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Preparation of germatranyl triflates: reactions of germatranes $N(CH_2CHRO)_3X$ ($X = Br, OTf, OSiMe_3$; $R = H, Me$) with lithium reagents

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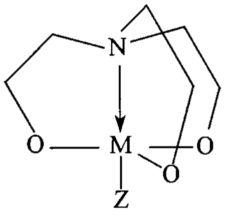
Abstract

New germatranes $N(CH_2CHRO)_3GeOTf$ (**4a**, $R = H$; **4b**, $R = Me$) were prepared in quantitative yield by treatment of $N(CH_2CHRO)_3GeOSiMe_3$ (**2a** and **2b**), with Me_3SiOTf. The reactions of germatranes $N(CH_2CHRO)_3GeX$ [**3a**, $X = Br$, $R = H$; **4a**, $X = OSO_2CF_3$, $R = H$; **4b**, $X = OSO_2CF_3$, $R = Me$; **2a**, $X = OSiMe_3$, $R = H$; **2b**, $X = OSiMe_3$, $R = Me$] with LiY reagents were studied. A series of germatranes $N(CH_2CHRO)_3GeY$ [**5a**, $R = H$, $Y = Ind$ (indenyl); **5b**, $R = Me$, $Y = Ind$; **6a**, $R = H$, $Y = N(SiMe_3)_2$; **6b**, $R = Me$, $Y = N(SiMe_3)_2$; **7a**, $R = H$, $Y = Cp$ (cyclopentadienyl); **7b**, $R = Me$, $Y = Cp$; **8a**, $R = H$, $Y = Flu$ (fluorenyl); **9a**, $R = H$, $Y = t\text{-}Bu$] were obtained by nucleophilic substitution with the corresponding LiY reagent. Reactions of $N(CH_2CHMeO)_3GeOSiMe_3$ (**2b**) and $N(CH_2CH_2O)_3GeBr$ (**3a**) with excess n-BuLi and of $N(CH_2CH_2O)_3GeOSiMe_3$ (**2a**) with excess $LiNMe_2$ led to the formation of $n\text{-}Bu_4Ge$ and $(Me_2N)_4Ge$. The structures of new germatranes **4a**, **4b**, **6b** and **7b** were confirmed by NMR spectroscopy, mass spectrometry and elemental analyses. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Germatranes; Lithium reagents

1. Introduction

Atranes of type (**A**) are cyclic esters containing a hypervalent atom M with a transannular interaction between M and the bridgehead nitrogen atom [1,2]. The nature of substituent Z affects the properties of atranes, such as biological activities [3a,b] and the strength of the transannular M←N bonding [4].



A

Most of the previous extensive work on metallatranes has been focused on the synthesis, physico-chemical properties and RSA studies of these compounds in order to confirm the supposed intramolecular M←N coordination. Much less attention has been directed toward chemical transformations of these compounds.

We are interested in the chemistry of metallatranes (M = Si, Ge) that contain the substituent Z with different steric and electronic properties, including studying the influence of the 'atrane' moiety on the stability, the reactivity and the ability to undergo chemical transformations [5a–d].

We have focused our attention on germatranes with germanium–carbon bonds containing a functional group neighbouring the germanium atom (M = Ge, Z = allyl [6a], phenylacetylenyl [6b], fluorenyl [6b,c,d], benzyl [6e], alkoxycarbonylmethyl [4]). These compounds have been found to be reactive precursors for new types of germatranes. For example, we have

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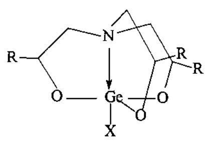
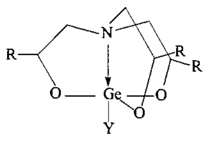
described two kinds of reactions proceeding with a retention of both the ‘atrane’ skeleton and the Ge–C bond: cyclopropanation of allylgermatranes with $CH_2N_2/Pd(OAc)_2$ [6a], and stannylation of 1-fluorenylgermatranes [6c,d]. A series of the above-mentioned germatranes [4,6a–e] was synthesized by a transmetallation reaction of trihalogenogermanes with stannyl esters of trialkanolamines. This organotin route to germatranes achieved excellent results and can be carried out using easily accessible trihalogenogermanes.

Here we report our studies with functionalized germatranes starting from the most simple and available germatranes — 1-hydroxygermatranes (**1a** and **1b**) [1].



1-4

	X	R
1a	OH	H
1b	OH	Me
2a	$OSiMe_3$	H
2b	$OSiMe_3$	Me
3a	Br	H
4a	OSO_2CF_3	H
4b	OSO_2CF_3	Me



5-8

	Y	R
5a	C_9H_7	H
5b	C_9H_7	Me
6a	$N(SiMe_3)_2$	H
6b	$N(SiMe_3)_2$	Me
7a	C_5H_5	H
7b	C_5H_5	Me
8a	$C_{13}H_9$	H
9a	*t*-Bu	H

Triisopropanolamine derivatives (R = Me) were synthesized in order to clarify the possible influence of steric crowding on the reaction pathways.

We demonstrate that these germatranes can be transformed via 1-trimethylsiloxygermatranes (**2a** and **2b**) to new germatranes $N(CH_2CHRO)_3GeOSO_2CF_3$ (**4a**, R = H) and (**4b**, R = Me). Germatranes **2**–**4** bearing a highly electronegative apical substituent X react with LiY reagents to yield the corresponding germatranes **5**–**8**. NMR data of the compounds **4a**, **4b**, **6b** and **7b** are reported. To the best of our knowledge, there have been no reports in the literature on the reaction of germatranes with lithium reagents [1,2]. Interestingly, the ‘atrane’ framework in **2**–**4** was found to be stable under reaction conditions with LiY when Y = Flu, Ind, Cp, and $N(SiMe_3)_2$. Treatment of **2b** and **3a** with *n*-BuLi as well as **2a** with $LiNMe_2$ gave the reaction products with the destruction of the ‘atrane’ fragment.

2. Results and discussion

The starting materials, 1-trimethylsiloxygermatranes (**2a** and **2b**) [7,8], were prepared by a silylation reaction of the monohydrates of 1-hydroxygermatranes (**1**) [1] (here and for other compounds: **a**, R = H, **b**, R = Me) with $(Me_3Si)_2NH$ (Eqs. (1) and (2))).

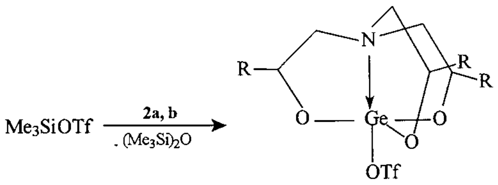
$$GeO_2 + N(CH_2CHROH)_3/H_2O \rightarrow \underset{\mathbf{1a,b}}{N(CH_2CHRO)_3GeOH} \cdot H_2O \quad (1)$$

$$(Me_3Si)_2NH \xrightarrow[-1/2(Me_3Si)_2O,\ -NH_3,\ -H_2O]{\mathbf{1a,b}} N(CH_2CHRO)_3GeOSiMe_3\ \mathbf{2a,b} \quad (2)$$

Compound **2a** was used for the preparation of 1-bromogermatrane (**3a**) [5a,8] (Eq. (3))

$$Me_3SiBr \xrightarrow[-(Me_3Si)_2O]{\mathbf{2a}} \underset{\mathbf{3a}}{N(CH_2CH_2O)_3GeBr} \quad (3)$$

The new 1-trifluoromethanesulfonatogermatranes (germatranyltriflates) (**4a** and **4b**) were obtained almost quantitatively by substitution of the $OSiMe_3$ group with the OSO_2CF_3(OTf) group from the reaction of (**2a** and **2b**) with Me_3SiOTf (Eq.(4)).



(4)

4a, b

The synthetic potential of $N(CH_2CHRO)_3GeX$ (X = Br, OTf, $OSiMe_3$) as precursors for functionally substituted germatranes was investigated in many reactions with lithium reagents.

2.1. *Reactions of 1-bromogermatrane **3a** with lithium reagents*

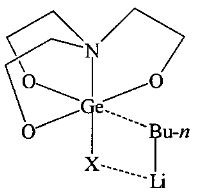
Halogenides of Ge(IV) are widely used as key reagents in the synthesis of functionalized germanes [9]. Exchange reactions between halogenogermanes and functionally substituted organotin compounds are a convenient approach for the synthesis of various functional germanes [9,10]. The question of whether 1-bromogermatrane (**3a**) was suitable as a starting material for an analogous route was explored by reacting it with different organotin reagents. We have recently shown that this method is applicable for the preparation of a variety of 1-organoxygermatranes by replacement of bromine in **3a** in a reaction with organoxytrialkylstannanes [5a]. However, our attempted reactions of germatrane **3a** with organotin ketoenol derivatives failed [11]. These results contrasted those obtained for tetracoordinated halogenogermanes in analogous reactions [10]. In our present work from **3a** and $Et_3SnN(SiMe_3)_2$ we obtained only an impure product in low yield.

Therefore, we investigated another approach to functionalized germatranes: reactions of germatrane **3a** with stronger nucleophilic reagents, e.g. with lithium reagents. The results of this reaction essentially depend on the nature of the lithium reagents; treatment of a suspension of **3a** in THF with an excess of *n*-butyllithium in *n*-hexane at room temperature for 4 h provides, after work-up, tetra-*n*-butylgermane in 61% yield. Therefore, *n*-butyllithium, acts as a strong, non-selective nucleophilic reagent, alkylates Ge–Br bonds and cleaves Ge–O bonds of the germatrane fragment (Eq. (5)).

$$\mathbf{3a} \xrightarrow{4\ n\text{-BuLi}} n\text{-Bu}_4\text{Ge}\ (61\%) \qquad (5)$$

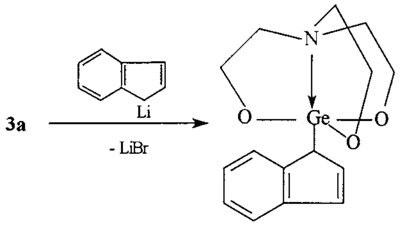
Conversion of **3a** into *n*-Bu_4Ge takes place even in the presence of only one equivalent of *n*-BuLi.

Our results contrast with those obtained for a recent study of the silicon analogue of **3a** (1-halosilatranes) with *n*-BuLi, where substitution, involving cleavage of the equatorial Si–O bond rather than of the Si–Hal linkage, takes place. The lower reactivity of the Si–Cl bond of halogenosilatranes in this case was interpreted as a consequence of the unusual molecular geometry of the 'atrane' framework [12a,b]. The X-ray crystal structure analysis of the 1-bromogermatrane (**3a**) [13] shows, that the Ge–Br bond is considerably longer than a Si–Cl bond (2.36 Å instead of 2.15 Å [14]). The Ge–Br bond elongation in the structure of $N(CH_2CH_2O)_3GeBr$ is correlated to the enhanced reactivity of the Ge–Br bond toward *n*-BuLi. In germatranes the germanium atom possibly becomes hexacoordinated and nucleophilic substitution of bromine may occur via the intermediate **B**:



B

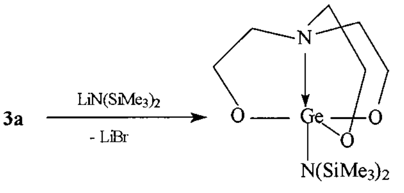
In contrast to *n*-butyllithium, indenyllithium gave with stoichiometric amounts of **3a** 1-(1-indenyl)germatrane (**5a**) in 56% yield. NMR control showed the absence of degradation products of the 'atrane' fragment (Eq. (6)).



(6)

5a (56%)

The Ge–O bonds remain unchanged in the case of the reaction of **3a** with $LiN(SiMe_3)_2$ (Eq. (7)). Compound **6a** was obtained in moderate yield when a solution of **3a** in THF was treated with equimolar amounts of $LiN(SiMe_3)_2$; the product was isolated as an analytically pure sample and identified by comparison with an authentic sample prepared earlier in our group by reaction of **1a** with $[(Me_3Si)_2N]_2Sn$ [15].



(7)

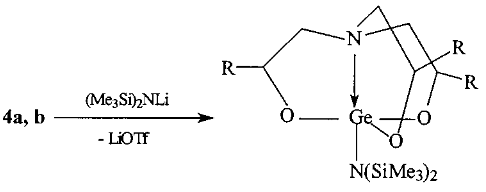
6a (65%)

Reaction (7) contrasts a known reaction of four-coordinate alkoxy and aryl germanium derivatives with $MN(SiMe_3)_2$ (M = Na, Li), where Ge–O bonds are cleaved to form Ge–$N(SiMe_3)_2$ bonds [16].

Treatment of germatrane **3a** with fluorenyllithium or 9-Me_3Ge-fluorenyllithium in THF at room temperature for 12 h results, after standard work-up, in the formation of a mixture of the starting material and unidentified products. In the case of CpLi, a reaction takes place; however, 1-(5-cyclopentadienyl)germatrane (**7a**) was only obtained in relatively low yield (29%).

2.2. Reactions of germatranyltriflates ***4a*** *and* ***4b*** *with lithium reagents*

Group 14 triflates are highly reactive reagents and have been widely used for metallation and catalysis [17a,b]. In this respect, germatranyltriflates **4** are analogous (or even more reactive) to 1-bromogermatrane (**3a**) in their reactions with lithium reagents. Treatment of triflates **4a** and **4b** (as a suspension in xylene) with solutions of $LiN(SiMe_3)_2$ in THF–hexane led to the formation of the corresponding 1-aminogermatranes **6a** and **6b** in good yields (Eq. (8)). A white solid **6b**, which was obtained after standard procedure as a mixture of two diastereomers, was further purified by sublimation.



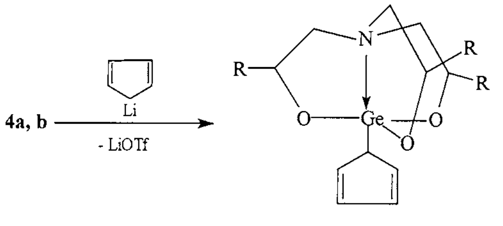
(8)

6a (76%)
6b (68%)

Note the substantial difference in reactivity between 1-bromogermatrane **3a** and germatranyltriflates **4a** and

4b toward $LiN(SiMe_3)_2$. It appears that the nature of the leaving group is not of great importance since the yields of **6a** from reactions (7) and (8) are comparable.

Likewise, the OTf group in compounds **4a** and **4b** can be easily replaced by a cyclopentadienyl group resulting in the formation of germatranes **7a** and **7b** in good yield (Eq. (9)):



(9)

7a (65%)
7b (70%)

Compound **7a** is a known compound and was made earlier by reacting Cl_3GeCp with $N(CH_2CH_2OSnEt_3)_3$ [18]. Although this organotin route to give **7a** has been reported in 98% yield, our approach (reaction (9)) in the case of this germatrane is preferable because of the readily available starting reagents. Purification of the reaction product from **4b** with CpLi, obtained in a 70% yield as a mixture of two diastereomers, gave almost solely the symmetric diastereomer of **7b** (NMR data). The second (unsymmetric) diastereomer does not sublime under these conditions.

However, extension of this method for synthesizing 1-(9-fluorenyl)germatrane (**8a**) was unsuccessful; all our attempts to react **4a** with fluorenyllithium failed. After standard work-up we obtained a complex mixture of products, all of which contained the starting material **4a**.

2.3. *Reactions of 1-trimethylsiloxygermatranes **2a** and **2b** with lithium reagents*

We have recently shown that 1-trimethylsiloxygermatranes **2a** and **2b** can serve as excellent starting materials for the preparation of a variety of 1-halogenogermatranes [5a,8] (Eq. (10)):

$$N(CH_2CHRO)_3GeOSiMe_3 \xrightarrow[-\ Me_3SiOE]{E\text{-}Hal} N(CH_2CHRO)_3\text{-}GeHal$$

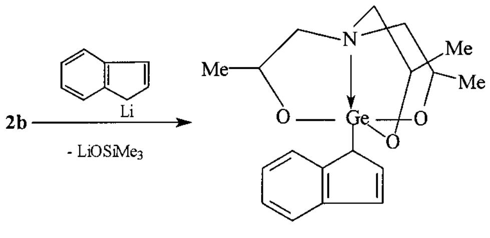
R = H, Me; E-Hal: HF, $SOCl_2$, Me_3SiBr, Me_3SiI (10)

Other results concerning the reactivity of 1-trimethylsiloxygermatranes have not been reported. Previously it has been described that the reaction of phenyllithium with $Me_3GeOSiMe_3$ quantitatively affords Me_3GePh (as a product of nucleophilic attack at the electrophilic germanium atom) [19].

Treatment of **2a** with one equivalent of $LiN(SiMe_3)_2$ in hexane–THF, analogous to reactions (7) and (8), produces the aminogermatrane **6a** in good yield (Eq. (11)):

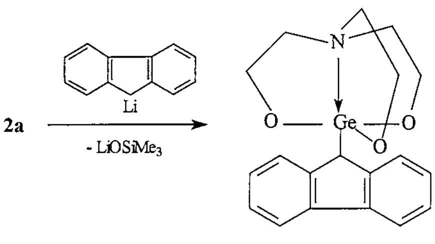
$$\mathbf{2a} \xrightarrow[-\ LiOSiMe_3]{LiN(SiMe_3)_2} \mathbf{6a}\ (71\%) \qquad (11)$$

This method is applicable for the synthesis of 1-indenyl-3,7,10-trimethylgermatrane **5b** and 1-(9-fluorenyl)-germatrane **8a** (Eqs. (12) and (13)):



(12)

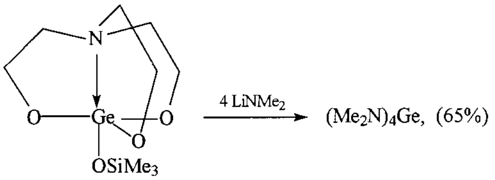
5b (45%)



(13)

8a (71%)

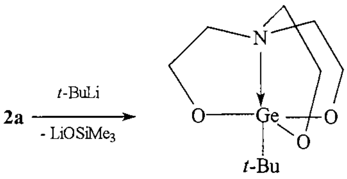
Cleavage of the endocyclic Ge–O bonds of the 'atrane' skeleton is the predominant reaction when **2a** was treated with an excess of $LiNMe_2$ (Eq. (14)) and *t*-BuLi (see Section 4).



(14)

2a

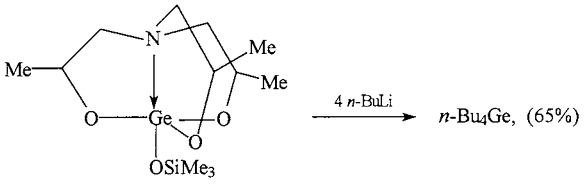
With one equivalent of *t*-BuLi and **2a** we could obtain 1-*t*-butylgermatrane (**9a**) in satisfactory yield (Eq. (15)):



(15)

(**9a**), 42%

Reaction (16) shows that methyl groups in positions 3, 7 and 10 of the 'atrane' fragment do not prevent the cleavage of the equatorial Ge–O bonds with *n*-BuLi. No reactions were detected from **2a** and CpLi or Me_4CpLi.

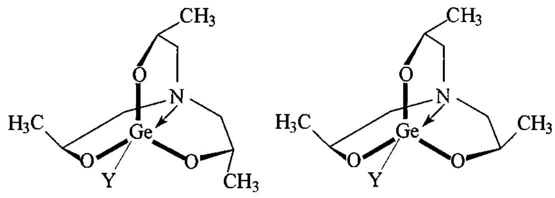


(16)

2b

All compounds were characterized by ^{1}H-, ^{13}C- (excluding **4a** and **4b**) and ^{19}F- (for **4a** and **4b**) NMR spectroscopy; new compounds **4a**, **4b**, **6b** and **7b** were also characterized by elemental analyses and mass spectrometry.

^{1}H- and ^{13}C-NMR spectra were in accordance with the suggested structures. In the ^{1}H-NMR spectrum of **4a**, signals of the methylene protons of the germatrane skeleton appear as a set of two pseudo-triplets, forming an AA′XX′ spin system ($J = 5.6$ Hz). This pattern is a general feature of the 'atrane' framework for a variety of germatranes [1,4,6]. 3,7,10-Trimethylsubstituted metallatranes **4b**, **6b** and **7b** are mixtures of two diastereomers which differ in the orientation of the methyl groups relative to the Ge–N-axis (Structures **C** and **D**).



C

symmetric
diastereomer

D

unsymmetric
diastereomer

Proton signals of the $OCH(CH_3)CH_2N$ groups of the 'atrane' framework appear in the ^{1}H-NMR spectra as complex multiplets ($ABMX_3$ spin system). This pattern is also a general feature of the 3,7,10-trimethylsubstituted 'atrane' framework. In this case the composition of mixtures can be examined by ^{13}C-NMR spectroscopy as described earlier for other 1-substituted germatranes [1,4,6]. In the ^{19}F-NMR spectrum of **4a** the signal of the fluorine atoms of the CF_3 groups appears at $\delta = -79.34$ ppm; in the ^{19}F NMR spectrum of **4b** two signals of the CF_3 group appear for two diastereomers at -78.81 and -79.18 ppm [20]. **5b** is a mixture of four diastereomers according to the ^{13}C-NMR spectrum.

3. Conclusions

In summary, we conclude that in our studies substitutive cleavage of equatorial Ge–O bonds as well as a cleavage of the apical bond opposite to the transannular Ge←N bond of germatranes takes place with the lithium reagents.

The reactions occur without degradation of the cyclic skeleton of the molecule. We have developed a simple and effective method of preparation under very mild conditions from 1-cyclopentadienyl-, 1-indenyl-, 1-(9-fluorenyl)- and 1-[bis(trimethylsilyl)amino]germatranes, $N(CH_2CHRO)_3GeY$, using reactions of lithium reagents with $N(CH_2CHRO)_3GeX$ ($X = Br$, OTf, $OSiMe_3$; $R = H$, Me) as easily available starting materials. We are attempting to further extend the scope of this method to functionally substituted germatranes.

4. Experimental

4.1. General comments

The synthesis of **4a**, **4b** and reactions with lithium reagents were carried out under an argon atmosphere using standard Schlenk techniques. All solvents (hexane, tetrahydrofuran (THF) and xylene) were dried by standard methods and distilled before use. Solutions of *n*-butyllithium in hexane were commercially obtained and analysed regularly by the Gilman double-titration method [21]. Commercially available Me_3SiBr, $Me_3SiOSO_2CF_3$ and $(Me_3Si)_2NH$ (Aldrich) were used without further purification. Organoelement compounds used in this study were prepared according to the literature method indicated: $N(CH_2CH_2O)_3GeOH{\cdot}H_2O$ [7], $N(CH_2CH_2O)_3GeOSiMe_3$ [7], $N(CH_2CHMeO)_3GeOSiMe_3$ [8], 9-trimethylgermyl-fluorene [22], 1-trimethylsilylindene [23], $N(CH_2CH_2O)_3GeBr$ [5a]. NMR spectra were recorded at 25°C in $CDCl_3$, C_6D_6 and CD_5CD_3 with internal deuterium lock, on Bruker AMX 400 and Varian VXR 400 spectrometers. Chemical shifts in the ^{1}H- and ^{13}C-NMR spectra are given in ppm relative to internal TMS; in ^{19}F-NMR experiments $CFCl_3$ was used as an external standard. Assignment of the ^{13}C-NMR data were supported by APT experiments. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University and by that of the Fachbereich Chemie of the Philipps-University Marburg (Heraeus-Rapid-Analyser). Mass spectra (EI-MS, 70 eV) were recorded on a Varian CH-7a device; all assignments were made with reference to the most abundant isotopes.

4.2. (1-Germatranyl)triflate, $N(CH_2CH_2O)_3GeOTf$ (**4a**)

To a solution of **2a** (0.85 g, 2.8 mmol) in xylene (10 ml) Me_3SiOTf was added (1 ml, 1.23 g, 5.5 mmol). The mixture was stirred at r.t. for 12 h; after removal of all volatiles in vacuo 1.03 g (100%) pure **4a** was left as a white solid, m.p. >250°C. ^{1}H-NMR ($CDCl_3$): δ 3.10

(t, 6H, NCH_2), 4.06 (t, 6H, OCH_2). ^{19}F NMR ($CDCl_3$): δ −79.34. EI MS *m*/*e* (rel. int.): [$M^+ - CH_2O$] 339 (20); [$M^+ - 2CH_2O$] 309 (24); [$M^+ - CF_3SO_3$] 220 (47); 100 (45); 86 (77); CF_3, 69 (100). Anal. Calc. for $C_7H_{12}F_3GeNO_6S$: C, 22.86; H, 3.29; N, 3.81. Found: C, 22.60; H, 3.30; N, 3.61%.

4.3. [1-(3,7,10-Trimethylgermatranyl)]triflate, $N(CH_2CHMeO)_3GeOTf$ (**4b**)

The procedure is analogous to that in Section 4.2. The reaction of **2b** (1.0 g, 2.9 mmol) in xylene (10 ml) with Me_3SiOTf (1 ml, 1.23 g, 5.5 mmol) gave 1.19 g (100%) of **4b** as a white solid, m.p. > 250°C. ^1H-NMR ($CDCl_3$): δ 1.30–4.30 ($ABXM_3$ system of NCH_2CH-MeO group protons). ^{19}F-NMR ($CDCl_3$): δ −78.81, −79.18; two diastereomers, **4b**-C and **4b**-D. EI MS *m*/*e* (rel. int.): [$M^+ - CH_3CHO$] 367 (20); [$M^+ - 2CH_3CHO$] 323 (24); [$M^+ - CF_3SO_3$] 262 (47); 128 (47); 100 (100); CF_3, 69 (61). Anal. Calc. for $C_{10}H_{18}F_3GeNO_6S$: C, 29.30; H, 4.43; Ge, 17.71. Found: C, 29.13; H, 4.53; Ge, 17.90%.

4.4. 1-(1-Indenyl)germatrane, $N(CH_2CH_2O)_3GeC_9H_7$ (**5a**)

A solution of IndLi, prepared from indene (0.10 g, 0.84 mmol) and *n*-BuLi (0.49 ml, 0.84 mmol) as a 1.72 M solution in hexane, was added to a solution of **3a** (0.25 g, 0.84 mmol) in THF (10 ml) at room temperature (r.t.). The reaction mixture was stirred for 12 h at r.t.; a precipitate was separated and volatiles were evaporated in vacuo. The residue was recrystallized twice from chloroform–hexane to give 0.16 g (56% yield) of **5a** as a white solid. ^1H- and ^{13}C-NMR data are consistent with those already published [24].

4.5. 1-(1-Indenyl)-3,7,10-trimethylgermatrane, $N(CH_2CHMeO)_3GeC_9H_7$ (**5b**)

A solution of IndLi, prepared from indene (0.15 g, 1.26 mmol) in THF (10 ml) and *n*-BuLi (0.72 ml, 1.26 mmol) as a 1.75 M solution in hexane, was added to a solution of **2b** (0.44, 1.26 mmol) in benzene (10 ml) at r.t. The reaction mixture was stirred for 12 h at r.t., a precipitate was separated and volatiles were evaporated in vacuo, the residue was recrystallized twice from chloroform–hexane to give 0.22 g (46% yield) of **5b** as a white solid (four diastereomers); ^1H- and ^{13}C-NMR data are consistent with those already published [24].

4.6. 1-[Bis(trimethylsilyl)amino]germatrane, $N(CH_2CH_2O)_3GeN(SiMe_3)_2$ (**6a**)

4.6.1. Reaction of 1-bromogermatrane **3a** with $LiN(SiMe_3)_2$

A solution of $LiN(SiMe_3)_2$, prepared from $(Me_3Si)_2NH$ (0.17 g, 1 mmol) in THF (10 ml) and *n*-butyllithium (0.6 ml, 1 mmol) as a 1.66 M solution in hexane, was added to a suspension of **3a** (0.30 g, 1 mmol) in THF (10 ml) at r.t. The reaction mixture was stirred for 24 h at r.t., then two thirds of the volatiles were evaporated in vacuo. A white precipitate was filtered off and volatiles were removed in vacuo. The residue was recrystallized from hexane–xylene, washed with hexane (2 × 5 ml). After drying in vacuo **6a** (0.25 g, 65%) was obtained as a white solid, m.p. 161–162°C (Ref. [15]: 161–163°C).

4.6.2. Reaction of (1-germatranyl)triflate **4a** with $LiN(SiMe_3)_2$

The synthesis of **6a** was analogous to that of **6a** in Section 4.6.1, except that a suspension of **4a** in xylene was used instead of a suspension of **4a** in THF. **6a** was obtained in 76% yield.

4.6.3. Reaction of 1-trimethylsiloxygermatrane **2a** with $LiN(SiMe_3)_2$

The synthesis of **6a** was analogous to that of **6a** in Section 4.6.1 except that a suspension of **2a** in toluene was used instead of a suspension of **4a** in THF. **6a** was obtained in 71% yield.

4.7. Reaction of **3a** with $Et_3SnN(SiMe_3)_2$

A mixture of **3a** (0.5 g, 1.7 mmol) and $Et_3SnN(SiMe_3)_2$ (1.23 g, 3.4 mmol) was heated at 100°C for 1 h. A mixture of Et_3SnBr and $Et_3SnN(SiMe_3)_2$ was separated by vacuum distillation, b.p. 60–80°C (1 Torr) (^1H-NMR data). ^1H and ^{13}C spectra of the residue showed the presence of **3a** and of product **6a**.

4.8. 1-[Bis(trimethylsilyl)amino]-3,7,10-trimethylgermatrane, $N(CH_2CHMeO)_3Ge\ N(SiMe_3)_2$ (**6b**)

Synthesis of **6b** was analogous to that of **6a** (Section 4.6.2.) except that triflate **4b** was used instead of **4a**. Colourless crystalline **6b** was obtained on sublimation at 80°C (2 Torr) with 68% yield, m.p. 149–151°C. ^1H-NMR ($CDCl_3$): δ 1.30–4.30 ($ABXM_3$ system of NCH_2CHMeO group protons); 0.48 (minor diastereomer, **6b**-C), 0.49 (major diastereomer, **6b**-D) (2s, 9H, $SiMe_3$). ^{13}C-NMR ($CDCl_3$): δ 2.92 ($SiMe_3$), 20.56, 20.71, 21.04, 23.18 (CH_3); 59.24, 62.09, 62.45, 62.95, 63.86, 64.18, 65.69, 66.11 (NCH_2, OCH). Two diastereomers. EI MS *m*/*e* (rel. int.): [$M^+ - Me$] 407 (100); [$M^+ - N(SiMe_3)_2$] 262 (4). Anal. Calc. for $C_{15}H_{36}GeN_2O_3Si_2$ (421.22): C, 42.77; H, 8.61; Ge, 17.23. Found: C, 42.38; H, 8.43; Ge, 17.60%.

4.9. 1-(5-Cyclopentadienyl)germatrane (**7a**)

4.9.1. Reaction of (1-germatranyl)triflate **4a** with cyclopentadienyllithium

A solution of cyclopentadienyllithium, prepared from cyclopentadiene (0.06 g, 0.95 mmol) in THF (10 ml) and *n*-butyllithium (0.6 ml, 0.95 mmol) as a 1.66 M solution in hexane, was added to a suspension of **4a** (0.35 g, 0.95 mmol) in xylene (10 ml). Using a procedure analogous to that of **6a** (Section 4.6.1), product **7a** (0.18 g, yield 65%) was obtained as a white solid, m.p. 127–129°C (dec.) (Ref. [18]: 128–129°C (dec.)). ^{1}H-NMR data are consistent with those already published [18].

4.9.2. Reaction of 1-bromogermatrane **3a** with cyclopentadienyllithium

A solution of cyclopentadienyllithium, prepared from cyclopentadiene (0.17 g, 2.6 mmol) in THF (10 ml) and *n*-butyllithium (1.64 ml, 2.6 mmol) as a 15% solution in hexane, was added to a suspension of **3a** (0.78 g, 2.6 mol) in THF (10 ml). at r.t. The reaction mixture was stirred for 24 h at r.t., then two thirds of the volatiles were evaporated in vacuo. A white precipitate was filtered off and the volatiles were removed in vacuo. The residue was recrystallized from pentane–toluene, washed with pentane (2 × 5 ml). After drying in vacuo product **6a** (0.29 g, 39%) was obtained as a white solid, m.p. 127–129°C (dec.) (Ref. [18]: 128–129°C (dec.)). ^{1}H-NMR data are consistent with those already published [18].

4.10. 1-(5-Cyclopentadienyl)-3,7,10-trimethylgermatrane (**7b**)

Synthesis of **7b** was analogous to that of **7a** (Section 4.9.) except that triflate **4b** was used instead **4a**. A white solid **7b** (1.1 g, yield 70%) was obtained as a mixture of two diastereomers. Sublimation at 80°C (2 Torr) afforded 0.33 g (m.p. 117–118°C (dec.) of pure symmetric diastereomer **7b**-D. ^{1}H-NMR (C_6D_6): δ 1.01–3.47 ($ABXM_3$ system of NCH_2CHMeO group protons); 4.09 (m, 1H, CHGe), 6.86 (m, 4H, Cp). ^{13}C-NMR (C_6D_6): δ 20.70 (CH_3), 38.95 (CHGe), 59.27 (NCH_2), 62.19 (OCH), 130.53 (CH=); 133.96 (CH=). EI MS *m*/*e* (rel. int.): [M^+] 326 (1); [$M^+ - C_5H_5$] 262 (100); [$M^+ - C_5H_5 - 2CH_3CHO$] 174 (20); [$M^+ - C_5H_5 - CH_3CHO - CH_2CH(CH_3)O$] 160 (21), [$M^+ - C_5H_5 - 2CH_3CHO - CH_2CH(CH_3)O$] 130 (8). Anal. Calc. for $C_{14}H_{23}GeNO_3$ (325.93): C, 51.59; H, 7.11; Ge, 22.27. Found: C, 52.08; H, 7.43; Ge, 22.60%.

4.11. 1-(9-Fluorenyl)germatrane (**8a**)

Synthesis of **8a** was analogous to that of **5a** (Section 4.4) except that fluorene was used instead of indene and **2a** was used instead of **3a**. **8a** was obtained in 71% yield; m.p. 240–241°C (Ref. [6b]: m.p. 240–242°C). ^{1}H- and ^{13}C-NMR data are consistent with those already published [6b].

4.12. Reactions of $N(CH_2CHRO)_3GeX$ with n-BuLi

4.12.1. Reaction of 1-bromogermatrane (**3a**) with n-BuLi

n-Butyllithium (2.0 ml, 3 mmol) as a 1.66 M solution in hexane was added to a suspension of **3a** (0.21 g, 0.7 mmol) in THF (10 ml). The mixture was stirred at r.t. for 4 h; after evaporation of volatiles (one third of the reaction mixture) under vacuo a precipitate was filtered off. Evaporation of the solvents from the filtrate under vacuo gave tetra-*n*-butylgermane (0.13 g) as a colourless liquid in 61% yield, n_D^{20} 1.4567 (Ref. [25]: n_D^{20} 1.4571). ^{13}C-NMR data are consistent with those already published [26].

4.12.2. Reaction of 1-trimethylsiloxy-3,7,10-trimethylgermatrane (**2b**) with n-BuLi

The procedure is analogous to that given in Section 4.12.1. except that **2b** was used instead **3a**. Tetra-*n*-butylgermane was obtained in 65% yield.

4.13. Reaction of 1-trimethylsiloxygermatrane (**2a**) with $LiNMe_2$

The procedure is analogous to that given in Section 4.12.1. except that **2a** was used instead **3a** and $LiNMe_2$ was used instead *n*-BuLi. Tetrakis(dimethylamino)germane was obtained in 65% yield as a pure colorless liquid, b.p. 49–50°C (3 Torr) (Ref. [27]: b.p. 82–83°C (12 Torr)). ^{1}H and ^{13}C-NMR data are consistent with those already published [28].

4.14. 1-tert-Butylgermatrane, $N(CH_2CH_2O)_3Ge^tBu$ (**9a**)

tert-Butyllithium (2.20 ml, 3.2 mmol) as a 15% solution in pentane was added to a suspension of **2a** (1.00 g, 3.2 mmol) in THF (10 ml) at r.t. The reaction mixture was stirred for 24 h at r.t., then two thirds of the volatiles were evaporated in vacuo. A white precipitate was filtered off and all volatiles were removed in vacuo. The residue was recrystallized from pentane–toluene and washed with pentane (2 × 5 ml). After drying in vacuo product **9a** (0.38 g, 42%) was obtained as a white solid. ^{1}H-NMR data are consistent with those already published [29]. ^{13}C-NMR ($CDCl_3$): δ 28.81 (CH_3), 30.88 (CHGe), 53.51 (NCH_2), 58.12 (OCH_2).

4.15. Reaction of 1-trimethylsiloxygermatrane (**2a**) with excess t-BuLi

tert-Butyllithium (11.00 ml, 16 mmol) as a 15% solution in pentane was added to a solution of **2a** (1.00 g, 3.2 mmol) in THF (20 ml) at r.t. The reaction mixture was stirred for 24 h at r.t., then all volatiles were evaporated in vacuo. The residue was extracted with pentane (2 × 10 ml) and the solvents were removed in vacuo. ^{1}H-NMR analysis of the residue gave evidence for a complex mixture of products.

4.16. *Attempted syntheses of $N(CH_2CHRO)_3GeY$*

Reactions of **2a** with CpLi, of **3a** with FluLi and (9-Me_3Ge)FluLi, and also of **4a** with FluLi (1-Me_3Si)IndLi, were carried out under standard conditions (Section 4.6.1.) resulting according to ^{1}H-NMR spectra in complex mixtures containing the starting germatranes as the only identifiable materials.

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