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A NEW ROUTE TO BIS(2,4,6-TRI-TERT-BUTYLPHENYL)DIPHOSPHENE VIA SILYLATED COMPOUND
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Summary : A new synthesis of stable diphosphene is reported. δ^{31} P value is reinvestigated.

Recently Yoshifuji and coll. described the synthesis of the first stable diphosphene 2 by reacting 2,4,6-tri-tert-butylphenyldichlorophosphine 1 with magnesium in tetrahydro-furan solution $(^{1})$.



The very bulky 2,4,6-tri-tert-butylphenyl substituent $\binom{2}{}$ appears to be a convenient group to stabilize dicoordinated phosphorus species. Thus we tried to synthesize a stable silaphosphimine **3**, such species being only known as intermediates with a very short lifetime $\binom{3}{}$. The dechlorosylilation reaction is well known as a route to phosphorus (II) compounds :

$$Me_{3}Si - Y - P \begin{pmatrix} R & -Me_{3}SiC1 \\ C1 & & & \\ Y = P - R \end{pmatrix}$$

$$Y = P - R$$

$$Y = C \begin{pmatrix} (^{4}) \\ (^{5}) \\ (^{5}) \end{pmatrix} = P - (^{6})$$

It seemed reasonable to extend this type of reaction to compounds where Y is a silicon atom. However, action of tris(trimethylsilyl)silyllithium $(^{7})$ with | led to a non silylated phosphorus derivative 4 $(^{8})$ probably via a P-chloro P-silyl (or P-lithio)phosphine intermediate.



Elemental analysis and ¹H and ¹³C NMR (⁹) are consistent with structure $(Ar-P)_n$ for derivative 4. The ³¹P NMR signal (+493, singlet) seemed to exclude structures where n is equal to 2 ($\delta^{31}P = -59$ (¹), to 3 or 5 (A_2B or A_3B_2 systems) or to 4 (¹⁰). So, 4 could be a phosphinidene (n=1).

Moreover heating 4 in tetrahydrofuran-benzene solution, in a sealed tube at 120°C, led to phosphine 5 $(^{12})$

This derivative 5 might come from hydrogen abstraction of the solvent by the phosphinidene 4 by analogy with nitrene isologues $(^{13})$.

However, mass spectrometry (M + 1 = 553) and osmometry in benzene (M = 548) were in good agreement with a diphosphene structure. On the other hand, UV and ¹H NMR spectra and the melting point were similar to those reported by Yoshifuji and coll. (¹).

Because of the large difference between the 31 P value reported for diphosphene 2 and for our derivative, an X-ray analysis was performed in order to determine the structure of 4.

Surprisingly, it was the same than the one described by Japanese group $(^1)$:



Elucidation of the mechanism of the diphosphene formation and of the possibility of thermal equilibrium between diphosphene and phosphinidene are under way.

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- (⁸) Tris(trimethylsily1)sily1lithium (⁷) in THF solution was added at -70°C to a solution of 2,4,6-tri-tert-buty1phenyldichlorophosphine in THF. The orange solution was allowed to warm up to room temperature and stirred for two hours. Evaporation of the solvent led to crude 4 which was purified by silica gel chromatography (pentane). Recrystallization from pentane gave pure 4.
- (⁹) ¹³C ¹H NMR (CDC1₃): 31.5 (s, p-C(<u>CH</u>₃)₃, 34.5 (s, o-C(<u>CH</u>₃)₃), 34.8 (s, p-<u>C</u>(CH₃)₃), 38.7 (s, o-<u>C</u>(CH₃)₃), 122.3 (s, m-C), 138.4 (m, ipso-C), 149.1 (s, p-C), 154.4 (t, ²J_{C-P}: 4.6 Hz, o-C).
- (¹⁰) The ³¹P chemical shift of (PhP)₄ being -49 ppm (¹¹) it seems reasonable to exclude (ArP)₄.
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- $\binom{12}{H}$ ¹_H NMR $(C_{6}D_{6})$: δ : 1.30 (s, p-C(CH₃)₃), 1.60 (s, o-C(CH₃)₃), 4.26 (d, ¹J(PH) : 209.5 Hz, PH), 7.60 (d, ⁴J(PH) ; 2.3 Hz, CH), ³¹_P {¹_H} : -131.4 .
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