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Stable germa-imines: synthesis and reactivity of orthosubstituted anilinodimesitylgerma-imines *

M. Rivière-Baudet, A. Khallaayoun [1] and J. Satgé

Laboratoire de Chimie des Organominéraux, UA 477 du CNRS, Université Paul Sabatier, 31062 Toulouse Cedex (France)

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Abstract

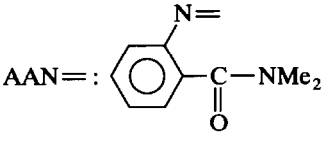
The orthosubstituted anilinodimesitylgerma-imines Mes_2Ge=NAA (**1**) and Mes_2Ge=NAE (**2**) where NAA is *N*-(dimethylanthranilamide) and NAE is *N*-(methylanthranilate) have been prepared by dehydrohalogenation of the corresponding halogenogermylamines. They are rare examples of thermally stable and monomeric germa-imines, probably stabilized by intramolecular C=O → Ge coordination. They readily undergo addition reactions with water, ethanol, germanols, phenylacetylene and chloroform to form adducts in which the protonic H is bonded to nitrogen. They also add to 3,5-ditert-butylorthoquinone, forming thermally unstable (2 + 4) and (2 + 2) adducts which rearrange to the expected digermadioxolane and dimesitylgermoxane respectively. By 1-3 cycloaddition, *N*-tert-butyl-phenylnitrone adds to germa-imines **1** and **2**, yielding the first stable 1-oxa-2,4-diaza-5-germolanes.

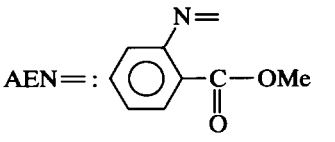
1. Introduction

The chemistry of germa-imines has recently been reviewed [1,2]; few stable germa-imines have been characterized and most were obtained by the reaction of a germylene with an azide [1,2]; only three have been characterized by X-ray analyses [3,4]. In our search for an easy route to germa-imines, we examined the dehydrohalogenation reaction starting with halogenogermylamines of the type $R_2Ge(X)$–NHR′. When such precursors are not sterically encumbered, the reaction gave cyclogermazanes (*i.e.*, germa-imines oligomers), whereas when bulky substituents are used in the hope of stabilizing the expected germa-imine, dehydrohalogenation did not easily occur [5].

2. Results and discussion

We recently found that from hindered precursors in which the germanium–halogen bond is "activated" by electron-withdrawing substituents on nitrogen and/or by nucleophilic assistance on germanium [6,7], dehydrohalogenation occurs readily even at low temperature to form stable germa-imines [8,9]. Using *ortho*-substituted anilines as nitrogen moieties, we obtained dimesitylgerma-imines in high purity: *N*-dimethylanthranilamide Mes_2Ge=NAA (**1**) and the *N*-methylanthranilate Mes_2Ge=NAE (**2**) where AAN= and AEN= are derived from anthranilic amide and methyl anthranilate, respectively.





Correspondence to: Professor M. Rivière-Baudet.

* Dedicated to Professor Michael Lappert in appreciation of his pioneer work in Main Group 14 chemistry as part of his many contributions to organometallic chemistry.

[1] On leave from Université Ibnou Zohr, Agadir (Morocco).

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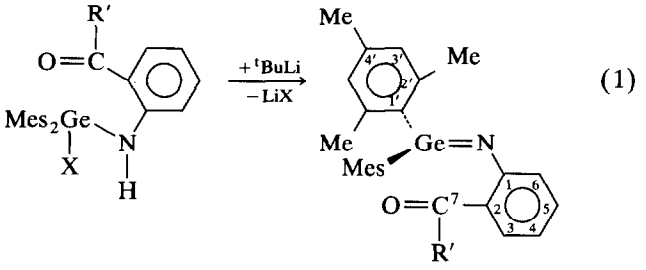
Our preliminary results [9] showed these compounds to be thermally stable and monomeric. We now report on their chemical behaviour, concentrating on **1** which is obtained in high yield (85%) by reaction (1):



(1)

R′ = NMe_2 **1**

R′ = OMe **2**

Compound **2** is formed in lower yield (17%), because of the well-known secondary reaction of tert-butyllithium with the carbonyl group of the ester [8,9].

The chlorogermyl secondary amine $Mes_2Ge(Cl)NHAE$ [7] was used to prepare **2**, whereas **1** required fluorogermylamine, $Mes_2Ge(F)NHAA$ [9], because the chlorogermyl precursor $Mes_2Ge(Cl)NHAA$ is unstable [7]. Alternatively, lithium dimethylamide reacts with the same fluorogermylamine to form the germa-imine **1** in appreciable yield (Scheme 1, route b).

1 crystallizes with one molecule either of diethylether or THF, but there is no evidence of complexation of either ether to the germanium. Each can easily be removed by dissolution of **1** in toluene and chloroform, followed by evaporation of the solvents, without decomposition of the germa-imine. Compound **2** behaves similarly.

The ^1H NMR spectra of **1** at 200 MHz at room temperature show inequivalence of the mesityl and *N*-methyl groups. Coalescence at about 55°C in $CDCl_3$ leads to singlets. One possible explanation is intramolecular interaction between the amido-group and germanium.

Mass spectra by chemical desorption of **1** and **2** showed that they are monomeric and the seven addition reactions which follow confirm beyond doubt that **1** and **2** react as monomers. If genuine dimers (*e.g.*, cyclodigermazane) or higher polymers were present, the resulting products would be completely different [10].

Compound **1** adds ethanol, as expected [1–3,11–15]. With water (eqn. (2)) a stepwise reaction occurs, giving first the corresponding germanol **3**.

$Mes_2Ge{=}NAA + H_2O \longrightarrow$

1

$Mes_2Ge(OH)-N(H)-AA$ (2)

3

Germanol **3** then reacts as an alcohol towards the germa-imine and, as a result, the main product of the reaction is the digermoxane **4** (eqn. (3a)). Reactions of germanols with germa-imines have not previously been reported.

$Mes_2Ge{=}NAA + Mes_2Ge(OH)-N(H)-AA \xrightarrow{(a)}$

1 **3**

$(Mes_2GeN(H)AA)_2O$ (3)

4

$2 \times 3 \xrightarrow{(b)} -H_2O$

Of course, under the same experimental conditions, there is no dehydration of [3] (eqn. (3b)), which is not surprising because the mesitylgermanols $Mes_2Ge(H)(OH)$, $Mes_2Ge(OH)_2$, Mes_3GeOH are also stable [16,17].

Further evidence for the addition of germanols to germa-imines is provided by the addition of dimesitylgermanol [16] to germa-imine **1** (eqn. (4))

$Mes_2Ge{=}NAA + Mes_2Ge(H)-O-H \longrightarrow$

1

$Mes_2Ge(NHAA)-O-Mes_2Ge(H)$ (4)

5

Germanol **3**, transiently formed and observed by ^1H NMR spectroscopy during the hydrolysis reaction (eqn. (2)), has been characterized by comparison with an authentic sample of **3** obtained by the slow hydrolysis in moist air of a benzene solution of the asymmetric *N*-dimethyl-*N*-(dimethylanthranilamide)germyldiamine (**6**) (eqn. (5)).

$Mes_2Ge(NMe_2)-NHAA \xrightarrow{H_2O}$

6

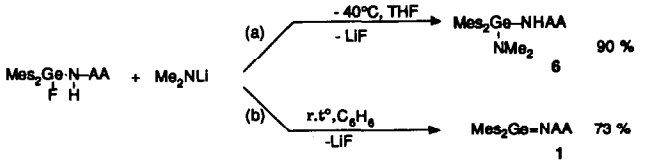
$Mes_2Ge(OH)-NHAA + Me_2NH$ (5)

3

Germanol **3** thus obtained reacts with germa-imine **1** to give germoxane **4**, confirming reaction **3**.

Compound **6** must be prepared at low temperature in THF (Scheme 1, route a) to avoid the competitive formation of germa-imine **1** (Scheme 1, route b).

We did not observe any spontaneous deamination of **6** such as could produce **1** by releasing Me_2NH.



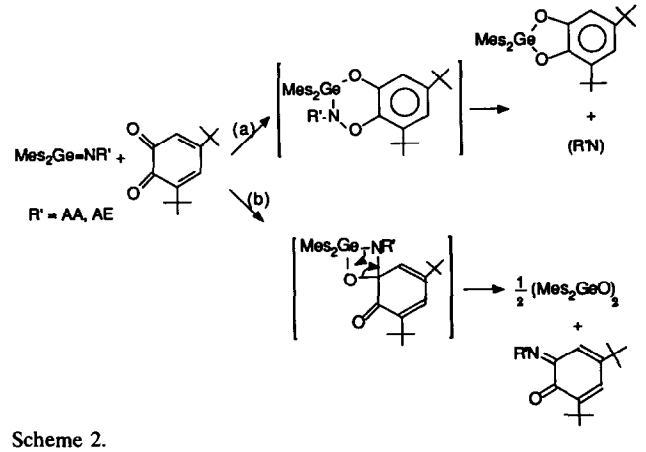
Scheme 1.

Other mild protic reagents such as phenylacetylene (eqn. (6)) [9] and chloroform (eqn. (7)) add across the germanium–nitrogen double bond of germa-imines, leading to functional germylamines, **7** and **8**, respectively.

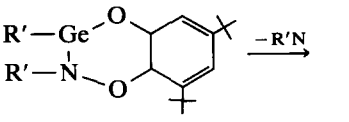
$$Mes_2Ge{=}NAA + PhC{\equiv}CH \longrightarrow \underset{\mathbf{1}}{} \quad \underset{\mathbf{7}}{Mes_2Ge(NHAA)(C{\equiv}C{-}Ph)} \qquad (6)$$

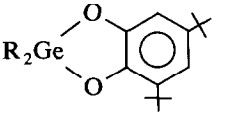
$$Mes_2Ge{=}NAA + CHCl_3 \longrightarrow \underset{\mathbf{1}}{} \quad \underset{\mathbf{8}}{Mes_2Ge(CCl_3)(NHAA)} \qquad (7)$$

Germa-imines **1** and **2** also give cycloaddition reactions. 1-4 Cycloadditions are the main reactions observed with 3,5-di-tert-butylorthoquinone. These transient adducts are not thermally stable and lead eventually, as previously observed [8,18] (eqn. (8)), to dimesitylgermadioxolane (Scheme 2, route a). 1-2 Cycloaddition occurs competitively, forming $(Mes_2GeO)_2$ (Scheme 2, route b), and the ratio of dimesitylgermadioxolane to $(Mes_2GeO)_2$ gives the ratio of 1-4 to 1-2 addition [8,18].



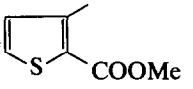
Scheme 2.





(8)

in ref. 18: R = Ph, R' = Me

in ref. 8: R = Me, R' = 

Germa-imines **1** and **2** react easily with *N*-phenyl [9] and *N*-tert-butyl-phenyl nitrone forming the first thermally stable 1-oxa-2,4-diaza-5-germolanes by 1-3 cycloaddition (eqn. (9)). Adducts of this type obtained from transient germa-imines are thermally unstable [19]. Stabilization is probably achieved here by the electron-withdrawing effects of the AA or AE substituents in addition to steric hindrance.

$$Mes_2Ge{=}NR' + Ph{-}CH{=}N{-}{}^tBu \longrightarrow \underset{\mathbf{9}}{} \qquad (9)$$

ref. 9: R' = AA **9**
R' = AE **10**

Because of their asymmetric carbon (C_3), compounds **9** and **10** show at room temperature inequivalent mesityl groups in the ^1H NMR spectra (*e.g.*: **9**, toluene-d_8, ppm, TMS): (*o*-Me: 2.87 (6H); 2.70 (6H); pMe 2.02 (3H); 2.29 (3H); NMe_2: 2.30 (6H). A decrease in temperature to −30°C enhances the inequivalence, suggesting a rigidity of the molecule which prevents free rotation of the methyl groups (*o*-Me: 3.11 (3H), 2.86 (3H); 2.83 (3H), 2.74 (3H); pMe: 2.06 (3H), 1.87 (3H); NMe_2: 2.35 (3H), 2.24 (3H)).

There is a significant decrease in ν(C=O) between the unsaturated compounds **1** or **2** and the corresponding adducts **3** to **10**, suggesting that any interaction (Ge ← O) between the carbonyl group and germanium in **1** and **2** disappears upon the formation of an adduct.

Among the factors which might favour the stability of compounds **1** and **2** are intramolecular coordination (Ge ← O), electron-withdrawal by the *ortho*-ester or amide group, and steric hindrance of the mesityl groups on germanium.

An X-ray crystal structure determination is necessary to decide which is most important.

3. Experimental section

All reactions were carried out under dinitrogen or argon and with dry solvents.

NMR spectra were recorded on Bruker AC 80 (^{1}H) and AC 200 (^{13}C) spectrometers; IR spectra on a Perkin-Elmer 1600 FT IR spectrometer; mass spectra on a Rybermag R10-10 spectrometer operating in the electron-impact mode at 70 eV or by chemical desorption (DCi/CH_4). Elemental analyses were performed by the Ecole Nationale Supérieure de Chimie, Toulouse, France.

3.1. Anthranilic imido(dimesityl)germanium Mes_2Ge=NAA 1

1 was prepared [9] according to eqn. 1 (85%). m.p. 194–200°C (with decomposition). IR ($CDCl_3$, cm^{-1}): ν(C=O) 1634. ^{1}H NMR (80 MHz, $CDCl_3$) δMes: *p*-Me 2.15 (s); *o*-Me 2.25 (s, broad); C_6H_2 6.57 (s); δAA: C_6H_4 6.69–700m; NMe_2 2.77 (s), 2.67 (s). ^{13}C NMR ($CDCl_3$) (for carbon numbering, see eqn. 1). δMes 132.33 ($C_{1'}$); 142.98 ($C_{2'}$); 128.72 ($C_{3'}$); 137.79 ($C_{4'}$); 20.89 (*o*-Me); 24.40 (*p*-Me); δAA, 148.88 (C_1); 131.58 (C_2); 127.43 (C_3, C_4); 127.85 (C_5); 120.50 (C_6); 170.53 (C_7); 39.16, 34.34 (NMe_2). MS (DCi/CH_4): 475 (M^++ 1, 15%). ^{1}H NMR (200 MHz; $CDCl_3$, room temp.) δN-methyl: 2.70 (broad s), 2.78 (s); δMes(*o*-Me 2.15, 2.27 (broad s), *p*-Me 2.15(s); C_6H_2 6.58 (broad singlet). Coalescence at about 55°C leads to singlets (NMe_2 2.74; *o*-Me 2.28; *p*-Me 2.16; C_6H_2 6.68).

A crystalline sample of **1** left in moist air for 18 h at room temperature showed only slight evidence of hydrolysis.

When **1** was heated in benzene for 18 h at 180°C, there was no evidence of decomposition.

3.2. Dimesityl-(N-methylanthranilatimido)germanium Mes_2Ge=NAE 2

Preparation [9] was according to eqn. 1 (17%) m.p. 201°C. IR (Nujol) ν(C=O): 1738 cm^{-1}. ^{1}H NMR (80 MHz, $CDCl_3$) δMes: *p*-Me 2.13 (5); *o*-Me 2.29 (s); C_6H_2 6.55 (s); δAE: OMe 3.65 (s); 7.45 (m) (H_3); 6.68 (s) (H_4 + H_5); 6.65 (s) (H_6). ^{13}C NMR ($CDCl_3$) δMes: 134.32 ($C_{1'}$); 142.94 ($C_{2'}$); 128.60 ($C_{3'}$); 137.93 ($C_{4'}$); 23.93 (*o*-Me); 20.91 (*p*-Me), δAA: 151.07 (C_1); 126.28 (C_2); 129.24 (C_3); 131.39 (C_5); 120.40 (C_6); 169.03 (C_7); 51.59 (OMe). MS (DCi/CH_4): 462 (M^++ 1, 100%).

3.3. Addition of ethanol to 1

Mes_2Ge(OEt)NHAA was obtained by addition of ethanol to a solution of **1** in $CHCl_3$ [9], yield 88%. m.p. 172°C. IR ($CDCl_3$) νNH 3384; ν(C=O) 1619 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ Mes: *o*-Me 2.46 (s); *p*-Me 2.23 (s); C_6H_2 6.79 (s); δEt: CH_2 3.73 (q), CH_3 1.17 (t) $J(CH_2$–$CH_3)$: 7 Hz; δAANH: NH 5.62 (s); NMe_2 2.99 (s); C_6H_4 6.5–7.0 (m). ^{13}C NMR ($CDCl_3$) δMes 132.04 ($C_{1'}$), 143.41 ($C_{2'}$), 129.53 ($C_{3'}$), 139.55 ($C_{4'}$), 21.08 (*p*-Me), 23.21 (*o*-Me); δEt: 19.03(CH_3), 59.43 (CH_2); δAA: 147.15 (C_1), 122.56 (C_2), 127.75 (C_3), 117.97 (C_4), 130.15 (C_5), 116.64 (C_6), 171.83 (C=O) MS (EI): 520 (M^+, 12%).

3.4. Hydrolysis of germa-imine 1

To Mes_2Ge=NAA (**1**) (0.08 g; 0.17×10^{-3} mole) dissolved in 0.5 ml of $CDCl_3$, droplets of water were progressively added. The reaction was followed by ^{1}H NMR measurements. After 15 min of moderate heating (50–60°C), **3** was formed (15%), identified by comparison with an authentic sample (see 3.5.3. below), and **4** (85%).

A sample of pure **3** (see 3.5.3 below), (0.05 g; 0.10×10^{-3} mole) dissolved in 0.5 ml of $CDCl_3$, heated for 15 min at 60°C did not show any change.

4 was obtained as follows: Mes_2Ge=NAA (**1**) (0.15 g; 0.31×10^{-3} mole) dissolved in 5 ml of moist $CHCl_3$ ($H_2O \sim 0.03\%$) and heated in a sealed tube for 4 h at 80°C led after evaporation of the solvents to pure $(Mes_2GeNHAA)_2O$ (**4**) (0.09 g), 59% m.p. 215°C. IR ($CDCl_3$) ν(NH): 3414; ν(C=O) 1622 cm^{-1}. ^{1}H NMR ($CDCl_3$) δMes: *o*-Me 2.22 (s); *p*-Me 2.15 (s); C_6H_2 6.58 (s); δAANH: NMe_2 2.90 (s), NH 5.45 (s), C_6H_4 6.50–7.00 (m). ^{13}C NMR ($CDCl_3$) δmes: 20.95 (*p*-Me); 23.07 (*o*-Me); 134.08 ($C_{1'}$); 143.08 ($C_{2'}$); 129.25 ($C_{3'}$); 138.81 ($C_{4'}$); δAANH: 146.26 (C_1); 122.79 (C_2); 127.29 (C_3); 118.23 (C_4); 129.25 (C_5); 116.14 (C_6); 171.50 (C_7). MS (DCi/CH_4): 963 (M^+ − 1, 3%); 993 (M^+ + 29, 1%); 801 (M^+ − NHAA, 100%); 845 (M^+ − Mes, 6%).

Analysis Calc. for $C_{54}H_{66}Ge_2N_4O_3$: C 67.26, H 6.89, N 5.81. Found C 66.91, H 6.77, N 5.85%. **4** was not obtained by spontaneous dehydration of **3**.

3.5. Syntheses of 3 from 6

3.5.1. Preparation at low temperature of $Mes_2Ge(NMe_2)$NHAA 6

Me_2NH (2 ml, 39.5×10^{-3} mole) dried on KOH pellets was condensed onto 5 ml of THF cooled to −40°C. LiBu (1.6 M in pentane; 1.2 ml; 1.87×10^{-3} mole) was added slowly with stirring and the mixture was warmed to room temperature and then stirred for

30 min. $LiMe_2N$ thus formed was transferred to a cooled (−40°C) THF solution of $Mes_2Ge(F)NHAA$ [9] (0.92 g; 1.87×10^{-3} mole). After 2 h stirring, LiF was removed by centrifugation, leaving after evaporation of the solvents 0.87 g of an amorphous powder of $Mes_2Ge(NMe_2)$ NHAA (**6**) (90%), m.p. 70°C. IR ($CDCl_3$) ν(NH): 3383; ν(C=O): 1620 cm^{-1}. ^1H NMR ($CDCl_3$) δMes: *o*-Me 2.36 (s); *p*-Me 2.24 (s); C_6H_2 6.79 (s); δAANH: NMe_2 2.96 (s), NH 4.84 (s); C_6H_4 6.5–7.2 (m); $\delta GeNMe_2$: 2.55 (s). ^{13}C NMR ($CDCl_3$) δMes: 21.00 (*p*-Me); 22.47 (*o*-Me); 133.94 ($C_{1'}$); 143.16 ($C_{2'}$); 129.42 ($C_{3'}$); 138.91 ($C_{4'}$); δAANH: 147.28 (C_1); 122.31 (C_2); 127.87 (C_3); 117.15 (C_4); 129.93 (C_5); 115.65 (C_6); 171.70 (C_7); $\delta GeNMe_2$: 39.66. MS (DCi/CH_4), 356 (M^+ − AANH, 10%). Analysis Calc. for $C_{29}H_{39}GeN_3O$ C 67.21, H 7.58, N 8.10. Found C 66.91, H 7.57, N 7.83%.

3.5.2. Preparation of 6 and 1 at room temperature according to Scheme 1

The THF from $LiMe_2N$ (1.17×10^{-3} mole) prepared as before was replaced by dry benzene (5 ml). $LiMe_2N$ was then transferred to a benzene solution (10 ml) of $Mes_2Ge(F)NHAA$ [9] (0.58 g, 1.17×10^{-3} mole) at room temperature. The reaction mixture was stirred for 2 h and LiF removed by centrifugation. The white residue obtained after evaporation of benzene was treated with pentane, affording a solution and a white precipitate (0.40 g) identified as germa-imine (**1**), 73% yield. The solution afforded on evaporation a white amorphous powder (0.14 g) identified as **6** (23%).

3.5.3. Synthesis of 3

A solution of **6** (0.87 g; 1.68×10^{-3} mole) in 4 ml C_6H_6 was slowly hydrolyzed in air. The reaction was followed by ^1H NMR spectroscopy. When **6** had disappeared (after 16 h) the benzene was evaporated *in vacuo* leaving an amorphous powder of pure $Mes_2Ge(OH)NHAA$ (**3**) (0.65 g) 79%. IR ($CDCl_3$) ν(NH): 3383; ν(OH) 3625; ν(C=O) 1620 cm^{-1}. ^1H NMR ($CDCl_3$) δMes: *o*-Me 2.42 (s); *p*-Me 2.25 (s); C_6H_2 6.82 (s). δNHAA: NH 5.23 (s); NMe_2 2.99 (s); C_6H_4 6.5–7.2 (m); δOH 1.68 (s). ^{13}C NMR ($CDCl_3$) δ Mes: 23.06 (*o*-Me); 21.10 (*p*-Me); 132.86 ($C_{1'}$); 143.35 ($C_{2'}$); 129.58 ($C_{3'}$); 139.95 ($C_{4'}$). δAANH: 146.66 (C_1); 122.15 (C_2); 128.27 (C_3); 117.25 (C_4); 130.48 (C_5); 116.66 (C_6); 171.52 (C_7). MS (Dci/CH_4) 493 ($M^+ + 1$, 15%); 475 (M^+ − OH, 20%); 329 (M^+ − $AANH_2$, 33%). Analysis Calc. for $C_{27}H_{34}GeN_2O_2$; C 66.02, H 6.97, N 5.70. Found C. 65.86, H 7.06, N 5.59%.

3.6. Addition of 3 to 1

To Mes_2Ge=NAA (**1**) (0.050 g; 0.10×10^{-3} mole) in 1 ml C_6H_6 was added $Mes_2Ge(OH)NHAA$ (**3**) (0.052 g; 0.10×10^{-3} mole) and the mixture was placed in a sealed tube for 14 h at 80°C. Evaporation of benzene led to 0.45 g of $(Mes_2GeNHAA)_2O$ (**4**) (90%).

3.7. Preparation of 5

A mixture of Mes_2Ge=NAA **1** (0.11 g, 0.23×10^{-3} mole) and $Mes_2Ge(H)(OH)$ (0.076 g, 0.23×10^{-3} mole) in 7 ml of benzene heated for 18 h at 80°C in a sealed tube gave 0.14 g of an amorphous powder identified as **5** (78%), m.p. 66°C. IR ($CDCl_3$) ν(NH) 3400; ν(Ge–H) 2061; ν(C=O) 1621 cm^{-1}. ^1H NMR ($CDCl_3$) δMes: *o*-Me 2.21 (s); *p*-Me 2.30 (s); C_6H_2 6.66 (s); δAANH: NH 5.68 (s); NMe_2 2.91 (s), C_6H_4 + GeH 6.5–7.0 (m). ^{13}C NMR ($CDCl_3$) δMes: 133.85, 133.80 ($C_{1'}$); 143.50, 143.04 ($C_{2'}$); 129.03, 128.58 ($C_{3'}$); 139.03, 138.66 ($C_{4'}$); 23.12, 22.19 (*o*-Me); 21.01 (*p*-Me); δNHAA: 146.77 (C_1); 122.40 (C_2); 127.53 (C_3); 117.92 (C_4); 129.63 (C_5); 116.13 (C_6); 171.68 (C_7). MS (DCi/CH_4): 803 ($M^+ + 1$, 69%); 683 (M^+-Mes, 37%); 639 (M^+ − AANH, 100%) Analysis Calc. for $C_{45}H_{56}Ge_2N_2O_2$; C 67.32, H 7.04, N 3.49. Found C 67.26, H 6.90, N 3.04%.

3.8. Preparation of $Mes_2Ge(C{\equiv}CPh)NHAA$ (7)

A mixture of **1** (0.255 g, 0.54×10^{-3} mole) and PhC≡CH (0.055 g, 0.54×10^{-3} mole) in 3 ml C_6H_6 heated for 14 h at 100°C in a sealed tube led to 0.28 g of **7** [9], 90%. M.p. 52°C.

3.8.1. Alternative route to 7

To PhC≡CH (0.110 g, 1×10^{-3} mole) in C_6H_6 (3 ml) at 0°C was added ^{t}BuLi (1×10^{-3} mole) with stirring. After 30 min further stirring at room temperature, Li(C≡CPh) was transferred to a benzene solution of $Mes_2Ge(F)NHAA$ [9] (0.53 g, 1×10^{-3} mole) stirred and cooled at 0°C. After 2 h at room temperature, LiF was removed by centrifugation and the solvent evaporated, yielding 0.46 g of **7**. Yield 80%. IR ($CDCl_3$) νNH: 3383; ν(C=O): 1620; νC≡C: 2160 cm^{-1}. ^1H NMR ($CDCl_3$): δMes: *o*-Me 2.50 (s), *p*-Me 2.27 (s), (C_6H_2) 6.85 (s); δAANH: NH 4.86(s); NMe_2 2.99 (s); δC_6H_4 + Ph 6.50–7.50 (m). ^{13}C NMR ($CDCl_3$) δMes: 131.87 ($C_{1'}$); 143.85 ($C_{3'}$); 129.72 ($C_{3'}$); 139.62 ($C_{4'}$); 21.09 (*p*-Me); 23.37 (*o*-Me); δAA: 146.95 (C_1); 122.50 (C_2); 127.88 (C_3); 117.74 (C_4); 129.98 (C_5); 116.16 (C_6); 171.73 (C_7); δPhC≡C: 123.46 ($C_{1''}$); 131.59 ($C_{2''}$); 128.21 ($C_{3''}$); 128.44 ($C_{4''}$); 106.22 (GeC); 93.97 (CPh). MS (EI): 576 M^+, 3%.

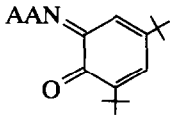
3.9. Preparation of $Mes_2Ge(CCl_3)NHAA$ (8)

A mixture of Mes_2Ge=NAA **1** (0.30 g, 0.63×10^{-3} mole) and dry $CHCl_3$ (1 ml) was heated for 2 h at 80°C in a sealed tube. After evaporation of the excess of chloroform, a brownish amorphous powder (0.35 g) of **8** remained. Yield 94%. M.p. 48°C. IR ($CDCl_3$): ν(NH):

3405; ν(C=O): 1620 cm^{-1}. ^1H NMR ($CDCl_3$) δMes: *o*-Me 2.46 (s); *p*-Me 2.25 (s); C_6H_2 6.82(s); δNHAA: N–H 6.56 (s), NMe_2 3.05 (s); C_6H_4 6.3–7.1 (m). ^{13}C NMR ($CDCl_3$) δMes: 133.47 ($C_{1'}$); 142.84 ($C_{2'}$); 130.04 ($C_{3'}$); 140.06 ($C_{4'}$); 24.54 (*o*-Me); 21.03 (*p*-Me). δAA: 124.78 (C_2); 127.45 (C_3); 117.92 (C_4); 129.70 (C_5); 117.21 (C_6); 171.51 (C_7). MS (DCi/CH_4): 593 (M^+, 1%). Analysis Calc. for $C_{28}H_{33}Cl_3GeN_2O$ C 56.74, H 5.61, N 4.72. Found C 56.38, H 5.63, C 4.39%.

3.10. Additions of 3,5-di-t-butyl orthoquinone with 1 and 2

To a solution of germa-imine **1** (0.156 g, 0.33×10^{-3} mole) in 5 ml C_6H_6, was added 3,5-di-*t*-butyl-*ortho*quinone (0.072 g, 0.33×10^{-3} mole), and the mixture was heated for 18 h at 80°C. ^1H NMR and MS analyses showed the formation of $(Mes_2GeO)_2$ and dimesitylgermadioxolane, which was identified by comparison with an authentic sample [20]. GC/MS analysis allowed the characterization of $AANH_2$, 164 ($M^{+\cdot}$), germadioxolane, 532 ($M^{+\cdot}$); and imine:



366 ($M^{+\cdot}$); 321 ($M^{+\cdot} - 3Me$). The relative proportions of $(Mes_2GeO)_2$ and dimesitylgermadioxolane as measured by ^1H NMR were 33%, 67% respectively, indicating that the 1-2 and 1-4 addition were in these same proportions.

In a similar way, germa-imine (**2**) (0.03 g, 0.064×10^{-3} mole) and 3,5-di-*t*-butyl*ortho*quinone (0.014 g, 0.064×10^{-3} mole) in 1 ml C_6D_6, heated in a sealed tube for 18 h at 80°C gave dimesitylgermadioxolane [20] and $(Mes_2GeO)_2$ which were characterized by ^1H NMR and MS (DCi, CH_4): germadioxolane 533 ($M^+ + 1$, 4%); $(Mes_2GeO)_2$ 655 ($M^+ + 1$, 2%). Relative proportions by ^1H NMR led to: addition 1-2 25%, addition 1-4 75%.

3.11. Preparation of 9

A mixture of **1** (0.150 g; 0.31×10^{-3} mole) and *n*-t-butyl-α-phenylnitrone (0.056 g; 0.31×10^{-3} mole) in 5 ml C_6H_6 was heated for 3 days at 100°C. Evaporation of solvent led to a sticky residue which, after treatment with pentane, afforded 0.12 g of a white powder of **9**. Yield 60%. m.p. 179°C. IR ($CDCl_3$) ν(C=O): 1608 cm^{-1}. ^1H NMR ($CDCl_3$) δMes: *o*-Me 2.56 (s), 2.42 (s), *p*-Me 2.30 (s), 2.17 (s), C_6H_2 6.85 (s), 6.68 (s); δAA: NMe_2 2.84 (s), C_6H_4 6.50–7.0 (m); δPhCHN^{t}Bu: ^{t}Bu 0.80 (s), CH 5.49(s); C_6H_5 7.13–7.63 (m). ^{13}C NMR ($CDCl_3$) δMes: 133.86 ($C_{1'}$); 142.74, 141.82 ($C_{2'}$); 128.98, 128.85 ($C_{3'}$); 137.92, 137.39 ($C_{4'}$), 21.18, 20.99 (*p*-Me); 23.88, 23.49 (*o*-Me); δAA: 172.76 (C_1), 130.06 (C_3), 116.35 (C_4), 131.20 (C_5), 119.77 (C_6), 211.04 (C_7); δCHPh: 79.53 (CH), 143.46 ($C_{1''}$), 127.59 ($C_{2''}$), 130.67 ($C_{3''}$), 127.44 ($C_{4''}$); δN^{t}Bu: 27.23 (CH_3), 58.35 (C_{IV}). MS (Ei): 651 (M^+, 8%), 399 (M^+-PhCHNAA, 48%). Analysis calc. for $C_{38}H_{47}GeN_3O_2$: C 70.17, H 7.28, N 6.46. Found: C 70.60, H 7.67, N 6.24%.

3.12. Preparation of 10

In a similar way, **2** and PhCH=N(O)^{t}Bu led to **10** [9] (95%). IR ($CDCl_3$) ν(C=O): 1660, ν(COC): 1240 cm^{-1}. ^1H NMR ($CDCl_3$) δMes: *o*-Me 2.60 (s), 2.39 (s), *p*-Me 2.32 (s), 2.16 (s), C_6H_2 6.88 (s), 6.67 (s); δAE: *o*-Me 3.66 (s), H_4 6.43 (d,d,d), J(3–4) 8.2 Hz; J(4–6) 2.4 Hz; J(4–5) 5.6 Hz, H_3, H_5, H_6, C_6H_5 7.14–7.76 (m, 8H); ^{t}Bu 0.74 (s); CH 5.39 (s). ^{13}C NMR ($CDCl_3$) δMes 133.96 ($C_{1'}$), 142.60, 140.86 ($C_{2'}$), 129.30, 129.10 ($C_{3'}$), 138.28, 137.39 ($C_{4'}$), 21.19, 20.95 (*p*-Me), 24.34, 23.35 (*o*-Me); δAE: 153.16 (C_1), 110.70 (C_2), 131.87 (C_3), 115.45 (C_4), 134.64 (C_5), 118.45 (C_6), 170.65 (C_7), 52.46 (OCH_3); δCHPh: 80.04 (CH), 140.21 ($C_{1''}$), 127.93 ($C_{2''}$), 131.04 ($C_{3''}$), 127.51 ($C_{4''}$); δN^{t}Bu: 58.35 (C_{IV}), 27.26 (CH_3). MS (Ei): 638 (M^+, 15%); 399 (M^+-PhCHNAE, 84%).

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