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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 $R_3SiCl\cdot$bipy complex of hypercoordinated silicon with electroactive ligand was formed instead, whose reduction requires about 1 V less negative potentials than bipyridine itself.

1. Introductione

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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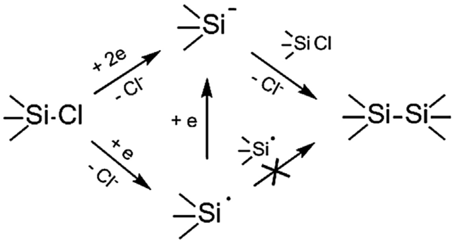
intermediacy of silyl radicals and radical pathway of formation of disilanes were ruled out already in earlier works: the addition of PhOH during the electroreduction of Ph_3SiCl lead to the quantitative protonation of triorganosilyl anion and no disilane products were formed under these conditions [5], Eq. (2).



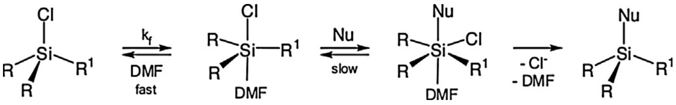
(1)

$$2Ph_3SiCl \overset{PhOH}{\underset{+2e}{\longrightarrow}} Ph_3SiH + Ph_3SiOPh \qquad (2)$$

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 $-3.2 \ldots -2.4$ V *vs.* SCE [9], whereas the $E_{1/2}$ of the couple $Ph_3Si^{\bullet}/Ph_3Si^{-}$, estimated by photomodulated voltammetry, is -1.39 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 R_3SiCl compounds but also the use of many electrophilic reagents susceptible to react with R_3Si^{-} 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, σ-carbanions of different nature (benzyl [31], aryl, allyl, vinyl [32] and alkyl [33]), electrogenerated via the reductive cleavage of C—X (X=Cl, Br, I) bonds at less negative potentials than those of the reduction of chlorosilanes, act as efficient C-nucleophiles towards the chlorosilanes themselves. These reactions were reported to result in silylated products with $Si—C_{sp3}$ bond. Therefore in order to minimize such S_N2-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 π-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 π-anion radicals.

On the other hand, in spite of some similarities outlined above, the patterns of bimolecular substitution mechanisms at C and Si are quite different: while S_N2 in carbon chemistry is a classical example of this type of processes, nucleophilic displacement at Si involves, by virtue of coordination extension ability of 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 N,N-dimethylaminopyridine, HMPA or DMF [1,38] that induce pentacoordination at Si prior its interaction with the proper nucleophile (Eq. (3)). Silaphilic additives such as DMPU (tetrahydro-1,3-dimethyl-2(1H)-pyrimidinone), HMPA or DMF were commonly used in organosilicon electrosynthesis and voltammetry [32,33,36,39–42] though their effect on the process studied is quite difficult to quantify.



(3)

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 (S_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 × 50 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 ($E^0_{Fc+/Fc}$(DMSO) = 0.31 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 × 20 × 0.5 mm Pt plate cathode and a 2.5 × 75 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 mm × 30 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 °C) neutral Al_2O_3. CH_3CN and THF were distilled before using from CaH_2 and from sodium benzophenone ketyl, respectively. Et_3SiCl and M_3SiCl were kept over Mg turnings and distilled prior to the electrolyses. The supporting electrolytes, Bu_4NPF_6 or Bu_4NBF_4 (Aldrich), activated in vacuum at 80 °C for 10 hours and kept in a vacuum desiccator over P_2O_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 Me_3SiCl in 20 mL THF/0.1 M

Bu_4NBF_4, containing the mediator and 1–2 mL of DMF, was electrolyzed at −1.0 V for 1.5 h to reduce the protons ←arising from the hydrolyses of the chlorosilane by residual water. After the pre-electrolysis was over, the target chlorosilane (10 mmol) was added through the syringe and the potential of the working electrode was switched to the E_p of the mediator used. At the end of the electrolysis, the catholyte was quenched with saturated aqueous solution of NaCl in order to transform unreacted chlorosilane into the corresponding $R_3SiOSiR_3$. The mixture was extracted by cyclohexane, the organic phase was then dried over Na_2SO_4, concentrated and filtered through a 3 cm SiO_2 cartridge. The products were analyzed by GC–MS by comparing with the authentic samples.

ZPE-corrected energies, NBO charges and profiles of potential energy have been calculated using Gaussian 03 suite [45] on DFT B3LYP/Lanl2DZ non-zero frequency optimized structures.

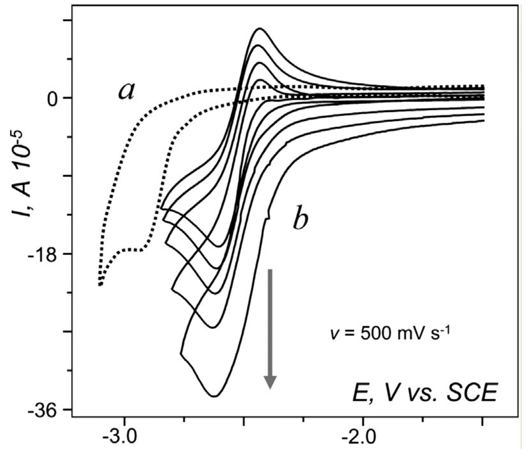


Fig. 1. (*a*) Reduction of Et_3SiCl ($5\,mmol\,L^{-1}$) and (*b*) the voltammograms of electroreduction of naphthalene ($10^{-2}\,mol\,L^{-1}$) at a GC disk electrode upon addition of Et_3SiCl (down the arrow: 0, 2, 4, 8 and $16\,mmol\,L^{-1}$). Solvent DMF + 0.1 M Bu_4NPF_6. Scan rate $v = 500\,mV\,s^{-1}$, T = 20 °C.

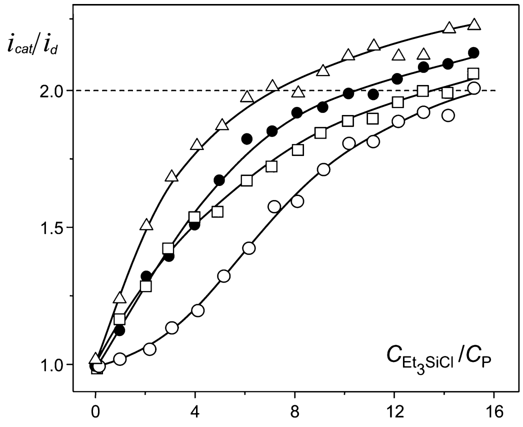


Fig. 2. Normalized kinetic currents i_p^{cat}/i_p^d of the reduction of: (△) naphthalene, (●) PhCN, (□) PhCOOMe and (○) anthracene ($C_P = 10^{-3}\,mol\,L^{-1}$ in DMF/0.1 M Bu_4NPF_6) in the presence of Et_3SiCl as a function of Et_3SiCl-to-mediator ratio. $v = 500\,mV\,s^{-1}$, T = 20 °C.

3. Results and discussion

3.1. General considerations

Several organic mediators (P) that form, upon one-electron uptake, relatively stable delocalized anion radicals (Q) and ranked according the reducing power that they provide to homogeneous electron transfer to chlorosilanes were considered (Table 1). 9,10-Dimethyl anthracene and benzonitrile were previously used for proving dissociative character of the cleavage of Si—Cl bond in Me_3SiCl via its indirect electroreduction. The synthetic outcome of this process was not studied then [36]. Three monochlorosilanes $R^1R^2R^3SiCl$ ($R^{1-3} = Me$; $R^{1-3} = Et$, and $R^{1,2} = Me$, $R^3 = t\text{-}Bu$), widely used both in silyl protection and in synthesis of silicon organic products, were considered as substrates all showing single irreversible two-electron reduction steps at −3.10, −2.87 and −2.82 V *vs.* SCE, respectively.

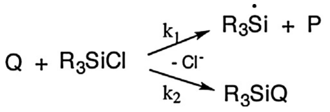
All mediators listed in Table 1 show the catalytic effect when a chlorosilane is added to the solution. As exemplified in Fig. 1 in case of naphthalene, the one-electron reduction current (i_p^d) of the mediator increases upon progressive addition of Et_3SiCl; at the same time the oxidation current of naphthalene anion radicals decreases up to its total disappearance (at the ratio $[Et_3SiCl]/[P] \geq 12/1$). It is seen that at this point the normalized kinetic current i_p^{cat}/i_p^d of the mediator only reaches the value of 2; other mediators show quite similar behavior (Fig. 2). This indicates that the reaction between the reduced form Q and the chlorosilane is not limited to pure electron transfer and includes a substrate-mediator addition [46,47]; the contribution of this side process limits the propagation of the catalytic scheme (Eq. (5b)).

$$P + e \rightleftarrows Q \tag{4}$$

Table 1
Aromatic redox mediators and the rate constants ($M^{-1}\,s^{-1}$) of the reactions of their anion radicals with chlorosilanes: electron transfer (ET)[a] vs. nucleophilic displacement (S_N)

Mediator	$-E^0_{P/Q}$, V[b]	Me_3SiCl		Et_3SiCl		t-$BuMe_2SiCl$	
		k_1 (ET)	k_2 (S_N)	k_1 (ET)	k_2 (S_N)	k_1 (ET)	k_2 (S_N)
Triphenylphosphine	2.65	4.78×10^7	1.69×10^8	5.61×10^6	2.39×10^8		
Biphenyl	2.55			1.34×10^6	7.01×10^7		
Naphthalene	2.50	6.92×10^6	3.02×10^7	6.32×10^5	3.59×10^7	1.04×10^5	3.25×10^6
Benzonitrile	2.23	1.18×10^5	6.60×10^5	6.87×10^3	5.21×10^5	1.38×10^3	5.49×10^4
Methylbenzoate	2.18	5.13×10^4	2.94×10^5	2.74×10^3	2.12×10^5	5.79×10^2	2.37×10^4
2,2'-Bipyridine[c]	2.10						
Pyrene	2.02	2.96×10^3	1.79×10^4	1.21×10^2	9.37×10^3	31.30	1.35×10^3
9,10-Dimethylanthracene	1.90	2.92×10^2	1.78×10^3			3.05	1.32×10^2
Anthracene	1.89	2.39×10^2	1.45×10^3	7.89	5.67×10^2	2.50	1.08×10^2
9-Phenylanthracene	1.83	70.74	4.25×10^2	2.11	1.43×10^2	0.74	31.57
9,10-Diphenylanthracene	1.79					0.32	13.65

[a] With $\Delta G_0^{\neq}$ obtained using the $\Delta G_{Si\text{-}Cl}$ from B3LYP/Lanl2DZ frequency analysis.
[b] V, vs SCE; DMF/0.1 M Bu_4NBF_4.
[c] Falls out of the reaction series, see text.



(5a)

(5b)

Under such circumstances, it is difficult to check whether primary $R_3Si^•$ radicals undergo second ET (either homo- or heterogeneous), or dimerization or else other radical reactions with the components of the solution. This situation can be simplified considering the following. With the mediators used in this study, the primary product R_3SiQ (Eqs. (5b), (10) and (11)) may only contain Si—C or Si—O bonds, both stable enough for not allowing any reverse reactions (supposing R_3SiQ to be kinetic product) that might lead to the disilane (thermodynamic) products. Though radical-radical dimerization is very fast and usually occurs at the diffusion limit (for $Me_3Si^•$, $k = 3 \times 10^9\ M^{-1}\ s^{-1}$ [48] and for $Et_3Si^•$, $k = 10^{10}\ M^{-1}\ s^{-1}$ [49]), the efficient reducing potential in the reaction space is such that the silyl radicals[5] (with own reduction potentials $E \approx -0.5 \ldots -1.4$ V [17,18]) are instantaneously transformed into silyl anions, which is consistent with the results of Corriu [12]. It is quite obvious then that if a disilane is formed in the process starting with eqs. ((1), (4), (5a), it could only have arisen from the reactions following the reduction of $R_3Si^•$ radicals (eqs. (6), (6a)). An S_N-like nucleophilic pathway is therefore assumed the only one accounting for the formation of Si-Si products.

$$R_3\dot{S}i \overset{+e}{\rightarrow} R_3Si^- \qquad (6)$$

$$R_3Si^- \underset{-Cl^-}{\overset{R_3SiCl}{\rightarrow}} R_3SiSiR_3 \qquad (6a)$$

In an *in situ* electrochemically dried solution (when the protonation of silyl anions is minimized), the nucleophilic attack of R_3Si^- (Eq. (6a)) on starting R_3SiCl is faster compared to its addition across the C=O or C≡N bonds [1,4] of the most electrophilic among the used mediators. Therefore, with R_3Si^- produced in the solution through Eqs. (4)–(6), the yield of the corresponding disilane can roughly be considered as reflecting the contribution from pure ET, Reaction (5a), k_1.

The anion radical of the mediator does not solely act as an outer-sphere electron donor towards Si-Cl substrates and the process involves several successive steps. Considering the process in its whole complexity, - involving multiple instable species and their interconversion depending on the reaction conditions, - in the absence of data on the coordination state of silyl intermediates and their interactions with various nucleophiles in the solution seems a non-realistic task, at least at the present. In fact, it would involve too many adjustable variables for obtaining reliable results. Therefore, we reduced the case to a simplified model, neglecting several seemingly secondary reactions (e.g. protonations and radical coupling of secondary radicals) and based on steady-state assumption for major intermediates (which holds sound in most practical situations [26]), developed for homogeneous reduction of alkyl halides [23]. In the following principal steps, provided an over-equimolar presence of DMF prior any ET, we assume $[R_3SiCl] = [R_3Si(DMF)Cl]$ (Eq. (3)). Otherwise, the competition between k_f and the processes with k_1, k_2, and k_6 should be considered.

$$P \overset{+e}{\rightleftarrows} Q \qquad (4)$$

ET (1e):

$$R_3SiCl + DMF \overset{k_f}{\rightleftarrows} R_3Si(DMF)Cl \qquad (7)$$

$$Q + R_3SiCl \underset{-Cl^-}{\overset{k_1}{\rightarrow}} R_3\dot{S}i + P \qquad (5a)$$

$$2R_3\dot{S}i \overset{k_{dim}}{\rightarrow} R_3SiSiR_3 \qquad (8)$$

$$R_3\dot{S}i + Q \overset{k_3}{\rightarrow} R_3Si^- + P \qquad (9)$$

$$R_3\dot{S}i + Q \overset{k_4}{\rightarrow} R_3SiQ^- \qquad (10)$$

S_N (2e):

$$Q + R_3SiCl \underset{-Cl^-}{\overset{k_2}{\rightarrow}} R_3SiQ^{\cdot} \qquad (11)$$

$$R_3SiQ^{\cdot} \underset{k_5}{\overset{Q}{\rightarrow}} R_3SiQ^- + P \qquad (12)$$

$$2R_3SiQ^{\cdot} \overset{k_{dim2}}{\rightarrow} R_3SiQQSiR_3 \qquad (13)$$

$$R_3SiQ^- \underset{k_6}{\overset{R_3Si\ Cl}{\rightarrow}} R_3SiQSiR_3 \qquad (14)$$

Two competing electron transfers (ET) trigger this sequence: a one-electron transfer, Eq. (5a) with ensuing radical coupling (Eq. (8), k_{dim}), and a two-electron (S_N2-like) attack of the mediator anion radical (by its site with highest negative charge localization) on the chlorosilane (Eq. (11)). The steps with k_1 and k_2 are supposed to be chemically irreversible since both involve Si—Cl bond cleavage (plus Q—Si bond formation, Eqs. (10), (11).

Admitting steady-state for $[R_3Si^•]$ in the ET scheme implies that k_1 is rate-limiting, i.e. $k_1 << (k_{dim} + k_3 + k_4)$, and the concentration of silyl radicals is manly determined by the competition between k_1 and their consumption in Reactions (8)–(10). The competition with the S_N-process (Eqs. (11)–(14) brings k_2 into the kinetic equation. Thus, without taking into account diffusion of reagents and the contribution of direct reduction of radical species at the cathode due to homogeneous character of the process, the rate law is

$$\begin{aligned}-d[Q]/dt = {} & [Q]((k_1 + k_2)[R_3Si\ Cl] + (k_3 + k_4)[R_3Si] \\ & + k_5([R_3SiQ])\end{aligned} \qquad (15)$$

Steady-state for $[R_3Si^•]$ (Eq. (16) implies that $k_{dim}[R_3Si^•]^2 \rightarrow 0$, even if k_{dim} is close to the diffusion limit

$$d[R_3S]/dt = k_1[Q][R_3Si\ Cl] - k_{dim}[R_3Si]^2 - (k_3 + k_4)[Q][][R_3Si] = 0 \qquad (16)$$

$$[R_3Si^•] = k_1[R_3Si\ Cl]/(k_3 + k_4) \qquad (17)$$

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[5] Dimerization of homologous $Ph_3Ge^{\cdot}$ radicals was postulated in [35]. However provided $E_{(1/2(Ph_3Ge\cdot/Ph_3Ge^-)} = -0.61$V vs SCE [17], an increase in the driving force of their reduction to germyl anions at the potential of $E = -2.1$ V, required for the reductive cleavage of Ge—Cl bond, is by 5×10^{12} times at the level of k_s. Most probably, no radical coupling could therefore compete with their reduction under these conditions.

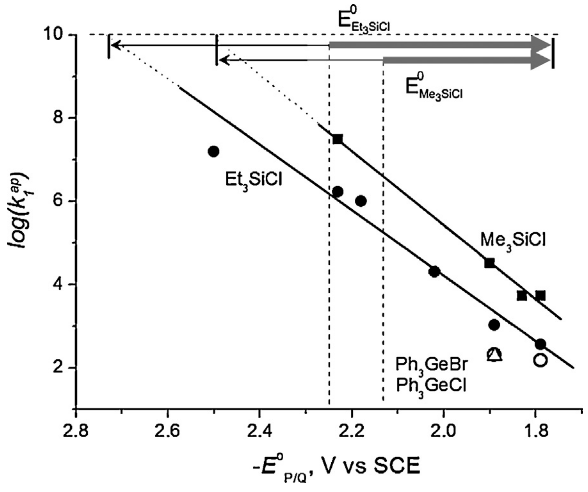

Fig. 3. Log(k_1^{ap}) versus E_o of redox mediators for the reaction of their anion radicals Q with triorgano chlorosilanes and the estimation of $E^0_{(SiCl/Si\bullet+Cl^-)}$. With Me_3SiCl (■), data from [26] are shown. (•) Et_3SiCl. For comparison, known values of k_1 for Ph_3GeCl (○) and Ph_3GeBr (△) [30] are plotted.

With the concentration of [$R_3SiQ^\bullet$] expressed as

$$d[R_3SiQ]/dt = [Q](k_2[R_3Si\,Cl] - k_5[R_3SiQ] = 0 \tag{18}$$

$$[R_3SiQ] = k_2[R_3SiCl]/k_5 \tag{19}$$

and with the ratio [$R_3Si^\bullet$]/[$R_3SiQ^\bullet$] = k_1/k_2, one obtains

$$-d[Q]/dt = (2k_1 + 2k_2)[Q][R_3SiCl] = k_1^{ap}[Q][R_3SiCl] \tag{20}$$

The corollary of this model is that $k_5 = k_3 + k_4$, i.e. the rate of consumption (SET, Eq. (12) of the primary radical product of the S_N step (Eq. (11), neglecting its dimerization under the conditions of voltammetry, equals the sum of the rates of disappearance of silyl radicals ($k_3 + k_4$) produced in the step 5a (k_1). Both electron transfers—one-electron (ET) and electron-pair (S_N)—are reflected in the kinetic law through the apparent rate constant[6] ($k_1^{ap} = 2k_1 + 2k_2$). Therefore, considering the mediator P/Q couple (through i_p(P)) in terms of the λ–i_p^{cat}/i_p^d analysis of redox catalytic mechanisms [23], the response of this system will be complex including the contributions form the two pathways. At this point, it is not possible to distinguish these contributions since they have similar reactants' energy profile and similar pre-exponential factors; their competition intervenes through the interplay of the corresponding activation energies in k_1 and k_2 in the apparent rate constant k_1^{ap}.

Now supposing for the process a catalytic EC mechanism with an additional solution electron transfer (SET) (Eq. (9)) while k_1^{ap} remains rate limiting step and using the working curve CAT–log(λ) (Fig. 1 from [23]; with $\lambda = k_1[P]\delta^2/D$, where δ and D are diffusion layer thickness and the diffusion coefficient of P) with catalytic efficiency taken as CAT = $2(i_p^{cat} - i_p^d)/i_p{}^d{}_{SiCl}$ (here i_p^{cat}, i_p^d and $i_p{}^d{}_{SiCl}$ are peak currents of P in the presence and the absence of R_3SiCl and the peak current of R_3SiCl, respectively) provided the values of log (k_1^{ap}), plotted as a function of $E^0_{P/Q}$ in Fig. 3.

Reduction of Me_3SiCl, Et_3SiCl and *t*-$BuMe_2SiCl$ with the mediators listed in Table 1 corresponds to an activation controlled process with the $\Delta\log(k_1)/\Delta E^0_{P/Q}$ slopes of −1/105 mV [36], 1/112 mV and 1/108 mV, respectively. For none of these chlorosilanes the zone of diffusion control by the back process was attained [25], so simple determination of $E^0_{(R_3SiCl/R_3Si\bullet+Cl^-)}$ by extrapolation of the line with 1/58 mV slope to log(k_D) is not possible. However, some estimation concerning their values can be made here. First, Cabasso et al. [8] reported that Ph_2SiCl_2 and $MePhSiCl_2$ show, at T = -41 °C, reversible reduction with E^0_{app} (as an average of E_p^c and E_p^a) of −2.8 . . . −3.0 V vs SCE. This value can be taken as lower limit for$E^0_{(R_3SiCl/R_3Si\bullet+Cl^-)}$ which is expected not to be more negative. Then, considering the shape of the log(k_1)-$E^0_{P/Q}$ plot (in an ideal case when $\alpha = 0.5$) can give another idea of the cathodic limit of $E^0_{(R_3SiCl/R_3Si\bullet+Cl^-)}$. The intercepts of the activation-controlled portion of the log(k_1)-$E^0_{P/Q}$ plot (Fig. 3) with two adjacent diffusion-controlled portions (with 0 and 1/58 mV slopes) are equidistant relative to $E^0_{(R_3SiCl/R_3Si\bullet+Cl^-)}$ (at $E^0_{(R_3SiCl/R_3Si\bullet+Cl^-)} - E^0_{P/Q=0}$). Such symmetry of the activation zone also implies that $\Delta E^0/0.058 < 2(\log(k_D) - \log(k_s))$ [24]. Therefore, from the half-spans of the visible activation zones, the values of $E^0_{(R_3SiCl/R_3Si\bullet+Cl^-)}$ of the chlorosilanes in question cannot be more negative than −2.13, −2.25 and −2.10 V for Me_3SiCl, Et_3SiCl and *t*-$BuMe_2SiCl$, respectively (Fig. 3).

The contribution of pure ET into k_1^{ap} was estimated through fitting the experimental points with Marcus curve [26] defining log (k_1) as

$$\log(k_1) = \log Z - \left(\frac{F}{2.3RT}\right)\Delta G_0^{\neq}\left(1 + \frac{\Delta G^0}{4\Delta G_0^{\neq}}\right)^2 \tag{21}$$

with homogeneous collision frequency Z estimated (6.7×10^{10} $M^{-1}\,s^{-1}$ for Me_3SiCl) from Debye-Smoluchovski equation [50], and $\Delta G_0^{\neq} = \lambda/4 = 0.125 \times (\lambda_P + \lambda_{SiCl})$. For aromatic anion radicals, solvent reorganization energies λ_P have close values that can be taken, following Kojima and Bard [51], as 0.63 eV. For chlorosilanes, the term λ_{SiCl} can be estimated as $\lambda_{SiCl} = D_{Si\text{-}Cl} + \lambda_0$ [26]. It has been previously shown [7,52] that in solution the Si—Cl bond undergoes substantial polarization preceding the electroreduction of chlorosilanes. If the gas phase bond strength $D_{Si\text{-}Cl}$ (5.49 eV [53]) sustained in the solution, chlorosilanes would not be reducible before -6 V vs SCE. So a good estimation of the effective Si-Cl bond energy in solution, $D_{Si\text{-}Cl}{}^{sol}$, is needed for assessing λ_{SiCl} and then $\Delta G_0^{\neq}$. First, it can be obtained according to the approximate Eq. (22) [54]

$$D^{sol}_{Si-Cl} \cong -2/3 \times (E_p - E^0_{Cl/Cl^-}) + C \tag{22}$$

which, with $E_p = -$ 3.1 V, and taking after Savéant $E^0{}_{Cl^\bullet/Cl^-} = 1.89$ V and C = 0.3 eV (for C- and N-haloderivatives [54–56]), provides $D_{Me_3Si\text{ - }Cl^{sol}} \cong 70.5\,\text{kcal mol}^{-1}(3.06\,\text{eV})$ as first estimate. Using more recent value $E^0{}_{Cl^\bullet/Cl^-} = 2.12$ V [57] and C = 0.27 eV that was directly calculated for the chlorosilane (as $C = 2\{(RT/\alpha F)\text{In}(Z_{het}(RT/\alpha F\nu D))$ - $0.78(RT/\alpha F)$ - $\lambda_0/2$ - $T(S_{Me_3SiCl}$ - $S_{Me_3Si^\bullet}$ - $S_{Cl^\bullet})\}/3$ [56] for $\nu = 0.1\,V\,s^{-1}$ with heterogeneous collision frequency $Z_{het} = (kT/2\pi M)^{1/2}$ [58], diffusion coefficient D form Stokes equation and the corresponding entropies obtained by DFT calculations at B3LYP/Lanl2DZ level), one obtains $D_{Me_3Si-Cl^{sol}} \cong 74.04\,\text{kcal mol}^{-1}(3.21\,\text{eV})$. Provided that bond strength is enthalpy, both these approaches have to treat the entropic contribution to energy, included in term C, either supposing it to be small and practically constant [54,55] or explicitly calculating it. A more complete way for estimation of $D_{Si\text{-}Cl}{}^{sol}$ ($\Delta G_{Si\text{-}Cl}$) can be calculating the profile of Gibbs energy of the reaction via frequency analysis (here at DFT B3LYP/Lanl2DZ level) when solvation is taken into account using an appropriate model (e.g. [59]). For Me$_3$Si-Cl, thus obtained free enthalpy of Si—Cl bond dissociation in DMF amounts to 2.048 eV (see Section 3.2).

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[6] Similar expression would result in the extreme case if the reduction of $R_3Si^\cdot$ (Eq. (6)) entirely occurs at the cathode, via heterogeneous ET (i.e. when $k_3 = 0$).

Table 2
Parameters of redox-mediated reduction of alkyl chlorosilanes in DMF/0.1 M Bu_4NBF_4

R_3SiCl	E_p, V[a]	$E^0_{(R_3SiCl/R_3Si^\bullet+Cl^-)}$ V[a]	λ_0[b]	$D_{Si\text{-}Cl}{}^{sol}$[b]	k_1 (ET)[c]	$\Delta G^{\neq}$ (ET)[b]	k_2 (S_N)[c]	$\Delta G^{\neq}$ (S_N)[b]
Me_3SiCl	−3.10	−2.06 (−1.89)	42.36 (1.836)[d]	74.04 (3.210)	0.053	19.18 (0.832)	4.73×10^4	11.07 (0.480)
			25.16 (1.091)	47.23 (2.048)	6.43×10^2	13.61 (0.590)	3.91×10^3	12.55 (0.544)
Et_3SiCl	−2.87	−2.11 (−1.94)	42.49 (1.842)	70.48 (3.056)	0.165	18.51 (0.803)	2.95×10^4	11.35 (0.492)
			26.34 (1.142)	47.99 (2.081)	1.29×10^3	13.20 (0.572)	4.59×10^4	11.09 (0.481)
t-$BuMe_2SiCl$	−2.82	−2.00 (−1.83)	42.58 (1.846)	69.72 (3.023)	0.201	18.39 (0.798)	3.61×10^2	13.96 (0.605)
			42.18 (1.829)	49.82 (2.160)	8.16	16.20 (0.703)	3.53×10^2	13.97 (0.606)

[a] V vs. SCE; in parentheses, the E^0 corrected for liquid-liquid potential for DMF/water, 0.172 V [57].
[b] kcal mol^{-1} (eV).
[c] $M^{-1} s^{-1}$
[d] Upper row values: derived with λ_0 from Born model [26] and $D_{Si\text{-}Cl}$ from Eq. (22); lower row: from DFT B3LYP/Lanl2DZ calculation of reaction ΔG profiles.

Similarly obtained values for other chlorosilanes seem consistent and were used in the following (Table 2).

Standard potentials E^0 of ET to alkylchlorosilanes, $E^0_{(R_3SiCl/R_3Si^\bullet+Cl^-)}$, necessary for $\Delta G_0{}^{\neq}$ determination, were obtained according to the thermochemical scheme [60] which proved efficient for calculating E^0 of alkyl halides [61]. Here, given the lack of consistent data on free enthalpies of formation of silyl radicals $\Delta G_f{}^0(R_3Si^\bullet)$ [53], the necessary energies of formation have been calculated for all entities at DFT B3LYP/Lanl2DZ level at T = 298.15 K and P = 1 bar (Ox = R_3SiCl, Red = $R_3Si^\bullet + Cl^-$). Solvation has been taken into account using Tomasi's isodensity polarized continuum model (IPCM) for model reaction field and analytic DFT energies calculation [59]. Obtained from DFT calculations, the values of E^0 are not related to any reference electrode, so they were brought to the SCE scale (E_{SCE} = 0.241 V vs. NHE), using recent value of absolute potential of standard hydrogen electrode proposed by Gennaro, $E^0{}_{H^+/H2}$ = 4.281 V [57]. The influence of ion pairing with Bu_4N^+ was supposed to be small, see [62].

$$E^0_{(R_3SiCl/R_3Si+Cl^-)}\text{vs.SCE} = \Delta G_f^0(Ox)^{(g)} - \Delta G_f^0(Red)^{(g)} + (\Delta G^0_{(R_3Si\ Cl)^{solv}} - \Delta G^0_{(R_3Si)}\text{solv} - \Delta G^0_{(Cl^-)^{solv}}) - 4.522 \tag{23}$$

Now with $D_{Si\text{-}Cl}{}^{sol}$ and $E^0_{(R_3SiCl/R_3Si^\bullet+Cl^-)}$ in hands, the corresponding standard activation energy $\Delta G_0{}^{\neq}$ could be determined and hence, from Eq. (21), the theoretical k_1 (Table 2). Plotted versus $E^0{}_{P/Q}$, the k_1 values (dotted lines in Fig. 4) thus correspond to the pure ET scheme. As is seen for Me_3SiCl, a fair fit of the experimental points with Marcus parabola, assuming pure ET (Fig. 4), was found with Z = 6.7×10^{10} and $E^0_{(Me_3SiCl/Me_3Si^\bullet+Cl^-)} = -2.06$V for $\Delta G_0{}^{\neq}$ = 0.34 eV. Similar trends with close values of $\Delta G_0{}^{\neq}$ were found for Et_3SiCl and *t*-$BuMe_2SiCl$. Obviously, such standard activation energy appears too small for a process including bond-breaking. Therefore, either the reduction of the chlorosilanes is not dissociative in its nature and involves transient anion radicals (though not detectable by voltammetry), as was supposed for the reduction of $ClCH_2TMS$ [36], or that bond breaking in chlorosilanes requires in fact much lower energy than estimated above. Following the model of parallel ET and S_N processes, it might also mean that the whole set of experimental log($k_1{}^{ap}$) values is uplifted relative to pure ET process (k_1) due to the contribution of parallel nucleophilic interaction of Q with R_3SiCl. Taking into account possible partial contamination of the catalytic current with some contribution from Eq. (12) would not explain such a large gap since this contribution is expected to be smaller than that of S_N. It is to be noted that similar excessive log(k_1) values were observed for homogeneous reduction of *n*-BuI compared to *sec*- and *tert*-BuI [61] when a substantial contribution from an S_N2 process was supposed.

As mentioned above, left sides of Eqs. (5a) and (5b) are similar but these reactions have different transition states. Now provided the rate constants k_1 and k_2 are included into $k_1{}^{ap}$ through Eq. (20), it is possible to separate them from Fig. 4 ($k_1{}^{ap}$ - 2 k_1 = 2k_2), using the calculated k_1 for pure ET case, and to determine the rate of the nucleophilic attack of the anion radical of any given mediator on the chlorosilane (Table 1). It is to note that with the $\Delta G_0{}^{\neq}$ estimated form the approximate model (Eq. (22), the k_2 values are superior to k_1 by the factor of ca. 10^5-10^6 (e.g. for Me_3SiCl/naphthalene, $k_1 = 1.98 \times 10^2$ and $k_2 = 6.27 \times 10^7 M^{-1} s^{-1}$), which seems greatly underestimating the contribution of ET. Using $\Delta G_{Si\text{-}Cl}$ from DFT calculations (see 3.2) provides better agreement with the experiment. Thermodynamic parameters of the S_N process can then be assessed from the values of k_2 using a retro-procedure through the transition state theory equation for the rate constant of a bimolecular reaction, $k_2 = \kappa P(kT/h) \exp(-\Delta G^{\neq}/RT)$ [63]. Here, the values of the transmission coefficient κ and steric factor P (as $\exp(\Delta S_{ster}{}^{\neq}/R)$, [64]) are not known; in first approach they are assumed to be equal to unity for Me_3SiCl and Et_3SiCl though they are supposedly smaller for *t*-$BuMe_2SiCl$. Thus estimated $\Delta G^{\neq}$ values correspond to quite low activation barriers (Table 2), which is consistent with high reactivity of chlorosilanes in S_N-reactions.

3.2. DFT calculations

Consistency of the electrochemical results was checked considering theoretical energy profiles of the corresponding processes. Potential energy (PE) and free Gibbs energy profiles for an ET-induced reductive cleavage of Si-Cl bond in Me_3SiCl have been calculated at DFT B3LYP/Lanl2DZ level in gas phase and in DMF (IPCM calculations, solvent cavity built using scaled van der Waals surface). PE profiles, plotted at zero driving force, are shown in Fig. 5. Remarkably, the PE profile for ($Me_3Si^\bullet + Cl^-$) system in the gas phase shows a shallow minimum which can be related to a −0.202 eV stabilized $Me_3SiCl^\bullet$ intermediate with ≈20% stretched Si—Cl bond (Fig. 5a). In DMF, solvation of the fragments overruns this stabilization and only repulsive part appears; the situation thus corresponds to a pure dissociative ET (Fig. 5b). For *t*-$BuMe_2SiCl$ (Fig. 6a), such a minimum is less pronounced and is shifted to longer $l_{Si\text{-}Cl}$, corresponding to long-term coordination interactions between *t*-$BuMe_2Si^\bullet$ radical and Cl^-.

For both chlorosilanes, Si-Cl bond dramatically weakens when going form the gas phase to solution (Figs. 5 and 6). Solution bond energies from the PE profiles seem more appropriate for calculating $\Delta G_0{}^{\neq}$ than those obtained using the approximate model (Eq. (22). Yet even better way of assessing Si—Cl energies and intrinsic barriers is to consider pure Gibbs energies (Fig. 5c) available from frequency analysis of the optimized configurations along the PE profile. Using these free energies of bond dissociation in DMF (Table 2), theoretical ET rate constants (k_1) are closer to the experimentally obtained $k_1{}^{ap}$ (Fig. 4). Now realizing the risk of direct comparison of the results of voltammetry and of large-scale electrolysis, a rough approximate of the ratio k_1/k_2 can be obtained from the practical ratio of ET to S_N products in large scale reductions, which is roughly ranging from ≈1:10 to ≈1:100 (e.g. for Me_3SiCl and Et_3SiCl using anthracene anion radicals, Table 3). Then the k_1 are supposed to be of the order of $k_1^{ap}/(20\ldots200)$, which is in a good accordance with the above theoretical estimates.

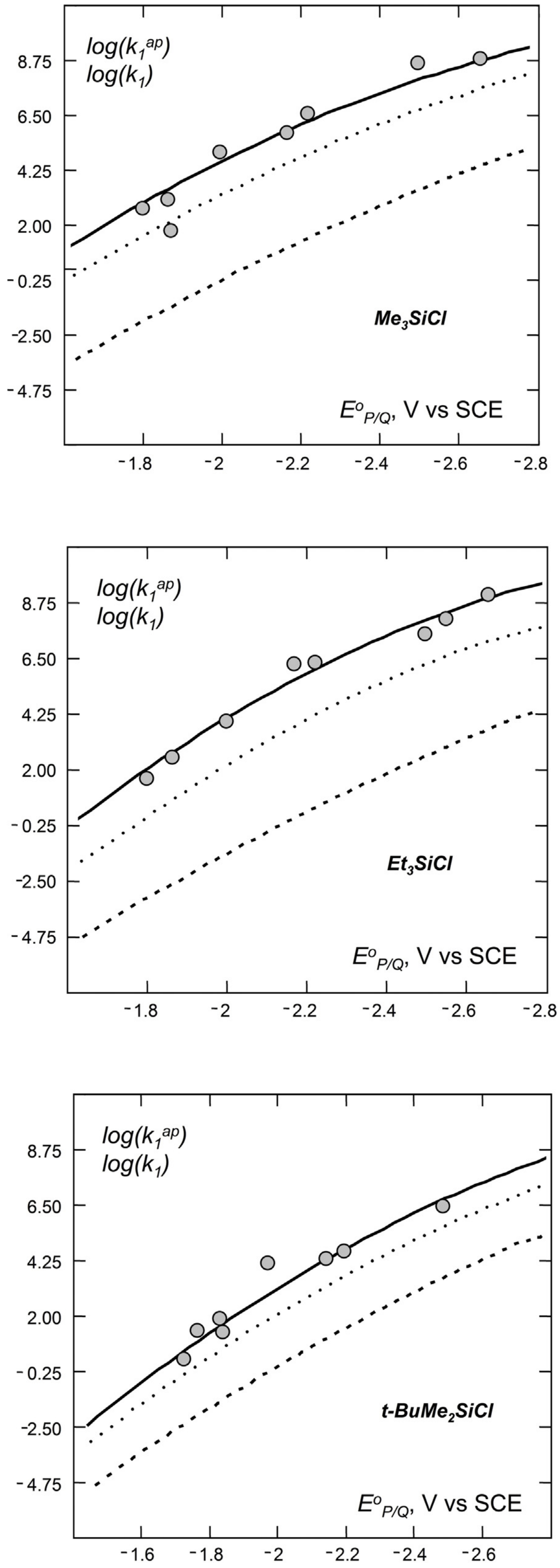


Fig. 4. Quadratic fits for the experimental k_1^{ap} (solid line) and Marcus plots for pure ET (dashed line: $D_{Si\text{-}Cl}$ from Eq. (22); dotted line: $\Delta G_{Si\text{-}Cl}$ from DFT calculations) for homogeneous reduction of three trialkyl chlorosilanes with aromatic anion radicals.

In DMF, which is more efficient silicophile than pyridine or even Me_3N [2], Si—Cl bond is affected not only by solvation but also by nucleophilic assistance of the solvent. To take this interaction into account, energy profile of the system $Me_3SiCl^{\bullet}DMF$ along the ET process has been calculated (Fig. 5d). Its striking feature is that the minimum related to the ground state geometry ($l_{Si\text{-}Cl}^{eq}$) is now only slightly marked: all following geometries (for $l_{Si\text{-}Cl} > 2.25$ Å) are almost equivalent in energy. The curve of the products shows that past equilibrium geometry, the energy decreases linearly with distance until ~3.7 A, after which it remains practically unchanged. The feature is quite similar for t-$BuMe_2SiCl$, though bond breaking energy is more pronounced (Fig. 6c), probably because approaching of DMF molecule is impeded by higher steric demand. Equilibrium geometries for both chlorosilanes clearly correspond to penta-coordinate species. Evidently, bond energies $D_{Si\text{-}Cl}$ in this situation are not the same and are not suitable for using in the model considered in 3.1.

Although electrochemistry of hyper-coordinate silicon species is still to be developed, some idea on relative electrophilicity of silicon in DMF-coordinated Me_3SiCl with respect to its non-coordinated form can be obtained from NPA charges and from the relative LUMO levels in these species (Scheme 1).

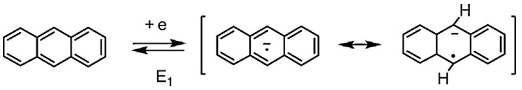
In spite of smaller partial positive charge on Si (1.608 vs. 1.721), LUMO level in DMF-associated penta-coordinated chlorosilane is 0.408 eV lower than in the non-associated form rendering the electron uptake easier. In Cl-silatrane, reduced at quite similar potentials and having strong intramolecular N → Si coordination [65], the charge at Si is remarkably more positive (2.228) while LUMO energy is only 0.1 eV higher than in $Me_3SiCl^{\bullet}DMF$. It seems that electron uptake in these systems is mainly orbital-controlled.

Thus donor interactions from an external or an internal silicophile do not increase LUMO energy in such species and therefore do not make their reduction more difficult, contrary to a common sense inspired by carbon chemistry. This additional energy is used for rearrangement of the orbitals of Si upon coordination expansion, generally lowering LUMO energy, promoting nucleophilicity and rendering the reduction easier. Evidently, careful quantification of nucleophilic assistance of silicophiles is needed for the development of a more elaborated model of reactivity of chlorosilanes.

3.3. Large scale reductions

3.3.1. Anthracene

When reducing anthracene in the presence of sub-equivalent amounts of Me_3SiCl, a kinetic pre-peak (E_{pp}) with $\Delta E = E_p - E_{pp} \cong 300$ mV appears on the voltammogram, caused by a fast nucleophilic attack of anthracene anion radicals on the chlorosilane. Very electrophilic character of Me_3SiCl renders its reactions with even poorly nucleophilic delocalized anion radicals quite efficient. Indeed, with $E^0_{P/Q} - E_p$ of 1.21 V, the estimated ratio of the rate constants of homogeneous ET to S_N between Q and Me_3SiCl (Table 1) can be compared with the reported alkylation of aromatic anion-radicals in a formal S_N2 process [26]. In the case of alkyl halides, the contribution from S_N2 was essentially neglected compared to ET mechanism [66]. For alkyl chlorosilanes, and to the greatest extend for Me_3SiCl, the situation is inversed: S_N-type process is systematically favored compared to ET.



(24)

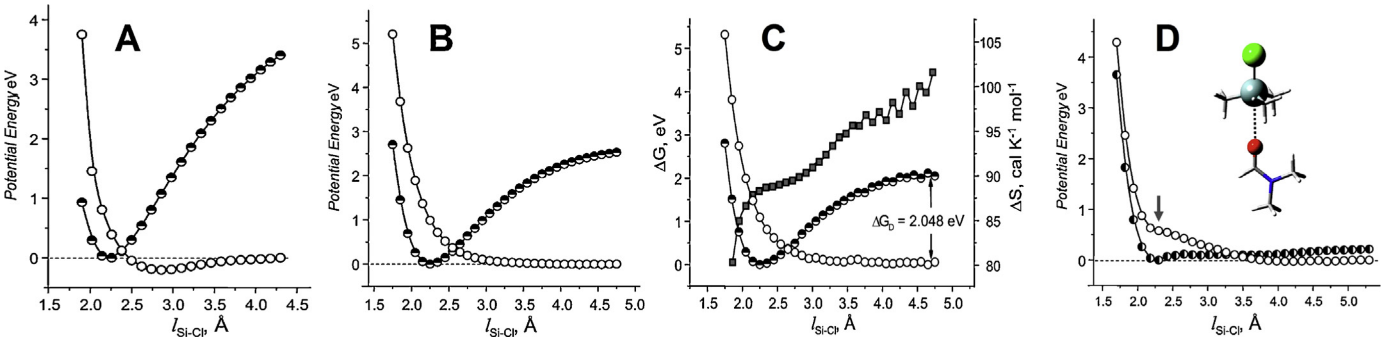


Fig. 5. Reduction of Me_3SiCl. (A) PE profile in the gas phase, (B) PE in DMF (polarized continuum with ε = 36.7). (C) Free Gibbs energy and ΔS (right scale, ■) in DMF. (D) PE profiles for the reduction in the presence of one molecule of DMF in DMF; the arrow corresponds to the structure shown. From DFT B3LYP/Lanl2DZ.

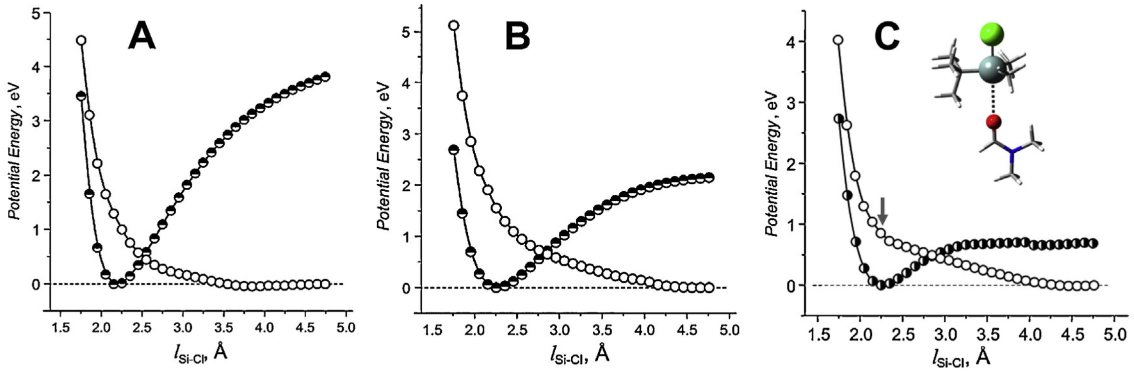
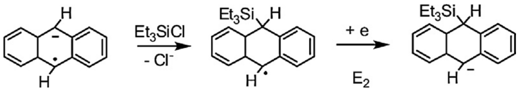


Fig. 6. PE profiles for the reduction of *t*-$BuMe_2SiCl$: (A) in the gas phase, (B) in DMF. (C) Reduction in the presence of one molecule of DMF (in DMF as solvent). From DFT B3LYP/Lanl2DZ.



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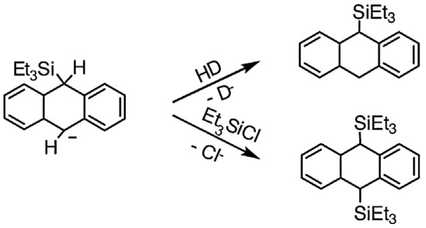
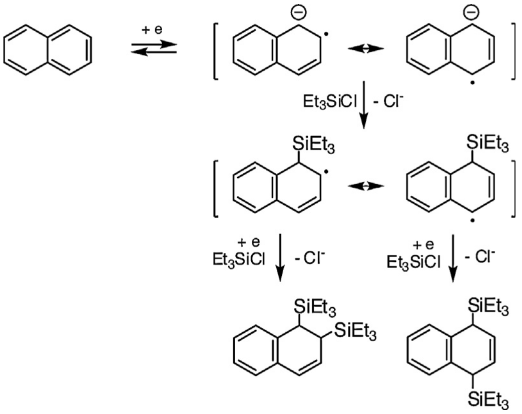


(26)

In the large scale reduction of the anthracene/chlorosilane mixture, only traces of the disilane (ET product) were observed by GC-MS. Instead, 9- and 9,10-silylated anthracenes were formed as main products (Table 3). Silyl-substitution at the benzylic position 9 in anthracene does not affect much electronic demand of the primary silylated radical but it neutralizes the negative charge of this species. Since neutral radicals are usually easier to reduce than the starting neutral molecule ($|E_2| < |E_1|$), once nucleophilic attack (Eq. (25)) produces silylated dihydroanthryl radical, it undergoes immediate reduction to form the corresponding anion. The mono-silylated anion follows second silylation at the position 10. Small amount of di-9,9'-silylated dimer of anthracene was also formed, arising from 10,10'-dimerization of 9-substituted intermediate radicals, in a way similar to that reported by Hammerich and Parker [67].

3.3.2. Naphthalene

With naphthalene, the contribution of ET process amounts to ≈8%, according to the amount of formed disilane. Instead, the silylation of naphthalene was quite efficient. Interestingly, two disilylated isomers - 1,4-bis(triethylsilyl)-1,4-dihydronaphthalene and 1,2-di(triethylsilyl)-1,2-dihydronaphthalene - were formed (Table 1), arising from two radical anion forms of naphthalene (Eq. (27)). The ratio of these products is 1:1.7, the major isomer being supposedly 1,2-silylated one. These results agree with those observed for the reaction of chemically prepared naphthyl lithium with Me_3SiCl [68] and Me_3SiCN [69]. Interestingly, the recovery of starting naphthalene was reported in the chemical version of this process, presuming that the $Naph^•$ also intervenes as electron transfer reagent providing an electron for the reduction of intermediate monosilylated naphthyl radical to the corresponding anion [68].



(27)

Table 3

Electroreduction of aromatic mediators (P) in the presence of trialkyl chlorosilanes in THF-DMF (10:1 v/v)/0.1 M Bu_4NBF_4

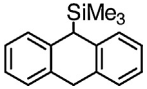
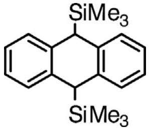
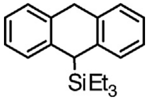
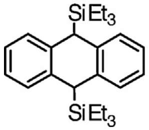
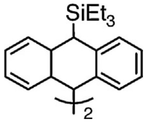
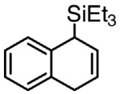
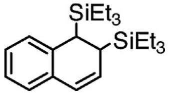
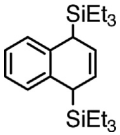
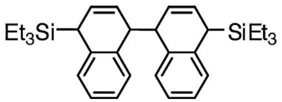
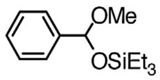
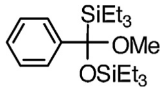
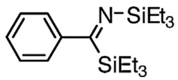
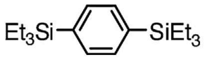
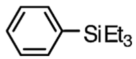
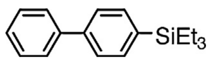
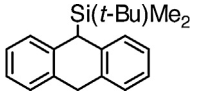
Chlorosilane	Mediator[a]	R[b]	B[c], %	Product	m/z, %	Yield, %[d]
Me_3SiCl	AN	3.0	traces		252 (M^+, 2), 237 (M-Me, 98), 179 (M-Me_3Si, 61), 91 ($C_7H_7^+$, 21), 77 (Ph), 73 (Me_3Si^+, 31), 65 ($C_5H_5^+$, 7), 51	73.2
					324 (M^+, 1), 309 (M-Me, 100), 294 (-2Me, 21), 251 (M-Me_3Si, 34), 91 ($C_7H_7^+$, 37), 77 (Ph), 73 (Me_3Si^+, 24), 65 ($C_5H_5^+$), 51	22.6
Et_3SiCl	AN	5.6	9.6		294 (M^+, 8), 279 (M-Me, 95), 265 (M-Et, 62), 179 (M-Et_3Si, 76), 115 (Et_3Si, 36), 65 ($C_5H_5^+$, 5), 51, 43	56.5
					408 (M^+), 379 (M-Et, 5), 350 (M-2Et, 27), 321 (M-$3Et_3$, 1), 293 (M-Et_3Si, 24), 115 (Et_3Si^+, 100), 91, 77, 65, 51	27.8
					293 (M/2, 19), 279 (M-Me, 71), 265 (M-Et, 100), 179 (M-Et_3Si, 52), 115 (Et_3Si, 47), 65 ($C_5H_5^+$), 51 ($C_4H_3^+$, 12), 43	< 5
Et_3SiCl	NP	3.5	8.2		244 (M^+, 2), 229 (M-Me, 15), 215 (M-Et, 27), 186 (M-2Et, 2), 157 (M-3Et, 2), 115 (Et_3Si, 34), 104, 91 ($C_7H_7^+$, 23), 77 (Ph, 11), 65 ($C_5H_5^+$), 51	47.6
					358 (M^+, 8), 343 (M-Me, 32), 329 (M-Et, 11), 243 (M-Et_3Si, 15), 115 ($SiEt_3^+$, 100), 91, 77, 51 ($C_4H_3^+$, 8), 43	23.3
					358 (M^+, 0.5), 343 (M-Me, 56), 329 (M-Et, 0.5), 301 (M-2Et, 12), 243 (M-Et_3Si, 6), 115 ($SiEt_3^+$, 100), 91, 77, 51	13.2
					486 (M^+, 2), 457 (M-Et, 9), 243 (M/2, 23), 215 (M/2–2Et, 8), 115 ($SiEt_3$, 100), 91, 77, 65	6.8

Table 3 (*Continued*)

Chlorosilane	Mediator[a]	R[b]	B[c], %	Product	*m/z*, %	Yield, %[d]
						
Et_3SiCl	MBA	3.5	16.2		252 (M^+, 32), 237 (M -Me, 9), 221 (M-OMe, 11), 115 (Et_3Si, 98), 122 ($C_7H_6O_2^+$, 13), 105 ($C_7H_5O^+$, 19), 77 (Ph, 25), 65, 51, 32 (CH_4O, 9)	78.1
					366 (M^+, 94), 337 (M -Et, 5), 309 (M-2Et, 8), 251 (M-Et_3Si, 23), 123 ($C_7H_7O_2^+$, 21), 115 (Et_3Si, 100), 105 ($C_7H_5O^+$, 8), 77 (Ph, 19), 65, 51	2.8
Et_3SiCl	BN	2.4	20.5	 *e*	333 (M^+, 7), 304 (M-Et, 100), 275 (M-2Et, 18), 218 (M-Et_3Si, 47), 115 (Et_3Si, 31), 102 (12), 77, 51	52.2
				[e] 	306 (M^+, 3), 277 (M-Et, 100), 249 (M-2Et, 25), 191 (M-Et_3Si, 32), 115 (Et_3Si^+, 56)	3.2
					192 (M^+, 5), 163 (M-Et, 100), 135 (M-2Et, 9), 115 (Et_3Si^+, 43), 105 ($C_7H_5O^+$, 6), 77, 42	7.4
					268 (M^+, 3), 253 (M-Me, 72), 239 (M-Et 93), 191 (M-Ph 48), 153 (M-$SiEt_3$, 61), 115 (Et_3Si, 100), 77 (Ph, 34), 65, 51	5.3
t-$BuMe_2SiCl$	AN	3.5	–	t-$BuMe_2SiH$	115 ($[M-H]^+$, 76), 100 (M-Me, 47), 65 (100), 58 (M-t-Bu, 15), 57 (t-Bu, 43), 43 (MeSi, 10)	53.5
					296 (M^+, 4), 281 (M-Me, 78), 115 (Et_3Si^+, 24), 181 (M-Et_3Si, 100), 91, 77 (Ph, 7), 65 ($C_5H_5^+$, 13), 57 (t-Bu, 11)	34.3

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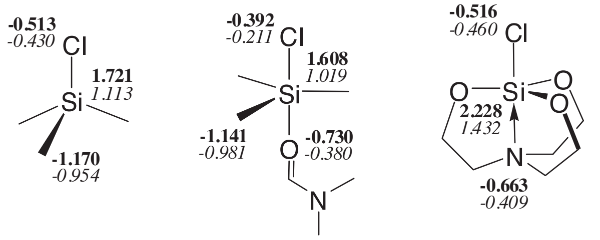
[a] AN: anthracene, MBA: methylbenzoate, NP: naphthalene, BN: benzonitrile.

[b] Ratio [Et_3SiCl]/[P].

[c] Yield of the corresponding disilane ($Me_3SiSiMe_3$,*m/z*: 146 (M^+, 17), 131 (M-Me, 38), 115 (M-2Me, 7), 73 (Me_3Si, 100); $Et_3SiSiEt_3$, *m/z*: 230 (M^+, 15), 201 (M-Et, 16), 115 (Et_3Si^+, 77)).

[d] Yields are based on the reacted R_3SiCl. Unreacted R_3SiCl was converted into corresponding disiloxane during the work-up procedure ($Me_3SiOSiMe_3$, *m/z*: 147 (M-Me, 100), 131 (M-2Me, 7), 117 (M-3Me, 1) 73 (Me_3Si, 15); $Et_3SiOSiEt_3$, *m/z*: 246 (M^+, 2), 217 (M-Et, 100), 188 (M-2Et, 79), 115 (Et_3Si, 37)).

[e] Supposed structure; ^1H NMR ($CDCl_3$, TMS): 7.78 (3H), 7.16 (2H), 1.10 (18H, CH_3), 0.63 (12H, CH_2).



Scheme 1. NPA (bold) and Mulliken (italic) charges in Me_3SiCl, $Me_3SiCl^{\bullet}DMF$ and chlorosilatrane in DMF from DFT B3LYP/Lanl2DZ calculations.

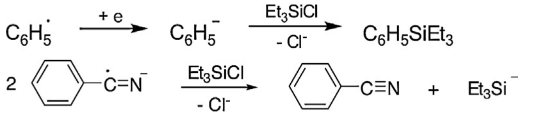
For comparison, Li-reduction of PhH in the presence of Me_3SiCl yielded 1,4-bis(trimethylsilyl)-1,4-dihydrobenzene [70] in a “silyl Birch reduction” of aromatics”.

3.3.3. Benzonitrile

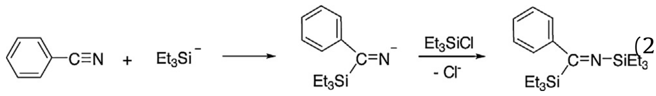
Although providing a considerable driving force for the ET ($E_p–E^0_{P/Q}$, Table 1) comparable to that of methylbenzoate, and being most efficient as ET reagents in the reaction series considered (Table 3), the anion radicals of benzonitrile have quite complex own reactivity.

The elimination of CN^- anion might generate $Ph^{\bullet}$ radical whose reactions could explain the formation of the silylated biphenyl, $PhC_6H_4SiEt_3$. This product might arise from radical phenylation of $PhSiEt_3$, formed through Eq. (28), or from nucleophilic substitution of $(C_6H_4)_2^{\bullet}$ anion radical on Et_3SiCl. Due to small electron-withdrawing effect ($\sigma_p = 0.02$ [71]), Et_3Si-group cannot lower the reduction potential of $PhSiEt_3$ to ensure its efficient separate reduction; in addition, electroreduction of the homologous $PhSiMe_3$ was reported to result in silylated cyclohexa-1,4-dienes [72]; such products were not formed in the electrolysis.

In neutral benzonitrile, charge distribution is such that carbon of the CN-group is most susceptible to nucleophilic attacks, but in the reduced forms of benzonitrile the negative charge is mostly localized on N atom according to ROHF/6–311 G calculations. This features account for the formation of the product of addition of Et_3Si^- anion across the CN bond followed by N-silylation of the resulting anion (Eq. (29)); this product (with $m/z = 333$) was tentatively characterized as N-silylated ketimine (sf. [73]).



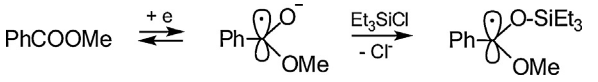
(28)



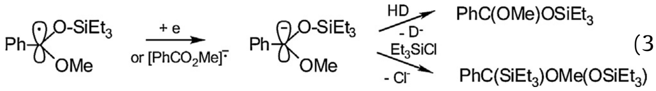
(29)

3.3.4. Methylbenzoate

Supposedly, because of large affinity of Si for O favoring the formation of O-silylated products, no phenyl silylation was detected, as in the reaction of benzophenone anion radical with 2-bromooctane [74]. This is consistent with the fact that O atom in carbonyl anion radicals acts as a nucleophilic center while C-atom mostly intervenes in ET processes [75].



(30)



(31)

Protonation and silylation of the carbanion resulting from the reduction of the intermediate silylated radical (Eq. (31)) lead to the main product, corresponding silyl(methyl) acetal. Contribution of pure ET from this mediator to Et_3SiCl, from the yield of $Et_3SiSiEt_3$, is 16% only.

3.3.5. Bipyridine

The anion radicals of 2,2'-bipyridine are π-delocalized akin to those of the above aromatic mediators, so they were expected to trigger similar reactions with chlorosilanes. However, 2,2'-bipyridine has lone pairs at N atoms, perpendicular to its π-system, so that it can manifest its silicophilic character both in the neutral form and in the anion radical. Being better silicophile than DMF [1], bipyridine is able to pre-coordinate with chlorosilanes before ET, thus making the whole reaction scheme different. Bipyridine is therefore falling out the reaction series of aromatic mediators (sf. Table 1), though the reduction of chlorosilanes in its presence also results in Si—Cl bond cleavage.

Upon progressive addition of R_3SiCl to 2,2'-bipyridine, initially showing a reversible redox system, the anodic counterpart of the reduction of bipyridine (at $E_p = -2.21$ V) progressively vanished but the reduction peak did not show any catalytic increase. At the same time, this system exhibited a new reduction peak at about $E_{p'} = -1.1$ V, the exact value depending on the chlorosilane taken.

The $E_{bipy} - E_{p'}$ for this new peak is too large to be provoked by the kinetic shift of the reduction of bipyridine, so it supposedly corresponds to the reduction of a complex between 2,2'-bipyridine and the chlorosilane. Such complexes have been prepared and isolated in case of triorganobromo- and iodo- silanes and polychlorosilanes [76], but not for monochlorosilanes. However, these complexes might exist in the solution, though with a small stability constant, and their formation is well seen through their voltammetric response (Fig. 7). Here, the peak p_1 ($E_p = -1.1$ V) arises from the reduction of $Et_3SiCl^{\bullet}bipy$ complex and the peak p_2 is the oxidation of Cl^- anion eliminated at the step p_1. The latter fact suggests the occurrence of intramolecular electron transfer between the two units: from SOMO (π-system of bipy) of the ligand anion radical to LUMO of the chlorosilane (Si-Cl σ^*-bond). The formation of complexes of electrophilic silicon halides with

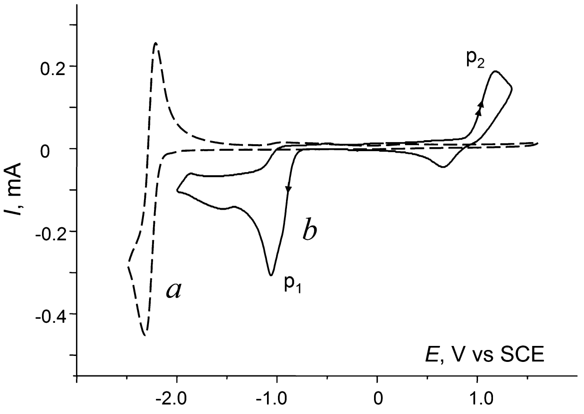


Fig. 7. Voltammograms of reduction of 2,2'-bipyridine (3×10^{-2} mol L^{-1}) in CH_3CN + 0.1 M Et_4NBF_4 at a GC electrode: (*a*)—before and (*b*)—after addition of Et_3SiCl (2.4×10^{-2} mol L^{-1}). Temperature 21 °C. $v = 500$ mV s^{-1}. With DMF used as solvent, electrode passivation occurred at $[Et_3SiCl] > 3 \times 10^{-3}$ mol L^{-1}.

2,2'-bipy and other N-bases is now well documented [77] and electroreduction of homologous complexes of germanium chlorides with 2,2'-bipyridine has been recently reported [78].

In terms of the reduction potential, the complexation of a chlorosilane with bipyridine formally corresponds to introduction of an acceptor substituent into the bipy moiety. Its equivalent electron-withdrawing ability was estimated through $E_{1/2}$–$\rho\sigma$ correlations from the reaction constants ($\rho = 0.9$–1.1) derived from the reduction $E_{1/2}$ of 4-R-2,2′-bipyridines and the ligand-based reduction of their RuL_3 complexes [79], and ligand-based reduction potentials of Re complexes with substituted bipyridines *fac*-$[4,4'\text{-X}2\text{–}2,2'\text{-bipy}]\text{Re(CO)}_3\text{Etpy}^+$ [80]. Thus obtained plot ($E_p = \rho\sigma_p - 2.1$) allowed assessing the σ-constant of an equivalent substituent at *p*-position of bipyridine that would provoke similar anodic shift in E_p of bipy as that due to the complexation with R_3SiCl. The obtained value, $\sigma_p = 1.8$ for a single 4-R substituent (or $\sigma_p = 0.9$ for each of two 4,4′-R_2- substituents), is equivalent to the electron-acceptor effect of *p*-$(CF_3)_3CSO_2$ group or of two *p*-$Me_2\,S^+$ groups [71]. Rough estimation of the complex formation constant, K_f, from E^0(bipy) and $E^0(\text{bipy}^{\bullet}R_3SiCl)$, assuming the reaction between $\text{bipy}^{\bullet}$ and R_3SiCl to be total with $K > 10^4$, provides $K_f < 8 \times 10^{10}$. The study of these systems is presently in progress.

4. Conclusions

In a series of representative alkyl chlorosilanes, the rates of their reactions with electrogenerated aromatic anion radicals were determined by homogeneous redox catalysis method. Thus found apparent rate constants k_1^{ap} are remarkably higher than those of pure one-electron transfer to alkyl chlorosilanes expected according to Marcus model. The difference between these constants arises from the contribution of the parallel two-electron (nucleophilic) interaction between the mediators and chlorosilanes. The rates of nucleophilic displacement at Si by aromatic anion radicals, estimated from the comparison of the experimental $\log(k_1^{ap})$ and theoretical $\log(k_1)$–$E_{P/Q}$ plot, are quite high amounting to 10^2-$10^8\,M^{-1}\,s^{-1}$. These values are comparable with those found for the total reaction (including both ET and S_N contributions) between aromatic anion radicals and hexyl iodide [34] and are higher than those determined for *n*-BuI after subtraction of the ET term [61], which agrees with higher electrophilicity of chlorosilanes compared to alkyl iodides.

For an S_N-like process, the steric demand determining the availability of Si becomes more important when going from Me_3SiCl to *t*-$BuMe_2SiCl$, so the rate of the nucleophilic reaction of alkyl chlorosilanes with the same aromatic nucleophile decreases in average by 4–9 times form Me_3SiCl to Et_3SiCl but may drop by about 200–300 when passing form Et_3Si to *t*-$BuMe_2Si$ derivatives. Steric hindrance brought by *t*-Bu group in *t*-$BuMe_2SiCl$ affects the S_N process to much lesser extent compared to *t*-Bu effect in carbon chemistry. This feature stems from longer Si—C bonds compared to C—C, generally providing poorer shielding of Si by alkyl substituents. Though this order is in good agreement with the general reactivity of electrophilic trialkylsilyl derivatives $Me_3Si > Et_3Si >> t\text{-}BuMe_2Si$ [1–4,81], steric demand of the nucleophile should also be taken into account for a more strict consideration. Corresponding activation energies agree with the observed contributions from ET and S_N pathways in all three reaction series. The approximate and the DFT-supported determinations of thermodynamic parameters for the ET model allowed assessing the Si-Cl bond strength in solution, which becomes more than 3 eV weaker compared to the gas phase because of polarization(/coordination) by(/with) the solvent and the interactions with the supporting electrolyte cation [6,52]. However, even if these two phenomena evidently account for a part of the reorganization energy and therefore influence the outcome of the formal Marcus treatment, their inclusion in the model is not simple and needs a special consideration. Coordination with the silicophilic solvent (DMF) is effective throughout the whole process. Its contribution supposedly evolves when going form one silylated intermediate to another but at the present state, it is impossible to provide a quantitative account for this phenomenon. Given a large excess of the silicophile at any moment, one can suppose that pseudo-first order conditions for these interactions were maintained, and hence, in a first approach, they could be neglected as supposedly constant.

Electrochemical silylation of delocalized aromatic anion radicals is not so chemoselective as in the case of σ-anions or of non-delocalized alkyl carbanions; charge delocalization and radical coupling account for the formation of multiple silylated products. Interestingly, that in case of *t*-$BuMe_2SiCl$, most favorable for observing ET chlorosilane, the *t*-$BuMe_2Si$-group is too bulky for an efficient S_N self-process of the silyl anion with the starting chlorosilane; under these conditions, no disilane was formed and *t*-$BuMe_2Si^-$ anion ends up as an electrochemically inactive hydrosilane *t*-$BuMe_2SiH$.

In general, the present study has shown that the use of redox mediators, in spite of its expected advantage as compared to direct cathodic reduction of chlorosilanes, is quite inefficient for preparing disilane products. On the contrary, silylation of the aromatic anion radicals via an S_N–like process seems to be a good complement to the conventional synthetic methods involving aromatic reductions with alkali metals but being free of the inconveniences of the latter. Electroactive silicophilic ligand 2,2'-bipyridine forms electroactive hyper-coordinated species whose low-potential cleavage of Si—Cl bonds merits a special study. Further works in this direction are under the progress.

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