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Invited Paper

Reactivity† of Hypervalent Species: Reactions of Anionic Penta-Coordinated Silicon Complexes towards Nucleophiles

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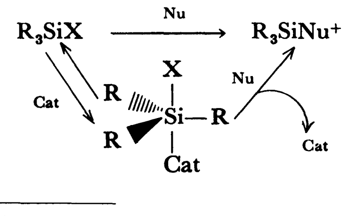
The reactivity of anionic penta-coordinated silicon complexes $[RSi(O_2C_6H_4\text{-}o)_2]^-Na^+$ **1** with nucleophilic reagents has been studied. **1** can be reduced to organosilanes $RSiH_3$ by metallic hydrides. Reactions with an excess of Grignard or organolithium reagents (R′MgX or R′Li) gave tetraorganosilanes $RSiR'_3$. When only two molar equivalents of Grignard reagents (R′MgX) or lithium reagents (R′Li) are added to complexes **1** functional silanes RR'_2SiX can be prepared.

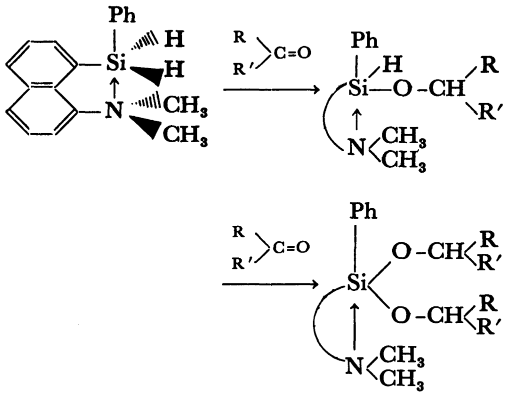
It has been known for a long time that silicon can expand its valence shell and several types of penta- and hexa-coordinated silicon compounds have been reported, in which silicon is surrounded by electronegative ligands[2–4] and more recently by nonelectronegative ones.[5] Numerous structural studies of hexa- and penta-coordinated silicon complexes have been reported[2,3,5,6] but little attention has been paid to the fundamental chemical behaviour of these species. Some reports which are in the literature suggested that these complexes may have unusual properties compared with those of their tetra-coordinated analogues. Kummer et al.[7] have observed that cationic bis(2,2′-bipyridine), 1,10-phenantroline, and pyridine *N*-oxide silicon complexes have unexpected properties. For instance $[SiX_2(bipy)_2]\,Cl_2$ may be dissolved in water or methanol without reaction of the SiX bond (X=Cl,Br). Kumada[4,8,9] has shown the unique reactivity of the carbon–silicon bond in organopentafluorosilicates and has exploited these properties in organic synthesis. Muller[10] has reported that reaction is possible between an organopentafluorosilicate and strong nucleophiles such as Grignard reagents:

$$[CH_3SiF_5]M_2 + 3C_2H_5MgBr \longrightarrow CH_3Si(C_2H_5)_3 \quad 25\%$$

Finally 1-hydrosilatrane has been shown to have some potential uses as a reducing agent.[11] All these examples illustrate very well the difference between the chemical behaviour of hypervalent silicon species and the tetra-coordinated ones. Moreover mechanistic studies of nucleophilic substitution at silicon performed in our laboratory[12] have established the nucleophilic activation of nucleophilic substitution at silicon. To explain these results, a mechanism has been proposed in which the rate-determining step is attack of the nucleophile, Nu, at a penta-coordinated silicon centre. This mechanism is now given further support by some recent results:

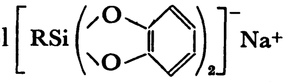


1) Reactivity of the Si–H bonds[13] in penta-coordinated silicon dihydrides towards nucleophiles is markedly greater than that of the corresponding tetra-coordinated species. For example these penta-coordinated silicon dihydrides react with carbonyl compounds without any catalyst as shown in the following reaction:



2) Other very recent experiments[14] have confirmed that penta-coordinated anionic trifluorosilicates $R_2SiF_3^-$ and difluorosilicates $R_3SiF_2^-$ react with nucleophiles faster than the corresponding fluorosilanes R_2SiF_2 and R_3SiF.

In this paper we describe the reactivity towards nucleophiles of anionic penta-coordinated silicon complexes of catechol



Na^+ **1**. These derivatives have been prepared by Frye[15] and the structure of tetramethylammonium (1,2-benzenediolato)phenylsilicate has been determined by X-ray diffraction,[6a] but the chemistry of theses anions however has not yet been explored.

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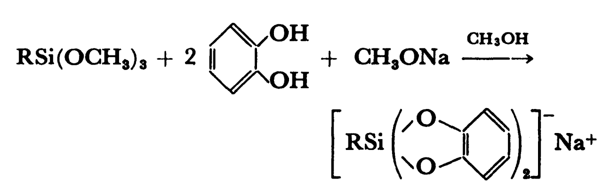
† Preliminary Communication Ref. 1.

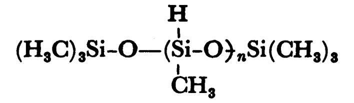
Results and Discussion

Synthesis of Anionic Penta-Coordinated Silicon Complexes of Catechol. The anionic penta-coordinated silicon complexes **1** have been synthesized according to the method described by Frye,[15]



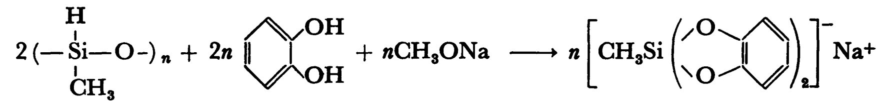
1a : R=Ph, **1b** : R=CH_3, **1c** : R=1-naphthyl

The complex **1b** can be also prepared with 90% yield from the polymer polymethylhydrosiloxane (PMHS):



$$(H_3C)_3Si\text{-}O\text{—}(\overset{H}{\underset{CH_3}{Si}}\text{-}O)_nSi(CH_3)_3$$

PMHS is obtained from methyldichlorosilane which is itself a by-product of the "direct synthesis" of dimethyldichlorosilane



Reactivity of Anionic Penta-Coordinated Silicon Complexes of Catechol towards Metal Hydrides. The reactivity of the anionic complexes **1a** and **1c** towards metal hydrides such as lithium aluminium hydride, diisobutylaluminium hydride and triethylaluminium/sodium hydride was investigated. The only product obtained is the monoorganosilane $RSiH_3$ in quite a good yield (Table 1).

Reactivity of Anionic Penta-Coordinated Silicon Complexes of Catechol towards Grignard and Organolithium Reagents. The reactivity of anionic complexes **1** with organometallic compounds (R′MgX and R′Li) has been studied. First, we have investigated the influence of the ratio complex/organometallic compound on the reaction products in order to examine the possible selectivty of the reaction.

Table 1. Reactions of Metalhydrides with Complexes **1**

Complex	Hydride	Reaction condition			Product (yield/%)[a]
		Solvent	T/°C	t/h	
1a	$LiAlH_4$(excess)	Ether	20	2	$PhSiH_3$ (72)
1a	NaH/Et_3Al 4eq/3eq	Hexane	20	1	$PhSiH_3$ (68)
1a	i-Bu_2AlH(5eq)	CH_2Cl_2	0	1	$PhSiH_3$ (65)
1c	$LiAlH_4$(excess)	Ether	35	4	1-$NpSiH_3$ (73)
1c	NaH/Et_3Al 4 eq/3 eq	Hexane	20	1	1-$NpSiH_3$ (65)

a) Yield of isolated product.

Table 2. Reaction of Methyllithium and Methylmagnesium Bromide with Complex **1a**. Influence of the Ratio Complex **1a**/Organometallic Compound on the Reaction Products[a]

CH_3M	Reaction condition			$PhSiH_3$	$PhCH_3SiH_2$	$Ph(CH_3)_2SiH$	$PhSi(CH_3)_3$
	Solvent	T/°C	t/h				
CH_3MgBr(1eq)	Ether	0	2,5	79	9	12	0
CH_3MgBr(1eq)	Ether	35	2	56	7	36	0
CH_3MgBr(1eq)	THF	60	2	54	5	41	0
CH_3MgBr(2eq)	Ether	35	2	6	6	85	3
CH_3MgBr(3eq)	Ether	35	2	0	4	58	38
CH_3Li(1eq)	Ether	35	2	48	7	44	0
CH_3Li(2eq)	Ether	35	2	12	4	81	4
CH_3Li(2eq)	THF	60	2	9	10	49	32
CH_3Li(3eq)	Ether	35	2	0	0	0	100

a) The ratio of the different reaction products was determined by GLC after reduction of the reaction mixture with $LiAlH_4$.

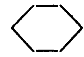
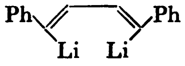
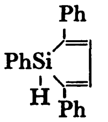
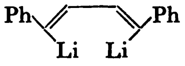
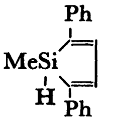
The results obtained after reduction of the reaction mixture with an excess of lithium aluminium hydride are reported in Table 2. It appears that:

1) The addition of 1 or 2 molar equivalents of organometallic reagents R′MgX or R′Li results mainly in the formation of two Si–C bonds whatever the reaction conditions (solvent, temperature, nature of the organometallic compound). This implies that the first substitution is rate-determining step.

2) The reaction of 2 molar equivalents of organometallic reagents (R′MgX or R′Li) followed by reduction with lithium aluminium hydride gives mainly organosilanes of type RR'_2SiH.

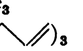
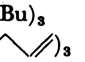
3) 3 molar equivalents of organolithium reagent R′Li lead only to the tetra-substituted silanes $RSiR'_3$ while the reaction with 3 molar equivalents of Grignard reagent R′MgX followed by reduction with lithium aluminium hydride gives a mixture of RR'_2SiH and $RSiR'_3$. The results of the reactions carried out with 2 or 3 molar equivalents of organometallic reagents are summarised in Tables 3 and 4 respectively. The great reactivity of the allylic and alkynyl Grignard reagents towards complexes **1a** and **1b** should be pointed out in that the tetra-substituted compounds $RSi(CH_2CH{=}CH_2)_3$ or $RSi(C{\equiv}CR')_3$ are the main products whatever the stoichiometry of the reactants. It is worth noting the preparation in one step of 1-methyl-2,5-diphenylsilacyclopentadiene and 1,2,5-triphenylsilacyclopentadiene with satisfactory yield (Table 3). The reactivity of *t*-butylmagnesium bromide towards **1a** is low. One molar equivalent of *t*-butylmagnesium bromide in the

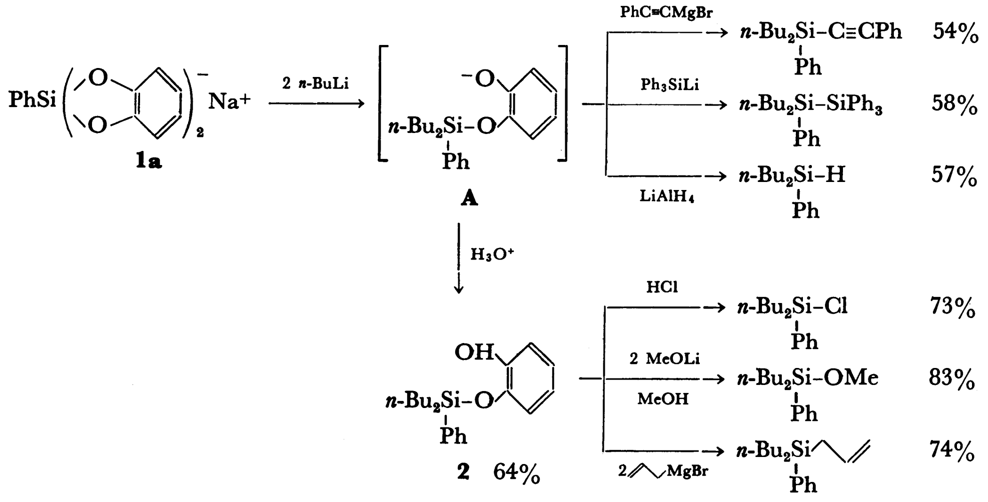
Table 3. Reactions in Ether of 2 Molar Equivalents of Organometallic Reagents (RMgX, RLi) with Complexes **1** Followed by Reduction of the Reaction Mixture with an Excess of $LiAlH_4$[a)]

Complex	Organometallic reagent	Reaction condition		Product (yield/%)	
		T/°C	t/h		
1a	MeLi	35	1	$PhMe_2SiH$	(37)
1a	EtMgBr	20	3	$PhEt_2SiH$	(40)
1a	EtLi	20	3	$PhEt_2SiH$	(43)
1a	*i*-PrMgBr	20	3	Ph(*i*-Pr)$_2$SiH	(45)
1a	*n*-BuLi	20	3	Ph(*n*-Bu)$_2$SiH	(57)
1a	*t*-BuMgBr[b)]	35	15	Ph(*t*-Bu)SiH_2	(16)
1a	-MgBr	20	15	$Ph(C_6H_{11})_2SiH$	(83)
1a		20	16		(50)
1b	PhLi	35	2	$MePh_2SiH$	(60)
1b	$PhCH_2MgBr$	35	6	$Me(PhCH_2)_2SiH$	(86)
1b		20	16		(51)

a) The reaction mixture has been heated about 4 hours at 35 °C after addition of an excess of $LiAlH_4$.
b) Only 1 molar equivalent of *t*-BuMgBr in presence of the cryptand TDA-1 was used to obtain Ph(*t*-Bu)SiH_2.

Table 4. Reactions of 3 Equivalents of Organometallic Reagents (RMgX,RLi) with Complexes **1** in Ether

Complex	Organometallic reagent	Reaction condition		Product (yield/%)	
		T/°C	t/h		
1a	MeLi	35	3	$PhSiMe_3$	(78)
1a	MgBr	35	1	PhSi()$_3$	(53)
1a	*n*-BuLi	35	2	PhSi(*n*-Bu)$_3$	(85)
1a	PhMgBr	20	3	Ph_4Si	(76)
1b	*n*-BuLi	35	2	MeSi(*n*-Bu)$_3$	(43)
1b	MgBr	35	1	MeSi()$_3$	(62)
1b	PhLi	35	2	$MeSi(Ph)_3$	(63)
1b	PhC≡CMgBr	35	4	MeSi(C≡CPh)$_3$	(82)



Scheme 1.

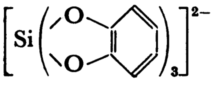
presence of one molar equivalent of the cryptand tris(3,6-dioxaheptyl)amine[16] (TDA-1) results in the formation of only one new Si–C bond giving after reduction with lithium aluminium hydride phenyl-*t*-butylsilane as the major product but in poor yield (16%) (Table 3) (without TDA-1 no reaction product at all was isolated). 3 molar equivalents of *t*-butylmagnesium bromide in the presence of 3 molar equivalents of TDA-1, react with **1a** to give after reduction with an excess of lithium aluminium hydride the unexpected product diphenyl-*t*-butylsilane in 31% yield.

$$\mathbf{1a} \xrightarrow[\text{2) LiAlH}_4]{\text{1) 3eq } t\text{-BuMgBr, 3eq TDA-1}} Ph_2SiH(t\text{-}Bu)\ (31\%)$$

The formation of this product can be explained by a disproportionation of phenyl-*t*-butylsilane induced by $LiAlH_4$/TDA-1. Indeed other examples of disproportionation of silanes promoted by $LiAlH_4$/TDA-1 have been observed.[17]

$$PhSiH_3 \xrightarrow[\text{TDA-1}]{LiAlH_4} Ph_2SiH_2 \longrightarrow Ph_3SiH$$

Two different substituents can be introduced in successive steps into the complex **1a** without isolating the intermediate **A** (Scheme 1). This one can react with different nucleophilic reagents to give further organosilicon compounds with moderate to good yield. However in some cases, for purification purposes, it is better to hydrolyze the intermediate **A** and isolate **2** before adding the second nucleophile. Analogous results have been obtained with the dianionic hexa-coordinated silicon complex



2Na+.[18]

In conclusion this work describes a new route to organosilicon compounds from penta-coordinated anionic species. From a mechanistic point of view the products obtained are the result of the reaction of a nucleophilic reagent with a negatively charged species. The mechanistic details of these nucleophilic reactions have yet to be elucidated. However these results open some new synthetic possibilities exploiting the reactivity of hypervalent silicon species.

Experimental

Reactions have been carried out under nitrogen. All solvents were purified by standard techniques before use. (All the compounds described in this paper have been characterized by usual techniques and analysis: CPV (Girdel,SE30). NMR spectra have been recorded with a Varian EM 360A spectrometer for ^1H, with a Bruker WP-80 for ^{13}C, with a Bruker WP-200 SY for ^{29}Si. All ^1H, ^{13}C, and ^{29}Si chemical shifts reported in ppm are relative to Me_4Si. IR spectra have been recorded with a Perkin Elmer 298 spectrophotometer, mass spectra with a JEOL JMS-DX 300 Mass Spectrometer. Microanalyses have been carried out by CNRS laboratories (Lyon).

Preparation of Complexes: Sodium Bis(1,2-benzenediolato)methylsilicate (1b) from MeSi(OMe)₃. A solution of $MeSi(OMe)_3$ (0.0475 mol) in 10 ml of MeOH was added at room temperature to a solution of MeONa (0.0475 mol) in 15 ml of MeOH. Then 10.34 g of catechol dissolved in 20 ml of MeOH were added dropwise at 25 °C. The mixture was heated for about 4 hours at 45 °C. MeOH was removed under vacuum. Complex was washed twice with ether and dried under vacuum at 100 °C for one day. 12 g (90%) of **1b** were obtained as a white powder. ^1H NMR (DMSO-d_6) δ=−0.1 (3H, s), 6.5—6.8 (8H,m); ^{13}C NMR (DMSO-d_6) δ=151.6, 120.8, 113.2, 1.2; ^{29}Si NMR (CD_3OD) δ=−73.77; IR (KBr) 1590, 1475, 1345, 1240, 1095, 1010, 895, 830, 750 cm^{-1}.

Sodium Bis(1,2-benzenediolato)methylsilicate (1b) from PMHS. 0.2 mol of catechol (22 g) and 0.2 mol of PMHS (12 g) were dissolved in about 50 ml of MeOH. 0.1 mol of MeONa dissolved in about 30 ml of MeOH was added slowly at room temperature. The reaction of MeONa with PMHS was exothermic. The mixture was stirred overnight during which time a precipitate from the polymer appeared. Then the solution was filtered and the solid washed twice with methanol. The methanol was removed from the whole filtrate; 25.3 g (90%) of a grey powder was obtained. The spectral data were the same as those of the complex prepared from $MeSi(OMe)_3$.

Sodium Bis(1,2-benzenediolato)phenylsilicate (1a). The preparation of **1a** from $PhSi(OMe)_3$ was the same as that of **1b** from $MeSi(OMe)_3$. ^1H NMR (DMSO-d_6) δ=6.28—6.78 (8H, m), 6.95—7.22 (3H, m), 7.28—7.60 (2H, m); ^{13}C NMR (DMSO-d_6) δ=150.6, 140.8, 135.4, 129.4, 127.9, 119.9, 112.0; ^{29}Si NMR (DMSO-d_6) δ=−87.4; IR (KBr) 1600, 1475, 1340, 1240, 1220, 1110, 1100, 1010, 890, 825, 730, 700 cm^{-1}.

Sodium Bis(1,2-benzenediolato)-1-napthylsilicate (1c). The complex **1c** was prepared from 1-$NpSi(OMe)_3$ as **1a** from $MeSi(OMe)_3$. ^1H NMR (DMSO-d_6) δ=6.1—6.7 (8H, m), 7.0—7.35 (3H, m), 7.35—7.78 (3H, m), 8.35—8.8 (1H, m); ^{13}C NMR (DMSO-d_6) δ=150.2, 132.7, 131.6, 130.1, 127.7, 127.1, 124.8, 124.6, 117.5, 110.1; ^{29}Si NMR (DMSO-d_6) δ=−84.64; IR (KBr) 1600, 1480, 1395, 1240, 1100, 1010, 890, 820, 740, 700 cm^{-1}.

Synthesis of Tetraorganosilanes $RSiR'_3$. The following is given as an example. **Methyltri(phenylethynyl)silane.** An excess of $PhC{\equiv}CMgBr$ (40 mmol) was added to a suspension of **1b** (10 mmol) in anhydrous ether (60 ml) at 20 °C. The mixture was stirred at 35 °C for about 4 hours, then hydrolyzed with aqueous 4M HCl. After 3 extractions with ether, the organic layer was washed 3 times with aqueous 2M NaOH then twice with water and once with brine. Evaporation of the solvent gave the crude $MeSi(C{\equiv}CPh)_3$ which was purified by recrystallization from pentane. 2.83 g (82%) of pure $MeSi(C{\equiv}CPh)_3$ was obtained, mp 125—6 °C (lit,[19] 126 °C).

The following products similarly prepared were: **Trimethylphenylsilane** (75%) bp 75—77 °C/30 Torr (lit,[20] 170.6 °C/760 Torr). **Triallylphenylsilane** (53%) bp 85—88 °C/0.4 Torr (lit,[21] 90—92 °C/0.8 Torr). **Tributylphenylsilane** (85%) bp 89—92 °C/0.05 Torr (lit,[22] 116—118 °C/0.9 Torr). **Tetraphenylsilane** (76%) mp 232—233 °C (lit,[23] 236.5—237 °C). **Tributylmethylsilane** (63%) bp 110—113 °C/14 Torr (lit,[24] 101—104 °C/9 Torr). **Triallylmethylsilane** (62%) bp 78—82 °C/35 Torr (lit,[25] 180.3 °C/745 Torr). **Methyltriphenylsilane** (63%) bp 150—160 °C/0.2 Torr (lit,[26] 196—200 °C/9 Torr). ***t*-Butylphenylsilane** (16%) bp 87 °C/30 Torr (lit,[27] 186—188 °C/760 Torr).

Synthesis of Triorganosilanes RR'_2SiH. The following is given as an example. **Dibutylphenylsilane.** Two molar equivalents of a molar solution of *n*-BuLi in ether were added to a suspension of **1a** (40 mmol) in 100 ml of ether at room temperature. The mixture was stirred at 20 °C about one hour then a suspension of 20 mmoles of $LiAlH_4$ in ether was added. The mixture was heated at 35 °C about 2 hours then hydrolyzed and extracted in the same way as for the isolation of $RSiR'_3$. 2.5 g (57%) of pure product was distilled at 75—79 °C/0.5 Torr (lit,[28]).

Similarly prepared were: **Dimethylphenylsilane** (37%) bp 89—91 °C/100 Torr (lit,[29] 159.3 °C/760 Torr). **Diethylphenylsilane** (40%) bp 115 °C/25 Torr (lit,[30] 97—100 °C/25 Torr). **Diisopropylphenylsilane** (45%) bp 120 °C/17 Torr (lit,[31] 58—60 °C/1.2 Torr). **Dicyclohexylphenylsilane** (83%) bp 145 °C/0.08 Torr (lit,[31] 124 °C/0.03 Torr). **Methyldiphenylsilane** (60%) bp 90—95 °C/1 Torr (lit,[32] 93.5 °C/1 Torr). **Dibenzylmethylsilane** (86%) bp 90—92 °C/0.05 Torr (lit,[33] 130—140 °C/3 Torr). **1-Methyl-2,5-diphenylsilacyclopentadiene** (51%) mp 97—99 °C (lit,[34] 97—98 °C). **1,2,5-Triphenylsilacyclopentadiene** (50%) mp 176—178 °C (lit,[35] 180—181 °C).

***t*-Butyldiphenylsilane.** 3 molar equivalents of *t*-BuMgCl in ether were added dropwise to a mixture of 20 mmoles of **1a** and 60 mmoles of TDA-1 in 100 ml of anhydrous ether. The pasty mixture was refluxed for 24 hours, then a suspension of 40 mmoles of $LiAlH_4$ in ether was added. The mixture was stirred at room temperature for one day, then hydrolyzed and extracted with ether. After the usual work-up the product was purified by silica-gel column chromatography to give 1.48 g of *t*-butyldiphenylsilane (31%). ^1H NMR (CCl_4) δ=1.0 (9H, s), 4.5 (1H, s), 7.05—7.55 (10H, m); IR (CCl_4) 2120 (SiH) cm^{-1} (lit,[36]).

Dibutylphenyl(2-hydroxyphenoxy)silane 2. 2 equivalents of *n*-BuLi in ether were added to a suspension of **1a** (20 mmol) in 150 ml of anhydrous ether at 20 °C. The mixture was stirred at room temperature for about one hour, then hydrolyzed with an aqueous solution of 4M HCl and extracted with ether three times. The combined organic extracts were washed 4 times with 2M NaOH, then with brine, dried ($MgSO_4$) and concentrated. The product was purified by distillation to give 4.2 g of **2** (64%). bp 153—5 °C/0.01 Torr. ^1H NMR (CCl_4) δ=0.42—2.02 (18H, m), 5.5 (1H, s), 6.5—7.0 (4H, m), 7.02—7.78 (5H, m); IR (CCl_4) 3560 (OH) cm^{-1}; Found: C, 73.21; H, 8.54; Si, 8,51%. Calcd for $C_{20}H_{28}O_2Si$: C, 73.17; H, 8.53; Si, 8.53%.

Dibutylphenyl(phenylethynyl)silane. 2 molar equivalents of *n*-BuLi in ether were added to a suspensition of **1a** (20 mmol) in 150 ml of anhydrous ether at 20 °C. The mixture was stirred at room temperature for one hour then one equivalent of $PhC{\equiv}CMgBr$ was added at 20 °C. The mixture was heated at reflux about 6 hours then hydrolyzed with an aqueous solution of 4M HCl, and extracted with ether; the extracts were washed with 2M NaOH four times then with brine, dried ($MgSO_4$) and concentrated. The product was distilled to give 3.5 g (54%) of dibutylphenyl(phenylethynyl)silane, bp 150—153/0.01 Torr. ^1H NMR (CCl_4) δ=0.15—1.90 (18H, m), 6.65—7.90 (10H, m); IR (CCl_4) 2150 (-C≡C-) cm^{-1}; Found C, 82.39; H, 8.77; Si, 8.74%. Calcd for $C_{22}H_{28}Si$: C, 82.50; H, 8.75; Si, 8.75%.

Allyldibutylphenylsilane. An excess of allylmagnesium bromide was added to a solution of 15 mmoles of the organosilane **2** in 50 ml of anhydrous ether at 20 °C. The mixture was heated about 20 hours at reflux then hydrolyzed with an aqueous solution of 4 M HCl and extracted with ether three times. The combined organic extracts were washed with 2M NaOH four times then with brine, dried ($MgSO_4$) and concentrated. The product was distilled to give 2.8 g (74%) of allyldibutylphenylsilane; bp 167 °C/13 Torr; ^1H NMR (CCl_4) δ=0.63—1.67 (18H, m), 1.87 (2H, d), 4.60—6.05 (3H, m), 7.05—7.70 (5H, m); IR (CCl_4) 1625 (C=C) cm^{-1}; Found: C, 78,38; H, 10.74; Si, 10.77%. Calcd for $C_{17}H_{28}Si$: C, 78.46; H, 10.76; Si, 10.76%.

Dibutylphenylmethoxysilane. 2 molar equivalents of MeOLi dissolved in 15 ml of MeOH were added to a solution of 9.1 mmoles of the organosilane **2** in 100 ml of MeOH. The mixture was stirred about 1.5 h at 20 °C, then MeOH was removed. The residue was extracted with pentane, the salts were filtered and the solvent was removed under vacuum. The product was distilled to give 2.9 g of dibutylphenylmethoxysilane (83%); bp 113 °C/0.02 Torr; ^1H NMR (CCl_4) δ=0.8—1.8 (18H, m), 3.6 (3H, s), 7.3—7.8 (5H, m); Found: C, 72.11; H, 10.43; Si, 11.18%. Calcd for

$C_{15}H_{26}OSi$: C, 72.00; H, 10.40; Si, 11.20%.

Dibutylphenylchlorosilane. 5 molar equivalents of HCl diluted in ether (100 ml) were added to a solution of 15 mmoles of the organosilane **2** in 50 ml of ether. The mixture was stirred at 20 °C for about 15 hours, then the solvent was removed and the residue taken up in pentane. The catechol was filtered and the product was purified by distillation; bp 164 °C/13 Torr (yield 73%); ^1H NMR (CCl_4) δ: 0.45—1.90 (18H, m), 6.95—7.82 (5H, m); Found: C, 66.11; H, 9.02, Cl, 13.92; Si, 10.97%. Calcd for $C_{14}H_{23}ClSi$: C, 66.01; H, 9.03; Cl, 13.94; Si, 11.00%.

1,1-Dibutyl-1,2,2,2-tetraphenyldisilane. 2 equivalents of *n*-BuLi were added to a suspension of **1a** (10 mmol) in 50 ml of anhydrous ether at 20 °C. The mixture was stirred at room temperature for one hour, then 10 mmoles of Ph_3SiLi[37] in 30 ml of THF were added at 20 °C. The mixture was stirred under reflux during 36 hours. After this time the reaction mixture was completely colourless. The salts were filtered and washed with ether. The combined ether extracts were washed with water until the aqueous layer was colourless. The ethereal solution was dried over anhydrous $MgSO_4$ and concentrated. The solid residue was recrystallized from ethanol to give white crystals [2,77 g (58%)] of 1,1-dibutyl-1,2,2,2-tetraphenyldisilane; mp 108—110 °C; ^1H NMR (CCl_4) δ=0.75—1.65 (18H, m), 7.25—7.7 (20H, m); Found: C, 80.26; H, 7.98; Si, 11.75%. Calcd for $C_{32}H_{38}Si_2$: C, 80.33; H, 7.95; Si, 11.70%.

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