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Influence of structural features of tri-functionalized aryl phosphates on the outcome of the $S_{RN}1$ process with stannyl anions: a DFT study†

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Under irradiation, 1,3-bis(diethoxyphosphoryloxy)-4-chlorobenzene (**2**), 1,4-bis(diethoxyphosphoryloxy)-3-chlorobenzene (**3**) and 1,3-bis(diethoxyphosphoryloxy)-5-chlorobenzene (**4**) react with trimethyltinsodium (**1**) in liquid ammonia giving entirely different distribution of stannylated products. These differences are explained through theoretical DFT studies. Experimental evidence for the involvement of an $S_{RN}1$ mechanism was obtained.

Introduction

The preparation of organotin compounds and their application as intermediates have become a very important aspect in organic chemistry.[1] For example, palladium-catalyzed reactions involving aryltin compounds have found wide application in the synthesis of aromatic and heterocyclic compounds.[2] In connection with the synthetic importance of these reactions, our group has been involved in searching new synthetic routes to organostannanes by the $S_{RN}1$ mechanism.[3]

Aromatic nucleophilic substitution *via* the $S_{RN}1$ mechanism enables the substitution of appropriate nucleofuges on unactivated aromatic systems with suitable nucleophiles.[4] The proposed mechanism is a chain process, as can be seen from Scheme 1 for a starting substrate supporting only one leaving group (ArX). In the initiation step there is an electron transfer (ET) from the nucleophile to the starting substrate (eqn (1)); if this ET is not spontaneous, it could be induced by UV light.[4] The key species of the process, $Ar^{\bullet}$, obtained by the reductive cleavage of $ArX^{\bullet-}$ (eqn (2)), combines with the nucleophile to give $ArNu^{\bullet-}$ (eqn (3)), which in turn reduces the starting aromatic substrate. The radical anion $ArX^{\bullet-}$ is regenerated according to eqn (4). It should be noted that the coupling with the nucleophile is not the only reaction that aryl radicals can undergo: hydrogen atom transfer from the solvent is one of the most important side reactions (eqn (5)). This competitive reaction is prevented by using liquid ammonia as solvent, which is a poor hydrogen atom donor.[4]

$$ArX + Nu^- \longrightarrow (ArX)^{\cdot-} + Nu^{\cdot} \quad (1)$$

$$(ArX)^{\cdot-} \longrightarrow Ar^{\cdot} + X^- \quad (2)$$

$$Ar^{\cdot} + Nu^- \longrightarrow (ArNu)^{\cdot-} \quad (3)$$

$$(ArNu)^{\cdot-} + ArX \longrightarrow ArNu + (ArX)^{\cdot-} \quad (4)$$

$$Ar^{\cdot} + SH \longrightarrow ArH + S^{\cdot} \quad (5)$$

Scheme 1 General $S_{RN}1$ mechanism.

We have demonstrated that substrates containing three leaving groups, such as 1,3,5-tris(diethoxyphosphoryloxy)benzene[3d] and 1,3-bis(diethoxyphosphoryloxy)-5-chlorobenzene (**4**),[5] react with **1** in liquid ammonia under irradiation yielding, by $S_{RN}1$, 1,3,5-tris(trimethylstannyl)benzene (**6**) together with 1,3-bis-(trimethylstannyl)benzene (**7**) in 92 : 8 and 88 : 12 relative percentages (GC), respectively.

Also, Córsico and Rossi have reported the synthesis of **6** by the reaction of 1,3,5-trichlorobenzene with an excess of **1** in liquid ammonia under irradiation.[6] So, both diethoxyphosphoryloxy- (DEP) and/or chloro 1,3,5-trisubstituted benzenes could be excellent starting materials for the synthesis of tris-tannylated products by an $S_{RN}1$ mechanism.

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† Electronic supplementary information (ESI) available: *xyz* coordinates and total energies in atomic units for all of the calculated structures. See DOI: 10.1039/c3nj40814k

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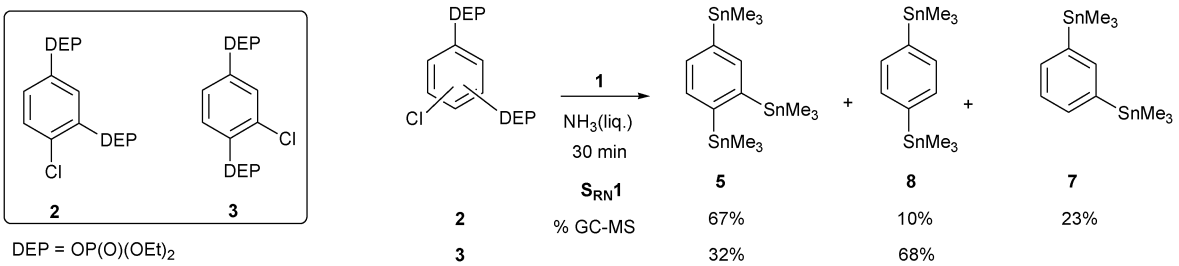
On the other hand, in previous works we have obtained 1,2-, 1,3- and 1,4-bis(trimethylstannyl)benzene in good to excellent yields, by $S_{RN}1$, starting from DEP and/or chloro disubstituted aryl compounds.[3b,e] It should be mentioned that, although tristannylated substrates would be interesting intermediates in organic synthesis, in addition to the above mentioned synthetic routes there are few and relatively limited methods available for the synthesis of such compounds, most of them using haloarenes as starting materials.[7] These antecedents prompted us to study the scope of the $S_{RN}1$ mechanism for the tristannylation of aromatic rings by the reaction of aryl phosphates, supporting three nucleofugal groups at different relative positions, with **1** in liquid ammonia as solvent. Moreover, with the purpose of explaining experimental results, a theoretical analysis was performed using DFT methods and the B3LYP functional.

Results and discussion

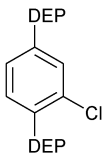
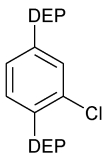
In order to synthesize 1,2,4-tris(trimethylstannyl)benzene (**5**) we used, as starting substrates, 1,3-bis(diethoxyphosphoryl)oxy-4-chlorobenzene (**2**) and 1,4-bis(diethoxyphosphoryl)oxy-3-chlorobenzene (**3**). Noticeably, as shown in Scheme 2, irradiation of **2** and **3** in the presence of **1** (1/3.3 ratio), in liquid ammonia, led to entirely different products distribution. With the aim of explaining these unexpected results we carried out a series of reactions under different conditions (Table 1).

As can be observed, when the reactions of **2** and **3** with **1** were quenched at short reaction time (entries 1 and 7) no starting substrate was detected and complex mixtures were obtained. The faster fragmentation of chlorine is supported by the detection of compounds **10** and **9**, probably generated by hydrogen atom transfer from the solvent to the first Ar radical

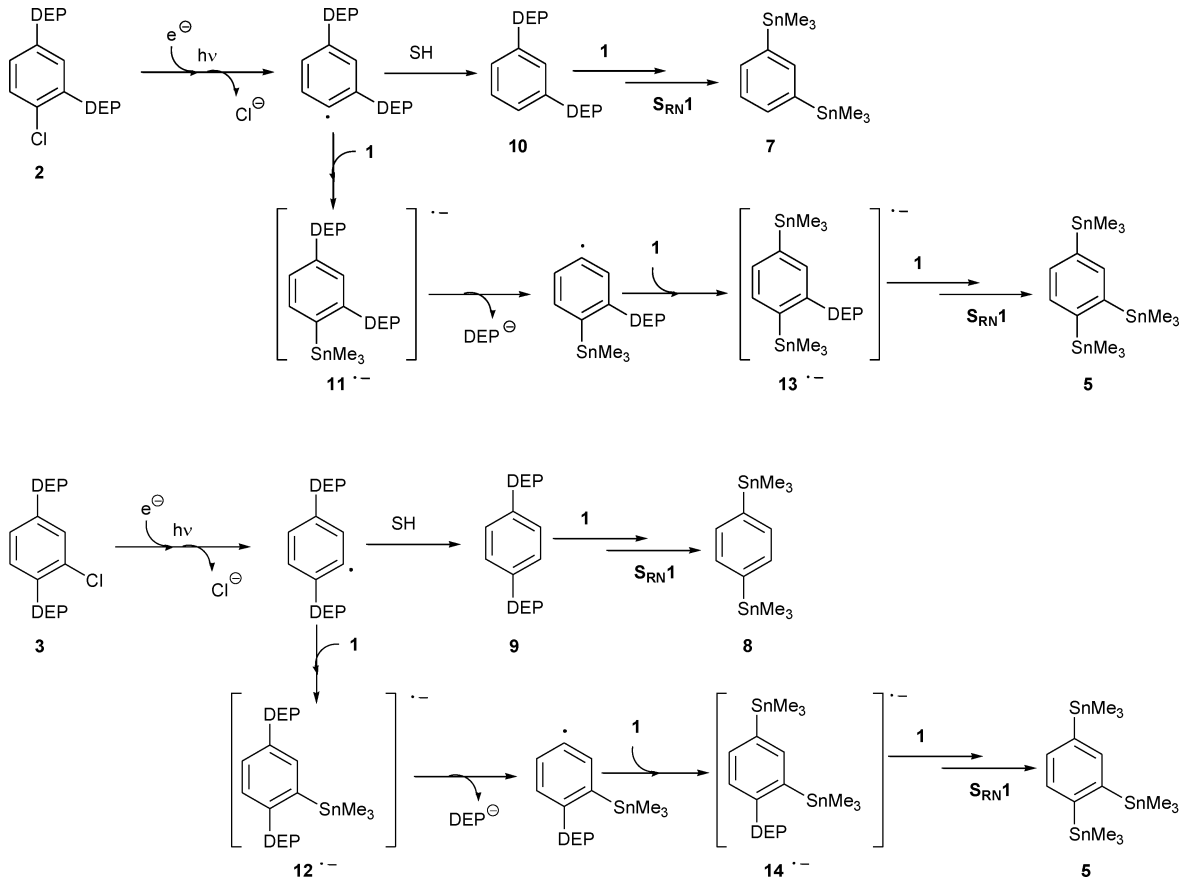


Scheme 2

Table 1 Reactions of **2** and **3** with Me_3SnNa in liquid ammonia[a]

Substrate	Entry	Reaction conditions	Relative percentage **5**	**8**	**7**	**13**	**14**	**10**	**9**	**2**	**3**
 **2**	1	5 min/$h\nu$	18	6	7	44		18		—	
	2	30 min/$h\nu$	**67**	10	23	Detected		—		—	
	3	30 min/dark	—	—	—	Detected		68		32	
	4[b]	30 min/dark 20% *p*-DNB	—	—	—	—		1		40	
	5[c,d,e]	10 min/Na(0)	14	15	62	—		—		—	
	6[d]	6 h/$h\nu$	50	15	35	—		—		—	
 **3**	7	5 min/$h\nu$	22	44	—		7		17		—
	8	30 min/$h\nu$	32	**68**	—		—		—		—
	9	30 min/dark	—	—	—		—		100		—
	10[b]	30 min/dark 20% *p*-DNB	—	—	—		—		49		3
	11[c,d,f]	10 min/Na(0)	10	72	8		—		—		—
	12[d]	6 h/$h\nu$	25	75	Detected		—		—		—

[a] Reaction conditions: substrate (1.0 equiv.), trimethylstannylsodium (3.3 equiv.), in liquid ammonia as solvent unless otherwise stated. [b] Together with the hydrolyzed starting substrate. [c] Reaction conditions: substrate (1.0 equiv.), trimethylstannylsodium (12 equiv.), in liquid ammonia as solvent. [d] 1,2-Bis-trimethylstannylbenzene was detected. [e] Together with trimethylstannylbenzene (9%). [f] Together with trimethylstannylbenzene (10%).

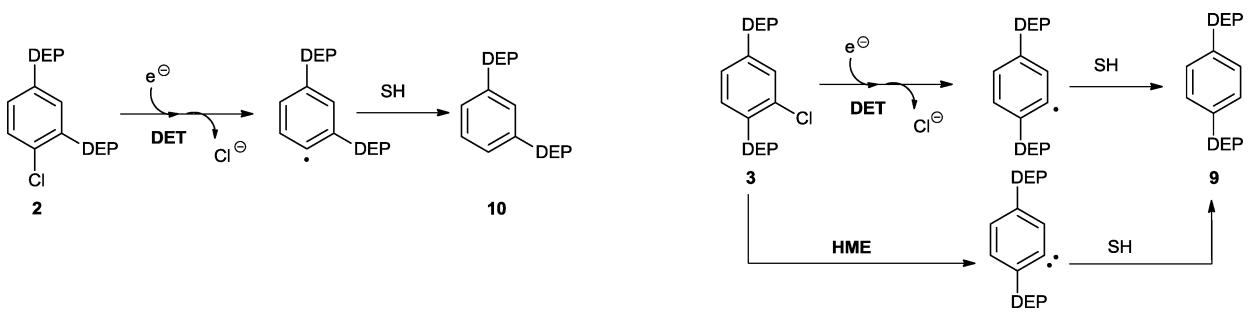


Scheme 3

intermediate formed from **2** and **3**, respectively. Then, these compounds react with **1** leading to the distannylated isomers **7** and **8**, respectively. These results are in agreement with the fact that chloro is a better leaving group than DEP towards **1** in liquid ammonia.[3b] On the other hand, formation of **13** and **14**[8] indicates that the fragmentation of the C–DEP bond, *ortho*-with respect to the stannyl moiety, does not compete efficiently for the generation of the second Ar radical. In Scheme 3 are sketched the different reaction steps proposed.

When the reactions were carried out for 30 min in the dark, meanwhile **2** afforded **10** together with substantial amounts of starting substrate, **3** yielded, exclusively, compound **9** and no starting substrate was detected (entries 3 and 9). Interestingly, the spontaneous ET initiation in the dark reaction was almost totally inhibited for **2** and partially (*ca.* 50%) inhibited for **3**, in the presence of *p*-dinitrobenzene (*p*-DNB, 20%), a well known inhibitor of $S_{RN}1$ reactions (entries 4 and 10). These results suggest that the cleavage of the C–Cl bond occurs through a spontaneous dissociative ET (DET) in substrate **2**, whereas it fragments through two different mechanisms in substrate **3**: by DET and by an ionic process named HME (halogen–metal exchange) followed by protonation of the intermediate anion (Scheme 4).

The existence of an HME mechanism competing with the $S_{RN}1$ process in substrate **3** would explain the generation of high yields of **8** in the photostimulated reactions (entries 7 and 8).



Scheme 4

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It should be mentioned that compound **5** together with different relationships of the three isomers of bis(trimethylstannyl)benzene were observed when we carried out the reaction of **1** with either **2** or **3** by solvated electron initiation (Na metal in liquid ammonia) (entries 5 and 11).

From the above mentioned results it is evident that, in the systems studied, the stannylated substitution products arise from the participation of the $S_{RN}1$ mechanism.

Besides the just explained observed differences in the reactivity of substrates **2** and **3**, we considered of interest to theoretically study their behavior under ET conditions.

Taking into account that the π* MO energy is not likely to be affected by the relative positions of the substituents on the ring, both substrates would have similar electron affinities making feasible their single-electron reduction. In order to obtain information on this matter, we theoretically study the neutrals and the radical anions of compounds **2′** and **3′**, the dimethoxyphosphoryloxy (DMP) analogs of **2** and **3**, respectively. Calculations were performed with the B3LYP DFT functional, the LACVP pseudopotential for Sn and the 6-31+G* basis set for C, H, O and P. The LUMO MOs of the neutral compounds have π symmetry and they are, as expected, similar in energy (−0.90 eV and −1.01 eV for **2′** and **3′**, respectively).[9]

Also, we considered of relevance to theoretically study the reactivity of $\mathbf{11}^{\bullet-}$ and $\mathbf{12}^{\bullet-}$ toward further substitutions through the ET process, taking into account that it could be responsible for the final product distribution.

In a previous theoretical study of the reactivity of 1- and 2-(diethoxyphosphoryl)oxy-1,3-cyclohexadienes towards **1**, under $S_{RN}1$ conditions, we have demonstrated that the spin distribution on the C-*ipso* to the leaving group changes with the position of the latter on the π system and can be taken as an indication of the easiness of dissociation of the corresponding radical anions.[3i]

Thereby, at first, we calculated in $\mathbf{11'}^{\bullet-}$ and $\mathbf{12'}^{\bullet-}$ (DMP analogs) the dissociation of the second DMP *para*- or *meta*- with respect to the stannyl moiety. No thermodynamic differences were found for the process, both being exothermic. Nevertheless, a thorough analysis of the SOMO OMs of these radical anions showed significant differences. Despite both having π symmetry, as can be seen in Fig. 1, $\mathbf{12'}^{\bullet-}$ has a C-*ipso* node at the *ortho* and *meta* C–DMP position with respect to the stannyl moiety. On the other hand, nodes are not observed at the reactive position of the radical anion of the stannyl derivative ($\mathbf{15}^{\bullet-}$) of compound **4** which, under the same reaction conditions, yielded mostly the tri-stannyl derivative.[5]

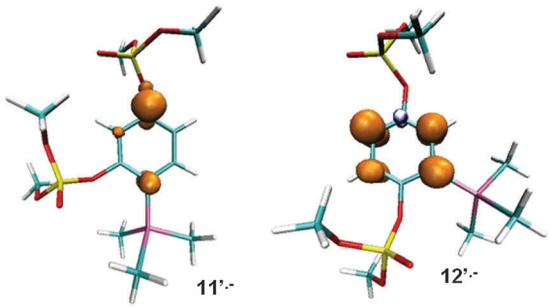


Fig. 2 Gas phase B3LYP/6-31+G* α and β spin density (orange and blue respectively)[10] of $\mathbf{11'}^{\bullet-}$ and $\mathbf{12'}^{\bullet-}$.

Besides, the unpaired spin distribution at the C-*ipso* to DMP in *meta* with respect to the stannyl moiety for $\mathbf{12'}^{\bullet-}$ is considerably lower than the spin density at the C-*ipso* to DMP in the *para*-position for $\mathbf{11'}^{\bullet-}$, that is, −0.06 and 0.65, respectively (Fig. 2).

On the other hand, the systematic inspection of the potential energy surface (PES) of both radical anions for the dissociation through an intramolecular DET (intra-DET) from the π system to the σ* C–OP bond shows, as expected from the low spin density at the C-*ipso* to its leaving groups, that radical anion $\mathbf{12'}^{\bullet-}$ dissociates at its *meta*-position with higher activation energy than $\mathbf{11'}^{\bullet-}$ at its *para*-position (3.2 kcal mol^{-1} *vs.* 0.14 kcal mol^{-1}), as can be seen from Fig. 3.

Through a subsequent sequence of coupling with **1** – fragmentation of the second C–DEP bond and a third coupling with **1**, substrates **2** and **3** afford radical anion $\mathbf{5}^{\bullet-}$.

We believe that these theoretical results support the experimental outcomes. This system is an interesting example of isomers whose radical anions dissociate with similar

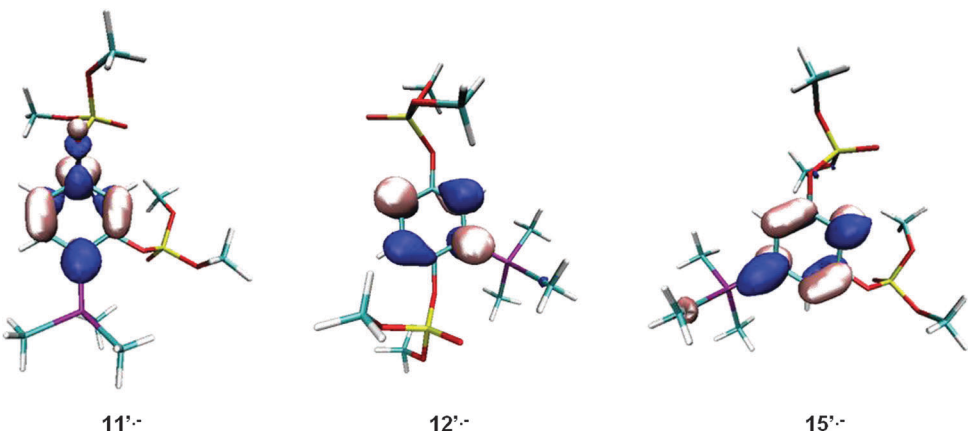


Fig. 1 SOMO OMs of $\mathbf{11'}^{\bullet-}$, $\mathbf{12'}^{\bullet-}$ and $\mathbf{15'}^{\bullet-}$.

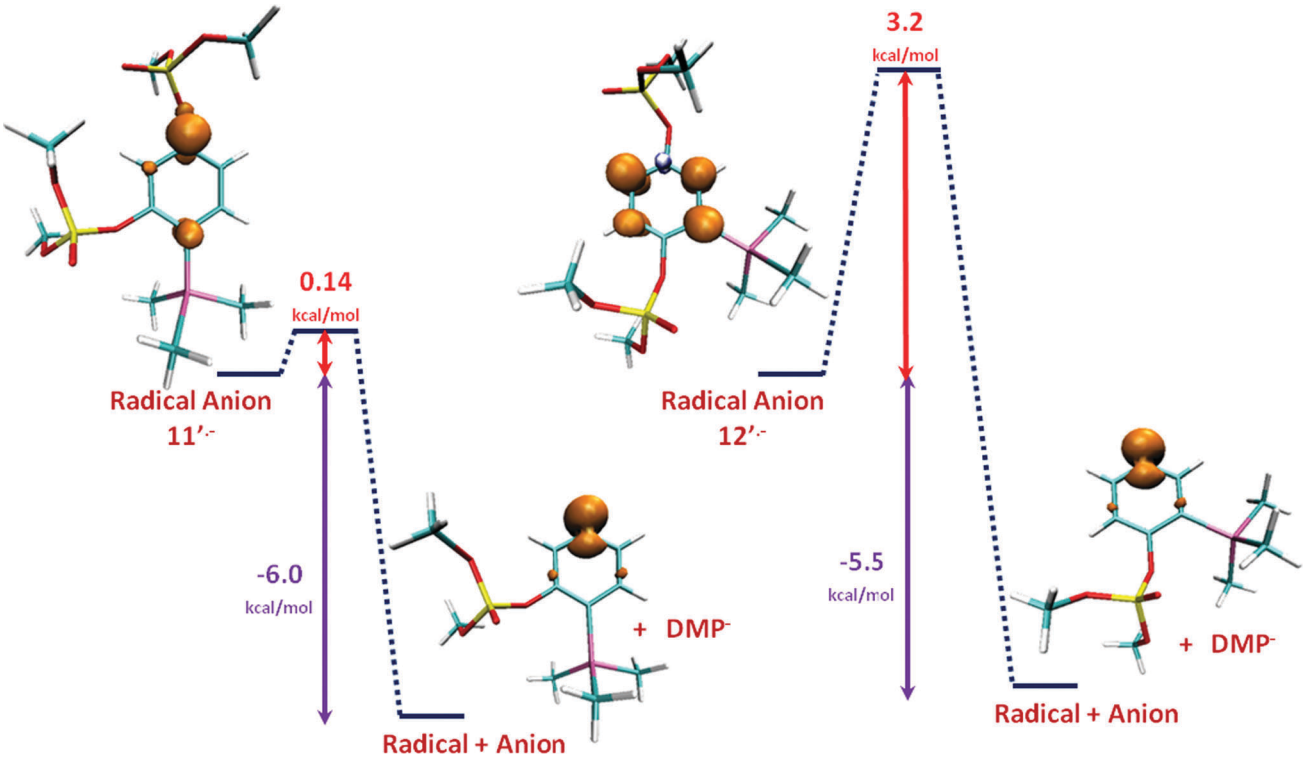


Fig. 3 PES for C–OP bond fragmentation of $\mathbf{11'}^{\bullet-}$ and $\mathbf{12'}^{\bullet-}$ (spin densities are shown).

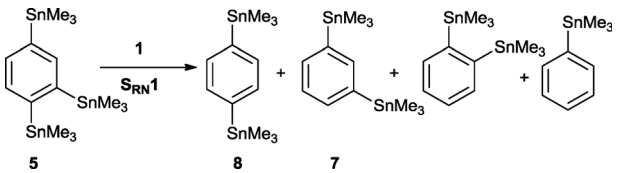
thermochemistry but different activation energy due to differences in their SOMO's composition.

From the above-mentioned results it is evident that the synthesis of compound **5** appears to be dependent on some structural features of the starting substrate. It should be noted that the undesired secondary products **7** and **8** derived from **2** and **3**, respectively, are formed by the most important side reaction in the $S_{RN}1$ process, that is, hydrogen atom transfer to the intermediate radicals and subsequent substitution. Moreover, the HME mechanism competes efficiently with the ET process in substrate **3**, affording higher amounts of **9** (see Scheme 4). This fact supports the experimental results: 1,4-bis(trimethylstannyl)benzene (**8**) is the main product in this reaction.

Also, it is essential to mention that $\mathbf{5}^{\bullet-}$ may suffer two competing reactions: ET to the starting substrate or generation of a radical (by expelling a trimethylstannyl anion) which ultimately leads to disubstitution by-products by hydrogen atom transfer from the solvent. This intra-DET cleavage corresponds to a radical anion process which becomes more important at long reaction times (Table 1, entries 6 and 12) and under strong electron donating conditions (Na in liquid ammonia) (Table 1, entries 5 and 11). Moreover, when substrate **5** was allowed to react with **1** under the studied reaction conditions, the starting substrate was observed together with a mixture of mono- and distannylated products (Scheme 5).

As can be seen from Fig. 4, the fragmentation pattern is in agreement with the unpaired spin distribution calculated for $\mathbf{5}^{\bullet-}$.

On the other hand, although $\mathbf{6}^{\bullet-}$ suffers fragmentation in the presence of solvated electrons, this reaction is not important and it is not a competitive process. This fact is also in agreement with the spin density distribution observed for this radical anion (Fig. 4).



Scheme 5

The reactivity of $\mathbf{15}^{\bullet-}$ toward further substitution (Fig. 1) together with the stability of **6** under ET conditions (Fig. 4) explains the efficient synthesis of 1,3,5-tristannylbenzene

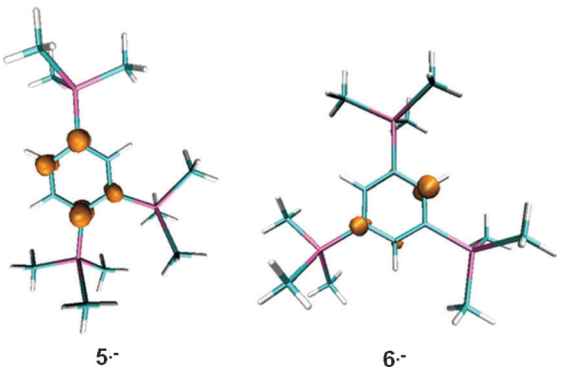


Fig. 4 Gas phase B3LYP/6-31+G*/LACVP (Sn) spin density (orange) of $\mathbf{5}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$.

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through an $S_{RN}1$ process, previously reported by Córsico and Rossi[6] and Chopa *et al.*[3d]

Conclusions

The reaction of Me_3SnNa (**1**) with isomeric aryl chloro phosphates supporting three nucleofugal substituents, under $S_{RN}1$ conditions, is another interesting example of structurally similar compounds that do not behave in the same way under ET conditions, this behavior being mainly due to differences in the SOMO composition of the intermediate radical anions. We have proved that meanwhile the $S_{RN}1$ route is adequate for the synthesis of 1,3,5-tristannylbenzene (**6**), it is rather limited for the synthesis of the 1,2,4-isomer (**5**), starting from different isomeric substrates (**2** and **3**). This limitation is due to the effective competition of an IMH process (starting from substrate **3**) and the proved instability of compound **5** under ET conditions. It should be mentioned that the presence of rather high amounts of the undesired distannylated compounds in the reaction mixtures makes it difficult the isolation of pure **5** in acceptable yields. DFT studies support the experimental results.

Experimental section

General

All moisture sensitive reactions were carried out under a nitrogen atmosphere. Anhydrous ammonia was freshly distilled from sodium. Other solvents used were treated prior to use by standard methods.[11] All starting materials were of the best available grade (Aldrich, Merck) and were used without further purification. Thin layer chromatography (TLC) was performed on precoated silica gel plates (Merck 60, F254, 0.25 mm). Irradiation was conducted in a reactor made of Pyrex, equipped with four 250 W UV lamps emitting maximally at 350 nm (water-refrigerated). To carry out the reaction in the dark, the reaction flask was wrapped with aluminum foil.

Instrumentation and analysis

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-300 spectrophotometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference (^1H and ^{13}C) and H_3PO_4 as external reference (^{31}P). Mass spectra (EI) were obtained at 70 eV on a Hewlett Packard HP-5890 GC/MS instrument equipped with a HP-5972 selective mass detector. The purity of volatile compounds was determined and the chromatographic analyses (GC) were performed using a Shimadzu GC-14B instrument equipped with a flame-ionization detector and a HP-5MS column (30 m × 0.25 mm × 0.25 μm), using nitrogen as carrier gas.

General procedure for the synthesis of aryl phosphate esters

Diethyl aryl phosphates were prepared by the Kenner and Williams[12] method, characterized by NMR spectroscopy, and used without further purification.

1,3-Bis(diethoxyphosphoryl)oxy-4-chlorobenzene (2). To a mixture of 4-chlorobenzene-1,3-diol (5.0 mmol, 0.72 g) with diethyl hydrogen phosphate (10.4 mmol, 1.34 mL) in CCl_4 (4 mL) as solvent in an ice bath was slowly added triethylamine (10.4 mmol, 1.57 mL) and left overnight at room temperature. After total conversion of the starting material (TLC), the resulting suspension was diluted with H_2O. The organic phase was washed with HCl 10%, NaOH 10% and H_2O. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated (20 mbar). The title compound was obtained as a pale yellow liquid (3.6 mmol, 1.51 g, 76%). ^1H NMR δ_H (300 MHz, $CDCl_3$, $SiMe_4$): 7.45–6.82 (3H, m); 4.15 (8H, m); 1.25 (12H, m). ^{13}C NMR δ_C (75 MHz, $CDCl_3$, $SiMe_4$): 149.8 ($^2J_{CP}$ = 6.4 Hz, C_{aryl}); 147.2 ($^3J_{CP}$ = 6.0 Hz, C_{aryl}); 130.9 (CH_{aryl}); 121.6 ($^2J_{CP}$ = 7.6 Hz, C_{aryl}); 117.5 ($^3J_{CP}$ = 4.7 Hz, CH_{aryl}); 113.8 (CH_{aryl}); 65.5 ($^2J_{CP}$ = 6.4 Hz, CH_2); 16.1 ($^3J_{CP}$ = 7.6 Hz, CH_3). ^{31}P NMR δ_P (121.4 MHz, $CDCl_3$, PPh_3): 44.30 and 43.92. MS-EI, *m/z* 416 (M^+, 14%), 418 (M + 2, 4.7), 381 (M − Cl, 70), 353 (29), 325 (19), 297 (38), 269 (100), 187 (36), 109 (36), 81 (78). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{14}H_{23}ClO_8P_2$, 416.0557; found 416.0556.

1,4-Bis(diethoxyphosphoryl)oxy-3-chlorobenzene (3). Pale yellow liquid (4.0 mmol, 1.67 g, 84%). ^1H NMR δ_H (300 MHz, $CDCl_3$, $SiMe_4$): 7.64–7.10 (3H, m); 4.28 (8H, m); 1.40 (12H, m, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 1.1 Hz). ^{13}C NMR δ_C (75 MHz, $CDCl_3$, $SiMe_4$): 147.6 ($^2J_{CP}$ = 7.0 Hz, C_{aryl}); 144.2 ($^3J_{CP}$ = 5.9 Hz, C_{aryl}); 126.1 ($^2J_{CP}$ = 7.6 Hz, C_{aryl}); 122.3 ($^3J_{CP}$ = 4.7 Hz, CH_{aryl}); 122.1 (CH_{aryl}); 119.6 ($^3J_{CP}$ = 6.4 Hz, CH_{aryl}); 65.2 ($^2J_{CP}$ = 6.4 Hz, CH_2); 16.2 ($^3J_{CP}$ = 7.0 Hz, CH_3). ^{31}P NMR δ_P (121.4 MHz, $CDCl_3$, PPh_3): 44.35 and 44.01. MS-EI, *m/z* 416 (M^+, 12%), 418 (M + 2, 4.2), 381 (M − Cl, 25), 353 (14), 325 (10), 297 (22), 269 (51), 187 (9), 109 (78), 81 (100). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{14}H_{23}ClO_8P_2$, 416.0557; found 416.0560.

1,3-Bis(diethoxyphosphoryl)oxy-5-chlorobenzene (4). Pale yellow liquid (3.0 mmol, 1.25 g, 60%). ^1H NMR δ_H (300 MHz, $CDCl_3$, $SiMe_4$): 7.18–7.02 (3H, m); 4.25 (8H, m); 1.39 (12H, dt, $^3J_{HH}$ = 7.05 Hz, $^4J_{HP}$ = 0.95 Hz). ^{13}C NMR δ_C (75 MHz, $CDCl_3$, $SiMe_4$): 151.9 ($^2J_{CP}$ = 6.4 Hz, C_{aryl}); 135.7 (C_{aryl}); 117.6 ($^3J_{CP}$ = 5.3 Hz, CH_{aryl}); 111.3 ($^3J_{CP}$ = 5.3 Hz, CH_{aryl}); 65.3 ($^2J_{CP}$ = 6.0 Hz, CH_2); 16.4 ($^3J_{CP}$ = 6.4 Hz, CH_3). ^{31}P NMR δ_P (121.4 MHz, $CDCl_3$, PPh_3): 44.19. MS-EI, *m/z* 416 (M^+, 12%), 418 (M + 2, 3.8), 381 (M − Cl, 50), 353 (28), 325 (18), 297 (40), 269 (100), 187 (39), 109 (28), 81 (75). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{14}H_{23}ClO_8P_2$, 416.0557; found 416.0559.

General procedure for photostimulated reactions in liquid ammonia

1,2,4-Tris(trimethylstannyl)benzene (5)[7b]. In a 250 mL two-necked round-bottomed flask, equipped with a cold finger condenser charged with acetone–liquid nitrogen, a nitrogen inlet and a magnetic stirrer were condensed 180 mL of Na-dried ammonia. Me_3SnCl (3.3 mmol, 0.66 g) was dissolved and small pieces of sodium metal (7.5 mmol, 0.17 g) were added until the blue color persisted for at least 5 min. When the blue color disappeared, **2** (1.0 mmol, 0.42 g) was added dropwise and the solution was irradiated under stirring. The reaction was quenched with IMe (3.3 mmol, 96 μL), 10 mL of Et_2O was added and, then, liquid ammonia was allowed to evaporate. The resultant solution was treated with H_2O and extracted with

Et_2O (3 × 30 mL). The crude extract was diluted with Et_2O to a volume of 100 mL and analyzed by MS-EI, *m/z* 551 ($M–CH_3^+$, 30%, Sn_3 pattern), 401 ($C_6H_3Sn_2(CH_3)_6^+$, 30), 371 ($C_6H_3Sn_2(CH_3)_4^+$, 21), 341 ($C_6H_3Sn_2(CH_3)_2^+$, 30), 165 ($Sn(CH_3)_3^+$, 100).

Computational procedure

The calculations were performed with Gaussian03.[13] The initial conformational analysis of compounds was performed using the semiempirical AM1 method. The geometry of the most stable conformers thus obtained was used as a starting point for the B3LYP[14] studies of their radical anions with the LACVP[15] pseudopotential for heavier elements (Sn) and the 6-31+G* (C, H, O, P). The exploration of the potential surface was carried out by varying the selected coordinate ($C_{aromatic}$–OP bond distance) with full optimization for the remainder degrees of freedom. The characterization of all stationary points was done by Hessian matrix calculations of geometries obtained with full optimization for a minimum and by using the TS methodology for a transition state. In all cases, the spin contamination along the whole fragmentation paths was negligible. The zero point energy corrections were made for the thermodynamic quantities. The energies in solution were obtained with full geometry optimization within the Tomasi's polarized continuum model (PCM)[16] as implemented in Gaussian03. The figures were built with the GaussView program using a spin density isosurface of 0.02.

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