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Chlorophosphaalkenyl- and chloroalkenylstibanes

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ABSTRACT

Mono-, bis- and tris(chlorophosphaalkenyl)stibanes have been obtained from Mes*P=C(SiMe$_3$)Li (Mes* = 2,4,6-tri-*tert*-butylphenyl) or from the phosphaalkene carbenoid Mes*P=C(X)Li (X = Cl) and SbF_3, Mes*Sb(OMes*)F or Mes*SbF_2. Bis[chloroalkenyl]stibanes [R_2C=C(Cl)]$_2$SbCl (R_2C = fluorenylidene and 2,7-di-*tert*-butylfluorenylidene) have also been obtained from R_2C=C(Cl)Li and $SbCl_3$.

1. Introduction

A great number of phosphorus derivatives have been synthesized. By contrast, going down group 15, arsenic, antimony and bismuth compounds are less abundant. One of the reasons could be the lack of As, Sb or Bi NMR spectroscopy for characterization of compounds, whereas ^{31}P NMR spectroscopy is extremely useful. Furthermore, the element–carbon bonds are less strong for the heavier group 15 congeners.

We planned to prepare novel types of stibanes R_nSbX_{3-n} (R = chloroalkenyl >C=C(Cl) and chlorophosphaalkenyl –P=C(Cl) groups). The presence of the C=C and C=P unsaturations and of halogen atoms allowing further substitution or functionalization should increase their synthetic utilities. As previously observed from similar models, a chlorine atom on the sp^2 carbon atom can be easily replaced using a lithium compound at low temperature to afford E=C(Li)–E′ derivatives (E = R_2C, E′ = R_2Ge [1a], R_2Sn [1b], RSb [1c]; E = P, E′ = R_2Si [1d,1e,1f], RP [1g], R_2Ge [1h,1i]). Depending on E′, stable lithium, vic-halolithium or heteroallenic compounds can be obtained.

We present in this paper the synthesis of chlorophosphaalkenylstibanes [Mes*P=C(Cl)]$_{3-n}$SbR$_n$ (R = Mes*, Cl; n = 0,1), silylphosphaalkenylstibane [Mes*P=C(SiMe$_3$)]Sb(F)Mes* and chloroalkenylstibanes [>C=C(Cl)]$_2$SbCl starting from the commercially available SbX_3 (X = F, Cl).

2. Results and discussion

2.1. Phosphaalkenylstibanes

Depending on the substituents on the phosphaalkenyl group and on the antimony atom, it is possible to direct the reaction towards the first mono-, bis- or tris(phosphaalkenyl)stibanes.

2.1.1. Tris(phosphaalkenyl)stibanes

Phosphaalkenes –P=C< need great steric hindrance around the phosphorus–carbon double bond to be stabilized as monomers (for reviews, see Ref. [2]); for this goal the very bulky 2,4,6-tri-*tert*-butylphenyl group (Mes* called supermesityl) has often been used on the phosphorus atom to prevent dimerization. Owing to this group, some phosphaalkenyl compounds of the type Mes*P=C(X)–ERR′ (X = Cl, Br; E = heavier element of group 15 such as P [1g,3], or As [4]) have previously been stabilized and isolated. The best route to substitute E by the chlorophosphaalkenyl group Mes*P=C(Cl) is to use the kinetically stabilized carbenoid Mes*P=C(Cl)Li [5] **1** obtained from Mes*P=CCl_2 through a halogen metal exchange.

Reaction of **1** with SbF_3 at low temperature led exclusively to the new tris(phosphaalkenyl)stibane **2**. Surprisingly, even with a large excess of SbF_3, only the trisubstituted antimony derivative **2** was obtained (Scheme 1).

Compound **2** was isolated in the form of an air-stable powder. The phosphaalkenyl groups display a single set of signals in ^{1}H and ^{13}C NMR spectroscopy. A singlet at δ = 299.3 ppm was observed in the ^{31}P NMR spectrum. This more deshielded signal, in comparison with that of the starting dichlorophosphaalkene, is expected upon substitution of a chlorine atom by a more

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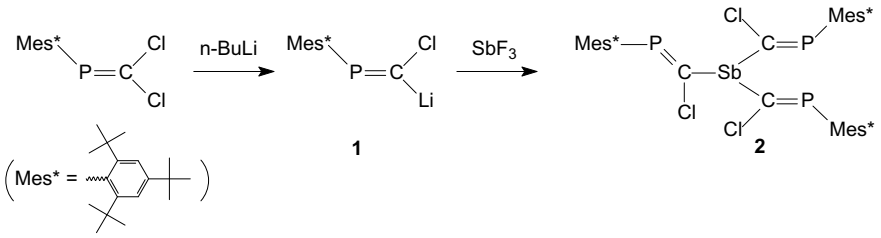


Scheme 1. Synthesis of tris(phosphaalkenyl)stibane **2**.

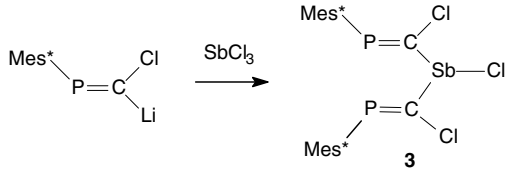
electropositive element [6]. According to these data, the three phosphaalkenyl groups adopt the same configuration, probably with the Mes* group and the Sb atom in a *trans* disposition since it has been demonstrated that the lithium halogen exchange preferentially takes place at the *E*-chlorine of Mes*P=CCl_2 and that phosphacarbenoid **1** is configurationally stable [5]. Unfortunately, a single crystal could not be obtained for the structural determination by X-ray to prove this stereochemistry.

2.1.2. Bis(phosphaalkenyl)stibanes

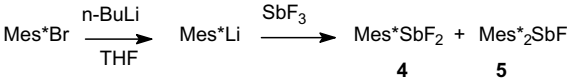
A bis(phosphaalkenyl)stibane (**3**) can be synthesized by using antimony trichloride, instead of antimony trifluoride, and two equivalents of carbenoid **1** (Scheme 2). A very small amount of tris(phosphaalkenyl)derivative **2** was also obtained. With a large excess of $SbCl_3$, a product with a ^{31}P chemical shift at 297.5 ppm was also formed in about 10% yield. As a further addition of carbenoid led to the disappearance of this product and an increase in amount of the bis- and trisubstituted derivatives, it can be tentatively assigned to the dichloro(phosphaalkenyl)stibane Mes*P=C(Cl)–$SbCl_2$. Few single crystals of **3** could be obtained and an X-ray analysis unambiguously proved its structure but, due to the poor quality of the crystal, a correct refinement was not possible. Compound **3** was also characterized by ^{31}P NMR spectroscopy with a unique signal at 300.3 ppm, very close to the signal observed for the trisubstituted derivative **2**. Like derivative **2**, **3** is probably obtained as the *E*,*E*-isomer.

Another class of antimony derivatives, with an aryl group instead of a halogen on the antimony atom, could be obtained starting from Mes*SbF_2 (the latter was obtained from the reaction of Mes*Li with SbF_3); whatever the experimental conditions (reactions at −78 °C, −30 °C or room temperature, addition of Mes*Li to SbF_3 or reverse addition and use of various solvent such as toluene, Et_2O or THF), a mixture of Mes*SbF_2 and Mes^*_2SbF was formed, but both compounds could be obtained in a pure state by fractional crystallization (Scheme 3). Thus, despite the high steric hindrance of the supermesityl group, two units can be easily put on antimony. Compound **4** was also prepared by a disproportionation reaction by heating equimolar amounts of Mes^*_2SbF **5** and SbF_3 under reflux in toluene.

In the reaction of carbenoid **1** with Mes*SbF_2, the exclusive formation of the bis(phosphaalkenyl)stibane **6** was observed in the form of only one isomer, probably the E, *E*-isomer for the reasons previously reported. As in the reaction of **1** with SbF_3, all the fluorine atoms are replaced, even when a large excess of **4** was used



Scheme 2. Synthesis of bis(phosphaalkenyl)stibane **3**.



Scheme 3. Synthesis of fluorostibanes **4** and **5**.

(Scheme 4). Interestingly, the same bis(phosphaalkenyl)stibane **6** could be obtained starting from alkoxyfluorostibane **7**, showing that both a fluorine or an alkoxy group, even extremely bulky, on antimony could be replaced by the phosphaalkenyl group.

Compound **6** presents an interesting structure for complexation of transition metals by the two phosphorus atoms, (for complexation of a transition metal by two Mes*P=C units, see Ref. [7]) and might be a potential precursor of a three-membered ring heterocycle of antimony by coupling of the two C(Cl) atoms.

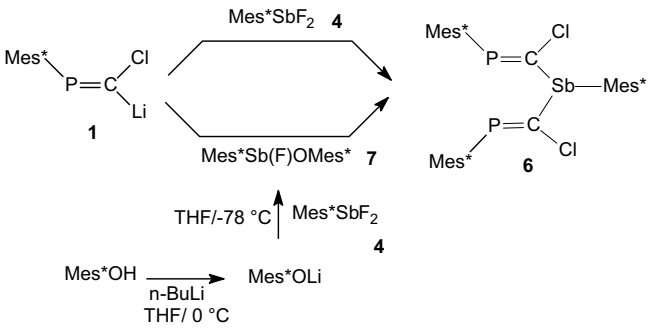
2.1.3. Mono(phosphaalkenyl)stibane

In order to obtain mono-substitution of the antimony atom by a phosphaalkenyl group, it was necessary to use the more hindered phosphaalkenyllithium compound **8** [5c], with a trimethylsilyl group instead of a chlorine atom, obtained from **9** [8]. Addition to the difluorostibane **4** led exclusively to **10** (Scheme 5).

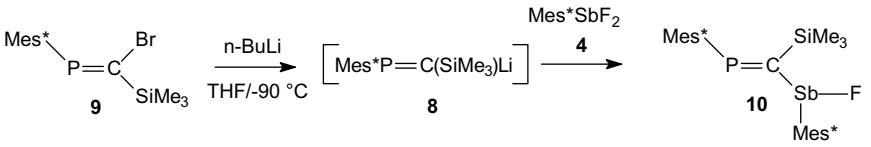
The greater bulkiness of the phosphaalkenyllithium **8** prevents the second fluorine atom in starting compound **4** from being replaced. Although lithium derivative **8** has been reported to isomerize rapidly [5c], the ^{31}P NMR analysis of the crude reaction mixture showed one isomer of fluoro(phosphaalkenyl)stibane **10** to predominate, probably the *E*-isomer since a similar result was noticed by Bickelhaupt et al. in the reaction of **8** with magnesium bromide or zinc chloride [5c].

2.2. Alkenylstibanes

Some mono-, bis- or tris(alkenyl)-substituted derivatives of antimony $[\gtrdot C{=}C(R)]_nSbR'_{3-n}$ have previously been prepared [9]; however most of them are substituted on the carbon atom bonded to antimony by hydrogen, alkyl or aryl groups which do not allow a further functionalization.



Scheme 4. Synthesis of bis(phosphaalkenyl)stibane **6**.



Scheme 5. Synthesis of mono(phosphaalkenyl)stibane **10**.

In order to increase the synthetic utility of alkenylstibanes, we planned to substitute, as in the case of phosphaalkenylstibanes, the sp^2 carbon atom bonded to antimony by a chlorine atom. Substituted fulvenyl groups $R_2C{=}C(Cl)$, with R_2C being a fluorenylidene or a 2,7-di-*tert*-butylfluorenylidene appeared promising: such groups, due to the bulkiness of the fluorenylidene moiety (3 fused rings), should display good stabilizing properties; moreover, compounds substituted by fluorenyl groups generally easily crystallize due in particular to their special planar geometry.

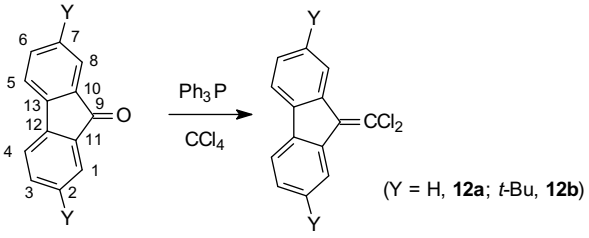
Like phosphaalkenyl derivatives, the best way to substitute antimony by the chloroalkenyl group $R_2C{=}C(Cl)$ is to use the kinetically stabilized alkene carbenoid $R_2C{=}C(Cl)Li$ **11a**,**b** obtained from $R_2C{=}CCl_2$ **12a**,**b** through a halogen/lithium exchange.

The starting new 9-(dichloromethylene)-2,7-di-*tert*-butylfluorene **12b** was prepared from 2,7-di-*tert*-butylfluorenone [10], according to the procedure described by Normant to synthesize **12a** [11] (Scheme 6). Compound **12b** was characterized by signals at 121.0 ($C{=}CCl_2$) and 150.3 ppm (CCl_2) in its ^{13}C NMR spectrum, and by an X-ray analysis which displays standard bond lengths and angles (Fig. 1) (Table 1).

Reaction of alkenylidene carbenoids **11a**,**b**, obtained from **12a**,**b** and *n*-BuLi at low temperature, with $SbCl_3$ led exclusively to the bis(alkenyl)stibanes **13a**,**b** (Scheme 7).

Derivatives **13a**,**b** have been characterized by mass spectrometry, ^1H and ^{13}C NMR spectroscopies which display as expected that all the proton and carbon atoms of a same fluorenylidene group are inequivalent and **13a** by an X-ray structural study (Fig. 2) (Table 1). C–Cl (1.750(6) and 1.755(7) Å), Sb–C (2.169(6) and 2.187(6) Å) and Sb–Cl (2.356(1) Å) bond lengths are close to the standard values: C–Cl (1.77 Å), Sb–C (2.13-2.20 Å) [12], Sb–Cl (2.36 Å) [13]. The $Cl_1C_1SbCl_3$ and $Cl_3SbC_{15}Cl_2$ torsion angles are quite different, showing a non-symmetrical molecule (see Fig. 2).

The formation of disubstitution derivatives **13** with alkenyllithium **11** must be compared to the formation of a mixture of bi- and trisubstitution compounds **3** and **2** with phosphaalkenyllithium **1** and $SbCl_3$. Even with an excess of $SbCl_3$, the compound with three $R_2C{=}C(Cl)$ groups was not formed. The decreasing in the substituting ability of $R_2C{=}C(Cl)Li$ compared to $Mes^*P{=}C(Cl)Li$ can be probably explained by a lower nucleophilicity of the more stabilized anion $[R_2C{=}CCl]^-$. This lower substituting ability of alkenyllithium **11** was also observed in the reaction of **11a** with Mes^*SbF_2, giving exclusively the mono(alkenyl)stibane **14a** (Scheme 8) [1c] whereas **1** led to the bis(phosphaalkenyl)stibane **6** (Scheme 4).



Scheme 6. Synthesis of fulvenes **12**.

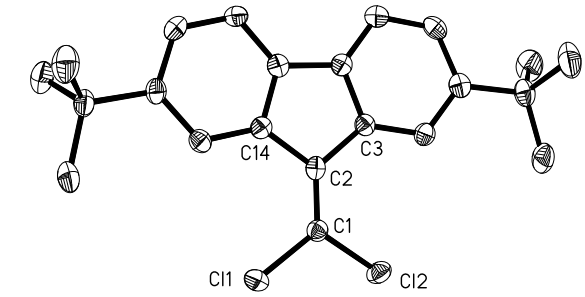
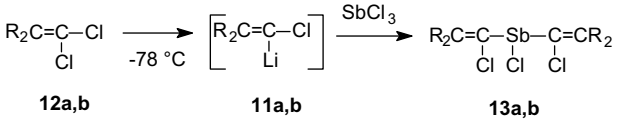


Fig. 1. Molecular structure (50% probability thermal ellipsoids) of **12b** with atom labeling scheme. Only one molecule of the two independent ones present in the asymmetric unit is depicted. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1–C2, 1.340(4); C1–Cl1, 1.723(3); C1–Cl2, 1.724(3); C2–C3, 1.491(3); C2–C14, 1.494(4); Cl1–C1–Cl2, 110.64(14); Cl1–C1–C2, 124.5(2); Cl2–C1–C2, 124.9(2); C1–C2–C3, 127.1(2); C1–C2–C14, 127.0(2); C3–C2–C14, 105.9(2).

Table 1
Crystal data for compounds **12b** and **13a**

	12b	**13a**
Empirical formula	$C_{22}H_{24}Cl_2$	$C_{28}H_{16}Cl_3Sb + CH_2Cl_2$
Formula weight	359.31	665.43
Temperature (K)	173(2)	193(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a (Å)	11.872(1)	20.557(2)
b (Å)	11.253(1)	5.577(1)
c (Å)	28.538(3)	22.146(2)
β	91.643(2)	
Volume (Å^3)	3811.0 (6)	2539.0(5)
Z	8	4
Absorption coefficient (mm^{-1})	0.341	1.631
Reflections collected	21834	12414
Independent reflections	7801	4547
R_{int}	0.0490	0.0517
Absorption correction	Semi-empirical	Semi-empirical
Minimum/maximum transmission	0.8193	0.5557
Data	7801	4547
Restraints	0	1
Parameters	445	317
Goodness-of-fit on F^2	0.982	1.012
Final R indices [$I > 2\sigma(I)$] R_1	0.0486	0.0422
wR_2	0.1106	0.0838
R indices (all data) R_1	0.0993	0.0589
wR_2	0.1330	0.0893
Largest difference in peak and hole (e Å^{-3})	0.329 and −0.268	0.735 and −0.599



Scheme 7. Synthesis of bis(alkenyl)stibanes **13**.

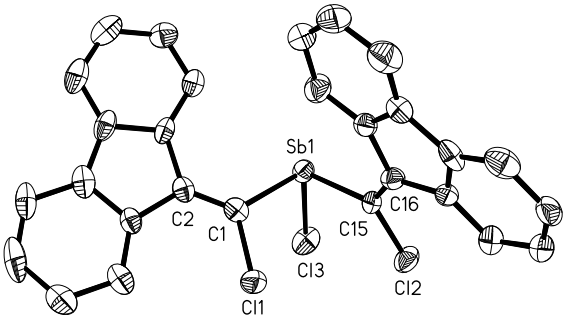
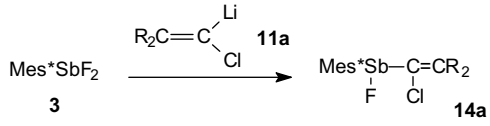


Fig. 2. Molecular structure (50% probability thermal ellipsoids) of **13a** with atom labeling scheme. Hydrogen atoms and a solvent molecule have been omitted for clarity. Selected bond lengths (Å), angles (°) and torsion angles (°): C1–C2, 1.348(9); C1–Cl1, 1.755(7); Sb–C1, 2.169(6); Sb–Cl3, 2.3558(14); Sb–C15, 2.187(6); C15–C16, 1.331(9); C15–Cl2, 1.750(6); Cl2–C15–Sb, 115.8(3); Cl2–C15–C16, 119.3(5); C1–Sb–C15, 94.7(3); C1–Sb–Cl3, 93.3(2); C2–C1–Cl1, 120.7(5); C2–C1–Sb, 128.6(5); Cl1–C1–Sb, 110.2(3); Cl3–Sb–C15, 96.9(2); Cl2–C15–Sb–Cl3, 9.0; Cl3–Sb–C1–Cl1, 51.9.



Scheme 8. Synthesis of monoalkenylstibane **14a**.

3. Conclusions

Various chlorophosphaalkenyl- and chloroalkenylstibanes have been obtained. It seems that the reaction rate increases from mono- to di- or trisubstitution of antimony by chlorophosphaalkenyl or chloroalkenyl groups. Indeed, the monosubstituted chlorophosphaalkenyl derivative **10** can only be obtained when the steric hindrance is large enough to prevent disubstitution.

These potentially functional chlorophosphaalkenyl- and chloroalkenylstibanes should be interesting building blocks in antimony chemistry. Their use as ligands with transition metals, as precursors of stibaallenes –Sb=C=X (X = C, P) by dehalogenation, and of three-membered rings of antimony are under active investigation.

4. 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 the vacuum line by several "freeze-pump-thaw" cycles. NMR spectra were recorded (with $CDCl_3$ as solvent) on the following spectrometers: ^{1}H, Bruker AC200 (200.13 MHz), Avance 300 (300.13 MHz); ^{13}C, Bruker AC200 (50.32 MHz), and Avance 300 (75.47 MHz) (reference TMS); ^{19}F, Bruker AC200 (188.30 MHz) (reference CF_3COOH); ^{31}P, Bruker AC200 (80.15 MHz) (reference H_3PO_4). 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. Carbon atoms of the fluorenylidene group are labeled as indicated in Scheme 6. SbF_3, Me_3SiCl, 2,4,6-tri-*tert*-butylphenol, *n*-BuLi (1.6 M in hexane) and *tert*-BuLi (1.5 M in pentane) were purchased from Acrōs.

4.1. Synthesis of [Mes*P=C(Cl)]$_3$Sb **2**

To a colorless solution of Mes*P=CCl_2 (0.82 g, 2.29 mmol) in THF (20 mL) were added dropwise, at −78 °C, 1.5 mL (2.40 mmol) of *n*-BuLi. The solution turned brown and was stirred at this temperature for 30 min. The lithium compound Mes*P=C(Cl)Li was then added to an excess of SbF_3 (0.82 g, 4.58 mmol) in THF (20 mL) cooled at −78 °C. The reaction mixture was stirred for 20 min and warmed up to room temperature. Solvents were removed in vacuo and the residue dissolved into pentane (20 mL). After removal of the lithium salts and excess of SbF_3 by filtration, the resulting solution was dried in vacuo to afford **2** (0.71 g, 86%) as a colorless powder (mp 215–217 °C).

^{1}H NMR (200.13 MHz): δ 1.32 (s, 27H, *p*-*t*-Bu), 1.48 (s, 54H, *o*-*t*-Bu), 7.39 (broad s, 6H, arom H).^{13}C NMR (50.32 MHz): δ 31.4 and 33.1 (*o*- and *p*-C(CH_3)$_3$), 35.1 (*p*-C(CH_3)$_3$), 37.9 (*o*-C(CH_3)$_3$), 122.0 (*m*-C), 136.2 (d, $^1J_{CP}$ = 71.3 Hz, *ipso*-C), 150.6 (*p*-C), 153.4 (*o*-C), 170.5 (dt, $^1J_{CP}$ = 96.3 Hz, $^3J_{CP}$ = 15.0 Hz, C(Cl)=P).^{31}P NMR: δ 299.3. MS (Cl/NH_3, *m*/*z*, %): 1127 (M+N_2H_7, 20), 1093 (M+1, 40), 1092 (M, 90), 769 (M−Mes*P=C(Cl), 100). Anal. Calc. for $C_{57}H_{87}Cl_3P_3Sb$: C, 62.62; H, 8.02. Found: C, 62.87; H, 7.89%.

4.2. Synthesis of [Mes*P=C(Cl)]$_2$SbCl **3**

The experimental process was the same as that for **2**, starting from 1.03 g (2.85 mmol) of Mes*P=CCl_2, 1.78 mL (2.85 mmol) of *n*-BuLi and 0.21 g, (0.95 mmol) of $SbCl_3$ in THF. The ^{31}P NMR analysis showed the formation of **3**, **2** and possibly Mes*P=C(Cl)—$SbCl_2$(δ^{31}P: 297.5 ppm) in the ratio 85/5/10. Due to similar solubility in various solvents, the complete purification of **3** was not possible, but crystallization from pentane afforded **3** (0.63 g, 55%) in about 95% purity, mixed with very small amounts of tris(phosphaalkenyl)stibane **2**.

^{1}H NMR (200.13 MHz): δ 1.29 (s, 18H, *p*-*t*-Bu), 1.36 (s, 36H, *o*-*t*-Bu), 7.34 (broad s, 4H, arom H), ^{31}P NMR: δ 300.3, MS (EI, 70 eV, *m*/*z*, %): 804 (M, 2), 769 (M−Cl, 2), 573 (M−Ar−Me, 18), 57 (*t*-Bu, 100).

4.3. Synthesis of Mes*SbF_2 **4**

A solution of *n*-BuLi (20.20 mL, 32.32 mmol) was added dropwise to a solution of Mes*Br (10.00 g, 30.76 mmol) in THF (100 mL), cooled to −80 °C. The solution was stirred at this temperature for 3 h. The lithium compound Mes*Li was then slowly added to a solution of SbF_3 (8.25 g, 46.10 mmol) in THF (50 mL) cooled to −80 °C. The reaction mixture was stirred for 10 min and warmed up to room temperature. A ^{19}F NMR analysis showed the presence of the two compounds Mes*SbF_2 and Mes*$_2$SbF in the ratio 50/50. After removal of solvents, 100 mL of pentane were added to the residue, lithium salts and excess of SbF_3 were removed by filtration. Recrystallization from pentane afforded first Mes*SbF_2 **4** (2.58 g, 21%) as a white powder (mp 84 °C) and then Mes*$_2$SbF **5** (3.25 g, 35%, mp 146 °C).

Compound **4**: ^{1}H NMR (300.13 MHz): δ 1.29 (s, 9H, *p*-*t*-Bu), 1.50 (t, J_{HF} = 1.0 Hz, 18H, *o*-*t*-Bu), 7.43 (s, 2H, arom H); ^{13}C NMR (75.47 MHz): δ 31.20 (*p*-C(CH_3)$_3$), 34.02 (t, J_{CF} = 2.2 Hz, *o*-C(CH_3)$_3$), 39.59 (*p*-C(CH_3)$_3$), 40.07 (*o*-C(CH_3)$_3$), 124.45 (*m*-C), 151.51 (*p*-C), 154.30 (t, $^2J_{CF}$ = 9.0 Hz, *ipso*-C), 158.53 (*o*-C); ^{19}F NMR: δ −50.9, MS (EI, 70 eV, *m*/*z*, %): 404 (M, 1), 385 (M−F, 1), 365 (M−2F−1, 1), 349 (M−2F−Me−2, 3), 245 (M−SbF_2, 15), 57 (*t*-Bu, 100). Anal. Calc. For $C_{18}H_{29}F_2Sb$: C, 53.36; H, 7.21; Found: C, 53.47; H, 7.33%.

Compound **5**: ^{1}H NMR (300.13 MHz): δ 1.17 (d, J_{HF} = 0.7 Hz, 36H, *o*-*t*-Bu), 1.27 (s, 18H, *p*-*t*-Bu), 7.33 (s, 4H, arom H); ^{13}C NMR (75.47 MHz): δ 31.37 (*p*-C(CH_3)$_3$), 33.85 (d, $^5J_{CF}$ = 2.5 Hz, *o*-C(CH_3)$_3$), 34.5 (*p*-C(CH_3)$_3$), 39.62 (*o*-C(CH_3)$_3$), 123.81 (*m*-C), 147.66 (d, $^2J_{CF}$ = 11.6 Hz, *ipso*-C), 149.61 and 158.4 (*o*- and *p*-C); ^{19}F NMR: δ −99.4; MS (EI, 70 eV, *m*/*z*, %): 611 (M−F, 1), 385 (M−Mes*, 15), 365 (Mes*Sb−1, 18), 57 (*t*-Bu, 100). Anal. Calc. for $C_{36}H_{56}FSb$: C, 68.68; H, 8.97. Found: C, 68.81; H, 9.05%.

4.4. Synthesis of Mes^*SbF_2 from Mes^*_2SbF

Mes^*SbF_2 can be obtained quantitatively according to a dismutation reaction of 4.0 g (6.35 mmol) of Mes^*_2SbF and 1.13 g (6.35 mmol) of SbF_3 by reflux in toluene for 2 h.

4.5. Synthesis of $Mes^*Sb[C(Cl)=PMes^*]_2$ **6**

1.6 mL (2.56 mmol) of *n*-BuLi were added dropwise to a solution of Mes^*PCCl_2 (0.88 g, 2.45 mmol) in THF (20 mL), cooled to −78 °C. After stirring for 30 min, the solution of $Mes^*PC(Cl)Li$ was cannulated to a solution of Mes^*SbF_2 (1.00 g, 2.45 mmol) in THF (25 mL) at −78 °C. The reaction mixture was stirred for 20 min and then warmed up to room temperature. Solvents were removed in vacuo and 15 mL of pentane were added. After removal of salts by filtration, recrystallization afforded **6** (1.02 g, 82%) as a white powder in 90% purity.

The same product **6** was obtained (0.43 g, 93%) when the lithium compound $Mes^*PC(Cl)Li$ (0.92 mmol) was added to a solution of $Mes^*Sb(OMes^*)F$ (0.60 g, 0.92 mmol) under the same conditions.

^1H NMR (200.13 MHz): δ 1.39, 1.40, 1.54 and 1.70 (4s, 81H, *o*- and *p*-*t*-Bu Mes^*Sb and Mes^*P), 7.46 (s, 2H, arom H Mes^*Sb), 7.53 (d, $^4J_{PH}$ = 1.2 Hz, 4H, arom H Mes^*P); ^{13}C NMR (50.32 MHz): δ 29.8–33.2 (*o*- and *p*-$C(CH_3)_3$ Mes^*P and Mes^*Sb), 34.1, 35.1, 38.0 and 38.8 (*o*- and *p*-$C(CH_3)_3$ Mes^*P and Mes^*Sb), 121.9 and 122.6 (*m*-C Mes^*P and Mes^*Sb), 135.0 (*ipso*-C Mes^*Sb), 137.3 (d, $^1J_{CP}$ = 74.9 Hz, *ipso*-C Mes^*P), 150.3, 150.6 and 153.4 (*o*- and *p*-C Mes^*P and Mes^*Sb), 174.6 (dd, $^1J_{CP}$ = 112.9 Hz, $^3J_{CP}$ = 12.2 Hz, *C*(Cl)=P); ^{31}P NMR: δ 295.3.

4.6. Synthesis of $Mes^*Sb(OMes^*)F$ **7**

1.3 mL (2.08 mmol) of *n*-BuLi were added dropwise at 0 °C to a yellow solution of 2,4,6-tri-*tert*-butylphenol (0.52 g, 1.97 mmol) in THF (15 mL). The solution turned colorless, was stirred for 10 min and was allowed to warm to room temperature. It was then added dropwise to a solution of Mes^*SbF_2 (0.80 g, 1.97 mmol) in THF (15 mL) cooled to −78 °C. The reaction mixture was stirred for 20 min and warmed up to room temperature. After removal of solvents, 20 mL of pentane were added and the lithium salts were removed by filtration. The residue was recrystallized from pentane to afford **7** (0.70 g, 55%) as a white powder (mp 135–137 °C).

^1H NMR (200.13 MHz): δ 1.15 (s, 18H, *o*-*t*-Bu $OMes^*$), 1.22 and 1.33 (2s, 2 × 9H, *p*-*t*-Bu $OMes^*$ and*p*-*t*-Bu Mes^*), 1.51 (s, 18H, *o*-*t*-Bu Mes^*), 7.10 (s, 2H, arom H $OMes^*$), 7.43 (s, 2H, arom H Mes^*); ^{13}C NMR (50.32 MHz): δ 31.3 and 31.7 (*p*-$C(CH_3)_3$ $OMes^*$ and $SbMes^*$), 32.9 and 34.0 (*o*-$C(CH_3)_3$ $OMes^*$ and $SbMes^*$), 35.5 and 39.9 (*o*- and *p*-$C(CH_3)_3$ $OMes^*$ and $SbMes^*$), 123.0 and 124.1 (*m*-C $OMes^*$ and $SbMes^*$), 141.4, 151.1 and 159.0 (*o*- and *p*-C, *ipso*-C $OMes^*$), 153.3 (d, J_{CF} = 9.2 Hz, *ipso*-C $SbMes^*$); ^{19}F NMR: δ −61.6. MS (EI, 70 eV, *m*/*z*, %): 646 (M, 1), 627 (M−F, 3), 626 (M−F−1, 3), 385 (M−$OMes^*$, 40), 365 (Mes^*Sb−1, 70), 57 (*t*-Bu, 100); Anal. Calc. for $C_{36}H_{58}FOSb$: C, 66.77; H, 9.03. Found: C, 66.59; H, 8.92%.

4.7. Synthesis of $Mes^*Sb(F)–C(SiMe_3)=PMes^*$ **10**

A solution of *n*-BuLi (1.5 mL, 2.40 mmol) was added dropwise to a solution of $Mes^*P=C(Br)SiMe_3$ (1.04 g, 2.26 mmol) in THF (25 mL), cooled to −90 °C. The reaction mixture was stirred for 30 min and was then allowed to warm to room temperature. The lithium compound $Mes^*P=C(SiMe_3)Li$ **8** was then added slowly to a solution of Mes^*SbF_2 (0.96 g, 2.37 mmol) in THF (25 mL) cooled to −78 °C. The solution was stirred for 10 min and warmed up to room temperature. After removal of solvents, 100 mL of pentane were added to the residue and the resulting mixture was filtrated to remove lithium salts. Recrystallization from pentane afforded **10** (1.23 g, 69%) as an orange powder (mp 115–117 °C).

^1H NMR (200.13 MHz): δ −0.26 (s, 9H, $SiMe_3$), 1.28 and 1.29 (2s, 2 × 9H, *p*-*t*-Bu Mes^*Sb and Mes^*P), 1.39 (s, 18H, *o*-*t*-Bu Mes^*Sb), 1.53 (d, 18H, $^4J_{PH}$ = 1.2 Hz, *o*-*t*-Bu Mes^*P), 7.27 (d, 2H, $^4J_{PH}$ = 1.5 Hz, arom H Mes^*P), 7.41 (s, 2H, arom H Mes^*Sb); ^{13}C NMR (50.32 MHz): δ 0.7 (d, $^3J_{CP}$ = 37.9 Hz, $SiMe_3$), 31.3, 33.6, 33.8 and 34.3 (*o*- and *p*-$C(CH_3)_3$ Mes^*Sb and Mes^*P), 34.3 and 34.5 (*p*-$C(CH_3)_3$ Mes^*Sb and Mes^*P), 38.3 (d, $^3J_{CP}$ = 7.4 Hz, *o*-$C(CH_3)_3$ Mes^*P), 38.7 (*o*-$C(CH_3)_3$ Mes^*Sb), 121.6 and 121.8 (*m*-C Mes^*Sb and Mes^*P), 149.8, 150.1, 152.3 (d, *J* = 1.8 Hz) and 153.5 (d, *J* = 3.7 Hz) (*o*- and *p*-C, *ipso*-C Mes^*), 205.6 (dd, $^1J_{CP}$ = 106.3 Hz, $^2J_{CF}$ = 9.0 Hz, P=*C*); ^{19}F NMR: δ −98.5 (d, $^3J_{PF}$ = 27.2 Hz); ^{31}P NMR: δ 392.5 (d, $^3J_{PF}$ = 27.2 Hz), MS (EI, 70 eV, *m*/*z*, %): 746 (M, 1), 689 (M−*t*-Bu, 5), 669 (M−*t*-Bu−F−1, 5), 598 (M−2*t*-Bu−F−Me, 3), 501 (M−Mes^*, 10), 445 (M−Mes^*−*t*-Bu+1, 25), 365 (Mes^*Sb−1, 24), 57 (*t*-Bu, 100); Anal. Calc. for $C_{40}H_{67}FPSbSi$: C, 64.25; H, 9.03. Found: C, 64.47; H, 9.21%.

4.8. Synthesis of 9-(dichloromethylene)-2,7-di-tert-butylfluorene **12b**

81.60 g (0.31 mol) of triphenylphosphine were added to a solution de 2,7-di-*tert*-butylfluorenone [10] (14.00 g, 48.0 mmol) in 250 mL of THF. The reaction mixture was heated at reflux and 190 mL (1.85 mol) of carbon tetrachloride were added dropwise for 5 h. The solution became dark brown; it was heated for one hour at 65 °C after completion of the addition. After cooling to room temperature, the reaction mixture was hydrolyzed, extracted with Et_2O and the organic layer was washed with saturated solutions of $NaHCO_3$ and NaCl then dried over Na_2SO_4. The solvents were removed under reduced pressure and the resulting brown solid was washed three times with pentane. A recrystallization from pentane led to 12.00 g (85%) of light yellow needles of *C*,*C*-dichlorofulvene **12b** (mp 140 °C).

^1H NMR (300.13 MHz): δ 1.48 (s, 18H, *t*-Bu), 7.42 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.7 Hz, 2H, H on C3 and C6), 7.58 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H on C4 and C5), 8.38 (d, $^4J_{HH}$ = 1.7 Hz, 2H, H on C1 and C8); ^{13}C NMR (75.47 MHz): δ 31.5 (*CMe*$_3$), 35.0 (*C*Me$_3$), 118.9, 122.9 and 126.3 (arom CH of CR_2), 121.0 (*C*=CCl_2), 134.8, 136.8 and 137.8 (arom C of CR_2), 150.3 (*C*Cl_2)MS (EI, 70 eV, *m*/*z*, %): 358 (M, 47) 343 (M−Me, 100), 57 (*t*-Bu, 20); Anal. Calc. for $C_{22}H_{24}Cl_2$: C, 73.54; H, 6.73. Found: C, 73.62; H, 6.85%.

4.9. Synthesis of $[R_2C=C(Cl)]_2SbCl$ **13a**

A solution of *n*-BuLi (3.9 mL, 6.37 mmol) was added dropwise to a solution of 9-dichloromethylenefluorene **12a** (1.50 g, 6.07 mmol) in THF (15 mL) cooled to −78 °C. The solution turned purple and, after stirring for 15 min, was added dropwise to a solution of SbF_3 (0.69 g, 3.02 mmol) in THF at −78 °C. The temperature was maintained for 10 min and the mixture was then slowly warmed to room temperature. Solvents were removed in vacuo, the residue was extracted with a solution of pentane/dichloromethane (50/50, 2 × 30 mL), and the insoluble precipitate (LiCl) was filtered out. Removal of the solvent in vacuo followed by recrystallization from CH_2Cl_2 yielded **13a** (1.07 g, 61%) as yellow crystals (mp 196 °C).

^1H NMR (300.13 MHz): δ 6.98 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.22–7.35 (m, 6H), 7.60–7.66 (m, 6H), 8.56 (d, $^3J_{HH}$ = 7.5 Hz, 2H); ^{13}C NMR (75.47 MHz): δ 120.09 and 120.53 (C_4C_5), 123.44, 127.07, 127.79, 127.98, 129.37 and 129.89 (CH of CR_2), 137.84, 137.87, 140.71, 140.91, 143.49 and 148.23 (C_{10-13} and C=C); MS (EI, 70 eV, *m*/*z*, %): 544 (M−Cl−1, 1), 509 (M−2Cl−1, 1), 471 (M−3Cl−2, 1), 422 (M−SbCl, 1), 404 (M−(C=CR_2), 15), 352 (M−$SbCl_3$, 40), 246 ($R_2C=CCl_2$, 30), 176 (R_2C=C, 100); Anal. Calc. for $C_{28}H_{16}Cl_3Sb$: C, 57.93; H, 2.78. Found: C, 57.88; H, 2.63% (the solvent molecule (CH_2Cl_2) observed by X-ray in the unit cell was removed in vacuo).

4.10. Synthesis of $[R_2C{=}C(Cl)]_2SbCl$ **13b**

Compound **13b** was prepared according to the same experimental process as **13a** from 4.3 mL (7 mmol) of a solution of *n*-BuLi (1.6 M in hexane), (2.5 g, 7 mmol) of dichlorofulvene **12b** in 15 mL of THF and (0.79 g, 7 mmol) of $SbCl_3$ in 15 mL of THF. 2.07 g (83%) of yellow crystals of $[R_2C{=}C(Cl)]_2SbCl$ **13b** (mp 250 °C) were obtained.

^{1}H NMR (300.13 MHz): δ 1.09 (s, 18H, *t*-Bu), 1.31 (s, 18H, *t*-Bu), 7.31 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.7 Hz, 2H, H on C6 or C3), 7.37 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.7 Hz, 2H, H on C3 or C6), 7.1 (dd, $^4J_{HH}$ = 1.7 Hz, $^5J_{HH}$ = 0.5 Hz, 2H, H on C8 or C1), 7.51 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H on C5 or C4), 7.52 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H on C4 or C5), 8,64 (dd, $^4J_{HH}$ = 1.7 Hz, $^5J_{HH}$ = 0.5 Hz, 2H, H on C1 or C8); ^{13}C NMR (75.47 MHz): δ 31.2 and 31.5 (CMe_3), 34.8 and 35.0 (CMe_3), 119.0, 119.7, 120.9, 124.7, 126.5 and 126.9 (arom CH of CR_2), 138.3, 138.4, 138.5, 142.4, 149.6 and 150.3 (C=CCl and arom C of CR_2), 150.8 (CCl); MS (EI, 70 eV, *m*/*z*, %): 804 (M, 1), 646 (M−SbCl, 3), 631 (M−SbCl−Me, 2), 611 (M−SbCl−Cl, 20), 576 (M−SbCl−2Cl, 18), 481 (M−$CClCR_2$, 12), 310 (CR_2+Cl−1, 26), 273 (CR_2−3, 26), 193 ($SbCl_2$, 60), 158 (SbCl, 10), 123 (Sb, 20), 57 (*t*-Bu, 100); Anal. Calc. for $C_{44}H_{48}Cl_3Sb$: C, 65.65; H 6.01. Found: C, 65.89; H, 5.95%.

4.11. X-ray structure determinations

All data for all structures represented in this paper were collected at low temperatures by using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods [14] and all non hydrogen atoms were refined anisotropically by using the least-squares method on F^2 [15].

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Appendix A. Supplementary material

CCDC 679867 and 679868 contain the supplementary crystallographic data for **12b** and **13a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.04.012.

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