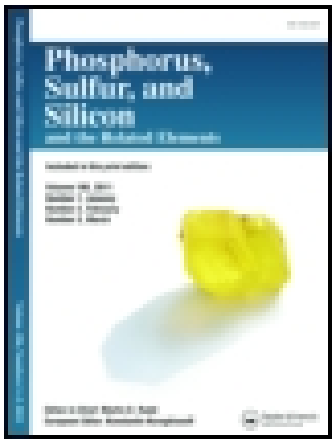

Phosphorus, Sulfur, and Silicon and the Related Elements

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New Halo Compounds of Si, P, As, AND Sb Bearing a Bulky Substituted Fluorenyl Group

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NEW HALO COMPOUNDS OF Si, P, As, AND Sb BEARING A BULKY SUBSTITUTED FLUORENYL GROUP

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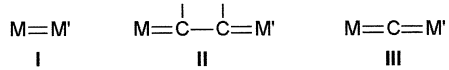
New halo compounds of Si, P, As, and Sb, potential precursors of doubly-bonded derivatives of these elements, have been synthesized: dichloro- and difluorosilanes ***2–6*** *bearing a methylfluorenyl group and a second substituent of various size (Me, Ph, Mes, R_2CMe); dichlorophosphines* ***13*** *and* ***14****, fluoro- and difluoroarsines* ***15*** *and* ***16*** *and fluorostibine* ***17****, substituted by the diphenyl (or dimesityl) phosphinofluorenyl group. Phosphine oxide and sulfide* ***9*** *and* ***10*** *also have been prepared.*

Keywords: Dichlorophosphines; dihalosilanes; fluorenyl compounds; fluoroarsines; fluorostibines; phosphine oxides; sulfides

The study of doubly-bonded systems of main group elements is currently under active investigation. Many groups in the world are working in derivatives containing one (**I**) or two double bonds (conjugated (**II**) or cumulated (**III**)):[1]



I II III

M, M' = C, Si, Ge, Sn, P, As, Sb

These compounds generally are stabilized by a large steric hindrance which prevents the approach of two monomers to form dimers or

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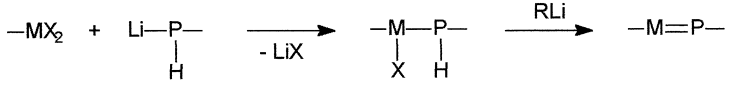
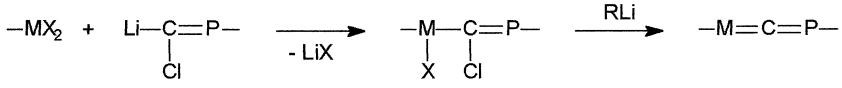
oligomers. Thus, the design of synthetically available routes to bound groups on M and M′ that present a great steric hindrance is extremely important. Moreover, as the dihalo compounds MX_2 (X = F, Cl, Br) of group 14 and 15 elements are generally involved in the process to derivatives **I–III**, their preparation must be the first step in the synthesis of the latter:





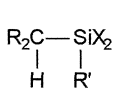
Thus, we report in this article the synthesis of dihalo derivatives of the type MX_2, with M being an element of group 14 (silicon) or 15 (phosphorus, arsenic, and antimony).

RESULTS AND DISCUSSION

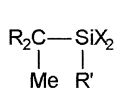
The choice of the bulky group on M is very important. In order to prepare large quantities of MX_2 compounds at the lowest possible price, it is necessary to use a group easily prepared from an inexpensive commercially available starting material, such as fluorene. Moreover, the fluorenyl group allows simple purification by easy crystallization and, due to the presence of three fused cycles, presents a large steric hindrance. Thus, we used it on all MX_2 compounds we have synthesized.

Dihalosilanes

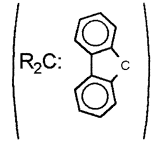
We have prepared derivatives of type **V** from **IV** where, in order to avoid side reactions that could occur (hydrogen easily substitutable by lithium), we have replaced hydrogen by an alkyl group such a methyl, which is the simplest one.



IV



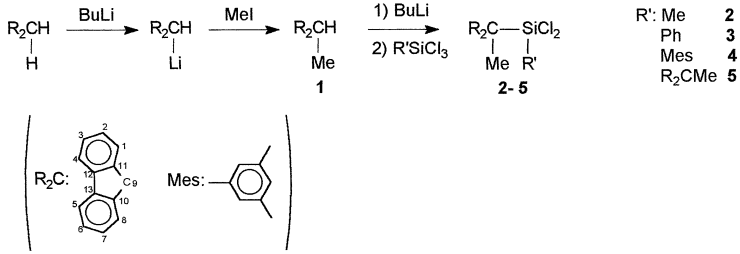
V



We have used groups R′ of various size on silicon (Me, Ph, Mes, R_2CMe) to obtain dihalosilanes $>SiX_2$, precursors of low-coordinated

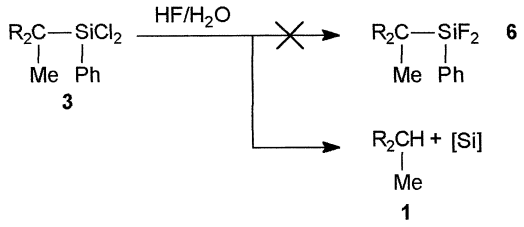
silicon species, presenting a large scale of steric hindrance. As $R'SiCl_3$, we generally have used $MeSiCl_3$ or $PhSiCl_3$, which are commercially available.

2–5 are synthesized nearly quantitatively from **1**, easily prepared from fluorene.[2]



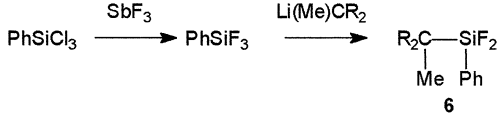
2–5 are characterized by ^1H and ^{13}C NMR and mass spectroscopy. In compounds **2–4**, the protons of the fluorenyl group appear in ^1H NMR as a complex multiplet. By contrast, in **5**, a first order spectrum is observed for the eight aromatic protons (two doublets and two triplets) with a high field shift of about 0.50 ppm compared to **2–4**. Such a phenomenon is due to the presence of a second fluorenyl group which presents a high magnetic anisotropy. The influence of a fluorenyl group on a second one previously has been reported in $Me_2Si(CMeR_2)_2$.[3]

As reduction, alkylation or monoelectronic transfers sometimes occur in the reaction of chlorosilanes with lithio compounds, we also have prepared in one case a difluorosilane derivative. Fluorination of chlorosilanes with hydrofluoric acid in water is generally a good route to the corresponding fluorosilanes,[4] but attempts to prepare **6** by such a route from **3** failed: We only have observed the cleavage of the benzylic Si—CR_2 bond with formation of **1** and of an unidentified silicon compound:



Note that in similar conditions, the Ge-CHR_2 bond is not cleaved and fluorine derivatives can be synthesized from their chloro analogues and HF/H_2O.[5] However, **6** was prepared in high yield by reaction of

$R_2C(Me)Li$ with phenyltrifluorosilane obtained from its trichloro analogue and antimony trifluoride.[6]

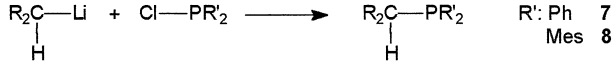


Dihalides of Group 15 Elements

Synthesis of Precursors

As there is only one substituent on M in $-MX_2$ (M = P, As, Sb), it is necessary to increase its size by comparison with the case of Si where there are two bulky substituents. So, we decided to use the fluorenyl group but, instead of a methyl on carbon **9**, we have chosen a bulkier group. As NMR of arsenic and antimony is not available, we used a phosphorus group in order to have a NMR probe allowing easy identification of derivatives even in a complex mixture.

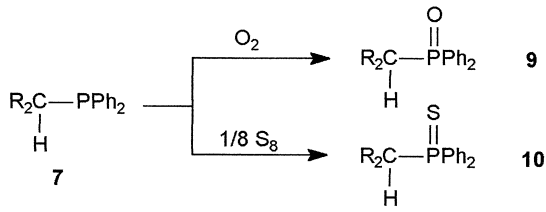
The phosphines **7** and **8** with phenyl or mesityl groups were prepared in excellent yield by reaction of the fluorenyllithium with chlorodiphenyl (or dimesityl) phosphine:



For the synthesis of **8**, it is possible to use the crude reaction mixture of Mes_2PCl/Mes_2PBr obtained from MesMgBr and PCl_3.[7]

A proof of the great steric hindrance of **8** is given by the ^1H NMR: Two singlets are observed for the aromatic hydrogens of the mesityl groups. Surprisingly, the six methyl groups (*ortho* and *para*) present the same chemical shift.

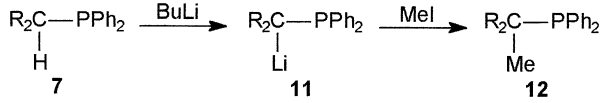
Due to the presence of two aromatic groups on phosphorus, **7** and **8** are not very air-sensitive and can be handled easily and used. However, **7** is oxidized by gaseous oxygen and sulfurized to form air-stable **9** and **10**:



As expected, larger J_{PC} coupling constants are observed for P_{IV} compounds **9** and **10** than for P_{III}. Whereas C_{2-7} do not couple with P in **7**

and **8**, $^4J_{PC}$ and $^5J_{PC}$ are observed between $C_{2,3,6,7}$ and P in **9** and **10**, and even $^4J_{PC}$ between $C_{4,5}$ and P in **10**.

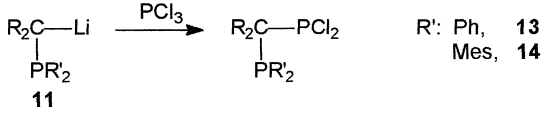
In order to see if this group $R_2C(PR'_2)$ is potentially available as substituent on M_{15}, we determined the experimental conditions to get the lithio compound $R_2C(Li)PR'_2$ **11**. The use of *n*-butyllithium in THF appeared to be suitable to give **11**, and the formation was evidenced by quenching with methyl iodide:



All the compounds **7–10** and **12** were characterized by NMR and mass spectroscopy. Note that whereas the $^2J_{HP}$ coupling constant in **7** is close to zero, a large $^3J_{HP}$ coupling (13.0 Hz) is observed for **12**.

Synthesis of Halophosphines, Arsines, and Stibines

Addition of **11** to phosphorus trichloride afforded the expected diphosphines **13** and **14**:



13 and **14** were characterized by ^{31}P NMR, which displays two doublets as expected. Note a shift of about 30 ppm at high field for the phosphorus of $PMes_2$ in comparison with the one of PPh_2, but the most striking feature is the extremely large difference between the two $^2J_{PP}$ coupling constants: 167.8 Hz in **13** and 409.0 Hz in **14**. The latter is very high and generally corresponds to a $^1J_{PP}$. This great coupling constant in **14** probably is due to the large size of mesityl groups which induce a nearly planar phosphorus atom and particularly to a special conformation of the P—C—P moiety. A similar huge difference in the $^2J_{PP}$ coupling constant previously has been observed in $ArP=C(Cl)—P(Cl)Tsi$ (Tsi: $(Me_3Si)_3C$) (89 and 457 Hz) and was related to the difference in the conformation.[8]

From **11** and AsF_3,[9] we also obtained, in addition to the expected dihalo derivative **15**, the monofluoroarsane **16**:

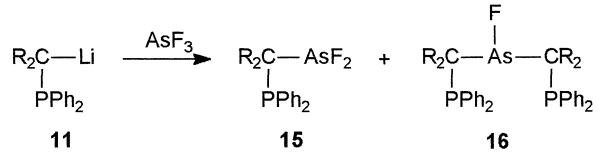


TABLE I ^{19}F and ^{31}P NMR Spectra of Fluoro- and Difluoroarsines

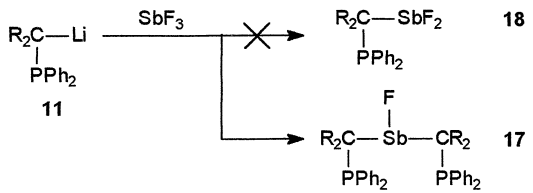
Difluorinated compound	Chemical shift in ^{19}F (ppm)	Monofluorinated compound	Chemical shift in ^{19}F (ppm)
$R_2C(PPh_2)$-AsF_2 **15**	−35.1	$[R_2C(PPh_2)]_2AsF$ **16**	−132.4
$ArAsF_2$[10] (Ar: 2,4,6-$tBu_3C_6H_2$)	−21.8	ArP=C(Br)-As(Dmt)F[11] (Dmt: 2,6-Mes_2-4-MeC_6H_2)	−114.4
$TsiAsF_2$[11] (Tsi: $(Me_3Si)_3C$)	−32.4	ArP=C(Cl)-As(Tsi)F[11]	−114.3

15 and **16** were identified in ^{19}F and ^{31}P NMR: They present characteristic chemical shifts in ^{19}F NMR for a fluoro- (−110/−135 ppm) or a difluoroarsine (−20/−30 ppm) as shown in Table I.

Moreover, the P—F coupling constants (d in ^{19}F and t in ^{31}P NMR for **15** and t in ^{19}F and d in ^{31}P NMR for **16**) unambiguously prove their structure.

The formation of mono- and disubstituted derivatives **15** and **16** contrasts with the results observed in the case of phosphorus. Indeed, only the smaller size of phosphorus allows monosubstitution on PCl_3 to give **13** and **14** while the larger radius of arsenic allows the disubstitution.

As very few doubly-bonded derivatives of antimony are known, it seemed interesting to synthesize dihalogeno compounds —SbX_2. However, in the reaction of **11** with SbF_3, only the disubstituted antimony compound **17** was formed:



The structure of **17** was evidenced by its high field shift in ^{19}F NMR (−125.0 ppm), characteristic of a monofluoroantimony derivative. Such types of chemical shifts already have been found in other R_2SbF compounds.[12] Although the target difluoroantimony compound **18** has not been obtained, this reaction is interesting since it leads to **17** which, due to its high steric hindrance and the presence of a flurine atom, could be used as a bulky protecting group.

The formation of the disubstituted arsenic and antimony derivatives **16** and **17** deserves some comments. Obviously the size of the M element (M = As, Sb) increasing from P to Sb going down the periodic table is important, but does not constitute the only determining factor. Indeed, whatever the experimental conditions we used (excess of MF_3,

temperature, addition of RLi to MF_3, or reverse addition), we always obtained the same results and we have been unable to prevent the disubstitution. Thus, it seems that the disubstitution is faster than the mono- one, contrary to what is expected on the basis of steric and electronic arguments. We currently are studying the mechanism of these reactions.

CONCLUSION

Two series of $R_2C(Me)$—$Si(R')X_2$ (X = F, Cl; R′ = Me, Ph, Mes, R_2CMe) and $R_2C(R'')$-MX_2 (X = F, Cl; M = P, As; R″ = PPh_2, $PMes_2$) derivatives which present various group **14** and **15** elements, halogens, and steric hindrance have been synthesized. Going down the periodic table, we observed exclusive monosubsitution on Si and P, both mono- and disubstitution on As and only disubstitution on Sb.

The use of the dihalo derivatives **2–5** and **13–15** for stabilizing low coordinated compounds is now under intensive investigation.

EXPERIMENTAL SECTION

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 in $CDCl_3$ on the following spectrometers: ^1H, Bruker AC200 (200.13 MHz) and sometimes when mentioned Bruker AC80 (80.13 MHz); $^{13}C\{^1H\}$, Bruker AC200 (50.32 MHz) (reference TMS); ^{19}F, Bruker AC80 (75.39 MHz) (reference CF_3COOH); $^{31}P\{^1H\}$, 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.

$MeSiCl_3$, $PhSiCl_3$, Ph_2PCl, and SbF_3 were available commercially Solutions of *n*-BuLi 1.6 M in hexane were used. Some starting products were synthesized according to the literature: $PhSiF_3$,[6] Mes_2PCl,[7] AsF_3,[9] $MesSiCl_3$.[13]

Synthesis of Dichloro(methyl)(methylfluorenyl)silane 2

To a solution of methylfluorene **1** (2.50 g, 13.9 mmol) in Et_2O (30 mL) cooled at −78°C were added 8.8 mL of a solution of *n*-BuLi (13.9 mmol). After .5 h of stirring at room temperature, the red solution of $R_2C(Me)Li$ was canulated to a solution of methyltrichlorosilane (2.07 g, 13.9 mmol)

in Et_2O (10 mL) cooled at −78°C. After stirring the mixture at 20°C for 2 h, LiCl was eliminated by filtration, then the solvents were removed in vacuo and the residue dissolved in 20 mL of pentane. Cooling at −20°C afforded white crystals of **2** (3.38 g, 83%, mp: 110°C).

NMR: ^{1}H (80 MHz): 0.01 (s, 3H, MeSi), 1.87 (s, 3H, C<u>Me</u>R_2), 7.35–7.90 (m, 8H, arom H).

^{13}C: 0.54 (MeSi), 17.81 (C<u>Me</u>R_2), 46.74 (C_9), 120.21 (C_4C_5), 125.03, 127.07, and 127.34 ($C_{1-3}C_{6-8}$), 140.61 ($C_{12}C_{13}$), 145.84 ($C_{10}C_{11}$).

MS: 292 (M, 18), 257 (M—Cl, 2), 179 ($CMeR_2$, 100).

The dihalogenosilanes **3–6** were synthesized by the same procedure as **2**.

Synthesis of Dichloro(phenyl)(methylfluorenyl)silane 3

$R_2C(Me)H$, 1.27 g (7.1 mmol); BuLi, 4.40 mL (7.1 mmol); $PhSiCl_3$, 1.50 g (7.1 mmol); **3** (2.04 g, 81%, m.p. 84–85°C).

NMR: ^{1}H (80 MHz): 1.99 (s, 3H, Me), 6.92–7.30 (m, 5H, arom H Ph), 7.32–7.83 (m, 8H, arom H CR_2).

^{13}C: 18.02 (Me), 47.23 (C_9), 120.08 (C_4C_5), 125.14, 126.82, 127.10 and 127.37 ($C_{1-3}C_{6-8}$ and *m*-CH Ph), 128.66 (*ipso*-C Ph), 131.31 (*p*-CH Ph), 134.10 (*o*-CH Ph), 140.95 ($C_{12}C_{13}$), 145.42 ($C_{10}C_{11}$).

MS: 354 (M, 18), 276 (M-Ph-1, 1), 179 ($CMeR_2$, 100).

Synthesis of Dichloro(mesityl)(methylfluorenyl)silane 4

$R_2C(Me)H$, 1.00 g (5.5 mmol); BuLi, 3.5 mL (5.5 mmol); $MesSiCl_3$, 1.40 g (5.5 mmol); **4** (1.57 g, 72%, m.p.: 118°C).

NMR: ^{1}H (80 MHz): 1.92 (s, 3H, Me), 2.03 (s, 6H, *o*-Me), 2.20 (s, 3H, *p*-Me), 6.67 (s, 2H, arom H Mes), 7.20–7.76 (m, 8H, arom H CR_2).

^{13}C: 19.44 and 20.15 (C<u>Me</u>R_2 and *p*-Me Mes), 26.39 (*o*-Me Mes), 49.70 (C_9), 120.38 (C_4C_5), 123.22 (*ipso*-C Mes), 125.16, 126.92 and 127.40 ($C_{1-3}C_{6-8}$), 130.34 (*m*-CH Mes), 141.07, 141.43, 146.09 and 145.78 (C_{10-13} and *o*- and *p*-C Mes).

MS: 396 (M, 15), 217 ($MesSiCl_2$, 78), 179 ($CMeR_2$, 91), 119 (Mes, 100).

Synthesis of Dichloro[bis(methylfluorenyl)]silane 5

$R_2C(Me)H$, 2.58 g (14.3 mmol); BuLi, 9.0 mL (7.1 mmol); $SiCl_4$, 1.21 g (7.1 mmol); **5** (2.14 g, 66%, m.p.: 243°C).

NMR: ^{1}H: 1.52 (broad s, 6H, Me), 6.85 and 7.08 (2t, $^3J_{HH}$: 7.1 Hz, 2 × 4H, H on $C_{2,3,6,7}$), 7.23 and 7.33 (2d, $^3J_{HH}$: 7.1 Hz, 2 × 4H, H on $C_{1,4,5,8}$).

^{13}C: 21.05 (broad, Me), 45.52 (C_9), 120.03 (C_4C_5), 124.70 (C_1C_8), 126.13, 126.74 (C_2C_7 and C_3C_6), 140.04 ($C_{12}C_{13}$), 145.81 ($C_{10}C_{11}$).

MS: 456 (M, 8), 421 (M-Cl, 1), 277 (M-$CMeR_2$, 10), 179 ($CMeR_2$, 100).

Synthesis of Difluoro(phenyl)(methylfluorenyl)silane 6

$R_2C(Me)H$, 1.10 g (6.1 mmol); BuLi, 3.8 mL (6.1 mmol); $PhSiF_3$, 0.99 g (6.1 mmol); 6 (1.12 g, 75%).

NMR: ^{1}H (80 MHz): 1.92 (s, 3H, Me), 6.90–7.78 (m, 13H, arom H).

^{13}C: 17.76 (Me), 43.21 (t, $^2J_{CF}$: 14.4 Hz, C_9), 120.13 (C_4C_5), 124.38 (C_1C_8), 125.18 (t, $^2J_{CF}$: 18.1 Hz, *ipso*-C Ph), 127.14, 127.23 and 127.62 (C_2C_7, C_3C_6 and *m*-CH Ph), 131.69 (*p*-CH Ph), 134.07 (*o*-CH Ph), 140.65 ($C_{12}C_{13}$), 146.06 ($C_{10}C_{11}$).

^{19}F: −72.3.

MS: 322 (M, 23), 244 (M-Ph-1, 5), 179 ($CMeR_2$, 100).

Synthesis of Diphenyl(fluorenyl)phosphine 7

19.70 mL (31.52 mmol) of *n*-BuLi were added to a suspension of fluorene (5 g, 30.12 mmol) in Et_2O (60 mL) at room temperature. The solution turned red and after .5 h of stirring was added dropwise to one equivalent of chlorodiphenylphosphine (6.64 g, 30.12 mmol) in solution in Et_2O (65 mL). The reaction mixture turned from red to yellow. 100 mL of water were added and an abundant yellow precipitate appeared. This yellow residue was recrystallized from THF to afford a white powder of pure **7** (8.92 g, 84%, m.p.: 192°C).

NMR: ^{1}H: 5.01 (broad s, 1H, HC_9), 6.97–7.32 (m, 18H, arom H).

^{13}C: 46.19 (d, $^1J_{CP}$: 24.0 Hz, C_9), 119.82 (C_4C_5), 125.10 (d, $^3J_{CP}$: 4.6 Hz, C_1C_8), 126.43 and 126.93 (C_2C_7 and C_3C_6), 128.15 (d, $^3J_{CP}$: 6.5 Hz, *m*-CH Ph), 129.14 (*p*-CH Ph), 133.80 (d, $^2J_{CP}$: 20.3 Hz, *o*-Hz, *o*-CH Ph), 135.78 (d, $^1J_{CP}$: 17.6 Hz, *ipso*-C Ph), 141.06 (d, $^3J_{CP}$: 1.8 Hz, $C_{12}C_{13}$), 143.72 (d, $^2J_{CP}$: 5.6 Hz, $C_{10}C_{11}$).

^{31}P: 3.6.

MS: 350 (M, 18), 185 (PPh_2, 43), 165 (R_2CH, 100).

Synthesis of Dimesityl(fluorenyl)phosphine 8

5.20 mL (8.30 mmol) of *n*-BuLi were added to a suspension of fluorene (1.32 g, 7.90 mmol) in Et_2O (30 mL) at room temperature and stirred for .5 h at this temperature. This solution was then added dropwise to a solution of Mes_2PCl/Mes_2PBr (30/70; 2.72 g, 7.90 mmol) in Et_2O (40 mL). The reaction mixture turned red and a white precipitate appeared. Then the solution turned green. After removal of the lithium

salts, recrystallization from pentane afforded a white powder of pure **8** (2.81 g, 82%, m.p.: 138–142°C (dec)).

NMR: ^{1}**H** (80 MHz): 2.27 (s, 18H, *p* and *o*-Me), 5.74 (d, $^{2}J_{PH}$: 3.1 Hz, 1H, HC_9), 6.80 and 6.83 (2s, 2 × 2H, arom H Mes), 6.97–7.83 (m, 8H, arom H CR_2).

^{13}**C:** 21.04 (*p*-Me Mes), 23.36 (d, $^{3}J_{CP}$: 15.7 Hz, *o*-Me Mes), 43.03 (d, $^{1}J_{CP}$: 28.7 Hz, C_9), 119.81 (C_4C_5), 125.68 (d, $^{3}J_{CP}$: 4.6 Hz, C_1C_8), 126.82 and 126.96 (C_2C_7 and C_3C_6), 130.36 (*m*-CH Mes), 131.63 (d, $^{1}J_{CP}$: 31.4 Hz, *ipso*-C Mes), 138.37 (s), 141.20 (s), 143.48 (d, J_{CP}: 16.6 Hz) and 145.04 (d, J_{CP}: 10.2 Hz) ($C_{10}C_{11}$, $C_{12}C_{13}$, *o*-C Mes and *p*-C Mes).

^{31}**P:** −14.3.

MS: 434 (M, 22), 419 (M-Me, 2), 315 (M-Mes, 1), 269 (M-R_2CH, 100), 165 (R_2CH, 1).

Synthesis of Diphenyl(fluorenyl)phosphine Oxide 9

A yellow solution of R_2CHPPh_2 7 (0.40 g, 1.14 mmol) in THF (10 mL) was oxidized by gaseous oxygen at room temperature. After 5 min under stirring, the solvent was removed in vacuo to afford a yellow powder of pure **9** (0.21 g, 50%, m.p.: 223–227°C).

NMR: ^{1}**H**: 5.12 (d, $^{2}J_{PH}$: 23.4 Hz, 1H, HC_9), 7.12–7.62 (m, 18H, arom H).

^{13}**C:** 50.68 (d, $^{1}J_{CP}$: 62.1 Hz, C_9), 119.95 (C_4C_5), 126.21, 126.90 and 127.79 (3d, J_{CP}: 2.6 Hz, 2.6 Hz and 1.7 Hz, C_1C_8, C_2C_7 and C_3C_6), 128.22 (d, $^{2}J_{CP}$: 12.2 Hz, *o*-CH Ph), 129.98 (d, $^{1}J_{CP}$: 99.4 Hz, *ipso*-C Ph), 131.74 (d, $^{3}J_{CP}$: 8.7 Hz, *m*-CH Ph), 132.08 (d, $^{4}J_{CP}$: 2.6 Hz, *p*-CH Ph), 139.07 and 141.90 (2d, J_{CP}: 4.3 Hz and 4.4 Hz, $C_{10}C_{11}$ and $C_{12}C_{13}$).

^{31}**P:** 31.7.

MS: 366 (M, 12), 201 (M-R_2CH, 100), 165 (R_2CH, 16).

Synthesis of Diphenyl(fluorenyl)phosphine Sulfide 10

0.10 g (0.39 mmol) of sulfur S_8 were added to a solution of R_2CHPPh_2 **7** (1.00 g, 2.80 mmol) in THF (25 mL); after 1 h of reflux under stirring, the solvent was removed in vacuo. Recrystallization from THF afforded pale yellow crystals of pure **10** (0.73 g, 72%, m.p.: 192–195°C).

NMR: ^{1}**H**: 5.23 (d, $^{2}J_{PH}$: 18.1 Hz, 1H, HC_9), 7.02–7.78 (m, 18 H, arom H).

^{13}**C:** 52.23 (d, $^{1}J_{CP}$: 45.3 Hz, C_9), 119.91 (d, $^{4}J_{CP}$: 1.7 Hz C_4C_5), 125.99, 126.69 and 128.17 (3d, J_{CP}: 3.5 Hz, 2.6 Hz and 2.6 Hz, C_1C_8, C_2C_7 and C_3C_6), 128.35 (d, $^{2}J_{CP}$: 12.2 Hz, *o*-CH Ph), 130.51 (d, $^{1}J_{CP}$: 80.2 Hz, *ipso*-C Ph), 131.82 (d, $^{4}J_{CP}$: 2.6 Hz, *p*-CH Ph), 132.19 (d, $^{3}J_{CP}$: 9.6 Hz, *m*-CH Ph), 139.26 and 142.17 (2d, J_{CP}: 4.4 Hz and 4.3 Hz, $C_{10}C_{11}$ and $C_{12}C_{13}$).

^{31}P: 48.9.

MS: 382 (M, 14), 217 (M-R_2CH, 100), 165 (R_2CH, 29), 139 (PhP(S)-1, 38).

Synthesis of Diphenyl(methylfluorenyl)phosphine 12

0.56 mL (0.90 mmol) of *n*-BuLi were added dropwise at room temperature to a suspension of **7** (0.30 g, 0.86 mmol) in THF (10 mL). The reaction mixture turned orange and was stirred for .5 h. 1.1 equivalent (0.94 mmol) of methyl iodide were added and after 1 h, 10 mL of water. Upon separation, the aqueous layer was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to afford a yellow powder of **12** (0.12 g, 38%, m.p.: 250°C (dec)).

NMR: ^{1}H: 2.61 (d, $^3J_{CP}$: 13.0 Hz, 3H, $R_2C\underline{Me}$), 6.77–8.18 (m, 18H, arom H).

^{31}P: 3.3.

MS: 364 (M, 100), 165 (R_2CH, 18).

Synthesis of Dichloro(diphenylphosphinofluorenyl)-phosphine 13

2.55 mL (4.1 mmol) of *n*-BuLi were added dropwise to a solution of 7 (1.36 g, 3.88 mmol) in THF (25 mL) cooled at −30°C. The mixture (turned yellow) was allowed to warm to room temperature, then stirred for .5 h, and finally was added dropwise to a solution of phosphorus trichloride (2 eq., 7.77 mmol) in THF (20 mL). The solution turned colorless. After removal of solvent, 20 mL of pentane and 20 mL of Et_2O were added. The lithium salts were removed by filtration, the filtrate evaporated and the residue recrystallized from pentane/Et_2O to afford a white powder of **13** (0.75 g, 43%).

NMR: ^{1}H (80 MHz): 7.10–8.10 (m, 18H, arom H).

^{13}C: 120.26 (C_4C_5), 125.45 (dd, $^3J_{CP}$: 4.8 Hz and 7.0 Hz, C_1C_8), 127.15 and 128.19 (C_2C_7 and C_3C_6), 128.27 (d, $^3J_{CP}$: 7.8 Hz, *m*-CH Ph), 129.96 (*p*-CH Ph), 132.88 (dd, $^1J_{CP}$: 18.3 Hz, $^3J_{CP}$: 5.2 Hz, *ipso*-C Ph), 134.84 (dd, $^2J_{CP}$: 22.7 Hz, $^4J_{CP}$: 2.6 Hz, *o*-CH Ph), 141.52 (dd, $^2J_{CP}$: 4.4 Hz and 10.5 Hz, $C_{10}C_{11}$), 141.57 (t, $^3J_{CP}$: 1.75 Hz, $C_{12}C_{13}$).

^{31}P: 6.4 (d, $^2J_{PP}$: 167.8 Hz, PPh_2), 179.8 (d, $^2J_{PP}$: 167.8 Hz, PCl_2).

Synthesis of Dichloro(dimesitylphosphinofluorenyl)-phosphine 14

1.55 mL (2.47 mmol) of *n*-BuLi were added to a solution of $R_2CHPMes_2$ **8** (0.98 g, 2.25 mmol) in THF (25 mL) cooled at −20°C. After 20 min of

stirring, the red solution was added dropwise at the same temperature to a solution of phosphorus trichloride (1.54 eq., 0.3 mL) in Et_2O (10 mL). The reaction mixture was allowed to warm to room temperature and then stirred for 1 h. After removal of the lithium salts, the product was unambiguously characterized by NMR spectroscopy but could not be isolated in pure form by crystallization. However, it can be used without further purification.

NMR: ^{31}P (THF): −26.4 (d, $^2J_{PP}$: 409.0 Hz, $PMes_2$), 167.2 (d, $^2J_{PP}$: 409.0 Hz, PCl_2).

Reaction of $R_2C(Li)PPh_2$ with AsF_3: Synthesis of 15 and 16

$R_2C(Li)PPh_2$ **11** was prepared as previously described from 0.50 g (1.40 mmol) of **7**. The reaction mixture was then added at room temperature to a solution of AsF_3 (0.28 g, 2.1 mmol) in THF (15 mL) and turned yellow. After .5 h of stirring, the mixture was analyzed and **15** (66%) and **16** (33%) were characterized by NMR spectroscopy. Fractional crystallization did not allow the separation of these two compounds.

NMR: 15: ^{19}F: −35.1 (d, $^3J_{PF}$: 28.1 Hz).
^{31}P: −6.1 (t, $^3J_{PF}$: 28.1 Hz).
16: ^{19}F: −132.4 (t, $^3J_{PF}$: 38.4 Hz).
^{31}P: 7.9 (d, $^3J_{PF}$: 38.4 Hz).

Reaction of $R_2C(Li)PPh_2$ with SbF_3: Synthesis of Fluoro[bis(diphenylphosphinofluorenyl)]antimony 17

$R_2C(Li)PPh_2$ **11** was prepared as previously described from 1.81 g (5.17 mmol) of **7**, and added dropwise to a solution of SbF_3 (1.8 g, 1.9 eq., 9.90 mmol) in THF (30 mL) cooled at −50°C. The reaction mixture turned orange and was allowed to warm to room temperature. The solution turned brown, and after removal of the lithium salts, a pale brown compound was obtained. **17** was not completely purified by crystallization but crude solution can be used for further reactions.

NMR: ^{19}F: −125.0 (t, $^3J_{PF}$: 27.8 Hz).
^{31}P: 2.6 (d, $^3J_{PF}$: 27.8 Hz).

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