

A Stable Compound with a Tin–Phosphorus Double Bond: the (2,4,6-Triisopropylphenyl)(supermesityl)stannaphosphene

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The stable bis(2,4,6-triisopropylphenyl)(supermesityl)stannaphosphene **1** (supermesityl : 2,4,6-tri-*tert*-butylphenyl) has been synthesized by dehydrofluorination of the corresponding fluorostannylphosphine by *tert*-butyllithium; its structure has been evidenced by NMR spectroscopy and by addition of methanol and water onto the tin–phosphorus double bond.

Despite the intensive studies performed on low coordinated species of heavier elements of group 14,¹ stable doubly-bonded compounds of tin are still rare: only two stannenes $>Sn=C<$ ² and a stannaphosphene $>Sn=P<$ ³ have been described. One of the distannenes has been characterized by NMR spectroscopy but oligomerizes above 0 °C,⁴ the other behaves as two stannylenes in solution,⁵ and exhibits a distannene structure only in the solid state,⁶ or in NMR below –100 °C.⁷ We present in this paper the nearly quantitative synthesis of a new stable doubly-bonded tin and phosphorus compound, the stannaphosphene **1**.

Substitution of metal by aryl groups generally enhances the stability of doubly-bonded main group elements and gives cleaner reactions in relation to alkyl groups:† it is for example the case in germanium compounds such as germenes, digermenes and germaphosphenes.^{1e} Moreover the use of a 2,4,6-triisopropylphenyl group (Is) as a substituent on tin appeared to be a good solution for steric stabilization of a stannaphosphene (mesityl or 2,4,6-triethylphenyl would be probably too small). We have substituted the phosphorus atom by the 2,4,6-tri-*tert*-butylphenyl group (supermesityl) which is very efficient for the stabilization of P^{II} compounds.⁸ A good route to doubly-bonded main group elements is usually the dehydrofluorination by lithio compounds of the corresponding fluoro precursors;^{1e} the first step in the synthesis of **1** was the preparation of the fluorostannylphosphine **5**, by addition of (2,4,6-tri-*tert*-butylphenyl)lithiophosphide **4** to the bis(2,4,6-triisopropylphenyl)difluorostannane **3**.‡

The stannaphosphene **1** was then obtained nearly quantitatively by dehydrofluorination of **5** with *tert*-butyllithium, via stannylithiophosphide intermediate **6**:§ the reaction, followed by NMR spectroscopy, showed the immediate formation of **6** at –78 °C and elimination of LiF at –50 °C (Scheme 1).

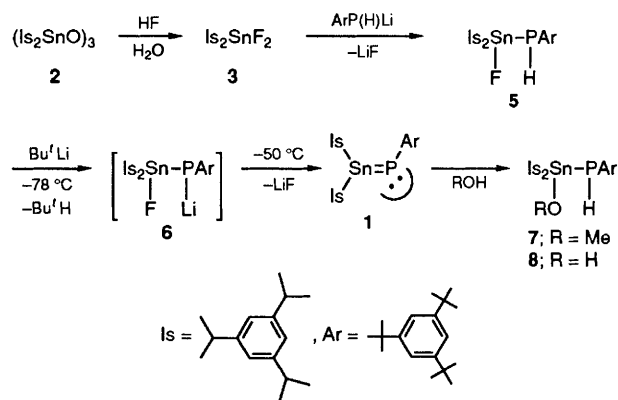
Intense blood-red solutions¶ of **1** are very air- and moisture-sensitive, however, crystals of **1** can be rapidly handled in air; they are highly soluble in common organic solvents. This stannaphosphene presents very good stability: under inert

atmosphere, it can be kept without change for a long period of time, and in solution it can be recovered unchanged after heating at 60 °C for some hours.

The structure of **1** was clearly evidenced from its NMR data. It displays in phosphorus and tin NMR low field chemical shifts (³¹P: $\delta + 170.7$ || and ¹¹⁹Sn: $\delta + 499.5$) characteristic of a phosphorus atom doubly bonded to a group 14 element (³¹P: $\delta 204.7$ in Bis₂Sn=PAR³ [Bis: (Me₃Si)₂CH], 156.6 to 173.6 in germaphosphenes^{1e,9} and 66 to 142 in silaphosphenes¹⁰) and for a doubly-bonded tin (¹¹⁹Sn: $\delta 658.3$ in Bis₂Sn=PAR,³ 427.3⁴ and 725⁷ in distannenes $>Sn=Sn<$, 647² and 835² in stannenes $>Sn=C<$). Moreover, the large tin–phosphorus coupling constant (¹J_{P117Sn} 2110 Hz, ¹J_{P119Sn} 2208 Hz) is supplementary proof of the stannaphosphene structure; for a single bond the coupling is generally only around 1000 Hz³ (¹J_{P117Sn} 954.0 Hz and ¹J_{P119Sn} 994.8 Hz in **5**).

The non equivalence of the two 2,4,6-triisopropylphenyl groups in the ¹H and ¹³C NMR spectral data is further evidence of the presence of the double bond between tin and phosphorus. A similar phenomenon has been observed previously in germaphosphene Mes₂Ge=PAR.¹¹

The double bond between tin and phosphorus is proved also by the chemical reactivity of **1**. As expected **1** reacts very easily toward protic reagents such as methanol and water to give the corresponding adducts **7** and **8**** in nearly quantitative yields.



Scheme 1

† For example the stannaphosphene Bis₂Sn=PAR³ [Bis: (Me₃Si)₂CH] could only be obtained with byproducts which prevent its isolation in pure form.

‡ Bis(2,4,6-triisopropylphenyl)difluorostannane **3**¹² was prepared by treatment of (Is₂SnO)₃⁴ **2** with an excess of hydrofluoric acid according to a procedure used by Masamune for the synthesis of Is₂SnCl₂.⁴

§ NMR data for **6**: (Et₂O–C₇D₈) ³¹P $\delta -32.5$ (d, ²J_{PF} 45.7 Hz, ¹J_{P119Sn} 2486 Hz). The very large P–Sn coupling constant and the low field shift in δ ³¹P [δ ³¹P of M_{1,4}–P(Li)Ar derivatives are generally round –100 to –130] could indicate a partial double-bonding character between tin and phosphorus such as (Et₂O)_nLi–F–SnIs₂=PAR. In fluorosilyllithioamines, formation of (thf)₃LiF–Si(R)₂=NR' (thf = tetrahydrofuran) has been reported by Klingebiel.¹³

¶ Like in other doubly-bonded group 14 and 15 elements^{1,9} some thermochromism has been observed: solution of **1** is orange–red at –78 °C and intense blood red at room temperature.

|| A rather important temperature dependence has been observed for the δ ³¹P of **1**: +25 °C, 170.7; –28 °C, 165.9; –65 °C, 159.3; –89 °C, 155.0. A similar phenomenon was also observed in germaphosphenes.⁹

** Selective NMR data for **5**: ³¹P $\delta -115.8$ (dd, ¹J_{PH} 205.0, ²J_{PF} 3.9, ¹J_{P117Sn} 954.0, ¹J_{P119Sn} 994.8 Hz); ¹⁹F $\delta -113.75$ (¹J_{119SnF} 2568.0, ¹J_{117SnF} 2691.6 Hz); ¹¹⁹Sn $\delta -33.95$. **7**: ³¹P $\delta -108.6$ (¹J_{PH} 206.7, ¹J_{P117Sn} 859.3, ¹J_{P119Sn} 899.5 Hz); ¹¹⁹Sn $\delta -56.1$. **8**: ³¹P $\delta -119.0$ (¹J_{PH} 202.5, ¹J_{P117Sn} 752.6, ¹J_{P119Sn} 787.3 Hz); ¹¹⁹Sn $\delta -65.1$.

The detailed experimental and physicochemical data for compounds **1**, **5**, **7** and **8** (NMR ¹H, ¹³C, ¹⁹F, ³¹P, ¹¹⁹Sn, mass spectroscopy, IR and melting points; 4 pages) are available by writing to the authors.

Further investigations of the chemical behaviour of **1**, which appears to be very reactive, are now in progress.

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