Method b. A mixture of 0.410 g (1.44 mmol) of $\{[Me_2Si(C_5H_4)_2]TiClMe\}$, 0.036 g (1.58 mmol) of 10% sodium amalgam, and 0.22 mL (1.58 mmol) of PMe_2Ph in 60 mL of toluene was stirred at −78 °C, allowed to warm to room temperature, and stirred for 12 h more. The resulting dark red solution was filtered and the solvent removed in vacuo, yielding 0.325 g (58.5%) of 4 as a dark red crystalline solid (being air sensitive, no elemental analysis was performed).

Synthesis of $\{[Me_2Si(C_5H_4)_2]Ti(CH_2SiMe_3)(PMe_2Ph)\}$ (5). A 0.094-g (1 mmol) sample of $LiCH_2SiMe_3$ in toluene was added to a solution of 0.370 g (0.90 mmol) of $\{[Me_2Si(C_5H_4)_2]TiCl(PMe_2Ph)\}$ in toluene at −78 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The dark red solution was filtered and evaporated in vacuo, to give 0.193 g (46.6% yield) of complex 5 as a dark red crystalline solid (being air sensitive, no elemental analysis was performed).

X-ray Data Collection, Structure Determination, and Refinement for $\{[Me_2Si(C_5H_4)_2]TiCl(PMe_2Ph)\}$ (3). A single crystal of 3 was sealed in Lindemann glass capillary under dry nitrogen and used for data collection. The crystallographic data are summarized in Table III. Unit cell parameters were determined from the θ values of 30 carefully centered reflections, having $25 < \theta < 40°$. Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using the nickel-filtered Cu Kα radiation and the $\theta/2\theta$ scan type. The reflections were collected with a variable scan speed of 3–12° min^{-1} and a scan width from $(\theta - 0.6)°$ to $(\theta + 0.6 + 0.142 \tan \theta)°$. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed following Lehmann and Larsen.[16] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.2623 and 0.7750).[17] Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed at their geometrically calculated positions (C–H = 1.00 Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 437 variables; after the last cycles, no parameters shifted by more than 0.32 esd. The biggest remaining peak in the final difference maps was equivalent to about 0.42 e/Å^3. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used; at convergence the K and g values were 0.3643 and 0.0068, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 18. All calculations were carried out on the CRAY X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the GOULD POWERNODE 6040 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[19] The final atomic coordinates for the non-hydrogen atoms are given in Table IV. The atomic coordinates of the hydrogen atoms and the thermal parameters are given in the supplementary material.

Acknowledgment. Generous financial support from the CICYT (PB86-0093), EEC [SC1/0137-C(AM)], and Ministerio de Educación y Ciencia for a fellowship to R.G. is gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, principal axes of the thermal ellipsoids, bond distances and angles, least-squares planes, and interatomic contacts (33 pages); a listing of observed and calculated structure factors from the final cycle of least-squares refinement (27 pages). Ordering information is given on any current masthead page.

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Reactivity of Dianionic Hexacoordinate Germanium Complexes toward Organometallic Reagents. A New Route to Organogermanes†

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Lithium and potassium tris(benzene-1,2-diolato)germanates (**2a** and **2b**, respectively) and potassium tris(butane-2,3-diolato)germanate (**3**) are easily prepared from GeO_2 in quantitative yields. They are very reactive toward organometallic reagents, the reactivity depending on the ligands on the germanium. Complexes **2** react with an excess of Grignard reagent to give the corresponding tetraorganogermanes R_4Ge while the less reactive complex **3** leads to the functional triorganogermanes R_3GeX. Tetraorganogermanes can also be prepared from complex **2b** by reaction with organic bromides in the presence of Mg (Barbier reaction). The influence of Cp_2TiCl_2 and $MgBr_2$ on the reactivity of Grignard reagents with these complexes was also investigated: in both cases formation of triorganogermanes was favored.

Introduction

We have shown recently that the hypervalent silicon complexes **1**, though negatively charged, react with organometallic reagents to give organosilanes[2] (Scheme I). The reactivity of these complexes depends on the cation, the lithium complex being much less reactive than the sodium or potassium complexes.[3]

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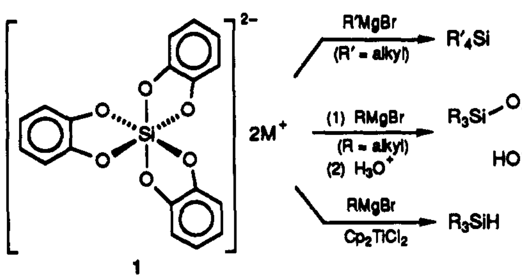
† For a preliminary communication, see ref 1.

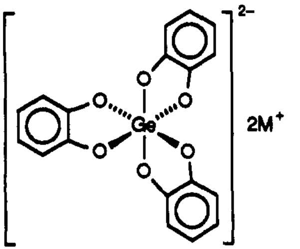
[1] Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reyé, C. *Organometallics* 1988, *7*, 786.

[2] Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reyé, C. *Organometallics* 1988, *7*, 1165.

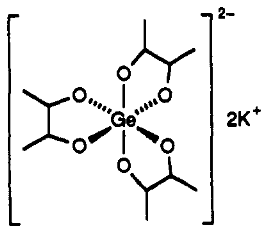
Scheme I



In this paper, we report the reactions of the hypervalent germanium complexes **2** and **3** with organometallic derivatives, the chemistry of such compounds having not previously been explored. Complexes **2** and **3** were selected in order to investigate the influence of the nature of the ligands. The role of the cation has also been considered.



2a: M = Li
b: M = K

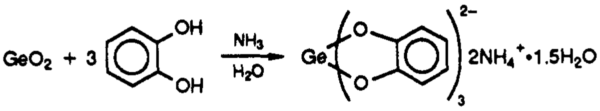


3

From the synthetic point of view it was interesting to find an alternative route for the preparation of organogermanes normally obtained from $GeCl_4$.[4]

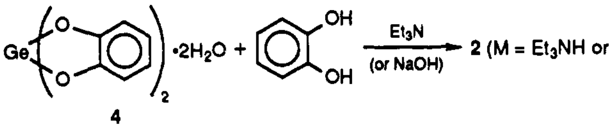
Results and Discussion

I. Preparation of Dianionic Hexacoordinate Germanium Complexes 2 and 3. Complexes **2** were prepared for the first time by Bevillard in 1954 by reaction of catechol on GeO_2 in basic aqueous solution[5] (eq 1).



(1)

They have also been prepared from the germaspiran **4**[6-8] according to eq 2.



(2)

We prepared complexes **2a** and **2b** by reacting GeO_2 with catechol in the presence of MeOLi or MeOK in MeOH (Scheme II). Under these conditions, the reaction is complete after reflux for 3 days. In contrast, 2,3-butanediol reacts easily with GeO_2 in the presence of MeOK to give complex **3** (which has not been prepared before) after reflux for 2 h (Scheme II). It is worth noting that the analogous silicon complexes of **3** have not been described up to now, reaction of $Si(OMe)_4$ with 1,2-diols leading to pentacoordinate silicon complexes[9] (eq 3).

Scheme II

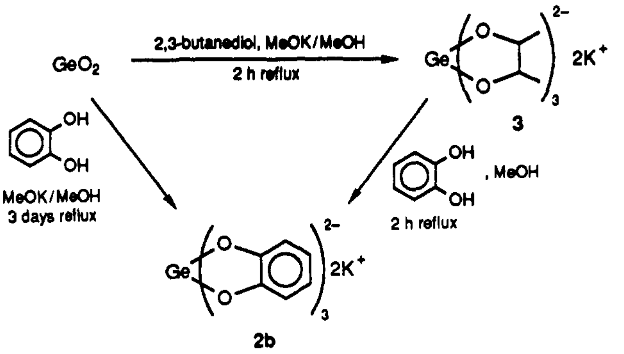
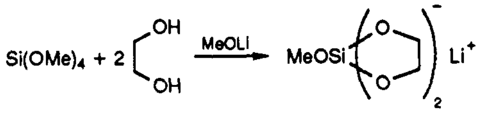


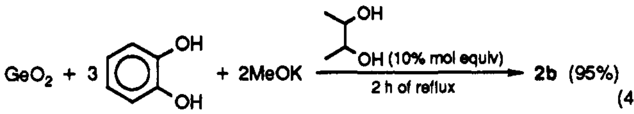
Table I. Reaction of Complex 2b with Organometallic Reagents (4.6–5 Molar Equiv)

reagent	solvent	temp, °C	time, h	R_4Ge yield, %
nBuMgBr	Et_2O	20	0.5	87
nBuLi	Et_2O	20	0.5	67
nBuZnBr	Et_2O/THF	50	20	0
$nBuCu/BF_3$	Et_2O/THF	50	20	0
HC≡CNa	Et_2O	35	20	0
EtSLi	Et_2O/THF	50	18	63



(3)

Ligand exchange takes place readily when complex **3** is treated with catechol, giving a quantitative yield of complex **2b**. On the basis of this finding, a convenient preparation of **2b** by reaction of catechol with GeO_2 in the presence of a catalytic amount of 2,3-butanediol was developed (eq 4).



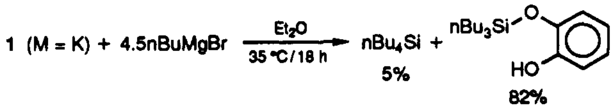
(4)

The germanium complexes are obtained as white, air-stable powders. The potassium complexes **2b** and **3** are insoluble in ether and THF, but the lithium complex **2a** is by contrast very soluble in THF.

II. Reactivity of Complexes 2a, 2b, and 3 with Organometallic Reagents. The reaction of an excess of different organometallic reagents with **2b** was studied (Table I). Though the reaction mixture was heterogeneous, **2b** reacted easily with Grignard and lithium reagents giving only tetrasubstituted germanes R_4Ge. No reaction was observed with zinc, copper, or sodium derivatives (Table I).

The germanium complex **2b** is more reactive toward nBuMgBr than the corresponding silicon complex **1** (M = K)[2] or $GeBr_4$[10] (eqs 5–7).

$$\mathbf{2b} + 4.5\,nBuMgBr \xrightarrow[20\,^\circ C/0.5\,h]{Et_2O} \underset{87\%}{nBu_4Ge} + \underset{0\%}{nBu_3Ge{-}X} \qquad (5)$$



(6)

$$GeBr_4 + 6nBuMgBr \xrightarrow[35\,^\circ C/0.5\,h]{Et_2O} \underset{74\%}{nBu_4Ge} + \underset{20\%}{nBu_3GeBr} \qquad (7)$$

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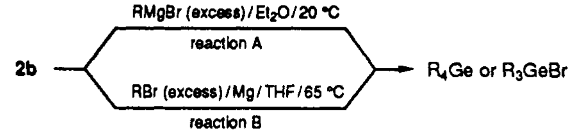
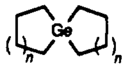
Table II. Yields of Organogermanes from Complex 2b by Reactions A and B

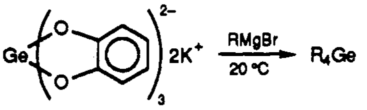


	reaction A		reaction B	
organogermane	yield, %	reaction time, h	yield, %	reaction time, h
Me_4Ge	69[a]	1		
Et_4Ge	83	0.5	78	2
nBu_4Ge	87	0.5	87	3.5
cHx_3GeBr	71	6	59	6
			55 (n = 1) 53 (n = 2)	1 1.75
$(CH_2{=}CH)_4Ge$	64[b]	1	7	1.5
$(CH_2{=}CH{-}$	68	0.5	49	4
$CH_2)_4Ge$	77	0.5	58[c]	3.5
Ph_4Ge	69	1	50	3.5
$(PhCH_2)_4Ge$	64	2		
$(CH_3C{\equiv}C)_4Ge$	78.5	0.5		
$(Me_3SiC{\equiv}C)_4Ge$	45[d]	12		
$(\alpha Np)_3GeBr$				

[a] The reaction was performed in nBu_2O. [b] In Et_2O/THF at 45 °C. [c] $(Ph_3Ge)_2$ (14%) was also obtained. [d] Obtained at 35 °C.

The reaction of organometallic reagents under different conditions with complexes **2a**, **2b**, and **3** has been studied in detail.

(a) Reaction of the Potassium Complex 2b with Grignard Reagents. Grignard reagents react with **2b** at room temperature in ether to give tetraalkyl- or tetraarylgermanes whatever the complex/Grignard reagent ratio (eq 8 and Table II).



(8)

R = primary alkyl, vinyl, allyl, benzyl, alkynyl

No byproduct (di- or polygermanes) was observed in contrast to the corresponding reactions of primary alkyl and vinylmagnesium compounds on $GeCl_4$.[11-13] For example tetravinylgermane was obtained in 64% yield from **2b** (Table II) and in 35% yield from $GeCl_4$[13] (eq 9).

$$GeCl_4 + CH_2{=}CHMgBr \rightarrow \underset{35\%}{(CH_2{=}CH)_4Ge} + \underset{26\%}{[(CH_2{=}CH)_3Ge]_2} \quad (9)$$

As already mentioned (eqs 5–7), **2b** is more reactive toward Grignard reagents than $GeCl_4$ or $GeBr_4$; this is particularly evident with PhMgBr (eqs 10 and 11).[14] To obtain a good yield of Ph_4Ge from $GeCl_4$ or $GeBr_4$, it is necessary to reflux the mixture in toluene[15] or in THF.[16]

$$GeBr_4 + PhMgBr\ (36\ equiv) \xrightarrow[35\ °C]{2\ h} Ph_4Ge \quad 40\% \quad (10)$$

$$GeBr_4 + PhMgBr\ (5\ equiv) \xrightarrow[20\ °C]{2\ h} Ph_3GeBr \quad 33\% \quad (11)$$

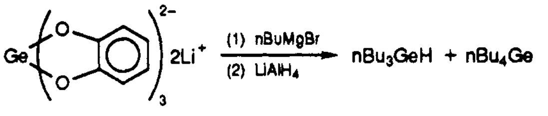
Table III. Comparison of the Reactivity of 2a toward nBuMgBr (4.6 Molar Equiv) in Ether and in THF at 20 °C Followed by LiAlH$_4$ Reduction: Yields[a] of nBu$_3$GeH and nBu$_4$Ge

	Et_2O		THF	
time	nBu_3GeH, %	nBu_4Ge, %	nBu_3GeH, %	nBu_4Ge, %
15 min	18	16	6	15
1 h	9	38	6	43
3 h	7	51	8	50
6 h	8	62	7	60

[a] Yields determined by GC with dibenzyl as internal standard.

In the case of hindered Grignard reagents (secondary alkyl or 1-naphthyl) trisubstituted bromogermane (R_3GeBr) are obtained (Table II) as from $GeCl_4$.[17]

(b) Reaction of the Lithium Complex 2a with Grignard Reagents. As already observed with the analogous silicon complex 1 (M = Li),[3] **2a** was found to be less reactive than **2b**. Nevertheless it reacts with nBuMgBr in heterogeneous (Et_2O) or homogeneous (THF) conditions to give a mixture of tri- and tetrasubstituted derivatives (eq 12). The reaction was monitored by GC and, as indicated in Table III, no preferential formation of nBu_3GeH was observed no matter what the solvent was.

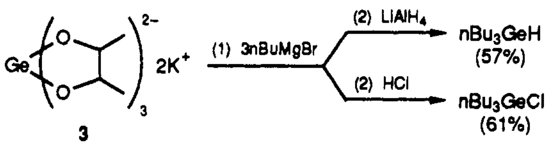


(12)

2a

From allyl and phenyl Grignard reagents (in THF at room temperature) only the corresponding tetraorganogermanes were obtained in 76% and 64% yield, respectively. No trisubstituted organogermane was detected even when the reaction was conducted at 0 °C.

(c) Reaction of the Potassium Complex 3 with Grignard Reagents. The reactivity of complex **3** toward primary aliphatic Grignard reagents is lower than that of **2a** and **2b** since only three Ge–C bonds are formed (eq 13).



(13)

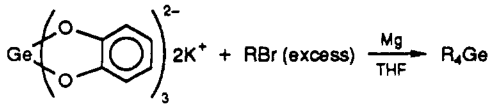
3

However PhMgBr reacts with **3** to give Ph_4Ge as unique product with a good yield (75%).

Trialkylgermanes and trialkylchlorogermanes can be prepared in a "one-pot" reaction from complex **3**. This method for the preparation of R_3GeH and R_3GeCl is more convenient than that from $GeCl_4$[4] shown by

$$GeCl_4 \xrightarrow{RMgBr} R_4Ge \xrightarrow{AlCl_3} R_3GeCl \xrightarrow{LiAlH_4} R_3GeH$$

(d) Reaction of Complexes 2a and 2b with Alkyl and Aryl Bromides in the Presence of Mg (Barbier Reaction[18]). In the presence of Mg, primaryl alkyl bromides react with complex **2b** upon refluxing in THF to give the corresponding tetraorganogermanes (eq 14 and Table II).



(14)

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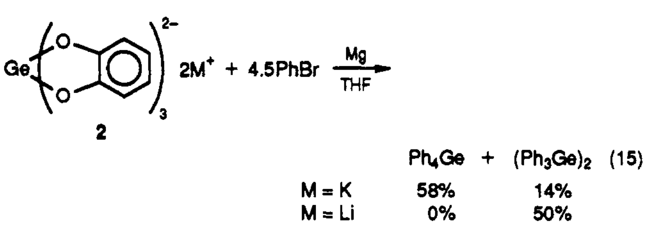
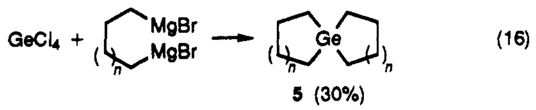
Table IV. Reaction of Complexes 2a, 2b, and 3 with 5 Molar Equiv of RMgBr in the Presence of 1-2 mol % of Cp_2TiCl_2

complex	solvent	temp, °C	time, h	R	R_3GeH (isolated yield), %
2b	Et_2O	35	1	C_2H_5	45
				nC_4H_9	75
				nC_8H_{17}	77
2a	Et_2O	35	1	nC_8H_{17}	62
2a	THF	65	1.5	nC_8H_{17}	78
		0	0.5	nC_8H_{17}	28
3	Et_2O	35	3.5	nC_8H_{17}	44

Complex **2b** reacts with secondary alkyl bromides under the same conditions to give bromotrialkylgermanes (Table II). In both cases, the yields are similar to those obtained with Grignard reagents. PhBr reacts with **2b** to give an 80/20 mixture of tetraphenylgermane and hexaphenyldigermane (eq 15). Under the same conditions, **2a** gives only hexaphenyldigermane (eq 15).



This reaction is useful for the preparation of symmetrical germaspirans. Thus the germaspirans **5** (*n* = 1, 2) are prepared in 55% yield (Table II) by reaction of **2b** with 1,4-dibromobutane and 1,5-dibromopentane. These germaspirans are obtained in lower yields by the reaction of the corresponding diorganomagnesium reagents with **2b** or $GeCl_4$[19,20] (eq 16).



(e) Reaction of Complexes 2a, 2b, and 3 with Grignard Reagents in the Presence of Cp_2TiCl_2. We reported recently a convenient preparation of hydrogenosilanes[21] in one step from the silicon complex 1 (M = Na) involving the reaction of Grignard reagents having a hydrogen atom in the β position activated by Cp_2TiCl_2.[22] Treatment of complexes **2a**, **2b**, and **3** with an excess of primary Grignard reagent, in the presence of Cp_2TiCl_2 (1–2% with respect to the Grignard reagent) gives monohydrogenogermanes (eq 17 and Table IV) in one step.

$$\textbf{2a, 2b, }\text{or }\textbf{3} \xrightarrow[Cp_2TiCl_2]{RMgBr} R_3GeH \qquad (17)$$

The reaction is selective and neither di- nor trihydrogenogermanes have been detected even from **3** or from **2a** in homogeneous conditions.

(f) Reaction of Complex 2b with Grignard Reagents in the Presence of $MgBr_2$. The addition of $MgBr_2$ to Grignard reagents modifies their reactivity toward complex **2b**. This one reacts with PhMgBr in the presence of $MgBr_2$ to give a mixture of tetra- and trisubstituted products (eq 18). A good yield of Ph_3GeH is obtained (after reduction of the reaction mixture) for a **2b**/PhMgBr/$MgBr_2$ ratio of 1/3/4 (Table V).

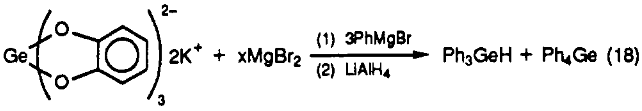


Table V. Reaction of PhMgBr (3 Molar Equiv) with 2b in Ether at Room Temperature (Influence of $MgBr_2$)

$MgBr_2$/**2b**	yield, %	ratio Ph_3GeH/Ph_4Ge[a]
0	77	0/100
2	56	55/45
4	78	90/10

[a] Ratio Ph_3GeH/Ph_4Ge obtained after reduction of the reaction mixture by $LiAlH_4$.

Table VI. Reaction of Complex 2b with RMgBr/$MgBr_2$ (Ratio 3/4), in Ether at 0 °C, Followed by HCl Hydrolysis (Procedure A) or $LiAlH_4$ Reduction before Hydrolysis (Procedure B)

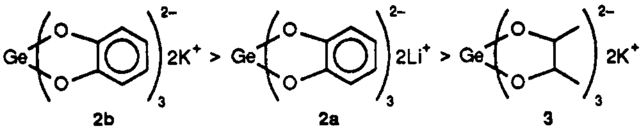
R	time, h	procedure	product	isolated yield, %
Ph	2	B	Ph_3GeH	65
	2	A	Ph_3GeCl	69
$CH_2{=}CH{-}CH_2$	2.5	A	$(CH_2{=}CH{-}CH_2)_4Ge$	58
nC_6H_{13}	1.5	B	$(nC_6H_{13})_3GeH$	80
	1.5	A	$(nC_6H_{13})_3GeCl$	75

When the Grignard reagent is prepared in the presence of 1,2-dibromoethane (3 molar equiv of RBr for 4 molar equiv of $C_2H_4Br_2$) a soluble reagent (RMgBr/$MgBr_2$) is obtained which reacts selectively with **2b** to give the trisubstituted derivative [R_3GeX/R_4Ge = 9 (the same selectivity (R_3GeH/R_4Ge = 9) is observed with **2a** in ether (heterogeneous conditions) but in homogeneous conditions (THF) poor selectivity is obtained (R_3GeH/R_4Ge = 1))] except with allylmagnesium bromide (Table VI).

An interesting application of this reaction is the one step synthesis of triphenylgermyl compounds (Table VI). This is the only way known at present to prepare these derivatives from complex **2b**.

Conclusion

In conclusion, a new way to prepare organogermanes from anionic hexacoordinate germanium complexes is described. Complexes **2a** and **3**, quantitatively obtained from GeO_2, react easily with organometallic reagents such as Grignard reagents. It is worth noting the high reactivity of these anionic hexacoordinate germanium complexes toward Grignard reagents. The reactivity of these complexes depends on the nature of the ligand and on that of the associated cation, decreasing in the order



According to the complex chosen, our method allows the preparation of either tetraorganogermanes R_4Ge or monofunctional organogermanes R_3GeH and R_3GeCl. The yields in tetraorganogermanes are comparable to those obtained by the classical method (starting from $GeCl_4$) and even better in some cases. Monofunctional organogermanes are obtained in one step in contrast to their preparation from $GeCl_4$ which requires several steps

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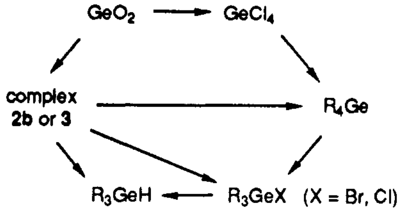
Scheme III



(Scheme III). Furthermore complexes 2 and 3 are more easily handled than $GeCl_4$.

Experimental Section

General Data. All experiments were carried out under nitrogen. Solvents were purified by standard techniques. IR spectra were recorded with a Perkin-Elmer 298 spectrophotometer, ^1H NMR spectra with a Varian EM 360 A, ^{13}C NMR with a Bruker WP-200 SY spectrometer, and mass spectra with a JEOL JMS-SX 300 spectrometer.

All the compounds described in this paper were identified by the usual techniques or compared with authentical samples. Their purity was checked by GC (10% SE 30 column) and was better than 95% unless stated otherwise.

Preparation of Complexes 2a, 2b, and 3. The preparation of potassium tris(benzene-1,2-diolato)germanate **2b** and potassium tris(butane-2,3-diolato)germanate **3** has been described in a previous communication.[1] The FAB mass spectrum of **2b** has been reported.[23]

Lithium Tris(benzene-1,2-diolato)germanate 2a. This compound was prepared in the same way as **2b**: 95%; IR (KBr) 1627 (m), 1691 (w), 1646 (s), 1335 (m), 1248 (s), 1102 (m), 1030 (w), 1020 (w), 916 (w), 876 (m), 800 (s), 762 (m), 738 (m), 658 (m) cm^{-1}.

Reaction of 3 with Catechol. A solution of 3.3 g (30 mmol) of catechol in 10 mL of MeOH was added to a solution of 4.1 g (10 mmol) of **3** in 35 mL of MeOH. The reaction mixture was stirred for 2 h. During this time a precipitate appeared. The methanol was then removed under vacuum and the solid residue washed with ether and dried under vacuum to give 4.7 g (99%) of **2b**.

2,3-Butanediol-Catalyzed Preparation of 2b. To a suspension of 26.1 g (0.25 mol) of GeO_2 in 50 mL of MeOH was added successively a solution of 35 g (0.5 mol) of MeOK in 100 mL of MeOH and then a solution of 82.5 g (0.75 mol) of catechol and 3 g (0.033 mol) of 2,3-butanediol in 100 mL of MeOH. The reaction mixture was refluxed for 2 h and MeOH removed under vacuum. The residue was washed twice with ether and dried under vacuum to give 115 g (97%) of **2b** as a white powder, characterized by its IR spectrum.[1]

Preparation of Tetraorganogermanes. Tetrakis(ethylthio)germane. EtSH (7.5 mL, 101 mmol) was added dropwise to a cooled (−15 °C) solution of 90.5 mmol of nBuLi in 60 mL of ether. The reaction mixture was stirred 2 h at room temperature and then a suspension of 9.2 g (19.4 mmol) of **2b** in 100 mL of THF was added in one portion. The reaction mixture was refluxed for 18 h, and the solvents were removed under vacuum. The viscous residue was treated with pentane in order to precipitate catechol. After filtration and evaporation of pentane, the distillation gave 3.9 g (63.5%) of tetrakis(ethylthio)germane, bp 100–107 °C (66.7 Pa) [lit.[24] bp 164–165 °C (6.7 hPa)].

Tetramethylgermane. In a 100-mL three-necked flask equipped with a magnetic stirrer, a dropping-funnel, and a fractionating column, 7.8 g (16.4 mmol) of **2b** was suspended in 10 mL of anhydrous nBu_2O. A solution of MeMgI in nBu_2O (44 mL, 78.3 mmol) was added dropwise at room temperature. The reaction mixture was heated and the fraction boiling between 40 and 80 °C was recovered. A second distillation gave 1.5 g (69%) of tetramethylgermane, bp 42–44 °C (101 kPa) [lit.[25] bp 43.4 °C (101 kPa)].

Tetraphenylgermane. PhMgBr (44 mmol) was added dropwise, at room temperature, to a suspension of 4.7 g (99 mmol) of **2b** in 50 mL of ether. After addition, the reaction mixture was stirred for 15 min and then hydrolyzed with 25% H_2SO_4. The gray solid which precipitated was filtered off (crude Ph_4Ge). The aqueous layer was extracted three times with $CHCl_3$ and the $CHCl_3$ extracts were washed once with water, twice with aqueous 2 M NaOH, twice with water, and once with brine and dried over $MgSO_4$. After evaporation of the solvent, the crude solid from the two crops was recrystallized from toluene to give 2.9 g (77%) of tetraphenylgermane, mp 231–233 °C [lit.[14] mp 230–231 °C; lit.[26] mp 235.7 °C].

Tetraphenylgermane was made from **2a**: 64%; mp 236.5–238.5 °C.

Tetraphenylgermane was made from **3**: 75%; mp 230–233 °C.

Tetrabutylgermane. nBuMgBr (50 mmol) in ether was added dropwise at room temperature to a suspension of 4.7 g (9.9 mmol) of **2b** in 50 mL of ether. The reaction mixture was stirred for 30 min, then hydrolyzed with 25% H_2SO_4, and extracted three times with ether. The organic extracts were washed once with water, twice with aqueous 2 M NaOH, twice with water, and once with brine and dried over $MgSO_4$. After evaporation of the solvent, distillation gave 2.6 g (87%) of tetrabutylgermane bp 168–171 °C (26.7 hPa) [lit.[10] bp 160–161 °C (22.7 hPa)].

The following products were similarly prepared (reaction times and temperatures are reported in Tables I and II).

Tetrabutylgermane made by reaction of nBuLi in ether: 67%; bp 160–161 °C (22.7 hPa).

Tetraethylgermane: 83%; bp 65 °C (33.3 hPa) [lit.[27] bp 163.5 °C (101 kPa)].

Tetravinylgermane: 64%; bp 66–68 °C (86.7 hPa) [lit.[13] 52–54 °C (36 hPa)].

Tetraallylgermane: 68%; bp 105–110 °C (24 hPa) [lit.[28] bp 106–107 °C (20 hPa)].

Tetraallylgermane (THF, 20 °C, 1 h): 75%; bp 110–115 °C (33.3 hPa).

Tetrabenzylgermane: 69%, mp 110.5–112.5 °C (EtOH); [lit.[29] mp 107–108 °C]. The raw material was washed with pentane to eliminate the dibenzyl present in the Grignard reagent.

Tetrapropynylgermane: 64%; mp 166.5–168.5 °C (toluene) [lit.[30] mp 168 °C].

Tetrakis[(trimethylsilyl)ethynyl]germane: 78%; mp 168–170 °C (hexane). Anal. Calcd for $C_{20}H_{36}GeSi_4$: C, 52.01; H, 7.86; Ge, 15.73; Si, 24.36. Found: C, 52.25; H, 7.92; Ge, 15.94; Si, 24.73.

Bromotricyclohexylgermane: 59% (purity 90%); mp 100–104 °C (EtOH); [lit[31] mp 110 °C].

Bromotri-1-naphthylgermane. 1-$C_{10}H_7$MgBr (55 mmol) in ether was added dropwise to a suspension of 4.7 g (9.9 mmol) of **2b** in 20 mL of anhydrous ether. The reaction mixture was refluxed for 12 h, then hydrolyzed with 25% H_2SO_4, and extracted with ether. The extracts were washed with water, aqueous 2 M NaOH, and water and dried over $MgSO_4$. The ether was removed and the residue distilled to eliminate naphthalene. The solid residue was recrystallized first in petroleum ether/$HCCl_3$ and then in ethyl acetate to give 2.6 g (49%) of bromo(1-naphthyl)germane, mp 239–243 °C [lit.[32] mp 242–243.5 °C].

Tributylgermane (from 3). nBuMgBr (45 mmol) in ether was added dropwise at 0 °C to a suspension of 6.2 g (15 mmol) of **3** in 50 mL of anhydrous ether. The reaction mixture was stirred for 1 h at 0 °C and for 4 h at 20 °C, then hydrolyzed with 25% H_2SO_4, and extracted with ether. The ether was evaporated, pentane was added, and the mixture was washed with water to eliminate 2,3-butanediol and dried over $MgSO_4$. The pentane was evaporated and the residue dissolved in 30 mL of ether. A suspension of 600 mg of $LiAlH_4$ in ether was added, and the

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reaction mixture was heated at reflux for 2 h. Usual workup gave 2.1 g (57%) of tributylgermane, bp 120–123 °C (26.7 Pa) [lit.[33] bp 123 °C (26.7 hPa)].

Chlorotributylgermane (from 3). nBuMgBr (30 mmol) in ether was added dropwise at −5 °C to a suspension of 4.1 g (10 mmol) of **3** in 75 mL of anhydrous ether. The reaction mixture was stirred for 3 h at 0 °C and for 2 at 20 °C. A 1.4 M ethereal solution of HCl (50 mL) was added to the reaction mixture and then stirred for 18 h at 20 °C. After filtration, the residue was extracted with pentane. After evaporation of pentane, distillation gave 1.7 g (61%) of chlorotributylgermane, bp 160 °C (26.7 hPa) [lit.[10] bp 139–140 °C (17.3 hPa)].

Reaction of 2a with an Excess of nBuMgBr. nBuMgBr (7.6 mL, 10.6 mmol) in ether was added in 5 min at 20 °C to a solution of **2a** (910 mg, 2.22 mmol) in 20 mL of THF in presence of 210 mg of dibenzyl used as internal standard. The reaction was monitored by GC after reduction of a little amount of the reaction mixture by $LiAlH_4$ in order to determine the yield in nBu_3GeH and nBu_4Ge. The same reaction was performed in ether. Results are indicated in Table III.

Preparation of Organogermanes by the Barbier Reaction. Tetrabutylgermane. A suspension of 1.25 g (52 mmol) of Mg and 5.1 g (10.7 mmol) of **2b** in 25 mL of THF was heated under stirring to 50–55 °C. A solution of 6.6 g (48.2 mmol) of nBuBr in 75 mL of THF was added dropwise. Gentle reflux was maintained during the addition, and then the reaction mixture was refluxed under stirring for 2 h. After cooling, 100 mL of ether was added and tetrabutylgermane was isolated as before. Distillation gave 2.8 g (87%), bp 84–85 °C (400 Pa) [lit.[10] bp 160–161 °C (22.7 hPa)].

The following products were similarly prepared (reaction times are reported in Table II).

Tetraethylgermane: 78%; bp 80–81 °C (70.7 hPa) [lit.[27] bp 163.5 °C (101 kPa)].

Tetraallylgermane: 49%; bp 103–107 °C (24 hPa) [lit.[28] bp 106–107 °C (20 hPa)].

Tetrabenzylgermane: 50%; (purity 85%); mp 102.5–106 °C (EtOH) [lit.[29] mp 107–108 °C]. The raw material was washed with pentane to eliminate dibenzyl formed during the reaction.

5-Germaspiro[4.4]nonane: 55%; bp 74–76 °C (21.3 hPa) [lit.[19] bp 188–189 °C (101 kPa)].

6-Germaspiro[5.5]undecane: 53%; bp 108–109 °C (25.3 hPa) [lit.[19] bp 124 °C (40 hPa)].

Bromotricyclohexylgermane. By reaction of 3.5 molar equiv of cyclohexyl bromide for 1 mol of **2b**; 59% (purity 93%); mp 108.5–110 °C (EtOH) [lit.[31] mp 110 °C].

Tetraphenylgermane. A suspension of 1.2 g (50 mmol) of Mg and 4.7 g (9.9 mmol) of **2b** in 30 mL of THF was stirred and heated to 50 °C. A solution of 7.1 g (45.5 mmol) of PhBr in 70 mL of THF was then added dropwise over a period of 1.5 h, and the reaction mixture was refluxed for 2 h. After cooling, 100 mL of ether was added and the reaction mixture was hydrolyzed with 25% H_2SO_4. A solid (2.3 g) precipitated, it was filtered off, washed with water, acetone, and ether, and dried. The filtrate was extracted with ether, and the organic extracts were washed with water, aqueous 2 M NaOH, water, and brine and dried over $MgSO_4$. Evaporation of the solvent gave some more solid (1.6 g). Recrystallization of the two crops in toluene gave 2.7 g (mp 229.5–233 °C) of a 80/20 mixture of Ph_4Ge and $(Ph_3Ge)_2$ as determined by GC.

Hexaphenyldigermane. A suspension of 675 mg (28.1 mmol) of Mg in a green solution of 3.25 g (7.9 mmol) of **2a** in 20 mL of THF was stirred and heated to 50 °C (the color turned brown). A solution of 3.7 g (23.6 mmol) of PhBr in 40 mL of THF was added over a period of 1 h, and the reaction mixture was refluxed for 2 h. During this time a precipitate formed. After cooling, the reaction mixture was hydrolyzed with 25% H_2SO_4 and the precipitate formed was filtered, washed with water, acetone, and ether, and dried. It was recrystallized in toluene to give 1.2 g (50%) of hexaphenyldigermane, mp 345–347.5 °C [lit.[25] mp 340 °C].

Trialkylgermanes by Reaction of Complexes 2a, 2b, and 3 with $RMgBr/Cp_2TiCl_2$. Tri-*n*-octylgermane. $nC_8H_{17}MgBr$ (24.5 mL, 37.3 mmol) in ether was added dropwise over a period of 15 min to a suspension of 3.6 g (7.6 mmol) of **2b** and 100 mg (0.4 mmol) of Cp_2TiCl_2 in 50 mL of anhydrous ether. The temperature of the reaction mixture rose from 24 to 33 °C. After the addition, the mixture was refluxed for 1 h. Usual workup gave 2.4 g (77%) of tri-*n*-octylgermane, bp 155–160 °C (53.3 Pa) [lit.[33] bp 179–180 °C (53.3 Pa)].

Solvents, temperatures, reaction times, and yields of the same reaction with **2a** and **3** are indicated in Table IV.

The following triorganogermanes were prepared by the same procedure.

Triethylgermane: 45%; bp 120–123 °C (101 kPa) [lit.[27] bp 124.4 °C (100 kPa)].

Tri-*n*-butylgermane: 75%; bp 123–125 °C (26.7 hPa) [lit.[33] bp 123 °C (26.7 hPa)].

Reaction of 2b with PhMgBr in the Presence of $MgBr_2$. A solution of 6.1 g (32.5 mmol) of 1,2-dibromoethane in 40 mL of ether was added dropwise to a suspension of 780 mg (32.5 mmol) of Mg in 10 mL of ether. The reaction mixture was stirred for 2.5 h and gave a two-phase solution of $MgBr_2$. A suspension of 3.85 g (8.1 mmol) of **2b** in 30 mL of anhydrous ether was added to this solution followed by 38 mL (24.2 mmol) of PhMgBr (over a period of 45 min at 20 °C). During the addition, the lower phase, containing the complex, became very viscous. The reaction mixture was stirred 1 h at 20 °C and an excess of $LiAlH_4$ was added. After 1 h reflux, usual workup gave 2.4 g of a 90/10 mixture of Ph_3GeH and Ph_4Ge (determined by GC).

The same reaction carried out in the presence of 2 molar equiv of $MgBr_2$ gave 1.6 g of a 55/45 mixture of Ph_3GeH and Ph_4Ge, starting from 3.5 g (7.5 mmol) of **2b**.

Preparation of $RMgBr/MgBr_2$ Mixtures. $PhMgBr/MgBr_2$ Mixture. A mixture of 47 g (0.3 mol) of PhBr and 75 g (0.4 mol) of 1,2-dibromoethane in 200 mL of anhydrous ether was added dropwise over a period of 6 h to an ice-cooled suspension of 17.2 g (0.72 mol) of Mg in 10 mL of anhydrous ether. A 0.92 M solution was obtained. $CH_2{=}CH{-}CH_2MgBr/MgBr_2$ and $nC_6H_{13}MgBr/MgBr_2$ mixtures were prepared in the same way. In this latter case the mixture was not as clear as the $PhMgBr/MgBr_2$ and $CH_2{=}CH{-}CH_2MgBr/MgBr_2$ mixtures and various amounts of sediments settled in the flask.

Reactions of 2b with $RMgBr/MgBr_2$ Mixtures. Triphenylgermane. The $PhMgBr/MgBr_2$ (24 mL, 22.1 mmol) mixture was added under stirring at 0 °C during 1 h to a suspension of 3.5 g (7.4 mmol) of **2b** in 50 mL of anhydrous ether. Excess of $LiAlH_4$ was then added and the reaction mixture was refluxed for 2 h. It was hydrolyzed by 25% H_2SO_4, filtered, and extracted with ether. The raw material (2.3 g) was crystallized in 20 mL of MeOH to give 1.3 g (58%) of triphenylgermane, mp 47–49 °C [lit.[26] mp 47 °C]. A second crop of crystals (180 mg) was obtained from the mother solution, giving an overall yield of 66%.

Tri-*n*-hexylgermane. Prepared in the same way: 80%; bp 105–107 °C (13.3 Pa) [lit.[34] bp 122–125 °C (66.7 Pa)].

Chlorotriphenylgermane. $PhMgBr/MgBr_2$ (21.6 mL, 19.9 mmol) was added at 0 °C to a suspension of 3.15 g of **2b** (6.64 mmol) in 50 mL of anhydrous ether. The reaction mixture was then hydrolyzed with an aqueous HCl solution. Usual workup gave a solid product which was treated with pentane. After filtration, the pentane was evaporated to give 2.2 g of raw material. Recrystallization in EtOH gave 1.55 g (69%) of chlorotriphenylgermane (purity 95%), mp 113.5–118 °C [lit.[29] mp 117–118 °C].

Chlorotri-*n*-hexylgermane. It was prepared in the same way: 75% (purity 90%); bp 122–140 °C (13.3 Pa) [lit.[34] bp 138–139 °C (66.7 Pa)].

Reaction of 2b with a $CH_2{=}CH{-}CH_2MgBr/MgBr_2$ Mixture. A $CH_2{=}CH{-}CH_2MgBr/MgBr_2$ mixture (36 mL, 22 mmol) was added dropwise under stirring at 0 °C during 1 h to a suspension of 3.5 g (7.4 mmol) of **2b** in 50 mL of ether. The reaction mixture was kept at this temperature for 1 h. Usual workup gave 750 mg (58%) of tetraallylgermane, bp 95–110 °C (20 hPa).

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