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Convenient route for the preparation of unsymmetrical phospholes via zirconacyclopentadienes☆

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Abstract

The unsymmetrical substituted zirconacyclopentadienes obtained by selective intramolecular cross-coupling of two different alkynes on zirconocene are used to prepare new unsymmetrical C-substituted phosphole compounds. The X-ray structures of a phosphole and its related sulfide are presented. © 2000 Elsevier Science S.A. All rights reserved.

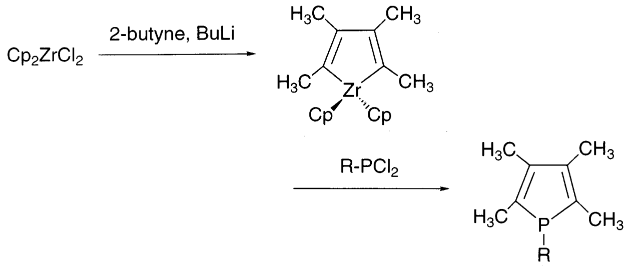
Keywords: Phosphorus heterocycle; Phospholes; Zirconacyclopentadienes

1. Introduction

As part of our continuing interest in the design and synthesis of new biphosphole compounds [1] as bidentate ligands with applications in catalysis, we have investigated the synthesis of some new phosphole moieties.

The chemistry of phospholes, the phosphorus analogue of the classic five-membered heterocycles (i.e. pyrroles, furans and thiophenes) and their preparations have been investigated and reviewed extensively [2]. Indeed, numerous phosphole derivatives with various substituents at the ring positions have been reported in the literature [2]. As most of the available synthetic routes to these heterocyclic compounds involve rather complicated multistep procedures and give rather low yields [2], we have been interested in developing a simple method for preparing unsymmetrical C-substituted phospholes with alkyl and aryl groups.

The synthesis of symmetrical phospholes using a simple one-pot procedure via zirconacyclopentadiene intermediates has been described in the literature [3]. This procedure involves in the first step the formation of a symmetrical zirconacyclopentadiene as an intermediate resulting from an alkyne–alkyne product of zirconocene. In the second step, the treatment of this intermediate by the electrophile $RPCl_2$ induces direct zirconium–phosphorus exchange and produces a symmetrical phosphole in a good yield (Eq. (1)). However, only a few phospholes have been prepared by this route [3,4].



(1)

Several methods have been reported to prepare unsymmetrical zirconacyclopentadienes [5] in which the key step is the addition of a second alkyne to a zirconocene alkyne complex thus preventing the formation of homo coupling products. However, these

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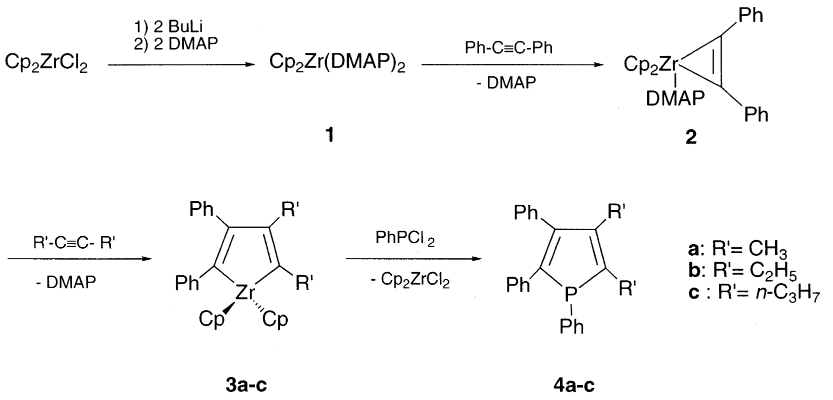


Scheme 1.

zirconacyclopentadienes are not used to produce unsymmetrical C-substituted phospholes. Among the methods described, we chose the method of Van Wagenen and Livinghouse [5e], which involves highly controlled conditions for selective cross-coupling reactions between two different alkynes. Using this method we have extended the synthesis utility of zirconacyclopentadienes to new compounds and further developed their applications in the preparation of phospholes.

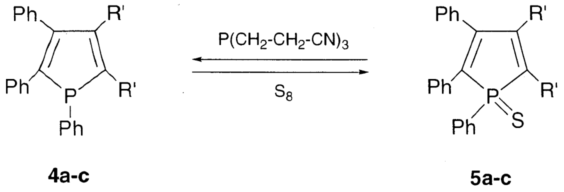
In this paper we describe the synthesis and the characterization of these new phospholes. The X-ray molecular structures of the 2,3-dimethyl-4,5-diphenyl-1-phenylphosphole and its sulfide derivative are discussed.

2. Results and discussion

2.1. Synthesis of phospholes **4**

The synthesis of unsymmetrical C-substituted phospholes **4a**–**c** was accomplished via zirconacyclopentadiene intermediates obtained according to the literature procedure [5e]. This method is based on reductive alkyne cross-coupling mediated by a stabilized 4-dimethylaminopyridine–zirconocene complex. This procedure involves reduction of Cp_2ZrCl_2 with two equivalents of *n*-BuLi under argon at −78°C followed by the addition of two equivalents of 4-dimethylaminopyridine (DMAP) which leads, at room temperature, to a stable 4-dimethylaminopyridine–zirconocene complex (**1**) (Scheme 1). This zirconocene complex reacts with the first alkyne to form the zirconacyclopropene intermediate **2** in 90 min. In the presence of a second alkyne, a cross-coupling reaction takes place between the two alkynes to form the zirconacyclopentadiene (**3**). This last compound does not need to be isolated. Treatment of the reaction mixture with one equivalent of $Ph–PCl_2$ at −78°C and warming to 25°C provides phospholes **4** (Scheme 1). Crude compounds isolated from the reaction mixture by extraction with pentane were identified by ^{31}P-NMR spectroscopy. The ^{31}P-NMR spectra exhibit only one resonance in the conventional region for such compounds [2], indicating the formation of pure phospholes except in the case of **4a**. In this case, the reaction leads to the formation of a mixture of two phospholes compounds in a 80/20 ratio. The major product is the unsymmetrical C-substituted phosphole **4a** whereas the minor product corresponds to a symmetrical phosphole resulting from a homo coupling of the two alkynes $CH_3–C≡C–CH_3$. This symmetrical phosphole has already been obtained by another zirconocene procedure [3].

Due to their sensitivity towards air and moisture, phospholes **4** have been isolated and purified as their P-sulfide derivatives. Crude phospholes **4a**–**c** were quantitatively transformed into the corresponding phosphole sulfides **5a**–**c** (Scheme 2) and have been obtained in a pure form as solids after silica column chromatography. These compounds have been fully characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy, mass spectroscopy, elemental analysis and single-crystal X-ray diffraction. The reduction of phosphole sulfides **5a**–**c** by the *tris*(2-cyanoethyl)-phosphine affords, quantitatively, phospholes **4a**–**c** (Scheme 2). A simple extraction of the reaction mixture by pentane leads to pure compounds **4** which have been isolated as solids and fully characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy. The structure of phosphole **4a** has been defined by X-ray diffraction analysis. The global yields of this procedure are rather modest (23–52%) but



Scheme 2.

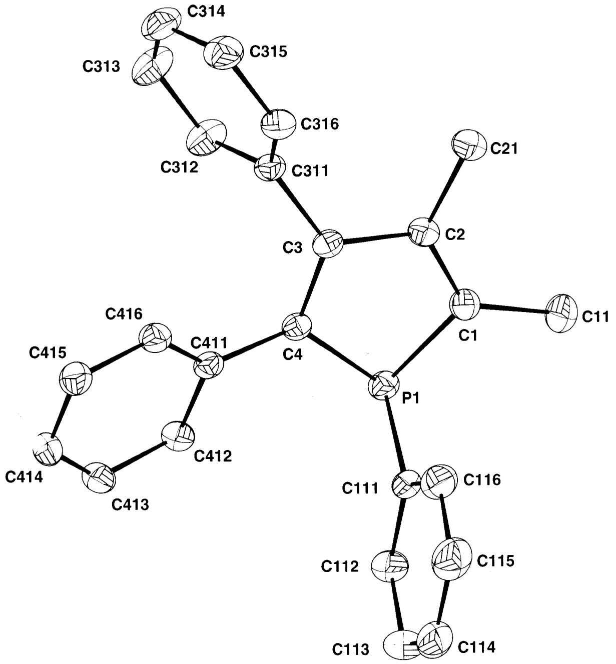


Fig. 1. Molecular structure of **4a**.

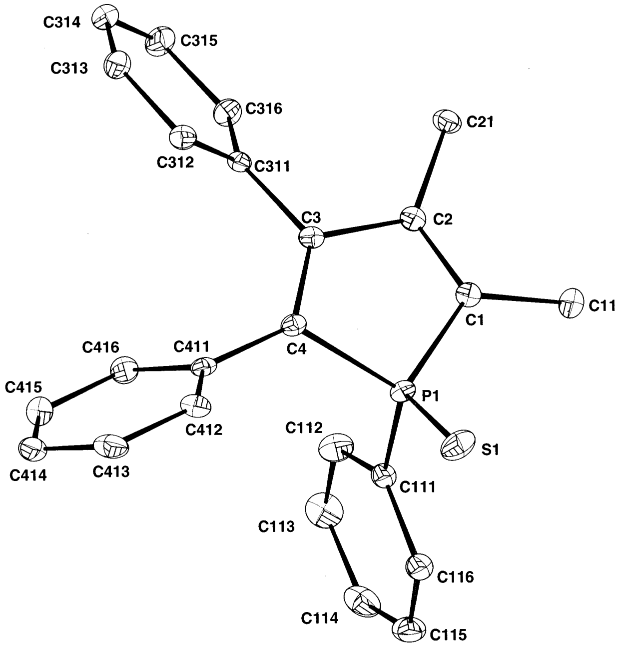


Fig. 2. Molecular structure of **5a**.

comparable to those reported for phospholes synthesized by other procedures [2]. According to Van Wagenen and Livinghouse [5e], unsymmetrical zirconacyclopentadiene (**3b**) was formed in quantitative yield, based on the 97% isolated yield of the unsymmetrical coupling product obtained after protonation. As the transformation of **3b** into phosphole **4b** by reaction with $PhPCl_2$ leads to the product in 50% yield, the limitation of this method seems to be the metallacycle transfer from zirconium to phosphorus. However, no improvement was obtained by using CuCl as noted in the preparation of stannacycles from zirconacycles [6].

2.2. Crystal structure of the phosphole 4a and its sulfide derivative 5a

The structures of the phosphole **4a** and the sulfide derivatives **5a**, **5b** and **5c** were confirmed by X-ray diffraction analyses. The molecular view of **4a** is shown in Fig. 1. As the three structures of the phospole sulfides are closely related, only the molecular structure of **5a** is depicted in Fig. 2.

As usual, the phosphole ring in **4a** is not planar with a half-chair conformation. The distance of the phosphorus atom to the butadiene fragment is 0.297 Å and the dihedral angle from the plane established by C(1)–P(1)–C(4) with respect to the butadiene is 13.71°. These values are within the range reported for other phosphole derivatives [7]. As also observed in related compounds, the phosphole ring and the phenyl attached to the phosphorus are roughly orthogonal with a dihedral angle of 85.8°. In the sulfide derivative **5a**, the phosphole ring is perfectly planar, the largest deviation from the plane being -0.026 Å at C(2). The S atom and the phenyl ring attached to the phosphorus are approximately in the same plane and orthogonal to the phosphole ring (86.8°).

A comparison of selected bond lengths and bond angles in the two phospholes **4a** and **5a** is provided in Table 1. It is seen that there is only a very slight difference in length within the phosphole rings, so the sulfuration does not seem to influence the bond distances although the framework of ring has been modified.

3. Conclusions

We have developed a convenient route to prepare unsymmetrical phospholes via zirconacyclopentadienes. This zirconium-based route allows the synthesis of new unsymmetrical C-substituted phospholes that are difficult to prepare by other available procedures. Further studies are in progress in order to improve and generalize this method of synthesizing unsymmetrical phospholes.

4. Experimental

All reactions were carried under an inert atmosphere of dry argon by using Schlenk glassware and vacuum line techniques. Solvents were freshly distilled from standard drying agents. Flash chromatography was carried out under argon on Merck silica gel (230–400

Table 1
Selected bond lengths (Å) and bond angles (°) for compounds **4a** and **5a**

4a		**5a**	
Bond lengths			
P(1)–C(1)	1.791(2)	S(1)–P(1)	1.9477(7)
P(1)–C(4)	1.806(2)	P(1)–C(1)	1.794(2)
P(1)–C(111)	1.830(2)	P(1)–C(4)	1.8096(17)
C(1)–C(2)	1.353(3)	P(1)–C(111)	1.8174(19)
C(1)–C(11)	1.492(3)	C(1)–C(2)	1.336(3)
C(2)–C(3)	1.468(3)	C(1)–C(11)	1.502(3)
C(2)–C(21)	1.500(3)	C(2)–C(3)	1.503(3)
C(3)–C(4)	1.369(3)	C(2)–C(21)	1.498(3)
C(3)–C(311)	1.495(3)	C(3)–C(4)	1.354(3)
C(4)–C(411)	1.466(3)	C(3)–C(311)	1.481(2)
		C(4)–C(411)	1.472(3)
Bond angles			
C(1)–P(1)–C(4)	91.7(1)	S(1)–P(1)–C(1)	114.57(7)
C(1)–P(1)–C(111)	107.38(11)	S(1)–P(1)–C(4)	119.22(6)
C(4)–P(1)–C(111)	106.8(1)	S(1)–P(1)–C(111)	114.37(7)
P(1)–C(1)–C(2)	109.61(17)	C(1)–P(1)–C(4)	93.41(8)
P(1)–C(1)–C(11)	123.09(18)	C(1)–P(1)–C(111)	107.02(9)
C(2)–C(1)–C(11)	126.8(2)	C(4)–P(1)–C(111)	105.82(8)
C(1)–C(2)–C(3)	114.1(2)	P(1)–C(1)–C(2)	109.66(14)
C(1)–C(2)–C(21)	124.3(2)	P(1)–C(1)–C(11)	121.56(14)
C(3)–C(2)–C(21)	121.63(19)	C(2)–C(1)–C(11)	128.70(19)
C(2)–C(3)–C(4)	114.20(18)	C(1)–C(2)–C(3)	113.80(17)
C(2)–C(3)–C(311)	121.28(19)	C(1)–C(2)–C(21)	124.37(17)
C(4)–C(3)–C(311)	124.3(2)	C(3)–C(2)–C(21)	121.77(16)
P(1)–C(4)–C(3)	108.23(15)	C(2)–C(3)–C(4)	115.28(16)
P(1)–C(4)–C(411)	122.26(15)	C(2)–C(3)–C(311)	120.62(16)
C(3)–C(4)–C(411)	129.46(19)	C(4)–C(3)–C(311)	124.09(16)
		P(1)–C(4)–C(3)	107.66(13)
		P(1)–C(4)–C(411)	122.68(13)
		C(3)–C(4)–C(411)	129.52(16)

mesh).^{1}H-, ^{13}C{^{1}H, ^{31}P}- and ^{31}P{^{1}H}-NMR spectra were recorded on a Bruker WMX 400 instrument operating at 400, 100, 162 MHz, respectively or on a Bruker AM 250 instrument operating at 250, 63, 101 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P). The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analyses were performed by the 'Service d'Analyse du Laboratoire de Chimie de Coordination' at Toulouse, France. Mass spectra were obtained on a Mermag R10-10 instrument. Melting points (uncorrected) were determined with a Stuart Scientific SMP1 apparatus.

4.1. General procedure for the preparation of phosphole 4

To a solution of zirconocene chloride (5.01 g, 17.1 mmol) in THF (60 ml) was added, dropwise, *n*-butyllithium (21 ml, 33.6 mmol, solution 1.6 M in hexane) at − 78°C and the mixture was allowed to stir for 15 min at − 78°C after the addition was complete. DMAP (4.1g, 33.6 mmol) was added rapidly and the mixture was warmed to room temperature (r.t.) and stirred for 90 min. The dark red solution thus obtained was cooled to 0°C, diphenylacetylene (3.0g, 16.8 mmol) was introduced and the solution was stirred for 90 min. A second alkyne (one equivalent) was added and the solution was warmed to r.t. and stirred for 2 h. The orange–red mixture thus obtained was cooled again to − 78°C and phenyldichlorophosphine (2.4 ml, 17.7 mmol) was added. The reaction mixture was then warmed to r.t. and stirred for 16 h during which time the orange–red color had dissipated. The solvent was then evaporated and the crude residue was extracted four to five times with dry pentane. After removal of the solvent, **4** was identified by ^{31}P-NMR spectroscopy and engaged in the subsequent sulfuration step.

Sulfur (two equivalents) were added to a solution of the crude phosphole **4** in dichloromethane (30 ml). The reaction mixture was stirred at r.t. for 4 h and filtered through celite. After removal of the solvent, **5** was purified by flash chromatography on silica gel (dichloromethane–pentane, 40/60 as eluent).

Pure phospholes **4** were obtained by reduction of phosphole sulfides **5**. *Tris*(2-cyanoethyl)phosphine (two equivalents) was added to a solution of the phosphole sulfide **5** in toluene (75 ml) and the resulting mixture was refluxed for 4 h. Once at r.t., the suspension was filtered through Celite. The solvent was evaporated in vacuo and the crude residue was extracted four times with dry pentane. After removal of the pentane, pure phosphole **4** was obtained as yellow powder.

2,3-Dimethyl-4,5-diphenyl-1-phenylphosphole (**4a**): (36%). Yellow crystals were isolated after crystallization from a pentane solution. m.p. = 97–99°C. ^{31}P-NMR ($CDCl_3$): δ 15.66. ^{1}H-NMR ($CDCl_3$): δ 1.85 (s, 3H, Me), 2.08 (d, 3H, $^3J_{HP} = 12$ Hz, Me), 7.03 (m, 5H, Ph), 7.22 (m, 5H, Ph), 7.33 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$): δ 13.33 (d, $^2J_{CP} = 22.3$ Hz, CH_3), 14.93 (s, CH3), 125.77–133.66 (Ph), 136.76 (d, $^2J_{CP} = 16.4$ Hz, *C*–Ph), 138.62 (s, *C*–Ph), 139.32 (s, *C*–Me), 142.67 (d, $^2J_{CP} = 8.9$ Hz, *C*–Me). MS *m*/*z* (rel. int.) 341 (MH^+, 100%). Anal. Calc. for $C_{24}H_{21}P$: C, 84.71; H, 6.18. Found: C, 84.24; H, 6.12.

2,3-Diethyl-4,5-diphenyl-1-phenylphosphole (**4b**): (52%). Yellow solid. ^{31}P-NMR ($CDCl_3$): δ 9.67. ^{1}H-NMR ($CDCl_3$): δ 0.92 (t, 3H, $^3J_{HH} = 7.5$ Hz, Me), 1.24 (t, 3H, $^3J_{HH} = 7.5$ Hz, Me), 2.51 (m, 2H + 1H, CH_2), 2.70 (m, 1H, CH_2), 7.10 (m, 5H, Ph), 7.40 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$): δ 14.56 (s, CH_3), 17.03 (d, $^2J_{CP} = 7.6$ Hz, *C*H_2–CH_3), 21.41 (s, CH_3), 21.69 (d, $^3J_{CP} = 19.5$ Hz, *C*H_2–CH_3),125.70–133.73 (Ph), 136.78 (d, $^2J_{CP} = 17.3$ Hz, *C*–Ph), 138.64 (s, *C*–Ph), 147.16 (s, *C*–Et), 148.74 (d, $^2J_{CP} = 8.1$ Hz, *C*–Et). MS *m*/*z* (rel. int.) 369 (MH^+, 100%).

2,3-Dipropyl-4,5-diphenyl-1-phenylphosphole (**4c**): (23%). Yellow solid. ^{31}P-NMR ($CDCl_3$): δ 10.98. ^{1}H-

NMR ($CDCl_3$): δ 0.72 (t, $^3J_{HH} = 7.3$ Hz, 3H, Me), 0.92 (t, $^3J_{HH} = 7.3$ Hz, 3H, Me), 1.19 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 2.30 (m, 2H + 1H, CH_2), 2.60 (m, 1H, CH_2), 6.96 (m, 5H, Ph), 7.23 (m, 5H, Ph), 7.32 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$): δ 14.23 (s, CH_3), 14.47 (s, CH_3), 22.24 (d, $^2J_{CP} = 22.5$ Hz, *C*H_2–CH_2–CH_3), 23.10 (s, CH_2–*C*H_2–CH_3), 30.36 (s, CH_2–*C*H_2–CH_3), 30.82 (d, $^3J_{CP} = 17.8$ Hz, *C*H_2–CH_2–CH_3), 125.68–133.86 (Ph), 136.78 (d, $^2J_{CP} = 17.3$ Hz, *C*–Ph), 138.65 (s, *C*–Ph), 146.14 (s, *C*–Pr), 147.55 (d, $^2J_{CP} = 8.0$ Hz, *C*–Pr). MS *m*/*z* (rel. int.) 397 (MH^+, 100%).

2,3-Dimethyl-4,5-diphenyl-1-phenylphosphole-sulfide (**5a**): (36%). Orange crystals were obtained by diffusion of pentane into a dichloromethane solution. m.p. = 143–145°C. ^{31}P-NMR ($CDCl_3$): δ 56.3. ^{1}H-NMR ($CDCl_3$): δ 1.87 (s, 3H, Me), 1.96 (d, 3H, $^3J_{HP} = 14$ Hz, Me), 6.90–7.56 (m, 13H, Ph), 7.88 (m, 2H, Ph). ^{13}C-NMR ($CDCl_3$): δ 9.90 (d, $^2J_{CP} = 14$ Hz, CH_3), 15.10 (d, $^3J_{CP} = 14.5$ Hz, CH_3), 127.50–132.40 (Ph), 132.50 (d, $^1J_{CP} = 79$ Hz, *C*–CH_3), 134.80 (d, $^1J_{CP} = 77.6$ Hz, *C*–Ph), 145.40 (d, $^2J_{CP} = 22.8$ Hz, *C*–Me), 151.60 (d, $^2J_{CP} = 22.5$ Hz, *C*–Ph). MS *m*/*z* (rel. int.) 373 (MH^+, 100%). Anal. Calc. for $C_{24}H_{21}PS$: C, 77.39; H, 5.68; S, 8.61. Found: C,76.76; H, 5.61; S, 8.62.

2,3-Diethyl-4,5-diphenyl-1-phenylphosphole-sulfide (**5b**): (52%). Yellow crystals were obtained by diffusion of pentane into a dichloromethane solution. m.p. = 148–150°C. ^{31}P-NMR ($CDCl_3$): δ 54.6. ^{1}H-NMR ($CDCl_3$): δ 0.85 (t, 3H, $^3J_{HH} = 7.6$ Hz, Me) 0.93 (t, 3H, $^3J_{HH} = 7.6$ Hz, Me), 2.43 (m, 2 + 1H, CH_2), 2.61 (m, 1H, CH_2), 7.02 (m, 5H, Ph), 7.25–7.51 (m, 8H, Ph), 7.88 (m, 2H, Ph). ^{13}C-NMR ($CDCl_3$): δ 13.60 (d, $^3J_{CP} = 2.1$ Hz, CH_3), 14.50 (s, CH_3), 19.06 (d, $^3J_{CP} = 13.0$ Hz, *C*H_2), 21.16 (d, $^2J_{CP} = 14.0$ Hz, *C*H_2), 127.40–135.60 (Ph), 135.90 (d, $^1J_{CP} = 76.6$ Hz, *C*–Et), 137.70 (d, $^1J_{CP} = 76.8$ Hz, *C*–Ph), 150.90 (d, $^2J_{CP} = 26.5$ Hz, *C*–Et), 151.30 (d, $^2J_{CP} = 21.0$ Hz, *C*–Ph). MS *m*/*z* (rel. int.) 401 (MH^+, 100%). Anal. Calc. for $C_{26}H_{25}PS$: C, 77.97; H, 6.50; S, 8.00. Found: C,77.51; H, 6.45; S, 8.12.

2,3-Dipropyl-4,5-diphenyl-1-phenylphosphole-sulfide (**5c**): (23%). Yellow crystals were obtained by diffusion of pentane into a dichloromethane solution. m.p. = 130–132°C. ^{31}P-NMR ($CDCl_3$): δ 55.0. ^{1}H-NMR ($CDCl_3$): δ 0.74 (t, 3H, $^3J_{HH} = 7.4$ Hz, Me), 0.80 (t, 3H, $^3J_{HH} = 7.4$ Hz, Me), 1.22 (m, 4H, $2CH_2$), 2.33 (m, 2 + 1H, CH_2), 2.57 (m, 1H, CH_2), 7.00 (m, 5H, Ph), 7.21–7.44 (m, 8H, Ph), 7.91 (m, 2H, Ph).^{13}C-NMR ($CDCl_3$): δ 14.10 (s, CH_3), 14.40 (s, CH_3), 22.20 (s, CH_2–*C*H_2–CH_3), 22.90 (s, CH_2–*C*H_2–CH_3), 28.30 (d, $^3J_{CP} = 12.3$ Hz, *C*H_2–CH_2–CH_3), 30.00 (d, $^2J_{CP} = 13.7$ Hz, *C*H_2–CH_2–CH_3), 127.40–132.30 (Ph), 135.65 (d, $^1J_{CP} = 76.9$ Hz, *C*–Pr), 137.10 (d, $^1J_{CP} = 76.6$ Hz, *C*–Ph), 150.20 (d, $^2J_{CP} = 20.2$ Hz, *C*–Pr), 151.10 (d, $^2J_{CP} = 26.2$ Hz, *C*–Ph). MS *m*/*z* (rel. int.) 429 (MH^+, 100%). Anal. Calc. for $C_{28}H_{29}PS$: C, 78.47; H,6.82; S,7.48. Found: C,78.24; H, 6.74; S, 7.13.

4.2. X-ray data collection and structure determination

Data for **5a**, **5c** and **4a** were collected on a Stoe IPDS diffractometer equipped with a graphite oriented monochromator using Mo–K_α radiation ($\lambda = 0.71073$). The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections. Data for **5b** were collected on an Enraf–Nonius CAD4 diffractometer and the final unit cell was derived from the refinement of 25 well centered reflections. In all cases, only statistical fluctuations were observed in the intensity monitors over the course of the data collections.

The four structures were solved by direct methods (SIR92) [8] and refined by least-squares procedures on F_o. All H atoms attached to carbon were introduced in the calculation in idealized positions (d(CH) = 0.96 Å) and their atomic coordinates were re-calculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they were attached. Least-squares refinements were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)2$, where F_o and F_c are the observed and calculated structure factors, respectively. The weighting scheme used in the last refinement cycles was $w = w'[1 - \{\Delta F/6\sigma(F_o)\}^2]^2$ where $w' = 1/\Sigma_1^n A_r T_r(x)$ with three coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$ where x was $F_c/F_c(\max)$ [9]. Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w\text{-}(F_o)^2]^{1/2}$, having the values listed in Table 2.

The calculations were carried out with the CRYSTALS package programs [10] running on a Pentium II. The molecular views were realized with the help of CAMERON [11]. Fractional atomic coordinates, anisotropic thermal parameters for non hydrogen atoms and atomic coordinates for H atoms have been deposited at the Cambridge Crystallographic Data Center.

5. Supplementary material

Tables of anisotropic temperature factors, hydrogen coordinates and observed and calculated structure factors are available from the Cambridge Crystallographic Data Center. Ordering information is given on any current masthead page.

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Table 2
Crystal data

Crystal parameters	**5a**	**4a**	**5c**	**5b**
Formula	$C_{24}H_{21}PS$	$C_{24}H_{21}P$	$C_{28}H_{29}PS$	$C_{26}H_{25}PS$
Formula weight (g)	372.47	340.41	428.57	400.52
Shape (color)	Box (colorless)	Box (yellow)	Needle (colorless)	Plate (yellow)
Size (mm)	0.25 × 0.25 × 0.125	0.65 × 0.24 × 0.22	0.72 × 0.168 × 0.152	0.63 × 0.50 × 0.05
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	10.104(2)	16.926(2)	10.001(1)	10.261(2)
b (Å)	12.129(1)	6.1384(6)	13.028(1)	12.262(2)
c (Å)	16.317(2)	17.924(2)	18.602(3)	18.340(9)
β (°)	100.19(2)	92.43(2)	102.13(2)	102.51(3)
V (Å^3)	1968.1(5)	1860.7(6)	2369.6(5)	2253(1)
Z	4	4	4	4
$F(000)$	785	720	913	849
$\rho_{calc.}$ (g cm^{-3})	1.257	1.215	1.201	1.181
μ (Mo–K$_\alpha$) (cm^{-1})	2.411	1.449	2.083	2.149
Data collection				
Diffractometer	Stoe IPDS	Stoe IPDS	Stoe IPDS	CAD4 Enraf–Nonius
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$)	Mo–K$_\alpha$ ($\lambda = 0.71073$)	Mo–K$_\alpha$ ($\lambda = 0.71073$)	Mo–K$_\alpha$ ($\lambda = 0.71073$)
Temperature (K)	160(2)	293(2)	180(2)	293(2)
Detector distance (mm)	80	70	70	
Scan mode	φ (oscillation)	φ(rotation)	φ (oscillation)	$\omega/2\theta$
φ range (°)	$0.0 < \varphi < 250.0$	$0.0 < \varphi < 199.5$	$0.0 < \varphi < 200.0$	
Scan range θ (°)				$0.9 + 0.345\mathrm{tg}\theta$
φ increase (°)	1.5	1.5	1.5	
Absorption method				Ψ scan
Exposure time (min)	5	3	6	
2θ range (°)	$2.9 < 2\theta < 48.4$	$4.8 < 2\theta < 52.3$	$4.2 < 2\theta < 52.0$	$3 < 2\theta < 50$
min. and max. correction				1.00, 1.107
No. of reflections collected	15652	14744	18467	4406
No. of unique reflections	2947	3653	4542	3951
Merging factor R_{int}	0.0345	0.0712	0.0582	0.016
Reflections used ($I > 2\sigma(I)$)	2280	2214	2914	2408
Refinement				
R	0.0323	0.0456	0.0317	0.0370
R_w	0.0390	0.0522	0.0364	0.0429
Weighting scheme	Chebyshev	Chebyshev	Chebyshev	Chebyshev
Coefficient ar.	1.49; 0.140; 1.08	2.45, 0.635, 2.09	1.37; −0.033; 1.03	1.17, 0.704, 0.814
$(\Delta/\sigma)_{max}$	0.02	0.048	0.04	0.078
$\Delta\rho_{min}/\Delta\rho_{max}$	$-0.272/0.312$	$-0.322/0.306$	$-0.236/0.240$	$-0.181/0.269$
Goodness-of-fit	1.034	1.092	1.089	1.092
Variable parameters	236	227	272	254

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