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PRELIMINARY NOTE

Novel Synthesis and Properties of N-Bis(trifluoromethyl)nitroxy-Germaimine, $(CF_3)_2NON{=}GeH_2$

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SUMMARY

$(CF_3)_2NON{=}GeH_2$, synthesized by a novel method involving the reactions of $(CF_3)_2NONO$ and GeH_4, underwent addition reactions with HI to give $(CF_3)_2NONHGeH_2I$ and substitution reactions to afford a number of derivatives, $(CF_3)_2NON{=}GeRR'$ [where R, R' = H, Cl and $ON(CF_3)_2$].

In recent years, there has been a growing interest in the chemistry of germaimines of the type $R_2Ge{=}NR'$, where the Ge=N double bond has been shown to be reactive and that it can be detected by the so-called trapping experiments [1]. Thus far, only one such compound has been isolated, namely $[(Me_3Si)_2N]_2Ge{=}N{-}N{=}C(COOMe)_2$, whose stability has been attributed to mesomeric effects [2, 3]. We now report a number of new stable germaimine derivatives, namely $(CF_3)_2NON{=}GeRR'$ (where R, R' = H, Cl, $ON(CF_3)_2$], whose stability can be attributed to the presence of highly electronegative $(CF_3)_2NO$ groups(s).

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The reactions of N-nitrosobis(trifluoromethyl)hydroxylamine with germane in a 1:1 molar ratio in an evacuated glass ampoule afforded N-bis(trifluoromethyl)nitroxy-germaimine, $(CF_3)_2NON{=}GeH_2$ in 35% yield, according to the equation:

$$(CF_3)_2NONO + GeH_4 \longrightarrow (CF_3)_2NON{=}GeH_2\ (A) + H_2O$$

A hygroscopic yellow solid was also formed in the reaction ampoule. The germaimine (A) was isolated as a white solid at -96°C on vacuum trap-to-trap fractionation. Its infrared spectrum gave the following peaks: 2261 cm^{-1}, (ν Ge-H); 890 cm^{-1}, (δ Ge-H); 1324, 1271, 1243 cm^{-1}, (νC-F); 1050 cm^{-1}, (ν N-O); and 720 cm^{-1}, (δC-F). The peak located at 1002 cm^{-1} can be attributed to the Ge=N stretching vibration, which is slightly higher than the band at 970 cm^{-1} reported for $F_2Ge{=}NPh$ [1]. Molecular weight determination by Regnault's method gave 255 g mol^{-1}; (compound (A) requires 256 g mol^{-1}).

The presence of the Ge=N double bond in the germaimine (A) was chemically confirmed by the addition reactions with hydrogen iodide to give $(CF_3)_2NONHGeH_2I$, as shown below:

$$(CF_3)_2NON{=}GeH_2 + HI \longrightarrow (CF_3)_2NON(H)\text{-}GeH_2(I)\ (B)$$

The addition compound (B) was isolated at -60 °C trap on vacuum fractionation as a pale yellow liquid. The following peaks were shown in its infrared spectrum: 3419 cm^{-1}, (νN-H); 2232 cm^{-1}, (νGe-H); 822 cm^{-1}, (δGe-H); 1497, 1324, 1270, 1243 cm^{-1}, (ν C-F); and 1050 cm^{-1}, (ν N-O). The Ge=N stretching vibration at 1002 cm^{-1} disappeared. The spectral data indicate that addition across the double bond occurred with the migration of hydrogen to the nitrogen atom and iodine to the germanium atom.

^1H NMR of the compound (B) consists of 2 peaks of 1:2 intensity: one (δNH) located at 11.6 ppm and the other (δGeH_2) at 2.1 ppm, both downfield w.r.t. TMS. The ^{19}F NMR shows a singlet (δCF_3) at 17.6 ppm downfield w.r.t. CF_3COOH. Analysis of iodine gave 32.67%; (compound (B) requires 33.02%).

The presence of the GeH_2 moiety was chemically confirmed by the reactions between the germaimine (A) and bis(trifluoromethyl)nitroxyl which is a powerful hydrogen abstractor and a radical scavenger [4]. Their reactions in 1:2 and 1:4 ratio afforded N-bis(trifluoromethyl)nitroxy derivatives (C) and (D) in 62% and 64% yields respectively:

$$(CF_3)_2NON{=}GeH_2 + 2(CF_3)_2NO \longrightarrow (CF_3)_2NON{=}GeHON(CF_3)_2\ (C) + (CF_3)_2NOH$$

$$(CF_3)_2NON{=}GeH_2 + 4(CF_3)_2NO \longrightarrow (CF_3)_2NON{=}Ge[ON(CF_3)_2]_2\ (D) + 2(CF_3)_2NOH$$

Both the reactions gave quantitative amounts of bis(trifluoromethyl)-hydroxylamine. The germaimines (C) and (D) were isolated at -40°C and -20°C traps respectively as colourless liquids.

The infrared spectrum of compound (C) shows peaks located at 1393, 1290, 1243 1050, 995, 721 cm^{-1} due to the presence of $(CF_3)_2NO$ groups; as well as 2271 and 1001 cm^{-1} due to Ge-H and Ge=N stretching vibrations respectively. Molecular weight determination of the germaimine (C) gave 420 g mol^{-1} (calcd. 423 g mol^{-1}).

The infrared spectrum of the germaimine (D) shows characteristic peaks due to the $(CF_3)_2NO$ group located at 1313, 1271, 1243 and 721 cm^{-1}, and the Ge=N stretching at 1001 cm^{-1}.

Compounds C and D underwent cleavage at the Ge-ON bonds when reacted with excess anhydrous hydrogen chloride to give the corresponding chloro derivatives, according to the equations:

$$(CF_3)_2NON{=}GeHON(CF_3)_2 + HCl \longrightarrow (CF_3)_2NON{=}GeHCl\ (E) + (CF_3)_2NOH$$

$$(CF_3)_2NON{=}Ge[ON(CF_3)_2]_2 + 2HCl \longrightarrow (CF_3)_2NON{=}GeCl_2\ (F) + 2(CF_3)_2NOH$$

In both the reactions, quantitative yields of bis(trifluoromethyl)-hydroxylamine were obtained.

Compound (E) shows peaks due to $(CF_3)_2NO$ group at 1286, 1214, 1148, 900 and 720 cm^{-1}, and the Ge=N stretching vibration at 1022 cm^{-1}. Analysis for chlorine gave 11.34%, (compound (E) requires 12.19%). Similarly, compound (F) shows peaks due to $(CF_3)_2NO$ group located at 1352, 1214, 1194 and 720 cm^{-1}, and Ge=N group at 1022 cm^{-1}. Analysis for chlorine gave 20.83%; (compound (F) requires 21.80%).

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