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An Eight-Membered Cyclic *C,N*-Bis(germadiyl) Bis(ketenimine)

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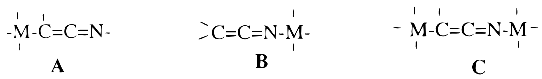
The reaction of *tert*-butyllithium with (fluorodimesitylgermyl)- and (chlorodimesitylgermyl)-phenylacetonitrile (**4a,b**) leads to the lithium salts **5a** (X = F) and **5b** (X = Cl), which exhibit an ambident character: $[{>}C^{-}{-}C{\equiv}N \leftrightarrow {>}C{=}C{=}N^{-}]Li^{+}$. Quenching of **5a** with triphenylbromomethane affords the germylketenimine **8**, $Mes_2FGeC(Ph){=}C{=}NCPh_3$. ^{1}H dynamic NMR spectroscopy allows the determination of the activation energy of the nitrogen inversion $\Delta G^* = 9.9 \pm 0.2$ kcal/mol. In the absence of a trapping reagent, **5** undergoes an elimination of lithium halide with formation of the eight-membered cyclic *C,N*-bis(germadiyl) bis(ketenimine) **1**, which is the first ring containing two ketenimine moieties. **1** has been characterized by IR (ν(C=C=N) 2015 cm^{-1}) and ^{13}C NMR spectroscopy (170.87 ppm for the sp carbon) and by an X-ray structure determination, which displays a "cyclohexane" type structure in a chair conformation.

Introduction

Ketenimines have attracted considerable attention because they are versatile synthetic reagents.[1] When substituted at nitrogen by heavy elements of Group 14 they may be useful synthons, due to the high reactivity both of the ketenimine moiety and of the Group 14 metal-nitrogen bond. Some silylketenimines[2] of type A, B or C and stannylketenimines[3] of type C have been reported, but no germylketenimines have been characterized or isolated thus far (Chart 1).

We report here the synthesis of two germanium-containing ketenimines, one of type A (**8**) and the other of type C (**1**). The latter represents a new class of compounds, since it contains two germanium−ketenimine moieties in a ring.

Chart 1



(M: Si, Sn)

Results and Discussion

The synthesis of **1** is based on the previous preparation of (fluorodimesitylgermyl)- and (chlorodimesitylgermyl)phenylacetonitrile (**4a,b**) by reaction of α-lithiophenylacetonitrile (**2**) in THF with the dihalodimesitylgermane **3** at −78 °C. **4a** can be converted quantitatively to **4b** upon refluxing in concentrated HCl. The products **4** were characterized by their spectroscopic data. As expected, in their ^{1}H and ^{13}C NMR spectra the two mesityl groups were nonequivalent and the IR spectra showed the characteristic C≡N vibrations at 2229 (**4a**) and 2215 (**4b**) cm^{-1} (Scheme 1).

Addition of *t*-BuLi to colorless solutions of **4** in Et_2O at −78 °C gave immediately deep yellow solutions which slowly lost their color with the formation of a precipitate of the lithio compounds **5**. When suspensions of **5** were warmed to room temperature, a lemon yellow compound precipitated after stirring overnight at 20 °C. After its purification by crystallization, spectroscopic studies showed it to be the bis(ketenimine) **1** (Scheme 2).

In ^{1}H NMR spectrum of **1** the four mesityl groups appear equivalent. Of course, the molecule has a center of symmetry and is not chiral, but the two mesityl

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(1) (a) Michael, J. P.; De Koning, C. B. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Elsevier: New York, 1995; Vol. 3, Chapter 3.17, p 555. (b) Aumann, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1456. (c) Gambaryan, N. P. *Russ. Chem. Rev. (Engl. Transl.)* **1976**, *45*, 630. (d) Krow, G. R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 435.

(2) (a) Matsuda, I.; Okada, H.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 528. (b) Okada, H.; Matsuda, I.; Izumi, Y. *Chem. Lett.* **1983**, 97. (c) Gabriel, A. O.; Riedel, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 384. (d) Prober, M. *J. Am. Chem. Soc.* **1956**, *78*, 2274. (e) Gillette, G. R.; Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1429. (f) Differding, E.; Vandevelde, O.; Roekens, B.; Van, T. T.; Ghosez, L. *Tetrahedron Lett.* **1987**, *28*, 397. (g) Yamakado, Y.; Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1981**, *103*, 5568. (h) Seyferth, D.; Langer, P.; Döring, M. *Organometallics* **1995**, *14*, 4457. (i) Sato, Y.; Niinomi, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 56. (j) Gillette, G. R.; Igau, A.; Baceiredo, A.; Bertrand, G. *New J. Chem.* **1991**, *15*, 393.

(3) Miller, E.; Sommer, R.; Neumann, W. P. *Liebigs Ann. Chem.* **1968**, *718*, 1.

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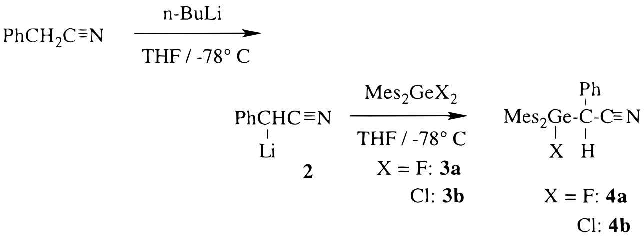
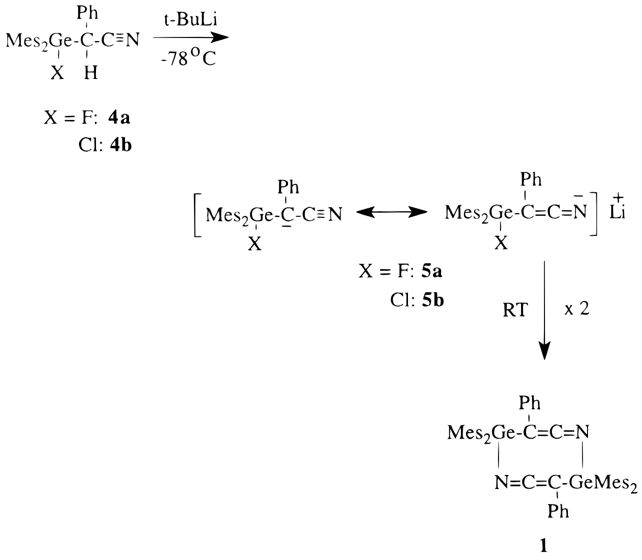
Scheme 1



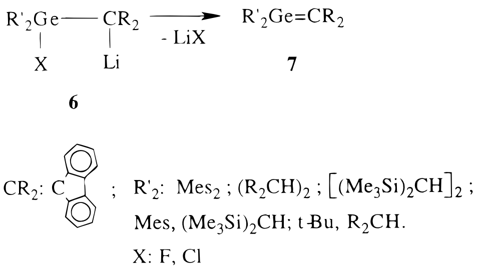
Scheme 2



groups on each germanium atom should be different. Since **1** has a “cyclohexane” type structure (see the X-ray structure determination), they are in “axial” and “equatorial” positions. However, attempts to differentiate them were unsuccessful, even at −100 °C. Such a result is not surprising, since the rapid axial−equatorial equilibrium generally occurs at even very low temperature. Also, the steric strain in **1** probably is not very high. The ^{13}C NMR spectrum shows a signal at 170.87 ppm, characteristic of the sp carbon of the C═C═N moiety.[1,4] The ketenimine structure was also evidenced in the IR spectrum by a strong band at 2015 cm^{-1}.[1] **1** is the first germanium-containing ketenimine and also the first compound with two ketenimine moieties in the same heterocycle. It is unexpectedly stable compared with the only known eight-membered cyclic ketenimine,[5] which was obtained as an unstable oil.

1 is poorly soluble in the usual organic solvents. It can be handled in air for some minutes without decomposition. The Ge−N bond, which generally is very reactive[6] and is easily cleaved by water, is relatively stable in this case, probably due to the steric protection caused by the bulky mesityl groups.[7] However, yellow solutions of **1** in commercial grade benzene or diethyl ether become colorless after 2 days because of decomposition.

Scheme 3



Elimination of lithium halide from ((halogermyl)-fluorenyl)lithium derivatives **6** generally occurs at low temperature to afford the corresponding germenes **7**[8−10] (Scheme 3). In contrast, in the case of **5**, such elimination of LiX, leading to germaacrylonitrile $Mes_2Ge{=}C(Ph)CN$, has never been observed.

The ambident character of intermediate Li salt **5a** was confirmed by trapping reactions with electrophiles. Thus, quenching of **5a** with Ph_3CBr at 20 °C quantitatively gives the germylketenimine **8** (Scheme 4). In contrast, when **5a** was quenched with Me_2SO_4 or MeI, only the C-alkylation product **9** was isolated in good yield. This result could be explained by steric control of the reaction, which leads to N-alkylation in the case of the bulky Ph_3C group and to C-alkylation with the less sterically hindered methyl group.

However, we cannot completely exclude an alternative possibility for the formation of **9**: previous N-alkylation of **5a** leading to the intermediate **10** followed by a ketenimine−nitrile rearrangement. Examples of such conversion have been previously reported.[11]

The presence of the ketenimine moiety in **8** was evidenced by a strong band at 2011 cm^{-1} in the IR spectrum[1] and by a low-field signal at 173.89 ppm in the ^{13}C NMR spectrum, which is characteristic for the sp carbon.[1,4]

Due to the chiral >C═C═N− moiety in **8**, the two mesityl groups are diastereotopic. However, in the ^{1}H NMR spectrum the two mesityl groups appeared equivalent, because of the rapid inversion of nitrogen. Low-temperature ^{1}H dynamic NMR spectra allowed the determination of the coalescence temperature of the *o*-Me groups of the mesityl groups (−55 °C) and of the activation energy of the nitrogen inversion ($\Delta G^* = 9.9 \pm 0.2$ kcal/mol). Such a value corresponds to the previously reported data for other N-substituted ketenimines.[12,13] Owing to the large steric hindrance caused

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[4] Firl, J.; Runge, W.; Hartmann, W.; Utikal, H. P. *Chem. Lett.* **1975**, 51.

[5] Firl, J.; Schink, K.; Kosbahn, W. *Chem. Lett.* **1981**, 527.

[6] Rivière, P.; Rivière-Baudet, M.; Satgé, J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol. 2, Chapter 5, p 139.

[7] For example, Mes_3GeNH_2 is very stable toward moisture due to the steric protection of the Ge−N bond: Rivière-Baudet, M.; Morere, A.; Britten, J. F.; Onyszchuk, M. *J. Organomet. Chem.* **1992**, *423*, C5.

[8] Couret, C.; Escudié, J.; Satgé, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, *109*, 4411.

[9] Lazraq, M.; Couret, C.; Escudié, J.; Satgé, J.; Soufiaoui, M. *Polyhedron* **1991**, *10*, 1153.

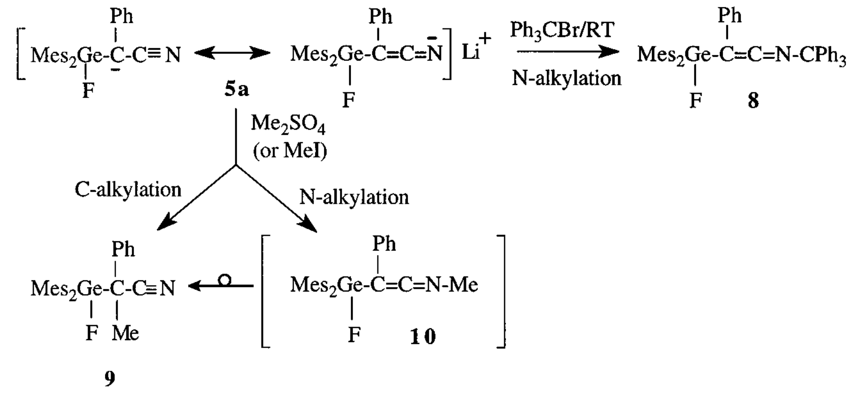
[10] Anselme, G.; Escudié, J.; Couret, C.; Satgé, J. *J. Organomet. Chem.* **1991**, *403*, 93.

[11] (a) A facile 1,3-rearrangement of the ketenimine $Ph_2C{=}C{=}NCHMePh$ to the nitrile $Ph_2C(CHMePh)C{\equiv}N$ has been reported by: Singer, L. A.; Lee, K. W. *J. Chem. Soc., Chem. Commun.* **1974**, 962. Lee, K. W.; Horowitz, N.; Ware, J.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 2622. (b) A similar rearrangement from the ketenimine $Me_3SiCH{=}C{=}NSiMe_3$ to the nitrile $(Me_3Si)_2CH{-}C{\equiv}N$ at room temperature has also been observed by Prober.[2d]

[12] (a) Jochims, J. C.; Herzberger, S.; Gambke, B.; Anet, F. A. L. *Tetrahedron Lett.* **1977**, *26*, 2255. (b) Jochims, J. C.; Lambrecht, J.; Burkert, U.; Zsolnai, L.; Huttner, G. *Tetrahedron* **1984**, *40*, 893. (c) Eberl, K.; Roberts, J. D. *Org. Magn. Reson.* **1981**, *17*, 180. (d) Jochims, J. C.; Anet, F. A. L. *J. Am. Chem. Soc.* **1970**, *92*, 5524.

[13] There is a large difference in ΔG* values between **1** and an eight-membered cyclic ketenimine,[5] for which the nitrogen inversion of the C═C═N moiety requires 19.0 kcal/mol due to the steric strain.

Scheme 4



Scheme 5

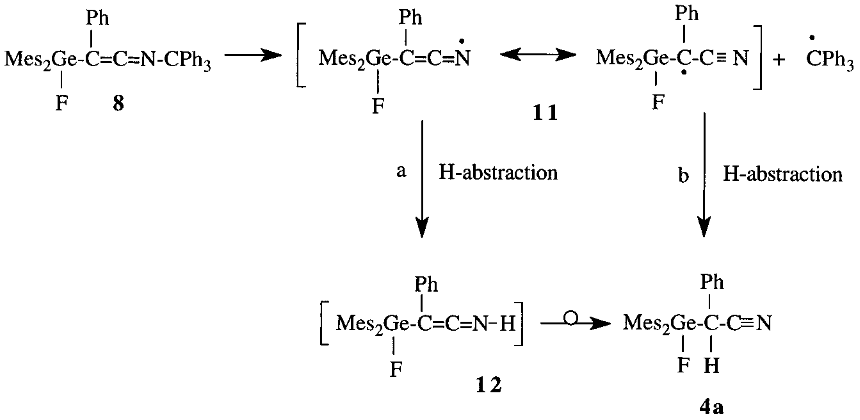


Table 1. Crystallographic Data, Experimental Conditions, and Summary of Structural Refinement for 1[a]

empirical formula	$C_{52}H_{54}Ge_2N_2$
mw	852.15
cryst size (mm)	0.5 × 0.5 × 0.2
cryst syst	monoclinic
space group	$P2_1/n$
cell dimens	
a (Å)	11.969(2)
b (Å)	10.758(2)
c (Å)	17.269(3)
β (deg)	96.27(1)
V (Å^3)	2210.3(7)
D_{calcd} (g cm^{-3})	1.28
Z	2
Mo Kα radiation	$\lambda = 0.710\ 69$ Å
$F(000)$	888
T (K)	293
$2\theta_{max}$ (deg)	55
no. of rflns collected	5064
no. of obsd rflns with $I > 2\sigma(I)$	2875
range of hkl	$0 < h < 15$, $0 < k < 13$, $-22 < l < 22$
refined ls R1 factor obsd ($F > 4\sigma(F)$)	0.06
refined ls wR2 factor obsd ($I > 2\sigma(I)$)	0.15
s	0.95
residual density, e Å^{-3}	−0.60 to +0.91

[a] $W = 1/[\sigma^2(F_o^2) + (0.124P)^2 + 0.384P]$, with $P = [F_o^2 + 2F_c^2]/3$.

by the bulky CPh_3 group, **8** is quite stable. It can be isolated in pure form.

8 is rather stable toward hydrolysis but slowly decomposes in benzene or chloroform solutions at room-temperature, reverting to the starting material **4a** and giving also some unidentified products. We suggest that the decomposition of **8** involves homolytic cleavage of the N−CPh_3 bond. This is supported by the work of Hegarty et al.,[14] who observed a facile thermal cleavage of the N−$CHPh_2$ bond in ketenimines via a radical mechanism. Thus, for ambident radical **11**, there are two possible processes: (a) H abstraction by the nitrogen atom followed by a rearrangement of the transient ketenimine **12** with final formation of **4a** and (b) H abstraction by the carbon atom leading directly to **4a** (Scheme 5).

X-ray Structure Determination. The structure of **1** was unambiguously proved by an X-ray study (see Tables 1−3 and Figure 1). The molecule is centrosymmetric. The sum of angles at C(2) is very close to 360° (359.3°), showing an almost complete planarity around the C(1)−C(2) double bond. The C(2)C(1)N arrangement is not completely linear but rather is bent to 171.8(5)°. It is in the normal range, since the C=C=N unit generally deviates from linearity by 5−10°.[12b,15] A more distorted C=C=N bond angle (163.8°) was even observed in a seven-membered-ring ketenimine.[16] Since the molecule is centrosymmetric, the four atoms NC(1)$N_aC(1_a)$ are exactly in the same plane. C(2) and C(2_a) are very close to this plane (±0.172(8) Å): this means that the six atoms NC(1)C(2)$N_aC(1_a)C(2_a)$ are approximately in the same plane. One of the germanium atoms is above and the other one below the mean plane NC(1)C(2)$N_aC(1_a)C(2_a)$ at a distance of 0.93(1) Å. Due to the centrosymmetry of **1**, the GeC(2) and $Ge_aC(2_a)$

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[14] Clarke, L. F.; Hegarty, A. F.; O'Neill, P. *J. Org. Chem.* **1992**, *57*, 362.

[15] Dely, J. J. *J. Org. Chem.* **1961**, *26*, 2801.

[16] Huisgen, R.; Langhals, E.; Nöth, H. *J. Org. Chem.* **1990**, *55*, 1472.

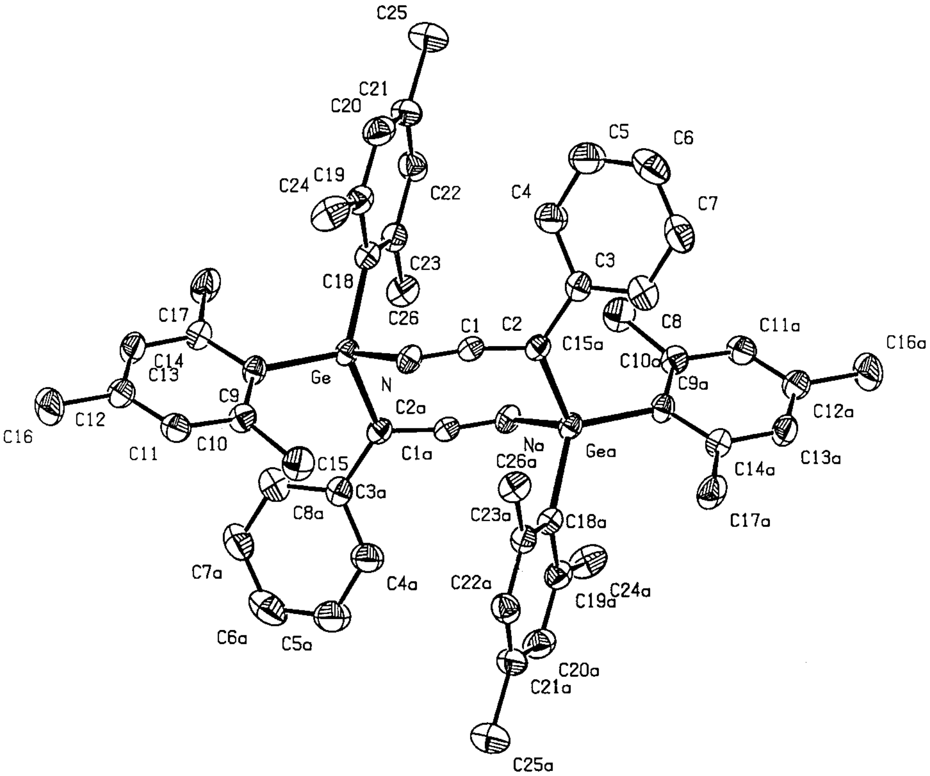


Figure 1. PLATON[19] view of **1** (ellipsoids are drawn at the 50% probability level).

Table 2. Selected Bond Lengths (Å) and Angles (deg)

Ge−N	1.926(4)	C(1)−N	1.215(6)
Ge_a−C(2)	1.939(5)	C(1)−C(2)	1.312(7)
Ge−C(18)	1.945(5)	C(2)−C(3)	1.469(7)
Ge−C(9)	1. 941(5)		
N−Ge−C(2_a)	98.2(2)	N−C(1)−C(2)	171.8(5)
N−Ge−C(18)	99.4(2)	C(1)−N−Ge	123.5(3)
C(2_a)−Ge−C(18)	120.5(2)	C(1)−C(2)−C(3)	121.9(4)
N−Ge−C(9)	108.0(2)	C(1)−C(2)−Ge_a	110.4(4)
C(2_a)−Ge−C(9)	110.6(2)	C(3)−C(2)−Ge_a	127.0 (4)
C(18)−Ge−C(9)	116.8(2)		

Table 3. Selected Torsion Angles (deg)

C(9)−Ge−N−C(1)	−178.2(4)
C(2)−C(1)−N−Ge	−109.3(3)
C(2_a)−Ge−N−C(1)	67.0(4)
N−Ge−C(2_a)−C(1_a)	−46.9(4)
N−Ge−C(2_a)-C(3_a)	123.8(4)

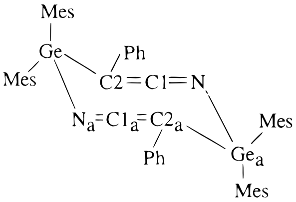
bonds, as well as the GeN and Ge_aN_a bonds, are parallel. From these data, it appears that **1** has a "cyclohexane" type structure in a "chair" conformation (Chart 2 and Figure 1).

The study of the reactivity of **1**, which seems according to our first experiments a good precursor of high-molecular-weight polymers, is now in progress.

Experimental Section

All experiments were carried out in flame-dried glassware under a nitrogen atmosphere using high-vacuum-line techniques. Solvents were dried and freshly distilled from sodium benzophenone ketyl and carefully deoxygenated on the vacuum line by several "freeze−pump−thaw" cycles. NMR spectra were recorded in $CDCl_3$ on the following spectrometers: ^1H, Bruker AC80 (80.13 MHz) and Bruker AC200 (200.13 MHz); $^{13}C\{^1H\}$, Bruker AC200 (50.32 MHz) (reference TMS); ^{19}F, Bruker AC80 (75.39 MHz) (reference CF_3COOH). Melting points were determined on a Wild Leitz-Biomed apparatus. Mass spectra were obtained on a Hewlett-Packard 5989A spectrometer by EI at 70 eV. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. The UV spectrum was recorded on a Hewlett-Packard 8453 UV−vis spectrometer. Elemental analyses were performed by the "Service de Microanalyse de l'Ecole de Chimie de Toulouse".

Chart 2



Mes_2GeCl_2 was synthesized according to the literature[17] from MesBr, Mg and $GeCl_4$. Mes_2GeF_2[18] was prepared from Mes_2GeCl_2 by treatment with MeOH/NEt_3 and then with HF/H_2O.

Synthesis of (Fluorodimesitylgermyl)phenylacetonitrile (4a). A solution of *n*-BuLi (9.5 mL, 1.6 M in hexane, 16.2 mmol) was added to a solution of phenylacetonitrile (1.72 g, 14.7 mmol) in THF (20 mL) at −78 °C. After 20 min the reaction mixture was transferred via cannula to a solution of Mes_2GeF_2 (5 g, 14.3 mmol) in THF (40 mL) stored at −78 °C. Stirring was continued at −78 °C for 40 min. Then the reaction mixture was warmed to room temperature and was stirred for 1 h. Solvents were removed in vacuo, the residue was dissolved in Et_2O, LiF was filtered out, and the filtrate was evaporated in vacuo. The residue was recrystallized from pentane, yielding 4.40 g (69%) of **4a** as white crystals (mp 149.0−149.5 °C).

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[17] Rivière, P.; Rivière-Baudet, M. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: New York, 1988; Vol. 4, p 542.

[18] Rivière, P.; Rivière-Baudet, M.; Castel, A.; Desor, D.; Abdennadher, C.; Satgé, J. *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *61*, 189.

[19] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

^{1}H NMR: δ 2.17 (d, $^5J_{\mathrm{H-F}} = 1.9$ Hz, 6H, o-Me), 2.27 (s, 6H, *p*-Me), 2.28 (d, $^5J_{\mathrm{H-F}} = 1.9$ Hz, 6H, *o*-Me), 4.14 (d, $^3J_{\mathrm{H-F}} = 4.8$ Hz, 1H, CH), 6.81 (s, 4H, H arom Mes), 7.11−7.26 (m, 5H, H arom Ph).

^{13}C NMR: δ 21.18 (*p*-Me), 22.98 and 23.04 (*o*-Me), 32.49 (d, $^2J_{\mathrm{C-F}} = 14.2$ Hz, C−H), 119.80 (d, $^3J_{\mathrm{C-F}} = 3.0$ Hz, C≡N), 127.34 (*p*-C Ph), 128.37 and 128.55 (*o*- and *m*-C Ph), 129.48 (*m*-C Mes), 130.50 (d, $^2J_{\mathrm{C-F}} = 9.3$ Hz, ipso-C Mes), 131.15 (ipso-C Ph), 131.53 (d, $^2J_{\mathrm{C-F}} = 10.5$ Hz, ipso-C Mes), 140.85 and 140.88 (*p*-C Mes), 142.74 and 143.09 (*o*-C Mes).

^{19}F NMR: δ −105.19 (s).

MS (EI, 70 eV, ^{74}Ge): *m/z* 447 (M, 5), 428 (M − F, 10), 331 (Mes$_2$GeF, 100), 311 (Mes$_2$Ge − 1, 22).

IR (KBr, cm^{-1}): ν(C≡N) 2229 (w).

Anal. Calcd for $C_{26}H_{28}FGeN$: C, 69.80; H, 6.26; N, 3.13. Found: C, 69.63; H, 6.19; N, 3.06.

Synthesis of (Chlorodimesitylgermyl)phenylacetonitrile (4b). A solution of *n*-BuLi (10.0 mL, 1.6 M in hexane, 16 mmol) was added dropwise to a solution of phenylacetonitrile (1.8 g, 15.38 mmol) in THF (20 mL) with stirring at −78 °C. The solution became bright yellow. After 15 min the reaction mixture was transferred via cannula to a solution of Mes$_2$GeCl$_2$ (5.64 g, 14.72 mmol) in THF (50 mL) stored at −78 °C. After the addition the reaction mixture was stirred at −78 °C for 30 min and then was warmed to room temperature with stirring for 1 h. The solvents were removed in vacuo, the residue was dissolved in Et$_2$O, LiCl was filtered out, and the filtrate was evaporated in vacuo. The crude product was recrystallized from *i*-PrOH to give 4.38 g (65%) of white crystals of **4b** (mp 138−140 °C).

^{1}H NMR: δ 2.18 (s, 6H, *o*-Me), 2.25 (s, 12H, *o*- and *p*-Me), 4.16 (s, 1H, CH), 6.77 (s, 4H, H arom Mes), 7.01−7.21 (m, 5H, H arom Ph).

^{13}C NMR: δ 21.06 (p-Me), 23.47 and 23.87 (*o*-Me), 34.92 (C−H), 120.50 (C≡N), 127.42 (*p*-C Ph), 128.17 and 128.81 (*m*-C Ph and *o*-C Ph), 129.87 (*m*-C Mes), 131.24 (ipso-C Ph), 132.34 and 133.78 (ipso-C Mes), 140.38 and 140.45 (*p*-C Mes), 141.84 and 142.58 (*o*-C Mes).

MS (EI, 70 eV, ^{74}Ge): *m/z* 463 (M, 4), 428 (M − Cl, 4), 347 (Mes$_2$GeCl, 100), 311 (Mes$_2$Ge − 1, 20).

IR (KBr, cm^{-1}): ν(C≡N) 2215 (w).

Anal. Calcd for $C_{26}H_{28}ClGeN$: C, 67.39; H, 6.05; N, 3.02. Found: C, 67.21; H, 6.16; N, 2.81.

Synthesis of 3,7-Diphenyl-2,2,6,6-tetrakis(2,4,6-trimethylphenyl)-2,6-digerma-1,5-diazacyclooctatetra-3,4,7,8-ene (1). A 1.4 mL amount of a 1.7 M solution of *t*-BuLi in pentane (2.38 mmol) was added to a solution of **4a** (0.99 g, 2.21 mmol) in Et$_2$O (30 mL) at −78 °C. The color immediately became bright yellow. After 10 min the cooling bath was removed and the reaction mixture was warmed to room temperature. The yellow color disappeared, and the white solid **5a** precipitated. After the mixture was stirred overnight, this white solid was converted to **1** in the form of a yellow solid. This yellow solid was filtered and dried in vacuo, yielding 0.90 g (95%) of **1**, which was recrystallized from benzene−hexane (30/70) to give lemon yellow crystals, mp 211−213 °C dec.

^{1}H NMR: δ 2.27 (s, 12H, *p*-Me), 2.35 (s, 24H, *o*-Me), 6.83 (s, 8H, H arom Mes), 6.58−6.99 (m, 10H, H arom Ph).

^{13}C NMR: δ 21.15 (*p*-C Me), 23.57 (*o*-C Me), 51.33 (*C*(Ph)=C=N), 122.37 (*p*-C Ph), 125.32 (*m*-C Ph), 128.46 (*o*-C Ph), 129.54 (*m*-C Mes), 134.08 (ipso-C Ph), 137.72 (ipso-C Mes), 139.74 (*p*-C Mes), 143.50 (*o*-C Mes), 170.87 (C(Ph)=*C*=N).

IR (KBr, cm^{-1}): ν(C=C=N) 2015 (vs).

UV ($\lambda_{\max}$ in cyclohexane): 202 ($\epsilon = 3859$), 286 ($\epsilon = 579$), 369 ($\epsilon = 8$) nm.

Anal. Calcd for $C_{52}H_{54}Ge_2N_2$: C, 73.29; H, 6.39; N, 3.29. Found: C, 73.24; H, 6.50; N, 3.16.

1 was also obtained in nearly quantitative yield from **4b** using the same procedure.

Synthesis of (Fluorodimesitylgermyl)methylphenylacetonitrile (9). a. From 5a and Methyl Iodide at −78 °C. The lithium derivative **5a** was prepared by reaction of 0.7 mL of a 1.7 M solution of *t*-BuLi in pentane (1.19 mmol) and **4a** (0.5 g, 1.12 mmol) in Et$_2$O (15 mL) at −78 °C. The color became bright yellow immediately. After 5 min MeI (0.23 g, 1.60 mmol) was added to the yellow solution at −78 °C. The reaction mixture was stirred for 30 min, was then warmed to room temperature, and was stirred for 1 h. Inorganic salts were filtered out, and the filtrate was concentrated in vacuo, giving 0.29 g (57%) of **9** as white crystals (mp 174−176 °C).

^{1}H NMR: δ 2.06 (d, $^5J_{\mathrm{H-F}} = 1.8$ Hz, 6H, *o*-Me), 2.07 (s, 3H, Me), 2.22 (s, 3H, *p*-Me), 2.29 (s, 3H, *p*-Me), 2.44 (d, $^5J_{\mathrm{H-F}} = 1.7$ Hz, 6H, *o*-Me), 6.72 (s, 2H, H arom Mes) and 6.87 (s, 2H, H arom Mes), 7.20−7.48 (m, 5H, H arom Ph).

^{13}C NMR: δ 21.09 (*p*-Me), 23.08 and 23.16 (*o*-Me), 23.89 (d, $^3J_{\mathrm{C-F}} = 4.2$ Hz, Me), 37.95 (d, $^2J_{\mathrm{C-F}} = 14.3$ Hz, *C*-Me), 123.67 (d, $^3J_{\mathrm{C-F}} = 3.3$ Hz, C≡N), 127.46 (*p*-C Ph), 128.39 and 128.68 (*o*- and *m*-C Ph), 129.33 and 129.80 (*m*-C Mes), 131.80 (d, $^2J_{\mathrm{C-F}} = 9.3$ Hz, ipso-C Mes), 132.05 (d, $^2J_{\mathrm{C-F}} = 9.9$ Hz, ipso-C Mes), 137.64 (ipso-C Ph), 140.57 and 140.63 (*p*-C Mes), 143.25 (*o*-C Mes).

^{19}F NMR: δ −103.86 (s).

MS (EI, 70 eV, ^{74}Ge): *m/z* 461 (M, 8), 442 (M − F, 2), 331 (Mes$_2$GeF, 100), 311 (Mes$_2$Ge − 1, 18).

IR (KBr, cm^{-1}): ν(C≡N) 2223 (w).

Anal. Calcd for $C_{27}H_{30}FGeN$: C, 70.28; H, 6.51; N, 3.04. Found: C, 70.03; H, 6.44; N, 3.18.

b. From 5a and Dimethyl Sulfate at Room Temperature. The lithium derivative **5a** was prepared at −78 °C as previously described. After 10 min the cooling bath was removed and the mixture was warmed to room temperature. At 20 °C the yellow color disappeared almost completely and a white solid precipitated. Me$_2$SO$_4$ (0.34 g, 2.7 mmol) was added at room temperature, and the reaction mixture was stirred for 1 h. Inorganic salts were filtered out, and the filtrate was concentrated in vacuo, giving 0.35 g (69%) of **9**.

Synthesis of *N*-(triphenylmethyl)(fluorodimesitylgermyl)phenylketenimine (8). The lithium derivative **5a** was prepared at −78 °C as previously described. After 10 min of stirring at −78 °C the cooling bath was removed and the mixture was warmed to room temperature. A white solid precipitated from the reaction mixture. Ph$_3$CBr (0.36 g, 1.12 mmol) was added at room temperature to the white solid, which disappeared in a few minutes. The yellow solution was stirred for 1 h at room temperature. LiBr was filtered out, and the filtrate was evaporated in vacuo. **8** formed in quantitative yield (according to ^{1}H NMR data). Recrystallization from pentane gave pale yellow crystals (mp 101−103 °C dec).

^{1}H NMR: δ 2.16 (d, $^5J_{\mathrm{H-F}} = 1.7$ Hz, 12H, *o*-Me), 2.24 (s, 6H, *p*-Me), 6.74 (s, 4H, H arom Mes), 6.67−7.30 (m, 20H, H arom Ph). At −70 °C the two Mes groups appeared to be nonequivalent with the following chemical shifts for the methyl groups: *o*-Me, 1.97 and 2.62 ppm (two broad s), *p*-Me, 2.31 ppm (s).

^{13}C NMR: δ 21.25 (*p*-Me), 22.81 and 22.88 (*o*-Me), 64.71 (d, $^2J_{\mathrm{C-F}} = 17.9$ Hz, *C*=C=N), 77.73 (*C*Ph$_3$), 124.85−130.15 (*o*-, *m*-, *p*-C Ph and *m*-C Mes), 132.12 (d, $^2J_{\mathrm{C-F}} = 11.9$ Hz, ipso-C Mes), 135.39 (ipso-C Ph), 139.97 (*p*-C Mes), 143.75 and 144.33 (*o*-C Mes and ipso-C CPh$_3$), 173.89 (C=*C*=N).

^{19}F NMR: δ −97.19 (s).

MS (EI, 70 eV, ^{74}Ge): *m/z* 446 (Mes$_2$Ge(F)-C(Ph)=C=N, 2), 331 (Mes$_2$GeF, 13), 243 (Ph$_3$C, 83), 165 (Ph$_3$C−Ph − 1, 78), 77 (Ph, 100).

IR (KBr, cm^{-1}): ν(C=C=N) 2011 (vs).

Anal. Calcd for $C_{45}H_{42}FGeN$: C, 78.37; H, 6.09; N, 2.03. Found: C, 78.52; H, 6.04; N, 2.10.

X-ray Crystallographic Analysis of 1. Yellow crystals of **1**, suitable for X-ray analysis, were obtained by slow evaporation of a saturated benzene−hexane (30/70) solution of **1** at room temperature. The data were collected on a Huber diffractometer with graphite-monochromated Mo Kα radiation

(λ = 0.710 69 Å). Final unit cell parameters for **1** were obtained by least-squares analysis of setting angles for 30 reflections; $14 < 2\theta < 30°$. The intensities of the standard reflection (0,−4,4) were measured every 50 reflections during the data collection, showing no significant variation. All calculations were performed with the programs SHELXS-86 and SHELXL-93 using F^2. Hydrogen atoms were placed in calculated positions, and all other atoms were refined with anisotropic thermal parameters. Residual densities close to germanium (d < 0.944 Å) are rather important. The other residual densities are in the normal range (−0.41 to 0.46 e Å^{-3}).

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Supporting Information Available: Tables of atomic coordinates, anisotropic temperature factors, bond lengths, bond angles, and torsion angles and additional PLUTO and crystal-packing diagrams (12 pages). Ordering information is given on any current masthead page.

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