Bull Soc Chim Fr (1996) 133, 33-37

Synthesis and X-ray crystal structure analysis of α-acetylenic phosphole derivatives

Serge Holand, François Gandolfo, Louis Ricard, François Mathey*

Laboratoire 'hétéroéléments et coordination', URA CNRS 1499, DCPH, École polytechnique, 91128 Palaiseau Cedex, France

(Received 10 October 1995; accepted 7 November 1995)

Summary – The reaction of 2-lithio-, 2-lithio-5-bromo-, and 2-lithio-5-(phenylethynyl) derivatives of 3,4-dimethyl-1-phenylphosphole with a series of aryl-alkynyl-sulfones affords the corresponding 2-alkynylphospholes. The X-ray crystal structure analysis of 2,5-bis(phenylethynyl)-3,4-dimethyl-1-phenylphosphole shows a pyramidalization of phosphorus and a lengthening of the intracyclic P-C bonds by comparison with 1-benzylphosphole. The alkynyl substituents appear to switch off the delocalization within the phosphole ring. The reaction of the 2-lithio-5-bromophosphole with bis(*tert*-butylsulfonyl)acetylene gives the expected bis(2-phospholyl)acetylene whose transformation into its 5,5′-bis(trimethylsilylethynyl) derivative has been achieved. Long (phosphole-ethynylene) chains are now accessible.

phosphorus-carbon heterocycle / phosphole / 2-alkynyl phosphole / 2,5-dialkynyl phosphole / organolithium compound

Résumé – Synthèse et analyse structurale par rayons X de phospholes α-acétyléniques. *La réaction des 2-lithio, 2-lithio-5-bromo- et 2-lithio-5-(phényléthynyl)-1-phényl-3,4-diméthylphospholes avec une série d'aryl-alcynyl-sulfones fournit les 2-alcynylphospholes correspondants. L'analyse de la structure X du 2,5-bis(phényléthynyl)-1-phényl-3,4-diméthylphosphole montre une pyramidalisation du phosphore et un allongement des liaisons P-C intracycliques par comparaison avec le 1-benzylphosphole. Il semble que les substituants alcynyles détruisent la délocalisation à l'intérieur du cycle phosphole. La réaction du dérivé 2-lithio-5-bromophosphole avec le bis(*tert*-butylsulfonyl)acétylène conduit au bis(2-phospholyl)acétylène attendu dont la transformation en dérivé 5,5′-bis(triméthylsilyléthynyle) a été réalisée. De longues chaînes (phosphole-éthynylène) sont maintenant accessibles.*

hétérocycle phosphore-carbone / phosphole / 2-alcynyl phosphole / 2,5-dialcynyl phosphole / composé organolithié

Introduction

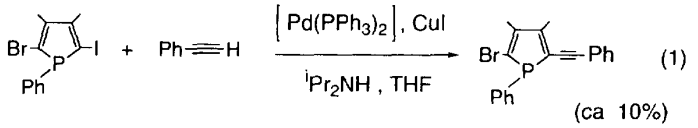
2,5-Difunctional phosphole derivatives are key intermediates in the synthesis of the phosphorus analogues of polypyrrole chains [1] or macrocycles [2]. With such targets in mind, we were interested in the possibilities offered by alkyne-functionalized phospholes. Clearly, the installation of an acetylenic bridge between the α-positions of two phosphole rings could serve to create fully conjugated polyphosphole chains. In the thiophene series, this idea has been illustrated by the synthesis of molecular wires based on (thiophene-ethynylene) oligomers [3]. Moreover, such C≡C bridges could be transformed into *Z*-vinylene bridges by *cis*-hydrogenation, 1,2-addition or cycloaddition, thus creating an ideal starting point for the synthesis of polyphosphole macrocycles. These considerations motivated a preliminary investigation of the synthesis and properties of some α-acetylenic phosphole derivatives.

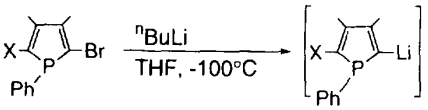
Results and discussion

Since the 2-bromo-[4] and 2,5-dibromo-[1] derivatives of 1-phenyl-3,4-dimethylphosphole are available, one of the most attractive routes to the desired acetylenic phospholes relied on a classical Stille coupling [5]. Using the tin derivative $PhC{\equiv}CSnMe_3$ as the reaction partner, we tried to perform the coupling in the presence of a $[PdL_2]$ catalyst without any success. In order to increase the reactivity of the halogenophosphole, we also investigated the possible use of the 2-iodo-5-bromo derivative, which was synthesized via the reaction of the 2-lithio-5-bromophosphole [1] with diiodomethane [6]. Even in this case, the Stille coupling failed. We had more success by using a different procedure devised by Hagihara [7] (eq 1).

The reaction appeared to be quite fast (10 min in boiling THF), but gave only a modest yield of the desired product (identified by ^{31}P NMR, MS and comparison with an authentic sample, see below) together with a variety of other unidentified materials.

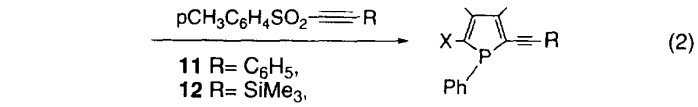
* Correspondence and reprints



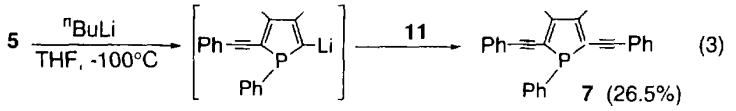


1 X= H
2 X= Br

1a X= H
2a X= Br



3 R= Ph, X= H, (67%)
4 R= $SiMe_3$, X= H, (28%)
5 R= Ph, X= Br, (25%)
6 R= $SiMe_3$, X= Br, (26%)



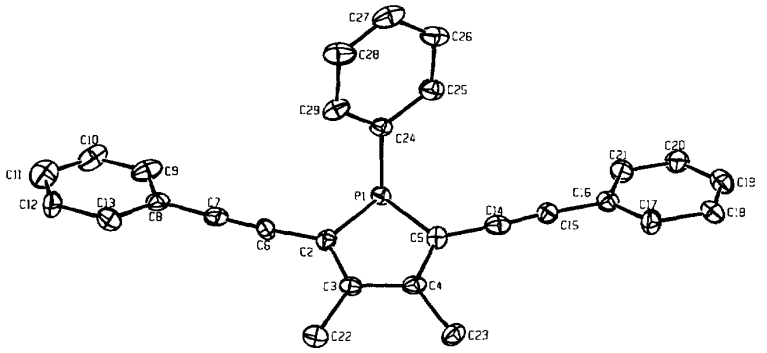


Fig 1. Ortep view of **7** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Important bond lengths (Å) and angles (deg): P(1)-C(2) 1.815(2), P(1)-C(5) 1.821(2), P(1)-C(24) 1.839(2), C(2)-C(3) 1.367(1), C(2)-C(6) 1.423(3), C(6)-C(7) 1.199(3), C(7)-C(8) 1.434(3), C(3)-C(4) 1.458(2), C(4)-C(5) 1.365(2), C(5)-C(14) 1.416(3), C(14)-C(15) 1.201(3), C(15)-C(16) 1.438(3); C(2)-P(1)-C(5) 89.19(8), C(2)-P(1)-C(24) 102.74(8), C(5)-P(1)-C(24) 100.42(8), P(1)-C(2)-C(3) 111.5(1), P(1)-C(2)-C(6) 122.3(1), C(2)-C(3)-C(4) 113.9(1), C(3)-C(4)-C(5) 113.3(2), P(1)-C(5)-C(4) 111.6(1), P(1)-C(5)-C(14) 122.5(1).

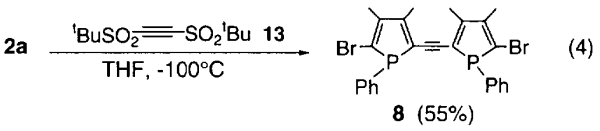
Since this first approach could not be considered acceptable, we decided to start from the highly reactive 2-lithio- and 2-lithio-5-bromophospholes [1, 4]. The problem was to find suitable acetylenic electrophiles. The answer was found in the work of Smorada and Truce on the reaction of arylsulfonylacetylenes with organolithium reagents [8]. Satisfactory results were thus obtained (eq 2).

A further advance was made when we found that the 5-bromo derivative **5** could be converted in turn into its corresponding 5-lithio analog using a classical metallation procedure (eq 3). This offered the possibility of grafting another functionality into the 5-position or, alternatively, preparing a 2,5-diacetylenic phosphole derivative. We checked this last point and obtained **7** in acceptable yield.

The X-ray crystal structure analysis of **7** (fig 1) allowed an examination of the effect of the acetylenic groups on the geometry of the phosphole ring. The structure of 1-benzylphosphole [9] serves as a reference for comparison. Phosphorus appears to be significantly more pyramidal in **7** than in 1-benzylphosphole: Σ (CPC angles) = 292.4 vs 302.7°. Moreover, the intracyclic P-C bonds are significantly longer in **7** than in 1-benzylphosphole: 1.815–1.821 vs 1.780–1.786 Å. These data clearly establish that the ring delocaliza-

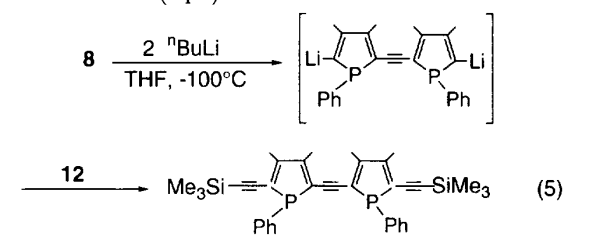
tion is almost switched off in **7**. The recent work of Schleyer [10] has clearly demonstrated that phospholes are weakly aromatic (ca 7 kcal mol^{-1} of aromatic stabilization energy) and that structural data constitute a valid criterion for assessing aromaticity in a five-membered heterocyle. In **7**, the weak aromaticity of the ring is destroyed by the conjugation of the dienic subunit with the two acetylenic substituents, with the result that the phosphorus lone pair no longer participates in any electronic delocalization.

The next step concerned the building of an acetylenic bridge between two phosphole units. The availability of the bis-sulfone **13** [11] allowed us to extend our procedure to the synthesis of the bis-phosphole **8** in fair yield (eq 4).



8 (55%) (4)

The bis-phosphole **8** is obtained as a 1:1 mixture of two diastereomers, which result from the presence of two chiral phosphorus centers. Their main spectroscopic differences concern the ^{31}P NMR and acetylenic ^{13}C NMR chemical shifts. Compound **8** is a versatile synthon which can be transformed into its 5,5′-dilithio derivative and, hence, gives access to a wide variety of 5,5′-bifunctional derivatives. Alternatively, it can serve to prepare 5,5′-bis-acetylenic derivatives. Thus, the compound **9** is also obtained as a mixture of two diastereomers (eq 5).



9 (20%) (5)

At this stage of our research, it is clear that we have at our disposal all the tools necessary to build phosphole-ethynylene oligomers. Since all the phosphorus centers are pyramidal, it must emphasized that these products will be obtained as complex mixtures of isomers.

Experimental section

All the reactions were carried under dry nitrogen, in a Schlenk tube previously dried at 130 °C, in solution in freshly distilled anhydrous THF. Degassed silica gel (70–230 mesh) was used for chromatographic separations. NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C and 81.01 MHz for ^{31}P. Chemical shifts (δ in $CDCl_3$) are expressed in ppm downfield from internal TMS (^{1}H and ^{13}C) or external 85% H_3PO_4 (^{31}P). The ^{1}H and ^{13}C numbering is given in the figure 2. The coupling constants (J) are given in Hz and concern only the ^{13}C–^{31}P couplings in the ^{13}C spectra. Mass spectra were obtained at 70 eV by the direct method with a Shimadzu QP 1000 spectrometer. The phospholyle anions **1a** and **2a** were generated according to references [4] and [1] respectively. The acetylenic sulfones **11** [12], **12** [13] and **13** [11] were prepared by published procedures.

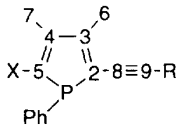


Fig 2

3,4-Dimethyl-1-phenyl-2-(phenylethynyl)phosphole **3** *and its sulfide*

To a solution of the 2-phospholyl anion **1a** (7×10^{-3} mol) in THF (20 mL) maintained between −95 and −100 °C was added, in one portion, the acetylenic sulfone **11** (1.96 g, 7.7×10^{-3} mol). The reaction mixture was stirred for 15 min at the same temperature and then allowed to warm at room temperature. After vacuum distillation of the solvent, the residue was chromatographed with hexane/toluene (8:2). Yield 1.36 g (67%) of a light yellow oil which slowly crystallized.

^{31}P NMR: δ 12.4.

^{1}H NMR: δ 2.02 (dd, ^{4}J(H-H) = 1.3, ^{4}J(H-P) = 3.2, 3H, 7 Me), 2.19 (d, ^{4}J(H-P) = 3.1, 3H, 6 Me), 6.38 (d, ^{2}J(H-P) = 38.7, 1H, 5 CH) , 7.20-7.40 (m, 10H, Ph).

^{13}C NMR: δ 16.0 (s, 6 Me), 17.97 (d, ^{3}J = 2.1, 7 Me), 86.34 (d, ^{3}J = 22.8, 9C), 98.26 (d, ^{2}J = 4.5, 8C), 123.82 (s, 9C-*C ipso*), 126.25 (d, ^{1}J = 2.9, 2C), 128.83 (d, ^{1}J = 4.6, 5C), 149.47 (d, ^{2}J = 4.7, 4C), 152.77 (d, ^{2}J = 13.7, 3C); P-phenyl C: 128.39 (d, ^{3}J = 7.6, *meta*), 128.98 (s, *para*), 131.90 (d, ^{1}J = 14.8, *ipso*), 132.77 (d, ^{2}J = 18.4, *ortho*); acetylenic phenyl C: 123.82 (s, *ipso*), 127.69 (s, *para*), 128.12 (s, *meta*), 131.13 (s, *ortho*).

Mass spectrum: m/z 288 (M^+, 40%), 273 (M^+ – Me, 40%).

Anal calc for $C_{20}H_{17}P$: C 83.3, H 5.94. Found: C 83.01, H 6.01.

• *Sulfide*: by standing of the phosphole **3** with 1.2 equiv sulfur in toluene overnight. Purified by chromatography, first with hexane then dichloromethane; white solid. Yield 85%.

^{31}P NMR: δ 51.0.

^{1}H NMR: δ 2.12 (pseudo t, ^{4}J(H-H) = 1.7, ^{4}J(H-P) = 1.7, 3H, 7 Me), 2.23 (d, ^{4}J(H-P) = 2.0, 3H, 6 Me), 6.10 (dt, ^{4}J(H-H) = 0.8, ^{4}J(H-P) = 30.7, 1H, 5 H); phenyl H: 7.25 (m, 3H), 7.44 (m, 5H) and 7.86 (m, 2H).

^{13}C NMR: δ 16.01 (d, ^{3}J = 12.2, 6 or 7 Me), 17.87 (d, ^{3}J = 16.4, 6 or 7 Me), 81.77 (d, ^{3}J = 14.9, 9 C), 102.09 (d, ^{2}J = 6.2, 8C), 123.10 (d, ^{1}J = 82.5, 5C), 123.29 (d, ^{1}J = 88.7, 2C), 154.17 (d, ^{2}J = 14.5, 3 or 4C), 154.57 (d, ^{2}J = 25.7, 3 or 4C); P-phenyl C: 126.98 (part of a doublet, *ipso*), 130.46 (d, J = 10.0, *meta* or *para*), 131.62 (d, J = 2.1, *para* or *meta*), 132.14 (d, ^{2}J = 2.8, *ortho*); acetylenic phenyl C: 122.65 (d, ^{4}J = 2.5, *ipso*), 128.17 (s, *meta* or *para*), 128.60 (s, *para* or *meta*), 128.83 (s, *ortho*).

3,4-Dimethyl-1-phenyl-2-(trimethylsilylethynyl) phosphole **4** *and its sulfide* **4a**

To a solution of anion **1a** (2.6×10^{-3} mol) was added, under the conditions described above, the acetylenic sulfone **12** (0.75 g, 3×10^{-3} mol). After warming to room temperature

the reaction mixture was acidified with a few drops of acetic acid. The THF was vacuum evaporated and the residue chromatographed with hexane/toluene (80:20) leading to 0.4 g of a mixture of **4** and 3,4-dimethyl-1-phenylphosphole (60:40 based on ^{1}H NMR spectra). Yield about 28%. Other attempts to purify the product were fruitless.

^{31}P NMR: δ **4** 13.7.

^{1}H NMR: δ **4** 0.17 (s, SiMe), 2.09 (dd, ^4J(H-H) = 1.0, ^4J(H-P) = 3.1, 7 Me), 2.17 (d, ^4J(H-P) = 3.2, 6 Me), 6.47 (d, ^2J(H-P) = 38.4, 5C), 7.35 and 7.81 (m, Ph).

^{13}C NMR: δ **4** 0.14 (s, SiMe), 16.08 (s, 6 Me), 18.07 (d, ^3J = 2.8, 7 Me), 101.57 (d, ^3J = 21.3, 9C), 102.58 (d, ^3J = 3.0, 8C), 126.23 (s, 2C), 128.29 (d, ^1J = 3.1, 5C) 149.50 (d, ^2J = 5.2, 4C), 153.74 (d, ^2J = 13.7, 3C); aromatic C: 132.20 (d, ^1J = 15.2, *ipso*), 128.48 (d, ^3J = 7.2, *meta*), 128.86 (s, *para*), 132.57 (d, ^2J = 18.2, *ortho*).

• *Sulfide*: the above mixture was heated with an excess of sulfur in toluene. Chromatography with hexane/toluene (80:20) gave first the sulfide **4a** of the acetylenic phosphole and subsequently the sulfide of dimethylphenyl phosphole (δ_P 46.2).

^{31}P NMR: δ 50.3.

^{1}H NMR: δ 0.15 (s, 9H, SiMe), 2.12 (t, ^4J(H-H) = 1.8, ^4J(H-P) = 1.8, 3H, 7 Me), 2.17 (d, ^4J(H-P) = 1.8, 3H, 6 Me), 6.08 (dq, ^4J(H-H) = 0.8, ^2J(H-P) = 30.5, 1H, 5H), 7.35 (m) and 7.81 (m, 5H, Ph).

^{13}C NMR: δ −0.9 (s, SiMe), 15.81 (d, ^3J = 12.3, 6C or 7C), 17.65 (d, ^3J = 16.4, 6C or 7C), 93.39, (d, ^3J = 13.8, 9C), 108.35 (d, ^2J = 6.0, 8C), 123.10 (d, ^1J = 82.5, 2C), 123.29 (d, ^1J = 88.7, 5C), 153.69 (d, ^2J = 13.18, 3C or 4C), 155.55 (d, ^2J = 5.5, 3C or 4C); aromatic C: 127.88 (d, ^1J = 86.5, *ipso*), 128.44 (d, J = 13.7), 130.24 (d, J = 12.1) and 131.41 (d, J = 2.9).

5-Bromo-3,4-dimethyl-1-phenyl-2-(phenylethynyl) phosphole **5**

The acetylenic sulfone **11** (0.8 g, 3.2×10^{-3} mol) was added in one portion to a solution of anion **2a** (2.9×10^{-3} mol) in THF (20 mL) maintained at −100 °C. After 15 min at −95 °C, the mixture was allowed to warm at room temperature. The solvent was then removed under vacuum and the residue chromatographed first with hexane then with a mixture of hexane/dichloromethane (9:1), leading to a yellow solid. Yield 0.25 g (25%).

^{31}P NMR: δ 20.2.

^{1}H NMR: δ 2.06 (d, ^4J(H-P) = 2.6, 3H, 7 Me), 2.28 (d, ^4J(H-P) = 3.2, 3H, 6 Me), 7.24 (m) and 7.35 (m, aromatic H).

^{13}C NMR: δ 16.05 (s, 6C), 16.98 (s, 7C), 85.57 (d, ^3J = 23.8, 9C), 96.65 (d, ^2J = 4.3, 8C), 123.59 (d, ^1J = 18.1, 5C), 124.60 (s, 2C), 147.04 (d, ^2J = 7.2, 4C), 152.93 (d, ^2J = 10.9, 3C); P-phenyl C: 130.28 (d, ^1J = 15.4, *ipso*), 128.79 (d, ^3J = 7.8, *meta*), 129.82 (s, *para*), 133.11 (d, ^2J = 19.0, *ortho*); acetylenic phenyl C: 123.55 (s, *ipso*), 127.89 (s, *meta*), 128.14 (s, *para*), 131.15 (s, *ortho*).

Mass spectrum: m/z 369 (M^+ for ^{81}Br, 97.5%), 367 (M^+ for ^{79}Br, 100%).

5-Bromo-3,4-dimethyl-1-phenyl-2-(trimethylsilylethynyl) phosphole **6**

The monoanion **2a** (5.8×10^{-3} mol) in THF (20 mL) at −100 °C was treated with the silylated acetylenic sulfone **12** (1.6 g, 6.35×10^{-3} mol). After 15 min, the reaction mixture was slowly heated to room temperature and then poured into ice-cold 5% aqueous hydrochloric acid solution. The products were extracted with dichloromethane, washed with water and dried over magnesium sulfate. After vacuum distillation of the solvent, the residue was chromatographed with a mixture of hexane/dichloromethane (9:1). Yield 0.6 g (26%) of a white solid.

^{31}P NMR: δ 21.2.

^{1}H NMR: δ 0.15 (s, 9H, SiMe), 2.05 (d, ^4J(H-P) = 2.6, 3H, 7 Me), 2.22 (d, ^4J(H-P) = 3.3, 3H, 6 Me), 7.21–7.46 (m, 5H, Ph).

^{13}C NMR: δ 0.22 (s, SiMe), 16.23 (s, 6 or 7 Me), 17.18 (s, 6 or 7 Me), 100.91 (d, ^3J = 21.4, 9C), 104.28 (s, 8C), 123.53 (d, ^1J = 18.3, 5C), 125.00 (s, 2C), 147.14 (d, ^2J = 7.4, 4C), 154.07 (d, ^2J = 11.1, 3C); aromatic C: 130.62 (d, ^1J = 15.4, *ipso*), 128.94 (d, ^3J = 7.7, *meta*), 129.89 (s, *para*), 131.85 (d, ^2J = 19.6, *ortho*).

Mass spectrum: m/z 364 (M^+ for ^{81}Br, 67%), 362 (M^+ for ^{79}Br, 63%), 349 (M^+ − Me for ^{81}Br, 29%), 347 (M^+ for ^{79}Br, 27%).

2,5-Bis(phenylethynyl)-3,4-dimethyl-1-phenyl-phosphole **7**

The synthesis of the diacetylenic compound **7** was performed from the dibromophosphole **2** (1 g, 2.9×10^{-3} mol), in a one-pot reaction. The first part of the reaction was conducted as described for the bromoacetylenic compound **5**. After the first addition of **11**, the solution was allowed to warm to −50 °C and then recooled to −100 °C. Butyllithium (2 mL, 3.2×10^{-3} mol) was then added by syringe and after 15 min at −100 °C, the sulfone **11** (0.8 g, 3.2×10^{-3} mol) was introduced. After 15 min the reaction mixture was slowly warmed to room temperature and then poured into iced water. The product was extracted with dichloromethane, washed with water and dried over magnesium sulfate. After vacuum distillation of the solvent, the residue was chromatographed with first hexane then toluene. Yield 0.3 g (26.5%) of yellow crystals; mp 185 °C.

^{31}P NMR: δ 22.6.

^{1}H NMR: δ 2.29 (d, ^4J(H-P) = 3.1, 6H, Me), 7.28, 7.40 and 7.54 (m, 15H, Ph).

^{13}C NMR: δ 16.62 (s, Me), 86.41 (d, ^3J = 21.7, 9 and 9′C), 99.50 (d, ^2J = 4.5, 8 and 8′C), 125.51 (s, 2 and 5C), 128.96 (d, ^1J = 6.8, P-C *ipso*), 155.40 (d, ^2J = 9.3, 3 and 4C).

Mass spectrum: m/z 388 (M^+, 88%), 373 (M^+ − Me, 100%).

Anal calc for $C_{28}H_{21}P$, % C 86.58, H 5.45, P 7.55. Found, % C 86.01, H 5.45, P 7.97.

• *X-ray Structure Determination for* **7** *[14]*: Crystals of **7**, $C_{28}H_{21}P$ were grown from an hexane solution of the compound. Data were collected at −150 ± 0.5 °C on an Enraf Nonius CAD4 diffractometer using Mo $K\alpha$ radiation(λ = 0.71073 Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf Nonius MOLEN package. The compound crystallizes in space group $Pca2_1$ (29), a = 11.753(1) Å, b = 23.619(2) Å, c = 7.540(1) Å; V = 2 093.04(63) Å^3; Z = 4; $d$calc = 1.233 g/cm^3; μ = 1.4 cm^{-1}; F(000) = 816. A total of 3 486 unique reflexions were recorded in the range $2° \leqslant 2\theta \leqslant 60.0°$ of which 934 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 2 552 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were refined isotropically in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.06. The final agreement factors were R = 0.031, R_ω = 0.041, GOF = 1.05.

1,2-Bis(5-bromo-3,4-dimethyl-1-phenyl-2-phospholyl) ethyne **8**

Disulfone **13** (1.4 g, 5.2×10^{-3} mol) was added to a solution of the anion **2a** (8.3×10^{-3} mol) in 100 mL of THF at −100 °C. After 15 min, the reaction mixture was warmed and the THF was vacuum removed. Chromatography of the residue with toluene gave 1.25 g (about 55% yield) of an orange oil which slowly crystallized. Recrystallization of an analytical sample in a mixture of dichloromethane/hexane lead to orange crystals, as a mixture of two diastereomers, A and B; mp 162 °C.

^{31}P NMR: δ 20.4 and 20.5.

^{1}H NMR: δ 2.05 (d, ^{4}J(H-P) = 2.4, 6H, 7 Me), 2.12 (d, ^{4}J(H-P) = 3.3) and 2.14 (d, ^{4}J(H-P) = 3.2, 6H, 6 Me of A and B), 7.32 (m, 10H, Ph).

^{13}C NMR: δ 16.10 (s, 6 or 7 Me), 16.92 (s, 6 or 7 Me), 95.00 (q, $^{2}J = 3.8$, $^{3}J = 22.8$) and 95.50 (q, $^{2}J = 4.3$, $^{3}J = 22.9$, acetylenic C of A and B), 122.93 (d, ^{1}J = 20.3, 5C), 125.46 (s, 2C), 147.50 (d, ^{2}J = 5.5, 4C), 151.65 (pseudo t, ^{2}J = 12.1 and ^{2}J = 7.3, 3C of A and B); aromatic C: 130.42 (d, ^{1}J = 16.9, *ipso*), 128.72 (d, ^{3}J = 8.8, *meta*), 129.66 and 129.75 (s, *para* of A and B), 132.94 (d, ^{2}J = 19.7) and 133.06 (d, ^{2}J = 19.7, *ortho* of A and B).

Mass spectrum: m/z 556 (M, 100%); isotope pattern for M^+: calc 559 (14.4%), 558 (51.7%), 557 (29.0%), 556 (100%), 555 (14.8%), 554 (50.3%). Found: 559 (14%), 558 (62%), 557 (29%), 556 (100%), 555 (14.5%), 554 (49%).

Anal calc for $C_{24}H_{22}Br_2P_2$: Br 28.73, P 11.14. Found: Br 28.51, P 11.86.

1,2-Bis[3,4-dimethyl-1-phenyl-5-(trimethylsilylethynyl)-2-phospholyl]ethyne **9**

To a solution of **8** (1.0 g, 1.8×10^{-3} mol) in THF (40 mL) at −100 °C, was added by syringe a solution of butyllithium in hexane (2.5 mL, 1.6 M, 4.0×10^{-3} mol), followed after 15 min at −95 °C, by the acetylenic sulfone **12** (1.1 g, 4.3×10^{-3} mol). The reaction mixture was slowly warmed to room temperature and then acidified with a few drops of acetic acid. The THF was removed and the residue chromatographed with a mixture of hexane/dichloromethane (from 9:1 to 8:2). Yield 0.2 g (about 20%) of a sticky deep-orange solid, mixture of two isomers, A (about 25–28%) and B (about 75–78%, by integration of the methyl ^{1}H NMR signals).

^{31}P NMR: δ 23.9, 24.2, 24.5 (pseudo triplet); small unidentified signal at 31.3.

^{1}H NMR: δ 0.24 (s, about 0.25 × 18H, SiMe isomer A), 0.31 (s, about 0.75 × 18H, SiMe isomer B), 2.23 (m, about 0.84 × 12H, 6 and 7 Me of B and 6 or 7 Me of A), 2.33 (d, ^{4}J = 3.9, about 0.14 × 12H, 6 or 7 Me of A), 7.35 and 7.56 (m, 10H, Ph).

^{13}C NMR: δ 0.25 (s, SiMe of B), 0.45 (s, SiMe of A), 16.20 (s) and 16.36 (s, 6 and 7 Me of A), 16.46 (s) and 16.52 (s, 6 and 7 Me of B), 96.54 (q, ^{2}J = 3.8, ^{3}J = 22.1 central triple bond of A or B), 96.80 (q, ^{2}J = 3.7, ^{3}J = 21.9, central triple bond of A or B), 101.64 (d, ^{3}J = 21.7, 9C of B), 101.85 (d, ^{3}J = 21.4, 8C of A), 104.82 (s, 8C of A), 105.19 (s, 8C of B), 124.23 (s, 2C of A), 125.17 (d, ^{1}J = 9.1, 2C of B), 125.99 (s, 5C of B), 126.27 (s, 5C of A); 152.18 (d, ^{2}J = 11.5), 154.50 (d, ^{2}J = 10.4) and 157.35 (d, ^{2}J = 4.7, 3C and 4C of A and B); aromatic C, A isomer: 128.35 (s, *para*), 128.62 (d, ^{3}J = 8.5, *meta*), 132.22 (d, ^{2}J = 18.1, *ortho*), 132.77 (d, ^{1}J = 14.1, *ipso*); B isomer: 128.74 (d, ^{3}J = 7.6, *meta*), 129.34 (d, ^{1}J = 14.4, *ipso*), 132.14 (d, ^{2}J = 18.0, *ortho*).

Mass spectrum: m/z 590 (M^+, 100%); isotope pattern for M^+: calc 590 (100), 591 (50.9), 592 (19.3), 593 (5.0), 594 (1.0); Found: 590 (100), 591 (53), 592 (19), 593 (5), 594 (1).

References

1 Deschamps E, Ricard L, Mathey F, *Angew Chem, Int Ed Engl* (1994) 33, 1158

2 Deschamps E, Ricard L, Mathey F, *J Chem Soc, Chem Commun* (1995) 1561

3 Pearson DL, Schumm JS, Tour JM, *Macromolecules* (1994) 27, 2348; see also: Dagani R, *Chem Eng News* (1993) March 22, 20

4 Deschamps E, Mathey F, *Bull Soc Chim Fr* (1992) 129, 486

5 Stille JK, Simpson JH, *J Am Chem Soc* (1987) 109, 2138

6 Deschamps E, unpublished results

7 Sonogashira K, Tohda, Hagihara N, *Tetrahedron Lett* (1975) 4467; see also: Nicolaou KC, Veale CA, Webber SE, Katerinopoulos H, *J Am Chem Soc* (1985) 107, 7515

8 Smorada RL, Truce WE, *J Org Chem* (1979) 44, 3444

9 Coggon P, Mc Phail AT, *J Chem Soc, Dalton Trans* (1973) 1888

10 Schleyer P von R, Freeman PK, Jiao H, Goldfuss B, *Angew Chem, Int Ed Engl* (1995) 34, 337

11 Backer HJ, Strating J, *Recl Trav Chim Pays Bas* (1954) 73, 565; Riera A, Cabré F, Moyano A, Pericàs MA, Santamaria J, *Tetrahedron Lett* (1990) 31, 2169; Riera A, Marti M, Moyano A, Pericàs MA, Santamaria J, *Tetrahedron Lett* (1990) 31, 2173

12 Mautner HG, Donnely B, Lee CM, Leddicotte W, *J Am Chem Soc* (1962) 84, 2020

13 Bhattacharya SN, Josiah Bm, Walton DRM, *Organometal Chem Synth* (1971) 1, 145

14 Supplementary material data for compound **7** have been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication N° SUP 9403 and are available on request from the Document Supply Centre