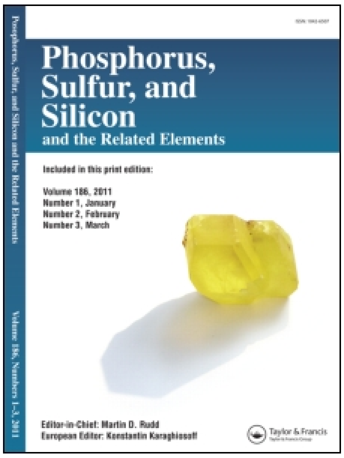


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# ATTEMPTED SYNTHESIS OF A TRANSITION-METAL STANNAPHOSPHENE COMPLEX

A. Kandri Rodi[a]; H. Ranaivonjatovo[a]; J. Escudié[a]; A. Kerbal[b]
[a] Hétérochimie Fondamentale et Appliquée, UPRES A 5069, Université Paul Sabatier, Toulouse cedex 04, France [b] Laboratoire de Chimie Organique, Faculté des Sciences Dhar El Mahraz, Université Sidi Mohamed Ben Abdellah, Fès, Maroc

**To cite this Article** Rodi, A. Kandri , Ranaivonjatovo, H. , Escudié, J. and Kerbal, A.(1997) 'ATTEMPTED SYNTHESIS OF A TRANSITION-METAL STANNAPHOSPHENE COMPLEX', Phosphorus, Sulfur, and Silicon and the Related Elements, 126: 1, 157 — 169

**To link to this Article: DOI:** 10.1080/10426509708043555

**URL:** http://dx.doi.org/10.1080/10426509708043555

*Phosphorus, Sulfur and Silicon*, 1997, Vol. 126, pp. 157-169
Reprints available directly from the publisher
Photocopying permitted by license only

# ATTEMPTED SYNTHESIS OF A TRANSITION-METAL STANNAPHOSPHENE COMPLEX

A. KANDRI RODI[a], H. RANAIVONJATOVO[a], J. ESCUDIÉ[a]
and A. KERBAL[b]

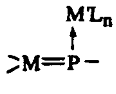
[a] *Hétérochimie Fondamentale et Appliquée, UPRES A 5069, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse cedex 04, France;* [b] *Laboratoire de Chimie Organique, Faculté des Sciences Dhar El Mahraz, Université Sidi Mohamed Ben Abdellah, BP 1796, Fès, Maroc.*

*(Received 1 February, 1997)*

Fluoro-, chloro- and bromostannylphosphines (**8-10**) complexed on phosphorus by tungsten pentacarbonyl have been synthesized by reaction between lithium mesityl(tungsten pentacarbonyl)phosphide **4** and the corresponding dihalo(diisityl)tin (isityl: 2,4,6-triisopropylphenyl). Reaction of **8** with tert-butyllithium afforded the stable lithium fluorostannylphosphide **11**. Addition of $Me_3SiCl$ or $MgBr_2$ to **11** gave the corresponding chloro- and bromoderivatives **14** and **15**. Similar compounds **16** and **17** were obtained from **9** and **10** and DBU. **11, 14, 15, 16** and **17** present a large $^1J_{SnP}$ coupling constant (2099.0 to 2151.4 Hz) indicating a partial Sn-P double bond.

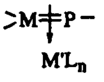
## INTRODUCTION

In the recent years, some stable metallaphosphenes >M=P- (M: Si[1,2], Ge[1,3], Sn[1,3g,4]) have been synthesized and physicochemically and chemically characterized However, if many doubly-bonded phosphorus compounds, particularly diphosphenes -P=P- [5] and phospha-alkenes >C=P- [6], have been stabilized by complexation with a transition metal, no metallaphosphene complexes such as A, B or C have been obtained so far:



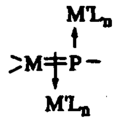
$>M=\overset{\overset{M'L_n}{\uparrow}}{P}-$

A



$>M\underset{\underset{M'L_n}{\downarrow}}{=}P-$

B



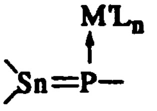
$>M\overset{\overset{M'L_n}{\uparrow}}{\underset{\underset{M'L_n}{\downarrow}}{=}}P-$

C

**(M: Si, Ge, Sn)**
**(M': transition metal)**

Such a complexation by a transition metal would be very interesting since, whereas extremely bulky groups are necessary to obtain stable >M=P- compounds and prevent their dimerisation, it would be possible in this case to stabilize metallaphosphenes substituted by small groups on P or both on M and P. Decomplexation would then afford hyperreactive >M=P- compounds.

We describe in this paper our first attempts to synthesize a stannaphosphene complex of type A:



**A**

## RESULTS AND DISCUSSION

Two routes to compounds A were a priori possible:

a. the direct complexation of a transient stannaphosphene >Sn=P- by a transition metal,

b. the complexation of a precursor of a stannaphosphene, such as a halostannylphosphine >Sn(X)-P(H)-, followed by its dehydrohalogenation.

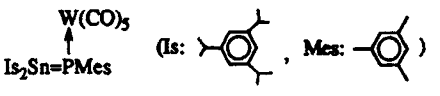
In these two cases we have used a tungsten complex, which is interesting in $^{31}P$ NMR owing to the $^{183}W$-$^{31}P$ coupling.

### 1) route a

Our preliminary attempts according to route **a** failed: addition of a solution of $W(CO)_5$.THF to a solution of $Is_2Sn{=}PIs$ **1** [7] (Is = isityl = 2,4,6-triisopropylphenyl) at –70°C did not give the complexed stannaphosphene $Is_2Sn{=}P[W(CO)_5]Is$; only decomposition products of starting stannaphosphene **1** were observed by warming to room temperature. One of the limitation of route **a** is that the complexation of phosphorus must occur at very low temperature which cannot be the case with a relatively bulky group such as a 2,4,6-triisopropylphenyl. Unfortunately, when phosphorus is substituted by a less bulky mesityl group, the corresponding stannaphosphene $Is_2Sn{=}PMes$ is too unstable, even at low temperature, to allow complexation.

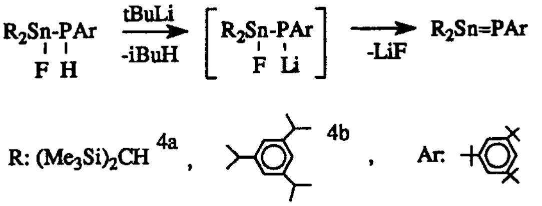
## 2) route b

In route **b**, as the phosphorus is complexed before the formation of the Sn=P double bond, a smaller group such as a mesityl can be used. Thus we have tried to prepare **2**, with two isityl groups on tin because such groups appeared very stabilizing for doubly-bonded tin derivatives[8-10]:

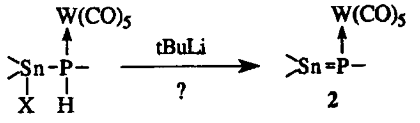


**2**

As uncomplexed stannaphosphenes were prepared in a good yield by dehydrofluorination of the corresponding fluorostannylphosphines by tert-butyllithium (eq. 1), we devised a similar route to complexed stannaphosphenes **2**(eq. 2):

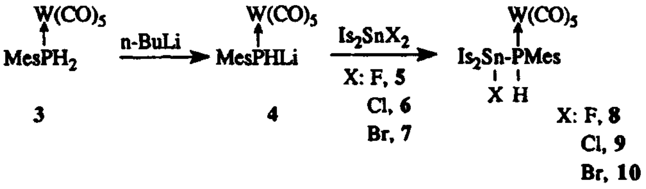


eq 1



eq 2

The synthesis of **2** involved the preliminary preparation of **8**, **9** or **10** according to the following process (eq. 3):



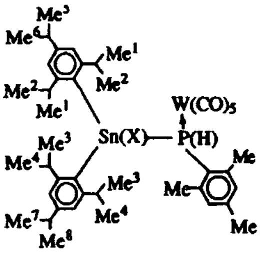
eq 3

Starting from **3**[11], the lithium phosphide **4** was prepared at low temperature. Solutions of **4** in THF were added to solutions of $Is_2SnF_2$[9a], $Is_2SnCl_2$[10a] or $Is_2SnBr_2$ (prepared from $(Is_2SnO)_3$[10a] and HBr) in pentane.

**8-10** were obtained as pure compounds after crystallization and characterized by $^1H$ (table I), $^{13}C$ (table II), $^{31}P$ and $^{119}Sn$ (table III) NMR, and by mass spectrometry.

TABLE I $^1H$ NMR ($CDCl_3$, δ (ppm), J (Hz))

| | *8* | *9* | *10* |
|---|---|---|---|
| o-$CH(C\underline{H}_3)_2$ (a) | 0.61, 1.08, 1.12 and 1.30 (4d, $^3J_{HH}$ : 6.8, 4 x 6H) | 0.64, 1.01, 1.03 and 1.19 (4d, $^3J_{HH}$ : 6.5, 4 x 6H) | 0.67, 0.99, 1.01, 1.16 (4d, $^3J_{HH}$ : 6.5, 4 x 6H) |
| p-$CH(C\underline{H}_3)_2$ (a) | 1.19 and 1.20 (2d, $^3J_{HH}$ : 6.8, 2 x 6H) | 1.15 and 1.17 (2d, $^3J_{HH}$ : 6.5, 2 x 6H) | 1.13 and 1.16 (2d, $^3J_{HH}$ : 6.5, 2 x 6H) |
| p-$CH_3$ | 2.30 (s, 3H) | 2.28 (s, 3H) | 2.26 (s, 3H) |
| o-$CH_3$ (b) | 2.56 and 2.60 (2s, 2 x 3H) | 2.53 and 2.56 (2s, 2 x 3H) | 2.53 and 2.58 (2s, 2 x 3H) |
| p– and o-$C\underline{H}(CH_3)_2$ | 2.45–3.15 (m, 6H) | 2.50–3.25 (m, 6H) | 2.53–3.20 (m, 6H) |
| P-H | 5.98 (dd, $^1J_{HP}$ : 304.0, $^3J_{HF}$ : 8.5, 1H) | 6.21 (d, $^1J_{HP}$ : 304.3, 1H) | 6.32 (d, $^1J_{PH}$ : 302.2, 1H) |
| H arom Is | 6.96 (s, $^4J_{HSn}$ : 28.0, 2H)<br>7.03 (s, $^4J_{Hsn}$ : 30.0, 2H) | 6.88 ($^4J_{HSn}$ : 31.0, 2H)<br>6.97 ($^4J_{HSn}$ : 26.2, 2H) | 6.86 ($^4J_{HSn}$ : 27.8, 2H)<br>6.95 ($^4J_{HSn}$ : 28.5, 2H) |
| H arom Mes (b) | 6.90 - 7.01 (m, 2H) | 6.90 - 7.00 (m, 2H) | 6.85 - 7.05 (m, 2H) |



(a) Due to chiral phosphorus, the two isityl groups are diastereotopic. As the two methyls of every iPr group are also diastereotopic, four doublets were expected and are really observed for the eight methyls of o-iPr: in the two o-iPr of every isityl, the methyl groups Me$^1$ and Me$^2$ or Me$^3$ and Me$^4$ are two on two equivalent. Four doublets are also expected for the methyls of p-iPr. However, as the prochiral tin is far away, Me$^5$ and Me$^6$ appear equivalent and give only one doublet, as well as Me$^7$ and Me$^8$.

(b) Two singlets are observed for the o-methyl groups (instead of one singlet expected) and a very broad multiplet for the aromatic hydrogens (instead of a doublet by coupling with phosphorus). This phenomenon is of course due to a hindered rotation of the mesityl group explained by the very large steric hindrance.

TABLE II $^{13}C$ NMR ($CDCl_3$, $\delta$ (ppm), J (Hz))

| | *8* | *9* | *10* |
|---|---|---|---|
| p-$CH_3$ | 21.01 | 21.02 | 21.03 |
| o-$CH_3$ p-$CH(\underline{C}H_3)_2$ o-$CH(\underline{C}H_3)_2$ | 23.28, 23.35, 23.84 24.43, 24.73, 24.87, 25.06 | 23.75, 23.86, 24.33, 24.53, 24.56, 24.86, 25.15 | 23.87, 24.21, 24.61, 25.06, 25.13, 25.32 |
| p-$\underline{C}H(CH_3)_2$ | 34.22, 34.32 | 34.17, 34.24 | 34.15, 34.22 |
| o-$\underline{C}H(CH_3)_2$ | 38.03 (d, $^{4}J_{CP}$ : 4.1) ($^{3}J_{CSn}$ : 48.4)<br>39.25 ($^{3}J_{CSn}$ : 41.1) | 38.15 (broad)<br>39.04 ($^{3}J_{CSn}$ : 43.4) | 38.47 (broad)<br>38.93 ($^{3}J_{CSn}$ : 43.3) |
| m-C Is | 122.79 ($^{3}J_{CSn}$ : 63.5)<br>123.17 ($^{3}J_{CSn}$ : 58.9) | 122.83 ($^{3}J_{CSn}$ : 61.4)<br>123.26 ($^{3}J_{CSn}$ : 59.8) | 122.81<br>123.28 |
| ipso-C Mes | 126.92 (d, $^{1}J_{CP}$ : 24.8) | 127.23 (d, $^{1}J_{CP}$ : 22.9) | 127.49 (d, $^{1}J_{CP}$ : 22.5) |
| m-C Mes (a) | 129.94 (d, $^{3}J_{CP}$ : 12.6)<br>129.97 | 130.06 (d, $^{3}J_{CP}$ : 14.7)<br>130.09 | 129.84 (d, $^{3}J_{CP}$ : 12.5)<br>129.87 |
| p-C Mes | 139.50 | 139.57 | 139.51 |
| o-C Mes (a) | 138.72<br>($^{3}J_{CSn}$ or $_{CW}$ : 19.8)<br>141.72 (d, $^{3}J_{CP}$ : 16.0) | 138.73<br>($^{3}J_{CSn}$ or $_{CW}$ : 20.1)<br>141.92 ($^{3}J_{CP}$ : 16.3) | 138.85<br>($^{3}J_{CSn}$ or $_{CW}$ :19.9)<br>141.86 (d, $^{2}J_{CP}$ : 16.2) |
| ipso-C Is | 138.24 (d, $^{2}J_{CP}$ : 5.0)<br>141.11 (dd, $^{2}J_{CP}$ and $^{2}J_{CF}$ : 10.0 and 4.7) (b) | 139.85 (d, $^{2}J_{CP}$ : 16.9)<br>142.28 (d, $^{2}J_{CP}$ : 4.0) | 139.89 (d, $^{2}J_{CP}$ : 15.8)<br>(c) |
| p-C Is | 152.02, ($^{4}J_{CSn}$ : 12.7) | 151.63, ($^{4}J_{CSn}$ : 12.7)<br>151.74, ($^{4}J_{CSn}$ : 12.4) | 151.47,<br>151.65 |
| o-C Is | 154.23 ($^{2}J_{CSn}$ : 60.0)<br>154.41 ($^{2}J_{CSn}$ : 54.5) | 153.51, ($^{2}J_{CSn}$ : 57.0)<br>154.03 (broad) | 153.37, ($^{2}J_{CSn}$ : 51.3)<br>153.78 (broad) |
| cis C=O (a) | 196.21 (d, $^{2}J_{CP}$ : 5.5) ($^{1}J_{CW}$ : 126.3) | 196.52 (d, $^{2}J_{CP}$ : 5.5) ($^{1}J_{CW}$ : 127.5) | 196.55 (d, $^{2}J_{CP}$ : 5.6) ($^{1}J_{CW}$ : 121.0) |
| trans C=O (a) | 198.74 (d, $^{2}J_{CP}$ : 23.3) | 198.81 (d, $^{2}J_{CP}$ : 23.9) | 198.75 (d, $^{2}J_{CP}$ : 24.1) |

(a) Two signals are observed for m-C (Mes) and also for o-C (Mes) due to a hindered rotation of the mesityl group: a singlet (with tin or tungsten satellites in the case of o-C Mes) and a doublet (coupling with phosphorus) for which the tin satellites are not observed.

(b) The attribution $J_{CP}$ or $J_{CF}$ could not be made,

(c) The second ipso-C Is could not be determined unambiguously.

(d) Cis and trans CO have been attributed according to literature data[12] which show that cis CO are more shielded and have a smaller $^{2}J_{CP}$ coupling constant than trans CO.

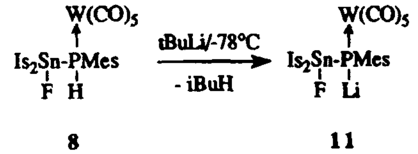
TABLE III $^{31}P$ and $^{119}Sn$ NMR (δ (ppm), J (Hz))

| | *8 (CDCl$_3$)* | *9 (C$_6$D$_6$)* | *10 (CDCl$_3$)* |
|---|---|---|---|
| $\delta^{31}P$ | -121.17 | -113.21 | -111.93 |
| $\delta^{119}Sn$ | -49.10 | -59.80 | -94.56 |
| $^1J_{P}119_{Sn}$ | 209.6 | 259.0 | 302.8 |
| $^1J_{P}117_{Sn}$ | 200.1 | 253.6 | 291.1 |
| $^1J_{PW}$ | 195.1 | 200.1 | 200.9 |
| $^1J_{PH}$ | 304.3 | 304.3 | 302.2 |
| $^2J_{PF}$ | 41.6 | | |

8: $^{19}F$ NMR (CDCl$_3$): – 110.42, $^1J_F117_{Sn}$: 2554.6, $^1J_F119_{Sn}$: 2669.0, $^3J_{FH}$ : 8.5 Hz.

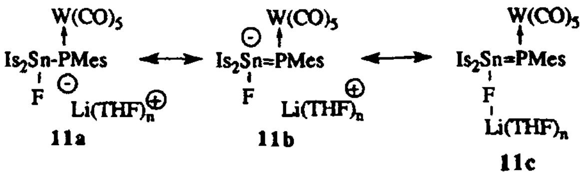
### *a) route involving lithio compounds*

Addition of tert-butyllithium to a solution of **8** in THF at low temperature afforded stable lithium phosphide **11** (eq. 4):



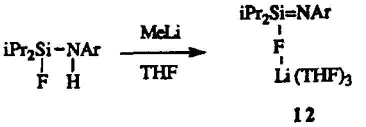
eq 4

The formation of **11** was unambiguously proved by $^{31}P$ NMR (no hydrogen on phosphorus) and by $^{119}Sn$ NMR which displayed a tin-fluorine coupling constant (see table IV). The most interesting feature was the great difference of $^1J_P119_{Sn}$ coupling constant between **8** (209.6 Hz) [13] and **11** (2099.0 Hz)[13]. The large increase of this coupling constant, as well as the deshielding of the $^{119}Sn$ NMR signal (from –49.1 to + 35.18 ppm) seem to indicate a partial double bond between tin and phosphorus. Thus, the structure of **11** could be described by the two forms **11a** and **11b**; however structure **11c** seems also possible (eq. 5):



eq 5

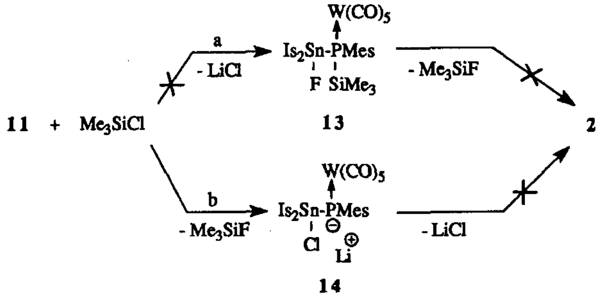
A structure analogous to **11c** has been described by Klingebiel[14] in the reaction between a lithio compound and a fluorosilylamine (eq. 6):



eq 6

Heating **11** did not give the expected stannaphosphene complex Is$_2$Sn=PMes[W(CO)$_5$] **2**.

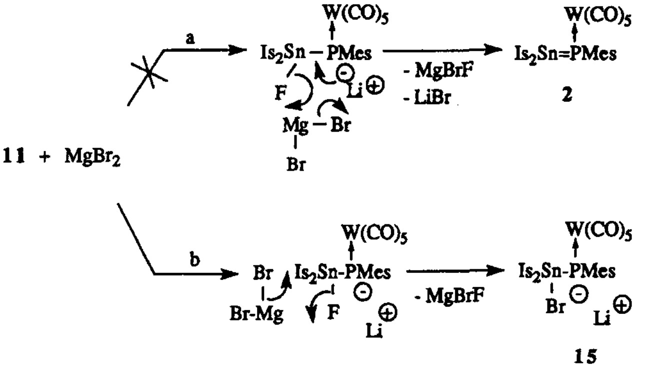
Addition of chlorotrimethylsilane to **11** could make easier the elimination of lithium fluoride according to route **a** or **b** (eq. 7) (for example addition of Me$_3$SiCl to **12** afforded the corresponding silanimine iPr$_2$Si=NAr via the chlorosilane intermediate iPr$_2$Si(Cl)N(Li)Ar[14]):



eq 7

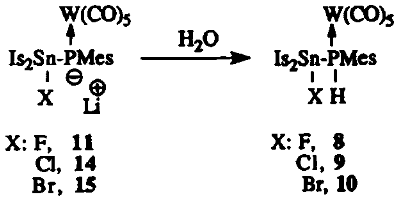
But only compound **14** was obtained, nearly quantitatively, according to route **b**, whereas the formation of **2** was not observed.

We have tried to eliminate lithium fluoride by adding MgBr$_2$ to **11**. Such an addition of magnesium bromide was successful to obtain germanimine >Ge=N- from lithium fluorogermylamide >Ge(F)-N(Li)-[15]. However, in our case, we did not obtain the expected stannaphosphene **2** via route **a**, but exclusively the lithium bromostannylphosphide **15** via route **b** (eq. 8):



eq 8

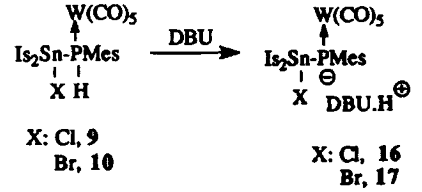
**11**, **14** and **15** were thermally stable but, as expected, extremely air- and moisture-sensitive. They are unambiguously characterized by $^{31}P$ and $^{119}Sn$ NMR with chemical shifts close to those of **11** (table IV), and by their reaction with water, leading to **8**, **9** and **10** respectively (eq. 9):



eq 9

### *b) route involving DBU*

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is a powerful dehydrohalogenating compound widely used in doubly-bonded phosphorus chemistry[5,6]. In our case, addition of an excess of DBU to **9** or **10** did not afford the stannaphosphene **2** but the chloro- or bromostannylphosphide **16** or **17** respectively (eq. 10):



eq 10

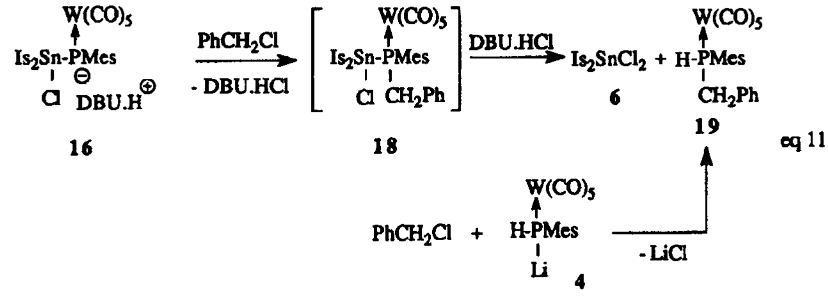
The $^{31}P$ and $^{119}Sn$ NMR analyses showed that **16** and **17** feature the same anions than **14** and **15**. The five compounds **11**, **14**, **15**, **16** and **17** present similar physico-chemical data with very large $^{1}J_{P}{}^{119}{}_{Sn}$ coupling constants (between 2099.0 and 2150.8 Hz) and deshielding of the $^{119}Sn$ NMR signal by about 60 ppm relatively to the corresponding halostannylphosphine analogues **8-10** (tables III and IV). Thus, they present very close structures, probably of the type **11a-11b**.

TABLE IV $^{31}P$ and $^{119}Sn$ NMR (δ (ppm), J (Hz))

| | *11* | *14* | *15* | *16* | *17* |
|---|---|---|---|---|---|
| $\delta^{31}P$ | –120.96 | –101.08 | –84.91 | –101.07 | –84.57 |
| $\delta^{119}Sn$ | 35.18 | –2.60 | –33.49 | –2.66 | |
| $^{1}J_{P}119_{Sn}$ | 2099.0 | 2155.2 | 2128.9 | 2150.8 | 2130.8 |
| $^{1}J_{P}117_{Sn}$ | 2023.0 | 2061.1 | 2031.9 | 2075.8 | 2036.0 |
| $^{1}J_{PW}$ | 97.0 | 98.0 | 99.7 | 96.4 | 100.1 |
| $^{2}J_{PF}$ | 33.8 | | | | |

**11**: $\delta^{19}F$: – 97.97, $^{1}J_{F}117_{Sn}$: 3004.0, $^{1}J_{F}119_{Sn}$: 3152.4 Hz.

Compound **16** has been chemically characterized by reaction with benzyl chloride leading to **6** and **19** (eq. 11):



The formation of **6** and **19** can occur from the intermediate **18** followed by a cleavage of the tin-phosphorus bond by DBU.HCl. **19** was easily prepared by an independent synthesis from benzyl chloride and **4**.

In conclusion, complexed halostannylphosphides present a different behaviour from those of uncomplexed halostannylphosphides which afford the corresponding stannaphosphenes at low temperature (generally below –50°C) in nearly quantitative yield. The lack of the lone pair on phosphorus is probably one of the main reason for this different behaviour.

## EXPERIMENTAL SECTION

As lithio compounds and derivatives with a tin-phosphorus bond are air- and moisture-sensitive, their synthesis and handling require high-vacuum techniques and the use of carefully deoxygenated solvents which must be freshly distilled from sodium benzophenone.

NMR spectra have been recorded on the following instruments:

| | |
|---|---|
| $^{1}H$ | Bruker AC 80 (80.1 MHz) and AC 250 (250.1 MHz) |
| $^{13}C$ | Bruker AC 200 (50.3 MHz) and AC 250 (62.89 MHz) (Ref. TMS) |
| $^{19}F$ | Bruker AC 80 (75.39 MHz) ($CF_3COOH$ ext. standard). |
| $^{31}P$ | Bruker AC 80 (32.43 MHz) and AC 200 (81.01 MHz)<br>($H_3PO_4$ 85 % ext. standard). |
| $^{119}Sn$ | Bruker AC 200 (74.63 MHz) ($Me_4Sn$ ext. standard). |

Solvent was $CDCl_3$ excepted when another solvent is reported.

Mass spectra were measured on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV. Melting points were determined on a Leitz microscope heating stage 350. Elemental analyses, performed by the "Service de Microanalyse de l'Ecole de Chimie de Toulouse, France" gave satisfactory results within 0.4% error and are not reported.

$Is_2SnF_2$[9a] and $Is_2SnCl_2$[10a] were prepared as previously described from $(Is_2SnO)_3$[10a] and HF or HCl respectively; $MesPH_2[W(CO)_5]$[11] was obtained from $MesPH_2$ and $W(CO)_5$.THF.

## Synthesis of $Is_2SnBr_2$ 7

To a solution of cyclotristannoxane $(Is_2SnO)_3$ (prepared as previously described[10a] from IsBr[16], Mg and $SnBr_4$, and followed by basic hydrolysis) (10.06 g, 6.20 mmol) in benzene (150 ml) were added 5 equivalents of a solution of hydrobromic acid in water (40 %). After 1/2 h of stirring at room temperature, the aqueous layer was extracted with benzene. All the organic layers were mixed; then benzene with unreacted HBr were removed *in vacuo*; 150 ml of pentane were added and the solution was dried over $Na_2SO_4$. After removal of pentane, crude $Is_2SnBr_2$ was recrystallized from $Et_2O$ in the form of white crystals (11.46g, 90 %, mp: 65°C).

**$^1$HNMR**: 1.14 (d, $^3J_{HH}$: 6.6 Hz, 24 H, o-CH$\underline{Me}_2$), 1.21 (d, $^3J_{HH}$: 6.8 Hz, 12 H, p-CH$\underline{Me}_2$), 2.85 (sept, $^3J_{HH}$: 6.8 Hz, 2 H, p-C$\underline{H}$Me$_2$), 3.36 (sept, $^3J_{HH}$: 6.6 Hz, 4 H, o-C$\underline{H}$Me$_2$), 6.99 (s, $^4J_{H119Sn}$: 39.3 Hz, 4 H, arom H).

**$^{13}$C NMR**: 24.00 (p-CH$\underline{Me}_2$), 24.64 ($^4J_{CSn}$: 35.3 Hz, o-CH$\underline{Me}_2$), 34.38 (p-$\underline{C}$HMe$_2$), 37.27 ($^3J_{CSn}$: 51.3 Hz, o-$\underline{C}$HMe$_2$), 122.89 ($^3J_{CSn}$: 74.7 Hz, m-C Is), 139.82 (ipso-C Is: the $^1J_{CSn}$ coupling constant could not be obtained because of a very small signal), 152.07 (p-C Is), 153.54 ($^2J_{CSn}$: 64.8 Hz, o-C Is).

**$^{119}$Sn NMR**: – 167.78.

**MS ($^{120}$Sn)**: 685 (M – 1, 1), 605 (M - Br, 3), 401 (IsSnBr – 1, 1), 202 (Is – 1, 100).

## Synthesis of stannylphosphine complexes 8, 9 and 10

2.43 ml of n-butyllithium 1.6 M in hexane were added to a solution of **3** (3.89 mmol) in THF (20 ml) cooled at –78°C. After 1/2 h of stirring at this temperature, one equivalent of $Is_2SnX_2$ (X: F, 2.19 g; Cl, 2.32 g; Br, 2.66 g) in solution in pentane (15 ml), cooled at –78°C was slowly added. Then the reaction mixture was allowed to warm to room temperature and turned yellow. After removal of the lithium salts, recrystallization from pentane afforded yellow crystals of respectively **8** (3.17 g, 80 %, mp: 140°C), **9** (3.58 g, 89 %, mp: 118–119°C) and **10** (3.57 g, 85 %, mp: 120°C).

**MS ($^{120}$Sn, $^{184}$W):**

**8**: (DCI/$CH_4$): 1019 (M+1, 4), 999 (M – F, 6), 787 (M – Is - CO, 1), 545 ($Is_2SnF$, 17), 476 ($MesPH_2.W(CO)_5$, 36), 419 ($MesPH.W(CO)_3$, 1), 355 ($P.W(CO)_5$, 40), 202 (Is – 1, 100).

**9**: (EI, 70 eV): 712 (M - $W(CO)_5$, 1), 677 (M – $W(CO)_5$ – Cl, 4), 561 ($Is_2SnCl$, 100), 449 ($MesPH_2.W(CO)_4$ + 1, 1), 419 ($MesPH.W(CO)_3$, 7), 202 (Is – 1, 63).

**10**: (EI, 70 eV): 645 (IsSn(Br)P.W(CO) – 1, 10), 605 ($Is_2SnBr$, 80), 475 ($MesPH.W(CO)_5$, 13), 419 ($MesPH.W(CO)_3$, 30), 202 (Is – 1, 100).

### Reaction of 8 with tBuLi

To a solution of **8** (1.10 g, 1.08 mmol) in THF (8 ml) cooled at –78°C was added one equivalent of a solution of tert-butyllithium 1.7 M in pentane. During warming to room temperature, the reaction mixture turned red. The NMR analysis showed the quantitative formation of **11**. Heating at reflux of THF or in a sealed tube at 100°C did not afford the expected stannaphosphene **2** but still **11** with unidentified decomposition products.

### Reaction of 11 with $Me_3SiCl$ or with $MgBr_2$

To a red solution of **11** (1.07 mmol) was added at room temperature one equivalent of chlorotrimethylsilane (0.11 g) or of $MgBr_2$ (0.20 g) (freshly prepared from 0.20 g of 1,2-dibromoethane, 0.03 g of Mg and 10 ml of THF). The NMR analysis proved the respective formation of the chloro- (**14**) or the bromo- (**15**) lithium stannylphosphides.

### Reaction of 9 or 10 with DBU

An excess of DBU (0.22 g, 1.44 mmol) was added to solutions of **9** (1.00 g, 0.96 mmol) or **10** (1.00 g, 0.92 mmol) in benzene (8 ml). An orange coloration appeared immediately. $^{31}$P and $^{119}$Sn NMR analyses showed the formation of **16** or **17**.

### Reaction of 11, 14 and 15 with water

To red solutions of **11** (1.07 mmol), **14** (1.07 mmol) and **15** (1.07 mmol) in $Et_2O$ (8 ml) was slowly added one equivalent of water in THF (3 ml) ; the reaction mixture turned immediately from red to yellow. After removal of lithium halide by filtration and of solvents *in vacuo,* recrystallization from pentane afforded respectively **8** (0.81 g, 74 %), **9** (0.90 g, 81 %) and **10** (0.88g, 76%) as yellow crystals.

## Reaction of 16 with benzyl chloride

To a solution of **16** (1.44 mmol) in benzene (8 ml) was slowly added at room temperature one equivalent of benzyl chloride (0.18 g) in $Et_2O$ (3 ml). After 1 h of stirring, the $^{119}$Sn NMR showed the formation of dichlorodiisitylstannane **6** (δ $^{119}$Sn: –64.13 ppm) [10a] and of **19**. Fractional crystallization did not allow the complete separation and purification of every compound; thus the formation of **19** was proved by its independent synthesis.

## Synthesis of 19

To a solution of **4** (1.73 mmol) in THF (20 ml) cooled at –78°C was added one equivalent of benzyl chloride (0.22 g, 1.73 mmol) in the same solvent (5 ml). After warming to room temperature, LiF was removed from the reaction mixture by filtration. Crude **19** was crystallized from pentane as yellow crystals (0.63 g, 64%, mp: 89°C).

**$^1$H NMR**: 2.10 (s, 6H, o-Me), 2.62 (s, 3H, p-Me), 4.10 (dd, $^2J_{HP}$: 7.1 Hz, $^3J_{HH}$: 7.1 Hz, 2H, $PhCH_2$), 6.26 (dt, $^1J_{HP}$: 347 Hz, $^3J_{HH}$: 7.1 Hz, 1H, PH), 6.60 – 7.40 (m, 7H, arom H (Mes + Ph)).

**$^{31}$P NMR**: –43.74, $^1J_{PW}$: 219.3 Hz, $^1J_{PH}$: 347 Hz

MS(EI, 70 eV): 566 (M, 40), 538 (M – CO, 14), 510 (M - 2CO, 6), 482 (M - 3CO, 50), 454 (M - 4CO, 31), 424 (MesP(W)=CHPh, 100), 391 (M - Mes - 2CO, 42).

## *References*

[1] For recent reviews on >M=P- compounds, see : F. Bickelhaupt, in *"Multiple bonds and low coordination in phosphorus chemistry"*, M. Regitz and O.J. Scherer Eds.; Georg Thieme Verlag: Stuttgart, New York, (1990), p. 287. J. Escudié, C. Couret, H. Ranaivonjatovo and J. Satgé, *Coordination Chem. Rev.*, **130**, 427 (1994). M. Driess, *Adv. Organomet. Chem.*, **39**, 193 (1996). M. Driess, *Coordination Chem. Rev.*, **145**, 1 (1995). A. Kandri Rodi, H. Ranaivonjatovo, J. Escudié and A. Kerbal, *Main Group Metal Chem.*, **19**, 199 (1996).

[2] C.N. Smit, F.M. Lock and F. Bickelhaupt, *Tetrahedron Lett.* **25**, 3011 (1984). C.N. Smit and F. Bickelhaupt, *Organometallics*, **6**, 1156 (1987). E. Niecke, E. Klein and M. Nieger, *Angew. Chem. Int. Ed. Engl.*, **28**, 751 (1989). Y. Van Den Winkel, H.M.M. Bastiaans and F. Bickelhaupt, *J. Organomet. Chem.*, **405**, 183 (1991). M. Driess, S. Rell and H. Pritzkow, *J. Chem. Soc. Chem. Commun.*, 253 (1995). H.R.G. Bender, E. Niecke and M. Nieger, *J. Am. Chem. Soc.*, **115**, 3314 (1993). M. Driess, *Angew. Chem. Int. Ed. Engl.*, **30**, 1022 (1991). R. Corriu, G. Lanneau and G. Priou, *Angew. Chem. Int. Ed. Engl.*, **30**, 1130 (1991).

[3] a) J. Escudié, C. Couret, J. Satgé, M. Andrianarison and J.D. Andriamizaka, *J. Am. Chem. Soc.*, **107**, 3378 (1985). b) J. Escudié, C. Couret, M. Andrianarison and J. Satgé, *J. Am. Chem. Soc.*, **109**, 386 (1987). c) J. Escudié, C. Couret, M. Andrianarison, A. Raharinirina and J. Satgé, *Phosphorus and Sulfur*, **30**, 377 (1987). d) M. Dräger, J. Escudié, C. Couret, H. Ranaivonjatovo and J. Satgé, *Organometallics*, **7**, 1010 (1988). e) H. Ranaivonjatovo, J. Escudié, C. Couret, J. Satgé and M. Dräger, *New. J. Chem.*, **13**, 389 (1989). f) H. Ranaivonjatovo, J. Escudié, C. Couret and J. Satgé, *J. Organomet. Chem.*, **415**, 327 (1991). g) K.M. Baines and W.G. Stibbs, *Adv. Organomet. Chem.*, **39**, 275 (1996).

[4] a) C. Couret, J. Escudié, J. Satgé, A. Raharinirina and J.D. Andriamizaka, *J. Am. Chem. Soc.*, **107**, 8280 (1985). b) H. Ranaivonjatovo, J. Escudié, C. Couret and J. Satgé, *J. Chem. Soc. Chem. Commun.*, 1047 (1992). c) H. Ranaivonjatovo, J. Escudié, C. Couret, A. Kandri Rodi and J. Satgé, *Phosphorus, Sulfur and Silicon*, **76**, 61 (1993).

[5] For reviews see: A.M. Caminade, J.P. Majoral and R. Mathieu, *Chem. Rev.*, **91**, 575 (1991). L. Weber, *Chem. Rev.*, **92**, 1839 (1992).

[6] For reviews see: J.F. Nixon, *Chem. Rev.*, **88**, 1327 (1988). L.N. Markovski and V.D. Romanenko, *Tetrahedron*, **45**, 6019 (1989). R. Appel and F. Knoll, *Adv. Inorg. Chem.*, **33**, 259 (1989). L. Weber, *Angew. Chem. Int. Ed. Engl.*, **35**, 271 (1996). R. Appel, in "*Multiple bonds and low coordination in phosphorus chemistry*", M. Regitz and O.J. Scherer Eds.; Georg Thieme Verlag: Stuttgart, New York, (1990), p 157. A. Marinetti, *Actualité Chimique*, **4**, 279 (1992).

[7] Stannaphosphene **1** was prepared by reaction between $Is_2SnF_2$ and $IsPLi_2$ in $Et_2O$ at −78°C. **1** is stable some hours at this temperature but decomposes above (A. Kandri Rodi, H. Ranaivonjatovo and J. Escudié, unpublished results).

[8] Some stannaphosphenes >Sn=P- [4b], stannenes >Sn=C< [9] and distannenes >Sn=Sn< [10] have been stabilized owing to this group.

[9] a) G. Anselme, H. Ranaivonjatovo, J. Escudié, C. Couret and J. Satgé, *Organometallics*, **11**, 2748 (1992). b) A. Schäfer, M. Weidenbruch, W. Saak and S. Pohl, *J. Chem. Soc. Chem. Commun.*, 1157 (1995).

[10] a) S. Masamune and L.R. Sita, *J. Am. Chem. Soc.*, **107**, 6390 (1985). b) M. Weidenbruch, A. Schäfer, H. Kilian, S. Pohl, W. Saak and H. Marsmann, *Chem. Ber.*, **125**, 563 (1992).

[11] S. Bauer, A. Marinetti and F. Mathey, *Heteroatom. Chem.*, **2**, 277 (1991).

[12] A. Marinetti, P. Le Floch and F. Mathey, *Organometallics*, **10**, 1190 (1991).

[13] A large difference was also observed between $Is_2Sn(F)P(H)Ar$ (Ar : 2,4,6-tri-tert-butylphenyl) ($^{1}J_{P^{119}Sn}$ : 994.8 Hz) and $Is_2Sn(F)P(Li)Ar$ ($^{1}J_{P^{119}Sn}$ : 2486.0 Hz) [4b].

[14] R. Boese and U. Klingebiel, *J. Organomet. Chem.*, **315**, C17 (1986).

[15] M. Rivière-Baudet, F. El Baz, J. Satgé, A. Khallaayoun and M. Ahra, *Phosphorus, Sulfur and Silicon*, **112**, 203 (1996).

[16] G. Whitesides, M. Eisenhut and W. M. Bunting, *J. Am. Chem. Soc.*, **96**, 5398 (1974).