Aryl–Cl vs heteroatom–Si bond cleavage on the route to the photochemical generation of σ,π -heterodiradicals

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Abstract

The photochemistry of aryl chlorides having a X–SiMe₃ group (X = O, NR, S, SiMe₂) tethered to the aromatic ring has been investigated in detail, with the aim to generate valuable σ,π -heterodiradicals. Two competitive pathways arising from the excited triplet state of the aromatics have been observed, namely heterolysis of the aryl–chlorine bond and homolysis of the X–silicon bond. The former path is found in chlorinated phenols and anilines, whereas the latter is exclusive in the case of silylated thiophenols and aryl silanes. A combined experimental/computational approach was pursued to explain such a photochemical behavior.

Graphical abstract

Keywords Aryl cations · Aryl chlorides · Heterodiradicals · Photoheterolysis · Photohomolysis

Dedicated to Prof. Angelo Albini in the occasion of his 75th birthday.

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1 Introduction

Radicals are intermediates of key importance in organic synthesis and have found application in several processes, although they were initially claimed as unstable and not useful for preparing target compounds [1, 2]. A peculiar case is represented by diradicals, intermediates where two unpaired electrons act (nearly) independently [3–5]. Although the thermal generation of these species in solution can be challenging, the access to several diradicals and their use

in organic synthesis is made possible by adopting a photochemical approach (Scheme 1) [6, 7].

As an example, cycloalkanones undergo either a Norrish type I (path a) [6–9] or a Norrish type II (path b) [6–8, 10–13] reaction affording diradicals that, in the latter case, may recombine via the well-known Norrish–Yang reaction [6, 7, 10–13]. Diradicals are also intermediates in photoextrusion reactions (path c) [6, 7] where the photorelease of a stable molecule, such as CO (in cyclic ketones) [14–16], dinitrogen (in azoalkanes) [17–20] or SO₂ (in sulfones, path c) [21], is followed by the concomitant radical–radical coupling of the radical sites in the resulting diradical. Diradicals are also key intermediates in photo-Fries rearrangements of lactones and lactams as illustrated in Scheme 1, path d [6, 7, 22].

One of the classes of intermediates which generation is particularly challenging is that of benzyne (σ,σ -diradicals). Indeed, while *o*-benzynes are formed under photochemical conditions by elimination of groups “X” and “Y” present in suitable *ortho* disubstituted aromatics (path e) [6, 7, 23–25], *p*-benzynes, are rarely obtained by photochemical means [6, 7], and their generation is mainly limited to cycloaromatization of an enediyne moiety [29–31]. The latter intermediates play a key role in the development of antitumorals [26–28] in view of their activity as cleaving agents of double-strand DNA [31], as in the case of antitumor antibiotic enediyne-based Dynemicin A [30].

Scheme 1 Photochemical generation of diradicals for synthetic applications

Another class of diradicals with potential biological applications is that of α,n -didehydrotoluenes (α,n -DHTs, σ,π -diradicals) usually formed by cyclization of an enyne-allene (**III**) via the Myers–Saito cyclization (albeit the $\alpha,3$ -DHT is the only isomer accessible Scheme 2a, right part) [29–33].

In the past, we developed a protocol that allows generating α,n -DHTs starting from a preformed aromatic nucleus (Scheme 2a, left part). UV irradiation in a protic medium of an aromatic derivative (**I**) bearing a leaving group (LG) and an electrofugal group (EG) in the benzylic position caused the detachment of the leaving group to form a triplet phenyl cation (**II**) [34, 35]. The following cleavage of the C–EG bond results in the formation of the desired α,n -DHT. The reaction is effective when starting from both the parent [36–39] and methoxy substituted [40] (chlorobenzyl) trimethylsilane isomers (LG = Cl, EG = Me₃Si). Electrofugal groups able to ameliorate the water solubility of α,n -DHT precursors have been likewise designed and efficiently tested in chlorophenylacetic acids (EG = COOH) [41] and chlorobenzylphosphonic acids (EG = P(O)(OH)₂) [42]. An alternative generation of α,n -DHTs involves the photolysis of (trimethylsilylmethyl)aryl sulfonates and phosphates (LG = OSO₂R, OP(O)(OEt)₂) [43].

Although it is relatively easy to generate diradicals where the two radical sites are on carbon atoms or both on heteroatoms (see the case of stable bis(nitroxides)) [3, 4], it is less common to find diradicals where each radical site resides on a different kind of atoms. The most famous example is the thermal generation of aryl/phenoxy diradical intermediate via Moore cyclization of enyne-ketenes that forms

a Previous works: Thermal and photochemical generation of σ,π diradicals

b This work: Attempted generation of σ,π diradicals having one radical site centered on a heteroatom

Scheme 2 **a** Generation of α,n -DHTs by cycloaromatization of enyne-allenes (right) and by photolysis of disubstituted aromatics (left). **b** Designed generation of diradicals **V** by photolysis of aromatics **IV**

$\alpha,3$ -didehydrophenols (or radical trapping products) [44–51] able to promote DNA cleavage [44–46]. In rare instances, $\alpha,3$ -didehydrophenylphosphanes (from phosphallenes) [52] and few nitrogen-based diradicals [53–56] including $\alpha,3$ -didehydroanilines (from ketenimines) [57] have been formed by a cycloaromatization step.

Intrigued by these premises, we wondered if σ,π diradicals having one radical site on the phenyl moiety and one on a heteroatom in benzylic position may be accessed using the same photochemical approach adopted in the photogeneration of α,n -DHTs. In our experience, the diradical precursors **IV** could be designed to allow the easy photoheterolysis of the Ar–LG bond followed by the easy detachment of EG⁺ to give diradical **V** (Scheme 2b). Among the different LG investigated, chloride anion is the most versatile [34, 35]. Furthermore, the presence of a heteroatom X directly linked to the aromatic ring may exert a sufficient electron-donating effect to drive the formation of the phenyl cation. Finally, the R₃Si group appears to be the elective choice in the role of EG due to the easy handling of the derived compounds **IV** and to the high stability of the corresponding cation (R₃Si⁺, Scheme 2b).

Accordingly, we embarked on the study of selected disubstituted chloroaromatics **IV** (Scheme 2b) to find if there will be the right conditions to generate diradicals **V** upon photolysis. The work was supplemented with theoretical calculations to give insights into the photoreactivity observed.

2 Results

As hinted above, Fig. 1 collects the chloroaromatics prepared and examined in the present work, namely silylated derivatives of phenols (**1**, **2**), of anilines (**3**, **4**), of thiophenol (**5**) and disilane (**6**).

Initially, we focused on aromatics having the LG group and the X–EG moiety placed in meta position (ethers **1**, **2**). Indeed, when diradical *p*-**V** (Fig. 2) is formed by irradiation of 4-halophenols [58–61] the reactivity observed (e.g., oxygen addition) is due to the resonant

Fig. 1 Compounds examined in the present work

Fig. 2 Possible resonant **VI**-like structures in diradicals **V**

4-oxocyclohexa-2,5-dienylidene carbene form (*p*-**VI**) [62–64]. The 2-oxocyclohexa-2,5-dienylidene carbene isomer *o*-**VI** has been described to be formed from the irradiation of diazocyclohexadienone [65–67]. Accordingly, to avoid the occurrence of **VI**-like structures, we focus on the possible generation of diradical *m*-**V**.

Silylated phenols **1**, **2** (and similarly, the other compounds tested) are not fluorescent in polar (protic) media ($\Phi_F < 0.1$, see Table S1 for further details). The products distribution observed in the photolysis of compounds **1**, **2** is shown in Table 1. Irradiations have been carried out at 254 nm in polar protic media (found suitable for the α,n -DHT generation) [76–80, 83] such as MeOH or aqueous methanol by a fixed time of 1 h. In both cases, dechlorinated derivatives **1a** and **2a** along with the photosubstitution products **1b** and **2b** were obtained in variable yields. The disappearance quantum yield (Φ_{-1}) of these compounds is rather low (< 0.1) and slightly increased in aqueous media [68]. Curiously, when changing the nature of the phenol protecting group, in silyl ether **2** the presence of water mainly drives to the formation of compound **2b**. No photocleavage of the O–Si bond, however, has been detected.

We then turned our attention to *N*-silyl anilines. Non-reproducible results have been obtained with the *N*-(trimethylsilyl) derivative of 3-chloro-*N*-methyl aniline due to the thermal lability of the N–Si bond under the reaction conditions. Accordingly, we shifted to the more stable derivative 1,2,5-azadisilolidine **3**, in turn prepared from 3-chloroaniline via treatment with bis(chlorodimethylsilyl) ethane. Compound **3** is thermally stable under the reaction conditions but unfortunately rather photostable ($\Phi_{-1} < 0.01$) as the parent 3-chloroaniline [69] and irradiation in MeOH gave only traces of the corresponding compound **3a** after 16 h irradiation (Table 2). We thus shifted to *p*-chloro derivative **4**. In analogy with 4-chlorophenol, a 4-iminocyclohexa-2,5-dienylidene carbene could be potentially formed in the reaction [70, 71], but we exploited the strong photoreactivity of 4-chloroaniline derivatives [72, 73] to test the feasibility of N–Si bond cleavage. Photolysis of aniline **4** was found efficient ($\Phi_{-1} > 0.5$) in different polar solvents, and dechlorinated product **3a** was the sole photoproduct obtained, while the integrity of the 1,2,5-azadisilolidine scaffold was maintained (Table 2)

Table 1 Photochemistry of compounds **1,2** in polar media

Compound	Solvent (Φ_{-1}) ^a	Time (min)	% Conversion	Products, yield %	
1	MeOH (0.02)	60	77	1a , 29	1b , 23
1	MeOH:H ₂ O 1:1 (0.07)	60	81	1a , 29	1b , 28
2	MeOH (0.03)	60	68	2a , 30	2b , 27
2	MeOH:H ₂ O 1:1 (0.05)	60	72	2a , 18	2b , 43

Irradiations were performed at 254 nm (8×15 W low-pressure Hg lamps) on a nitrogen-saturated 0.01 M solution of **1, 2** in the chosen media

^aDetermined at $\lambda = 254$ nm

Table 2 Photochemistry of compounds **3,4** in polar media

Compound	Solvent (Φ_{-1}) ^a	Time (min)	% Conversion	3a , yield %
3	MeCN (<0.01)	60	traces	Traces
3	MeCN	960	1.4	<0.2
4	MeCN (0.68)	5	35	23
4	MeCN	10	56	36
4	MeCN	20	76	49
4	MeCN	50	100	64
4	MeCN:H ₂ O 9:1 (0.75)	30	100	13
4	MeOH (0.57)	30	100	17
4	MeOH:H ₂ O 9:1 (0.62)	30	96	12
4	MeOH:H ₂ O 9:1	60	100	13

Irradiations were performed at 310 nm (8×15 W phosphor-coated Hg lamps) on a nitrogen-saturated 0.01 M solution of **3, 4** in the chosen media

^aDetermined at $\lambda = 254$ nm

Table 3 Photochemistry of compound **5** in polar media

Solvent (Φ_{-1}) ^a	Time (min)	% Conversion	Products, yield %	
			5a	5b
MeCN (0.05)	20	40	18	0
MeCN	40	75	69	3
MeCN	60	100	90	5
MeOH (0.09)	20	100	19	14
MeOH ^b	20	100	19	12

Irradiations were performed at 310 nm (8 × 15 W phosphor-coated Hg lamps) on a nitrogen-saturated 0.01 M solution of **5** in the chosen media

^aDetermined at $\lambda = 254$ nm

^bReaction carried out in the presence of acetone (10% v/v)

independently by the presence of a protic source in the reaction media.

Since in the previous cases, the photoheterolytic cleavage of the Ar–Cl bond succeeded but it was not followed by the desired Me_3Si^+ detachment, we shifted to compound **5** having a more labile S–Si bond [74] confident with the possible generation of the corresponding phenyl cation in analogy with chlorothioanisoles [75]. The consumption of **5** upon UV irradiation was quite inefficient (Φ_{-1} ca. 0.1) and cleavage of the S–Si bond to give thiophenol **5a** and disulfide **5b** took place in variable amounts depending on the solvent used, instead of the expected dechlorination (Table 3). Sensitization experiments carried out in MeOH in the presence of acetone (10% v/v) gave roughly the same products distribution.

Finally, we tested chlorodisilane **6**. The compound was quite photoreactive (Φ_{-1} up to 0.29) in both organic solvents and water/organic solvent mixtures (Table 4), but all the irradiation experiments tested led to desilylated product **6a** in variable amounts, where the experiments in MeOH under sensitized conditions gave the best mass balance.

We then decided to perform a computational analysis to explain the different photochemical behavior of chloroaromatics **1–6** trying to understand why diradicals are never formed in comparison with (chlorobenzyl)trimethylsilane.

2.1 Computational analysis

Computational analysis was carried out using DFT at the PW6B95-D3/def2-SVP level of theory incorporating the implicit contribution of methanol using the SMD solvent method [76]. PW6B95-D3 [77] is recognized as one of the best global hybrid functionals to reliably model thermochemistry, kinetics, and non-covalent interactions [78–80], being able to accurately predict open-shell species [81].

2.2 Comparison between S_0 and T_1 states

We started with the assumption that each photochemical process occurring in compounds **1–6** arose from their triplet state in analogy with other chloroaromatics [34, 35]. We then focused our attention on the optimized geometry of the compounds **1,2,4–6** both in their ground state (S_0 , Fig. S10 in the Supporting Information section) and in the triplet state (T_1 , Fig. 3). Table 5 collects the variation of selected bond lengths upon excitation. In all of the S_0 states the Ar–Cl bond is in the same plane as the aromatic core. Shifting from S_0 to T_1 geometry modifies the structural features of the substrates. In compounds **1–4**, the Ar–Cl bond in T_1 is puckered out-of-plane and it is longer than the one computed for the respective S_0 geometries. These features are known for triplet aryl halides and are extensively described in our previous works [82, 83]. The

Table 4 Photochemistry of compound **6** in polar media

Solvent (Φ_{-1}) ^a	Time (min)	% Conversion	6a , yield %
MeOH (0.1)	10	9	5
MeOH	20	33	18
MeOH	60	53	42
MeOH	120	80	63
MeOH ^b	30	40	30
MeOH ^b	60	100	95
MeOH:H ₂ O 1:1 (0.17)	10	15	11
MeOH:H ₂ O 1:1	30	35	32
MeOH:H ₂ O 1:1	60	79	62
MeOH:H ₂ O 1:1	120	100	78
MeCN:H ₂ O 1:1 (0.29)	10	48	3
MeCN:H ₂ O 1:1	30	100	6

Irradiations were performed at 310 nm (8×15 W phosphor-coated Hg lamps) on a nitrogen-saturated 0.01 M solution of **6** in the chosen media

^aDetermined at $\lambda = 254$ nm

^bReaction carried out in the presence of acetone (10% v/v)

C₁–C₆ and C₁–C₂ bonds adjacent to the C–Cl possess a more marked single-bond character at the T₁, due to the non-aromaticity of the structure [84]. Interestingly, in **35**, it is the sulfur atom (and not the Cl atom) that leaves planarity. Silane **6** is an exception because it is characterized by a fully broken Si–Si bond at the T₁. Therefore, the ring is characterized by fewer bond length variations compared to the S₀. Also, the X–Si bond lengths (except for **6**) differ only minimally between S₀ and T₁, while the Ar–Cl bond is longer in T₁ except in the case of **5** and **6** where it is slightly shortened in the first case and of the same length in the second case.

We also investigated the S₀ and T₁ structures of 4-chlorobenzylsilane (**BzS**) at the same level of theory for the sake of comparison. The molecule in S₀ has the Ar–Cl bond in the same plane of the aromatic core, while in the T₁, the Ar–Cl bond is longer and leaves planarity, influencing the adjacent C₁–C₆ and C₁–C₂ bonds, which, as seen previously, possess a more pronounced single-bond character.

2.3 Which is the first photocleavage event?

We then evaluated which bond between Ar–Cl and X–Si bonds was more susceptible to cleave in the triplet state by analyzing the difference in the energy between the detachment of the chlorine atom in the C–Cl bond and the detachment of the silane group in the R₃Si–X bond (see Fig. 4 and additionally Tables S2–S8 for a more complete overview of the relaxed scans performed).

4-Chlorobenzylsilane (**BzS**) was used as the reference, and significant differences have been found in the examined compounds (Fig. 4). The Ar–Cl bond scans have been carried out by a relaxed scan of the Ar–Cl bond in the triplet states of the molecules analyzed to obtain an approximated activation energy of the photocleavage of the chlorine atom tethered to the aromatic core. These scans were limited by the fact that the chloride anion, once detached from its previous position, formed π stacking interactions with the orbital of the aromatic core of the analyzed molecules. This limitation was a consequence of the method chosen. To accurately model the fate of the leaving group after detachment, an explicit solvent method is needed. However, this peculiar treatment does not fall into the scope of the present study, because we are solely focusing on the energies needed to cleave the photoactivatable bonds and not to determine which molecule will react with the group detached from the reagent.

As for compounds **1–4**, the photo-detachment of the chloride anion was by far more preferred than the X–Si cleavage. In the case of **1**, the energy needed to cleave the O–Si bond was 55.4 kcal mol^{−1}, whereas only 1.8 kcal mol^{−1} are required to break the Ar–Cl bond. Similar results were obtained in the case of **2** (26.6 kcal mol^{−1} for the O–Si bond and only 1.2 kcal mol^{−1} for the Ar–Cl bond). On the other hand, the cleavage of the N–Si and the Ar–Cl bonds in **4** has been evaluated to need 70.1 kcal mol^{−1} and 10.9 kcal mol^{−1}, respectively. Interestingly, in the case of compound **5**, the two cleavages require a comparable energy, with the cleavage of the S–Si bond slightly favored (for 2.5 kcal mol^{−1}) with respect to the Ar–Cl bond (12.1 kcal mol^{−1} vs 14.7 kcal mol^{−1}). As reported in Table 5, the Si–Si bond was found already cleaved in **36**, thus preventing any Ar–Cl cleavage. Finally, in **3BzS**, the cleavage of the Ar–Cl bond is favorable with respect to the CH₂–Si bond cleavage (11.1 kcal mol^{−1} vs 30.9 kcal mol^{−1}). As apparent in Fig. 4, only compounds **1–4** were suitable candidates for the initial formation of a triplet phenyl cation required for the diradical generation.

2.4 Isodesmic reactions

Isodesmic reactions were carried out to calculate the energy difference between the singlet and the triplet cations possibly

Fig. 3 Optimized geometry of the T_1 of aryl chlorides **1–6** and **BzS**

involved in the photochemistry of compounds **1–4**. For the sake of comparison, we likewise performed the calculations on compounds **1'** and **2'** (the para chloro isomers of compounds **1** and **2**, see also Supporting Information section). The results pointed out that the most stable state may depend on the silyl group used for the protection of the phenol.

Indeed, the singlet-state cation is slightly more stable for compound **1'** and the triplet is slightly more stable for compound **2'** ($0.28 \text{ kcal mol}^{-1}$ for the former and $0.30 \text{ kcal mol}^{-1}$ for the latter, Fig. 5). The situation completely changed when calculations are performed on both triplet and singlet cations **1⁺** and **2⁺**. In this case, the singlet states are by far

Table 5 Changes in the bond lengths of compounds **1–6** and **BzS** switching from S_0 to T_1 (SMD(MeOH)-PW6B95-D3/def2-SVP level of theory)

1 $R_1, R_2 = \text{Me}$ $R_3 = t\text{-Bu}$ 2 $R_1, R_2, R_3 = i\text{-Pr}$					
Bond	Length in S_0 [Å]	Length in T_1 [Å]	Bond	Length in S_0 [Å]	Length in T_1 [Å]
1			2		
C ₁ –Cl	1.74	1.82	C ₁ –Cl	1.74	1.82
C ₁ –C ₂	1.39	1.45	C ₁ –C ₂	1.39	1.47
C ₁ –C ₆	1.39	1.46	C ₁ –C ₆	1.39	1.45
C ₅ –O	1.34	1.34	C ₅ –O	1.34	1.34
O–Si	1.72	1.71	O–Si	1.72	1.72
3			4		
C ₁ –Cl	1.76	1.84	C ₁ –Cl	1.74	2.26
C ₁ –C ₂	1.39	1.41	C ₁ –C ₂	1.39	1.41
C ₁ –C ₆	1.39	1.47	C ₁ –C ₆	1.39	1.41
C ₅ –N	1.39	1.37	C ₄ –N	1.34	1.36
N–Si	1.79	1.81	N–Si	1.79	1.82
5			6		
C ₁ –Cl	1.74	1.72	C ₁ –Cl	1.74	1.74
C ₃ –C ₄	1.40	1.47	C ₃ –C ₄	1.39	1.39
C ₄ –C ₅	1.40	1.48	C ₄ –C ₅	1.39	1.39
C ₄ –S	1.78	1.75	C ₄ –Si	1.89	1.87
S–Si	2.20	2.21	Si–Si	2.34	Broken
BzS					
C ₁ –Cl	1.74	1.84			
C ₁ –C ₂	1.39	1.46			
C ₁ –C ₆	1.39	1.46			
C ₄ –CH ₂	1.49	1.47			
CH ₂ –Si	1.90	1.92			

more stable, and the energy difference is 6.40 kcal mol^{−1} and 6.72 kcal mol^{−1}, respectively. On the contrary, the presence, in compound **4** of the 1,2,5-azadisilolidine substituent in para position with respect to the chlorine atom, exerted a strong stabilization on the triplet state of the corresponding cation **³4⁺** (the energy gap is ca. 11.22 kcal mol^{−1}). The singlet cation became again the most stable one in **BzS⁺** (for ca. 4 kcal mol^{−1}).

2.5 Cleavage of the X–Si bond from cations **³1⁺**, **³2⁺**, **³4⁺** and **³BzS⁺**

The feasibility of the X–Si cleavage from triplet phenyl cations **³1⁺**, **³2⁺**, **³4⁺** leading to the desired diradical was finally investigated. These scans were conducted by stretching the X–Si bond in the already optimized triplet cation. We decided to approximate the point at which the bond was considered broken when a discontinuity was found. Such discontinuities could arise from interactions of the Si atom with the ring or larger geometry changes, which are possibly

Fig. 4 Ar–Cl and Si–X bond dissociation energies in **31**, **32**, **34**, **35** and **3BzS**. Energies are reported as the differences between the value obtained at the chosen X–Si or Ar–Cl length and the energy at the

equilibrium geometry taken as reference, using the SMD(MeOH)-PW6B95D3/def2-SVP level of theory

unrealistic in a more complex matrix like the one represented by a solution.

The energy needed to cleave the O–Si bond in $^3\mathbf{1}^+$ is $\Delta G = 44.8 \text{ kcal mol}^{-1}$ (similar to that required to break the same bond in $^3\mathbf{1}^{'+}$, $\Delta G = 44.4 \text{ kcal mol}^{-1}$ Fig. 6a). In compound $^3\mathbf{2}^+$, 43.4 kcal mol^{-1} are needed to break the O–Si bond (compare 44.0 kcal mol^{-1} for the isomer $^3\mathbf{2}'^+$). These graphs highlight how the substituent group on the silicon atom and the cation position have a marginal effect on the energy needed to photocleave the O–Si bond. The detachment of the N–Si bond in cation $^3\mathbf{4}^+$ is even more troublesome since it requires 58.1 kcal mol^{-1} (Fig. 6b). Finally, the energy needed to break the CH_2 –Si bond in $^3\mathbf{BzS}^+$ is only 17.9 kcal mol^{-1} , the lowest value found in all of the compounds analyzed in the present work (Fig. 6c).

3 Discussion

The photochemistry of compounds **1–6** can be summarized in Scheme 3. Each compound tested could in principle be suitable to undergo photoheterolytic cleavage of the Ar–Cl bond in $^3\mathbf{1}^+$ – $^3\mathbf{6}^+$, since the XSiR_3 group has a sufficient electron-donating ability to stabilize the corresponding triplet phenyl cation (path a) [36–39]. Sensitization experiments in the presence of acetone as triplet sensitizer did not affect somehow the distribution of products (see Tables 3, 4) pointing to the involvement of an excited triplet state in the reaction. Quite surprisingly, however, the detachment of

the chloride anion took place efficiently only in silyl ethers **1,2** and aniline **4**. The pronounced photostability of *meta*-chloro anilines previously reported [31] was also confirmed herein for derivative **3**. Nonetheless, the resulting cations $^3\mathbf{1}^+$, $^3\mathbf{2}^+$ and $^3\mathbf{4}^+$ failed to undergo loss of the R_3Si^+ cation and formation of the desired (hetero)diradical (path d), due to the high-energy barrier in the O–Si or N–Si cleavage. Thus, the intermediates due to its dual aryl radical cation/radical nature, showed a typical reactivity of a triplet phenyl cation (Fig. 5) namely hydrogen atom abstraction from the solvent (e.g., methanol or acetonitrile, path b') to give hydrodechlorinated derivatives **1a–3a** [34, 35]. However, in the case of $^3\mathbf{1}^+$, $^3\mathbf{2}^+$, intersystem crossing (ISC, path c) to the more stable singlet cations (Fig. 5) is also feasible [85, 86]; the addition of a nucleophilic solvent then yielded ethers **1b** and **2b** (path c' and Table 1) avoiding any desilylation pathways to σ,π -diradicals (path e).

Moving to silylated thiophenol **5**, makes the photohomolysis of the S–Si bond and subsequent formation of chlorinated compounds **5a,b** from the resulting thiyl radical intermediate, the only path observed (path f, Table 3). The presence of a labile Si–Si bond likewise diverts completely the photochemistry of aryl chloride **6**, in comparison with the photoheterolytic cleavage of the Ar–Cl bond observed in (4-chlorophenyl)trimethylsilane [87]. The photochemistry of compound **6** can be in part explained by the typical behavior of disubstituted phenyl pentamethyldisilane upon excitation in polar solvents. In fact, when the aromatic ring of the disilane is substituted with a more photolabile moiety, as the

Fig. 5 Relative energy of the spin states of isomeric phenyl cations deriving from compounds **1**, **2**, **4** and **BzS** using the SMD(MeOH)-PW6B95D3/def2-SVP level of theory. $^1\text{C}_6\text{H}_5^+$ was chosen as zero

OCOMe group in (2-acetoxyphenyl)pentamethyldisilane, the disilane structure remains untouched after the reaction [88]. However, other substituted phenyldisilanes showed a varied photoreactivity including the formation of a silylene intermediate or the nucleophilic attack of a protic solvent (e.g., an alcohol) at the β -silicon atom or the photohomolytic cleavage of the Si–Si bond [89–93]. In the latter examples, the fate of the reaction depends on the structure of the disilane in combination with the media used albeit the Si–Si bond was always photocleaved. In the case of compound **6**, a photocleavage of the Si–Si bond [92] from the triplet state can be envisaged as supported by the photosensitization experiments in the presence of acetone (Table 4).

Analyzing compounds **1–6**, we were then intrigued to find out why the formation of a diradical was not feasible.

We decided to make a comparison with (4-chlorobenzyl)trimethylsilane **BzS** taken as a model which has proven in recent literature to be a promising source of diradical, in particular of α,n -DHT depending on the position on the aromatic core of the chlorine atom [36, 43].

The observed difference arises from the geometrical arrangement of the benzylic substituent in the different molecules that may have access to the aryl cation reactivity (see Fig. 3). Indeed **BzS** is the only compound where the X–Si group is perpendicular to the aryl ring (Fig. 7a), allowing a positive interaction between the radical cation delocalized on the π system and the X–Si bond, favoring the detachment contrary to what calculated when X = O, N (see structures described in Fig. 7b, c).

Fig. 6 Barrier for the detachment of the silyl group from the different compounds analyzed. Energies are reported as the differences between the value obtained at the chosen X–Si length and the energy

at equilibrium of the system, taken as reference using SMD(MeOH)-PW6B95D3/def2-SVP level of theory

Scheme 3 Proposed mechanistic pathways in the photochemistry of compounds **1–6**

The NBO analysis [94] offers quantitative support to this hypothesis (see Sect. 3.4 in the Supporting Information). Among the triplet cations studied, **³BzS⁺** is the only compound where it is possible to find a strong $\pi_{CC} \rightarrow \sigma_{XSi}$ interaction (20 kcal mol^{−1}) between the ring and the benzylic X–Si σ bond. In all the other cases, any $\pi_{CC} \rightarrow \sigma_{XSi}$ was below the threshold limit of 0.05 kcal mol^{−1} and consequently considered to be negligible. Moreover, if we compare the X–Si bond lengths in compounds **1**, **2**, **3**, **4** and **BzS** in S₀ and in the corresponding triplet cations (Table S9), in the latter substrate, we have the more pronounced difference ($\Delta L = 1.4 \text{ \AA}$) thus confirming our hypothesis.

4 Conclusion

A competition between two photo-induced processes, namely Ar–Cl heterolysis and heteroatom–Si homolytic cleavage, was observed to take place from the triplet state of different chloroaromatics investigated as potential diradical precursors. Indeed, triplet aryl cations are efficiently generated from chlorinated silyl phenols and anilines, but the absence of an interaction between the radical cation delocalized on the π system and the O–Si or the N–Si σ -bond, preclude the formation of the desired heterodiradical. On the contrary, in silylated thiophenols and arylsilanes, the lability of the X–Si bond makes its cleavage the only observed phenomena. Such results further points out how rare is the formation of these heterodiradicals apart from the cycloaromatization approach.

5 Experimental section

5.1 General

¹H and ¹³C NMR spectra were recorded on a 300 e 75 MHz spectrometer, respectively. The attributions were based on ¹H and ¹³C NMR experiments; chemical shifts are reported in ppm downfield from TMS. HPLC analysis were carried out by means of a Jasco LC-NET II/ ADC, equipped with a Supelco Discovery C20 HPLC Column (25 cm × 4.6 mm, 5 μ m particle size). Solvents used for the elution process were H₂O and MeCN, and a flow rate of 0.7 mL min^{−1} was used. The UV detector was set to operate at 230 nm and 240 nm. UV–Vis analyses were carried out using UV–VIS Jasco V-550 spectrometer. Fluorescence spectra were recorded using Perkin Elmer precisely LS 55 spectrofluorometer. GC analyses were performed using a HP SERIES 5890 II equipped with a fire ion detector (FID, temperature 350 °C). Analytes were separated using a Restek Rtx-5MS (30 m × 0.25 mm × 0.25 μ m) capillary column with nitrogen as a carrier gas at 1 mL/min. The injection in the GC system was performed in split mode, and the injector temperature was 250 °C. The GC oven temperature was held at 80 °C for 2 min, increased to 250 °C by a temperature ramp of 10 °C min^{−1}, and held for 10 min. The synthesis of compound **5** was performed as previously reported [95] and the spectroscopic data of the silane were in accordance with literature data [95].

Fig. 7 Optimized geometry for **a** $^3\text{BzS}^+$, **b** $^3\text{2}^+$ and **c** $^3\text{4}^+$

5.2 Photochemical experiments

Irradiations were performed at room temperature using nitrogen-purged solutions of **1–6** (0.01 M) in quartz tubes in a multilamp reactor fitted with 8×15 W phosphor-coated Hg lamps (maximum of emission at 310 nm) or with 8×15 W low-pressure Hg lamps (maximum of emission at 254 nm). Quantum yields were measured at 254 nm (1 Hg lamp, 15 W). Solvents of HPLC purity were employed. The reaction course was followed by both GC and HPLC analyses. Photophysical analyses of substrates were carried out using quartz cuvette High Precision Cell with optical length of 10 mm and using Spectra Manager as software. Photophysical analyses were carried out using a methanolic solution of 4-chloroanisole as the standard.

5.3 General procedure for the synthesis of compounds **1**, **1a** and **1b**.

Compounds **1**, **1a** and **1b** have been prepared by adapting a known procedure starting from the corresponding phenols [96]. A solution of the chosen phenol (4 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1 equiv) and *tert*-butylchlorodimethylsilane (1.15 equiv) in benzene (4 mL) was stirred overnight at room temperature. The solvent was then evaporated and the resulting mixture purified by column chromatography (eluant: cyclohexane:acetate mixture).

5.3.1 *tert*-Butyl(3-chlorophenoxy)dimethylsilane (**1**)

Starting from 0.50 g (4 mmol) of 3-chlorophenol, 0.7 g (4.6 mmol) of *tert*-butylchlorodimethylsilane and 0.6 mL (4 mmol) of DBU in 4 mL of benzene. Purification was carried out by silica gel chromatographic column (eluant: cyclohexane/ethyl acetate 99:1) and afforded 0.44 g of **1** (colorless oil, 50% yield). Spectroscopic data are in accordance with the literature [97]. ^1H NMR (300 MHz, CD_3COCD_3) δ 7.28 (t, $J=8.1$ Hz, 1H), 7.02 (ddd, $J=8.0$, 2.1, 0.9 Hz, 1H), 6.97–6.82 (m, 2H), 1.01 (s, 10H), 0.25 (s,

6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_3COCD_3) δ 157.9, 135.4, 131.9 (CH), 122.8 (CH), 121.5 (CH), 119.9 (CH), 31.0, 30.7 (CH₃), –4.1 (CH₃); IR (neat) ν cm^{-1} : 2958, 2901, 1568, 1480, 975.

5.3.2 *tert*-Butyldimethyl(phenoxy)silane (**1a**)

Starting from 0.50 g (5.3 mmol) of phenol, 0.7 mL (4.6 mmol) of *tert*-butylchlorodimethylsilane and 0.6 mL (4 mmol) of DBU in 4 mL of benzene. Purification was carried out by silica gel chromatographic column (eluant: cyclohexane/ethyl acetate 99:1) and afforded 0.21 g of **1a** (colorless oil, 48% yield). Spectroscopic data of compound **1a** were in accordance with literature data [98].

5.3.3 *tert*-Butyl(3-methoxyphenoxy)dimethylsilane (**1b**)

Starting from 0.50 g (3.5 mmol) of 3-methoxyphenol, 0.7 mL (4.6 mmol) of *tert*-butylchlorodimethylsilane and 0.6 mL (4 mmol) of DBU in 4 mL of benzene. Purification was carried out by silica gel chromatographic column (eluant: cyclohexane/ethyl acetate 99:1) and afforded 0.19 g of **1b** (colorless oil, 50% yield). Spectroscopic data of compound **1b** were in accordance with literature data [99].

5.4 General procedure for the synthesis of compounds **2**, **2a** and **2b**

Compounds **2**, **2a** and **2b** were prepared by adapting a procedure described for the synthesis of triisopropyl(2,3,6-trifluorophenoxy)silane [100]. The chosen phenol (5 mmol) and imidazole (1 equiv) were dissolved in DMF (2.5 mL) and triisopropylsilyl chloride (1 equiv) was added in small portions. The resulting mixture was stirred overnight, poured into water (50 mL) and extracted with dichloromethane (3×20 mL). The organic phases

were reunited, washed with water (2×20 mL), the solvent evaporated and the crude residue purified by column chromatography (eluant: cyclohexane in the presence of TEA 1%_{v/v}).

5.4.1 (3-Chlorophenoxy)triisopropylsilane (2)

From 0.60 g (5 mmol) of 3-chlorophenol, 0.96 g (5 mmol) of triisopropylsilyl chloride and 0.34 g (5 mmol) of imidazole in 2.5 mL of DMF. Purification by column chromatography (eluant: cyclohexane in the presence of TEA 1%_{v/v}) afforded 0.804 g of **2** (colorless oil, 80% yield). Spectroscopic data of compound **2** were in accordance with literature data [100].

5.4.2 Triisopropyl(phenoxy)silane (2a)

From 0.50 g (5 mmol) of phenol, 0.96 g (5 mmol) of triisopropylsilyl chloride, 0.34 g (5 mmol) of imidazole and 2.5 mL of DMF. Purification by column chromatography (eluant: cyclohexane in the presence of TEA 1%_{v/v}) afforded 0.92 g of **2a** (colorless oil, 78% yield). Spectroscopic data of compound **2a** were in accordance with literature data [101].

5.4.3 Triisopropyl(3-methoxyphenoxy)silane (2b)

From 0.70 g (5 mmol) of 3-methoxyphenol, 0.96 g (5 mmol) of triisopropylsilyl chloride, 0.34 g (5 mmol) of imidazole and 2.5 mL of DMF. Purification by column chromatography (eluant: cyclohexane in the presence of TEA 1%_{v/v}) gave 1.1 g of **2b** (colorless oil, 77% yield). ¹H NMR (300 MHz, CD₃COCD₃) δ 7.15 (t, *J* = 8.1 Hz, 1H), 6.68–6.28 (m, 3H), 3.77 (s, 3H), 1.39–1.22 (m, 3H), 1.13 (d, *J* = 7.0 Hz, 18H); ¹³C{¹H} NMR (75 MHz, CD₃COCD₃) δ 161.5, 156.2, 130.6 (CH), 115.0 (CH), 108.4 (CH), 55.8 (CH₃), 18.6 (CH₃), 16.7 (CH); IR (neat) ν cm⁻¹: 2944, 2867, 1599, 1491, 883. Anal. Calcd. For C₁₇H₃₀OSi: C, 73.31; H, 10.86; Found: C, 73.2; H, 10.7.

5.5 General procedure for the synthesis of **3**, **4**, **4a**, **5** and **6**

Compounds **3**, **4** and **4a** have been prepared by adapting a known procedure [102]. A stirred solution of the chosen aniline (10 mmol) and triethylamine (TEA, 2.05 equiv) in dichloromethane was cooled at 0 °C, then 1,2-bis(chlorodimethylsilyl)ethane (1 equiv) was added in small portions. The resulting solution was stirred overnight, then 100 mL of hexane was added, and the solid residue was eliminated by filtration. The resulting solution was thus evaporated, and the crude residue purified by aluminum oxide column chromatography (eluant: hexane/DCM mixture in the presence of TEA 0.5% v/v).

5.5.1 1-(3-Chlorophenyl)-2,2,5,5-tetramethyl-1,2,5-azadisilolidine (**3**)

From 1.28 g (10 mmol) of 3-chloroaniline, 3.0 mL (21 mmol) of TEA in DCM (20 mL) and 2.0 g (10 mmol) of 1,2-bis(chlorodimethylsilyl)ethane. Purification by aluminum oxide column chromatography (eluant: hexane/DCM 5:1 mixture in the presence of TEA 0.5% v/v) afforded 0.304 g of **3** (colorless oil, 11% yield). ¹H NMR (300 MHz, CD₃COCD₃) δ 7.25–6.85 (m, 4H), 1.10 (s, 4H), 0.25 (s, 12H); ¹³C{¹H} NMR (75 MHz, CD₃COCD₃) δ 148.1, 135.1, 130.9 (CH), 122.3 (CH), 116.7 (CH), 114.4 (CH), 30.7 (CH), 22.9 (CH₂), 0.4 (CH₃); IR (neat) ν cm⁻¹: 2947, 2923, 2972, 1584, 1498, 1253, 936, 773. Anal. Calcd. For C₁₂H₂₀ClNSi₂: C, 53.40; H, 7.47; N, 5.19 Found: C, 53.2; H, 7.6; N, 5.0.

5.5.2 1-(4-Chlorophenyl)-2,2,5,5-tetramethyl-1,2,5-azadisilolidine (**4**)

From 1.28 g (10 mmol) of 4-chloroaniline, 3 mL (21 mmol) of TEA in DCM (20 mL) and 2 g (10 mmol) of 1,2-bis(chlorodimethylsilyl)ethane. Purification by aluminum oxide column chromatography (eluant: hexane/DCM 5:1 mixture in the presence of TEA 0.5% v/v) afforded 0.82 g of **4** (pale yellow oil, 30% yield). ¹H NMR (300 MHz, CD₃COCD₃) δ 7.56–6.61 (dd, *J* = 9 Hz, 4H), 0.91 (s, 4H), 0.22 (s, 12H); ¹³C{¹H} NMR (75 MHz, CD₃COCD₃) δ 147.6, 130.0, 126.5 (CH), 126.3 (CH), 125.4 (CH), 123.7 (CH), 32.7 (CH), 23.6 (CH₂), 0.3 (CH₃); IR (neat) ν cm⁻¹: 2954, 2919, 2892, 1592, 1489, 1269, 922, 783. Anal. Calcd. For C₁₂H₂₀ClNSi₂: C, 53.40; H, 7.47; N, 5.19 Found: C, 53.1; H, 7.5; N, 4.9.

5.5.3 2,2,5,5-Tetramethyl-1-phenyl-1,2,5-azadisilolidine (**4a**)

From 0.9 mL (10 mmol) of freshly distilled aniline, 3 mL (21 mmol) of TEA in 20 mL di DCM and 2 g (10 mmol) of 1,2-bis(chlorodimethylsilyl)ethane. Purification by aluminum oxide column chromatography (eluant: hexane/DCM 5:1 mixture in the presence of TEA 0.5% v/v) afforded 0.952 g of **4a** (pale yellow oil, 40% yield). ¹H NMR (300 MHz, CD₃COCD₃) δ 7.62–6.45 (m, 5H), 0.90 (s, 4H), 0.21 (s, 12H); ¹³C{¹H} NMR (75 MHz, CD₃COCD₃) δ 130.1, 125.0 (CH), 121.9 (CH), 120.3 (CH), 31.0 (CH), 29.7 (CH₂), 0.5 (CH₃); IR (neat) ν cm⁻¹: 2954, 2917, 2891, 1596, 1498, 1484, 1253, 927, 783. Anal. Calcd. For C₁₂H₂₁NSi₂: C, 61.21; H, 8.99; N, 5.95; Found: C, 61.2; H, 9.0; N, 6.0.

5.5.4 Synthesis of ((4-chlorophenyl)thio)triisopropylsilane (5)

The synthesis of **5** was performed by adapting a known procedure [95]. A solution of 4-chlorothiophenol (1.21 g, 8.40 mmol) in dry THF was kept under vigorous stirring, then 2 mL of TEA (14.5 mmol) was added dropwise. The resulting mixture was stirred for ten minutes, then 3 mL of TIPS-Cl (14.0 mmol) was added and the reaction was stirred overnight. The slurry was filtered and the filtrate was washed with saturated NaHCO₃ solution. The aqueous layer was extracted with hexane (10 mL × 3) and the combined organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by activated alumina gel as stationary phase (cyclohexane as the eluant) to give 2.39 g of **5** (colorless oil, yield: 95%). Spectroscopic data were in accordance with literature data [95].

5.5.5 Synthesis of 1-(4-chlorophenyl)-1,1,2,2,2-pentamethylidisilane (6)

The synthesis of **6** was performed by adapting a procedure reported in the literature [103]. A solution of 1-bromo-4-chlorobenzene (2.05 g, 10 mmol) in anhydrous THF was cooled to −78 °C under nitrogen atmosphere. *n*-BuLi (1M in *n*-Hexane, 12 mL) was added dropwise, and the resulting mixture was allowed to reach room temperature. 1-Chloro-1,1,2,2,2-pentamethylidisilane (2.40 mL 12.4 mmol) was added dropwise and the resulting solution was stirred overnight. Diethyl ether (20 mL) was then added, and the mixture was washed with brine (2 × 20 mL) and extracted with Et₂O (3 × 20 mL). The organic solution was dried on Na₂SO₄ and the solvent evaporated under reduced pressure. Purification by column chromatography (eluant cyclohexane/DCM 9:1 mixture) afforded 2.2 g of **5** (colorless oil, 90% yield). ¹H NMR (300 MHz, CD₃COCD₃) δ 7.52–7.49 (d, 2H), 7.41–7.38 (d, 2H), 0.37 (s, 6H), 0.08 (s, 9H); ¹³C{¹H} NMR (75 MHz, CD₃COCD₃) δ 139.4, 136.6 (CH), 136.2, 135.0 (CH), 129.09 (CH), 129.04 (CH), 3.56 (CH₃), 1.85 (CH₃). Anal. Calcd. For C₁₁H₁₉ClSi₂ C, 54.39; H, 7.88; Found: C, 54.4; H, 7.9.

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Declarations

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