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Nucleophilic substitution of bromonorbornenes and derivatives by electron transfer reactions†

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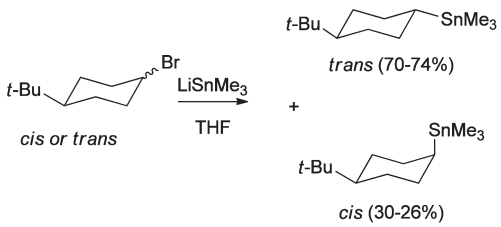
The photoinitiated substitution reactions of *anti*-7-bromobenzonorbornadiene (**5**), its *syn* isomer **6**, *exo–anti*-13-bromobenzocyclobutanorbornene (**7**), *syn*-7-bromonorbornene (**8**) and bromonorbornane (**9**) with Me_3Sn^- and Ph_2P^- anions, in liquid ammonia, are here informed to occur with good yields of substitution. The stereochemical outcome is discussed in terms of calculations with the B3LYP functional and the 6-31+G* basis set; the solvent being included as a continuum through the PCM model. The experimental relative chemical reactivity of pairs of substrates toward a given anion is also presented.

Introduction

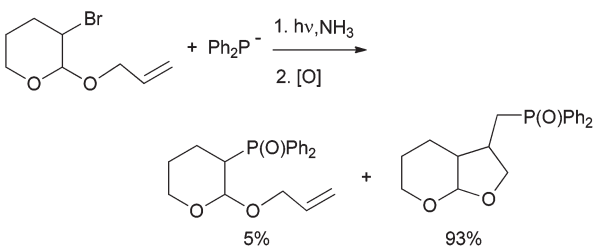
It is known that organic halides that are unreactive by polar nucleophilic mechanisms can be substituted by an electron transfer (ET) process named $S_{RN}1$.[1] Neopentyl, *t*-butyl, bridgehead-bicyclic and polycyclic halides are examples of this type of compound.[1] Fewer investigations have been carried out for cyclic secondary halides, however, from these the cyclopropyl derivatives of the halonorcarane family have been the most studied.

Carbanions and anions from Sn (R_3Sn^- (R = Me, Ph)), P (Ph_2P^-) and S are nucleophiles frequently used within the aliphatic family of substrates. Some examples for the *sec*-cycloalkyl halides family are the substitution of *c*-C_5H_9Br by $NaSnMe_3$ in THF, proposed to proceed 90% by ET with only 7% of a polar component,[2] and the substitution of *c*-C_4H_7Br, *c*-C_5H_9Cl and *c*-$C_6H_{11}X$ (X = Cl, Br) by Ph_2P^- ions in $NH_{3(l)}$, proposed to proceed by a variable extent of $S_{RN}1$ and cage-collapse pathways.[3] The lack of stereospecificity in the substitution of 2-, 3-, and 4-alkylcyclohexyl bromides (*trans* and *cis*) by $MSnMe_3$ (M = Li, Na, K) was one piece of the evidence used to propose that this reaction proceeds mainly by a free-radical pathway (eqn (1)).[4]



(1)

Also, the formation of straightforward and cyclized substitution products in the reaction of the radical probe 3-bromo-2-tetrahydropyranyl allyl ether with Ph_2P^- ions suggested the reaction proceeded through cyclohexyl radicals intermediates (eqn (2)).[3]



(2)

2-Haloadamantanes (2-XAd), a special case of *sec*-cyclohexyl halides, have been substituted by Me_3Sn^- (halogen = Cl,[5] Br[2]) and by Ph_2P^- (halogen = Br)[5,6] under ET conditions. Also, when a good leaving group is present, as in the case of 2-IAd, substitution by carbanions is possible under irradiation in DMSO.[7]

7-Halonorcaranes are one of the most studied derivatives of the cyclopropyl family. The 7-iodo-bicyclo[4.1.0]heptane (*ca.* 1 : 1 of *exo* : *endo* isomers) is substituted by $PhCOCH_2^-$, 2-NaphCOCH_2^-, and $O_2NCH_2^-$ ions under irradiation in DMSO with prevalence of the *exo* product (eqn (3)).[8]

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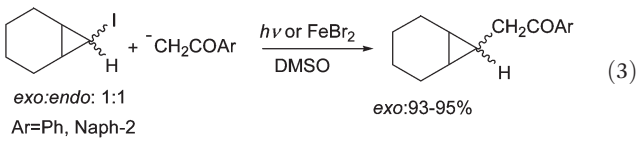
†Electronic supplementary information (ESI) available: Representative experimental procedure, ^{1}H-NMR, ^{13}C-NMR and 2D NMR of compounds **6**, **10a**, **10b**, **11a**, **11b**, **12a**, **12b**, **13a**, **14a**, **15**, **16**, **17** and **18**. Coordinates (*xyz*) for all stationary points evaluated. Estimation of activation free energies by Marcus Theory or Savèant's model. See DOI: 10.1039/c2ob26768c

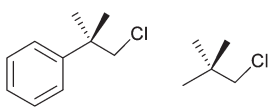


(3)

Also, the reaction of the 7-bromo compound with Ph_2P^-, Ph_2As^-, PhS^- and pinacolone enolate ions, in $NH_{3(l)}$, has been informed.[9]

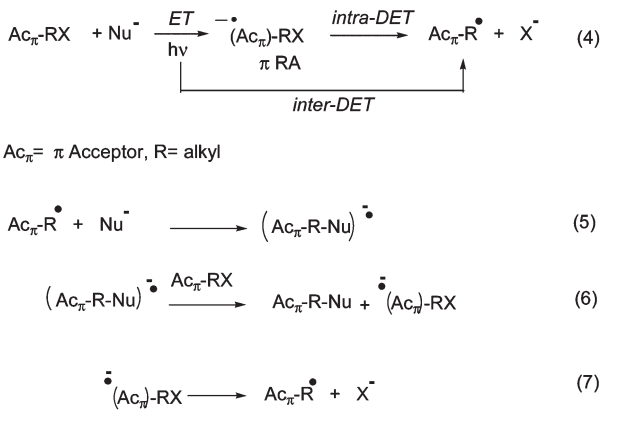
The $S_{RN}1$ mechanism, proposed as the reaction pathway for most of these substitutions, is a cyclic process which, for alkyl halide substrates, is photochemically initiated. In some cases, spontaneous or thermal ET is also possible.[1] Under irradiation, an electron is transferred from the anionic nucleophile to the substrate to initiate the cycle. This event can be dissociative, meaning that the carbon–halogen bond breaks as the electron is being transferred (intermolecular dissociative ET (inter-DET)), or it can follow a two-step pathway with formation of radical anion intermediates (eqn (4)). These intermediates fragment in a second step, through an intramolecular dissociative ET (intra-DET) from the π system to the σ* C–halogen bond to afford the radicals that enter the propagation cycle (eqn (5)–(7)), as shown in Scheme 1.

The initiation (eqn (4)) and step 6 of the propagation are favoured by the presence of good electron acceptors such as π substituents that increase the electron affinity of RX. This has been shown to be the case for neopentyl and bicyclic bridgehead alkyl halides. Thus, based on relative reactivity measurements, we have demonstrated that neophyl chloride (**1**) is about nine times more reactive than neopentyl chloride (**2**) toward Ph_2P^- ions.[10]

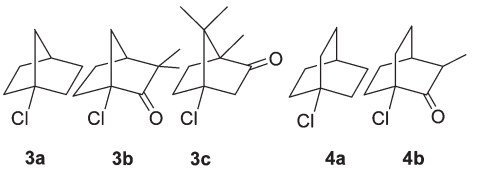


1 **2**

This π catalysis has also been reported for the subfamilies of compounds **3** and **4** (Chart 1).[11] While the unsubstituted compounds **3a** and **4a** are unreactive under ET conditions, the presence of an oxo substituent α- or β- to the halide was shown to be crucial to achieve the substitution.



Scheme 1



3a **3b** **3c** **4a** **4b**

Chart 1

It has been demonstrated on experimental and theoretical basis that this intramolecular π catalysis depends on the relative position of the oxo substituent with respect to the leaving group as well as on the strain of the aliphatic bridge.[12]

Taking into account the previous work on the subject, we consider the study of the potentiality of 7-bromobicyclo[2.2.1]-hep-2-ene and derivatives, a special case of *sec*-cyclopentyl bromides, toward nucleophilic substitution under $S_{RN}1$ conditions of interest.

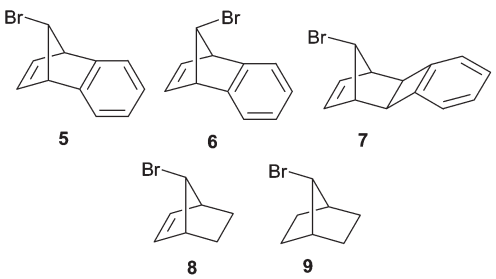
The compounds of study (Chart 2) are candidates to be substituted under the latter conditions. For example, the rate constant for solvolysis of 7-*anti*-bromobenzonorbornadiene (**5**) was determined to be 2.4×10^{-8} seg^{-1} (25 °C) and that of the *syn*-isomer **6** 1.05×10^{-3} seg^{-1} (25 °C) with a ratio $k_{syn}/k_{anti} = 4.4 \times 10^4$.[13] This low degree of reactivity under polar mechanisms provides interest for the study of reactivity under ET conditions and its synthetic scope.[14]

Also, the series can be used as a model to study the influence of the π system, its dimension and geometric disposition on the global reactivity of the compounds. Compounds **5** and **6** characterize by the presence of a double bond and a condensed phenyl group at different spatial disposition with respect to the C–Br bond. The phenyl group is at a longer distance from the halogen in **7** and it is absent in **8**. Meanwhile, **9** lacks any π substitution.

Results

Table 1 summarizes the results obtained in the photoinitiated reactions of compounds **5–9** with Ph_2P^- and Me_3Sn^- anions in $NH_{3(l)}$ as solvent as well as the reaction of **5** with Ph_3Sn^- ions.

Starting from the *anti*-**5** or *syn*-**6** bromo substrates a mixture of *syn* and *anti* substitution products is formed. In the reactions with Me_3Sn^- anions a similar *anti*-**10a** : *syn*-**10b** ratio of products is obtained starting with either substrate; the



5 **6** **7** **8** **9**

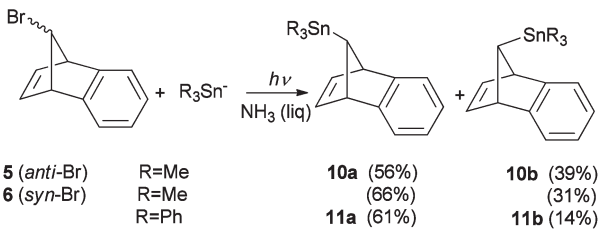
Chart 2

Table 1 Photochemical reactions of *anti*-7-bromobenzonorbornadiene (**5**), its *syn* isomer **6**, *exo–anti*-13-bromobenzocyclobutanorbornene (**7**), *syn*-7-bromonorbornene (**8**) and 7-bromonorbornane (**9**) with anions from tin and phosphorous in $NH_{3(l)}$ [a]

Expt	Substrate (mM)	Nu^- (mM)	Irradiation time (min)	% Br^- [b]	Products yields[c] (%) RNu (*anti*) RNu (*syn*)
1	**5** (2.44)	Me_3Sn^- (2.93)	120	99	**10a** (59) **10b** (40)
2	**5** (2.44)	Me_3Sn^- (2.93)	5	91	**10a** (56) **10b** (39)
3[d]	**5** (2.26)	Me_3Sn^- (2.69)	5	65	**10a** (47) **10b** (23)
4	**5** (2.36)	Me_3Sn^- (11.36)	5	>90	**10a** (64) **10b** (31)
5[e,f]	**5** (2.17)	Me_3Sn^- (2.68)	5	30	**10a** + **10b** (25)
6[g,h]	**5** (2.66)	Me_3Sn^- (3.22)	5	<1	—
7	**6** (1.16)	Me_3Sn^- (1.35)	120	100	**10a** (66) **10b** (31)
8	**5** (2.36)	Ph_3Sn^- (3.19)	5	>95	**11a** (61) **11b** (14)
9	**5** (1.80)	Ph_2P^- (2.18)	120	89	**12a** (47) **12b** (40)
10	**5** (2.63)	Ph_2P^- (3.13)	5	91	**12a** (49) **12b** (40)
11[i]	**5** (2.66)	Ph_2P^- (3.18)	5	65	**12a** (33) **12b** (28)
12[e]	**5** (2.14)	Ph_2P^- (3.27)	5	<4	—
13	**6** (2.21)	Ph_2P^- (2.45)	120	98	**12a** (54) **12b** (46)
14	**7** (1.67)	Me_3Sn^- (2.06)	120	88	**13a** (62) **13b** (—)
15	**7** (1.93)	Ph_2P^- (2.28)	120	50	**14a** (30) **14b** (—)
16	**8** (3.19)	Me_3Sn^- (6.92)	30	90	**15** (96)
17[j,e]	**8** (3.37)	Me_3Sn^- (7.95)	30	49	**15** (49)
18[k,l]	**8** (3.37)	Me_3Sn^- (7.88)	30	6	—
19[m]	**8** (3.37)	Ph_2P^- (7.24)	75	89	**16** (87)
20[e]	**8** (3.37)	Ph_2P^- (7.95)	75	<6	—
21[n]	**9** (3.20)	Me_3Sn^- (7.37)	30	75	**17** (72)
22[e,o]	**9** (3.09)	Me_3Sn^- (7.13)	30	43	**17** (33)
23[p]	**9** (3.09)	Me_3Sn^- (7.12)	30	<6	—
24	**9** (3.04)	Ph_2P^- (6.98)	75	98	**18** (97)
25[e]	**9** (3.04)	Ph_2P^- (7.01)	75	<6	—

[a] Reactions carried out in liquid ammonia $NH_{3(l)}$ (−33 °C) irradiated in a photochemical reactor equipped with two high pressure lamps model Philips HPI-T plus 400-W. [b] Halides quantified by potentiometric titration with $AgNO_3$. [c] Quantified by GC with the internal standard method. [d] In $NH_{3(l)}$ (−77 °C). [e] Reaction performed in the dark. [f] RBr unreacted (75%). [g] Dark reaction in the presence *p*-DNB (24.8% with respect to the substrate). [h] RBr unreacted (>96%). [i] Reaction performed in the presence of DTBN (32.2% with respect to the substrate). [j] RBr unreacted (53%). [k] Dark reaction in the presence *p*-DNB (29% with respect to the substrate). [l] RBr unreacted (97%). [m] RBr unreacted (16%). [n] RBr unreacted (31%). [o] RBr unreacted (64.5%). [p] Dark reaction in the presence *p*-DNB (20% with respect to the substrate).

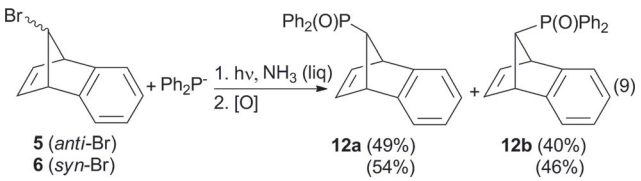
anti-substitution prevailing (*anti* : *syn* = 1.4 and 2.1 with **5** and **6**, respectively) (eqn (8), Table 1, expts 1, 7).



(8)

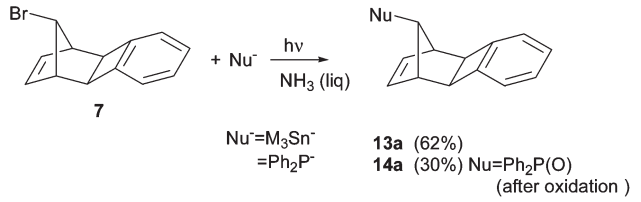
Neither the decrease of the reaction time or temperature nor the increase of the nucleophile : substrate ratio significantly modifies the *anti* : *syn* ratio of products formed in the reaction of **5** with Me_3Sn^- ions (Table 1, expts 2, 3 and 4, respectively).

The yield of *syn* substitution decreases, as shown in eqn (8), when **5** reacts with the bulky Ph_3Sn^- anion (Table 1, expt 8); the *anti* substitution prevails as in the previous reactions. A similar percentage of *anti*-**12a** and *syn*-**12b** phosphineoxides was obtained by reaction of **5** or **6** with Ph_2P^- ions (*anti*-**12a** : *syn*-**12b** = 1.2 with both substrates) (eqn (9), Table 1, expts 9, 10, 13)).



(9)

The reaction of Me_3Sn^- and Ph_2P^- ions with the *exo–anti* **7** affords the substitution product with high stereospecificity. Only the *exo–anti* isomers were formed (62% and 30% yield of products **13a** and **14a**, respectively) (eqn (10), Table 1, expts 14, 15).



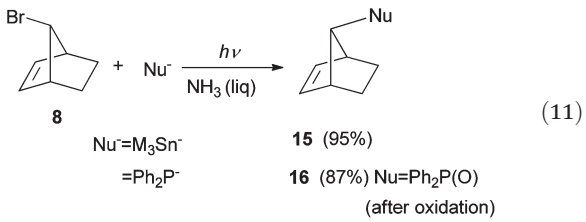
(10)

On the other hand, in the reaction of both anions with substrate **8** the major products formed were the *anti* isomers accompanied by traces of the *syn* ones (eqn (11), Table 1, expts 16, 19).

Table 2 Competition experiments between pairs of substrates toward Ph_2P^- or Me_3Sn^- ions in $NH_{3(l)}$ [a]

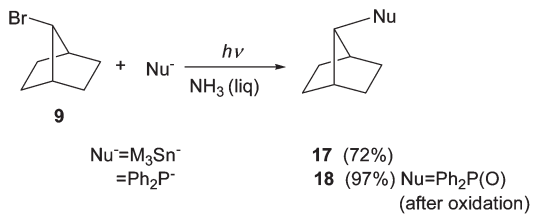
Expt	R_1X (mM)	R_2X (mM)	Nu^- (mM)	% RX unreacted	Substitution products[b] (%)	Relative reactivity[c]
1	**5** (1.94)	**6** (1.94)	Ph_2P^- (1.57)	**5** (30) **6** (42)	**11a** (36); **11b** (32)	k_5/k_6 = 1.4
2	**5** (1.35)	**6** (1.35)	Me_3Sn^- (1.57)	**5** (28) **6** (36)	**10a** (43); **10b** (21)	k_5/k_6 = 1.2
3	**5** (1.89)	**7** (1.89)	Ph_2P^- (3.74)	**5** (35) **7** (70)	**11a** (38); **11b** (25); **13** (24)	k_5/k_7 = 2.9
4	**5** (2.10)	**7** (1.98)	Me_3Sn^- (4.08)	**5** (14) **7** (47)	**11a** (47); **11b** (23); **13** (39)	k_5/k_7 = 2.6
5	**5** (4.00)	**8** (3.38)	Ph_2P^- (3.38)	**5** (28) **8** (79)	**11a** (32); **11b** (36); **15** (15)	k_5/k_8 = 5.4
6	**5** (3.90)	**8** (4.00)	Me_3Sn^- (4.29)	**5** (37) **8** (68)	**10a** (41); **10b** (22), **14** (27)	k_5/k_8 = 2.2
7	**5** (3.63)	**9** (3.67)	Ph_2P^- (3.64)	**5** (32) **9** (84)	**11a** (32); **11b** (38); **17** (14)	k_5/k_9 = 6.0
8	**5** (3.63)	**9** (3.63)	Me_3Sn^- (3.63)	**5** (35) **9** (65)	**10a** (38); **10b** (21); **16** (35)	k_5/k_9 = 3.2
9	**5** (3.31)	**9** (3.38)	Me_3Sn^- (6.56)	**5** (9) **9** (50)	**10a** (56); **10b** (30); **16** (51)	k_5/k_9 = 3.4

[a] Reactions carried out in $NH_{3(l)}$ (−33 °C) irradiated in a photochemical reactor equipped with two high pressure lamps model Philips HPI-T plus 400-W. [b] Quantified by GC with the internal standard method. [c] Determined according to ref. 15.



(11)

A good percentage of substitution product was also obtained in the irradiated reaction of compound **9** with both anions (eqn (12), Table 1, expts 21, 24).



(12)

The yields of substitution decreased in reactions performed in the presence of di-*t*-butylnitroxide (DTBN), a known radical trap (expt 11) or in the absence of light (expts 5, 12, 17, 20, 22, 25 and were almost completely inhibited by the addition of *p*-dinitrobenzene (*p*-DNB), a well known radical anion trap (expts 6, 18, 23).

Relative reactivities

The relative reactivity of pairs of substrates was determined under competition experiments towards a given nucleophile and evaluated as previously reported,[15] with concentrations under which both substrates remain unreacted at the final reaction time.

An average relative reactivity k_5/k_6 = 1.4 and 1.2 was obtained for substrates **5** and **6** with Ph_2P^- and Me_3Sn^- anions respectively (Table 2, expts 1, 2). The relative reactivities determined for **5** *vs.* **7**, **8** and **9** toward Ph_2P^- ions (k_5/k_7 = 2.9, k_5/k_8 = 5.4 and k_5/k_9 = 6, Table 2, expts 3, 5, 7) indicate the higher reactivity of **5** under ET conditions. Lower relative reactivities were determined toward Me_3Sn^- mainly for substrates **8** and **9** (k_5/k_7 = 2.6, k_5/k_8 = 2.2 and k_5/k_9 = 3.3, Table 2, expts 4, 6, 8–9).

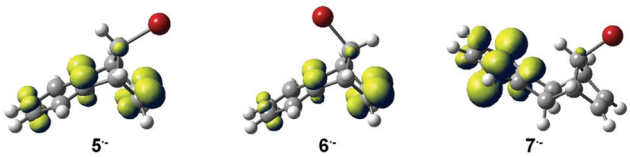


Fig. 1 B3LYP/6-31+G* unpaired spin density evaluated for radical anions of compounds **5**, **6** (value of isodensity = 0.004) and **7** (value of isodensity = 0.003) in the presence of a continuum solvent.

Discussion

Based on the experimental information obtained in reactions performed in the dark, conditions under which a considerable decrease of substitution is obtained, and on the inhibition exerted by *p*-DNB and DTBN, we propose the reactions to proceed through the $S_{RN}1$ mechanism (initiation and propagation cycle presented in Scheme 1, eqn (4)–(7)).

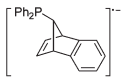
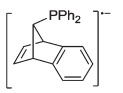
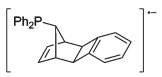
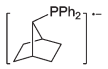
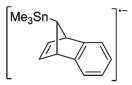
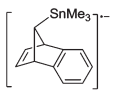
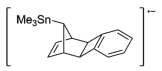
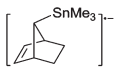
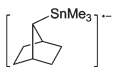
The electron donor, along the propagation cycle of this mechanism (eqn (6)), is the radical anion of the substitution product ($RNu^{-\bullet}$) formed by eqn (5). As mentioned, the ET from $RNu^{-\bullet}$ to the RBr substrates can follow an inter-DET or a stepwise pathway, with radical anions as intermediates. The latter is the favoured path for compounds that bear a stabilized π system that acts as the primary electron acceptor centre.

Calculations of the anionic potential energy surfaces (PES) of compounds **5–7** with the B3LYP functional and the 6-31+G* basis set, in the presence of a continuum solvent, lead to the finding of radical anions as intermediates;[12] their unpaired spin density being presented in Fig. 1.

The thermochemistry evaluated for the ET from $RNu^{-\bullet}$ to RBr (eqn (6)) is presented in Table 3.

As seen from the table, the outer sphere ET from $RPPh_2^{-\bullet}$ to **5** and **6** (entries 1–5) is slightly endothermic; the endothermicity being higher for the ET to **7**. For the latter compound, the evaluation of $\Delta G^{\#}_{ET}$ by the Marcus–Hush theory[16] (for a stepwise pathway) or Savèant's model[17] (for an inter-DET), favours the stepwise pathway (see ESI†). On the other hand, the ET from $RSnMe_3^{-\bullet}$ to **5–7** is exothermic (entries 6–9, Table 3).

Table 3 B3LYP/6-31+G* thermochemistry for the reaction $RNu^{-\cdot}$ + RBr → RNu + $RBr^{-\cdot}$ ($R^{\cdot}$ + Br^{-})[a]

		ΔE[b] (kcal mol^{-1})		
Entry	$RNu^{-\cdot}$	$RNu^{-\cdot}$ + (RBr) → RNu + $RBr^{-\cdot}$		
1	 **12a-desoxi**	(**5**) 2.95	(**6**) 3.08	(**7**) 7.92
2	 **12b-desoxi**	(**5**) 2.85	(**6**) 2.98	(**7**) 7.81
3	 **14a-desoxi**	(**5**) 2.31	(**6**) 2.44	(**7**) 7.28
4	 **16-desoxi**	(**5**) 2.50	(**6**) 2.63	(**7**) 7.47
5	 **18-desoxi**	(**5**) 2.05	(**6**) 2.19	(**7**) 7.02
6	 **10a**	(**5**) −5.61	(**6**) −5.47	(**7**) −0.64
7	 **10b**	(**5**) −5.65	(**6**) −5.52	(**7**) −0.68
8	 **13a**	(**5**) −8.94	(**6**) −8.81	(**7**) −3.97
9	 **15**	(**5**) −17.56	(**6**) −17.43	(**7**) −12.59
10	 **17**	(**5**) −13.00	(**6**) −12.97	(**7**) −8.13

[a] Evaluation includes the presence of the solvent as a continuum through the PCM model. [b] Zero point energy corrected.

It can be concluded that for this set of substrates the better electron acceptors are **5** and **6**, the extra electron being accommodated in the phenyl and olefinic π systems (see the unpaired spin density shown in Fig. 1). On the other hand, only the phenyl system acts as main acceptor centre in **7**, fact that accounts for its lower electron acceptor capacity.

Once $RBr^{-\cdot}$ are formed, they dissociate into radicals with very low ($\mathbf{5}^{-\cdot}$, $\mathbf{6}^{-\cdot}$ (0.1 and 0.4 kcal mol^{-1}, respectively)) or none ($\mathbf{7}^{-\cdot}$) activation energy (E_a) (eqn (7), Scheme 1). The normal mode of the intrinsic reaction path for dissociation of $\mathbf{6}^{-\cdot}$ involves, besides the trivial C–Br stretching, a distortion of one olefin–CH bond which approaches the C_{Br} centre assisting the halide departure from its back side (Fig. 2). A similar intrinsic path is observed for $\mathbf{5}^{-\cdot}$, but with the participation of the phenyl ring (Fig. 2).[18]

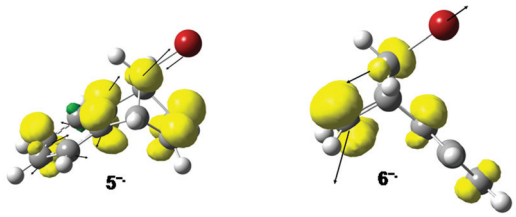
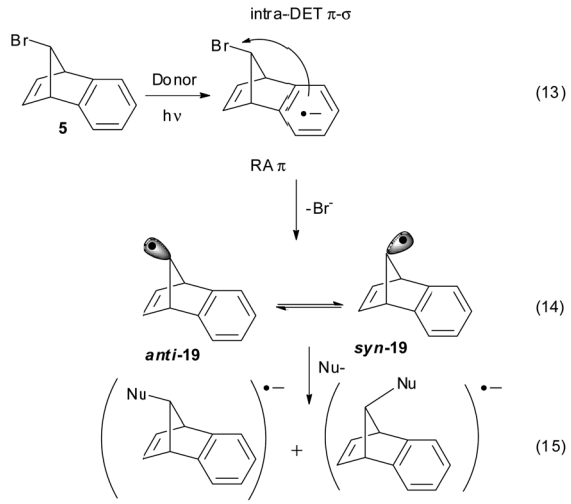


Fig. 2 Spin density and main heavy atoms displacement vectors of the π–σ* C–Br intra-DET transition states for bond dissociation of $\mathbf{5}^{-\cdot}$ and $\mathbf{6}^{-\cdot}$.



Scheme 2

In $\mathbf{7}^{-\cdot}$, despite the π_{phenyl} system is farther from the C–Br bond, a slight spin density spreads over the C–Br bond favouring the spontaneous dissociation of this intermediate.

The ET to **8** and **9** follows a inter-DET step; no RAs being located on their anionic PES. Applying Savèant's model a $\Delta G^{\#}_{ET} \approx 11$ kcal mol^{-1} is estimated for the ET from desoxi-$\mathbf{12a}^{-\cdot}$ or $\mathbf{12b}^{-\cdot}$ and ≈8 kcal mol^{-1} for the ET from $\mathbf{10a}^{-\cdot}$ or $\mathbf{10b}^{-\cdot}$ to **8** and **9**, respectively (see ESI†).

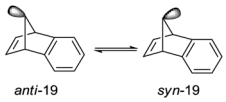
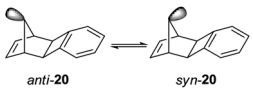
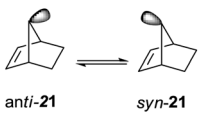
Stereochemistry of the coupling

The radicals formed by dissociation of **5–8** may experience a fast *syn–anti* isomerization[4,8,19] as shown in Scheme 2 for **5**, as a representative.

The most stable radicals are those in which the radical centre is *anti* to the olefinic-π system. In Table 4, the ΔE for the isomerization of the radicals is presented together with their estimated *anti*/*syn* percentage at equilibrium.

The NBO[20,21] analysis shows the *anti* and *syn* radicals **19** to be stabilized by hyperconjugative second order perturbation. This perturbation is due to the interaction between the radical-SOMO and the π bond of the phenyl or olefinic system, respectively; the stabilization being higher for *syn*-**19** (6.79 kcal mol^{-1}) with respect to *anti*-**19** (5.18 kcal mol^{-1}).[22] Similar effects are responsible for the higher stabilization for

Table 4 B3LYP/6-31+G* energy change for radicals isomerization together with radical percentage at equilibrium

Radicals	Isomerization $\Delta E_{syn-anti}$ [a] (kcal mol^{-1})	K[b]	Radical % at equilibrium
 anti-19 syn-19	−0.17	1.43	% *anti*-**19** = 41 % *syn*-**19** = 59
 anti-20 syn-20	−1.00	8.20	% *anti*-**20** = 11 % *syn*-**20** = 89
 anti-21 syn-21	0.73	0.22	% *anti*-**21** = 82 % *syn*-**21** = 18

[a] Zero point Corrected. E_a for isomerization lower than 1 kcal mol^{-1}. [b] Evaluated form $\Delta E = -RT \ln K$ (T = 240 K).

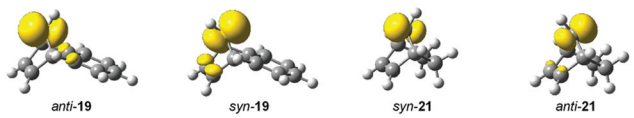


Fig. 3 NBO second order perturbative stabilization interactions for radicals *anti*-**19**, *syn*-**19**, *syn*-**21** and *anti*-**21**.

syn-**20** (5.61 kcal mol^{-1}) *vs.* *anti*-**20** (1.59 kcal mol^{-1}) and for *anti*-**21** (4.23 kcal mol^{-1}) *vs.* *syn*-**21** (1.14 kcal mol^{-1}) (see Fig. 3 and Table 4).

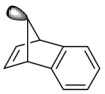
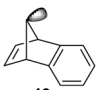
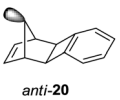
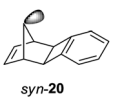
Taking into consideration the low E_a for isomerization (less than 1 kcal mol^{-1}), the radicals equilibration could be attained. Given this condition, the stereochemistry of the products will depend both on the difference in energy between the two radicals and their relative E_a for coupling with the nucleophile (Curtin–Hammett principle). In Table 5 the E_a evaluated for the reaction of *syn*- and *anti*-**19**, *syn*- and *anti*-**20** and *syn*- and *anti*-**21** with Ph_2P^- anion is presented together with the corresponding thermochemistry.

The percentage of *syn*-**19** formed by dissociation of $\mathbf{5}^{-\cdot}$ or $\mathbf{6}^{-\cdot}$, is approximately 16% higher than that of *anti*-**19**. On the other hand, *anti*-**19** couples with Ph_2P^- anion with a slightly lower E_a than the *syn* radical (3.2 *vs.* 3.9 kcal mol^{-1}). As a whole, these data justified the *anti* : *syn* = 1.2 ratio of products formed by reaction of **5** or **6** with Ph_2P^- anion (see eqn (9)).

Upon dissociation of intermediate $\mathbf{7}^{-\cdot}$, *syn*-**20** is evaluated as the preferred radical (86% *vs.* 14% (*anti*-**20**)). However, *syn*-**20** couples with Ph_2P^- anions with considerable higher E_a than *anti*-**20** (8.8 *vs.* 4.6 kcal mol^{-1}, see Table 5). Moreover, coupling through the *anti* face is considerably more exothermic than through the *syn* face and thus, the *anti*-coupling becomes the experimentally observed (Fig. 4 (see also eqn (10))).

Upon dissociation of **8**, *anti*-**21** prevails with respect to *syn*-**21** (83 : 17%). On the other hand, the coupling of Ph_2P^- anions with *anti*-**21** is slightly disfavoured (by ≈0.2 kcal mol^{-1}) with respect to coupling with *syn*-**21**. Based on these calculations a

Table 5 6-31+G* thermochemistry and activation energy for coupling of radicals with Nu^-=Ph_2P^- in the presence of a continuum as solvent[a]

Radical	E_a (kcal mol^{-1}) $R^{\cdot} + Nu^- \rightarrow RNu^{-\cdot}$	ΔE [a] (kcal mol^{-1}) $R^{\cdot} + Nu^- \rightarrow RNu^{-\cdot}$
 anti-19	3.2	−8.2
 syn-19	3.9	−8.0
 anti-20	4.6	−7.3
 syn-20	8.8	0.8
 syn-21	5.0	−8.4
 anti-21	5.2	−7.8

[a] Zero point energy corrected.

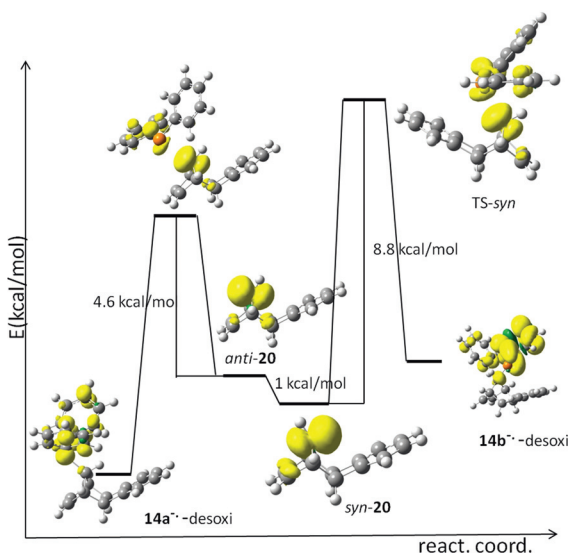
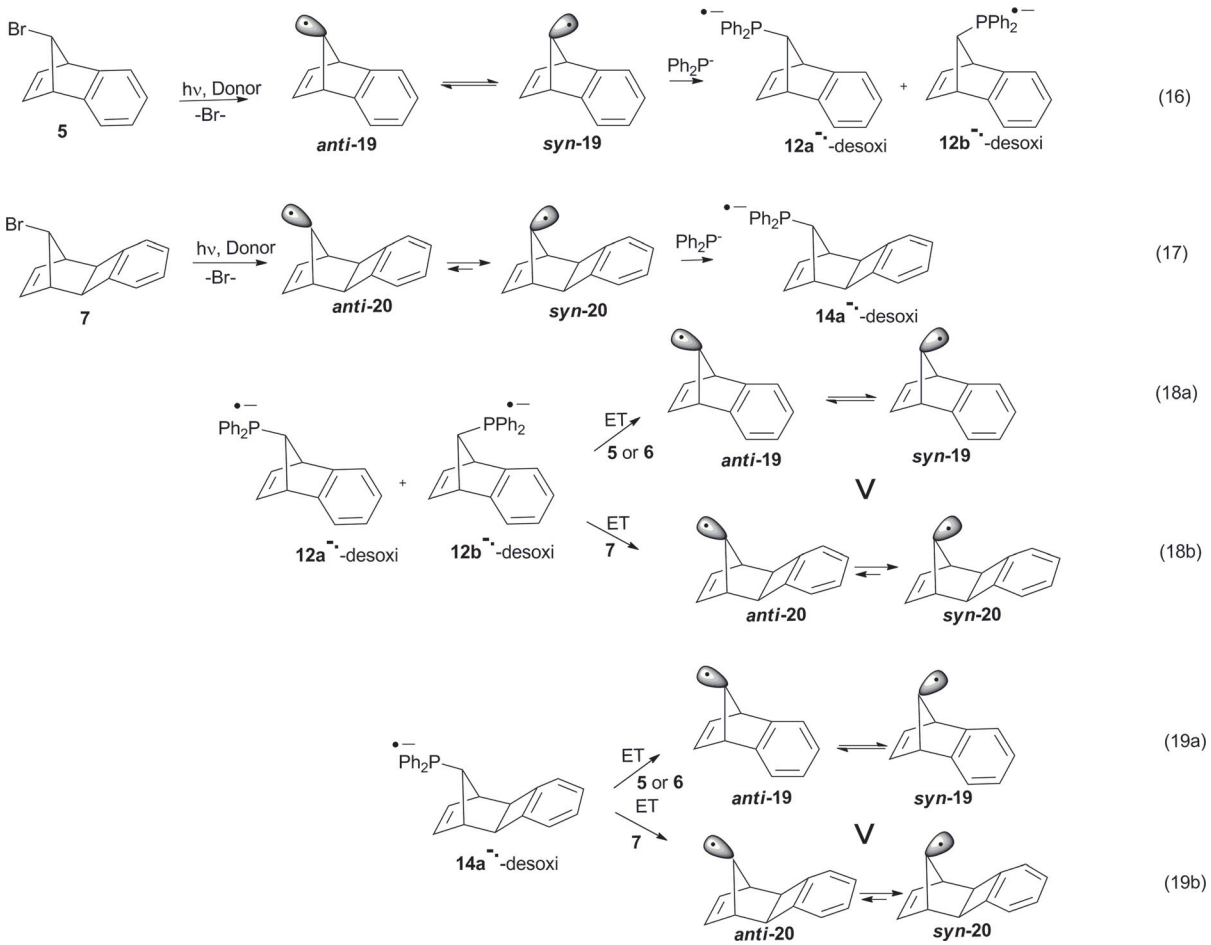


Fig. 4 B3LYP/6-31+G* PES (in the presence of a continuum) for the coupling of radical **20** (*anti* and *syn*) with Ph_2P^- anion.[23]

75 : 25% yield of *anti* : *syn* substitution would be expected (see ESI†). The main products formed by reaction of **8** with Ph_2P^- and Me_3Sn^- are *anti*-**15** and *anti*-**16** (eqn (11)). It is important to mention that in the reaction of *syn*-**8** with both anions, traces of the *syn*-products were detected. On these basis, B3LYP calculations, which clearly favour the *anti* products with respect to the *syn* ones stand as a valuable predictive tool.



Scheme 3

Competitions experiments of pair of substrates (R_1X, R_2X) toward Ph_2P^- are shown in Scheme 3 (R_1X = **5** and R_2X = **7**, as representative). Radicals **19** (*anti* and *syn*) couple with Ph_2P^- ion with similar E_a and lower than that of **20** (*anti*) (Table 5, eqn (16) and (17)).

It is expected that $RPPh_2^{-\bullet}$ will transfer its extra electron to the better acceptor **5** ≈ **6** > **7** in order to continue the propagation cycle (Scheme 3, eqn (18) and (19)). The energetic calculated for this ET (Table 3) explains the similar reactivity of compounds **5** and **6** (k_5/k_6 = 1.4) and the higher reactivity of **5** *vs.* **7** (k_5/k_7 = 2.9).

The higher reactivity of **5** *vs.* **8** (k_5/k_8 = 5.4) or **9** (k_5/k_9 = 6.0) is also attributed to their relative electron acceptor capability order (**5** > **8** ≈ **9**). The **5** > **8** reactivity is also supported by the E_a evaluated for the reaction of Ph_2P^- with radicals **19** *vs.* radicals **21** (Table 5).[24,25]

Conclusions

In this work we studied the reactivity of a series of 7-bromo norbornenes and derivatives in nucleophilic substitution reactions mediated by ET processes with Me_3Sn^- and Ph_2P^- nucleophiles. For substrates **5** and **6** good yields of both *anti* and *syn* substitution products were obtained. For compounds **7** and **8** the reaction is stereospecific with formation of the *anti* substitution products in both cases.

The experimental outcome of these mediated ET nucleophilic substitutions can be interpreted by the dissociation of compounds **5–8** into radicals followed by a fast equilibration between their isomeric forms. The favoured substitution products are justified, as stated by the Curtin–Hammett principle, by the thermodynamic of this equilibrium and the kinetic of the radical–anion coupling.

The computational studies explain the fast *anti–syn* equilibration of the radicals. Moreover, the theoretical studies of the radical–nucleophile coupling offer the possibility to understand the stereospecificity of the reaction for radicals **20** and **21**; no stereospecificity being observed with radical **19**.

Also, we established an experimental reactivity order (**5** ≈ **6** > **7** > **8** ≈ **9**), which is understood on the basis of the preferred inter-ET reaction between the different $RNu^{-\bullet}$/RBr pairs and on the differences in the coupling reactivity of the radicals, formed upon RBr dissociation, with the nucleophiles.

Unfortunately, we were unable to find a good yielding route to synthesize compounds *syn*-**7** and *anti*-**8**. However, as

discussed along the manuscript, the experimental outcome obtained with the different substrates relates pretty well with the theoretical predictions. On these bases, we believe that the complementarity of the experimental and theoretical work presented here may have a highly predictive scope for the expected experimental reactivity of compounds *syn*-**7** and *anti*-**8**.

Computational procedure

All the calculations were performed with the Gaussian03 or Gaussian09 program,[26] the B3LYP[27] DFT functional and the 6-31+G* basis set for C, H, Br and P.[28] The LACVP pseudopotential was used for Sn.[29]

Calculations were performed with full geometry optimization including in all cases the effect of the solvent (methanol as polar solvent) through the Tomasi's polarized continuum model (PCM)[30] as implemented in the Gaussian package. The transition states (TS) and intermediates were localized by the scan of the distinguished reaction coordinate (C–Br bond dissociation and C–P, C–Sn bond forming or breaking). After refinement the characterization of stationary points was done by Hessian matrix calculations, with all positive eigenvalues for a minimum and only one negative eigenvalue for the TSs. The energy informed for TSs and radicals includes zero-point corrections.

Experimental section

General methods

Irradiation was conducted in a reactor equipped with two high pressure lamps model Philips HPI-T plus 400-W, CH_3I contaminated (air- and water-refrigerated).

Materials

Compounds **5** and **7**[31] were prepared following the procedures previously described in the literature and characterized accordingly. Compound **6** was synthesized by an improved procedure, from a mixture of 2-*exo*–7-*syn*-dibromobenzonorborn-5-ene[32,33] (1.0 g, 3.31 mmol, see ESI†) by reaction with potassium *tert*-butoxide-THF solution (450 mg in 8 mL) in dry and fresh distilled THF (10 mL). The resulting reaction mixture was stirred at rt for 15 h. After this time, the solvent was evaporated. The mixture was diluted with water and the aqueous solution was extracted with ether (3 × 30 mL), washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was filtered on a short florisil column (10 g) eluted with *n*-hexane to give 732 mg (92%) of monobromide **6** as the sole product. It was recrystallized from methylene chloride/*n*-hexane. Compounds **8** and **9** were commercially available.

Photostimulated reaction of 5 with Ph_2P^- in liquid ammonia

The following procedure is representative of all the reactions. Into a three-necked round-bottomed flask equipped with a coldfinger condenser charged with dry ice ethanol, a nitrogen inlet, and a magnetic stirrer was condensed 300 mL of ammonia previously dried with Na metal under nitrogen. Ph_3P (1.6 mmol) and Na metal (3.2 mmol) were added to form Ph_2P^- ions, and *t*-BuOH (3.2 mmol) was added to neutralize the amide ions formed. To this solution was added **5** (1.6 mmol) and then the solution was irradiated for the time indicated in Tables 1 and 2. The reaction was quenched by adding ammonium nitrate in excess, and the ammonia was allowed to evaporate. The residue was dissolved with water and extracted twice with Cl_2CH_2 (20 mL each). The products were oxidized with H_2O_2 and then quantified by GLC with the internal standard method. The same procedure was followed when the reaction was performed in the presence of *p*-DNB or DTBN, except that a given mol% with respect to the substrate of *p*-DNB or DTBN was added to the solution of nucleophile prior to the substrate addition.

Generation of Me_3Sn^- and Ph_3Sn^- anions

To 300 mL of dried and distilled ammonia Me_3SnCl (1.6 mmol) was added. Afterwards Na metal (3.2 mmol) was added to form Me_3Sn^- ions. Starting with Ph_3SnCl the same procedure was followed to generate Ph_3Sn^- ions.

Product characterization

The stereochemistry of the substitution products was unambiguously assigned on the basis of their ^3J(Heteroatom (Sn, P)^{13}C). Based on Karplus equation, the coupling constant depends on the value of the dihedral angle formed between the heteroatom and a fourth carbon separated by three bonds.[34] The highest ^3J value corresponds to a dihedral angle of 180°, an intermediate value to a dihedral of 0° with a minimum located at a dihedral around 80–100°. Calculations performed with the B3LYP functional and the 6-31+G basis set show the dihedral angle between the heteroatom and the nearest $C_{aromatic}$ for the *anti* compounds **10a–12a** to be −178.692°; the dihedral with the $C_{olefinic}$ being around −71.143° (−68.901°). The opposite holds for the *syn* isomers **10b–12b**. Similarly, for compounds **13–14** the dihedral with the $C_{olefinic}$ is around 71.83° and approximately 178.204° with the cyclobutyl carbons. For compounds **15–16** the dihedral heteroatom-olefinic carbon is around 180°.

***syn*-7-Bromobenzonorbornadiene (6).** White solid, mp = 56–57 °C; lit[32a] mp = 61.1–61.7 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 3.99 (2H, m); 4.65 (1H, m); 6.82 (2H, m); 7.08 (2H, AA′ part of AA′BB′ system); 7.32 (2H, BB′ part of AA′BB′ system); ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 57.2; 75.4; 123.9; 125.6; 142.1; 147.1. Mass: MS (EI, 70 eV) 221/219 (M+, 19), 141 (M+ − Br, 100), 115 (indenyl cation, 42), 90 (6), 63 (7). Elemental analyses: C, 59.99; H, 4.04 (found); C, 59.76; H, 4.10 (calculated).

(1*R*(*S*),2*S*(*R*),9*R*(*S*),10*S*(*R*))-13-*anti*-Bromotetracyclo[8.2.1.0^{2,9}.0^{3,8}]-trideca-3,5,7,11-tetraene (7). Colorless crystals from methylenchloride/*n*-hexane (1 : 5). m.p. 91 °C; lit[31a] m.p. 93–93.5 °C (from methanol). ^{1}H-NMR (200 MHz, $CDCl_3$): δ_H: 7.27–7.01 (4H); 6.25 (2H, m); 3.64 (1H, m); 3.30 (2H, m); 3.09 (2H, m). ^{13}C-NMR (50 MHz, $CDCl_3$): δ_C: 145.9; 136.5; 129.9; 124.2; 65.7; 51.6; 49.0. *m*/*z* 247/246 (M+, 6); 167 (M+ − Br, 100); 152 (49); 115 (10); 102 (55); 82 (35).[31b]

***anti*-7-Trimethylstannylbenzonorbornadiene (10a).**[35] Colorless liquid. Isolated by column chromatography eluted with hexane. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 0.07 (9H, s, $^{CH_3\text{-}Sn}J$ = 26.0 Hz); 2.55 (1H, s); 4.00 (2H, b s); 6.81 (2H, b t, J = 1.7 Hz); 6.88 (2H, AA′ part of AA′BB′ system); 7.18 (2H, BB′ part of AA′BB′ system). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: −9.2; 54.2; 78.5; 120.5; 123.7; 144.3; 154.1 ($^{C\text{-}Sn}J$ = 26.2 Hz). ^{3}J(Sn–$C_{aromatic}$) = 26.2 Hz, ^{3}J(Sn–$C_{olefinic}$) = 0 Hz. *m*/*z*: 115.1 (52.2); 141.1 (100); 142.1 (12.8); 163.05 (8.45); 165.05 (10.72); 287.05 (23.6); 288.05 (16.1); 289.05 (42.1); 290.0 (17.6); 291.1 (56.3). HR MS (EI) calcd for $C_{14}H_{18}Sn$ 306.0425, found 306.0419.

***syn*-7-Trimethylstannylbenzonorbornadiene (10b).** Colorless liquid. Isolated (18%) by column chromatography eluted with hexane. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: −0.31 (s, 9H, $^{CH_3\text{-}Sn}J$ = 25.9 Hz); 2.45 (t, 1H, J = 1.2 Hz); 3.94 (dd, 2H, J = 1.8; 1.5 Hz); 6.83 (AA′ part of AA′BB′ system, 2H); 6.92 (t, 2H, J = 1.8 Hz); 7.13 (BB′ part of AA′BB′ system, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: −10.9; 54.4; 76.9; 121.8; 124.1; 146.0 ($^{C\text{-}Sn}J$ = 27.3 Hz); 152.5. ^{3}J(Sn–$C_{aromatic}$) = 0 Hz, ^{3}J(Sn–$C_{olefinic}$) = 27.3 Hz. *m*/*z*: 115.1 (39.8); 141.1 (100); 142.1 (12.9); 163.05 (6.9); 165.05 (9.3); 287.05 (19.9); 288.05 (13.1); 289.05 (33.7); 290.0 (14.4); 291.05 (42.8). HR MS (EI) calcd for $C_{14}H_{18}Sn$ 306.0425, found 306.0419.

***anti*-7-Triphenylstannylbenzonorbornadiene (11a).** Colorless liquid. Isolated (30%) by column chromatography eluted with hexane. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 3.05 (1H, t, J = 1.1 Hz); 4.09 (1H, c, J = 1.6 Hz); 6.68 (2H, t, J = 1.9 Hz); 6.79 (2H, AA′ part of AA′BB′ system); 7.08 (2H, BB′ part of AA′BB′ system); 7.20–7.48 (15H, cplx. m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 54.3; 78.4; 120.9; 124.0; 128.4; 128.68; 128.74; 128.8; 137.1; 137.5; 139.1; 139.6; 145.3; 153.0 ($^{C\text{-}Sn}J$ = 31.2 Hz). ^{3}J(Sn–$C_{aromatic}$) = 31.2 Hz, ^{3}J(Sn–$C_{olefinic}$) = 0 Hz. *m*/*z*: 115.2 (75); 116.05 (35.4); 117.05 (13.3); 118.1 (45.5); 119.15 (18.8); 119.15 (18.85); 120.05 (53.38); 141.2 (100); 193.15 (28.3); 194.1 (11.7); 195.05 (37.6); 196.15 (18.1); 197.1 (52.3); 270.1 (12.2); 271.1 (11.4); 272.1 (26.3); 273.05 (13.4); 274.1 (29.3); 347.05 (27.77); 348.15 (20.4); 349.1 (51.1); 350.1 (29.1); 351.2 (63), 352.3 (17.2); 353. (11); 414.1 (4.96); 415.1 (10.7); 416.05 (4.11). HR MS (EI) calcd for $C_{29}H_{24}Sn$ 492.0895, found 492.0886.

***syn*-7-Triphenylstannylbenzonorbornadiene (11b).** Colorless liquid. Isolated (10%) by column chromatography eluted with hexane. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 3.04 (1H, t, J = 1.2 Hz); 4.10 (2H, c, J = 1.7 Hz); 6.60 (2H, AA′ part of AA′BB′ system); 6.82 (2H, BB′ part of AA′BB′ system); 6.91 (2H, b t, J = 1.8 Hz); 7.14–7.27 (15H, cplx. m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 54.2; 76.9; 122.3; 124.3; 128.1; 128.5; 137.0; 138.6; 145.7 ($^{C\text{-}Sn}J$ = 31.8 Hz); 151.7. ^{3}J(Sn–$C_{aromatic}$) = 0 Hz, ^{3}J(Sn–$C_{olefinic}$) = 31.8 Hz. *m*/*z*: 115.20 (50.76); 118.05 (19.42); 120.05 (23.63); 141.20 (100); 193.15 (17.76); 195.40 (21.85); 196.05 (10.64); 197.15 (28.64); 208.20 (14.34); 218.25 (42.02); 347.20 (26.23); 348.05 (19.88); 349.10 (50.58); 350.05 (26.56); 351.20 (62.95); 352.15 (13.03). HR MS (EI) calcd for $C_{29}H_{24}Sn$ 492.0895, found 492.0886.

***anti*-7-Diphenylphosphineoxidebenzonorbornadiene (12a).** White wax. Isolated (30%) by column chromatography eluted with CH_2Cl_2/ethyl ether (80/20). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 3.62 (1H, dt, J = 4.5, 1.1 Hz); 4.17 (2H, m); 6.60 (2H, t, J = 1.9 Hz); 6.93 (2H, AA′ part of AA′BB′ system); 7.20 (2H, BB′ part of AA′BB′ system); 7.40–7.56 (6H, cplx. m); 7.68–7.78 (4H, cplx. m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 51.9; 80.4 ($^{C\text{-}P}J$ = 68.4 Hz); 121.3 ($^{C\text{-}P}J$ = 0.7 Hz); 124.6 ($^{C\text{-}P}J$ = 0.7 Hz); 128.5 ($^{C\text{-}P}J$ = 11.5 Hz); 131.0 ($^{C\text{-}P}J$ = 8.9 Hz); 131.5 ($^{C\text{-}P}J$ = 2.7 Hz); 133.6 ($^{C\text{-}P}J$ = 98.0 Hz); 140.7; 151.7 ($^{C\text{-}P}J$ = 12.7 Hz). ^{3}J(P–$C_{aromatic}$) = 12.7 Hz, ^{3}J(P–$C_{olefinic}$) = 0 Hz. ^{31}P-NMR ($CDCl_3$) δ_P: 23.8. *m*/*z* 77.1 (22.6); 115.1 (37); 128.0 (7); 141.15 (34.2), 183.05 (13.9); 201.1 (46.8); 202.1 (27.0); 215.05 (15.5); 216.0 (14.5); 217.05 (17.97); 341.1 (35.9); 342 (100); 343.1 (28.9). HR MS (ESI) calcd for $C_{23}H_{19}OPH$ 343.1246, found 343.1238.

***syn*-7-Diphenylphosphineoxidebenzonorbornadiene (12b).** White wax. Isolated (30%) by column chromatography eluted with CH_2Cl_2/ethyl ether (80/20). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 3.68 (1H, b c, J = 1.2 Hz); 4.18 (2H, b q, J = 1.6 Hz); 6.71 (2H, AA′ part of AA′BB′ system); 6.89 (2H, BB′ part of AA′BB′ system); 6.97 (2H, b dd, J = 3.5, 1.7 Hz); 7.28–7.52 (10H, cplx. m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 51.9; 79.4 ($^{C\text{-}P}J$ = 65.6 Hz); 122.4; 125.7; 128.2 ($^{C\text{-}P}J$ = 11.6 Hz); 130.7 ($^{C\text{-}P}J$ = 9.0 Hz); 131.1 ($^{C\text{-}P}J$ = 2.8 Hz); 133.1 ($^{C\text{-}P}J$ = 97.4 Hz); 145.2 ($^{C\text{-}P}J$ = 13.3 Hz); 147.9. ^{3}J(P–$C_{aromatic}$) = 0 Hz, ^{3}J(P–$C_{olefinic}$) = 13.3 Hz. ^{31}P-NMR ($CDCl_3$) δ_P: 222.4. *m*/*z*: 77.1 (21.9); 115.1 (47); 128.0 (17); 141.15 (95.5), 183.05 (11.6); 201.1 (39.8); 341.2 (75.6); 342 (100); 343.1 (29.5). HR MS (ESI) calcd for $C_{23}H_{19}OPH$ 343.1246, found 343.1247

***anti*-7-Trimethylstannylcyclobutabenzonorbornene (13a).** Colorless liquid. Isolated (40%) by column chromatography eluted with hexane. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: −0.084 (9H, s, $^{CH3\text{-}Sn}J$ = 25.2 Hz); 0.92 (1H, b s); 2.88 (2H, cplx. m); 3.21 (2H, s); 6.20 (2H, td, J = 1.8, 0.4 Hz); 7.07 (2H, AA′ part of AA′BB′ system); 7.2042 (2H, BB′ part of AA′BB′ system). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: −9.1; 40.0; 45.5; 48.4 ($^{C\text{-}Sn}J$ = 26.5 Hz); 121.8; 127.0; 137.7 ($^{C\text{-}Sn}J$ = 4.7 Hz); 146.2. ^{3}J(Sn–$C_{cyclobutyl}$) = 26.5 Hz, ^{3}J(Sn–$C_{olefinic}$) = 4.7 Hz. *m*/*z*: 102.1 (21.75); 152.1 (31.7); 161 (36.2); 162 (21.4); 163 (48.4); 164 (29.2); 165.1 (66.3); 166.1 (17.7); 166.7 (100); 168.2 (24.9); 169.05 (14.8); 185.0 (11.95); 313 (17); 314.05 (11.6); 315 (28.3); 316 (13.5); 317 (34.1). HR MS (EI) calcd for $C_{16}H_{20}Sn$ 332.0587, found 332.0594.

***anti*-7-Diphenylphosphineoxidecyclobutabenzonorbornene (14a).** White wax. Isolated (30%) by column chromatography eluted with CH_2Cl_2/ethyl ether (80/20). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 2.30 (1H, s); 3.12 (2H, b s); 3.28 (2H, d, J = 2.9 Hz); 6.05 (2H, b s); 7.13 (2H, AA′ part of AA′BB′ system); 7.28 (2H, BB′ part of AA′BB′ system); 7.31–7.49 (10H, cplx. m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 44.0; 48.6 ($^{C\text{-}P}J$ = 12.4 Hz); 52.2 ($^{C\text{-}P}J$ = 80.30 Hz); 122.2; 127.9; 128.3 ($^{C\text{-}P}J$ = 11.54 Hz); 130.8 ($^{C\text{-}P}J$ = 8.73 Hz); 131.1 ($^{C\text{-}P}J$ = 2.74 Hz); 134.0 ($^{C\text{-}P}J$ = 1.2 Hz); 134.3 ($^{C\text{-}P}J$ = 98.4 Hz); 144.9. ^{3}J(P–$C_{cyclobutyl}$) = 12.4 Hz, ^{3}J(P–$C_{olefinic}$) = 1.2 Hz. ^{31}P-NMR ($CDCl_3$) δ_P: 227.7. *m*/*z*: 51.1 (16.1); 77.1 (37.1); 102.1 (95.7); 103.1 (13.8); 115.1 (12.7); 152.1 (21); 155.2 (12.9); 165.1 (71.1); 166.1 (100); 167.1 (36.3); 183.05 (11.9); 201.1 (89.1); 202.1 (46.7); 203.1 (74.8); 204 (12); 367.1 (25.7); 368.1 (26.9); 369.1 (8.9). HR MS (EI) calcd for $C_{25}H_{21}OPH$ 369.1403, found 369.1407.

***anti*-7-Trimethylstannylnorbornene (15).** Colorless liquid. Isolated (60%) by column chromatography eluted with hexane. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 0.07 (9H, s, $^{CH3\text{-}Sn}J$ = 24.8 Hz); 1.04 (2H, dm, J = 7.7); 1.33 (1H, m, J = 1.22 Hz); 1.59 (2H, dm, J = 7.89 Hz); 3.04 (2H, m, J = 1.5 Hz); 6.23 (2H, t, 1.75 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: −10.3; 24.9; 45.5; 51.2; 138.2 ($^{C\text{-}Sn}J$ = 33.5 Hz). ^{3}J(Sn–$C_{olefinic}$) = 33.5 Hz. m/z 77.05 (24.74); 91.10 (35.33); 93.15 (100); 94.10 (7.50); 133 (4.71); 135.00 (5.97); 161.00 (6.08); 163.05 (9.89); 165.05 (13.37); 241.05 (13.16); 243.05 (17.62); 247.05 (2.99); 258.05 (2.76). HR MS (EI) calcd for $C_{10}H_{18}Sn$ 258.0425, found 258.0435.

***anti*-7-Diphenylphosphineoxidenorbornene (16).** White wax. Isolated (70%) by column chromatography eluted with CH_2Cl_2/ethyl ether (80/20). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 0.94 (2H, d, J = 7.2 Hz); 2.22 (1H, d, J = 1.6 Hz); 2.24 (2H, d, J = 8.4 Hz); 2.92 (2H, s); 6.11 (2H, b d, J = 1.4 Hz); 7.40 (6H, m); 7.68 (4H, dd, J = 10.9, 6.9 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 23.4; 43.8; 56.0 ($^{C\text{-}P}J$ = 67.0 Hz); 128.6 ($^{C\text{-}P}J$ = 11.3 Hz); 130.8 ($^{C\text{-}P}J$ = 8.7 Hz); 131.5 ($^{C\text{-}P}J$ = 2.7 Hz); 133.3 ($^{C\text{-}P}J$ = 96.7 Hz); 137.7 ($^{C\text{-}P}J$ = 15.7 Hz). ^{3}J(P–$C_{olefinic}$) = 15.7 Hz. m/z: 51.0 (9.9); 65.0 (8.4); 77.0 (34.4); 91.0 (20.3); 93.1 (8.8); 125.0 (9.4); 155.2 (23.2); 183.0 (8.7); 201.1 (79.9); 202.1 (100.0); 203.1 (23.1); 293.1 (8.4); 294.1 (55.1); 295.1 (11.7). HR MS (EI) calcd for $C_{19}H_{19}OPH$ 295.1246, found 295.1249.

7-Trimethylstannylnorbornane (17). Colorless liquid. Isolated (50%) by column chromatography eluted with hexane. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 0.04 (9H, s, $^{CH3\text{-}Sn}J$ = 25.1 Hz); 1.019 (1H, b m); 1.16 (2H, dm, J = 7.1 Hz); 1.29 (2H, cplx. m); 1.35–1.47 (4H, cplx. m); 2.38 (2H, b dd, J = 5.5, 4.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: −9.8; 30.0 ($^{C\text{-}Sn}J$ = 5.9 Hz); 31.4 ($^{C\text{-}Sn}J$ = 32.3 Hz); 38.8; 40.3. m/z 67.10 (25.17); 95.15 (19.71); 130.95 (10.72); 132.00 (6.62); 132.95 (17.67); 134.95 (22.62); 147.00 (26.16); 148.00 (17.51); 149.00 (40.98); 150.00 (21.50); 151.00 (52.79); 161.00 (31.32); 162.00 (17.33); 163.00 (52.87); 164.00 (20.18); 165.00 (69.76); 167.00 (9.62); 169.00 (12.12); 241.05 (43.30); 242.05 (27.37); 243.05 (74.37); 244.05 (32.16); 245.05 (100); 247.05 (14.38); 249.10 (17.06); 260.10 (1.88). HR MS (FD) calcd for $C_{10}H_{20}Sn$ 260.0582, found 260.0574.

7-Diphenylphosphineoxidenorbornane (18). White wax. Isolated (60%) by column chromatography eluted with CH_2Cl_2/ethyl ether (80/20). ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 1.16 (2H, b d, J = 7.2 Hz); 1.25 (2H, dd, J = 7.4, 5.7 Hz); 1.56 (2H, m); 2.13 (3H, b m); 2.41 (2H, b m); 7.34–7.47 (6H, cplx. m); 7.66–7.74 (4H, cplx. m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C: 29.0 ($^{C\text{-}P}J$ = 1.0 Hz); 31.5 ($^{C\text{-}P}J$ = 15.4 Hz); 39.7 ($^{C\text{-}P}J$ = 0.9 Hz); 48.7 ($^{C\text{-}P}J$ = 75.7 Hz); 128.5 ($^{C\text{-}P}J$ = 11.4 Hz); 130.7 ($^{C\text{-}P}J$ = 8.8 Hz); 131.4 ($^{C\text{-}P}J$ = 2.7 Hz); 134.1 ($^{C\text{-}P}J$ = 97.0 Hz). ^{31}P-NMR ($CDCl_3$) δ_P: 29.9. m/z: 77.05 (27.77); 78.10 (10.32); 125.05 (17.79); 155.15 (22.43); 183.10 (11.79); 132.95 (17.67); 134.95 (22.62); 147.00 (26.16); 148.00 (17.51); 149.00 (40.98); 150.00 (21.50); 151.00 (52.79); 161.00 (31.32); 162.00 (17.33); 163.00 (52.87); 164.00 (20.18); 165.00 (69.76); 167.00 (9.62); 169.00 (12.12); 192.10 (16.61); 201.10 (56.92); 202.10 (61.60); 203.10 (10.48); 241.10 (55.40); 242.10 (100.00); 243.15 (14.92); 267.10 (41.67); 268.15 (8.77); 295.10 (50.60); 296.10 (67.18); 297.15 (11.60). HR MS (ESI) calcd for $C_{19}H_{21}OPH$ 297.1403, found 297.1407.

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24 Based on theoretical grounds and even higher reactivity than the experimental one would have been expected for **5** or **6** (E_a for *anti*-coupling = 3 kcal mol^{-1}) *vs.* **8** (E_a for *anti*- or *syn*-coupling ≈ 5 kcal mol^{-1}) (see Table 5).

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