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Reactivity of Dianionic Hexacoordinated Silicon Complexes toward Nucleophiles: A New Route to Organosilanes from Silica†

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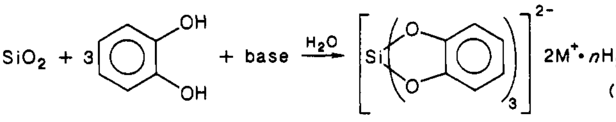
A general route for the preparation of organosilanes from silica is described. Depolymerization of silica is easily performed by chelating agents such as catechol in the presence of a base such as sodium methoxide with formation of a monomeric hexacoordinated complex $[Si(o\text{-}O_2C_6H_4)_3]^{2-}2M^+$ (1). The reaction of an excess of Grignard or organolithium reagent leads to the formation of R_4Si or $R_3SiO\text{–}C_6H_4\text{–}(o\text{-}OH)$ depending on the nature of the reagent. Functional organosilanes R_3SiX can be prepared in a one-pot reaction from 1. Silane (SiH_4) is obtained in quantitative yield under very mild conditions from 1. Interestingly, hypervalent anionic silicon species 1 react efficiently with strong nucleophiles, the products obtained corresponding to the result of a nucleophilic displacement at silicon.

Introduction

Elemental silicon is the starting material for the preparation of organosilicon compounds: the "direct" synthesis of Me_2SiCl_2, $SiCl_4$, and $HSiCl_3$.[2] Furthermore, $SiCl_4$ and $HSiCl_3$ are the starting materials for the preparation of organosilanes using the organometallic route[3] or hydrosilylation.[4]

It is an interesting problem for chemists to find a direct way to transform silica into organosilanes avoiding the transformation into elemental silicon. Some attempts have been reported in which silica was used as the starting material,[5] but they appear not very successful.

This paper describes a possible route for the transformation of silica into organosilanes using hypervalent silicon species. The use of hexacoordinated anionic species of silicon originates from the work of Rosenheim,[6] who reported the transformation of silica into hexacoordinated complexes using catechol as complexing agent under basic conditions (reaction 1).

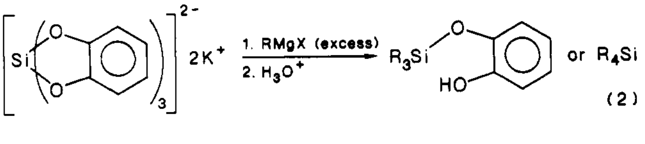


(1)

base = NH_4OH, KOH,...; $M^+ = NH_4^+$, $n = 9$; $M^+ = K^+$, $n = 8$

This complexation is a very efficient and very mild way to depolymerize any kind of silica into monomeric salts and was previously reported in water.[6,7]

We describe here the transformation of these anionic hexacoordinated silicon species into organosilanes. The nucleophilic attack of organometallic reagents (RLi, RMgX) on these complexes leads to the formation of silicon–carbon bonds[1,8] (reaction 2).



(2)

It might appear rather surprising to perform the reaction of strong nucleophiles at a silicon center that is surrounded by six ligands and included in a negatively charged complex.[9] In such hypervalent anionic species, the silicon atom could at first be thought to be less electrophilic and much too crowded to be the center of a nucleophilic attack. However, there are indications in the literature that such compounds are not totally inert toward nucleophiles. (i) Müller[10] showed that $[CH_3SiF_5]Na_2$ reacted with ethylmagnesium bromide to give $CH_3(C_2H_5)_3Si$ albeit in low yield (reaction 3). (ii) A similar observation was made by

$$Na_2[CH_3SiF_5] + 3C_2H_5MgBr \xrightarrow{Et_2O} \underset{25\%}{CH_3(C_2H_5)_3Si} \qquad (3)$$

Soshestvenskaya[11] with salts of fluosilicic acid under drastic conditions. (iii) Some studies have been performed on hydrolysis of cationic complexes of silicon containing three bidentate ligands (tropolone, aminotropinimine,[12] acetylacetone[13–15]). In the case of the complexes formed with 2,2′-bipyridine, 1,10-phenanthroline, and pyridine *N*-oxide, Kummer[16–18] showed that the reactivity is very unusual. For instance, the complexes of bipyridine $[SiX_2(bpy)_2]Cl_2$ (X = Cl, F) are soluble and unusually

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† For a preliminary communication, see ref 1.

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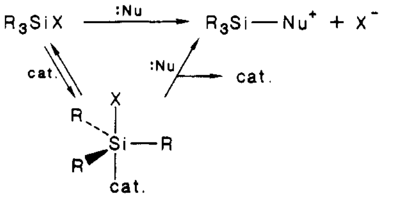
stable in methanol and water.[16d] (iv) Kumada and Tamao[19] illustrate very well the reactivity of the Si–C bond in the case of pentafluorosilicates $RSiF_5^{2-}$ and use these properties in organic synthesis.

Furthermore, we have also very recently reported the high reactivity of pentacoordinated anionic silicon catecholates,[20] pentacoordinated difluoro- and trifluorosilicates,[21] and pentacoordinated neutral hydro[22] and alkoxy[23] silanes toward nucleophiles relative to the tetracoordinated species.

These facts are in agreement with the explanation we have proposed for the mechanism of the nucleophilic activation of nucleophilic substitution at silicon.[24] In spite of other interpretations,[9,25] we have proposed a process in which the activation originates from the high reactivity of the pentacoordinated intermediate:



cat. = F$^-$, RCO$_2^-$, HMPA, ...

This mechanism can explain most of the uses of silicon in organic synthesis involving the activation by fluoride ion.[26] Finally, one of the most illustrative cases is the group-transfer polymerization for which the transfer of a silyl group was shown to take place through an hexacoordinated intermediate corresponding to the nucleophilic coordination of a methacrylate unit on a silicon atom which was already pentacoordinated.[27]

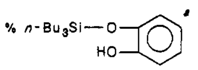
All these facts and discussions led us to consider as a possible chemical way the reaction of strong nucleophiles with hypervalent anionic species of silicon as described in reaction 2.

Results and Discussion

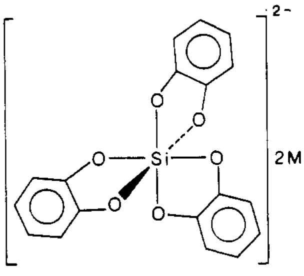
I. Preparation of Dianionic Hexacoordinated Silicon Complexes.

I. Preparation of Dianionic Hexacoordinated Silicon Complexes. Hypervalent anionic silicon species have been known for a long time.[28] Catechol in aqueous basic solutions reacts with silica gel, colloidal silica, and even finely divided quartz to form coordination complexes of silicon.[6,7] This reaction corresponds to a depolymerization of SiO_2 with formation of a monomeric hexacoordinated silicon complex 1.

Table I. Reaction of *n*-Butylmagnesium Bromide with Complex 1a (Reaction 5). Influence of the Ratio 1a/BuMgBr on the Reaction Products

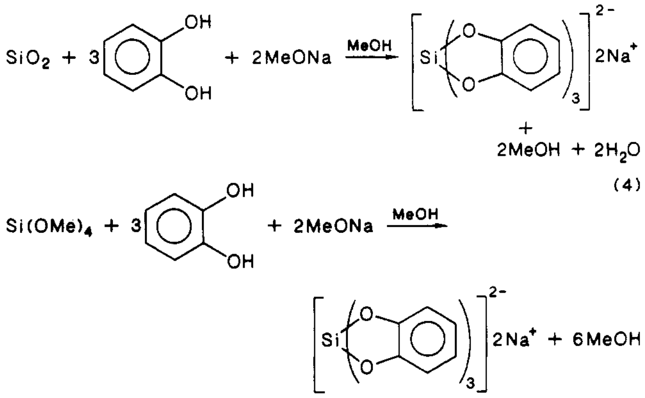
	x			
	1, 2	2	3	4, 5[b]
 [a]	29	50	72	82

[a] Isolated product. [b] After 18-h reflux (less than 4% n-Bu$_4$Si were obtained).



1a, M = Na
b, M = K

All the known preparations were carried out in water, leading to complexes that contained some water of crystallization. In order to study the reactivity of such species toward organometallic reagents or metallic hydrides, we have prepared lithium, sodium, or potassium complexes under anhydrous conditions[1,8] in analogy with previous work of Frye[29] on the preparation of pentacoordinated silicon complexes. Indeed treating silica gel or tetramethoxysilane with a methanolic solution of catechol in the presence of sodium (or potassium) methoxide in methanol, we obtained very stable sodium (or potassium) salts (reaction 4).



II. Reaction of Grignard and Organolithium Reagents with Complexes 1.

We have studied the reactivity of strong nucleophiles toward the complex 1. These complexes are very reactive, and three or four silicon–carbon bonds are formed depending on the nature of the reagent RM and of the solvent.

(a) Influence of the Reagent RM. We observed the following results. (1) When the reaction is performed under heterogeneous conditions (solvent Et_2O), use of an alkyl or benzyl Grignard results in formation of three

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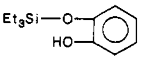
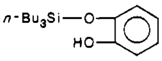
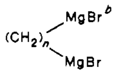
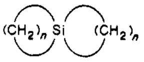
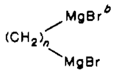
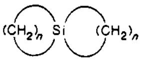
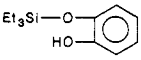
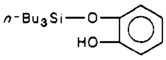
Table II. Reaction of an Excess of Alkyl Grignard Reagent (4.8 Equiv) with 1a Followed by Acid Hydrolysis (Procedure A) or by LiAlH$_4$ Reduction before Hydrolysis (Procedure B)

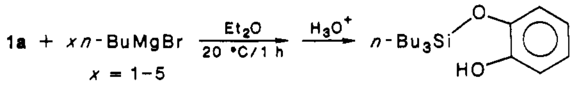
Grignard reagent	solv	temp, °C	time, h	proc	products (yield, %)
MeMgI	n-Bu$_2$O[a]	20	0.5	A	Me$_4$Si (73)
EtMgBr	Et$_2$O	35	2	A	 (72)
n-BuMgBr	Et$_2$O	35	2	A	 (82)
n-BuMgCl	THF	15	12	A	n-Bu$_3$SiOH (66) + n-Bu$_4$Si (13)
n-BuMgCl	THF	60	48	A	n-Bu$_3$SiOH (18) + n-Bu$_4$Si (76)
n-HexMgBr	THF	60	48	A	n-Hex$_3$SiOH (32) + n-Hex$_4$Si (60)
i-PrMgBr	Et$_2$O	20	4	B	i-Pr$_3$SiH (58)
i-BuMgBr	Et$_2$O	20	15	B	i-Bu$_3$SiH (71)
PhCH$_2$MgCl	Et$_2$O	20	4	B	(PhCH$_2$)$_3$SiH (73)
n-C$_{12}$H$_{25}$MgBr	Et$_2$O	35	4	B	(n-C$_{12}$H$_{25}$)$_3$SiH (62)
 $(CH_2)_n(MgBr)_2$[b]	Et$_2$O	35	15	A	 (n = 4) (33) (n = 5) (41)
 $(CH_2)_n(MgBr)_2$[b]	THF	60	20	A	 (n = 4) (54)

[a] Solvent n-Bu$_2$O because it is impossible to separate Me$_4$Si from Et$_2$O by distillation. [b] 2.4 equiv of the doubly functional Grignard reagent in these cases.

Table III. Reaction of an Excess of an Organolithium Reagent (4.8 Equiv) with 1a in Ether

organolithium	temp, °C	time, h	products (yield, %)
EtLi	35	18	 (38) + Et$_4$Si (35)
n-BuLi	35	18	 (37) + n-Bu$_4$Si (41)

silicon–carbon bonds whatever the ratio 1a/RM (reaction 5) as reported in Table I. It is impossible to perform successive reactions. We always observe the formation


(5)

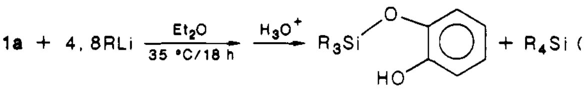
of the trisubstituted silane with the exception of MeMgBr that leads to the formation of Me$_4$Si in good yield. Di-Grignard reagents lead to the corresponding spirosilanes.

(2) When the reaction of an alkyl Grignard reagent is performed under homogeneous conditions (THF), it is less selective than in ether, and a mixture of tri- and tetraorganosilanes is obtained at room temperature, the tetrasubstituted silane being obtained in quite good yield in refluxing THF (reaction 6).

$$1a + 4,8\, n\text{-BuMgCl} \xrightarrow[\text{room temp or reflux}]{\text{THF}} \xrightarrow{H_3O^+} n\text{-Bu}_3\text{SiOH} + n\text{-Bu}_4\text{Si} \quad (6)$$

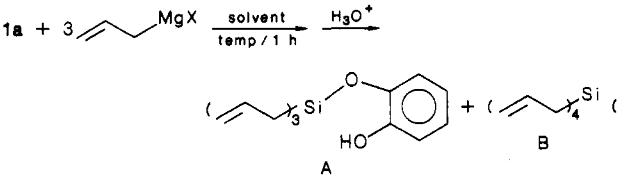
In contrast to the reaction performed in Et$_2$O, in this case the hydrolysis product trialkylsilanol is always obtained instead of trialkyl(2-hydroxyphenoxy)silane. However, it is important to point out that even under drastic conditions (48 h in refluxing THF), the tetrasubstitution is never complete: some trisubstituted silanol (18%) is always obtained. All these results are reported in Table II.

(3) When RM is an alkyllithium reagent, the reaction is again not very selective and a mixture of tri- and tetraorganosilanes (reaction 7) is obtained (Table III).


(7)

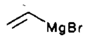
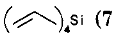
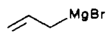
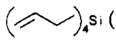
(4) When RM is an allyl, vinyl, phenyl, or alkynyl Grignard or phenyllithium, the tetraorganosilane R$_4$Si is directly formed whatever the ratio of 1/RM at room temperature (Table IV).

(b) Influence of the Solvent and the Temperature in the Case of Allylmagnesium Halide. We studied the influence of the solvent and the temperature in reaction 8. We observed that 1a is very reactive toward allylmagnesium bromide even at low temperature, the best selectivity being observed in ether at room temperature to obtain B and at −10 °C to obtain A as major products (see Table V).


(8)

(c) Preparation of Various Silanes R$_3$SiX. In order to develop a preparative route, we have studied a possible

Table IV. Reaction of Excess of an Organometallic Reagent (4.8 Equiv) with 1a

organometallic reagent	solvent	temp, °C	time, h	products (yield, %)
	THF	60	16	 (72)
	Et$_2$O	20	1	 (78)
CH$_3$C≡CMgCl	Et$_2$O/THF	45	1.5	(CH$_3$C≡C)$_4$Si (74)
n-BuC≡CMgCl	THF	60	1.5	(n-BuC≡C)$_4$Si (74)
PhC≡CMgCl	THF	45	1	(PhC≡C)$_4$Si (73)
Me$_3$SiC≡CMgCl	Et$_2$O/THF	48	1	(Me$_3$SiC≡C)$_4$Si (45)
PhMgBr	Et$_2$O	35	3	Ph$_4$Si (58)
PhLi	Et$_2$O	35	3	Ph$_4$Si (53)

Scheme I

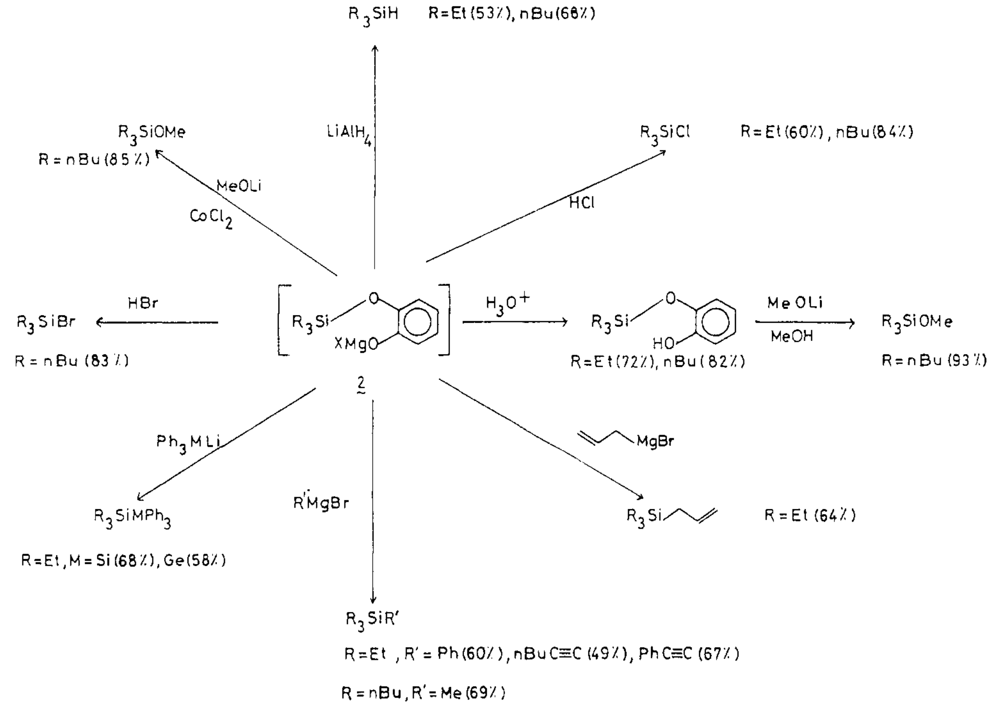
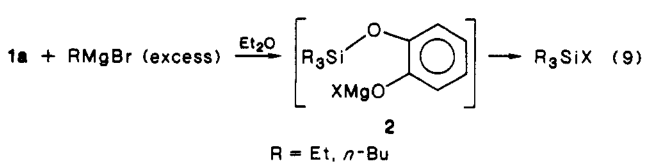


Table V. Influence of the Solvent and the Temperature in the Case of Allylmagnesium Halides

solvent	X	temp, °C	A/B[a]	crude yield, %
ether	Br	20→35	0/100	100
ether	Br	0	15/85	100
ether	Br	-10	80/20	100
ether	Br	-25→0	50/50	100
pentane	Br	-15	0/100	70
THF	Cl	-15	35/65	100

[a] % determined by GPC.

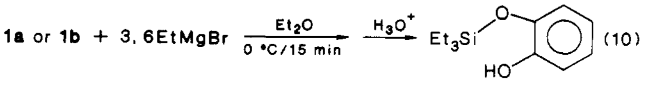
one-pot reaction leading to R_3Si-X. Thus various silanes R_3Si-X have been prepared directly from **1a**, without isolating intermediate **2** (reaction 9). **2** can react with



different nucleophiles to give organosilanes in good yields (Scheme I). These very clean reactions have been performed in ether under mild conditions. Furthermore catechol is quantitatively recovered in this process.

(d) All these results show that always three or four silicon-carbon bonds are formed and never one or two. This means that the slowest step in the substitution process is the initial attack at the silicon center. Indeed, we obtain the same results (formation of three or four Si-C bonds) when the reaction is performed under heterogeneous (Et_2O) or homogeneous (THF) conditions.

(e) Finally, it is interesting to stress the great reactivity of these hypervalent dianionic silicon species toward Grignard reagents. Indeed, 65% and 75% yields of triethyl(2-hydroxyphenoxy)silane are formed by reaction of, respectively, **1a** and **1b** with EtMgBr in ether at 0 °C in 15 min (reaction 10).



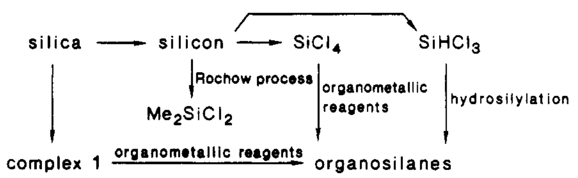
II. Reaction of Reducing Agents with 1a. When **1a** is treated by a reducing agent such as $LiAlH_4$, silane, SiH_4, is formed in quantitative yield under very mild conditions:

$$\mathbf{1a} + LiAlH_4 \xrightarrow[\text{room temp}]{Et_2O\text{ or }n\text{-}Bu_2O} \underset{100\%}{SiH_4}$$

In the same way catechol is quantitatively recovered in this reaction.

Conclusion

In conclusion, we describe a new chemical way to transform silica into organosilanes. Silica is depolymerized under very mild anhydrous conditions into monomeric dianionic hypervalent species of silicon accompanied by alkaline cations. Then, these species can form Si-C bonds by reaction with organometallic reagents. If we compare the two routes for transformation of silica into organosilanes



we note that ours is a very mild way to transform selectively silica into functional trisubstituted silanes (cf. Scheme I). Interestingly, complexes 1 are more easily handled than $SiCl_4$ or $HSiCl_3$, and the catechol can be quantitatively recovered.

Another noteworthy aspect is the high reactivity of the hypervalent species of silicon. Complexes 1 can undergo nucleophilic displacements of catecholates by using organometallic reagents: this fact illustrates the chemical possibilities of hypervalent species which were not extensively considered until now.[9,10]

We are working now to elucidate the mechanism of the displacements on the hypervalent species (penta- and

hexacoordinated), since in contrast to nucleophilic displacement at tetracoordinated silicon, we never observe successive substitutions, only tri- or tetrasubstitution is observed.

Experimental Section

General Data. All experiments were carried out under nitrogen, using standard vacuum line techniques. Solvents were dried, distilled, and deoxygenated. Starting materials were commercial products or were prepared by literature methods. Melting points were taken in a Tottoli apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer 298 spectrophotometer, ^{1}H NMR spectra with a Varian EM 360 spectrometer, and ^{13}C and ^{29}Si NMR spectra with a Bruker WP-200 SY. Chemical shifts, δ, are relative to Me_4Si in all cases.

All the compounds described in this paper were identified by the usual techniques or compared with authentic samples. Purity of these compounds was checked by GPC and found $\geq$95%.

Sodium Tris(benzene-1,2-diolato)silicate (1a) from Silica. A solution of 80 mmol of MeONa in 40 mL of methanol was added to silica gel (2.7 g, 45 mmol). Then a solution of catechol (13.2 g, 120 mmol) in 40 mL of methanol was added. The resulting mixture was stirred and refluxed during 18 h. The methanol was then evaporated and the solid residue washed with ether. This black solid was taken up in 400 mL of THF and the resulting solution heated 1 h in presence of charcoal. After filtration and evaporation of the solvent, the complex **1a** was isolated as a white powder (12.53 g, 70%): ^{1}H NMR (Me_2SO-d_6) δ 6.5–6.8; ^{13}C NMR (CD_3OD) δ 111.7, 118.6, 151.3, ^{29}Si NMR (CD_3OD) δ −143.4.

Sodium Tris(benzene-1,2-diolato)silicate (1a) from Si(OMe)$_4$. MeONa (15 g, 278 mmol) was dissolved in 80 mL of methanol. A solution of $Si(OMe)_4$ (22.5 g, 148 mmol) in 20 mL of methanol was then added, followed by a solution of pyrocatechol (47.5 g, 432 mmol) in 50 mL of methanol. The mixture was heated for 1 h at 60 °C. The methanol was then evaporated under vacuum and the solid residue washed with ether to remove unreacted methyl silicate and catechol. Complex **1a** was then dried under vacuum at 150 °C for 30 h. **1a** was isolated as a white, amorphous, air-stable powder (54.5 g, 98%).

Trisubstituted (2-Hydroxyphenoxy)silanes. Triethyl(2-hydroxyphenoxy)silane. This preparation is given as example. Complex **1a** (7.96 g, 20 mmol) was suspended in 100 mL of anhydrous ether. Ethylmagnesium bromide (4.8 molar equiv) was added dropwise at room temperature. The reaction mixture was heated under reflux for about 2 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 N solution of NaOH, twice with water, and then with brine and dried over $MgSO_4$. After evaporation of the solvent, the silicon derivative was purified by distillation to give 3.22 g (72%) of silane: bp 120–123 °C (130 Pa); ^{1}H NMR (CCl_4) δ 0.5–1.3 (15 H, m, ethyl protons), 5.2 (1 H, s, OH), 6.5–6.9 (4 H, m, aromatic). Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.28; H, 8.93; O, 14.28; Si, 12.5. Found: C, 64.02; H, 9.12; O, 14.13; Si, 12.72.

Tributyl(2-hydroxyphenoxy)silane was similarly prepared (82%): bp 140–155 °C (66 Pa); ^{1}H NMR (CCl_4) δ 0.6–1.1 (15 H, m, CH_3 and CH_2Si), 1.1–1.6 (12 H, m, CH_2CH_2), 5.33 (1 H, s, OH), 6.7–6.95 (4 H, m, aromatic). Anal. Calcd for $C_{18}H_{32}O_2Si$: C, 70.07; H, 10.45; Si, 9.10. Found: C, 69.87; H, 10.72; Si, 8.89.

Triallyl(2-hydroxyphenoxy)silane was prepared in the same way. In this case, the reaction was carried out at −30 °C and the mixture allowed to warm to −15 °C, and then it was hydrolyzed and treated in the usual way. The silane was obtained (43%): bp 106–108 °C (13 Pa); ^{1}H NMR (CCl_4) δ 1.85 (6 H, d, CH_2Si), 4.6–5.2 (6 H, m, $CH_2{=}$), 5.4–6.2 (4 H, m, $={CH}$ and OH), 6.6–7 (4 H, m, aromatic). Anal. Calcd for $C_{15}H_{20}O_2Si$: C, 69.18; H, 7.74; Si, 10.79. Found: C, 69.36; H, 8.92; Si, 10.88. In this reaction, tetrallylsilane was also formed and isolated (11%): bp 104–107 °C (28.6 hPa) [lit.[30] bp 103.4 °C (1.95 hPa)].

Trisubstituted Hydrosilanes R_3SiH. Triisopropylsilane. This preparation is given as example. Complex **1a** (7.96 g, 20 mmol) was suspended in 100 mL of anhydrous ether. *i*-PrMgBr (4.8 molar equiv) was added dropwise at room temperature. The mixture was stirred for about 4 h at room temperature. In order to prevent any formation of SiH_4, the reaction mixture was hydrolyzed with 4 M HCl before reduction. The crude product was then treated with an excess of $LiAlH_4$ (2 g) and stirred under reflux for 3 h. The reaction mixture was then hydrolyzed with 2 mL of water, 2 mL of a solution of NaOH (15%), and then 6 mL of water. The precipitate formed was filtered and washed with ether. The combined ethereal solutions were washed with water and dried over $MgSO_4$. The solvent was evaporated, and the silane was purified by distillation. Triisopropylsilane (1.83 g, 58%) was obtained: bp 70–75 °C (3.9 hPa) [lit.[31] bp 60 °C (1.3 hPa)].

The following products were similarly prepared.

Triisobutylsilane (71%): bp 100–105 °C (2.6 hPa) [lit.[32] bp 205.2 °C (10^5 Pa)].

Tribenzylsilane (73%): mp 90.5–91 °C (lit.[33] mp 90–91 °C).

Tridodecylsilane (62%): bp 220–222 °C (1.3 Pa) [lit.[34] bp 218–220 °C (1.3 Pa)].

Triethylsilane (53%): bp 40–45 °C (104 hPa) [lit.[35] bp 108.7 °C (10^5 Pa)].

Tributylsilane (68%): bp 115–117 °C (26 hPa) [lit.[32] bp 104–106 °C (15.6 hPa)].

Tetramethylsilane. Complex **1a** (8.1 g, 20.3 mmol) was suspended in 50 mL of anhydrous *n*-Bu_2O. MeMgI (89 mmol) in *n*-Bu_2O were added dropwise at room temperature. The reaction mixture was stirred for 30 min, and then Me_4Si was distilled. Me_4Si was obtained (1.3 g, 73%): bp 28–30 °C (10^5 Pa) [lit.[36] bp 26.6 °C (10^5 Pa)].

5-Silaspiro[4.4]nonane. Complex **1a** (7.96 g, 20 mmol) was suspended in 100 mL of anhydrous ether and treated by 2.4 equiv of butane-1,4-dimagnesium dichloride. The reaction mixture was refluxed for 15 h. Usual workup led to 0.92 g (33%) of spirosilane, bp 70–72 °C (26 hPa) [lit.[37,38] bp 173–174 °C (980 h Pa), bp 178.5 °C (10^5 Pa)]. The same reaction carried out in refluxing THF yields, 1.51 g (54%) of spirosilane.

6-Silaspiro[5.5]undecane was obtained in the same manner (41%): bp 115–118 °C (26 hPa) [lit.[38] bp 227 °C (10^5 Pa)].

Tributylsilanol and Tetrabutylsilane. Complex **1a** (19.9 g, 50 mmol) was dissolved in 200 mL of THF. *n*-BuMgCl (4.8 molar equiv) in THF were added dropwise at room temperature. The reaction mixture was then heated under reflux for 48 h and then hydrolyzed with an aqueous solution of 4 M HCl. Organic products were then extracted with ether and organic layers treated in the same manner as in other cases. The crude product was then distilled and gave a mixture of tributylsilanol and tetrabutylsilane. The two organosilanes were separated by column chromatography on silica gel. *n*-Bu_4Si (9.73 g, 76%) and 2.1 g of *n*-Bu_3SiOH (18%) were respectively eluted with pentane and ether and compared with authentic samples.[39] *n*-Bu_3SiOH: ^{1}H NMR (CCl_4) δ 0.5 (6 H, m, CH_2Si), 0.9 (9 H, t, CH_3), 1.35 (12 H, m, CH_2CH_2), 4.05 (1 H, s, OH).

Trihexylsilanol and tetrahexylsilane were similarly prepared (*n*-Hex_3SiOH, 32%; *n*-Hex_4Si, 60%).

Triethyl(2-hydroxyphenoxy)silane and Tetraethylsilane. Complex **1a** (7.96 g, 20 mmol) was suspended in 100 mL of anhydrous ether. An excess (4.8 equiv) of EtLi was added dropwise at room temperature. The resulting mixture was refluxed for 18 h, then hydrolyzed with an aqueous solution of 4 M HCl, and extracted three times with ether. Usual workup was used, and

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the products were separated by distillation. Et_4Si (1 g, 35%; bp 155 °C (10^5 Pa) [lit.[40] bp 108 °C (260 hPa)]) and 1.7 g of triethyl(2-hydroxyphenoxy)silane [38%; bp 120–123 °C (130 Pa)] were obtained.

Tributyl(2-hydroxyphenoxy)silane and Tetrabutylsilane. These products were obtained in the same manner. Tributyl(2-hydroxyphenoxy)silane (37%): bp 200–210 °C (26 hPa). n-Bu_4Si (41%): bp 140–160 °C (26 hPa) [lit.[39a] bp 156–157 °C (28.6 hPa)].

Preparation of Tetraorganosilanes R_4Si. Tetravinylsilane. This preparation is given as example. Complex **1a** (3.98 g, 10 mmol) was suspended in 50 mL of anhydrous THF. Vinylmagnesium bromide (4.8 equiv) was added dropwise at room temperature. The reaction mixture was heated to reflux for 16 h. It was then hydrolyzed with 4 M HCl. The silane was isolated in the same way as described above. Tetravinylsilane (0.98 g, 72%) was obtained: bp 60–67 °C (130 hPa) [lit.[41] bp bp 130.6 °C (10^5 Pa)].

The following products were similarly prepared (solvent, reaction time, and temperature are reported in Table IV).

Tetraallylsilane (78%): bp 104–107 °C (28.6 hPa) [lit.[30] bp 103.4 °C (19.5 hPa)].

Tetrapropynylsilane (74%): mp 176–178 °C (toluene) (lit.[42] mp 170 °C).

Tetrahexynylsilane (74%): bp 164–172 °C (1.3 Pa); ^1H NMR (CCl_4) δ 0.95 (3 H, t, CH_3), 1.3–1.7 (4 H, m, CH_2CH_2), 2.22 (2 H, t, $CH_2C\equiv$). Anal. Calcd. for $C_{24}H_{36}Si$: C, 81.82; H, 10.22; Si, 7.95. Found: C, 81.73; 71.73; H, 10.45; Si, 7.80.

Tetra(phenylethynyl)silane (73%): mp 193–194 °C (CCl_4) (lit.[43] mp 198 °C).

Tetra((trimethylsilyl)ethynyl)silane (45%): mp 161.5–164.5 °C (hexane). Anal. Calcd for $C_{20}H_{36}Si_5$: C, 57.69; H, 8.65; Si, 33.65. Found: C, 57.54; H, 8.68; Si, 33.42.

Tetraphenylsilane (58%): mp 236–237 °C (toluene) (lit.[44] mp 236.5–237 °C).

Preparation of Organosilanes R_3SiX. Triethylchlorosilane. Complex **1a** (7.96 g, 20 mmol) was suspended in 80 mL of ether. EtMgBr (70 mmol) was added and the resulting mixture refluxed 0.5 h. An ethereal solution of HCl (15 molar equiv) was then added, and the mixture was stirred for 1.5 h. A solid precipitated. It was filtered. The filtrate was concentrated and the residue taken up with pentane. The catechol was filtered, and the product was purified by distillation. Et_3SiCl (1.8 g, 60%) was obtained: bp 80–86 °C (127.5 hPa) [lit.[45] bp 145.8–146 °C (10^5 Pa)].

Tributylchlorosilane was prepared in the same way (84%): bp 124–127 °C (18.2 hPa) [lit.[39b] bp 142–144 °C (37.7 hPa)].

Tributylbromosilane was prepared in the same manner by using an excess of an ethereal solution of HBr. n-Bu_3SiBr was obtained (83%): bp 135–138 °C (18.2 hPa); ^1H NMR (CCl_4) δ 0.7–1.1 (5 H, m, CH_3 and CH_2Si), 1.1–1.6 (4 H, m, CH_2CH_2).

Triethylphenylsilane. Complex **1a** (5.9 g, 14.8 mmol) was suspended in 70 mL of anhydrous ether. EtMgBr (47 mmol) was added and the resulting mixture heated 0.5 h under reflux. PhMgBr (23 mmol) was then added and the mixture refluxed for 7 days. It was then hydrolyzed and extracted with ether. After usual workup, the product was purified by column chromatography on silica gel (pentane) and then distilled. Triethylphenylsilane (1.7 g, 60%) was obtained: bp 100–110 °C (18.2 hPa) [lit.[46] bp 122–125 °C (26 hPa)].

Tributylmethylsilane was prepared in the same manner (69%): bp 110–113 °C (18.2 hPa) [lit.[47] bp 101–104 °C (11.7 hPa)].

Triethyl(1-hexynyl)silane. Complex **1a** (7.96 g, 20 mmol) was suspended in 70 mL of anhydrous ether. EtMgBr (63 mmol) was added and the resulting mixture refluxed 0.5 h. Then 22 mmol of $CH_3(CH_2)_3C\equiv CMgBr$ prepared in 50 mL of THF was added at 20 °C. The mixture was stirred under reflux for 3 h, then hydrolyzed with an aqueous solution of 4 M HCl, and extracted with ether. After usual workup the crude product was distilled to give 1.92 g of triethyl(1-hexynyl)silane (49%): bp 125 °C (45.5 hPa) [lit.[48] bp 110 °C (32.5 hPa)].

Triethyl(phenylethynyl)silane. Complex **1a** (7.96 g, 20 mmol) was suspended in 70 mL of anhydrous ether and treated with 63 mmol of EtMgBr. The mixture was refluxed 0.5 h, and then 22 mol of $PhC\equiv CMgBr$ prepared in 50 mL of THF was added at 20 °C. The mixture was stirred under reflux for 2 h, then hydrolyzed with an aqueous solution of 4 M HCl, and extracted with ether. After usual workup the crude product was distilled to give 2.9 g of triethyl(phenylethynyl)silane (67%): bp 150 °C (32.5 hPa) [lit.[49] bp 132–133 °C (13 hPa)].

Triethylallylsilane. Complex **1a** (7.96 g, 20 mmol) was suspended in 70 mL of anhydrous ether. EtMgBr (63 mmol) was added and the resulting mixture refluxed 0.5 h. Then an excess of allylmagnesium bromide was added at 20 °C. The mixture was stirred under reflux for 48 h, then hydrolyzed with an aqueous solution of 4 M HCl, and extracted with ether. After usual workup, the crude product was distilled to give 2 g (64%) of triethylallylsilane; bp 75–80 °C (45.5 hPa) [lit.[50] bp 170–171.5 °C (980 hPa)].

1,1,1-Triphenyl-2,2,2-triethyldisilane. Complex **1a** (7.08 g, 17.8 mmol) was suspended in 60 mL of anhydrous ether. EtMgBr (56 mmol) was added and the resulting mixture refluxed for 0.5 h. Then 17.8 mmol of Ph_3SiLi[51] in 50 mL of THF was added at 20 °C. The mixture was stirred under reflux for 5 h. After this time, the reaction mixture was colorless. The salts were filtered and washed with ether. The combined ether extracts were washed with water. The ethereal solution was dried over anhydrous $MgSO_4$ and concentrated. The crude product (6.2 g) was obtained and recrystallized twice from 95% ethanol to give white crystals of 1,1,1-triphenyl-2,2,2-triethyldisilane (4.5 g, 68%): mp 92–93 °C [lit.[52] mp 92.5–93.5 °C].

(Triethylsilyl)triphenylgermane. Complex **1a** (4.77 g, 12 mmol) in suspension in 50 mL of anhydrous ether was treated by 39 mmol of EtMgBr. The mixture was refluxed for 0.5 h. Then, 12 mmol of Ph_3GeLi[53] in 30 mL of ether was added at 20 °C. The mixture was stirred for 16 h at room temperature. The white salts were then filtered and washed with ether. The ethereal extracts were washed with water, then dried over $MgSO_4$, and concentrated. The solid residue was recrystallized in ethanol to give 2.9 g of $Et_3SiGePh_3$ (58%): mp 93–94 °C [lit.[54] mp 93.5 °C].

Tributylmethoxysilane. From Tributyl(2-hydroxyphenoxy)silane. Tributyl(2-hydroxyphenoxy)silane (6.16 g, 20 mmol) dissolved in 100 mL of methanol was treated with 2 molar equiv of MeOLi dissolved in 15 mL of methanol. The mixture was stirred for about 1 h at room temperature; then methanol was evaporated. The residue obtained was extracted with pentane, the salts were filtered, and then the solvent was evaporated under vacuum. The liquid residue was distilled and yielded 4.3 g of n-Bu_3SiOMe (93%): bp 115–120 °C (19.5 hPa) [lit.[55] bp 239 °C (10^5 Pa)].

From Sodium Tris(benzene-1,2-diolato)silicate (1a). 1a (7.96 g, 20 mmol) suspended in 150 mL of ether was treated with 72 mmol of BuMgBr. The reaction mixture was stirred 3 h at room temperature; then a solution of 7.79 g (60 mmol) of $CoCl_2$

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and 6.08 g (160 mmol) of MeOLi in 50 mL of methanol was added. The resulting mixture was stirred for 30 min. The solvent was evaporated and the solid residue taken up with pentane. The salts were filtered, and then the solvent was evaporated. The residue was distilled and yielded 3.9 g of n-Bu_3SiOMe (87%): bp 110–120 °C (19.9 hPa) [lit.[55] bp 239 °C (10^5 Pa)].

Silane. Complex **1a** (0.447 g, 1.12 mmol) in 2 mL of n-Bu_2O was treated with 14.6 mmol of a solution of $LiAlH_4$ in n-Bu_2O. A gas evolved and was collected in a measuring glass tube initially filled with inert oil. Gas (25 mL, 100%) was collected and identified as silane by IR spectroscopy;[56] IR (CCl_4) ν_{Si-H} 2180 cm^{-1}. Caution! SiH_4 is an air-flamable gas.

General Procedure To Recover Catechol. After acidic hydrolysis of the reaction mixture, the organosilane was extracted with ether. The combined extracts were washed with water and then with a 2 M solution of NaOH. These basic waters were then acidified and extracted three times with ether. Ether was evaporated, and crude catechol was obtained quantitatively in every case.

Registry No. **1a**, 101519-12-4; HO-*o*-C_6H_4–OH, 120-80-9; $Si(OMe)_4$, 681-84-5; Et_3SiO-*o*-C_6H_4–OH, 101541-79-1; n-Bu_3SiO-*o*-C_6H_4–OH, 101541-83-7; $(CH_2{=}CHCH_2)_3Sio$-*o*-C_6H_4–OH, 106702-38-9; $(i\text{-}Pr)_3SiH$, 64885-79-6; $(CH_2{=}CHCH_2)_4Si$, 1112-66-9; Ph_3SiLi, 791-30-0; $(i\text{-}Bu)_3SiH$, 64885-81-0; $(PhCH_2)_3SiH$, 1747-92-8; $(n\text{-}C_{12}H_{25})_3SiH$, 18817-82-8; Et_3SiH, 617-86-7; n-Bu_3SiH, 998-41-4; Me_4Si, 75-76-3; n-Bu_3SiOH, 56889-90-8; n-Bu_4Si, 994-79-6; n-Hex_3SiOH, 60782-58-3; n-Hex_4Si, 3429-81-0; $(CH_2{=}CH)_4Si$, 1112-55-6; $(CH_3C{\equiv}C)_4si$, 20143-21-9; $(n\text{-}BuC{\equiv}C)_4Si$, 106702-39-0; $(PhC{\equiv}C)_4Si$, 18769-86-3; $(Me_3SiC{\equiv}C)_4Si$, 13888-92-1; Ph_4Si, 1048-08-4; Et_3SiCl, 994-30-9; n-Bu_3SiCl, 995-45-9; n-Bu_3SiBr, 2116-80-5; Et_3SiPh, 2987-77-1; n-Bu_3SiMe, 995-43-7; $Et_3Si(C{\equiv}CBu)$, 21693-13-0; $Et_3Si(C{\equiv}CPh)$, 4131-43-5; $Et_3Si(CH_2CH{=}CH_2)$, 17898-21-4; $Et_3SiGePh_3$, 18771-58-9; Ph_3GeLi, 3839-32-5; n-Bu_3SiOMe, 15811-64-0; SiH_4, 7803-62-5; Pentane-1,5-dimagnesium dichloride, 106702-37-8; butane-1,4-dimagnesium dichloride, 22758-42-5; 5-silaspiro[4.4]nonane, 176-51-2; 6-silaspiro[5.5]undecane, 181-09-9.

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Activation and Desulfurization of Thiophene and Benzothiophene by Iron Carbonyls

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The synthesis, reactivity, and structure of thiaferroles $Fe_2(R_2C_4H_2S)(CO)_6$ and benzothiaferroles $Fe_2(C_8H_6S)(CO)_6$ (1) are surveyed. These compounds are prepared by the reaction of $Fe_3(CO)_{12}$ with thiophenes and benzothiophenes. The benzothiaferrole 1 undergoes oxidative demetalation to give the cyclic thioester thiocoumarin C_9H_6OS. Solutions of 1 are stable at 185 °C under N_2; at 160 °C, high pressures of CO convert 1 into $Fe(CO)_5$ and benzothiophene, i.e. reductive elimination. Solutions of 1 react with H_2 to give primarily ethylbenzene together with 2-ethylbenzenethiol and bis(2-ethylphenyl) sulfide. Compound 1 survives flash vacuum pyrolysis up to ~280 °C whereupon it eliminates benzothiophene. In contrast to the considerable thermal stability of thiabenzoferrole, solutions of the thiaferroles decompose at ~80 °C to give the ferroles regiospecifically and in high yield. The structure of the PPh_3 derivative of 1 was studied in the solid state. $Fe_2(C_8H_6S)(CO)_5(PPh_3)$ crystallizes in the triclinic space group $P\bar{1}$, with $a = 12.498$ (2) Å, $b = 13.138$ (2) Å, $c = 10.618$ (2) Å, $\alpha = 113.00$ (1)°, $\beta = 111.22$ (1)°, and $\gamma = 100.37$ (1)°. Refinement of 3389 reflections converged to a final R of 0.030 ($R_w = 0.031$). The structure of this benzothiaferrole consists of a $Fe_2(CO)_5(PPh_3)$ core bridged by a C_8H_6S fragment involving both mercaptide and σ,π-vinyl bridging groups. One Fe center is six-coordinate, and the other Fe center is seven-coordinate. The low-temperature ^{13}C NMR spectrum of 1 shows six CO signals. Two dynamic processes are observed at higher temperatures: one involves turnstile rotation at one of the $Fe(CO)_3$ groups and the other, which equivalences all six CO groups, involves flip-flop of the organic ligand.

Introduction

The interaction of thiophenes with transition metals is of technological importance and scientific interest for three reasons. First, the poisoning of metal catalysts by organic sulfur compounds, commonly thiophenes, is a major problem in the petroleum industry.[1] Second, the desulfurization of thiophenes and sulfides is the objective of catalytic hydrodesulfurization (HDS), one of the largest industrial applications of transition-metal catalysis.[2] Third, transition metal reagents, e.g. Raney nickel, are often used to stoichiometrically abstract sulfur from thiophenes as well as organosulfur compounds.[3]

Several recent studies have provided definitive information on the interaction of thiophenes with the surfaces of metals and metal sulfides. Temperature-programmed desorption studies and vibrational spectroscopy under ultrahigh vacuum (10^{-10} Torr) have shown that thiophene binds to Mo(100) surfaces in both η^1,S- and η^5-modes.[4] At higher temperatures the coordinated thiophene is observed to undergo stepwise dehydrogenation. Thiophene also binds to Pt(111) in both an η^1,S- and an η^5-manner.[5,6] On Pt(111) the coordinated thiophene rearranges to metallacycles and sulfide at higher temperatures.[5,6] The initial coordination events on Ni(111) and Ni(100) appear to be

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