Mes_3GeNH_2 + LiCl \qquad (3)$$

In reaction 2, ammonia was used in excess because metallic sodium must be absent to avoid the formation of $\mathrm{Mes_3GeH}$ (eq. 4)

$$\mathrm{Mes_3GeCl} \xrightarrow[-\mathrm{NaCl}]{\mathrm{Na}} \mathrm{Mes_3Ge^{\cdot}} \xrightarrow[\text{solvent}]{\mathrm{H^{\cdot}}} \mathrm{Mes_3GeH} \qquad (4)$$

Trimesitylgermylamine melts at 166°C, is not moisture-sensitive and is soluble in most polar and non-polar organic solvents [6,7*].

In contrast to most germanium-nitrogen compounds [4,5] the hydrolysis of $\mathrm{Mes_3GeNH_2}$ is very slow, requiring 6 h at 140°C for completion (eq. 5).

$$\mathrm{Mes_3GeNH_2 + H_2O} \xrightarrow{\mathrm{C_6H_6},\ 140^\circ\mathrm{C}} \mathrm{Mes_3GeOH + NH_3} \qquad (5)$$

The reaction with methanol (eq. 6), producing $\mathrm{Mes_3GeOMe}$ [7*], is only 72% complete after 20 h at 80°C in a sealed tube:

$$\mathrm{Mes_3GeNH_2 + MeOH} \longrightarrow \mathrm{Mes_3GeOMe + NH_3} \qquad (6)$$

Similarly, aqueous hydrochloric acid (12 *N*) reacts gradually with $\mathrm{Mes_3GeNH_2}$ in benzene or diethyl ether solution to give $\mathrm{Mes_3GeCl}$ in quantitative yield after 5 h at 20°C.

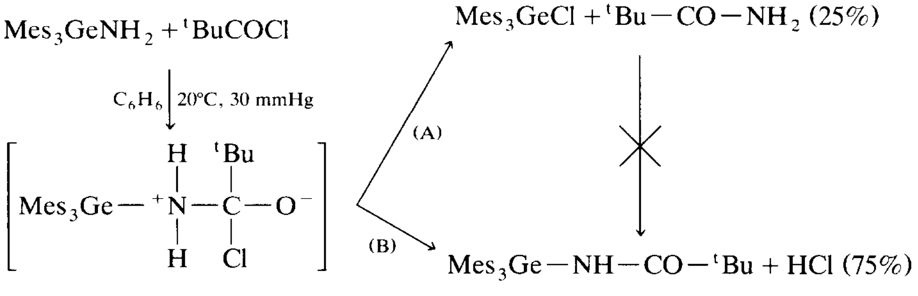
By contrast, gaseous HCl reacts (eq. 7) instantaneously and exothermally with $\mathrm{Mes_3GeNH_2}$ in ether solution.

$$\mathrm{Mes_3GeNH_2 + 2HCl} \xrightarrow{\mathrm{Et_2O}} \mathrm{Mes_3GeCl + NH_4Cl} \qquad (7)$$

In the reaction of $\mathrm{Mes_3GeNH_2}$ with 4-methylphenol, we were able to characterize the intermediate ammonium salt (eq. 8) which decomposes on heating to trimesitylgermylparamethylphenoxide $\mathrm{Mes_3GeOAr}$ [7*].

$$\mathrm{Mes_3GeNH_2 + HOAr} \longrightarrow \underset{(\mathrm{Ar} = p\text{-}\mathrm{CH_3C_6H_4}\text{-})}{[\mathrm{Mes_3GeNH_3}]^+[\mathrm{OAr}]^-} \xrightarrow[-\mathrm{NH_3}]{} \mathrm{Mes_3GeOAr} \qquad (8)$$

Apparently, when protonation on nitrogen is effective, secondary attack of a nucleophile on the germanium center is strongly dependent upon its steric hindrance. This is true in reactions with acid chlorides, in which trimethylacetyl chloride, $^t\mathrm{BuCOCl}$, produces not only the chlorogermane, as is usually observed in the case of germylamines [4,5] (Scheme 1, A), but also the Ge–N bonded amide [7*], as in the classical reaction of primary organic amines (Scheme 1, B).



Scheme 1.

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* Reference number with asterisk indicates a note in the list of references.

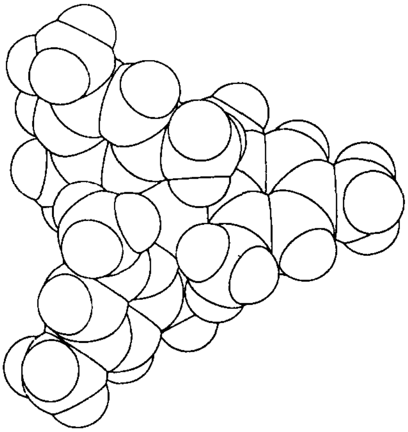

Fig. 1. Model of Mes_3GeNH_2 with atoms having van der Waals radii, viewed along the pseudo-C_3 axis, showing the protection of the central Ge atom.

The reactivity and exceptional stability of Mes_3GeNH_2 is consistent with the presence of a tetrahedral germanium atom sterically protected by the large mesityl groups, leaving the attached nucleophilic nitrogen atom more exposed to electrophilic attack. This is confirmed by its structure based on preliminary single crystal X-ray diffraction measurements [8*]. The Ge atom has approximate tetrahedral coordination, with an average Ge–C bond length of 1.978(3) Å and a Ge–N bond length of 1.854(3) Å. A propeller-like arrangement of the mesityl groups results in a pseudo-C_3 axis along the Ge–N vector and thereby hinders the approach of potential reactants along this direction, as evident from models with atoms having appropriate van der Waals radii (Figs. 1 and 2).

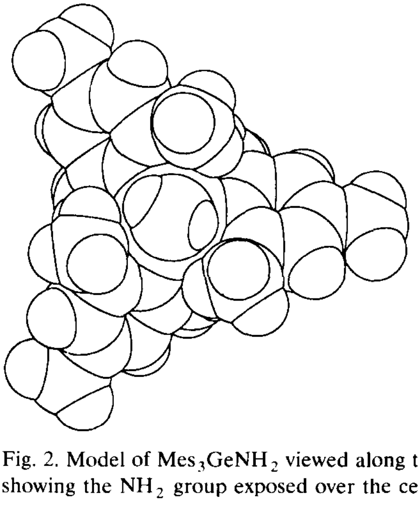

Fig. 2. Model of Mes_3GeNH_2 viewed along the pseudo-C_3 axis, with atoms having van der Waals radii, showing the NH_2 group exposed over the central Ge atom.

References and notes

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7 Physical data for new products were as follows.

Mes_3GeNH_2: m.p. 166°C. IR: ν_{as}(NH) 3420, ν_s(NH) 3340 cm^{-1} (C_6H_6 solution). ^1H NMR (C_6D_6): δ C_6H_2, 6.74 (s, 6H): o-CH_3, 2.32 (s, 18H); p-CH_3, 2.11 (s, 9H); NH_2, 0.55 (s, 2H, displaced by D_2O) ppm. ^{13}C NMR ($CDCl_3$) δ C1, 140.52; C2, 144.55; C3, 130.83; C4, 139.35; o-CH_3, 25.55; p-CH_3, 21.98 ppm. MS (EI): M^+, 447; ($M^+ - NH_3$), 430; (M^+ − Mes), 328.

Mes_3GeOMe: m.p. 176°C, and ^1H NMR ($CDCl_3$) δ C_6H_2, 6.84 (s, 6H); o-CH_3, 2.32 (s, 18H); p-CH_3, 2.29 (s, 9H); CH_3O, 3.41 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$) δ C1, 136.92; C2, 143.61; C3, 129.35; C4, 136.66; o-CH_3, 23.59; p-CH_3, 21.04; CH_3O, 52.61 ppm. Mass (Dci CH_4)$M^+ - 1$: 461.

$[Mes_3GeNH_3]^+[OC_6H_4CH_3]^-$: IR: $\nu(NH_3{}^+)$: strong, large, mult., abs. band 2577 cm^{-1} (CCl_4). ^1H NMR: (C_6D_6) δ CH_{ar}, 6.65 (10H); o-CH_3, 2.25 (s, 18H); p-CH_3, 2.08 (12H); NH_3, 3.47 (s, 3H) ppm.

$Mes_3GeOC_6H_4CH_3$: m.p. 180–185°C; and ^1H NMR (C_6D_6) δ CH_{ar}, 6.65 (10H); o-CH_3, 2.34 (s, 18H); p-CH_3, 2.07 (12H) ppm. ^{13}C NMR ($CDCl_3$) δ (Mes group): C1, 137.31; C2, 143.20; C3, 129.52; C4, 139.06; o-CH_3, 23.91; p-CH_3, 21.11 ppm. (Phenyl group): C1, 153.72; C2, 115.24; C3, 130.02; C4, 129.52; p-CH_3, 20.54 ppm.

$Mes_3GeNHCO^tBu$: m.p. 179°C, IR: ν(NH) 3438, ν(C=O) 1660 cm^{-1} (C_6H_6). ^1H NMR (C_6D_6) δ C_6H_2, 6.73 (s, 6H); o-CH_3, 2.43 (s, 18H); p-CH_3, 2.07 (s, 9H); ^tBu, 1.06 (s, 9H); NH, 5.42 (s, 1H) ppm. ^{13}C NMR (C_6D_6) δ C1, 137.37; C2, 143.56; C3, 130.12; C4, 138.82; CO, 180.22; ^tBu, CH_3, 28.08; C^{IV}, 39.95; o-CH_3, 23.67; p-CH_3, 20.95. MS (EI): M^+, 531; (M^+ − Mes), 412.

8 Crystal data: $C_{27}H_{35}GeN$, FW = 446.17, monoclinic, space groups $P2_1/c$, a 11.201(2), b 12.449(1), c 18.011(2) Å, β 106.777(9)°, U 2404.6(4) $Å^3$, D_c 1.139 g cm^{-3}, $Z = 4$, Cu-K_α radiation, λ 1.54178 Å, μ 10.77 cm^{-1}. A Rigaku AFC5R diffractometer at the McGill X-ray Crystal Structure Laboratory was used to collect data at 23 ± 1°C with the $\omega - 2\theta$ scan technique to a maximum 2θ of 119.9°, resulting in 3977 reflections of which 3765 were unique (R_{int} 0.027). Final $R = 0.037$, $R_w = 0.047$ for 298 parameters, using 2846 reflections with $I > 3\sigma(I)$. Hydrogen atoms were placed in calculated positions and refined with a fixed thermal parameter. The TEXAN structure-solving program of the Molecular Structure Corporation, Texas, was used in all calculations. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.