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# Key Intermediates in the Synthesis of 2,2′-Biphosphole

OLIVIER TISSOT, MARYSE GOUYGOU, JEAN-CLAUDE DARAN AND GILBERT BALAVOINE

*Laboratoire de Chimie de Coordination, UPR-CNRS 8241, 205 Route de Narbonne, 31077 Toulouse CEDEX, France. E-mail: daran@lcc-toulouse.fr*

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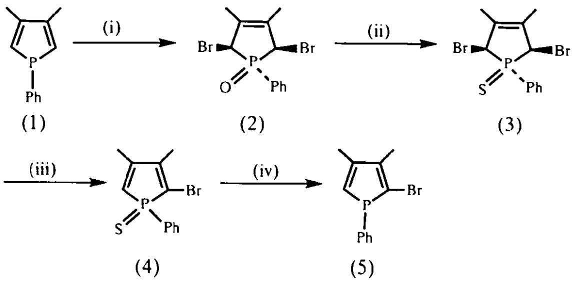
## Abstract

The crystal structures of three key intermediates in the synthesis of 2,2′-biphosphole are reported. Molecules of 2,5-dibromo-3,4-dimethyl-1-phenyl-2,5-dihydrophosphole 1-oxide, $C_{12}H_{13}Br_2OP$, and 2,5-dibromo-3,4-dimethyl-1-phenyl-2,5-dihydrophosphole 1-sulfide, $C_{12}H_{13}Br_2PS$, each contain a phospholene ring with a chair conformation. In the molecules, the $\alpha$-H atoms are *trans* to the P=O or P=S groups, thus demonstrating that the sulfurization takes place with the retention of the stereochemistry at phosphorus. In 2-bromo-3,4-dimethyl-1-phenylphosphole 1-sulfide, $C_{12}H_{12}BrPS$, the phosphole ring is perfectly planar.

## Comment

Within the framework of a project concerning the design and synthesis of new $C_2$-symmetry chiral bidentate ligands, we were interested in 2,2′-biphosphole and the possibility of formation of transition metal complexes with this chiral ligand (Gouygou *et al.*, 1997). Two approaches to the synthesis of 2,2′-biphosphole have been reported (Mercier *et al.*, 1986; Deschamps & Mathey, 1992). We have used the most attractive route, which involves the preparation of 2-bromophosphole. The synthesis of 2-bromo-3,4-dimethyl-1-phenylphosphole, (5), proceeds in four steps starting from 3,4-dimethyl-1-phenylphosphole, (1). Although the formation and spectroscopic characterizations of the intermediates (2) (2,5-dibromo-3,4-dimethyl-1-phenyl-2,5-dihydrophosphole 1-oxide), (3) (2,5-dibromo-3,4-dimethyl-1-phenyl-2,5-dihydrophosphole 1-sulfide) and (4) (2-bromo-3,4-dimethyl-1-phenylphosphole 1-sulfide) have already been mentioned, they have not been fully characterized by X-ray analysis. We have isolated (2), (3) and (4) as crystals suitable for X-ray investigations and their structures are reported here.



(i) (*a*) m-Cl-$C_6H_4$-$CO_3H$, $CH_2Cl_2$, 273 K
(*b*) $pyH^+Br_3^-$, $CH_2Cl_2$, 298 K
(ii) 0.5eq. $P_4S_{10}$, toluene, reflux
(iii) KOH, MeOH/$CH_2Cl_2$, 298 K
(iv) $PMe_3$, toluene, reflux

The structure of compound (2) is shown in Fig. 1. As observed in the related compound 3,4-dimethyl-1-supermesityl-3-phospholene (Li *et al.*, 1992), the phospholene ring has a chair conformation with a dihedral angle of 22.7 (3)° between the C1—C2—C3—C4 and C1—P1—C4 planes. The $\alpha$-H atoms are *trans* to the P=O group, which confirms the stereochemistry

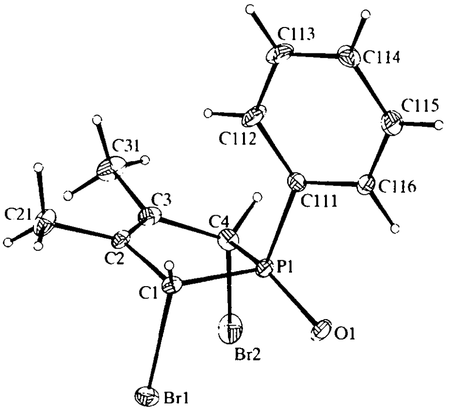


Fig. 1. Molecular view of molecule (2) showing 50% probability displacement ellipsoids.

proposed by Deschamps & Mathey (1992) based on NMR data, in particular the low $^2J$(P–α-H). The phenyl-ring plane, which makes a dihedral angle of 84.0 (2)° with the C1—C2—C3—C4 plane, is nearly coplanar with the O atom [displaced by only 0.13 (5) Å]. The C—Br bond lengths of 1.977 (4) and 1.984 (5) Å are significantly longer than that of 1.919 Å observed in 2,3-dibromo-1-phenylphospholane 1-oxide (Stults & Moedritzer, 1979).

Compound (3) crystallizes with two independent but roughly identical molecules, *A* and *B*, in the asymmetric unit. The molecular structures of the two molecules, as shown in Fig. 2, compare well with that of (2). As in (2), the phospholene ring has a chair conformation with dihedral angles of 16.8 (8) and 20.8 (8)° for molecules *A* and *B*, respectively. The α-H atoms are *trans* to the P=S group and thus demonstrate that the sulfurization takes place with the retention of the stereochemistry at phosphorus. In each molecule, the phenyl ring is roughly perpendicular to the phospholene ring [dihedral angles 89.0 (4) and 86.5 (3)° in *A* and *B*, respectively]. The C—Br distances [1.963 (9) and 1.953 (9) Å in *A*, and 1.960 (10) and 1.960 (9) Å in *B*] are slightly shorter than those in (2).

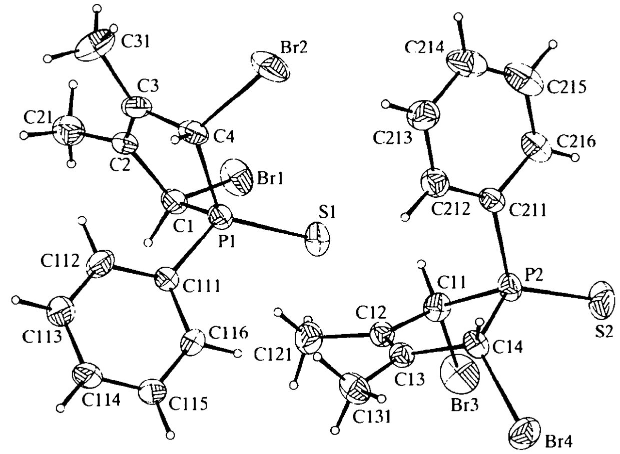


Fig. 2. Molecular view of molecule (3) showing 50% probability displacement ellipsoids.

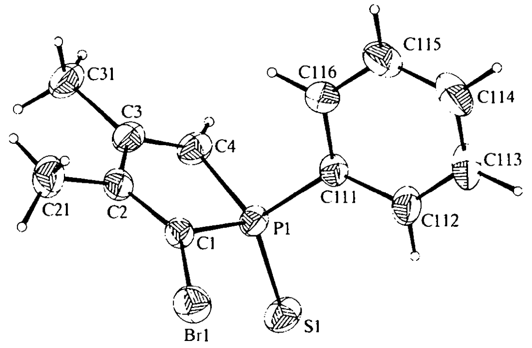


Fig. 3. Molecular view of molecule (4) showing 50% probability displacement ellipsoids.

The crystal structure of (4) is shown in Fig. 3. The phosphole ring is almost perfectly planar, with the largest deviation being −0.013 (5) Å (for C1). The P—S bond length of 1.946 (2) Å compares well with that of 1.947 Å observed in 2-carboxy-3,4-dimethyl-1-phenylphosphole sulfide (Craig *et al.*, 1980). The C—Br bond length of 1.871 (4) Å is slightly shorter than those in compounds (2) and (3).

## Experimental

Compounds (2), (3) and (4) were synthesized according to the reported procedure of Deschamps & Mathey (1992). Compounds (2) and (4) were obtained as powders. Intermediate (2) was recrystallized from dichloromethane, whereas (4) was obtained by slow diffusion between dichloromethane and pentane. Intermediate (3) was first obtained as an oil and was difficult to crystallize. However, the use of a diffusion procedure between dichloromethane and pentane allowed the formation of crystals suitable for X-ray analysis.

### Compound (2)

*Crystal data*

$C_{12}H_{13}Br_2OP$
$M_r = 364.02$
Monoclinic
*Cc*
$a = 14.135\,(2)$ Å
$b = 9.884\,(1)$ Å
$c = 10.877\,(1)$ Å
$\beta = 118.95\,(1)°$
$V = 1329.6\,(3)$ Å$^3$
$Z = 4$
$D_x = 1.818$ Mg m$^{-3}$
$D_m$ not measured

Mo *K*α radiation
$\lambda = 0.71073$ Å
Cell parameters from 5000 reflections
$\theta = 2.64$–$28.18°$
$\mu = 6.194$ mm$^{-1}$
$T = 180\,(2)$ K
Flat needle
0.50 × 0.16 × 0.08 mm
Colourless

*Data collection*

Stoe IPDS diffractometer
φ rotation scans
Absorption correction: numerical (Stoe & Cie, 1996*c*)
$T_{min} = 0.318$, $T_{max} = 0.654$
7891 measured reflections
3105 independent reflections

2766 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 28.18°$
$h = -18 \rightarrow 18$
$k = 0 \rightarrow 13$
$l = -14 \rightarrow 14$

*Refinement*

Refinement on $F^2$
$R(F) = 0.031$
$wR(F^2) = 0.073$
$S = 1.172$
3105 reflections
145 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 2.6194P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.466$ e Å$^{-3}$
$\Delta\rho_{min} = -0.517$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.02 (1)

Table 1. *Selected geometric parameters (Å, °) for (2)*

| | | | |
|---|---|---|---|
| Br1—C1 | 1.977 (4) | P1—C4 | 1.830 (5) |
| Br2—C4 | 1.984 (5) | C1—C2 | 1.508 (6) |
| P1—O1 | 1.470 (3) | C4—C3 | 1.502 (7) |
| P1—C111 | 1.813 (5) | C2—C3 | 1.341 (6) |
| P1—C1 | 1.825 (4) | | |
| O1—P1—C111 | 112.6 (2) | C3—C4—P1 | 105.0 (3) |
| O1—P1—C1 | 120.0 (2) | C3—C4—Br2 | 110.0 (3) |
| C111—P1—C1 | 104.0 (2) | P1—C4—Br2 | 109.7 (2) |
| O1—P1—C4 | 117.5 (2) | C3—C2—C21 | 126.2 (4) |
| C111—P1—C4 | 107.2 (2) | C3—C2—C1 | 116.4 (4) |
| C1—P1—C4 | 93.1 (2) | C21—C2—C1 | 117.3 (4) |
| C2—C1—P1 | 104.5 (3) | C2—C3—C31 | 127.1 (5) |
| C2—C1—Br1 | 111.2 (3) | C2—C3—C4 | 115.2 (4) |
| P1—C1—Br1 | 110.4 (2) | C31—C3—C4 | 117.7 (4) |

**Compound (3)**

*Crystal data*

$C_{12}H_{13}Br_2PS$
$M_r = 380.08$
Monoclinic
$P2_1/c$
$a = 7.843$ (1) Å
$b = 26.024$ (3) Å
$c = 14.003$ (2) Å
$\beta = 96.95$ (2)°
$V = 2837.1$ (8) Å$^3$
$Z = 8$
$D_x = 1.780$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5000 reflections
$\theta = 2.14$–$24.27°$
$\mu = 5.946$ mm$^{-1}$
$T = 293$ (2) K
Flat box
0.36 × 0.23 × 0.12 mm
Yellow

*Data collection*

Stoe IPDS diffractometer
$\varphi$ rotation scans
Absorption correction: numerical (Stoe & Cie, 1996*c*)
$T_{\min} = 0.140$, $T_{\max} = 0.506$
21 397 measured reflections
4432 independent reflections

2535 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.064$
$\theta_{\max} = 24.27°$
$h = -9 \rightarrow 8$
$k = 0 \rightarrow 29$
$l = 0 \rightarrow 16$

*Refinement*

Refinement on $F^2$
$R(F) = 0.051$
$wR(F^2) = 0.142$
$S = 1.531$
4432 reflections
289 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 9.9777P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.754$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.590$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (3)*

| | | | |
|---|---|---|---|
| Br1—C1 | 1.963 (9) | Br3—C11 | 1.960 (10) |
| Br2—C4 | 1.953 (9) | Br4—C14 | 1.960 (9) |
| P1—C111 | 1.814 (9) | P2—C211 | 1.809 (9) |
| P1—C1 | 1.841 (10) | P2—C11 | 1.831 (9) |
| P1—C4 | 1.843 (10) | P2—C14 | 1.840 (9) |
| P1—S1 | 1.928 (4) | P2—S2 | 1.920 (4) |
| C1—C2 | 1.498 (12) | C11—C12 | 1.484 (12) |
| C2—C3 | 1.332 (13) | C12—C13 | 1.311 (12) |
| C3—C4 | 1.494 (14) | C13—C14 | 1.495 (12) |
| C111—P1—C1 | 104.2 (4) | C211—P2—C11 | 103.5 (4) |
| C111—P1—C4 | 104.0 (4) | C211—P2—C14 | 106.1 (4) |
| C1—P1—C4 | 92.4 (4) | C11—P2—C14 | 91.8 (4) |
| C111—P1—S1 | 114.9 (3) | C211—P2—S2 | 114.2 (3) |
| C1—P1—S1 | 118.7 (3) | C11—P2—S2 | 118.7 (3) |
| C4—P1—S1 | 119.3 (3) | C14—P2—S2 | 119.4 (3) |
| C2—C1—P1 | 105.6 (7) | C12—C11—P2 | 105.5 (6) |
| C2—C1—Br1 | 110.8 (6) | C12—C11—Br3 | 110.2 (6) |
| P1—C1—Br1 | 112.9 (5) | P2—C11—Br3 | 113.5 (5) |
| C3—C2—C21 | 125.8 (9) | C13—C12—C11 | 116.2 (8) |
| C3—C2—C1 | 116.2 (9) | C13—C12—C121 | 125.7 (9) |
| C21—C2—C1 | 118.0 (9) | C11—C12—C121 | 118.0 (8) |
| C2—C3—C4 | 116.4 (9) | C12—C13—C14 | 116.5 (8) |
| C2—C3—C31 | 126.0 (10) | C12—C13—C131 | 125.6 (9) |
| C4—C3—C31 | 117.5 (9) | C14—C13—C131 | 117.9 (8) |
| C3—C4—P1 | 106.0 (7) | C13—C14—P2 | 105.1 (6) |
| C3—C4—Br2 | 112.4 (6) | C13—C14—Br4 | 110.7 (6) |
| P1—C4—Br2 | 112.0 (5) | P2—C14—Br4 | 112.7 (5) |

**Compound (4)**

*Crystal data*

$C_{12}H_{12}BrPS$
$M_r = 299.16$
Triclinic
$P\overline{1}$
$a = 7.354$ (2) Å
$b = 7.946$ (2) Å
$c = 11.731$ (2) Å
$\alpha = 92.61$ (2)°
$\beta = 96.96$ (2)°
$\gamma = 109.53$ (2)°
$V = 638.5$ (2) Å$^3$
$Z = 2$
$D_x = 1.556$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3713 reflections
$\theta = 2.73$–$24.27°$
$\mu = 3.473$ mm$^{-1}$
$T = 180$ (2) K
Prism
0.80 × 0.64 × 0.42 mm
Colourless

*Data collection*

Stoe IPDS diffractometer
$\varphi$ rotation scans
Absorption correction: numerical (Stoe & Cie, 1996*c*)
$T_{\min} = 0.157$, $T_{\max} = 0.311$
3713 measured reflections
1866 independent reflections

1611 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\max} = 24.27°$
$h = -8 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = 0 \rightarrow 13$

*Refinement*

Refinement on $F^2$
$R(F) = 0.036$
$wR(F^2) = 0.100$
$S = 1.072$
1866 reflections
136 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 1.8879P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.552$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.395$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (4)*

| | | | |
|---|---|---|---|
| Br1—C1 | 1.871 (4) | P1—S1 | 1.9460 (18) |
| P1—C4 | 1.785 (5) | C1—C2 | 1.331 (7) |
| P1—C1 | 1.805 (5) | C2—C3 | 1.499 (7) |
| P1—C111 | 1.810 (5) | C3—C4 | 1.336 (7) |
| C4—P1—C1 | 90.6 (2) | P1—C1—Br1 | 120.5 (3) |
| C4—P1—C111 | 108.3 (2) | C1—C2—C3 | 112.1 (4) |
| C1—P1—C111 | 105.6 (2) | C1—C2—C21 | 125.9 (5) |
| C4—P1—S1 | 118.66 (17) | C3—C2—C21 | 122.0 (4) |
| C1—P1—S1 | 116.01 (16) | C4—C3—C31 | 124.7 (5) |

| | | | |
|---|---|---|---|
| C111—P1—S1 | 114.69 (16) | C4—C3—C2 | 114.4 (4) |
| C2—C1—P1 | 111.9 (3) | C31—C3—C2 | 120.9 (5) |
| C2—C1—Br1 | 127.6 (4) | C3—C4—P1 | 111.0 (3) |

The data were collected on a Stoe Imaging Plate Diffraction System (IPDS) [equipped with an Oxford Cryosystems Cryostream cooler device (Cosier & Glazer, 1986) in the cases of (2) and (4)]. For (2), the crystal-to-detector distance was 60 mm. For (3) and (4), the crystal-to-detector distance was chosen to be 80 mm, thus resulting in a $\theta$ limitation at 24.27°. For (2) and (3), 125 exposures were obtained with $0 < \varphi < 250°$ and with the crystal rotated through 2° in $\varphi$. For (4), 80 exposures were obtained with $0 < \varphi < 200°$ and with the crystals rotated through 2.5° in $\varphi$. Coverage of the unique set was over 99% complete to at least 28° for (2), over 96% complete to at least 24° for (3), and over 94% complete to at least 24° for (4). Crystal decay was monitored by measuring 200 reflections per image.

For all compounds, data collection: *IPDS Manual* (Stoe & Cie, 1996*a*); cell refinement: *IPDS Manual*; data reduction: *X-RED* (Stoe & Cie, 1996*b*); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993) for (2) and (3); *SHELXL*97 (Sheldrick, 1997) for (4). For all compounds, molecular graphics: *CAMERON* (Watkin *et al.*, 1996). Software used to prepare material for publication: *SHELXL*93 for (2) and (3); *SHELXL*97 for (4).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1134). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). C**54**, 679–681

# 1,2-Bis(5-methyl-4-methylthio-1,3-dithiolium-2-ylidene)-1,2-diphenylethane Bis(triiodide) and 1,2-Bis(4-methoxyphenyl)-1,2-bis(5-methyl-4-methylthio-1,3-dithiolium-2-ylidene)ethane Diperchlorate

Christian Rimbaud,[a] Pierre Le Magueres,[a] Lahcene Ouahab,[a] Dominique Lorcy[b] and Albert Robert[b]

[a]*Groupe Matériaux Moléculaires, Laboratoire de Chimie du Solide et Inorganique Moléculaire (CNRS, UMR 6511), Université de Rennes 1, Avenue du General Leclerc, 35042 Rennes CEDEX, France, and* [b]*Laboratoire de synthese et électrosynthese organiques (UMR 6510), Université de Rennes 1, Avenue du General Leclerc, 35042 Rennes CEDEX, France. E-mail: ouahab@univ-rennes1.fr*

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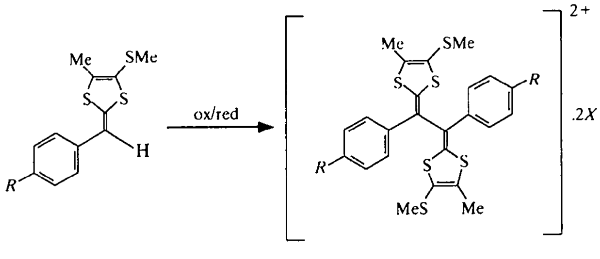
## Abstract

The non-planar organic donor 1,2-diaryl-1,2-bis(5-methyl-4-methylthio-1,3-dithiol-2-ylidene)ethane forms dication charge-transfer salts with iodine, $C_{24}H_{22}S_6^{2+}.2I_3^-$, and with perchlorate, $C_{26}H_{26}O_2S_6^{2+}.2ClO_4^-$. In the former salt, mixed stacks of triiodide and dications are observed, while separated organic and inorganic columns are found in the perchlorate salt.

## Comment

Extended tetrathiafulvalenes (TTF) which possess a conjugated spacer group between the two dithiole rings have stimulated a lot of work in the field of organic conductors (for a review, see Ogura *et al.*, 1992). The TTF vinylogue derivatives (1*a*) and (1*b*) were prepared by electrochemical synthesis starting from 1,4-dithiafulvene (2) (Lorcy *et al.*, 1995).



(2)

(1*a*) $R$ = H, $X$ = $I_3$
(1*b*) $R$ = MeO. $X$ = $ClO_4$

The stoichiometries of the title charge-transfer salts were determined by X-ray structure analysis: in both cases, there is one donor dication for two anions. Figs. 1 and 2 show the molecular structures of the title compounds. In both of these, the lengths of the