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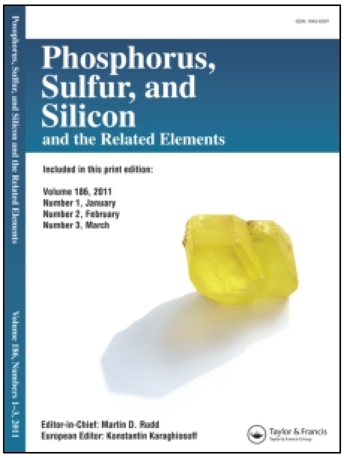

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DIBISYLDIPHOSPHENE: NEW ROUTES AND FIRST ASPECTS OF ITS REACTIVITY

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DIBISYLDIPHOSPHENE: NEW ROUTES AND FIRST ASPECTS OF ITS REACTIVITY

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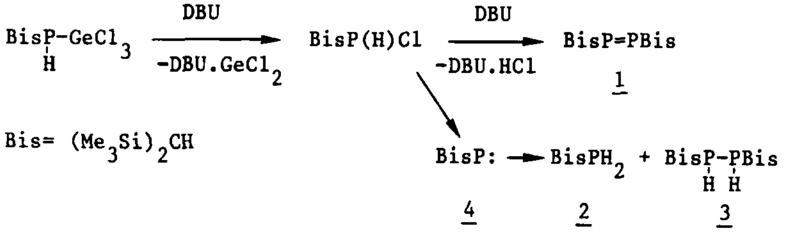
Dibisyldiphosphene, **1**, one of the least crowded stable diphosphenes, has been obtained in high yield by two new routes starting with fluorophosphines. **1** dimerizes slowly at room temperature, reacts very easily with 2,3-dimethylbutadiene and cyclopentadiene to give cycloadducts **14** and **15**, with selenium to form selenadiphosphirane **16**, and is reduced by lithium aluminium hydride to give **18**.

INTRODUCTION

Since the synthesis of the first stable diphosphene by Yoshifuji,[1] many other stable diphosphenes have been prepared and stabilized by bulky groups;[2] as steric hindrance decreases the reactivity of —P═P— double bonds, many aspects of their chemical behaviour are still unknown.

We have recently described the synthesis of dibisyldiphosphene, **1**,[3] (bisyl: $(Me_3Si)_2CH$), one of the least crowded stable diphosphenes, which should be a highly reactive species. However, the previously described synthesis from trichlorogermylphosphines[3] could not afford a completely pure diphosphene. The by-products were principally the bisylphosphine, **2**, and the dibisyldiphosphine, **3**, probably arising from an intermediate phosphinidene, **4**:



(1)

We now present two new routes a and b which lead to a more pure diphosphene, **1**, and involve diphosphine intermediates such as BisP(F)P(H)Bis, **5** (route a), and BisP(F)P($SiMe_3$)Bis, **6** (route b).

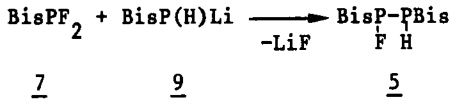
RESULTS AND DISCUSSION

The first step in the synthesis of **5** and **6** was the preparation of bisyldifluorophosphine, **7**, by fluorination of its chloro analog, **8**,[4] with zinc difluoride:

$$\underset{\underline{8}}{\mathrm{BisPCl_2}} \xrightarrow{ZnF_2/80^\circ C/C_6H_6} \underset{\underline{7}}{\mathrm{BisPF_2}} \qquad (2)$$

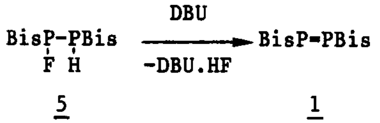
a) Synthesis of diphosphene **1** *via route a*

Reaction of bisyldifluorophosphine, **7**, with the lithiobisylphosphide, **9**, then afforded diphosphine, **5**, in a nearly quantitative yield:



$$\underset{\underline{7}}{\mathrm{BisPF_2}} + \underset{\underline{9}}{\mathrm{BisP(H)Li}} \xrightarrow[-\mathrm{LiF}]{} \underset{\underline{5}}{\mathrm{Bis}\underset{F}{\mathrm{P}}-\underset{H}{\mathrm{P}}\mathrm{Bis}} \tag{3}$$

5 is stable at room temperature and was characterized by its physical properties as two diastereoisomeric forms, **5a** and **5b**. Dehydrofluorination of **5** with DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) afforded diphosphene **1** in high yield (85%):



$$\underset{\underline{5}}{\mathrm{Bis}\underset{F}{\mathrm{P}}-\underset{H}{\mathrm{P}}\mathrm{Bis}} \xrightarrow[-\mathrm{DBU.HF}]{\mathrm{DBU}} \underset{\underline{1}}{\mathrm{BisP{=}PBis}} \tag{4}$$

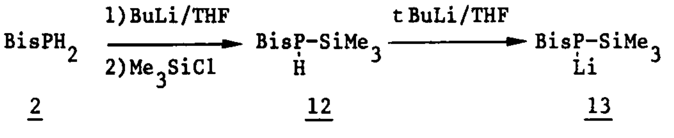
Tetrabisylcyclotetraphosphine, (BisP)$_4$, **10** was always obtained in minor quantities (5–10%).

Addition of DBU to the chlorodiphosphine RP(Cl)P(H)R, **11**, led also to **1** almost quantitatively, but **11** was obtained only in poor yield (about 20%); **11** was too unstable to be isolated in pure form, but it was identified in solution by ^{31}P NMR and mass spectrometry of the crude product.

b) Synthesis of diphosphene **1** *via route b*

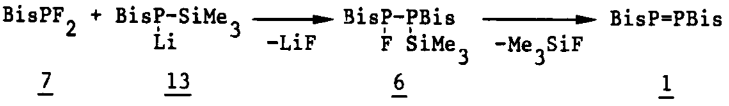
Dehalosilylation reactions between dichlorophosphines and disilylated phosphines are a good source of less hindered diphosphenes.[5] Unfortunately, with very bulky substituents, the coupling of the two phosphorus moieties is more difficult and takes place only after prolonged heating.[6] Therefore, we decided to prepare diphosphene **1** by using a new route involving the first formation of a diphosphine followed by an intramolecular dehalosilylation reaction.

Lithiophosphide, **13**, was prepared from bisylphosphine, **2**, according to:



$$\underset{\underline{2}}{\mathrm{BisPH_2}} \xrightarrow[2)\mathrm{Me_3SiCl}]{1)\mathrm{BuLi/THF}} \underset{\underline{12}}{\mathrm{Bis}\underset{H}{\mathrm{P}}-\mathrm{SiMe_3}} \xrightarrow{t\mathrm{BuLi/THF}} \underset{\underline{13}}{\mathrm{Bis}\underset{Li}{\mathrm{P}}-\mathrm{SiMe_3}} \tag{5}$$

Addition of **13**, characterized by ^{31}P NMR(−213.5 ppm), to the difluorophosphine, **7**, at −50°C, followed by warming to room temperature, led to a mixture of 1-fluoro-2-silyldiphosphine, **6**, and diphosphene, **1**:



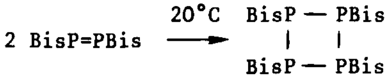
$$\underset{\underline{7}}{\mathrm{BisPF_2}} + \underset{\underline{13}}{\mathrm{Bis}\underset{Li}{\mathrm{P}}-\mathrm{SiMe_3}} \xrightarrow[-\mathrm{LiF}]{} \underset{\underline{6}}{\mathrm{Bis}\underset{F}{\mathrm{P}}-\underset{SiMe_3}{\mathrm{P}}\mathrm{Bis}} \xrightarrow[-\mathrm{Me_3SiF}]{} \underset{\underline{1}}{\mathrm{BisP{=}PBis}} \tag{6}$$

Subsequent stirring at 20°C for 30 mn led to the complete defluorosilylation of **6**, and **1** was isolated in 85% yield together with the dimer, (RP)$_4$, **10**, in 10% yield.

Diphosphene **1** obtained by these two routes can be used in crude form after separation of DBU · HF (route a) of LiF (route b) by filtration.

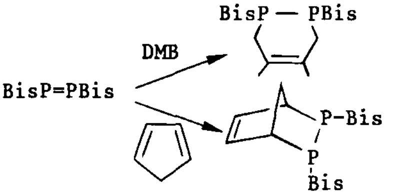
c) Reactivity of diphosphene **1**

Diphosphene, **1**, dimerizes slowly at room temperature, its half-life being about a week at 20°C, to give exclusively **10**:



1 10 (7)

10 was purified by chromatography on silica (eluent pentane) and characterized by its physical properties. **1** is very reactive towards 2,3-dimethylbutadiene and cyclopentadiene giving spontaneously cycloadducts **14** and **15**, respectively in nearly quantitative yield:

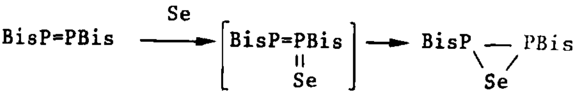


14 15 (8)

Such cycloaddition reactions have already been observed with di-tert-butyl- and tert-butyl(mesityl)diphosphene, but not with most of the stable diphosphenes for steric reasons, the only exception being the relatively less hindered bis[bis(trimethylsilyl)amino]diphosphene.[7]

We also studied reactivity of **1** towards sulfur and selenium. In the case of sulfur, we have not observed the formation of the expected three-membered heterocycle thiadiphosphirane, $\underset{S}{\text{RP—PR}}$, previously obtained with other stable diphosphenes[7–9] or by another route.[10] The ^{31}P NMR spectrum of the product showed several signals, which have not yet been unambiguously attributed; however, the major product (+100 ppm) is probably a heterocyclic oligomer $(RP{-}S)_n$. Attempts to isolate and characterize it were unsuccessful.

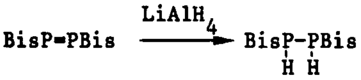
The reaction of **1** with selenium in the presence of triethylamine gave the expected three-membered heterocycle **16**:



1 17 16 (9)

Such catalysis by amines is well known in reaction between sulfur or selenium and phosphorus compounds.[9,11,14] The high-field ^{31}P NMR signal of **16** consisting of two equivalent phosphorus atoms and the coupling constant $^1J(^{31}P\text{-}^{77}Se)$ were similar to that obtained by Yoshifuji[11] and Baudler[10] in other selenodiphosphiranes. The first step is probably the formation of **17** which isomerises rapidly to **16**. The value of the ^{31}P-^{77}Se coupling constant for **17** should be much higher.[12,13]

Lithium aluminium hydride reduces the phosphorus–phosphorus double bond of **1** with formation of the diphosphine **18** in two diastereoisomeric forms in the ratio 50/50:



$$\mathrm{BisP{=}PBis} \xrightarrow{\mathrm{LiAlH_4}} \underset{\mathrm{H}}{\mathrm{BisP}}\text{-}\underset{\mathrm{H}}{\mathrm{PBis}} \qquad (10)$$

1 **18**

Similar reactions have already been observed with two stable diphosphenes.[8,15,16]

These initial results confirm the greater reactivity of **1** by comparison with other more stable diphosphenes. Other reactions of **1** are being studied in hope of gaining more information about the reactivity of phosphorus–phosphorus double bond.

EXPERIMENTAL

^1H NMR spectra were recorded at 60 MHz on a Varian EM 360 A spectrometer. ^{13}C and ^{31}P NMR were recorded at 22.6 and 36.4 MHz respectively on a Bruker WH 90 and ^{19}F at 84.6 MHz on a Perkin Elmer R 32 spectrometer. NMR spectra were measured in C_6D_6 using TMS (^1H and ^{13}C), H_3PO_4 85% (^{31}P) and CF_3COOH (^{19}F) as references. Mass spectra were obtained on a Varian MAT 311 A spectrometer operating at 70 eV. Melting points are uncorrected. Elemental analyses were done by the "Service Central de Microanalyse du CNRS" at Vernaison. The reactions were done under an atmosphere of dry nitrogen.

Synthesis of bis(trimethylsilyl)methyl difluorophosphine **7**

A mixture of zincdifluoride (11.89 g, 115 mmoles), dried prior to use, **8** (15.0 g, 57.5 mmoles) and benzene (35 ml) was heated at 80°C for 6 h. After elimination of zincdichloride by filtration, distillation gave 8.2 g of **7** (b.p. 94°C/80 mm, 63% yield).

NMR: ^1H: 0.07 (s, 18H, Me_3Si), 0.50 (dt, $^2J(HP)$: 10.0 Hz, $^3J(HF)$: 24.0, 1H, CH) ^{13}C, δ 1.90 (dquart, $^3J(PC)$: 4.4 Hz, $^1J(CH)$: 119.1 Hz, Me_3Si), 33.6 (ddt, $^1J(CP)$: 64.0 Hz, $^2J(CF)$: 7.4 Hz, $^1J(CH)$: 105.1 Hz, SiCP)

^{19}F δ -5.3 (dd, $^1J(FP)$: 1166 Hz, $^3J(FH)$: 24.0 Hz);

^{31}P $\{^1H\}$ $+256.8$ (t, $^1J(PF)$: 1166 Hz).

Anal. $C_7H_{19}F_2PSi_2$ Calcd.: C 36.81; H 8.39; F 16.64 Found: C 36.72; H 8.31
F 16.73

Synthesis of fluorodiphosphine **5**

A solution of lithiophosphide **9** (prepared from 0.93 g of bis(trimethylsilyl)methylphosphine (4.84 mmoles), the stoechiometric quantity of tert-butyllithium 1.4 M in pentane and 10 ml of diethyleter) was slowly added to a solution of **7** (1.10 g, 4.84 mmoles) in 10 ml of pentane at 0°C. The reaction appeared complete almost instantaneously. NMR analysis of the solution showed the nearly quantitative formation of **5**.

NMR (C_6D_6): ^{31}P: **5a** (40%) P(F): 229.7 (ddt, ^1J(PP): 219.7, ^1J(PF): 878.9, ^2J(PPH and PCH): 11.5 Hz); P(H): −64.3 (dddd, ^1J(PP): 219.7, ^1J(PH): 207.5, ^2J(PF): 109.9, ^2J(PH): 14.7 Hz)

5b (60%) P(F): 212.9 (ddt, ^1J(PP): 268.5, ^1J(PF): 927.7, ^2J(PPH and PCH): 15.8 Hz); P(H): −56.4 (dddd, ^1J(PP): 268.5, ^1J(PH): 189.2, ^2J(PF): 61.0, ^2J(PH): 25.0)

Mass spectrum (EI): *m/e*: 400 (M^+)

Synthesis of **1** *from* **5** *(route a)*

Addition of DBU (0.13 g, 0.8 mmole) to a solution of **5** (0.33 g, 0.8 mmole) in pentane gave immediately a yellow reaction mixture and a white precipitate of DBU·HF which was eliminated by filtration. NMR analysis showed the formation of **1**[3] (85%) and **10** (5–10%) (see further).

NMR **1** ^{31}P: + 517 ppm.

Synthesis of **11** *and* **1**

Chlorodiphosphine **11** was obtained according to the same experimental procedure as its fluoro analog **5** from **9** (3.2 mmoles) and **8** (0.84 g, 3.2 mmoles). **11** (yield 20%) could not be purified because of its low stability.

NMR ^{31}P **11**: P(Cl): 131.7 (d, ^1J(PP): 256.4 Hz) P(H): −37.5 (dd, ^1J(PH): 186.0 Hz). Mass spectrum (EI): *m/e*: 416 (M^+).

11 gave **1** quantitatively after addition of DBU.

Synthesis of **12**

To a solution of phosphide **9** (78.1 mmoles), prepared as previously described, was added dropwise a solution of trimethylchlorosilane (8.47 g, 78.1 mmoles) in pentane (30 ml) at 0°C. The reaction mixture was then warmed to room temperature and LiCl separated by filtration. Distillation afforded **12** (bp 108–110°C/15 mm, 77% yield).

NMR (C_6H_6): ^1H: 0.20 (d, ^4J(PH): 0.8 Hz, 18H, Me_3Si-C); 0.26 (d, ^3J(PH): 4.2 Hz, 9H, Me_3Si-P), 2.04 (d, ^1J(PH): 189.0 Hz, 1H, PH).

^{13}C {^1H} : + 1.78 (s, $(\underset{\smile}{C}H_3)_3SiC$), 1.80 (d, ^3J(CP): 16 Hz, $(CH_3)_3Si$-P), −2.99 (d, ^1J(CP): 45.6 Hz, C-P).

^{31}P: −161.4 (d, ^1J(PH): 189.0 Hz).

Anal. $C_{10}H_{29}PSi_3$ Calcd.: C 45.39; H 11.05 Found: C 45.28; H 11.0

Synthesis of **1** *from* **7** *and* **12** *(route b)*

Lithiophosphide **13** was obtained by addition of a solution of tert-butyllithium (1.4 M in pentane) (2.9 mmoles) to a stoechiometric amount of **12** (0.76 g) in 10 ml of diethylether. After 15 mn stirring, the solution of **13** was added dropwise to **7** (0.66 g, 2.9 mmoles) in 5 ml of diethylether at −50°C.

The reaction mixture was allowed to warm to room temperature and immediate analysis by NMR showed the formation of a mixture of **6** and **1**. Subsequent stirring at 20°C for 30 mn led to almost complete transformation of **6** into **1**, with only a minor quantity of **10** (10–15%). **6** was not isolated but clearly characterized by its $^{31}P\{^1H\}$NMR:P(F): 227.2 (dd, ^1J(PP): 391.2, ^1J(PF): 891.6 Hz), P($SiMe_3$): −67.9 (dd, ^1J(PP): 391.2, ^2J(PF): 85.4 Hz).

Synthesis of cyclotetraphosphine **10**

A yellow benzene solution of **1** prepared by route b (1.10 g, 2.9 mmoles) was heated at reflux until complete decoloration (about 15 h). After removal of the solvent in vacuo, crude **10** was recrystallized from pentane to afford 0.85 g white crystals: (mp: 157–160°C (dec), 77% yield).
NMR: ^1H: 0.48 (s, Me_3Si)

$^{31}P\ \{^1H\}$: −17(s)

Mass spectrometry: desorption m/e 760 (M).
EI: *m/e*: 760 (M^+, 40%), 745 (M–Me, 10%), 601 (M-Bis, 50%), 380 (BisP = PBis, 100%).
Anal. $C_{28}H_{76}P_4Si_8$ Calcd.: C 44.16; H 10.06 Found: C 44.24; H 10.13

Reaction of **1** *with* 1,3-*dienes*

A twofold excess (7, 80 moles) of 2,3-dimethylbutadiene (or cyclopentadiene) was added to a solution of **1** (1.5 g, 3.9 mmoles prepared in pentane (15 ml) by route b). The reaction mixture was stirred at 20°C for an hour. After removal of the solvent in vacuo **14** (or **15**) were obtained as white solids.
14 NMR ^1H 0.33 (s, 9H, $SiMe_3$), 1.75 (s, 6H, MeC=), 2.12–2.58 (m, 4H, CH_2)

$\delta^{31}P\ \{^1H\}$: −24.9 (s)

15 NMR ^1H 0.20 (s, 9H, endo-Me_3Si), 0.30 (s, 9H, exo-Me_3Si).

$\delta^{31}P\ \{^1H\}$: AB spectrum P_A: −11.0, P_B: −14.7 $^1J(P_AP_B)$: 326.5 Hz

Reaction of **1** *with selenium*

A solution of **1** (4.2 mmoles), prepared in THF (10 ml) by route b, was added to a suspension of selenium (0.33 g) in a mixture of THF (5 ml) and triethylamine (5 ml). After removal of the solvents in vacuo, crude **16** was identified by its physico-chemical data.
NMR $^{31}P\ \{^1H\}$: −72.4 $^1J(P\text{-}^{77}Se)$: 114.7 Hz
Mass spectroscopy (EI) (^{77}Se) *m/e*: 457 (M^+).

Reduction of **1** *with lithium aluminium hydride*

A suspension of 0.034 g (0.89 mmoles) of lithium aluminium hydride in 20 ml of THF was added, at room temperature, to a solution of **1** (0.67 g, 1.75 mmoles, prepared in pentane (10 ml) by route b). The mixture was stirred for half an hour, hydrolyzed, extracted with Et_2O and dried over Na_2SO_4. After removal of solvents, the crude material was analyzed by NMR:
NMR (C_6D_6): ^1H: **18a** (65%): 0.16 (s, $SiMe_3$); **18b** (35%): 0.20 (s, $SiMe_3$)

^{31}P $\{^1H\}$: **18a**: −90.1; **18b**: −97.7

Anal. $C_{14}H_{40}P_2Si_4$ Calcd.: C 43.93; H 10.53 Found: C 43.87; H 10.47

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