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AN ELECTROCHEMICAL METHOD FOR THE SYNTHESIS OF SILICON—SILICON BONDS

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Summary

An electrochemical method for the preparation of compounds containing Si—Si bonds has been developed and its scope investigated.

Introduction

Recently we reported an efficient electrochemical synthesis of disilane derivatives, such as hexamethyldisilane and hexaphenyldisilane, by cathodic reduction of the corresponding chlorosilanes [1,2]. There are few Si—Si bond-forming reactions [3], and therefore we wanted to define the scope of this new method. The electrolyses were performed in a divided, H-shaped cell. It was necessary to use an aprotic solvent of high dielectric constant and high cathodic reduction potential. The solvent must dissolve the starting materials and be unreactive toward them. The solvent of choice was found to be 1,2-dimethoxyethane (DME). A number of other aprotic solvents were tried. For example, acetonitrile gave undesirable products probably because it is attacked by the electrochemically generated reactive intermediates. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte. Mercury or cadmium were successfully used as the anode. The latter became passivated on extended electrolysis. The metal chlorides ($HgCl_2$ or $CdCl_2$) formed during the electrolysis are insoluble in DME and separated in the anode compartment.

$$M + 2\,Cl^- \xrightarrow{-2e^-} MCl_2$$

When iron is used as the anode, the iron chlorides are soluble in DME and form relatively stable dark red complexes. However, this advantage is more than balanced out by decomposition of metallic iron at the cathode, which leads to much lower current yields. A platinum cathode was normally employed but mercury, lead, titanium or iron may be used.

Results and discussion

As we have previously noted [2], there are two possible reaction mechanisms for the formation of the disilane derivatives by electrolysis of chlorosilanes. A mechanism involving one-electron transfer is proposed for trimethylchlorosilane because only one reduction wave appears in its polarogram.

$$(CH_3)_3SiCl \xrightarrow{+e^-} (CH_3)_3Si^{\cdot} + Cl^- \qquad E_{1/2} = 2.2\text{v vs. } 0.001\ M\ AgClO_4\ (0.1\ M\ \text{TBAP in DME})/AG$$

$$2(CH_3)_3Si^{\cdot} \rightarrow (CH_3)_3SiSi(CH_3)_3$$

The resulting trimethylsilyl radicals can dimerize to give hexamethyldisilane.

On the other hand, the electrolysis of a mixture of trimethylchlorosilane and triphenylchlorosilane yields only the asymmetric 1,1,1-trimethyl-2,2,2-triphenyldisilane. This suggests that the reaction involves a triphenylsilyl anion intermediate which may be generated in a two-electron transfer step

$$Ph_3SiCl \xrightarrow{+2e^-} Ph_3Si^-\!: + Cl^-$$

$$Ph_3Si^-\!: + (CH_3)_3SiCl \rightarrow Ph_3SiSi(CH_3)_3 + Cl^-$$

In support of this mechanism, we found two reduction waves in the polarogram of triphenylchlorosilane. The first, at $E_{1/2} = -1.2$ V, may be due to the formation of a radical, while the second, at -3.1 V, may be due to the formation of an anion which attacks trimethylchlorosilane to yield product. A similar mechanism has been observed with arylchlorogermanes [4]. The existence of the triphenylsilyl anion intermediate is consistent with the greater stability of triphenylsilyl alkali metal compounds [3] compared with trimethylsilyl alkali metal compounds. The electron affinity and electron delocalizing ability of the aryl groups may be the reason for this different behavior.

The formation of the 1,1,1-trimethyl-2,2,2-triphenyldisilane may result from nucleophilic attack by the triphenylsilyl anion on trimethylchlorosilane in preference to attack on triphenylchlorosilane. This decreased reactivity of triphenylchlorosilane may result from two factors; first, back-bonding in triphenylchlorosilane, which results in a higher electron density at the silicon atom, and, second, steric hindrance. Coelectrolysis of tris(*p*-fluorophenyl)-chlorosilane or tri(*p*-tolyl)chlorosilane with trimethylchlorosilane also gave the asymmetric disilanes, 1,1,1-trimethyl-2,2,2-tris(*p*-fluorophenyl)disilane (46%) and 1,1,1-trimethyl-2,2,2-tris(*p*-tolyl)disilane (60%), along with small yields of the corresponding symmetrical hexaaryldisilanes.

To explore the scope of this method, difunctional chlorosilanes were used as starting materials. The electrolysis of diphenyldichlorosilane yields the strained octaphenylcyclotetrasilane and a small amount of polymeric materials.

$$4\ Ph_2SiCl_2 \xrightarrow{+8e^-} (Ph_2Si)_4 + 8\ Cl^-$$

Octaphenylcyclotetrasilane is insoluble in DME and is precipitated at the cathode. It is noteworky that no larger rings $(Ph_2Si)_n$, $n = 5, 6$, are formed [5]. The reaction may proceed via a stepwise build-up of catenated dichloroperphenylpolysilanes. This proposal is supported by the fact that the electrolysis of 1,2-dichlorotetraphenyldisilane gives (along with 1,4-dichlorooctaphenyltetrasilane) only octaphenylcyclotetrasilane.

$Cl(SiPh_2)_2Cl \xrightarrow{4e^-} Si_4Ph_8$

$Cl(SiPh_2)_4Cl \xrightarrow{2e^-} Si_4Ph_8$

Similarly, electrolyses of bis(*p*-fluorophenyl)dichlorosilane gave the hitherto unknown octa(*p*-fluorophenyl)cyclotetrasilane in good yield. This compound was also insoluble in 1,2-dimethyoxyethane.

$(p\text{-}FC_6H_4)_2SiCl_2 \xrightarrow{+8e^-} [(p\text{-}FC_6H_4)_2Si]_4$

Electrolysis of 1-chloropentaphenyldisilane did not yield the expected decaphenyltetrasilane, but instead octaphenyltrisilane and hexaphenyldisilane, both of which are only slightly soluble in DME.

$Ph_3SiSiPh_2Cl \rightarrow Ph_3SiSiPh_3 + Ph_3SiSiPh_2SiPh_3$ + oligomers

Completely different behavior was found for dimethyldichlorosilane. Its electrolysis gave no cyclic products and only polymeric material was obtained. Investigation of this polymeric mixture by infrared and Raman spectroscopy showed the presence of Si—O bonds in addition to Si—Si and Si—C bonds. Presumably, the Si—O bonds are formed by the reaction of reactive silicon intermediates with the DME solvent. Electrolysis of α,ω-dichloropermethylpolysilanes such as 1,2-dichlorotetramethyldisilane and 1,5-dichlorodecamethylpentasilane gave the same result. These results should be considered in relation to the electrochemical investigations by Allred, who found that the reduction potential of α,ω-dichloropermethylpolysilanes becomes less negative with increasing chain length [6]. If one considers a mechanism which, in the first step produces 1,2-dichlorotetramethyldisilane, which is more easily reduced than dimethyldichlorosilane, α,ω-dichloropermethyloligosilanes will be preferentially formed. It may be that the cyclic products which are formed undergo further reduction [7,8,9]. Such cyclic permethylpolysilane anion radicals are only stable at low temperatures. At room temperature, they might react with solvent, starting materials, or with intermediate dichloropermethylpolysilanes to yield polymeric product. The fact that we were able to isolate 1,2-dichloro-1,2-dimethyl-1,2-diphenyldisilane from the electrolysis of methylphenyldichlorosilane is evidence that α,ω-dichloropolysilanes are formed as intermediates. In addition (2-methoxyethoxy)-methylphenylchlorosilane was isolated from this reaction and can only be formed by a radical reaction with the DME solvent.

$MePhSiCl_2 \xrightarrow{e^-} MePh\dot{S}iCl + Cl^-$

$2\ MePh\dot{S}iCl \rightarrow ClMePhSiSiPhMeCl$

$MePh\dot{S}iCl \xrightarrow{DME} MePhClSiOCH_2CH_2OCH_3$

The low yield of identified products in relation to the number of coulombs of the electricity used (the current yield) suggests that 1,2-dichloro-1,2-dimethyl-1, 2-diphenyldisilane may undergo further reduction to give higher polysilanes, which we were unable to separate or characterize.

We electrolysed t-BuMeSiCl$_2$ and were able to isolate a small amount of 1,2,3,4-tetra-t-butyltetramethylcyclotetrasilane as expected by analogy to the reduction with Na/K alloy [10], but the yield was low.

In summary, we can say that the electrolysis of difunctional silane derivatives gives satisfactory yields of cyclic compounds only if the cyclic reaction products are insoluble and thus not able to react further. On the other hand, disilanes, which are formed by electrolysis of triorganochlorosilanes, are stable against further electrochemical attack. Therefore, the formation of soluble products such as Me$_3$SiSiMe$_3$ is possible. The electrochemical coupling of triorganochlorosilanes to give disilanes is a mild method which is valuable because it permits the synthesis of hitherto unknown aryldisilanes which could not be obtained by conventional methods. For example, alkali metal coupling of tris(p-fluorophenyl)chlorosilane gives only a poor yield of hexakis(p-fluorophenyl)disilane [11]. On the other hand, this compound is formed in 80% current yield on the electrolysis of tris(p-fluorophenyl)chlorosilane. Likewise, tetrakis(p-fluorophenyl)dimethyldisilane, which can be made in a current yield of 50% by electrolysis of bis(p-fluorophenyl)methylchlorosilane, not be obtained at all by alkali metal coupling.

The coelectrolysis of 1 : 1 mixtures of triarylchlorosilane and trimethylchlorosilane is a very convenient method for preparing asymmetric disilanes, which are not accessible by conventional methods.

$$\mathrm{R_3SiCl + Me_3SiCl \xrightarrow{+2e^-} R_3SiSiMe_3}$$

$$\mathrm{R} = \mathrm{C_6H_5},\ p\text{-}\mathrm{FC_6H_4},\ p\text{-}\mathrm{CH_3C_6H_4}$$

The electrochemical formation of Si—Si bonds is thus a synthetically valuable method for the preparation of symmetric and asymmetric disilanes.

Experimental

General comments

All reactions were carried out under an atmosphere of purified nitrogen in a divided H-shaped cell. DME was dried by refluxing over LiAlH$_4$ for 3 days and was distilled immediately prior to use. The TBAP was purified by dissolving it in DME and precipitating it with distilled water. The procedure was repeated three times. Afterwards, TBAP was placed in a Soxhlet extraction cup and was extracted with Et$_2$O for 24 h. Finally, it was dried in vaccuo at 80°C. NMR spectra, ^{1}H and ^{29}Si, were run on a Brucker WH90 spectrometer. ^{29}Si NMR spectra were run with proton decoupling with TMS as internal standard. IR spectra were run on a Perkin-Elmer 325 IR spectrometer, Raman spectra were determined on a SPEX Ramalog with He/Ne excitation. Mass spectra were obtained on a Varian MAT 212 spectrometer at a ionizing voltage of 70 eV. Melting points and boiling points were not corrected. Many of the starting materials and products are known compounds. They had physical and spectral properties in agreement with literature values.

TABLE 1

REACTION CONDITIONS

Starting material	Conc. of starting material (mol/l)	Conc. TBAP (mol/l)	Starting voltage (V)	Starting current (mA)	Reaction time (h)	Current yield (%)	Yield [9]	Products	Work-up procedure
1. Me_3SiCl	5.3	0.04	75	40	96	100	10.5	$(Me_3Si)_2$	B
2. Ph_3SiCl	0.6	0.33	50	60	24	100	13.9	$(Ph_3Si)_2$	A
3. $(p\text{-}FC_6H_4)_3SiCl$	0.40	0.28	50	30	8	82	2.3	$[(p\text{-}FC_6H_4)_3Si]_2$	B
4. $(p\text{-}FC_6H_4)_2MeSiCl$	0.16	0.19	50	41	15	50	3	$[(p\text{-}FC_6H_4)_2MeSi]_2$	B
5. Ph_3SiCl/Me_3SiCl	0.45 0.45	0.18	65	40	24	100	6.5	$Ph_3SiSiMe_3$	B
6. $(p\text{-}FC_6H_4)_3SiCl/$ Me_3SiCl	0.45 0.45	0.17	52	30	48	16 46	2.2 4	$[(p\text{-}FC_6H_4)_3Si]_2$ $(p\text{-}FC_6H_4)_3SiSiMe_3$	B
7. $p\text{-}Tol_3SiCl/Me_3SiCl$	0.38 0.38	0.17	−3.2 vs. 0.001 *M* $AgClO_4/Ag$	20	39	6 61	0.4 2.3	$(p\text{-}Tol_3Si)_2$ $p\text{-}Tol_3SiSiMe_3$	B
8. Me_2SiCl_2	1.00	0.23	70	62	24			Si—O polymer	B
9. $Cl(SiMe_2)_5Cl$	0.16	0.19	45	40	24			Si—O polymer	B
10. $MePhSiCl_2$	2.20	0.39	45	50	48	20 9	2.0 1.3	$Cl(SiMePh)_2Cl$ $MePhSiOCH_2CH_2OCH_3$	B
11. $t\text{-}BuMeSiCl_2$	0.10	0.29	40	48	24		traces	$[Me(t\text{-}Bu)Si]_4$ Si—O polymers	B
12. Ph_2SiCl_2	1.77	0.38	60	75	12	100	3	$(Ph_2Si)_4$	A
13. $Cl(SiPh_2)_2Cl$	0.23	0.31	−3.4 vs. 0.001 *M* $AgClO_4/Ag$	30	10	43	0.5	$(Ph_2Si)_4$	A
14. $Cl(SiPh_2)_4Cl$	0.05	0.19	40	40	5	100	2.7	$(Ph_2Si)_4$	A
15. $(p\text{-}FC_6H_4)_2SiCl_2$	0.57	0.15	60	33	23	70	1.5	$[(p\text{-}FC_6H_4)_2Si)_4$	A
16. $Ph_3SiSiPh_2Cl$	0.16	0.16	43	33	39		0.3 1.1	$(Ph_3Si)_2$ Ph_8Si_3	A + B

Electrolysis

A solution of TBAP, the chlorosilane (see Table 1), and DME was transferred into the electrolysis cell by syringe. A voltage was applied to give a current of 30—50 mA. In some experiments with high concentration of the substrate, the value of the starting current was maintained over the entire reaction time, but in most cases it slowly decreased to 15—20 mA. When the electrolysis current reached this level, or when evolution of gas at the cathode began, the electrolysis was terminated.

The reaction mixtures were worked up by one of two methods as described below. The choice depended on the solubility of the products.

Method A was used for insoluble products. The cathodic precipitate was separated from the electrolysis solution by filtration through a glass frit. This precipitate was washed several times with DME. In most cases no further purification of the solid product was necessary.

Method B was used for soluble products. The electrolysis solution was filtered through a sintered glass frit and the volatile components were removed in vacuo. Ether or n-pentane was added to the residue to crystallize the recovered TBAP. TBAP was removed by filtration and was washed with ether or *n*-pentane. In reactions 1, 8, 9 and 10 the filtrate was combined with the volatiles and this mixture was fractionally distilled. In reactions 4, 5, 6, 7 and 11 all the Et_2O was removed in vaccuo. The residue was recrystallized from Et_2OH to give the product. In reaction 3 the slow evaporation of the ether caused the hexakis(*p*-fluorophenyl)disilane to crystallize. The perarylated disilanes precipated out in the electrolysis cell and were isolated by method A in reactions 5, 6, 7 and 16.

Characterization of the new compounds prepared

Hexakis(p-fluorophenyl)disilane. Raman/IR: 964vw/967vw, 946vw/945vw, —/935vw, —/838m, 820vvs/818vs, —/800(sh), 750m/—, 714w/720vw, —708w, 676vw/670vw, 634s/635w, —/630vw, —/620vw, —/590vvw, 548m/—, 528w/—, —/512s, 500m/—, 448m/453vvw, —/428s, —/420(sh), 412w/—, —/398m, —/380m, 328vs/315vvw cm^{-1}.

Anal. Found: Si, 8.97; C, 69.54; H, 3.63. calcd. for $C_{36}H_{24}F_6Si_2$: Si, 8.96%; C, 68.99%; H, 3.86%. M.P.: 305°C.

1,1,2,2-Tetrakis(p-fluorophenyl)-1,2-dimethyldisilane. Raman/IR: 990w/990 (sh), 973w/—, —/935m, —/820vs, 812vvs/811s, —/800 (sh), —/783s, —/765s, 746w/—, —/732m, 714s/710s, 698m/698s, 662w/—, 628s/630m, 607m/—, —/591m, 512m/512s, —/507s, 480vs/—, —/458w, 420m/418s, —/414s, —/386s, —/370s, 364s/360 (sh), —/342m cm^{-1}. Raman only: 316s, 289s, 200s, 162m cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 7.33 (m, 16 H), 0.70 ppm (s, 6 H). ^{29}Si NMR (CD_3COCD_3, ^{1}H-decoupled): δ —22.99 ppm (s). M.P.: 125°C.

1,1,1-Tris(p-tolyl)-2,2,2-trimethyldisilane. Raman/IR: —/832s, —822s, 804vvs/798s, —/740w, —/730w, —/710m, 688m/688m, —/648m, 640m/640s, —/628s, 598w/597m, 570w/—, —/555vw, 522w/515s, —/497s, 464w/—, —/450w, 434w/430m, —/428m, 355vw/352vw, 308s/304w cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 7.28 (m, 12 H), 2.33 (s, 9 H), 0.20 ppm (s, 9 H). Mol. wt.: found: 367 (ebull.), calcd. for $C_{24}H_{30}Si_2$: 374.7. M.p.: 93—94°C.

1,1,1-Tris(p-fluorophenyl)-2,2,2-trimethyldisilane. Raman/IR: —/972vvw, —/960w, —/939w, —841vvs, 824s/820vvs, 775vw/—, 742w/741m, —/708m, 696m/691ms, 664w/—, 634s/638m, —/628w, —/625w, 604w/596ms, 524w/522s, —/513s, 484m/480m, 440vw/435s, 414vw/405m, 322m/322ms cm^{-2}. Raman only: 194vs, 164m cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 7.42 m (12 H), 0.24 ppm (s, 9 H). ^{29}Si NMR (C_6D_6, ^{1}H-decoupled): —18.17 (s), —20.28 ppm (s). Anal. found: Si, 14.82; C, 65.95; H, 5.11. Calcd. for $C_{21}H_{21}F_3Si_2$: Si, 14.53; C, 65.25; H, 5.48%. M.P.; 126—127°C. Mol. wt. found: 389 (ebull.), calcd. for $C_{21}H_{21}F_3Si_2$:386.6

1,2-Diphenyl-1,2-dimethyl-1,2-dichlorodisilane. ^{1}H NMR. ($CDCl_3$): δ 7.74 (m, 10 H), 0.82 (s, 3 H), 0.78 ppm (s, 3 H). B.p.: 104—106°/0.01 mmHg.

2-(Methoxyethoxy)methylphenylchlorosilane. ^{1}H NMR: ($CDCl_3$): δ 7.47 (m, (m, 5 H), 3.89 (t, 2 H), 3.44 (t, 2 H), 3.29 (s, 3 H), 0.66 ppm (s, 3 H). B.p.: 50—57°C/0.02 mmHg.

Octa(p-fluorophenyl)cyclotetrasilane. Raman/IR: 828m/—, —/815vs, 716vw/—, —/702vw, 640m/632vw, 620m/—, 598w/—, 538m/—, —/508s, 408vs/—, —/420m, 410w/409w, —/358 (sh), 374vw/372m, 332w/328m cm^{-1} Raman only: 224s, 154vs cm^{-1}. Mass spectrum: parent m/e 872 (2%), p-C_6H_4F m/e 777 (1%), (p-$FC_6H_4)_3Si$ m/e 313 (100%), (p-$FC_6H_4)_2Si$ m/e 218 (16%), (p-FC_6H_4)Si m/e 123 (30%). Anal. found: Si, 13.10; C, 65.45; H, 4.03. Calcd. for $C_{48}H_{40}F_8Si_4$: Si, 12.88; C, 66.03; H, 4.62%. M.p.: 380—385°C (reversible color change at 150°C).

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References

1 E. Hengge and G. Litscher, Angew. Chem., 88 (1976) 414.
2 E. Hengge and G. Litscher, Monatsh. Chem., 109 (1978) 1217.
3 E. Hengge, Topics Curr. Chem., 51 (1976) 1.
4 R.J.P. Corriu, G. Davosi and M. Martineau, J. Chem. Soc. Chem. Commun., (1977) 649.
5 H. Gilman and G.L. Schwebke, Adv. Organometal. Chem., 1 (1964) 89.
6 W.G. Boberski and A.L. Allred, J. Organometal. Chem., 88 (1975) 73.
7 E. Carberry, R. West and T.E. Glass, J. Amer. Chem. Soc., 91 (1969) 5446.
8 R. West and E.S. Kean, J. Organometal. Chem., 96 (1975) 323.
9 A.C. Buchanan and R. West, J. Organometal. Chem., 172 (1979) 273.
10 M. Biernbaum and R. West, J. Organometal. Chem., 131 (1977) 173.
11 H. Kelling, Z. Chem., 7 (1968) 237.