and an α-chloro-substituted organic ligand. We have recently shown that the inverse situation, a chloro ligand at the metal and a silyl group at the metal-bonded carbon atom, also can be used to generate metal–carbon double bonds by R_3SiX elimination: on reaction of 1-chloro-1-(trimethylsilyl)alkenes with $Cp(CO)_2Mn$ fragments vinylidene complexes are formed, probably by Me_3SiCl elimination.[18]

Acknowledgment. We thank Johanna Kron for the NMR measurements and Jürgen Meyer and Wolfgang Hepp for the X-ray measurements.

Registry No. 1, 112533-44-5; 2, 112533-45-6; $[MeCp(CO)_2MnSiMePh_2]^-$, 112533-46-7; $[(Ph_3P)(CO)_3FeSiMePh_2]^-$, 112533-47-8; 1,1-dichloro-2,3-diphenylcyclopropene, 2570-00-5.

Supplementary Material Available: Details of the solution of the structure and listings of final atomic parameters, anisotropic *B*'s, and interatomic distances and angles (11 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Reactions of Nucleophilic Reagents with Dianionic Hexacoordinated Germanium Complexes: A New Convenient Route to Functional Organogermanes from Germanium Dioxide

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Summary: Tetraorganogermanes and triorganogermanes can be prepared in two steps from GeO_2: the preparation of the anionic hexacoordinated germanium complexes followed by reaction of these with Grignard reagents to give the organogermanes.

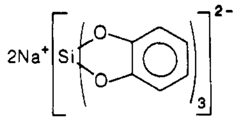
New routes for the preparation of functional organogermanes are attractive since the usual syntheses generally are long and difficult. For example, Ph_3GeH[1] is prepared as shown in Scheme I and other triorganogermanes are generally prepared in this way.[2]

Scheme I

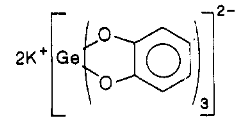
$$GeCl_4 \xrightarrow[\text{toluene}]{PhMgBr} GePh_4 \xrightarrow{Br_2} Ph_3GeBr \xrightarrow{LiAlH_4} Ph_3GeH$$

We previously have described[3] a novel synthesis of organosilicon compounds by reaction of organometallic reagents with the hexacoordinated silicon complex of catechol 1 which may be directly prepared from silica.

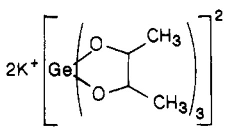
We now report that the germanium complexes 2 and 3 which can be prepared directly from GeO_2 under anhydrous conditions[4] can similarly be converted to germanes.



1

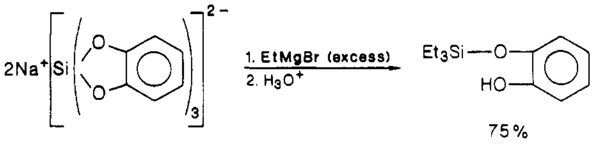


2

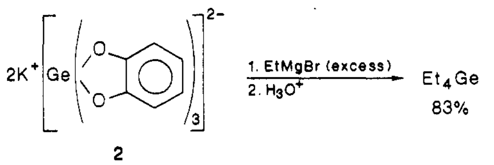


3

The results obtained with **2** are reported in Table I. Whatever the organometallic compound and the reaction conditions (solvent, temperature, and stoichiometry), only the tetrasubstituted organogermane is obtained. It is worth noting that the reactivity of **2** is greater than that of the analogous silicon complex **1**[3] since in the latter case an excess of alkyl Grignard reagent leads to the formation of only three Si–C bonds (eq 1a and 1b).



1 (1a)



2 (1b)

Complex **2** also is more reactive than $GeCl_4$ or $GeBr_4$. Indeed, in ether a large excess of PhMgBr is necessary to prepare Ph_4Ge from $GeCl_4$ or $GeBr_4$ (eq 2 and 3).[5] To obtain a good yield of $GePh_4$ from $GeCl_4$ or $GeBr_4$, it is necessary to use THF[6] or toluene[7] as the solvent and to reflux the mixture.

$$GeBr_4 + 36 \text{ equiv of } PhMgBr \xrightarrow[35\ °C]{2\ h} \underset{40\%}{Ph_4Ge} \qquad (2)$$

$$GeBr_4 + 5 \text{ equiv of } PhMgBr \xrightarrow[20\ °C]{2\ h} \underset{33\%}{Ph_3GeBr} \qquad (3)$$

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(4) Preparation of Potassium Tris(1,2-benzenediolato)germanate (2). The reaction was carried out under nitrogen. A solution of MeOK (10.5 g, 0.15 mol) in methanol (75 mL) was added to a suspension of GeO_2 (7.83 g, 0.075 mol) in methanol (40 mL). Then a solution of catechol (24.75 g, 0.225 mol) in methanol (75 mL) was added at room temperature. The resulting mixture was stirred and heated at reflux for 72 h. The methanol was removed under vacuum and the solid residue washed twice with ether; 33.9 g of complex 2 was isolated as a white powder (95% yield): ^1H NMR (CD_3OD) δ 5.80–6.35 (m); ^{13}C NMR (CD_3OD) δ 151.2; 118.2, 112.8; IR (KBr) 1615 (m), 1580 (m), 1475 (F), 1325 (m), 1240 (F), 1090 (m), 1010 (m), 910 (f), 870 (m), 860 (m), 790 (F), 740 (F), 640 (F) cm^{-1}. Preparation of Potassium Tris(2,3-butanediolato)germanate (3). The reaction was carried out under nitrogen. A solution of MeOK (2.8 g, 0.04 mol) in 40 mL of methanol was added to a suspension of GeO_2 (2.09 g, 0.020 mol) in 20 mL of methanol. Then a solution of 5.4 g of 2,3-butanediol in 20 mL of methanol was added at room temperature. The resulting mixture was stirred and refluxed for 1 h. The methanol then was removed under vacuum and the solid residue washed twice with ether; 8.12 g of complex 3 was isolated as a white powder (97% yield): ^1H NMR (CD_3OD) δ 0.60 (d, 6 H, CH_3), 2.5–3.18 (m, 2 H, CH); ^{13}C NMR (CD_3OD) δ 73.8, 20.5; IR (KBr) 2940 (m), 1650 (m), 1440 (m), 1365 (F), 1120 (m), 1075 (F), 920 (F), 815 (F), 670 (m), 620 (m) cm^{-1}.

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Table I. Reaction in Diethyl Ether of 4 Molar Equiv of Nucleophilic Reagents with Complex 2

nucleophilic reagent	reactn conditns		product (yield %)
	time, h	*t*, °C	
PhMgBr	0.25	20	Ph_4Ge (77)
EtMgBr	0.5	20	Et_4Ge (83)
n-BuMgBr	0.5	20	*n*-Bu_4Ge (87)
$CH_2{=}CHCH_2MgBr$	0.5	20	$(CH_2{=}CHCH_2)_4Ge$ (68)
$MeC{\equiv}CMgBr$	2	20	$(MeC{\equiv}C)_4Ge$ (64)
$Me_3SiC{\equiv}CMgBr$	0.5	20	$(Me_3SiC{\equiv}C)_4Ge$ (78)
$EtSLi/Et_2O$–THF	18	50	$(EtS)_4Ge$ (63)
1-NpMgBr	12	35	$(1\text{-}Np)_4Ge$ (45)

The reactivity of Grignard reagents having a hydrogen atom in the β-position and activated by Cp_2TiCl_2 (Cp = cyclopentadienyl) also was investigated. This system is known[8] to be a very efficient reducing agent. In this manner, organogermanes of type R_3GeH[9] have been prepared in one step directly from **2** (eq 4).

$$2 + 5\ \text{equiv of RMgX} \xrightarrow[\substack{Et_2O\\ \text{4-h reflux}}]{5\%\ Cp_2TiCl_2} \begin{array}{c} R_3GeH \\ R = Et\ (45\%) \\ R = n\text{-}Bu\ (75\%) \end{array} \tag{4}$$

The reactivity of complex **3** toward Grignard reagents is lower than that of **2** since it was found that only three Ge–C bonds are formed with **3**, except in the case of PhMgX, which gives Ph_4Ge in good yield (75%). The "one-pot" preparation of R_3GeH from **3** is achieved by addition of 3 molar equiv of an alkyl Grignard reagent followed by reduction with $LiAlH_4$.

$$3 \xrightarrow[\substack{2.\ LiAlH_4\\ (\text{2-h reflux})}]{\substack{1.\ 3n\text{-}BuMgBr,\ Et_2O\\ 1\ h\ at\ 0\ ^\circ C;\ 0 \rightarrow 20\ ^\circ C\\ \text{during 4 h}}} \begin{array}{c} n\text{-}Bu_3GeH \\ 58\% \end{array} \tag{5}$$

It is clear from the results described above that hexacoordinate, anionic germanium complexes, which are readily prepared from GeO_2, are useful starting materials in organogermanium synthesis.

Registry No. **2**, 112712-64-8; **3**, 112712-66-0; GeO_2, 1310-53-8; Ph_4Ge, 1048-05-1; Et_4Ge, 597-63-7; *n*-Bu_4Ge, 1067-42-1; $(CH_2{=}CHCH_2)_4Ge$, 1793-91-5; $(MeC{\equiv}C)_4Ge$, 20143-28-6; $(Me_3SiC{\equiv}C)_4Ge$, 13963-42-3; $(EtS)_4Ge$, 15800-73-4; $(1\text{-}Np)_4Ge$, 112712-65-9; PhMgBr, 100-58-3; EtMgBr, 925-90-6; *n*-BuMgBr, 693-03-8; $CH_2{=}CHCH_2MgBr$, 1730-25-2; $MeC{\equiv}CMgBr$, 16466-97-0; $Me_3SiC{\equiv}CMgBr$, 61210-52-4; EtSLi, 30383-01-8; 1-NpMgBr, 703-55-9; Cp_2TiCl_2, 1271-19-8; Et_3GeH, 1188-14-3; *n*-Bu_3GeH, 998-39-0; catechol, 120-80-9; 2,3-Butanediol, 513-85-9.

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(9) The following preparation is given as an example. Complex **2** (7.11 g, 0.015 mol) was suspended in 100 mL of anhydrous diethyl ether with 5 mol % of Cp_2TiCl_2 (0.187 g) under nitrogen. Five molar equiv of *n*-BuMgBr was added dropwise at room temperature. The reaction mixture was heated under reflux for about 4 h, then hydrolyzed with an aqueous solution of 4 M HCl, and extracted three times with ether. The combined organic extracts were washed once with water, twice with a 2 M solution of NaOH, twice more with water, and then with brine and dried over $MgSO_4$. After evaporation of the solvent, the organogermane was purified by distillation to give 3 g of tri-*n*-butylgermane (83%), bp 123–125 °C (2.66 kPa) [Lit.[2] bp 123 °C (2.66 kPa)].

Preparation and Reaction with $(CH_3)_3SiF_2^-$ of an Iron [(Trimethylsilyl)vinyl]carbene Complex. An Unprecedented and Highly Stereoselective Si to C Methyl Migration

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Summary: Introduction of $[(CH_3)_2N]_3S^+SiF_2(CH_3)_3^-$ to $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Fe{=}C(OCH_3)C{=}CHSi(CH_3)_3^+BF_4^-$ induces stereoselective methyl migration from Si to an adjacent carbon in the carbene ligand to give the (methoxyallyl)silane complex $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)FeC(OCH_3){=}CHCH(CH_3)Si(CH_3)_2F$.

Organic synthetic applications focussed on stereospecific conversions of organic ligands complexed to chiral transition metals is of interest due to the metal center's steric and electronic flexibility.[1] Among recent reports, carbene complexes have been utilized as enolate equivalent synthons[1,2] and acyl complexes of iron and cobalt have been studied as carbonyl–enolate synthetic reagents.[3]

We have recently initiated studies concerning the preparation and reactions of (trimethylsilyl)vinyl-substituted carbene complexes. Such compounds are unique, having in theory a partial cationic charge resident on the carbon (C_α) adjacent to the silicon (i.e., Figure 1), and are potentially useful as synthetic reagents in organic synthesis.[4] Here we report our initial studies concerning the preparation, and stereoselective reaction with fluoride, of a [(trimethylsilyl)vinyl]carbene complex of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)^+$ to give a σ-complex containing an allylsilane

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