2222 *Organometallics* **1998,** *17,* 2222−2227

Synthesis, Structural Characterization, and Reactivity of (8-Methoxynaphthyl)hydridogermanium Triflates and Iodides

F. Cosledan, A. Castel, P. Rivière,* and J. Satgé

Laboratoire "Hétérochimie Fondamentale et Appliquée", Université Paul Sabatier,
118, Route de Narbonne, 31062 Toulouse Cédex 04, France

M. Veith and V. Huch

Institute of Inorganic Chemistry, University of Saarland, P.O. Box 151150,
D-66041 Saarbrücken, Germany

Received November 4, 1997

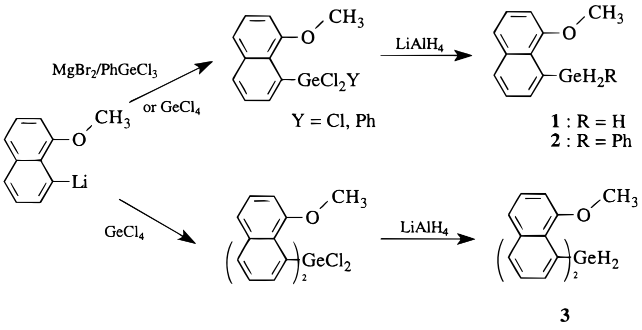
New 8-(methoxynaphthyl)hydridogermanium triflates and iodides were synthesized by treatment of the corresponding germanes with trifluoromethanesulfonic acid or I_2. Their characterization by ^1H and ^{13}C NMR and IR spectroscopy is reported. In the solid state, bis(8-methoxynaphthyl)hydridogermanium triflate (**6**) exhibits a 5-coordinate germanium atom weakly linked to the triflate anion. The germyl iodide rapidly gives the germoxolene with loss of MeI when it is heated in CH_3CN. With H_2O, amine, and DMSO, the germyl triflates react quantitatively to form new complexes which can be isolated and characterized. The X-ray crystal structure of the hydrate of bis(8-methoxynaphthyl)hydridogermanium triflate (**11**) shows the predominant formation of a hydrated germyl cation. Several tentative approaches to prepare germanols failed and always gave stable germoxanes instead.

Introduction

We have recently described the stabilization of organogermyllithiums[1] by the 8-methoxynaphthyl group and have shown a weak coordinative interaction between germanium and methoxy oxygen atoms giving a germanium(V) center in the starting organogermanes. Moreover, the stabilizing effect of O-chelation has been illustrated in the case of 2-oxo-1-hexahydroazepinylmethyl ligands.[2] X-ray diffraction analysis showed a possible coordinative interaction between the germanium center and the oxygen of the carbonyl group when the metal was surrounded by halogen atoms. The authors suggested the possibility of ionic dissociation of these compounds in sufficiently polar solvents. We herein describe the synthesis and reactivity of various (8-methoxynaphthyl)germanium iodides and triflates. Their behavior as possible germyl cations[3] will be discussed on the basis of an X-ray structure and spectroscopic data.

Results and Discussion

The dichloroorganogermanes were prepared by an organomagnesium route or by the direct reaction of the corresponding organolithium. Their reduction by $LiAlH_4$ gave the expected organogermanes **1**−**3** (eq 1).



(1)

Treatment of the (8-methoxynaphthyl)germanes **1**−**3** with trifluoromethanesulfonic acid in diethyl ether or with I_2 in benzene gave the corresponding germanium triflates **4**−**6**[4] and iodides **7** and **8**[4] in good yields (eq 2). These compounds are very air-sensitive powders, insoluble in common hydrocarbon solvents but soluble in chlorinated solvents (CH_2Cl_2 and $CHCl_3$).

The X-ray structure of the triflate **6** is shown in Figure 1. Some of the important bond lengths and angles are assembled in Table 1, and a summary of crystallographic data is given in Table 2. The geometry at germanium is very close to trigonal bipyramidal. The two 8-methoxynaphthyl ligands and the hydrogen atom form the central plane. The sum of the bond angles in the equatorial plane deviates by 3.2° from the ideal

---

(1) Castel, A.; Rivière, P.; Cosledan, F.; Satgé, J.; Onyszchuk, M.; Lebuis, A. M. *Organometallics* **1996**, *15*, 4488.

(2) (a) Ovchinnikov, Yu. E.; Struchkov, Yu. T.; Baukov, Yu. I.; Shipov, A. G.; Kramarova, E. P.; Bylikin, S. Yu. *Russ. Chem. Bull. (Engl. Transl.)* **1994**, *43*, 1346. (b) Ovchinnikov, Yu. E.; Struchkov, Yu. T.; Baukov, Yu. I.; Shipov, A. G.; Bylikin, S. Yu. *Russ. Chem. Bull. (Engl. Transl.)* **1994**, *43*, 1351. (c) Ovchinnikov, Yu. E.; Struchkov, Yu. T.; Shipov, A. G.; Smirnova, L. S.; Baukov, Yu. I.; Bylikin, S. Yu. *Mendeleev Commun. (Engl. Transl.)* **1994**, 178.

(3) (a) Belzner, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1277. (b) Schleyer, P. v. R. *Science* **1997**, *275*, 39.

(4) Cosledan, F.; Castel, A.; Rivière, P. *Main Group Met. Chem.* **1997**, *20*, 5.

S0276-7333(97)00963-1 CCC: $15.00

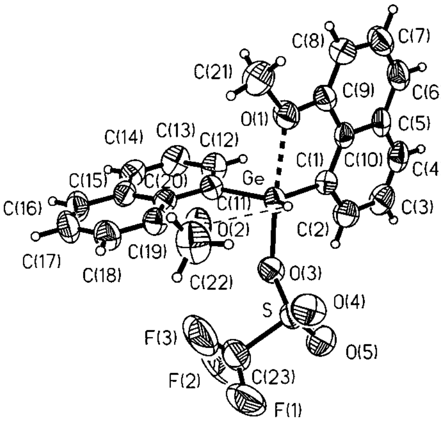
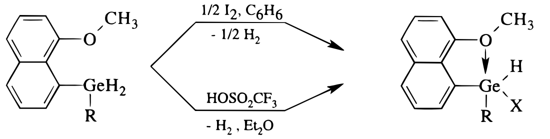


Figure 1. ORTEP drawing of **6**.



(2)

1 : R = H
2 : R = Ph
3 : R = (8-MeO)Np

4: R = H, X = OSO_2CF_3
5 : R = Ph, X = OSO_2CF_3
6 : R = (8-MeO)Np, X = OSO_2CF_3
7 : R = Ph, X = I
8 : R = (8-MeO)Np, X = I

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 6

Ge−O(1)	2.357(3)	C(11)−Ge	1.938(4)
Ge−O(2)	2.799(3)	C(1)−Ge	1.945(4)
Ge−O(3)	1.988(3)	S−O(3)	1.483(3)
Ge−H	1.33(3)	S−O(4)	1.406(3)
O(2)−H	2.46(3)	S−O(5)	1.417(3)
O(4)−H	2.78(3)	C(1)−C(2)	1.379(6)
C(11)−C(12)	1.369(5)	C(1)−C(10)	1.414(5)
C(11)−C(20)	1.428(5)		
C(1)−Ge-C(11)	112.81(15)	H−Ge−C(11)	127.8(12)
C(1)−Ge-O(3)	98.29(14)	H−Ge−C(1)	116.4(12)
C(1)−Ge-O(1)	76.84(14)	H−Ge−O(1)	84.9(13)
C(11)−Ge-O(3)	93.04(14)	H−Ge−O(3)	96.1(13)
C(11)−Ge-O(1)	90.19(14)	C(21)−O(1)-C(9)	118.5(4)
O(3)−Ge-O(1)	174.93(10)	C(22)−O(2)-C(19)	119.6(3)

Table 2. Summary of Crystallographic Data for Compounds 6 and 11

	6	**11**
empirical formula	$C_{23}H_{23}F_3GeO_5S$	$C_{23}H_{21}F_3GeO_6S$
M_r	541.06	555.05
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a/Å	10.209(2)	10.286(2)
b/Å	17.049(3)	11.052(2)
c/Å	12.918(3)	12.449(2)
α/deg	90	67.55(3)
β/deg	95.15(3)	67.69(3)
γ/deg	90	68.76(3)
V/Å^3	2239.3(8)	1170.3(4)
Z	4	2
F(000)	1104	564
D_c/Mg m^{-3}	1.605	1.575
T/K	293(2)	293(2)
cryst size/mm	0.2 × 0.12 × 0.08	0.3 × 0.2 × 0.15
θ range/deg	1.98−24.13	1.84−22.39
no. of rflns collcd	11 832	7545
no. of indep rflns	3348	2818
no. of obsd rflns	2378	1995
GOF on F^2	0.906	1.06
final R indices ($I > 2\sigma(I)$)	R1 = 0.039	R1 = 0.059
R indices (all data)	R1 = 0.061	R1 = 0.087
wR2	0.0951	0.1609

Table 3. Kinetics Parameters for Compounds 6 and 8

compd	T_c (K)	k_c (s^{-1})	ΔG_c* (kcal/mol)
6	223	239.7	10.50
8	232	308.4	10.82

value of 360°. The angles C(11)−Ge-C(1) and H−Ge−C(1) are decreased to 112.81(15)° and 116.4(12)°, whereas H−Ge−C(11) is widened to 127.8(12)°. The two distances Ge−C(1) (1.945(4) Å) and Ge−C(11) (1.938(4) Å) are similar and correspond to normal covalent bonds (1.90−2.05 Å).[5] The Ge−H bond (1.33(3) Å) is significantly shorter than a Ge−H covalent bond (1.46−1.70 Å),[5] even considering that the position of H in the X-ray structure lacks precision. A similar shortening of the Si−H bond has been observed in the case of a silylium cation stabilized by amino groups.[6] The axial positions are occupied by one methoxy group (O(1)) and the triflate anion (O(3)). The Ge−O(1) distance, 2.357(3) Å, is longer than that of the Ge−O covalent bond (1.75−1.85 Å)[5] but appreciably shorter than the sum of the van der Waals radii (3.40 Å), suggesting a coordinative interaction between the Ge and this methoxy oxygen atom. In contrast, the second methoxy group (O(2)) seems almost not linked to the germanium atom (Ge−O(2) = 2.799(3) Å); the steric hindrance of the triflate group and the hydrogen atom on germanium probably prevents the second complexation. Further NMR spectroscopic measurements may confirm the presence of a pentacoordinated germanium atom. The Ge−O(3) (triflate group) distance, 1.988(3) Å, is slightly longer than a covalent Ge−O bond. From the same observation in the silicon series,[6,7] Jutzi et al. concluded that the lengthening of the Si−O bond, a minor one, indicates a polar character of this bond. Similarly, we think that the methoxy chelation of the germanium center enhances the polarity of the Ge−O bond.

At room temperature, the ^{1}H NMR spectra of compounds **6** and **8** show broadened signals due to the methoxy groups which presumably are the result of an exchange process at the germanium center. When the temperature is decreased, two resolved signals of equal intensity appear. Coalescence temperature and kinetic parameters, estimated on the basis of the NMR measurements,[8] are collected in Table 3. These results suggest that a single mechanism operates throughout the temperature range (~100 K) because the Eyring plots are linear.[9] Several explanations are possible: (1) intramolecular nondissociative processes (Berry[10] pseudorotation for bipyramidal geometry or a Bailar[11] twist in the case of an ideal octahedral geometry) or (2) a dissociative process (rapid interconversion of the chelating groups). In our compounds **6** and **8**, the high

---

[5] Baines, K. M.; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157.

[6] Belzner, J.; Schär, D.; Kneisel, B. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 1840.

[7] Mix, A.; Berlekamp, U. H.; Stammler, H.-G.; Neumann, B.; Jutzi, P. *J. Organomet. Chem.* **1996**, *521*, 177.

[8] For simple coalescence cases, the barriers determined at the coalescence temperature by $k_c = 2.2\ \Delta\nu$ are reliable. The Eyring plot of data from line-shape analysis is given in the Supporting Information.

[9] Breliere, C.; Corriu, R. J. P.; Royo, G.; Zwecker, J. *Organometallics* **1989**, *8*, 1834.

[10] Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; p 1241 and references therein.

[11] Bailar, J. C. *Inorg. Nucl. Chem.* **1958**, *6*, 165.

Scheme 1

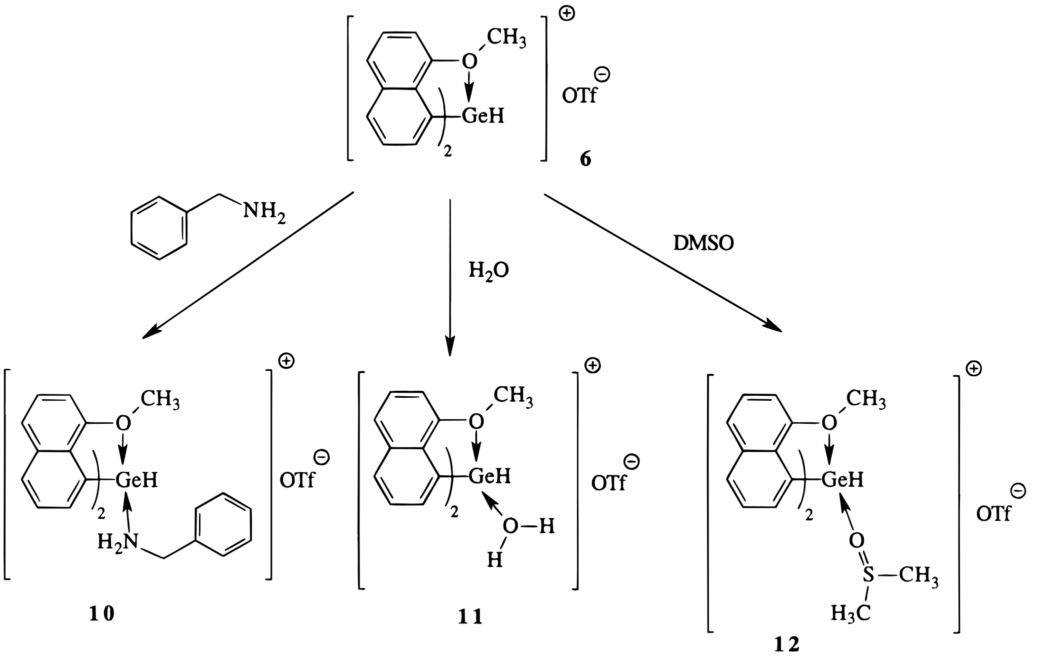


Table 4. Variation of δ (ppm) of the Germyl Triflates and Iodides Compared with Starting Compounds

	^{1}H NMR (CDCl$_3$, ppm)		^{13}C NMR (CDCl$_3$, ppm)		IR (cm^{-1})
compd	δ(GeH)	Δδ(GeH)	δ(C$_{ipso}$)^a	Δδ(C$_{ipso}$)	ν(GeH)
4	6.69	+2.06	122.35	−5.40	2121, 2109
5			123.10	−6.35	2151
6	7.85	+2.04	128.32	−4.98	2170
7	6.91	+1.45	123.10	−6.35	2095
8	7.35	+1.54	131.32	−1.98	2122

[a] Ipso C of naphthyl group.

apicophilicity[12] of the oxygen atom (in methoxy or triflate groups) compared with the carbon or hydrogen atoms allows us to eliminate the nondissociative processes. Moreover, the values of the energy of activation are similar to those previously obtained by Willcott[13] for a dissociative process. Thus, it is possible to explain the nonequivalence of the methoxy groups at low temperature in terms of their rapid interconversion which averages the NMR signals at room temperature.

The ^{1}H NMR Ge−H resonances in compounds **4**−**8** are shifted drastically to higher frequency in comparison with the corresponding neutral precursors ($\Delta\delta = +1.45$ to +2.06) (cf. Table 4). This finding is in agreement with the presence of deshielded hydrogen atoms, particularly for **6** where δ = (Ge−H) is higher than that in Cl_3GeH (7.66 ppm).[14] In the IR spectra, we observed very high values for ν(Ge−H), consistent with a positively charged hydrogen atom. Shifts of the ipso aromatic carbon atom resonances (cf. Table 4) toward higher field also suggest a localization of positive charge on the germanium atom.

The ionic structure of the compound **6** in solution is confirmed by conductivity measurements. The conductivity of a dichloromethane solution containing bis(8-methoxynaphthyl)hydridogermane (**3**) increases when trifluoromethanesulfonic acid is added until 1 mol equiv of reagent was added. We have previously verified that the starting derivatives show no significant conductivity.

These results show that compounds containing two 8-methoxynaphthyl ligands appear to be five-coordinate with only one methoxy group bonded to germanium at a time. The methoxy chelation of the germanium center seems to enhance the polarity of the Ge−O (triflate) bond so that a contact ion pair nearly is formed. This also is supported by the possibility of nucleophilic complexation of the germanium center in such derivatives.

Indeed, the degree of complexation of silylium cations by solvent[15] was the best argument to determine the "free" character of such species. We sought to verify if the cationic character of our germylated derivatives involves a positive charge on the Ge sufficiently large to facilitate coordination of a molecule of solvent. It was found that treatment of stoichiometric amounts of **6** with benzylamine, water, or DMSO led to quantitative formation of the corresponding complexes **10**−**12**, respectively (Scheme 1).

Compound **10** was too unstable to allow its isolation, but it was identified by ^{1}H NMR. Complexes **11** and **12** were obtained as air-sensitive white powders.

Single-crystal X-ray analysis of **11** revealed the presence of a dimeric form in which O−H interactions between the hydrogen of H_2O and the oxygen atom of the triflate anion connected the two monomers (Figure 2). Selected bond lengths and bond angles are shown in Table 5. The most notable features are the complexation of only one methoxy group to the germanium atom and a long Ge−O(3) bond (1.951(6) Å), as had been observed for compound **6**. The germanium atom shows

---

(12) Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; de Saxcé, A.; Young, J. C. *J. Organomet. Chem.* **1990**, *395*, 1.

(13) Benin, V. A.; Martin, J. C.; Willcott, M. R. *Tetrahedron Lett.* **1994**, *35*, 2133.

(14) Rivière, P.; Rivière-Baudet, M.; Satgé, J. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, U.K., 1982; Vol. 2, pp 399, 1995; *Ibid.*,Vol. 2, p 137.

(15) Arshadi, M.; Johnels, D.; Edlund, V.; Ottosson, C. H. Cremer, D. *J. Am. Chem. Soc.* **1996**, *118*, 5120.

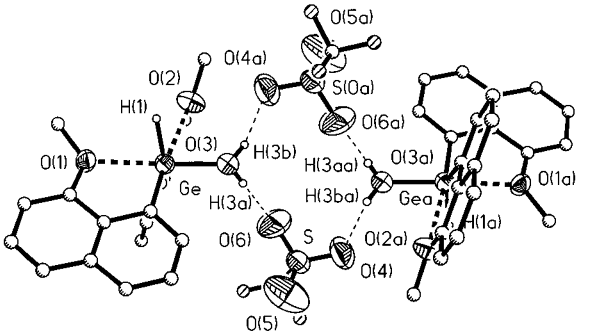


Figure 2. ORTEP drawing of **11**.

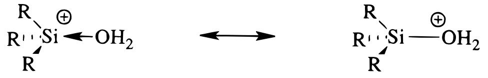
Table 5. Selected Bond Lengths (Å) and Angles (deg) for 11

Ge−O(1)	2.425(5)	O(3)−O(4)	2.624(9)
Ge−O(2)	2.785(6)	O(3)−O(6)	2.549(9)
Ge−O(3)	1.951(6)	Ge−C(9)	1.928(8)
Ge−H	1.51(6)	Ge−C(20)	1.953(8)
O(1)−H	2.54(5)	S−O(4)	1.425(7)
O(2)−H	2.71(5)	S−O(5)	1.404(8)
O(3)−H	2.60(5)	S−O(6)	1.415(8)
C(9)−Ge−C(20)	110.4(3)	O(3)−Ge−O(1)	168.4(2)
C(20)−Ge−H	131(2)	O(4)−O(3)−O(6)	117.4(3)
C(9)−Ge−H	111(2)	O(3)−Ge−C(9)	97.2(3)
O(1)−Ge−H	77(2)	O(3)−Ge−C(20)	102.0(3)
O(2)−Ge−H	71(2)	O(2)−Ge−C(9)	175.2(3)
O(3)−Ge−H	97(2)	C(12)−O(2)−C(22)	119.0(8)
C(1)−O(1)−C(11)	118.4(6)		

a slightly distorted trigonal bipyramidal geometry (omitting the rather long Ge−O(2) distance) with the apical sites occupied by one methoxy group and the H_2O molecule. The three S−O distances are in the same range: 1.425(7), 1.404(9), and 1.415(8) Å, suggesting a dissociated form consisting of the triflate anion and the hydrated germyl cation in the solid state.

The ^1H NMR and IR spectra support this hypothesis. The low-field chemical shift displacement of the GeH resonance (7.76 ppm) and the very high value for ν(Ge−H) (2165 cm^{-1}) are consistent with a positive by charged germanium center.

In the silicon series, Reed[16] also proposes a predominance of silyl cation character (A) for his protonated silanol:

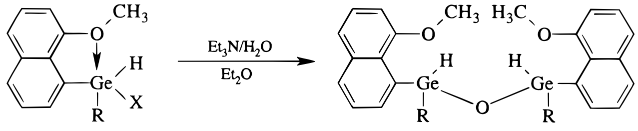


(A) (B)

The bond length data and the spectroscopic study of **11** suggest a similar preponderant form A with a remaining positive charge on the germanium atom.

In contrast, with DMSO (compound **12**), a delocalization of the positive charge onto the sulfur atom can be envisaged. The infrared spectrum of **12** shows a shift of ν(Ge−H) to lower frequency, in agreement with a decreasing positive charge on germanium. Moreover, the resonances of the methyl groups of DMSO are shifted slightly to lower field ($\Delta\delta(CH_3S) \approx 0.40$ ppm) as a result of the positive character of the sulfur atom.

Several attempts to prepare germanols have been made. All the reactions of germyl triflates and iodides with an excess of H_2O/Et_3N gave the germoxanes directly (eq 3). Thus, under the experimental conditions used, the germanols appear to be too unstable to be isolated, supporting the idea that a B type form for compound **11** is less probable than A.

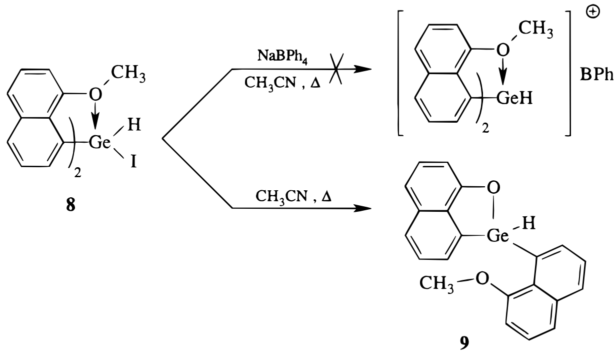


4 R = H, X = OTf
5 R = Ph, X = OTf
6 R = (8-MeO)Np, X = OTf
7 R = Ph, X = I
8 R = (8-MeO)Np, X = I

13 R =H
14 R = Ph
15 R = (8-MeO)Np

(3)

Treatment of germyl iodide **8** with $NaBPh_4$ (eq 4) in CH_3CN does not give the expected anion exchange product; rather, the germoxolene **9** is formed with loss of MeI.



8

9

(4)

The donation of a lone electron pair of the methoxy oxygen atom to the positive germanium center will generate a partial positive charge on oxygen. This in turn will result in inductive release of electron density from the methyl group to oxygen, making the CH_3 carbon atom more electrophilic and thus faciliting attack at the methyl carbon by I^-. A polar solvent (CH_3CN) will favor such a nucleophilic substitution.

Experimental Section

General Comments. All reactions were performed under a dry argon atmosphere using standard Schlenk techniques. The hydrocarbon solvents were dried and distilled from sodium under an inert atmosphere. The compounds were characterized by the usual analytical techniques: ^1H NMR, AC 80 Bruker; ^{13}C NMR, AC 200 and ARX 400 Bruker; IR, Perkin-Elmer 1600 FT; mass spectra, Ribermag R 10 10 (EI or CI, CH_4) and HP 5989 A. Melting points were measured on a Reichert microscope. Elemental analyses were performed by the Centre de Microanalyse de l'Ecole Nationale Supérieure de Chimie de Toulouse.

Compounds **2** and **3** were prepared as described in ref 1.

Synthesis of (8-Methoxynaphthyl)germane (1). A solution of (8-methoxynaphthyl)lithium[17] (8.52 g, 52 mmol) in 100 mL of THF was added dropwise at 20 °C to a suspension of 54.6 mmol of $MgBr_2$ in 40 mL of THF. The mixture was refluxed for 2 h and then added to a solution of freshly distilled $GeCl_4$ (11.16 g, 52 mmol) in 40 mL of THF. The mixture was stirred at room temperature overnight and then reduced by $LiAlH_4$ (3.95 g, 104 mmol) in 60 mL of THF. After 1 h at

---

[16] Xie, Z.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2519.

[17] Shirley, D. A.; Cheng, C. F. *J. Organomet. Chem.* **1969**, *20*, 251.

reflux, hydrolysis, extraction, drying with Na_2SO_4, and concentration, the residue was distilled, resulting in a mixture of **1** (60%) and methoxynaphthalene (40%) according to the ^1H NMR spectrum. The mixture was dissolved in the least amount of diethyl ether possible and cooled to −30 °C until compound **1** precipitated. The crystals were isolated by decantation and dried in vacuo.

1: 3.90 g (32%); mp 54−56 °C; ^1H NMR ($CDCl_3$) δ 3.95 (s, 3H, OCH_3), 4.63 (s, 3H, GeH_3), 6.82 (dd, $J^3 = 5.7$ Hz, $J^4 = 2.9$ Hz, 1H, H_7), 7.25−7.49 (m, 3H, $C_{10}H_6$), 7.73 (dd, $J^3 = 6.9$ Hz, $J^4 = 1.5$ Hz, 1H, H_2), 7.80 (dd, $J^3 = 7.9$ Hz, $J^4 = 1.5$ Hz, 1H, H_4); ^{13}C NMR ($CDCl_3$) δ 54.50 (OCH_3), 104.81, 121.31, 125.91, 126.10, 127.75, 129.41, 134.87, 136.17, 155.94 ($C_{10}H_6$); IR (neat) 2072.1, 2023.5 cm^{-1} (GeH); MS (EI, 50 eV) *m/z* 234 ((M^+), 32%) 216 ((M − 2H − CH_4), 18%). Anal. Calcd for $C_{11}H_{12}GeO$: C, 56.75; H, 5.20. Found: C, 56.79; H, 5.21.

General Procedure for the Synthesis of 4−6. Trifluoromethanesulfonic acid (1 mmol) was added slowly to a solution of the respective (8-methoxynaphthyl)germane (**1**−**3**; 1 mmol) in diethyl ether (15 mL). The reaction mixture was stirred for 1 h at 30 °C. After evaporation of the solvent in vacuo, 10 mL of pentane was introduced with stirring until a white solid precipitated. This powder was washed with freshly distilled pentane (2 × 3 mL) and then isolated by decantation and drying in vacuo.

4 (85%): mp 115−117 °C; ^1H NMR ($CDCl_3$) δ 4.14 (s, 3H, OCH_3), 6.69 (s, 2H, GeH_2), 6.95 (dd, $J^3 = 6.8$ Hz, $J^4 = 1.8$ Hz, 1H, H_7), 7.35−8.05 (m, 5H, $C_{10}H_6$); ^{13}C NMR ($CDCl_3$) δ 56.25 (OCH_3), 105.08, 122.35, 122.70, 126.31, 127.66, 130.39, 132.89, 134.01, 152.96 ($C_{10}H_6$), 119.19 (q, $J_{CF} = 318.2$ Hz, CF_3); ^{19}F NMR ($CDCl_3$) δ −2.40 (s); IR (Nujol) 2121.4, 2109.6 cm^{-1} (GeH); MS (EI, 70 eV) *m/z* 382 ((M^+), 59%); 233 ((M − OSO_2CF_3), 100%). Anal. Calcd for $C_{12}H_{11}F_3GeO_4S$: C, 37.84; H, 2.91. Found: C, 37.71; H, 2.86.

5 (42%): mp 131−134 °C; ^1H NMR ($CDCl_3$) δ 3.74 (s, 3H, OCH_3), 6.84 (dd, $J^3 = 7.1$ Hz, $J^4 = 1.5$ Hz, 1H, H_7), 7.25−7.80 (m, 9H, $C_{10}H_6$, C_6H_5, GeH), 8.02 (dd, $J^3 = 8.3$ Hz, $J^4 = 1.4$ Hz, 1H, H_4), 8.16 (dd, $J^3 = 6.8$ Hz, $J^4 = 1.4$ Hz, 1H, H_2); ^{13}C NMR ($CDCl_3$) δ 55.15 (OCH_3), 104.90, 122.53, 123.10, 126.34, 127.66, 131.19, 133.68, 134.14, 152.77 ($C_{10}H_6$), 128.93, 130.68, 133.12, 133.82 (C_6H_5); ^{19}F NMR ($CDCl_3$) δ −2.43 (s); IR (Nujol) 2151.5 cm^{-1} (GeH); MS (EI, 70 eV) *m/z* 458 ((M^+), 100%) 309 ((M − OSO_2CF_3), 40%). Anal. Calcd for $C_{18}H_{15}F_3GeSO_4$: C, 47.31; H, 3.31. Found: C, 46.65; H, 3.30.

6 (85%): mp 122−125 °C; ^1H NMR ($CDCl_3$) δ 3.76 (s, 6H, OCH_3), 6.86 (dd, $J^3 = 6.6$ Hz, $J^4 = 2.1$ Hz, 2H, H_7), 7.32−7.80 (m, 8H, $C_{10}H_6$), 7.85 (s, 1H, GeH), 7.94 (dd, $J^3 = 7.9$ Hz, $J^4 = 1.5$ Hz, 2H, $C_{10}H_6$); ^{13}C NMR ($CDCl_3$) δ 54.80 (OCH_3), 105.17, 121.88, 126.36, 126.74, 127.52, 128.32, 130.68, 133.73, 134.58, 154.23 ($C_{10}H_6$); ^{19}F NMR ($CDCl_3$) δ −2.56 (s); IR (Nujol) 2170.5 cm^{-1} (GeH); MS (CI, CH_4) *m/z* 539 ((M + 1), 1%), 538 ((M^+), 4%), 389 ((M − OSO_2CF_3), 75%). Anal. Calcd for $C_{23}H_{19}F_3GeSO_5$: C, 51.44; H, 3.57. Found: C, 51.43; H, 3.73. Crystals suitable for X-ray analysis were obtained by recrystallization from dry and degassed cyclohexane.

General Procedure for the Preparation of Germyl Iodides 7 and 8. Iodine (0.29 mmol) was added to a solution of the (8-methoxynaphthyl)germane (0.65 mmol) in benzene (10 mL). The mixture was stirred for 2 h at room temperature. The solvent was reduced by half and 30 mL of pentane was added. After 48 h at −30 °C, the white solid was isolated by decantation, washed with pentane (2 × 5 mL), and dried in vacuo.

7 (48%): mp 122 °C; ^1H NMR ($CDCl_3$) δ 3.60 (s, 3H, OCH_3), 6.78 (dd, $J^3 = 6.8$ Hz, $J^4 = 1.8$ Hz, 1H, H_7), 6.91 (s, 1H, GeH), 7.23−7.73 (m, 8H, $C_{10}H_6$ and C_6H_5), 7.95 (dd, $J^3 = 8.2$ Hz, $J^4 = 1.3$ Hz, 1H, H_4), 8.44 (dd, $J^3 = 6.8$ Hz, $J^4 = 1.3$ Hz, 1H, H_2); ^{13}C NMR ($CDCl_3$) δ 54.16 (OCH_3), 104.86, 121.66, 123.10, 126.14, 126.82, 127.91, 130.59, 138.56, 138.84, 154.00 ($C_{10}H_6$), 128.36, 129.57, 132.42, 134.56 (C_6H_5); IR (Nujol) 2094.9 cm^{-1} (GeH); MS (EI, 20 eV) *m/z* 436 ((M^+), 1%), 435 ((M − H), 5%), 309 ((M − I), 100%). Anal. Calcd for $C_{17}H_{15}GeIO$: C, 46.96; H, 3.48. Found: C, 46.71; H, 3.38.

8 (87%): mp 132−134 °C; ^1H NMR ($CDCl_3$) δ 3.63 (s, 6H, OCH_3), 6.78 (dd, $J^3 = 6.4$ Hz, $J^4 = 2.3$ Hz, 2H, H_7), 7.23−7.53 (m, 6H, $C_{10}H_6$), 7.35 (s, 1H, GeH), 7.78−7.90 (m, 4H, $C_{10}H_6$); ^{13}C NMR ($CDCl_3$) δ 54.26 (OCH_3), 105.15, 121.45, 126.08, 126.37, 127.32, 129.89, 131.32, 134.94, 135.20, 154.97 ($C_{10}H_6$); IR (Nujol) 2122.0 cm^{-1} (GeH); MS (EI, 10 eV) *m/z* 389 ((M − I), 35%), 374 ((M − CH_3I), 100%). Anal. Calcd for $C_{22}H_{19}GeIO_2$: C, 51.32, H, 3.72. Found: C, 51.03; H, 3.67.

Thermolysis of 8. A solution of **8** (0.23 g, 0.44 mmol) in CH_3CN (5 mL) was heated at reflux for 24 h. After concentration of the solvent in vacuo, the residue was washed with pentane (3 × 4 mL), giving a white powder which was isolated by decantation and drying.

9: 0.14 g (85%); mp 222−224 °C; ^1H NMR ($CDCl_3$) δ 4.35 (s, 3H, OCH_3), 7.19 (s, 1H, GeH), 6.97−7.91 (m, 11H, $C_{10}H_6$), 8.11 (dd, $J^4 = 1.4$ Hz, $J^3 = 6.7$ Hz, 1H, H_2); ^{13}C NMR ($CDCl_3$) δ 56.36 (OCH_3), 104.85, 122.22, 125.90, 126.97, 128.55, 130.55, 132.22, 132.56, 134.40, 161.72 (free $C_{10}H_6$), 107.18, 116.17, 126.97, 127.95, 128.32, 128.40, 129.61, 133.38, 154.35 (cyclic $C_{10}H_6$); IR (Nujol) 2086.6 cm^{-1} (GeH); MS (EI, 70 eV) *m/z* 374 ((M^+), 68%), 358 ((M − CH_4), 18%). This compound is unstable in solution and cannot be recrystallized.

Reaction of 6 with Benzylamine. Benzylamine (2.44 mL, 0.02 mmol) was added to a solution of **6** (0.012 g, 0.02 mmol) in 0.4 mL of $CDCl_3$ in an NMR tube. The quantitative formation of compound **10** was observed: ^1H NMR ($CDCl_3$) δ 3.29 (s, 8H, OCH_3 and CH_2N), 6.58 (d, $J^3 = 6.7$ Hz, 2H, H_7), 7.15−7.61 (m, 11 H, $C_{10}H_6$, NH_2 and GeH), 7.75 (d, $J^3 = 7.4$ Hz, 2H, H_2).

Reaction of 6 with H_2O. H_2O (0.012 g, 0.66 mmol) was added to a solution of **6** (0.35 g, 0.66 mmol) in diethyl ether (20 mL) at room temperature. The solvent was evaporated in vacuo to give a white powder identified as **11**: 0.36 g (quantitative yield). Crystals suitable for X-ray analysis were obtained by dissolving the powder in a large excess of diethyl ether. The solution was decanted and cooled at 5 °C for 3 weeks.

11: mp 120−140 °C dec; ^1H NMR ($CDCl_3$) δ 3.77 (s, 6H, OCH_3), 6.86 (dd, $J^3 = 6.5$ Hz, $J^4 = 2.1$ Hz, 2H, H_7), 7.33−7.60 (m, 6H, $C_{10}H_6$), 7.76 (d, $J^3 = 6.3$ Hz, 3H, $C_{10}H_6$ and GeH), 7.94 (dd, $J^3 = 7.9$ Hz, $J^4 = 1.2$ Hz, 2H, $C_{10}H_6$), 7.33−8.00 (m, 2H, H_2O); ^{13}C NMR ($CDCl_3$) δ 54.91 (OCH_3), 105.21, 122.00, 126.45, 126.85, 127.64, 128.44, 130.78, 133.85, 134.71, 154.36 ($C_{10}H_6$); ^{19}F NMR ($CDCl_3$) δ −2.55 (s); IR (Nujol) 2165.3 (GeH), 3000.0 cm^{-1} ($HOSO_3$). Anal. Calcd for $C_{23}H_{21}F_3GeO_6$: C, 49.77; H, 3.81. Found: C, 49.78; H, 3.75.

Reaction of 6 with DMSO. DMSO (43 mL, 0.59 mmol) was added to a solution of **6** (0.32 g, 0.59 mmol) in $CHCl_3$ (3 mL) and pentane (2 mL). The mixture was stirred for 10 min at room temperature. After evaporation of the solvent, ^1H NMR analysis showed the formation of complex **12**. Five milliliters of $CHCl_3$ was added to the residue, and the solution was cooled to −30 °C for 3 weeks to give colorless crystals. These were washed with pentane (3 × 5 mL) and dried under a current of argon, leading to **12**.

12 0.39 g (89%); mp 58−70 °C dec; ^1H NMR ($CDCl_3$) δ 2.92 (s, 6H, CH_3S), 3.81 (s, 6H, OCH_3), 6.93 (dd, $J^3 = 6.1$ Hz, $J^4 = 2.4$ Hz, 2H, H_7), 7.37−7.83 (m, 9H, $C_{10}H_6$ and GeH), 7.97 (dd, $J^3 = 7.2$ Hz, $J^4 = 2.2$ Hz, 2H, $C_{10}H_6$); ^{13}C NMR ($CDCl_3$) δ 37.87 (CH_3S), 55.39 (OCH_3), 106.16, 122.47, 126.79, 127.60, 128.26, 131.22, 133.32, 134.78, 154.04 ($C_{10}H_6$); ^{19}F NMR ($CDCl_3$) δ −3.52 (s); IR (Nujol) 2121.4 cm^{-1} (GeH). Anal. Calcd for $C_{23}H_{21}F_3GeSO_6$ ($CHCl_3$): C, 42.51; H, 3.57. Found: C, 42.03; H, 3.54.

Preparation of Germoxanes 13−15. A stoichiometric mixture of H_2O and Et_3N was added to a solution of germyl triflate **4**, **5**, or **6** (1 mmol). The mixture was stirred for 1 h at room temperature. An excess of water was then introduced. After extraction with ether and drying over Na_2SO_4, the solution was concentrated in vacuo and gave white powders, which were identified as the corresponding oxides.

13 (45%): mp 106−109 °C; ^{1}H NMR (CDCl$_3$) δ 3.97 (s, 6 H, OCH$_3$), 6.12 (s, 4H, GeH$_2$), 6.83 (dd, $J^3 = 6.4$ Hz, $J^4 = 2.1$ Hz, 2H, H$_7$), 7.27−7.66 (m, 6H, C$_{10}$H$_6$), 7.86 (dd, $J^3 = 8.1$ Hz, $J^4 = 1.2$ Hz, 2H, H$_4$), 8.25 (dd, $J^3 = 6.6$ Hz, $J^4 = 1.2$ Hz, 2H, H$_2$); ^{13}C NMR (CDCl$_3$) δ 54.74 (OCH$_3$), 104.52, 121.37, 125.71, 126.51, 128.51, 128.91, 130.99, 133.12, 134.73, 155.88 (C$_{10}$H$_6$); IR (Nujol) 2063.0 and 2042.4 (GeH), 739.8 cm^{-1} (GeOGe); MS (EI, 70 eV) *m/z* 480 ((M$^+$), 2%), 322 ((M − (CH$_3$O)N$_p$H), 13%). Correct analyses were obtained by recrystallization from THF. Anal. Calcd for $C_{22}H_{22}Ge_2O_2$: C, 55.10; H, 4.62. Found: C, 54.81; H, 4.66.

14 (37%): mp 140 °C; two diastereoisomers were obtained in the ratio 50/50; ^{1}H NMR (CDCl$_3$) δ 3.52 (s, 6H, OCH$_3$), 6.58 and 6.59 (s, 2H, GeH), 6.69 (dd, $J^3 = 6.9$ Hz, $J^4 = 1.9$ Hz, 2H, H$_7$), 7.16−7.68 (m, 16H, C$_{10}$H$_6$ and C$_6$H$_5$), 7.86 (dd, $J^3 = 8.2$ Hz, $J^4 = 1.9$ Hz, 2H, H$_4$), 8.34 and 8.42 (dd, $J^3 = 6.7$ Hz, $J^4 = 1.5$ Hz, 2H, H$_2$); ^{13}C NMR (CDCl$_3$) δ 54.01 (OCH$_3$), 104.36, 121.29, 125.67, 126.48, 129.20, 129.35, 131.36 and 131.48, 134.30 and 134.42, 134.79, 155.66 (C$_{10}$H$_6$), 127.93, 128.70, 133.47, 140.77 and 140.82 (C$_6$H$_5$); IR (Nujol) 2046.8 cm^{-1} (GeH); MS (EI, 20 eV) *m/z* 632 ((M$^+$), 2%). Anal. Calcd for $C_{34}H_{30}Ge_2O_3$: C, 64.64; H, 4.79. Found: C, 64.41; H, 4.91.

15 (47%): mp 225−230 °C; ^{1}H NMR (CDCl$_3$) δ 3.25 (s, 12H, OCH$_3$), 6.53 (dd, $J^3 = 6.8$ Hz, $J^4 = 2.0$ Hz, 4H, H$_7$), 7.01 (dd, $J^3 = 6.8$ Hz, $J^4 = 7.9$ Hz, 4H, H$_5$), 7.08 (s, 2H, GeH), 7.19−7.48 (m, 8H, C$_{10}$H$_6$), 7.56 (dd, $J^3 = 7.0$ Hz, $J^4 = 1.4$ Hz, 4H, H$_2$), 7.69 (dd, $J^3 = 8.1$ Hz, $J^4 = 1.4$ Hz, 4H, H$_4$); ^{13}C NMR (CDCl$_3$) δ 53.94 (OCH$_3$), 104.21, 120.93, 125.23, 126.12, 128.37, 128.74, 134.21, 134.76, 135.76, 156.18 (C$_{10}$H$_6$); IR (Nujol) 2069.9cm^{-1} (GeH); MS (CI, CH$_4$) *m/z* 793 ((M + H), 7%). Correct analyses were obtained by recrystallization from THF. Anal. Calcd for $C_{44}H_{38}Ge_2O_5$: C, 66.73; H, 4.83. Found: C, 66.31; H, 4.86.

X-ray Crystallography. Suitable crystals of **6** and **11** were sealed in a capillary. The data collection was carried out on a Stoe ′IPDS image system with MoKa radiation. The structures were solved by direct methods. The full-matrix least-squares refinement was done on F^2 and the hydrogen atoms (expect Ge−H) were geometrically fixed on the appropriate carbon and oxygen atoms.[18] Crystal data and the results of the refinement are collected in Table 2.[19]

Supporting Information Available: Tables of crystal data, atom coordinates, thermal parameters, and bond distances and angles for **6** and **11** and a plot of conductivity measurements (13 pages). Ordering information is given on any current masthead page.

OM970963F

---

(18) Sheldrick, G. M. SHELXS-86 and SHELXL-93, Programs for Crystal Structure Determination; University of Göttingen, Göttingen, Germany.

(19) Further details of the crystal structure investigation have been deposited at the CCDC and may be obtained on quoting the depository number (No. 101463), the names of the authors, and the journal citation.