I he Unexpected Chemistry of a Bis(phospholyl)acetylene

Matthew P. Duffy, Bruno Donnadieu, and François Mathey

Department of Chemistry, UCR–CNRS Joint Research Laboratory, University of California Riverside, Riverside, CA 92521-0403

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ABSTRACT: The reaction of lithium 3,4-dimethylphospholide with tetrachloroethylene gives the corresponding 1,2-bis(phospholyl)acetylene that has been characterized by X-ray crystal structure analysis of its bis(pentacarbonylmolybdenum) complex. The reaction with sulfur leads to the corresponding disulfide that spontaneously undergoes a self-condensation via a Diels–Alder cycloaddition between the C=C triple bond and the phosphole dienic system giving, after aromatization by loss of the phosphorus bridge, the corresponding 1,2-bis(phospholyl)benzene. © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:537– 541, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20457

INTRODUCTION

Conjugated oligomers incorporating phosphorus heterocycles as modulating units are now studied in some depth in view of their potential applications in the manufacture of organic light-emitting diodes (OLED's) and organic transistors [1,2]. In particular, the group of Chujo has described the synthesis of several oligomers including phosphole and alkyne units [3,4]. On our side, we have prepared several α -substituted alkynylphospholes from a 2-lithiophosphole [5], but the yields were relatively low and the overall scheme was somewhat cumbersome. Our initial aim in the present study was to check

whether it was possible to use the [1,5]-sigmatropic shifts of R-groups from P to C α that are characteristic of phosphole chemistry [6] to install an alkynyl group between the α -positions of two phospholes. In a preliminary work, we demonstrated that such a shift is possible on one phosphole, although polymerization by self-condensation between the C=C triple bond and the 2*H*-phosphole is difficult to avoid [7]. We report hereafter on the unexpected outcome of our study.

RESULTS AND DISCUSSION

Our primary target was the bis(3,4-dimethylphospholyl)acetylene (1). It must be noted here that the bis(2,3,4,5-tetraethylphospholyl)acetylene has already been prepared by the group of Yoshifuji using the chemistry of zirconacyclopentadienes [8]. Our synthetic approach is entirely different. We first decided to investigate the reaction of the 1-cyanophosphole (2) [9] with the readily available dilithioacetylene [10] (Eq. (1)).



Whatever the conditions, the reaction always yielded the monosubstituted acetylene (**3**), which was characterized by its 31 P resonance at -45 ppm and by X-ray analysis of its P-sulfide.

We then decided to follow a procedure reported in the literature for the synthesis of bis(diphenylphosphino)acetylene [11]. Accordingly,

Correspondence to: François Mathey; e-mail: françois.mathey@ ucr.edu.

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we reacted the lithium 3,4-dimethylphospholide with tetrachloroethylene (Eq. (2)).

deg. This cannot be due to the repulsion between the two bulky molybdenum units since the bending



We reproducibly obtained a 1:1 mixture of the desired bis(phospholyl)acetylene (1) ($\delta^{31}P$ -45) and the 1,1'-biphospholyl (4) ($\delta^{31}P$ -29). The formation of the biphospholyl suggests that dichloroacetylene is intermediately formed in the reaction. The postulated mechanism is shown in Eq. (3).

is directed toward the metals. A similar bending of the C=C triple bond has been observed previously in several bis(diphenylphosphino)acetylene complexes [12].

The preliminary C=C shift experiments at high temperature were negative, but, while studying the



The yield of (1) is 20% versus a maximum theoretical yield of 50%. The highly reactive biphospholyl was destroyed by the reaction with sulfur at room temperature. Bis(phospholyl)acetylene is inert under such conditions. A quick chromatography allowed to get (1) in the pure state. It was characterized by mass spectrometry and ¹H, ¹³C, and ³¹P NMR spectroscopy. A further characterization was performed by X-ray crystal structure analysis of its bis(pentacarbonylmolybdenum) complex (5) (Fig. 1). The structure shows a very short P–C(sp) bond at 1.782(4) Å, significantly shorter than the endocyclic P–C bonds (1.807(4) and 1.813(4) Å), but the most characteristic phenomenon is the nonlinearity of the C=C triple bond: P–C=C 170.49(15) sulfurization of (1) at 60°C, we made a surprising observation. The initial disulfide (6) (δ^{31} P 11 ppm) rapidly evolves to give a new sulfide (7) at δ^{31} P 41 ppm. The ¹³C spectrum of (7) shows two types of methyl groups and two types of sp²-C directly linked to P at 126.23 (¹*J*_{C-P} = 86.1 Hz) (CH) and 133.53 (¹*J*_{C-P} = 89.9 Hz, ²*J*_{C-P} = 8.2 Hz) (C). The mass spectrum indicates that one C₆H₈ unit has been added to (1) (*m*/*z* = 391 (M + H)). The X-ray crystal structure analysis (Fig. 2) shows that this product results from the self-condensation of (6), involving the Diels–Alder condensation of the C=C triple bond with the phosphole dienic unit, leading, after aromatization by loss of the P(S)R bridge, to the *ortho*diphospholylbenzene (7) (Eq. (4)).





FIGURE 1 X-ray crystal structure of molybdenum complex (5). Ellipsoids are scaled to enclose 50% of the electronic density. Main bond lengths (Å) and angles (deg.): P-C1 1.782(4), C1-C1 1.216(9), P-C2 1.807(4), P-C5 1.813(4), P-Mo 2.5177(18); P-C1-C1 170.49(15), Mo-P-C1 110.64(11), C2-P-C5 91.4(2).

The molecule is sterically congested as shown by the P1-C1-C6 and P2-C6-C1 angles larger than 120°. (126.24(19) and 126.6(2)) and by the relatively long C1-C6 bond at 1.410(4) Å versus 1.387(4)-1.400(4) A for the other C–C bonds of the benzene ring. It must be recalled here that monomeric 3,4dimethylphosphole sulfides are known to be quite reactive dienes in the Diels-Alder reactions and that the [4+2] cycloadducts thus obtained often lose their phosphorus bridges [13]. Besides, the reaction of lithium 3,4-dimethylphospholide with 1,2dibromobenzene in the presence of a nickel catalyst essentially stops at the monosubstitution [14] and only one ortho-diphospholylbenzene has been obtained previously by a rather complex sequence of reactions [15]. Finally, the bis(phospholyl)acetylene disulfide prepared by the group of Yoshifuji [8] does not undergo this kind of chemistry, probably because the phosphole dienic reactivity is quenched by the tetraethyl substitution.

EXPERIMENTAL

Nuclear magnetic resonance spectra were obtained on a Bruker-Avance 300 and Varian-Inova spectrometer operating at 300.13 MHz for ¹H, 75.45 MHz for ¹³C, and 121.496 MHz for ³¹P. Chemical shifts are expressed in parts per million downfield from external TMS (¹H and ¹³C) and external 85% H₃PO₄ (³¹P). Mass spectra were obtained on VG 7070 and Hewlett–Packard 5989A GC/MS spectrometers.



FIGURE 2 X-ray crystal structure of disulfide (7). Ellipsoids are scaled to enclose 50% of the electronic density. Main bond lengths (Å) and angles (deg.): P1–S1 1.9507(9), P2–S2 1.9508(10), P1–C1 1.826(3), P2–C6 1.833(3), P1–C7 1.791(3), P1–C10 1.791(3), P2–C11 1.784(3), P2–C14 1.799(3), C1–C6 1.410(4); P1–C1–C6 126.24(19), P2–C6–C1 126.6(2), C7–P1–C10 91.97(13), C11–P2–C14 91.48(13), C1–P1–S1 113.88(9), C6–P2–S2 114.67 (9).

Bis(3,4-*dimethylphospholyl*)*acetylene* (1)

To a Schlenk flask containing tetrachloroethylene (1.09 mL, 10.6 mmol) in THF (80 mL) was added dropwise via cannula, at room temperature under nitrogen a solution of lithium 3,4dimethylphospholide (42.5 mmol) in THF (240 mL). After stirring for 30 min, the reaction was monitored by ³¹P NMR. To destroy the biphospholyl by-product, sulfur (0.68 g, 21.3 mmol) was added and the solution was stirred for 1 h and monitored by ³¹P NMR. Once all the biphospholyl was destroyed, the solvent was removed under vacuum, the residue was dissolved in a minimum amount of methylene chloride and chromatographed on silica. The compound was eluted with an 80:20 hexane:methylene chloride mixture. Solvent was removed under vacuum, and the product was checked by ³¹P NMR. Yield 1.07 g (4.3 mmol, 20%) of an orange-yellow solid.

³¹P NMR (CDCl₃) δ: -38.1 ppm; ¹H NMR (CDCl₃) δ: 2.09 (d, ⁴*J*(P-H) = 3.3 Hz, 12H, CH₃), 6.30 (d, ²*J*(P-H) = 39.2 Hz, 4H, =CH); ¹³C NMR (CDCl₃) δ: 17.92 (s, CH₃), 100.44 (d, ¹*J*(P-C) = 26.0 Hz, =C), 124.92 (s, =CH), 150.45 (m, =CMe) ppm. Mass spectrum (FAB+): 247 (MH⁺)

Decacarbonyldimolybdenum Complex (5)

To a Schlenk flask with bis(phospholyl)acetylene (1) (0.752 g, 3.05 mmol) in acetonitrile (10 mL) was added dropwise under nitrogen a solution of freshly made $Mo(CO)_5(MeCN)$ (6.1 mmol) in acetonitrile

(20 mL). The reaction mixture was stirred overnight and monitored by ³¹P NMR. Solvent was removed under vacuum, and the residue was purified by column chromatography on silica with 97:3 petroleum ether:ethyl acetate as the eluent, yielding 0.50 g (0.7 mmol) of a pale yellow solid (23.0%).

³¹P NMR (CDCl₃) δ: -4.0 ppm; ¹H NMR (CDCl₃) δ: 2.14 (s, 12H, CH₃), 6.26 (d, ²J(P-H) = 38.8 Hz, 4H, =CH); ¹³C NMR (CDCl₃) δ 17.71 (d, ³J(P-C) = 12.0 Hz, CH₃), 99.11 (d, ¹J(P-C) = 44.9 Hz, =C), 125.85 (d, ¹J(P-C) = 44.9 Hz, =CH), 152.48 (d, ²J(P-C) = 11.4 Hz, CMe), 204.58 (d, ²J(P-C) = 8.2 Hz, Mo-C=O eq), 209.40 (d, ²J(P-C) = 20.3 Hz, Mo-C=O ax) ppm. Mass spectrum: 719 (MH⁺).

4,5-Dimethyl-1,2-bis(3,4dimethylphospholyl)benzene Disulfide (**7**)

To a Schlenk flask with bis(phospholyl)acetylene (1) (0.13 g, 0.53 mmol) in THF (5 mL) under nitrogen, sulfur (0.037 g, 1.2 m mol) at room temperature was added. The mixture was stirred overnight and monitored by ³¹P NMR to confirm the formation of the bis(phospholyl)acetylene disulfide (**6**). Then, the reaction mixture was heated at 60°C for 3 h and monitored by ³¹P NMR till there was no longer any bis(phospholyl)acetylene disulfide left, leaving only the final product (**7**). After the solvent was removed under vacuum, the residue was purified by column chromatography on silica with hexanes and methylene chloride. The product was finally eluted with diethyl ether to yield 0.04 g (0.10 mmol) of a light yellow solid (18.9%).

³¹P NMR (CDCl₃) δ : +40.7 ppm; ¹H NMR (CDCl₃) δ : 2.09 (s, 12H, CH₃), 2.24 (s, 6H, CH₃), 6.80 (d, ²J(P-H) = 28.7 Hz, 4H, =CH), 7.57 (m, ³J(P-H) + ⁴J(P-H) = 19.3 Hz, 2H, H benzene); ¹³C NMR (CDCl₃) δ : 17.68 (m, CH₃), 19.98 (s, Ph-CH₃) 126.23 (d, ¹J(P-C) = 86.1 Hz, =CH), 133.5 (dd, ¹J(P-C) = 89.9 Hz, ²J(P-C) = 8.2 Hz, P-C = C-P), 134.4 (m, Ph), 140.8 (m, Ph), 152.4 (m, =CMe) ppm; Mass spectrum (FAB+): 391 (MH⁺).

X-Ray Structure Determination of 5 and 7

Compounds were measured at low temperature T = 100(2) K, on an X8-APEX Bruker Kappa four circles X-ray diffractometer system (Mo-radiation, $\lambda = 0.71073$ Å). An optimized data collection strategy was defined using Cosmo [16]. Frames were integrated with the aid of Bruker Saint software [17] included in the Bruker APEX2 package [18] and us-

ing a narrow-frame integration algorithm. The integrated frames yielded for.

5: A total of 6677 reflections at a maximum 2θ angle of 46.52° of which 2062 were independent reflections ($R_{int} = 0.0488$, $R_{sig} = 0.0465$, completeness = 99.9%) and 1807 (87.63%) reflections were greater than $2\sigma(I)$. A monoclinic cell space group C2/c was found; the unit cell parameters were a = 25.368(19) Å, b = 9.006(7) Å, c = 13.883(11) Å, $\alpha = 90.0^{\circ}$, $\beta = 115.486(8)^{\circ}$, $\gamma = 90.0^{\circ}$, V = 2863(4) Å³, Z = 8, calculated density $D_c = 1.666$ Mg/m³.

7: A total of 26,584 reflections at a maximum 2θ angle of 51.76°, of which 3916 were independent reflections ($R_{int} = 0.0645$, $R_{sig} = 0.0450$, completeness = 99.9%) and 2700 (68.95%) reflections were greater than $2\sigma(I)$. A orthorhombic cell space group *Pbca* was found, the unit cell parameters were a = 15.8034(15) Å, b = 15.3256(15) Å, c = 16.6866(16) Å, $\alpha = \beta = \gamma = 90.0^{\circ}$, V = 4041.4(7) Å³, Z = 8, calculated density $D_c = 1.283$ Mg/m³.

Absorption corrections were applied for data using the SADABS [19] program. The program SIR92 [20] was used for phase determination and structure solution, followed by some subsequent difference Fourier maps. From the primary electron density map got most of the non-hydrogen atoms were located, and with the aid of subsequent isotropic refinement all of the non-hydrogen atoms were identified. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix leastsquares procedure on F^2 . The H-atoms were included in the refinement in calculated positions riding on the C atoms to which they were attached. The refinement converged for.

5 at $R_1 = 0.0391$, w $R_2 = 0.0998$, with intensity, $I > 2\sigma(I)$, **7** at $R_1 = 0.0400$, $wR_2 = 0.0915$ with intensity, $I > 2\sigma(I)$. Drawings of molecules were performed using of ORTEP32 [21]. (Further details on the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ UK, on quoting the full journal citation.

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