



# Nucleophilic displacement versus electron transfer in the reactions of alkyl chlorosilanes with electrogenerated aromatic anion radicals



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## ABSTRACT

Anion radicals of a series of aromatic compounds ( $C_6H_5CN$ ,  $C_6H_5COOEt$ , anthracene, 9,10-dimethyl-, 9,10-diphenyl- and 9-phenylanthracene, pyrene and naphthalene) react with trialkyl chlorosilanes  $R^1R^2R^3SiCl$  ( $R^{1-3} = Me, Et; R^{1,2} = Me, R^3 = t-Bu$ ) in multiple ways, following classical bimolecular schemes. The ratio of one-electron transfer (ET) to a two-electron process ( $S_N2$ -like nucleophilic attack of the reduced form of mediator on the chlorosilane, with  $k_2 \cong 10^2-10^8 M^{-1} s^{-1}$ ) is inversely related to the steric availability of Si for nucleophilic displacement reactions. The nucleophilic substitution pathway mainly results in mono- and disilylated aromatic products. Paralleling the electrochemical data with DFT calculations, the role of silicophilic solvent (DMF) in  $S_N$  process was shown to be quite complex because of its involvement into coordination extension at silicon, dynamically modifying energetics of the process along the reaction coordinate. Although 2,2'-bipyridine also forms delocalized persistent anion radicals, they do not induce neither ET nor  $S_N$  reactions in the same manner as aromatic mediators. Silicophilicity of 2,2'-bipyridine being superior to that of DMF, a  $R_3SiCl$ -bipy complex of hypercoordinated silicon with electroactive ligand was formed instead, whose reduction requires about 1 V less negative potentials than bipyridine itself.

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## 1. Introduction

Silyl protection-deprotection methodology as well as many synthetic procedures of organosilicon compounds are based on nucleophilic reactions exploiting large versatility of electrophilic properties and steric bulk of  $R_3SiY$  ( $Y = Hal, AlkO, MeCOO, R_2N, CN$  etc) precursors [1,2]. With all importance of the chemistry of introduction and removal of silyl groups, it is surprising that relatively few quantitative studies on the fundamentals of reactivity of chlorosilanes are available [2]. Corriu evoked the

possibility of both single electron transfer (ET) and a pure nucleophilic pathway in nucleophilic reactions of chlorosilanes [3]. The first one involves one-electron transfer from an electron-rich nucleophile to an electrophilic chlorosilane, supposedly with the intermediacy of an anion radical of the chlorosilane [4]. Since the reduction of chlorosilanes requires very negative potentials [5] and—at least of those with aliphatic substituents—occurs via dissociative ET mechanism [6,7], the ET pathway seems less probable, though in the case of aryl chlorosilanes this possibility cannot be ruled out [7,8]. On the other hand, it is well documented that heterogeneous ET to alkyl chlorosilanes induces cleavage of the Si–Cl bonds leading to the reduction products with Si–Si or Si–H bonds [9].

Direct cathodic reduction of chlorosilanes, pioneered by Bobersky [10], Hengge [11] and Corriu [5,12], includes two-electron cleavage of the Si–Cl bond resulting in silyl anions. The nucleophilic attack of these latter on the starting molecule or on other chlorosilane, added to the solution [13–15], leads to stable final products via the formation of a Si–Si bond (Eq. (1)). The

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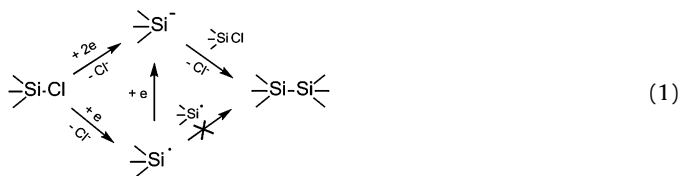
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intermediacy of silyl radicals and radical pathway of formation of disilanes were ruled out already in earlier works: the addition of PhOH during the electroreduction of  $\text{Ph}_3\text{SiCl}$  lead to the quantitative protonation of triorganosilyl anion and no disilane products were formed under these conditions [5], Eq. (2).

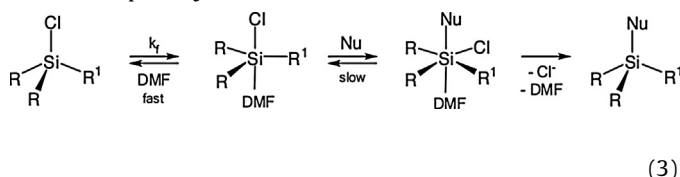


The reduction of chlorosilanes looks therefore quite similar to that of haloalkanes [16]. Dissociative electron transfer triggering the reduction of alkyl chlorosilanes requires about 1.5 V more negative potentials than the reduction of silyl radicals to the corresponding silyl anions, which totally bans the occurrence of any radical reactions in this process. Indeed, the reduction of the majority of chlorosilanes is usually observed at  $-3.2 \dots -2.4 \text{ V vs. SCE}$  [9], whereas the  $E_{1/2}$  of the couple  $\text{Ph}_3\text{Si}^\bullet/\text{Ph}_3\text{Si}^-$ , estimated by photomodulated voltammetry, is  $-1.39 \text{ V vs. SCE}$  [17]; this latter also agrees with the generation of silyl radicals from the oxidation of silyl anions at close potentials, as shown by real-time EPR-spectroelectrochemistry [18]. Thus this fundamental limitation precludes not only the intermediacy of silyl radicals and radical-based reactions in the direct cathodic reduction of  $\text{R}_3\text{SiCl}$  compounds but also the use of many electrophilic reagents susceptible to react with  $\text{R}_3\text{Si}^-$  anions because these electrophiles undergo own reduction at less negative potentials. A possible solution for debugging this situation could be the use of redox mediators, e.g. aromatic anion radicals, which would convey homogeneous character to the process and expectedly reduce the applied potentials by up to 0.6 V. Since first reports in mid-seventies on the reduction of aliphatic halides by anion radicals of aromatic hydrocarbons—homogeneous redox catalysis [19–21],—a great progress was accomplished in this field as summarized in the comprehensive review [22]. An analytical approach for such reactions has been developed by Savéant et al. using direct consideration of homogeneous redox catalysis [23–26] and by Lund and Daasbjerg using competition method between ET and coupling of alkyl radicals with the mediator [27–30].

Meanwhile,  $\sigma$ -carbanions of different nature (benzyl [31], aryl, allyl, vinyl [32] and alkyl [33]), electrogenerated via the reductive cleavage of  $\text{C-X}$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ) bonds at less negative potentials than those of the reduction of chlorosilanes, act as efficient  $\text{C}$ -nucleophiles towards the chlorosilanes themselves. These reactions were reported to result in silylated products with  $\text{Si-C}_{\text{sp}^3}$  bond. Therefore in order to minimize such  $\text{S}_{\text{N}}2$ -like nucleophilic interactions, similar to those between aromatic anion radicals and alkyl halides [34], and to act as outer-sphere mediators, the anion radicals must be rather of  $\pi$ -type, quite delocalized and weakly nucleophilic. So far, only few accounts were available on homogeneous reduction of germanium [35] and silicon chlorides [36,37] using such  $\pi$ -anion radicals.

On the other hand, in spite of some similarities outlined above, the patterns of bimolecular substitution mechanisms at  $\text{C}$  and  $\text{Si}$  are quite different: while  $\text{S}_{\text{N}}2$  in carbon chemistry is a classical example of this type of processes, nucleophilic displacement at  $\text{Si}$  involves, by virtue of coordination extension ability of  $\text{Si}$ , the formation of penta- or hexa-coordinate intermediates. Depending on whether

Berry pseudorotation occurs or not in such transients, it results in the products with retention or inversion of configuration [1]. Moreover, nucleophilic reactions at silicon are often promoted by silicophilic co-reagents such as  $\text{N,N}$ -dimethylaminopyridine, HMPA or DMF [1,38] that induce pentacoordination at  $\text{Si}$  prior its interaction with the proper nucleophile (Eq. (3)). Silicophilic additives such as DMF (tetrahydro-1,3-dimethyl-2(1H)-pyrimidinone), HMPA or DMF were commonly used in organosilicon electrochemistry and voltammetry [32,33,36,39–42] though their effect on the process studied is quite difficult to quantify.



Given the wide use of chlorosilanes as protecting groups in organic and organosilicon chemistry, examination of the reactions of electrogenerated anion radicals with alkyl chlorosilanes might provide an important insight into the ratio between electron transfer and nucleophilic substitution ( $\text{S}_{\text{N}}$ ) pathways in their reactivity. In the present paper, we checked the feasibility and efficiency of redox mediated reduction of model alkyl chlorosilanes versus silylation of aromatic mediators in view of assessing the synthetic potential of these processes for preparing the corresponding organosilicon products.

## 2. Experimental

A PAR-2273 and an EG&G 362 potentiostats were used for voltammetry and large-scale electrolyses, respectively. For cyclic voltammetry, a 2 mm in diameter glassy carbon (GC) and a 1 mm Pt disk working electrodes were used. A  $2.5 \times 50 \text{ mm}$  GC rod, separated from the analyte by a sintered glass diaphragm, was used as counter electrode. Peak potentials  $E_p$  were measured relative to Pt wire electrode electrochemically covered with polypyrrole and corrected using ferrocenium/ferrocene reversible system ( $E_{\text{Fc}^+/\text{Fc}}^0(\text{DMSO})=0.31 \text{ V vs. SCE}$  [43]). The working electrode was carefully polished with Struers FEPA P 4000 paper and rinsed consecutively with acetonitrile, ethanol and diethyl ether before each run. Large-scale electrolyses were carried out in a 40 mL two-compartment cell fitted with a  $30 \times 20 \times 0.5 \text{ mm}$  Pt plate cathode and a  $2.5 \times 75 \text{ mm}$  GC rod anode.

Chromatographic control of the electrolyses and GC-MS analyses, providing the distribution of products before any separation or a macro work-up, were performed using an HP-5973 MSD (EI mode, 70 kV) apparatus (Agilent Technologies) with a  $0.25 \text{ mm} \times 30 \text{ m}$  capillary column (OPTIMA-240 from Mackerel-Nägel).

DMF was used as a solvent (kinetic measurements) or was added to THF (approx. 1/10 v/v) for large-scale electrolyses. Analytical grade DMF (Aldrich) was passed through a column with vacuum-activated (at  $150^\circ\text{C}$ ) neutral  $\text{Al}_2\text{O}_3$ .  $\text{CH}_3\text{CN}$  and THF were distilled before using from  $\text{CaH}_2$  and from sodium benzophenone ketyl, respectively.  $\text{Et}_3\text{SiCl}$  and  $\text{M}_3\text{SiCl}$  were kept over Mg turnings and distilled prior to the electrolyses. The supporting electrolytes,  $\text{Bu}_4\text{NPF}_6$  or  $\text{Bu}_4\text{NBF}_4$  (Aldrich), activated in vacuum at  $80^\circ\text{C}$  for 10 hours and kept in a vacuum desiccator over  $\text{P}_2\text{O}_5$ , were used as 0.1 M solutions. The mediators used, all from ACROS, were used as received. 2,2'-Bipyridine (Aldrich) was additionally sublimed before using. All experiments were carried out under an inert Ar atmosphere.

Typically, preceding the main process, a pre-electrolysis was carried out for *in situ* drying the solution, as was suggested by Biran [44]. For this, the solution of 1 mmol of  $\text{Me}_3\text{SiCl}$  in 20 mL THF/0.1 M  $\text{Bu}_4\text{NBF}_4$ , containing the mediator and 1–2 mL of DMF, was

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