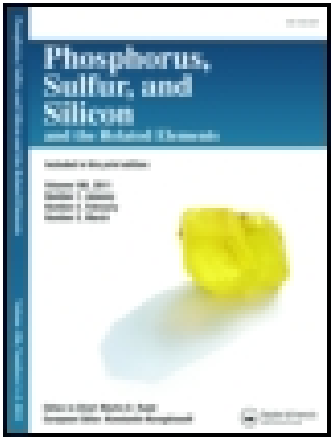

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N-GERMYL DERIVATIVES OF 4-NITROPHENYLAMINE: GERMYLAMINES, STABLE GERMA-IMINE

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N-GERMYL DERIVATIVES OF 4-NITROPHENYLAMINE: GERMYLAMINES, STABLE GERMA-IMINE

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N-germyl secondary amines of 4-nitrophenylamine were obtained by transamination from N-trialkylgermyldimethylamine, by transmetallation from the N-lithium derivative of 4-nitrophenylamine, or by intermolecular dehydrohalogenation between the corresponding halogermane and p-nitrophenylamine. Halogermylamines formed by the same methods are always obtained as a mixture with the corresponding diamine bis(4-nitrophenylamino)dimesitylgermane, and cannot be used as germa-imine precursors. However, elimination reactions from N-dimethylaminodimesitylgermyl-4-nitrophenylamine and N-dimesitylchlorogermyl-4-nitrophenylamine, formed from N-triethylgermyl N-dimesitylchlorogermyl-4-nitrophenylamine, yielded the thermally stable N-(4-nitrophenyl)dimesitylgerma-imine as a deep red amorphous powder. This germa-imine is moisture-sensitive, yielding (4-nitrophenylamino)dimesitylgermanol which adds to the germa-imine forming bis(4-nitrophenylaminodimesitylgermyl)oxide which was isolated as an orange powder.

N-4-nitrophenyl)dimesitylgerma-imine adds readily to chloroform yielding N-dimesitylchlorogermyl-4-nitrophenylamine. The 3+2 addition of the germa-imine to N-t-butyl-phenylnitrone gave an adduct whose thermal decomposition began at 100°C yielding benzylidene-4-nitrophenylamine and dimesitylgermoxane. The germa-imine addition to 4,5-di-t-butyl ortho-quinone led to the corresponding dimesitylgermadioxolane through decomposition at room temperature of a transient adduct. The formation of isobutene in this reaction is constitent with a Single Electron Transfer mechanism in the first step.

Keywords: N-4-nitrophenyl-halogermylamines; N-4-nitrophenyl-germylamines; bis(4-nitrophenylamino)dimesitylgermane; stable N-4-nitrophenyldimesitylgerma-imine

* Corresponding Author.

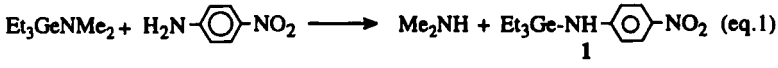
INTRODUCTION

We previously obtained stable germa-imines using the p-toluenesulfonamide group[1] or the less sterically hindered aromatic trifluorophenyl substituent[2] on nitrogen. In both cases, the stabilization was attributed to the withdrawing effects of these substituents on nitrogen. In order to confirm this hypothesis and to know if the result could be generalized, we used the electron withdrawing 4-nitrophenyl substituent on nitrogen.

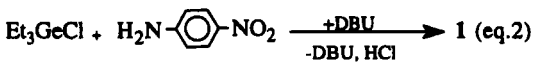
The N-germyl derivatives of 4-nitroaniline described here are the first compounds of this type. Within group 14, only three silylamines are known[3–8]and no metal-imino compounds have ever been characterized.

RESULTS AND DISCUSSION

One of the best starting material for the formation of a germa-imine is the corresponding halogermylamine which can be obtained by transamination, dehydrohalogenation, or transmetallation[9,10]. To obtain the best experimental conditions for the formation of such a compound, we began our study by the synthesis of N-triethylgermyl-4-nitrophenylamine **1**, which is easily obtained by transamination from N-triethylgermyldimethylamine (eq. 1).

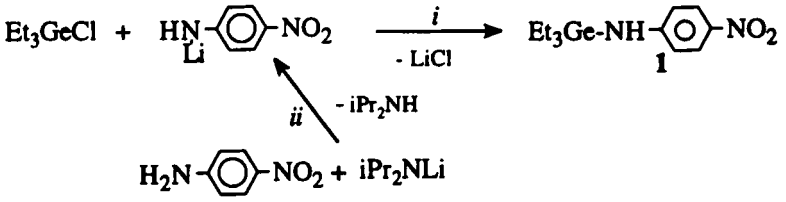


Dehydrohalogenation between triethylchlorogermane and 4-nitrophenylamine is difficult in the presence of triethylamine, but nearly quantitative in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (eq. 2).



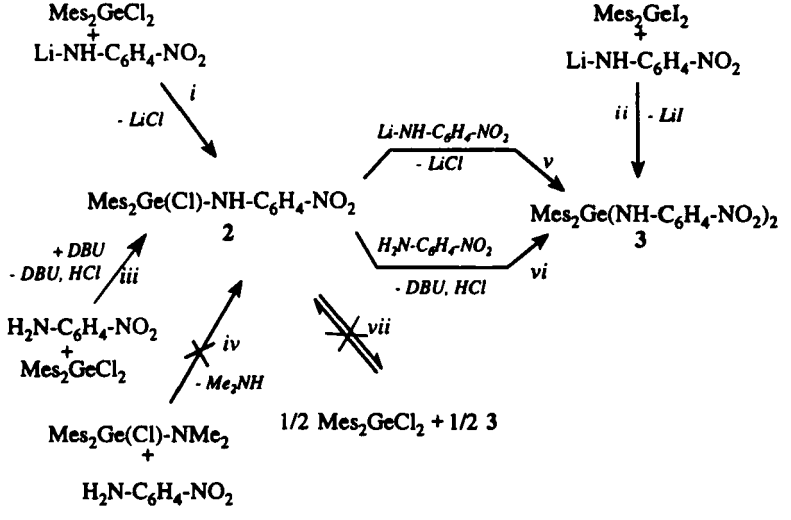
Transmetallation (Scheme 1, i) leads also to **1** in high yield if the lithium derivative of 4-nitroaniline itself is prepared by transmetallation

(Scheme 1, ii) using LDA to avoid secondary reactions with the nitro group.



SCHEME 1

When the transmetallation reaction is used (Scheme 2, i) for the preparation of N-dimesitylchlorogermyl-4-nitrophenylamine **2**, the main product is the corresponding diamine **3** (Scheme 2). The same result is obtained from dimesitylgermyldiodide (Scheme 2, ii), or by the dehydrohalogenation reaction (Scheme 2, iii). The transamination reaction which led to **1** (eq. 1) did not allow the formation of **2** (Scheme 2, iv). This surprising result can be explained by Pearson's HSAB concept; the soft nitrogen base of 4-nitroaniline is unable to attack the much harder acid germanium in N-dimesitylchlorogermyldimethylamine.

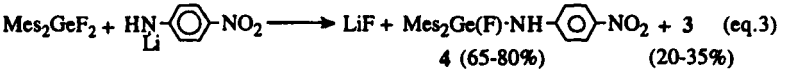


SCHEME 2

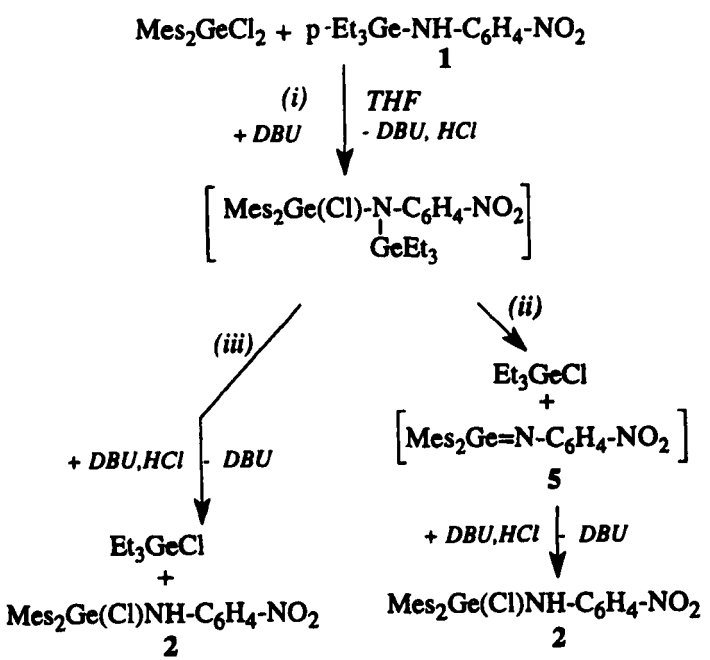
Diamine **3** is formed by a further transmetallation or dehydrochloration of **2** (Scheme 2, v, vi) and not by a rearrangement of **2**. We verified that **2** does not result in a disproportionation equilibrium involving diamine **3** (Scheme 2, vii).

Diamine **3** is thermally stable but very moisture-sensitive, as are most of the compounds in this series.

By contrast, the N-dimesitylfluorogermyl-4-nitrophenylamine **4** is obtained as the main product of the transmetallation reaction (eq. 3), but unfortunately, the diamine, inseparable by recrystallisation, is still formed in too great a proportion to make the compound a good starting material for the preparation of a pure germa-imine.



(eq.3)



SCHEME 3

In order to obtain germa-imine **5**, we tried the elimination of triethylchlorogermane from the corresponding N-triethylgermyl N-dimesitylchlorogermyl-4-nitrophenylamine (Scheme 3). Contrary to the silicon series[11,12], tertiary amines of the type $Ar_2Ge(Cl)N(R')GeR_3$ which we previously studied were stable compounds[13,14] but N-triethylgermyl N-dimesitylchlorogermyl-4-nitrophenylamine was not stable at room temperature under the reaction conditions. In THF, in which amine chlorhydrate is soluble, the final products are halogermylamine **2** and triethylchlorogermane. Compound **2** can be formed either via the germa-imine **5** (Scheme 3, ii), or by cleavage of the digermylamine by the amine chlorhydrate formed in the first step of the reaction (Scheme 3, iii).

The germa-imine **5** (Scheme 3, ii), if formed, like other germa-imines[2,9,10], would add to amine chlorhydrate acting as a protic species and the products isolated, would be chlorogermylamine **2** and 1,8-diazabicyclo[5.4.0]undec-7-ene.

There is no exchange reaction between dimesityldichlorogermane and N-triethylgermyl-4-nitrophenylamine **1**. After eigtheen hours of heating at 80°C in THF (eq. 4), the starting materials are recovered unchanged which means that triethylchlorogermane in Scheme 3 can be formed only by reactions ii or iii.

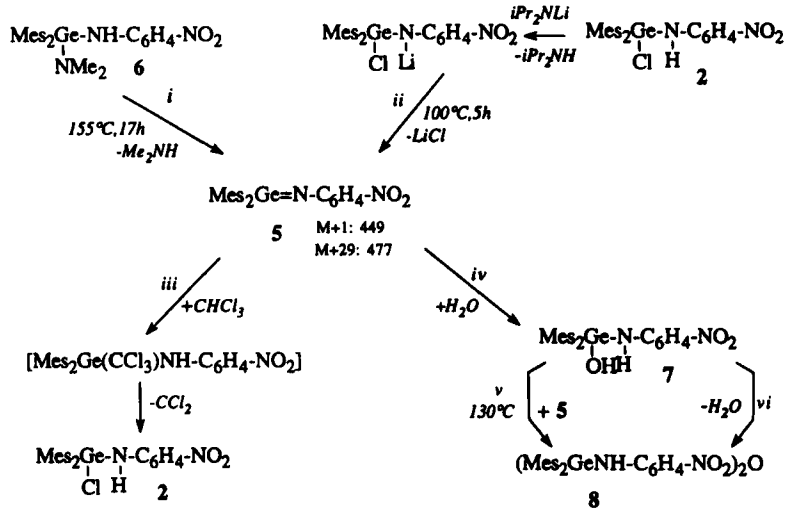
$$Mes_2GeCl_2 + \mathbf{1} \xrightarrow[THF]{18h,\ 80°C} \mathbf{2} + Et_3GeCl \quad \text{(eq.4)}$$

We tried to isolate germa-imine **5** using two different ways (Scheme 4, i and ii), starting from **2** obtained by Scheme 3 or from the unsymetrical diamine **6**. Diamine **6** is obtained by transamination from bis(dimethylamino)dimesitylgermane (eq. 5).

$$Mes_2Ge(NMe_2)_2 + H_2N\text{-}C_6H_4\text{-}NO_2 \xrightarrow[-\ Me_2NH]{36h,130°C} \underset{\displaystyle NMe_2}{\overset{\displaystyle |}{Mes_2Ge}}\text{-}NH\text{-}C_6H_4\text{-}NO_2 \quad \text{(eq.5)}$$

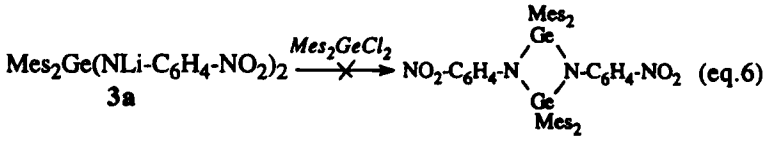
6

Both elimination reactions (Scheme 4, i and ii) yielded a dark red amorphous powder identified as germa-imine **5**. We never obtained the oligomeric cyclogermazane, confirming that germa-imine **5** is more stable thermally than the N-mesityl- or N-phenyl-substituted germa-imines pre-



SCHEME 4

viously characterized as transient species[15,16,17]. This germazane is not obtained by the usual method of preparation of such compounds[15] (eq. 6), probably because of the steric effects of the aromatic substituents both on nitrogen and on the metal. The × ray structure of **3** (Figure 1) shows that the aromatic substituents (Mes or $NPhNO_2$) adopt a propeller like disposition around a tetrahedral germanium, the hydrogen atoms on N1 and N3 being in « trans » positions. Furthermore, the shortening of the N1-C19 and N3-C25 is consistent with a conjugation of the lone pair on nitrogens with the phenyl rings. Nitrogen N3 is nearly planar (Σ angles: 359.2°), while N1 is only sligthly pyramidal (Σ angles: 351.1°) Table I. The electron withdrawing 4-nitro substituents, chosen to stabilise germa-imine **5** and prevent its dimerisation, also impede the formation of cyclodigermazane from equation 6.



(eq.6)

TABLE I selected bond lengths (Å) and angle (°) for germyldiamine **3**

Ge1-N3	1.835(4)	N3-Ge1-N1	103.22(17)
Ge1-N1	1.844(4)	N3-Ge1-C10	118.02(17)
Ge1-C10	1.940(3)	N1-Ge1-C10	102.58(15)
Ge1-C1	1.945(4)	N3-Ge1-C1	102.05(16)
N1-C19	1.382(5)	N1-Ge1-C1	118.95(17)
N3-C25	1.391(5)	C19-N1-Ge1	131.7(3)
N3-H	0.731	H-N3-C25	104.70
N1-H	0.642	H-N3-Ge1	123.61
		C25-N3-Ge1	130.9(3)
		H-N1-Ge1	102.77
		H-N1-C19	116.64

Germa-imine **5** is very moisture-sensitive, its colour changing from deep red to orange and finally to yellow. A mass spectrometric analysis of the red powder, using DCi/CH_4, showed the ions M+1 and M+29 characteristic of germa-imine **5**. The formation of **7** (Scheme 4) confirms the germa-imine structure of **5**, since hydrolysis of the corresponding dimer would not lead to **7** or **8**, as previously established[18,19]. Addition of germanol (Scheme 4, v), such as **7**, to germa-imines was previously observed[20,21]. However, **7** being not too sterically hindered can undergo intermolecular dehydratation to **8** (Scheme 4, vi). Therefore, **8** can be formed by either route v or vi of Scheme 4.

Germa-imine **5** is insoluble in benzene, pentane and ether, but soluble in THF, and it reacts readily with chloroform acting as a protic species. The adduct, as previously observed for such compounds[1,2], decomposes into the corresponding chloride **2** (Scheme 4, iii). The reaction transforming **5** into **2** is a further proof of the germa-imine structure when **5** is prepared from **6** (Scheme 4, i) or from **4**. It is also an easy way to determine by ^1H NMR the yields of **5** and **7**, on the one hand because **5** is less soluble in usual organic solvents than its hydrolysis products **7** and **8**, and on the other hand because **7** reacts with **5**(leading to **8**), but not with **2**.

Stoechiometric amounts of water react with **5** to form 4-nitrophenylamine and tetramesityldigermoxane (Scheme 5).

Dimesitylaminogermanol **7** was prepared in a pure form by slow hydrolysis of diamine **3** (Scheme 6). We could not obtain **7** from diamine **6** in

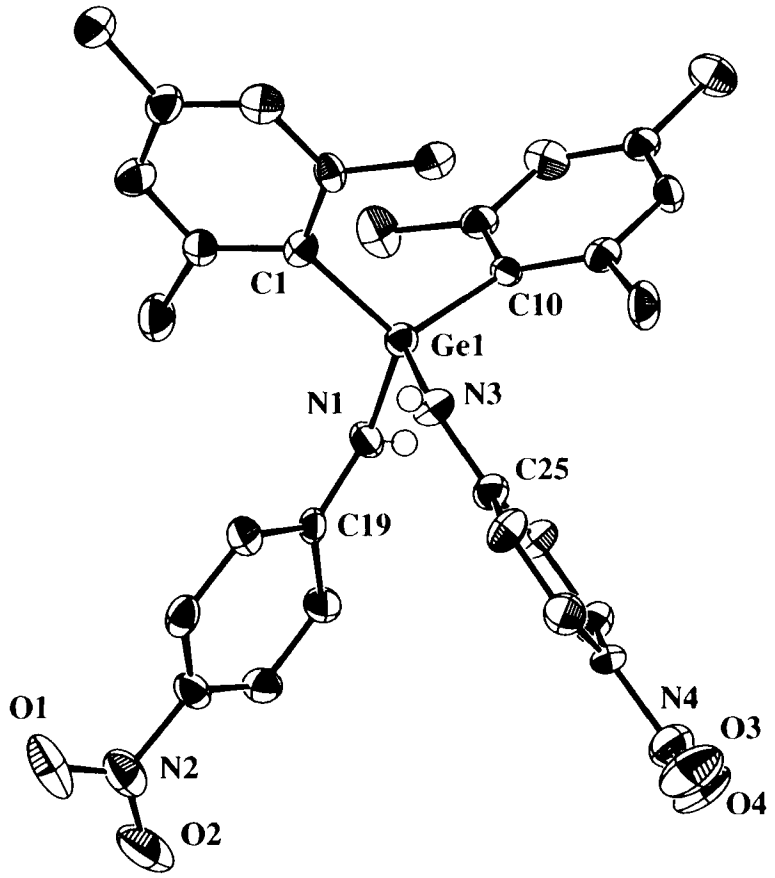
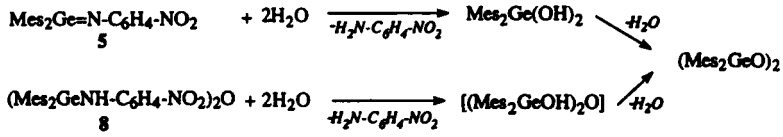


FIGURE 1 X ray structure of **3** displaying N1H and N3H in « trans ». Other hydrogens and two molecules of THF were omitted for clarity

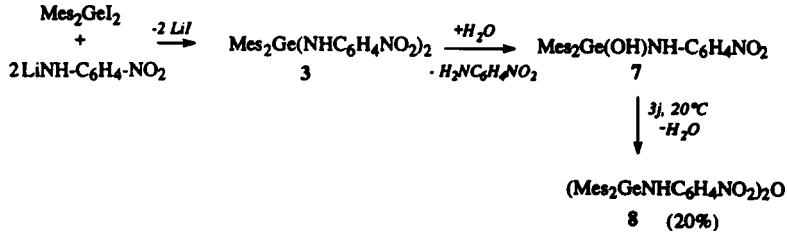
which the Ge-N-4-nitrophenyl bond is the first to be hydrolyzed. However, **7** is not thermally stable, its decomposition leads slowly to **8** and is easily followed by ^{1}H NMR at room temperature. Since **7** is observed only as a transient species in the presence of germa-imine **5**, we think that **8** in Scheme 4 is mainly formed by addition of germanol **7** to germa-imine **5** (Scheme 4, v), as previously observed with other stable germa-imines[20,21].

The use of the electron withdrawing 4-nitrophenyl substituent on nitrogen led to a stable germa-imine which is very reactive as it is not sterically



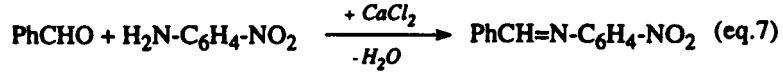
SCHEME 5

hindered. Besides additions to protic species (Scheme 4), 4-nitrophenyldimesitylgerma-imine **5** reacts easily with the 1–3 and 1–4 dipoles of N-t-butylphenylnitrone and 3,5-di-t-butyl ortho-quinone.

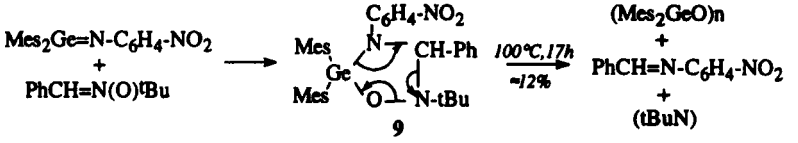


SCHEME 6

With N-t-butyl phenylnitrone (Scheme 7), **5** led to the adduct **9**. Like similar adducts obtained from other stable germa-imines[2,21], **9** is thermally stable at room temperature. However, after several hours of heating at 100°C, we detected small amounts of the decomposition products expected for the less sterically hindered diazagermaoxolanes[9] (Scheme 7). Benzylidene 4-nitrophenylimine was clearly identified by comparison with an authentic sample prepared by dehydratation between benzaldehyde and 4-nitrophenyl-amine (eq. 7).

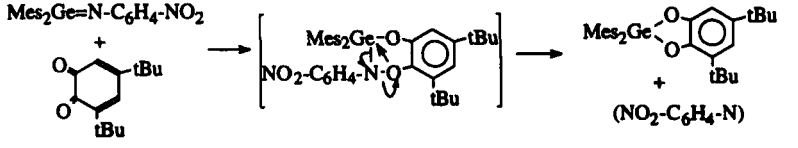


The addition of germa-imine **5** to 3,5-di-t-butyl ortho-quinone occurs at room temperature and is very similar to the reaction observed between the same quinone and another imino germanium compound, the dimesitylger-



SCHEME 7

mylidene p-toluenesulfonamide[1]. The reaction yields (Scheme 8) dimesitylgermadioxolane as the main product, as expected from thermal decomposition of similar 1–4 adducts[1,9,17,21,22]. There is no evidence of 1–2 addition to the carbonyl groups which would lead to other decomposition products[1,9,17,21,22].



SCHEME 8

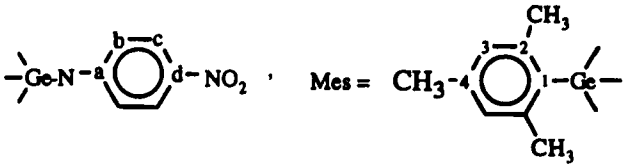
The formation of isobutene in the reaction confirms that the reaction occurs by single electron transfer in the first step as previously demonstrated[1] by the general reaction mechanism of that quinone with germanium-nitrogen compounds[9,22].

EXPERIMENTAL

All reactions were carried out under nitrogen or argon and with dry solvents. NMR spectra were recorded on Bruker AC80 (^{1}H) and AC 200 (^{13}C) spectrometers (δ ppm/TMS), ^{19}F on Bruker AC 80 (δppm/CF_3COOH); IR spectra on a Perkin-Elmer 1600 FT IR spectrometer; mass spectra on a HP 5989 instrument in the electron impact mode (70 eV) or on a Rybermag R10–10 spectrometer operating in the electron impact mode, or by chemical desorption (DCi/CH_4). Melting points were

measured on a Leitz microscope. Elemental analyses could not be obtained because all the new compounds were too moisture-sensitive.

Discrimination of carbons in ^{13}C NMR was achieved by the Jmod sequence. Identification of aromatic carbons is as follow:



N-triethylgermyl 4-nitrophenylamine 1

By transamination

In a Schlenk tube, the addition of Et_3GeNMe_2 (1.48 g, 7.2 mmol) to a solution of 4-nitroaniline (1.01 g, 7.2 mmol) in 8 ml of THF, gave immediate evolution of dimethylamine[23]. Evaporation of the solvents under vacuo resulted in 2.10 g of a slightly viscous liquid identified as **1**. Yield 98%.

B.P.: 150°C/0.2 mm Hg.IR: ($CDCl_3$) ν cm^{-1}: 3395 (NH). ^1H NMR ($CDCl_3$) δppm: 1.07 (s, 15H, EtGe); 3.99 (s, 1H, NH); 6.46 (d, 2H, Hb, $^3J_{HH}$: 9Hz); 7.97 (d, 2H, Hc, $^3J_{HH}$: 9Hz); (C_6D_6) δppm: 0.76 – 0.86 (m, 15H, EtGe); 3.36 (s, 1H, NH); 6.08 (d, 2H, Hb, $^3J_{HH}$: 9 Hz); 7.99 (d, 2H, Hc, $^3J_{HH}$: 9 Hz). ^{13}C NMR ($CDCl_3$) δ ppm: 6.44 (CH_2); 8.18 (CH_3); 158.07 (Ca); 114.25 (Cb); 126.51 (Cc); 137.17 (Cd).

^{13}C NMR (C_6D_6) δ ppm: 6.34 (CH_2); 8.21 (CH_3); 157.45 (Ca); 114.35 (Cb); 126.50 (Cc); 138.28 (Cd). MS(Ei) $M^{+\cdot}$ = 298 (25%); $M^{+\cdot}$ – Et = 269 (100%).

By dehydrohalogenation

Triethylchlorogermane (2.81 g, 14.4 mmol) was added to a solution of 4-nitroaniline (2.00 g, 14.4 mmol) and DBU (2.20 g, 14.4 mmol) in 10 ml of THF. DBU, HCl was filtered after 3h of stirring at 20°C. Evaporation of the solvent under vacuo gave 4.24 g of nearly pure **1** (yield 98%), which was distilled affording 2.5 g of pure **1**. Yield 59%.

Another attempt using Et_3N instead of DBU gave a mixture of **1** (50%), Et_3GeCl (25%), and H_2N-C_6H_4-NO_2 (25%). The reaction mixture when

heated in a sealed tube for 3 days at 80°C, led also to **1** (60%) in a mixture with the starting materials.

By transmetallation between LiNH-C_6H_4-NO_2 and Et_3GeCl

To diisopropylaminolithium, prepared by addition at 20°C of t-BuLi (1.7 M in pentane, 2.13 ml, 3.6 mmol) to diisopropylamine (0.36 g, 3.6 mmol) in 7 ml of ether stirred for 1 hour at room temperature, a solution of 4-nitroaniline (0.50 g, 3.6 mmol.) in 5 ml of THF was added dropwise with stirring. After 30 min. further stirring, Et_3GeCl (0.70 g, 3.6 mmol) was added dropwise. After 15 min. further stirring, LiCl was centrifuged and the solvents evaporated under vacuo, resulting in 0.95 g of **1**. Yield 88%.

A similar reaction using t-BuLi instead of iPr_2NLi to prepare LiNH-C_6H_4-NO_2 led to **1** in a mixture with unidentified decomposition products.

N-dimesitylchlorogermyl-4-nitrophenylamine 2

Attempt by dehydrohalogenation

To Mes_2GeCl_2 (2.01 g, 5.2 mmol) in 14 ml of THF, was added a mixture of H_2N-C_6H_4-NO_2 (0.72 g, 5.2 mmol) and DBU (0.80 g, 5.2 mmol) in 6 ml of THF. After 5h at room temperature with stirring and filtration of DBU.HCl, the solvents were evaporated under vacuo. The remaining residue, when analyzed by ^1H NMR, showed Mes_2GeCl_2 (38%), diamine **3** (28%), and N-dimesitylchlorogermyl-4-nitrophenylamine **2** (34%). Characteristics of **2** (**2** is obtained as a pure sample using Scheme 3) .

M.P.: 98–100°C. IR: ($CDCl_3$) ν cm^{-1}: 3386 (NH). ^{1}HNMR ($CDCl_3$) δppm: 2.36 (s, 12H, oMe); 2.24 (s, 6H, pMe); 4.95 (s, 1H, NH); 6.85 (s, 4H, C_6H_2); 6.53 (d, 2H, Hb, $^3J_{HH}$: 9Hz); 7.81 (d, 2H, Hc, $^3J_{HH}$: 9Hz); (C_6D_6) δppm: 2.36 (s, 12H, oMe); 2.05 (s, 6H, pMe); 4.95 (s, 1H, NH); 6.70 (s, 4H, C_6H_2); 6.34 (d, 2H, Hb, $^3J_{HH}$: 9Hz); 7.84 (d, 2H, Hc, $^3J_{HH}$: 9Hz). ^{13}C NMR ($CDCl_3$) δ ppm: 154.53 (Ca); 115.47 (Cb); 125.93 (Cc); 130.67 (Cd); Mes: 22.81 (oMe); 21.05 (pMe); 138.63 (C1); 143.08 (C2); 130.37 (C3); 141.02 (C4). MS(Ei) $M^{+\cdot}$ = 484 (10%).

Atttempt by transmetallation between LiNH-C_6H_4-NO_2 and Mes_2GeCl_2

LiNH-C_6H_4-NO_2 (3.6 mmol) prepared as for **1**, was added to dimesityldichlorogermane (1.38 g, 3.6 mmol) in 10 ml of THF, at room temperature

with stirring. After centrifugation of LiCl and evaporation of the solvents under vacuo, analysis by ^{1}H NMR showed Mes_2GeCl_2 (50%) and diamine **3** (50%). The mixture when treated with ether gave pure **3**, the dichlorogermane Mes_2GeCl_2 remaining in ether solution.

Attempt by transamination

4-nitrophenylamine (0.28 g, 2.1 mmol) in 4 ml of THF solution when added dropwise with stirring to $Mes_2Ge(Cl)NMe_2$ (0.80 g, 2.1 mmol) did not lead to evolution of dimethylamine even after 17h of heating at 80°C.

Thermal stability of 2

A solution of **2** in $CDCl_3$, under dry nitrogen, when examined by ^{1}H NMR after 24h at room temperature did not show any transformation into diamine **3** and dimesityldichlorogermane.

A similar study using equimolecular amounts of Mes_2GeCl_2 and **3** failed to show the formation of **2**.

Bis-(4-nitrophenylamino)dimesitylgermylamine 3

By transmetallation between LiNH-C_6H_4-NO_2 and Mes_2GeI_2

a) preparation of Mes_2GeI_2

To Mes_2GeH_2[24] (5.01 g, 16 mmol) in 20 ml of dry THF and catalytical amounts of AIBN (azo-bis-isobutyronitrile) was added an excess of methyl iodide (7.98 g, 56 mmol). the mixture was heated at 100°C for 18h in a sealed tube. Evaporation of solvents under vacuo led to 8.57 g of Mes_2GeI_2. Yield 95%.

M.P.: 149–150°C. ^{1}H NMR ($CDCl_3$) δppm: 2.62 (s, 12H, oMe); 2.35 (s, 6H, pMe); 6.86 (s, 4H, C_6H_2). ^{13}C NMR ($CDCl_3$) δ ppm: 24.10 (oMe); 21.31 (pMe); 142.28 (C1); 140.48 (C2); 130.43 (C3); 134.87 (C4). MS (Ei) ($M^{+\cdot}$ -I) = 439 (100%); ($M^{+\cdot}$-Mes) = 447 (10%).

b) preparation of **3** from Mes_2GeI_2

Mes_2GeI_2 (1.02 g, 1.81 mmol) was added to LiNH-C_6H_4-NO_2 (1.81 mmol) prepared as for **1**, in 8 ml of THF at room temperature with stirring. After one hour of further stirring, 7/8 of the THF was replaced by benzene and the solution was centrifuged to eliminate the lithium salt. The remaining solution when concentrated under vacuo gave crude **3**. This res-

idue after being washed several times with Et_2O to eliminate traces of Mes_2GeI_2, afforded 0.94 g of pure yellow powder of **3**. Yield 89%.

M.P: 195°C. IR: ($CDCl_3$) ν cm^{-1}: 3385 (NH). ^1H NMR ($CDCl_3$) δppm: 2.41 (s, 12H, oMe); 2.29 (s, 6H, pMe); 4.52 (s, 2H, NH); 6.90 (s, 4H, C_6H_2); 6.54 (d, 4H, Hb, $^3J_{HH}$: 9Hz); 7.86 (d, 4H, Hc, $^3J_{HH}$: 9Hz). ^{13}C NMR ($CDCl_3$) δ ppm: 154.06 (Ca); 115.45 (Cb); 126.02 (Cc); 130.57 (Cd); Mes: 22.78 (oMe); 21.02 (pMe); 139.02 (C1); 143.01 (C2); 130.48 (C3); 141.19 (C4). MS (DCi/CH_4): $(M+1)^+$= 587 (10%).

c) preparation of **3** from Mes_2GeCl_2

iPr_2NLi (7.86 mmol) prepared from iPr_2NH (7.86 mmol, 1.5 M in pentane) was added to the 4-nitrophenylamine (7.86 mmol, 1.08 g) in 4 ml of THF. After one hour stirring at room temparature, Mes_2GeCl_2 (3.93 mmol, 1.5 g) in 5 ml of THF was added to the mixture. After further stirring for 4 hours, THF was evaporated under vacuo and replaced by benzene. LiCl was then centrifuged. The evaporation of the benzene gave a powder which was then washed twice with ether affording 2.31 g of **3**. Yield: 85%. **3** was recristallized in a mixture THF/ether at −30°C affording crystals suitable for X-ray analysis.

Thermal stability of 3

Diamine **3** (0.10 g, 0.17 mmol) dissolved in THF was placed in a sealed tube and heated at 120°C for 1 day, without change.

N-dimesitylfluorogermyl-4-nitrophenylamine 4

By transmetallation between LiNH-C_6H_4-NO_2 and Mes_2GeF_2

LiNH-C_6H_4-NO_2 (1.80 mmol) prepared as before was added dropwise over 1h to Mes_2GeF_2 (0.63 g, 1.8 mmol) in 4 ml of THF. After further stirring for 0.5h, THF was evaporated under vacuo and the residue when analyzed by ^1H NMR showed the presence of **4** (70%) and diamine **3** (30%). The residue was washed six times with 5 ml of Et_2O leaving a powder of **3** and LiF. Evaporation of the solvent gave crude **4** which was then washed twice with pentane affording 0.41 g of **4** containing only 20% of **3**. Yield: 49%. ^1H NMR ($CDCl_3$) δppm: 2.29 (s, 12H, oMe); 2.40 (s, 6H, pMe); 4.67 (d, 1H, NH, $^3J_{HF}$: 3.2 Hz); 6.89 (s, 4H, C_6H_2); 6.69 (d, 2H, Hb, $^3J_{HH}$: 9Hz); 7.98 (d, 2H, Hc, $^3J_{HH}$: 9Hz). ^{13}C NMR ($CDCl_3$) δ ppm: 154.07

(Ca); 115.66 (Cb); 126.22 (Cc); 130.57 (Cd); Mes: 22.80 (oMe); 21.10 (pMe); 140.34 (C1); 143.59 (C2); 129.82 (C3); 141.59 (C4). ^{19}F NMR ($CDCl_3$) δppm: – 87.04 (s, GeF). MS (DCi/CH_4): $(M+1)^+$: 469 (2%); (Ei): ($M^{+\cdot}$- Mes) = 349 (10%).

Attempt to characterize N-4-nitrophenyldimesitylgerma-imine 5 from N-triethylgermyl N-dimesitylchlorogermyl-4-nitrophenylamine: isolation of pure 2

Transient N-triethylgermyl N-dimesitylchlorogermyl-4-phenylamine: in the presence of DBU,HCl (Scheme 3)

To a mixture of **1** (0.51 g, 1.7 mmol) and Mes_2GeCl_2 (0.65 g, 1.7 mmol) in 6 ml of THF was added dropwise under stirring DBU (0.26 g, 1.7 mmol). There was immediate formation of a white precipitate. After 30 min further stirring, CPV analysis and ^1H NMR showed the quantitative formation of Et_3GeCl and the disapearance of **1**. The filtered precipitate was identified as DBU.HCl (0,06 g; 20%). After evaporation of the solvent a light yellow residue resulted; it was washed twice with ether and identified as 0.49 g of pure **2**. Yield 74%.

The reaction required nucleophilic assistance from THF. The same mixture (**1**, DBU, Mes_2GeCl_2) in benzene did not give DBU.HCl, even after 17h of heating at 130°C.

Treatment of a 1/1 mixture of 1 and Mes_2GeCl_2

A 1 to 1 mixture of **1** and Mes_2GeCl_2 in THF was heated in a sealed tube for 18h at 80°C without formation of triethylchlorogermane. The starting materials were recovered unchanged.

Preparation of 6

A) preparation of $Mes_2Ge(NMe_2)_2$

Mes_2GeCl_2 (2.44 g, 6.4 mmol) in 25 ml of benzene was added to dimethylaminolithium (12.8 mmol) in 10 ml of THF. The mixture was placed in a Carius tube and heated for 5 days at 80°C after which THF was replaced by benzene and the LiCl filtered. Evaporation of the solvent led to 1.65 g of a very viscous liquid identified as $Mes_2Ge(NMe_2)_2$. Yield: 65%. ^1H

NMR ($CDCl_3$) δppm: 2.23 (s, 18H, o+ p Me); 6.74 (s, 4H, C_6H_2); 2.54 (s, 12H, NMe_2); (C_6D_6) δppm: 2.35 (s, 12H, o-Me); 2,10 (s, 6H, p-Me); 6.72 (s, 4H, C_6H_2); 2.61 (s, 12H, NMe_2). ^{13}C NMR ($CDCl_3$) δ ppm: 22.68 (oMe); 21.01 (pMe); 40.68 (NMe_2); 135.65 (C1); 143.18 (C2); 128.81 (C3); 138.10 (C4). MS (Ei) $M^{+\cdot}$ = 400 (5%); ($M^{+\cdot}$ -NMe_2) = 356 (100%).

B) preparation of 6 by transamination from $Mes_2Ge(NMe_2)_2$ and H_2N-C_6H_4-NO_2

A mixture of $Mes_2Ge(NMe_2)_2$ (0.50 g, 1.25 mmol) and 4-nitrophenylamine (0.17 g, 1.25 mmol) in 3 ml of dry THF solution was heated in a sealed tube for 36 hours at 130°C. The solvents were evaporated under vacuo leaving a brown residue of crude **6**. The residue was washed twice with pentane yielding 0.61 g of a light brown powder of pure **6**. Yield: 98%.

M.P.: 62–64°C. I.R. ($CDCl_3$); 3386 cm^{-1}(NH). ^1H NMR ($CDCl_3$) δppm: 2.35 (s, 12H, o- Me); 2.25 (s, 6H, p-Me); 4.36 (s, 1H, NH); 2.52 (s, 6H, NMe_2); 6.84 (s, 4H, C_6H_2); 6.52 (d, 2H, Hb, $^3J_{HH}$: 9Hz); 7.98 (d, 2H, Hc, $^3J_{HH}$: 9Hz); (C_6D_6) δppm: 2.33 (s, 12H, o-Me); 2.08 (s, 6H, p-Me); 4.05 (s, 1H, NH); 2.42 (s, 6H, NMe_2); 6.70 (s, 4H, C_6H_2); 6.14 (d, 2H, Hb, $^3J_{HH}$: 9Hz); 7.95 (d, 2H, Hc, $^3J_{HH}$: 9Hz);^{13}C NMR ($CDCl_3$) δ ppm: 156.27 (Ca); 115.73 (Cb); 126.04 (Cc); 132.77 (Cd); Mes: 22.38 (oMe); 21.04 (pMe); 39.62 (NMe_2); 137.95 (C1); 143.44 (C2); 129.74 (C3); 139.72 (C4). MS (Ei) $M^{+\cdot}$ = 493; ($M^{+\cdot}$ -NMe_2) = 449; ($M^{+\cdot}$ – $HNPhNO_2$)= 356.

Preparation of 5

By dehydrohalogenation of 4

The aminolithium derivative of **4** (0.88 mmol) was obtained by addition of diisopropylaminolithion (0.88 mmol.) to **4** (0.41 g of 80% purity, containing 20% of **3**) in 5 ml of THF at –56°C. The yellow solution turns to blood red. The reaction was followed by ^1H NMR. Elimination of LiF was very slow (about 3 days at 20°C to obtain the full disappearance of the starting dimesityfluorogermyl compound). ^1H NMR analysis in $CDCl_3$ showed formation of compounds **8** (70 %) (by hydrolysis of **5**) in a mixture with **2** (10 %) (by addition of $CHCl_3$ to **5**), besides the remaining impurity [**3** in the starting material **4** (20%)].

Dehydrohalogenation of 2

The aminolithium derivative of **2** (0.82 mmol) was obtained by slow addition (3h) at –60°C of iPr_2NLi (0.82 mmol) to **2** (0.40 g, 0.82 mmol). The mixture was warmed to room temperature. After 3h at room temperature, a ^1H NMR sample of the mixture in C_6D_6 showed complete disappearance of the starting germylated material. Only the hydrolysis products of **5** were detected in the C_6D_6 solution (**7** 66%; **8** 33 %). The mixture was then centrifuged to remove LiCl and THF was evaporated in vacuo. The residue was washed twice with ether leaving 0.22 g of a deep red powder of **5**. Yield 59%.

M.P.: 112–114°C. ^1H NMR (THF D8) δppm: 2.38 (s, 18H, o- Me); 2.18 (s, 6H, p-Me); 6.83 (s, 4H, C_6H_2); 6.67 (d, 2H, Hb, $^3J_{HH}$: 9Hz); 7.74 (d, 2H, Hc, $^3J_{HH}$: 9Hz). ^{13}C NMR (THF D8) δ ppm: 156.28 (Ca); 118.28 (Cb); 125.80 (Cc); 139.07 (Cd); Mes: 23.50 (oMe); 20.90 (pMe); 136.45 (C1); 143.41 (C2); 130.60 (C3); 139.07 (C4). MS (DCi/CH_4): $(M+1)^+$ =449 (21%); (M+29)= 477 (37%).

Evaporation of the ether solution gave a mixture of **7** (40%) and **8** (60%). The mixture when heated at 100°C for 5h led to 0.12 g of an orange powder of **8**. Yield 32%.

The same reaction mixture (same proportions, processed in the same way but without isolating **5**) was transferred under air and heated at 100°C for 5 hours in a Carius tube. After centrifugation of LiCl and evaporation of the solvents, a dark residue was obtained, which was extracted with 2 ml of Et_2O. The ether solution was evaporated under vacuo to give 0.31 g of an orange-brown powder of pure **8**. Yield 83%.

M.P.: 74–75°C with decomposition. IR ($CDCl_3$): 3346 cm^{-1} (NH). ^1HNMR ($CDCl_3$) δppm: 2.25 (s, 18H, o+p Me); 4.21 (s, 1H, NH); 6.79 (s, 4H, C_6H_2); 6.10 (d, 2H, Hb, $^3J_{HH}$: 9Hz); 7.77 (d, 2H, Hc, $^3J_{HH}$: 9Hz). ^1H NMR (C_6D_6) δppm: 2.32 (s, 12H, o-Me); 2.04 (s, 6H, p-Me); 4.26 (s, 1H, NH); 6.63 (s, 4H, C_6H_2); 6.10 (d, 2H, Hb, $^3J_{HH}$: 9Hz); 7.77 (d, 2H, Hc, $^3J_{HH}$: 9Hz). ^{13}C NMR ($CDCl_3$) δ ppm: 154.63 (Ca); 115.08 (Cb); 125.89 (Cc); 133.66 (Cd); Mes: 23.22 (oMe); 21.08 (pMe); 138.42 (C1); 142.84 (C2); 130.12 (C3); 140.85 (C4). ^{13}C NMR (C_6D_6) δ ppm: 154.21 (Ca); 115.33 (Cb); 125.96 (Cc); 134.17 (Cd); Mes: 23.43 (oMe); 20.98 (pMe); 139.52 (C1); 143.04 (C2); 130.45 (C3); 140.87 (C4). MS (DCi/CH_4): (M+1) = 913 (78%); (M+29) = 941 (17%).

Elimination from 6

$Mes_2Ge(NMe_2)NH\text{-}C_6H_4\text{-}NO_2$ **6** (0.20 g, 0.41 mmol) in 2 ml of THF was placed in a Carius tube and heated for 20 h at 155°C. Evaporation of Me_2NH and the solvent under vacuo left a deep red sticky powder whose ^1H NMR in chloroform showed 30% of unreacted **6** and 70% of **2** characteristic of the addition of **5** to chloroform.

Hydrolysis of 5

A solution of **5** (0.08 g, 0.18 mmol) in THF (not dried) allowed the characterization by mass spectrometry of **7** and **8** besides the molecular ions of **5**.

MS (DCi/CH_4): **5** $(M+1)^+$= 449 (32%); $(M+29)^+$= 477 (22%); $Mes_2Ge(OH)NH\text{-}C_6H_4\text{-}pNO_2$ **7**: $(M+1)^+$= 467 (7%); $(M+29)^+$= 495 (30%); $(Mes_2GeNHC_6H_4\text{-}pNO_2)_2O$ **8**: $(M+1)^+$= 913 (78%); $(M+29)^+$= 941 (16%).

The red powder of **5** left in a Schlenk tube slowly (5 to 10 h) changed from red to orange and then yellow. After three weeks, ^1H NMR analysis showed complete disappearance of **5** and a mixture of $Mes_2Ge(OH)_2$ (11 %), $(Mes_2GeO)_2$(38 %), and $H_2N\text{-}C_6H_4\text{-}NO_2$ (51%).

4-nitrophenylaminodimesitylgermanol 7 from hydrolysis of 3

The powder of **3** (0.50 g, 0,85 mmol) was left in a Schlenk tube for 7 to 10 days. Then, the powder was washed with benzene. After evaporation of the benzene solution, 0.05 g resulted of a yellow residue of nearly pure **7** analyzed in C_6D_6. Yield 12%.

IR (C_6D_6): 3370 cm^{-1} (NH); 3375 cm^{-1} (shoulder, OH). ^1H NMR (C_6D_6) δppm: 2.26 (s, 12H, o-Me); 2.05 (s, 6H, p-Me); 4.11 and 3.90 (s, OH, NH); 6.68 (s, 4H, C_6H_2); 6.02 (d, 2H, Hb, $^3J_{HH}$: 9Hz); 7.81 (d, 2H, Hc, $^3J_{HH}$: 9Hz). ^{13}C NMR (C_6D_6) δppm: 153.88 (Ca); 115.52 (Cb); 125.88 (Cc); 138.79 (Cd); Mes: 22.82 (oMe); 20.96 (pMe); 139.67 (C1); 143.29 (C2); 130.63 (C3); 141.17 (C4).

Slow hydrolysis of **6** never led to **7** but to $H_2N\text{-}C_6H_4\text{-}NO_2$ and the corresponding germylhydroxide and oxides.

Attempt to prepare N,N′-4-nitrophenyl tetramesitylcyclodigermazane, caracterisation of 3a

A) characterization of 3a

To diamine **3** (0.41 g, 0.69 mmol) in 5 ml of THF was added iPr_2NLi (1.39 mmol) in 2 ml of Et_2O. After 2h stirring at room temperature, the inhomogenous reaction mixture was centrifuged. The precipitate (0.04 g, 10%) was identified as unreacted **3**. The liquid phase, by evaporation of THF under vacuo, yielded an orange-brown powder of the lithium derivative **3a**.

M.P.: decomposition. ^1H NMR (DMSO) δppm: 2.31 (s, 12H, o-Me); 2.13 (s, 6H, p-Me); 6.56 (s, 4H, C_6H_2); 6.36 (d, 4H, Hb, $^3J_{HH}$: 9Hz); 7.73 (d, 4H, Hc, $^3J_{HH}$: 9Hz). **3a** treated with chloroform led to diamine **3**.

B) addition of Mes_2GeCl_2 on 3a

3a was prepared from **3** (0.48 g, 0.82 mmol) and iPr_2NLi (1.64 mmol) as before. After 2h of stirring at room temperature, Mes_2GeCl_2 (0.31 g, 0.82 mmol) in 3 ml of THF was added to the THF solution of **3a**. After 4h at room temperature with no precipitation of LiCl, the reaction mixture was placed in a Carius tube and heated for 3 days at 100°C. Evaporation of the solvents under vacuo led to a black sticky residue unidentifiable by NMR, but in which, mass spectroscopic analysis (DCi/CH_4) showed **3** (7%), $(Mes_2GeO)_3$(M+1: 981, 35%) and no ion characteristic of the expected digermazane. The same experiment but with the reaction mixture heated at 85°C for 24h led to similar results.

Addition of 5 to N-t-butyl phenylnitrone

Germa-imine **5** (0.04 g, 0.08 mmol) and N-t-butylphenylnitrone (0.014 g, 0.08 mmol) in 1 ml of C_6D_6 were heated in a Carius tube for 17h at 100°C. ^1H and ^{13}C NMR analysis allowed the detection of 49% of the adduct **9** soluble in C_6D_6, besides the hydrolysis product **8** (29%), tetramesityldigermoxane (11%) and benzylidene 4-nitrophenylimine (9%). The last compound was clearly identified by ^{13}C NMR and mass spectroscopy by comparison with an authentic sample.

Spectroscopic characteristic of **9**: ^1H NMR (C_6D_6) δppm: 2.60 (s, 12H, o-Me); 2.05 (s, 6H, p-Me); 6.54 (s, 4H, C_6H_2); 5.99 (d, 2H, Hb, $^3J_{HH}$:

9Hz); 7.93 (d, 2H, Hc, $^3J_{HH}$: 9Hz); 8.36–8.49 (m, 3H, C_6H_5); 7.10–7.20 (m, 3H, CH-C_6H_5); 1.27 (s, 9H, tBu). ^{13}C NMR (C_6D_6) δppm: 154.37 (Ca); 112.97 (Cb); 126.36 (Cc); 134.13 (Cd); Mes: 23.06 (oMe); 21.05 (pMe); 135.56 (C1); 143.10 (C2); 129.23 (C3); 138.82 (C4); CHPh: 130.45, 128.78, 129.63, 129.73; tBu: 28.14. MS (Ei) $M^{+\cdot}$ = 593 (100%); ($M^{+\cdot}$ -PhNO$_2$) = 489 (87%).

Benzilidene 4-nitrophenylamine

An authentic sample was obtained as follow: a mixture of benzaldehyde (0.302 g, 2.70 mmol), 4-nitrophenylamine (0.372 g, 2.70 mmol) and $CaCl_2$ (0.12 g) in 4 ml of THF was heated in a Carius tube for 22h at 90°C. The THF solution when concentrated under vacuo gave a yellow residue which was washed twice with 1ml of ether, leaving 0.17 g of a yellow powder of benzylidene 4-nitrophenylimine. Yield: 28%.

M.P.: 89°C. ^1H NMR ($CDCl_3$) δppm: 7.89–8.25 (m, 2H, C_6H_5); 7.49 (m, 4H, CHPh); 6.59 (d, 2H, Hb, $^3J_{HH}$: 9Hz); 8.10 (d, 2H, Hc, $^3J_{HH}$: 9Hz); (C_6D_6): 7.6–7.9 (m, 2H, C_6H_5); 7.17 (m, 3H, CH=C_6H_5); 6.65 (d, 2H, Hb, $^3J_{HH}$: 9Hz); 7.88 (d, 2H, Hc, $^3J_{HH}$: 9Hz). ^{13}C NMR ($CDCl_3$): 129.37 (C2); 129.06 (C3); 132.49 (C4); 121.34 (Cb); 125.13 (Cc); 162.77 (CH=); (C_6D_6): 129.53 (C2); 129.07 (C3); 132.38 (C4); 121.31 (Cb); 125.01 (Cc); 162.44 (CH=). MS. (Ei): $M^{+\cdot}$= 226 (100%); ($M^{+\cdot}$- HNO$_2$) = 179 (20%).

Addition of 5 to 3,5-di-t-butyl ortho-quinone

To germa-imine **5** (0.051 g, 0.11 mmol) was added a solution of quinone (0.025 g, 0.11 mmol) in 1 ml of C_6D_6. The mixture was kept in a sealed tube for 18h at room temperature, and then analyzed by ^1H and ^{13}C NMR. The heptuplet of isobutene was clearly visible in the ^1H NMR spectrum, but the main product of the reaction was dimesitylgermadioxolane identified by comparison with an authentic sample[25].

^1H NMR (C_6D_6) δppm: 2.49 (s, 12H, oMe); 2.00 (s, 6H, pMe); 6.60 (s, 4H, C_6H_2); 1.35 (s, 9H, tBu); 1.62 (s, 9H, tBu); 7.09 (d, 1H, H4); 7.32 (d, 1H, H6, $^3J_{HH}$: 6Hz). Besides the characteristic ions of dimesitylgermadioxolane [Ei: $M^{+\cdot}$ = 532 (90%); $M^{+\cdot}$-Me = 517 (88%)], a mass spectroscopic analysis of the reaction mixture showed ions belonging to the adduct of germa-imine **5** with quinone [$M^{+\cdot}$-Me = 653 (5%); $M^{+\cdot}$-2Me = 637 (10%)] and to ($NO_2C_6H_4N)_2$($M^{+\cdot}$- 2O$_2$ = 208 (2%).

X-Ray analysis of 3

Crystal data for **3**: $C_{38}H_{48}GeN_4O_6$, M = 729.39, orthorhombic, Pbca, a = 15.816(1) Å, b = 15.924(2) Å, c = 28.578(2) Å, V = 7197.5(11) Å^3, Z = 8, ρ_c 1.346 Mg m^{-3}, *F(000)* = 3072, λ = 0.71073 Å, T = 173(2) K, μ (Mo Kα) = 0.903 mm^{-1}, crystal size 0.7 × 0.1 × 0.05 mm, 2.31° < Θ < 23.25°, 58825 reflections (5166 independent, R_{int}= 0.1575) were collected at low temperatures using an oil-coated shock-cooled crystal[26]on a STOE-IPDS diffractometer. The structure was solved by direct methods (SHELXS-97)[27] and 481 parameters using 47 restraints were refined using the least-squares method on F^2 [28]. Largest electron density residue: 0.203 e Å^{-3}, R_1 (for $F>2\sigma(F)$) = 0.031 and wR_2 = 0.054 (all data) with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. A disorder of a THF molecule was refined anisotropicaly using ADP and distances restraints.

Crystallographic data (excluding structure factors) for the structure of **3** have been deposited with the Cambridge Crystallographic Data center as supplementary publication n° CCDC-135929. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB21EZ, UK (fax(+44)1223–336–033; e-mail: deposit@ccdc.cam.ac.uk).

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