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The first evidence for a transient stibaallene ArSb=C=CR_2

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Abstract

Dechlorofluorination of ArSb(F)–C(Cl)=CR_2 (CR_2 = fluorenylidene, Ar = 2,4,6-tri-*tert*-butylphenyl) by *tert*-butyllithium afforded a 3,4-bis(fluorenylidene)-1,2-distibacyclobutane. The formation of the latter probably involves the transient stibaallene ArSb=C=CR_2 followed by a head-to-head dimerization via two Sb=C double bonds. Molecular orbital calculations at the ab initio and DFT levels support the head-to-head dimerization of ArSb=C=CR_2 with the formation of a 1,2-distibacyclobutane.
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1. Introduction

A growing variety of compounds containing stable double bonds between carbon and main group heavy elements have been reported in the last years. More recently, much has been accomplished in the synthesis of stable heteroallenes E=C=E′ (E, E′ = C, Si, Ge, Sn, P, As, O, S) [1]. Based on their unique geometric and electronic structures, compounds containing cumulated double bonds to a group 14 or 15 element are particularly interesting and important molecules. In the field of –E_{15}=C=C< compounds, ketenimines (E = N) have been known for a long time, many phosphaallenes (E = P) have been prepared [1a,1c,1d] since the synthesis of the first one by both Appel and Yoshifuji [2], and one arsaallene (E = As) [3] has been obtained and isolated as an air and moisture stable derivative.

By contrast, no stibaallene (E = Sb) could be until now isolated or even postulated as a transient intermediate: antimony–carbon doubly bonded compounds have a higher tendency to dimerize than their phosphorus or arsenic analogues since the stabilization of such low coordinate derivatives is more and more difficult going down a column.

We present in this paper the first evidence for the formation of the transient stibaallene ArSb=C=CR_2.

2. Results and discussion

As phospha- and arsaallenes ArE=C=CR_2 (Ar = 2,4,6-tri-*tert*-butylphenyl, CR_2 = fluorenylidene) (E = As [3], P [4]) could be easily isolated, we chose to substitute the antimony atom by the same well-known stabilizing "supermesityl" group and to include the terminal carbon atom in a fluorenylidene group which provides a large steric hindrance with three fused cycles.

Many phosphaallenes –P=C=C< [1a,1c,1d] and the arsaallene ArAs=C=CR_2 [3] have been prepared by routes involving the initial formation of the P(or As)=C double bond. Such pathways were successful owing to the rather good stability of P=C [1c,5] and As=C [3,6]

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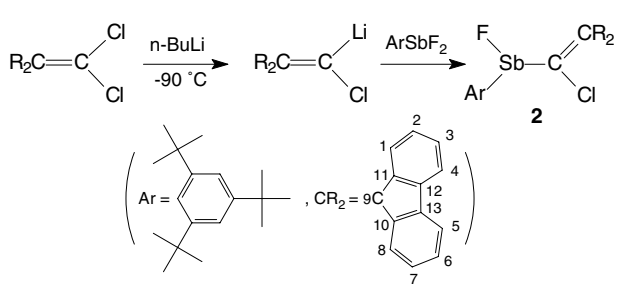
double bonds provided that the steric protection around the double bonds was important enough. But it is significantly more difficult to form and isolate compounds with Sb=C bonds [7]. Only few of them have been isolated as crystalline products: the stibaenols R(CO)Sb=C(OH)R (R = *t*-Bu, Mes, Ar) [8] and two 2,3-distibabutadienes R′(Me_3SiO)C=Sb–Sb=C(Me_3-SiO)R′ (R′ = Mes, Ar) [9]. The stibaalkene 2-Pyr(Me_3-Si)$_2$C–Sb=C($SiMe_3$)2-Pyr (Pyr = C_5H_4N) [10] has been obtained as an oil and other two have been physicochemically or chemically characterized [11]. Thus, for the synthesis of the stibaallene ArSb=C=CR_2, it appeared better to create the Sb=C double bond in the final step by a dechlorofluorination of a 2-chloro-3-fluorostibapropene with *tert*-butyllithium. Such a route was successfully used for the preparation of a heteroallene with a heavy group 14 element, the germaallene Tbt(Tip)Ge=C=CR_2 [12] (Tbt = 2,4,6-tris[bis(trimeth- ylsilyl)methyl]phenyl).

Stibapropene **2** was obtained nearly quantitative yield from the aryldifluorostibane $ArSbF_2$ (prepared from trifluoroantimony and ArLi), and the carbenoid R_2C=C(Cl)Li (obtained in situ from R_2C=CCl_2 [13]) (see Scheme 1).

Compound **2** was characterized by mass spectrometry and particularly by NMR spectroscopy which displays as expected non equivalent aromatic rings of the fluorenylidene group: four doublets were observed for $H_{1,4,5\,\text{and}\,8}$ in ^{1}H NMR and eight signals for the aromatic carbons in the ^{13}C NMR spectrum. The protons of the *o*-*tert*-butyl groups appear in the form of a broad singlet indicative of a slow rotation of the Ar group. This is confirmed by the ^{13}C NMR spectrum in which the methyl groups of *o*-*tert*-butyl groups also appear as a broad signal.

Addition of *tert*-butyllithium to a THF solution of **2** at low temperature afforded 1,2-bis(2,4,6-tri-*tert*-butylphenyl)-3,4-bis(9-fluorenylidene)-1,2-distibacyclobutane **3**.

Suitable single crystals for an X-ray analysis could not be obtained for **3**. However, its structure has been unambiguously determined by other physicochemical methods. In mass spectrometry by chemical ionization (NH_3), the protonated molecula peak was observed at



Scheme 1.

m/*z* 1087. Two main fragments were detected at 543 and 352, corresponding to ArSb=C=CR_2 + H and R_2C=C=C=CR_2, respectively, obtained by a [2 + 2] decomposition of **3** according to routes (a) and (b) (Scheme 2). By electronic impact, one of the major fragments correspond to *m*/*z* 352. The head-to-head dimeric structure of **3** indicated by mass spectrometry was confirmed by ^{1}H and ^{13}C NMR data very similar spectra to those of the stibapropene **2**, with the non equivalence of carbon and proton atoms of the two six-membered rings in both fluorenylidenes. This result rules out the head-to-tail dimer, in which these two six-membered rings should be equivalent, leading to two doublets and two triplets for the protons of the CR_2 group in ^{1}H NMR, and only four signals for C_{1-8} in ^{13}C NMR.

Whereas the head-to-tail dimer **4** could have resulted from the coupling of two molecules of the intermediate lithio-compound R_2C=C(Li)–Sb(F)Ar, the head-to-head dimer **3** can only be obtained from the transient stibaallene **1**. This reaction represents the first evidence for the formation of a stibaallenic compound. Moreover, to the best of our knowledge, such a four-membered heterocycle containing two adjacent antimony atoms has never been previously reported.

Similar transient allenes substituted by a fluorenylidene group have been evidenced by their dimer: the transient chloroallene R_2C=C=C(Ph)Cl has been postulated to give the 1,2-bis(9-fluorenylidene)cyclobutane **5** by a head-to-head dimerization as in the case of **1** [14] (see Scheme 3).

A ^{1}H NMR spectrum similar to that of **3**, with unequivalent protons and carbons in both fluorenylidene groups, was observed [14]. Some head-to-head dimerizations by the Si=C double bond of silaallenes Ar'_2Si=C=C($SiMe_3$)$_2$ (Ar′=Ph [15a,15b], *o*-, *m*- and *p*-Tol [15c]) leading to 1,2-disilacyclobutanes with two exocyclic C=C bonds have also been reported.

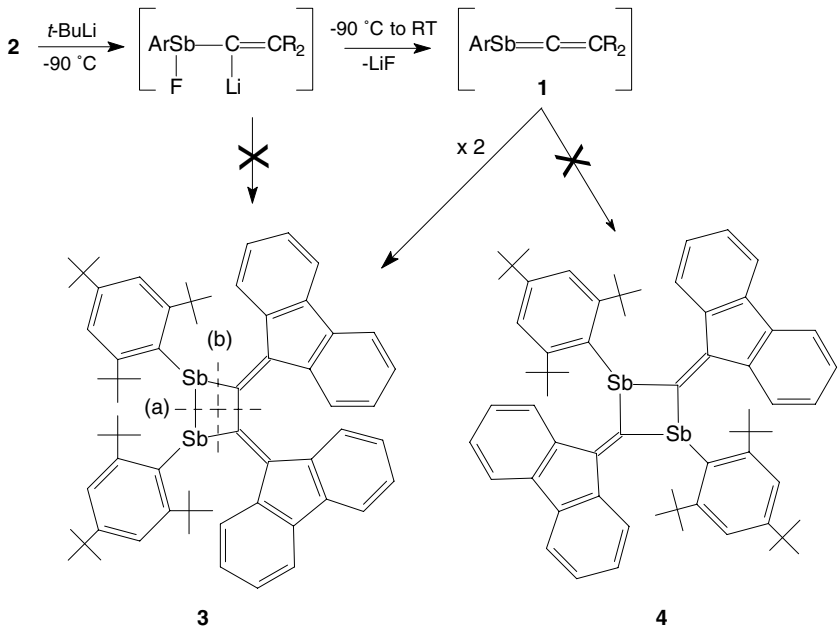
2.1. A molecular orbital insight into the dimerization of *1*

Molecular orbital calculations at the PM3 level have been carried out on the transient stibaallene ArSb=C=CR_2 **1** and its head-to-head **3** and head-to-tail **4** (*cis* and *trans*) dimers. The parent compound HSb=C=CH_2, **1H** and its dimers **3H** and **4H** have been considered also by ab initio and DFT treatments.

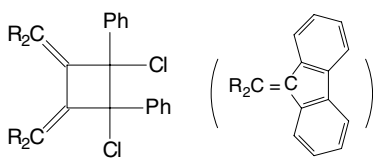
Fig. 1 shows the optimized structure of the lowest energy (*trans*-**3**) head-to-head dimer and Table 1 includes the calculated enthalpies of formation of **1**, **3** and **4**.

Data of Table 1 shows that there is a copious stabilization of the dimer against the monomeric stibaallene and that the head-to-head dimer **3** is much more favored than the head-to-tail dimer **4**. In both cases, the *trans* isomer is lower in energy.

More elaborate methods (ab initio and DFT) have been applied to **1H**, **3H** and **4H** in order to learn more



Scheme 2.



Scheme 3.

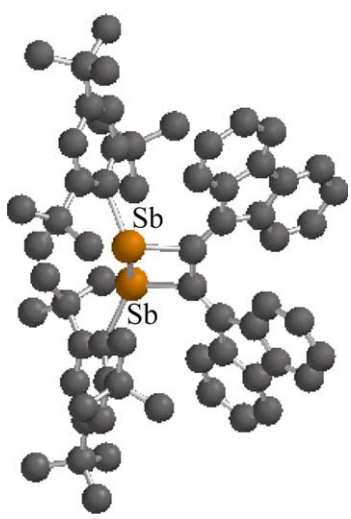


Fig. 1. The PM3 calculated structure of *trans*-**3** (hydrogen atoms omitted). Relevant geometry data for the Sb_2C_2 cycle: Sb–Sb = 2.733 Å, Sb–C = 2.175 Å, C–C = 1.435 Å, ∠SbCC = 102.40°, ∠CSbC = 69.95°, fold angle (along the Sb···C diagonal of the Sb2C2 ring) = 42.25°.

about the dimerization of the stibaallene. Table 2 includes the calculated energies at these two levels of theory.

Table 1
PM3 calculated enthalpies (kcal/mol) of **1**, **3** and **4**

System	ΔH_f	Dimerization energy ΔH_f(dimer)-2 × ΔH_f(monomer)	*cis–trans* relative energies
1	121.349		
cis-**3**	164.223	−78.475	+4.828
trans-**3**	159.395	**−83.303**	**0.0**
cis-**4**	193.967	−48.731	+8.520
trans-**4**	185.447	−57.251	0.0

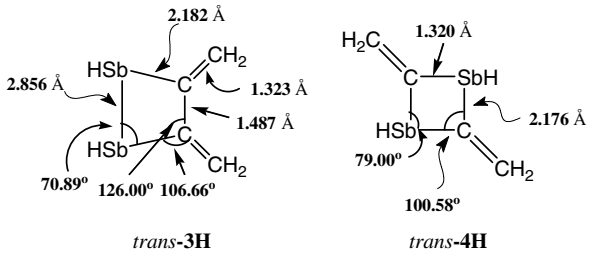
The main results coming out of these calculations are that the order of preference for the head-to-head dimerization is maintained and the HF method gives stabilization energies in the same range as the PM3 method. The DFT results are also in agreement with the preferred formation of the head-to-head *trans*-**3H** isomer. Note that similar finding has been reported from a HF study on the phosphagermaallene $H_2Ge{=}C{=}PH$ [16] where the Ge–Ge head-to-head [2 + 2] cycloaddition product was significantly more stable than the head-to-tail dimer.

Geometry data on the *trans* isomers of **3H** and **4H** are given in Scheme 4. While **4H** is predicted to be planar, **3H** is bent along the Sb···C diagonal. The two $C{=}CH_2$ moieties are in the same plane in *trans*-**4H** and twisted around the ring C–C bond in *trans*-**3H** by 42.58° (RHF). Some of the conjugation between the two $C{=}CH_2$ is however maintained since the central CC bond (1.487 Å) is still shorter than a normal single bond (as noticed also at the PM3 level within the real systems).

The inspection of the frontier orbitals of **1H** (Scheme 5) reveals that HOMO (−8.000 eV) and LUMO (1.497 eV) are composed mainly from antimony 5p and the

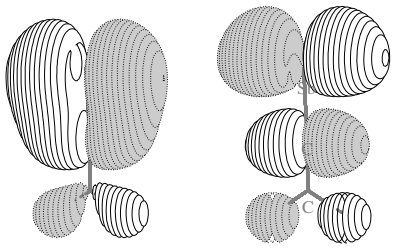
Table 2
Total (a.u.) and dimerization energies (kcal/mol) of the investigated models

System	RHF/gen		B3LYP/lanl2dz(dp)	
	Total	E(dimer) − 2 × E(monomer)	Total	E(dimer) − 2 × E(monomer)
1H	−316.6286888		−83.3271427	
cis-**3H**	−633.3844506	−79.75	−166.7586775	−65.51
trans-**3H**	−633.3897640	**−83.08**	−166.7635318	**−68.56**
cis-**4H**	−633.3488112	−57.39	−166.7334955	−49.71
trans-**4H**	−633.3483974	−57.12	−166.7335072	−49.71



trans-**3H** *trans*-**4H**

Scheme 4.



HOMO LUMO

Scheme 5.

central carbon 2p orbitals. Since the relative contributions from antimony are higher, it is expected that the primary interaction of two stibaallene fragments occurs between these two atoms and, first the Sb–Sb bond is formed.

Thus, both HOMO–LUMO interactions as well as the energy data support the experimental observation of the head-to-head dimers of **1**. The driving force for the head-to-head dimerization could be the formation of a dienic structure. Our efforts are now directed towards stabilization of stibaallenes using bulkier groups in order to avoid the approach of two molecules to dimerize.

3. Experimental

All experiments were carried out in flame-dried glassware under a nitrogen atmosphere using high-vacuum-line techniques. Solvents were dried and freshly distilled from sodium benzophenone ketyl and carefully deoxygenated on a vacuum line by several "freeze–pump–thaw" cycles. NMR spectra were recorded in $CDCl_3$ on the following spectrometers: ^{1}H, Bruker AC200 (200.13 MHz); ^{13}C{^{1}H}, Bruker AC200 (50.32 MHz) (reference TMS); ^{19}F, Bruker AC200 (188.30 MHz) (reference CF_3COOH). Melting points were determined on a Wild Leitz–Biomed apparatus. Mass spectra were obtained on a Hewlett–Packard 5989A spectrometer by EI at 70 eV and on a Nermag R10-10 spectrometer by CI.

HF ab initio and B3LYP hybrid DFT methods have been used to fully optimize the model HSb=C=CH_2 allene **1H** as well as the head-to-head and head-to-tail dimers of **1H.** The basis sets used were cc-pVDZ-PP for Sb [17] and 6-31G* on carbon and hydrogen for the HF calculations and Lanl2dz with (d, p) polarization functions [18] for antimony. Note that both of the basis functions on antimony account for the relativistic effects.

The ab initio and DFT calculations have been performed by using G98 suite of programs [19]. The basis sets and pseudopotentials were retrieved from the Pacific Northwest's Basis Set Library [20]. Semiempiric PM3 calculations on the real systems have been performed by using Spartan'02 from Wavefunction [21].

3.1. Synthesis of stibapropene 2

To an orange solution of 9-dichloromethylenefluorene (1.57 g, 6.36 mmol) in 15 ml of THF were added dropwise, at −78 °C, 4.2 ml (6.72 mmol) of *n*-BuLi (1.6 M in hexane); the solution turned purple and was stirred at this temperature for 15 min. The lithium compound was then added to a solution of $ArSbF_2$ (2.58 g, 6.36 mmol) in 15 ml of THF cooled at −78 °C. The reaction mixture turned green during stirring for 10 min, then it was allowed to warm to room temperature and turned yellow. Solvents were removed in vacuo and the residue dissolved in 20 ml of pentane/dichloromethane (50/50). After removal of the lithium salts by filtration, the resulting solution was crystallized to afford 3.18 g (83%) of **2** as a yellow powder (m.p. 155–160 °C). ^{1}H NMR δ: 1.35 (s, 9H, *p*-*t*-Bu); 1.42 (broad s, 18H, *o*-*t*-Bu); 7.24 and 7.35 (2t, $^3J_{HH}$ = 7.6 Hz, 2 × 2H, $HC_{2,3,6,7}$ CR_2); 7.43 (s, 2H, arom H Ar); 7.68 and 7.70 (2d, $^3J_{HH}$ = 7.6 Hz, 2 × 1H, two of $HC_{1,4,5,8}$ CR_2); 8.12 (d, $^3J_{HH}$ = 7.6 Hz, 1H, one of $HC_{1,4,5,8}$ CR_2); 8.56 (d, $^3J_{HH}$ = 7.6 Hz, 1H, one of $HC_{1,4,5,8}$ CR_2).

^{13}C NMR δ: 31.4 (p-C(CH$_3$)$_3$ Ar); 33.4 (broad s, o-C(CH$_3$)$_3$); 34.8 and 39.8 (o- and p-C(CH$_3$)$_3$); 119.3 and 119.9 (C$_4$ and C$_5$ CR$_2$); 124.1 (m-C Ar); 124.9 (d, J_{CF} = 2.8 Hz), 126.9, 127.7, 128.2 (d, J_{CF} = 4.6 Hz), 128.7 and 129.3 (CH CR$_2$); 138.1, 140.8, 142.8, 143.1, 145.3, 151.0, 156.4, 156.8 and 158.6 (o-, p- and $ipso$-C Ar, C=C and C$_{10–13}$ CR$_2$). ^{19}F NMR δ: −103.1. MS (EI, 70 eV, m/z, %): 598 (M, 1); 578 (M–F-1, 3); 385 (M-R$_2$C=C(Cl), 5); 365 (M-R$_2$C=C(Cl)–F– , 17); 245 (Ar, 28); 57 (t-Bu, 100). Anal. Calc. for C$_{32}$H$_{37}$SbClF (M = 597.85): C, 64.29; H, 6.24. Found: C, 64.50; H, 6.31%.

3.2. Synthesis of distibacyclobutane 3

1.20 ml (1.88 mmol) of t-BuLi (1.5 M in pentane) were added dropwise to a solution of ArSb(F)C(Cl)=CR$_2$ (1.02 g, 1.70 mmol) in a mixture THF/Et$_2$O (25/5 ml) cooled at −78 °C. The reaction mixture turned blue, was stirred for 10 min at this temperature and then allowed to warm to room temperature. After 30 min of stirring, solvents were removed under vacuum, 20 ml of pentane were added and the lithium salts were removed by filtration. Fractional crystallizations from pentane afforded 0.46 g (49%) of **3** as an orange powder (m.p. 170–173 °C). ^{1}H NMR δ: 1.37 (s, 18H, p-t-Bu Ar); 1.47 (s, 36H, o-t-Bu Ar); 7.04 (t, $^3J_{HH}$ = 7.6 Hz, 2H, two of HC$_{2,3,6,7}$ CR$_2$); 7.18–7.35 (m, 6H, six of HC$_{2,3,6,7}$ CR$_2$); 7.48 (s, 4H, arom H Ar); 7.64 (d, $^3J_{HH}$ = 7.6 Hz, 4H, four of HC$_{1,4,5,8}$ CR$_2$); 8.13 (d, $^3J_{HH}$ = 7.9 Hz, 2H, two of HC$_{1,4,5,8}$ CR$_2$); 8.64 (d, $^3J_{HH}$ = 7.9 Hz, 2H, two of HC$_{1,4,5,8}$ CR$_2$). ^{13}C NMR δ: 31.4 (p-C(CH$_3$)$_3$ Ar); 34.0 (o-C(CH$_3$)$_3$ Ar); 35.1 (p-C(CH$_3$)$_3$ Ar); 40.0 (o-C(CH$_3$)$_3$ Ar); 119.2, 119.6, 119.7, 123.3, 125.7, 126.5, 127.5, 128.2 and 128.9 (m-C Ar and CH CR$_2$); 138.2, 138.7, 139.8, 140.4, 140.7, 147.2, 150.0, 150.8 and 159.0 (o-, p- and $ipso$-C Ar, C=C and C$_{10–13}$ CR$_2$). MS (EI, 70 eV, m/z, %): 366 (ArSb, 6); 352 (R$_2$C=C–C=CR$_2$, 29); 245 (Ar, 49); 176 (C=CR$_2$, 8); 57 (t-Bu, 100). (CI/NH$_3$, m/z, %): 1087 (M + H, 5); 859 (M-Ar + NH$_4$, 4); 841 (M–Ar, 1); 577 (ArSb–C=CR$_2$ + N$_2$H$_7$, 100); 560 (ArSb–C=CR$_2$ + NH$_4$, 9); 543 (ArSb–C=CR$_2$ + H, 10); 367 (ArSb + H, 25); 280 (Ar + N$_2$H$_7$, 60); 246 (Ar + H, 62). Anal. Calc. for C$_{64}$H$_{74}$Sb$_2$ (M = 1086.79): C, 70.73; H, 6.86. Found: C, 70.50; H, 6.61%.

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