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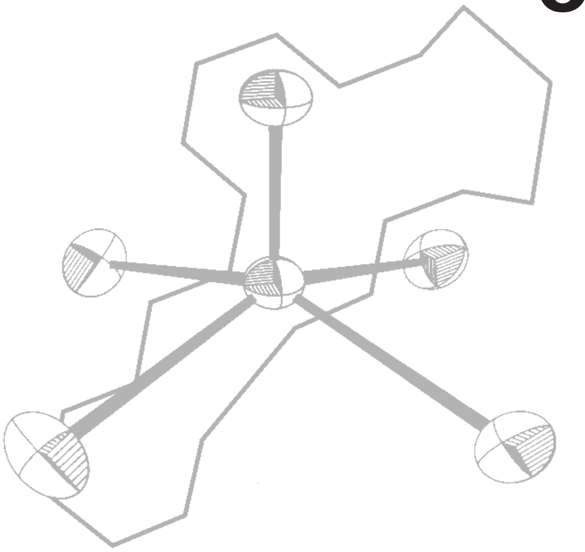

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Synthesis and Structure of Two Isomers of Di(indenyl)phenylphosphine Sulfide

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Dichlorophenylphosphine reacts with indenyllithium in tetrahydrofuran followed by sulfur to yield di(1*H*-inden-3-yl)phenylphosphine sulfide (2). The same reaction sequence in toluene yields di(1*H*-inden-1-yl)phenylphosphine sulfide (3) as a mixture of (±) and two *meso* isomers. The structures of (2) and (±)-(3) were determined [(2): $C_{24}H_{19}PS$, M_r 370·42, monoclinic, $P\,2_1/n$, a 14·329(4), b 7·0936(10), c 19·405(5) Å, β 99·18(2)°, Z 4, R 0·060 for 2422 observed reflections; (3): $C_{24}H_{19}PS$, M_r 370·42, monoclinic, $P\,2_1/n$, a 9·521(5), b 16·223(8), c 12·930(6) Å, β 107·41(3)°, Z 4, R 0·105 for 923 reflections].

Introduction

The interest in metallocene catalysis with Group 4 *ansa*-metallocenes as stereospecific olefin polymerization catalysts[1,2] and as catalysts for enantioselective organic transformations[3] has resulted in reports of a number of bridged dicyclopentadienyl compounds. These ligands consist of two cyclopentadiene fragments which are connected by a bridge. The bridge can be a carbon-atom chain of two or more carbon atoms[4–8] or the bridge linking the two cyclopentadiene fragments can be a single atom. Examples of single-atom bridges reported thus far contain boron,[9] carbon,[10] silicon,[11] germanium[12] and phosphorus.[13] Ligands containing two indenyl or two tetrahydroindenyl fragments are important for the formation of chiral C_2 symmetric metallocene complexes. There has been a report of an *ansa*-bisindenyl ligand with a phosphorus atom as the single-atom bridge although it was not isolated and characterized.[14] Di(cyclopentadienyl)phenyl phosphine has been reported, as well as the synthesis of a zirconium and a titanium complex with this ligand.[15,16] We are interested in developing novel indenyl-containing ligands as part of our work on novel Group 4 metal catalysis chemistry.[17–19] In this paper we report the synthesis of di(indenyl)phenylphosphine, a potential Group 4 *ansa*-ligand with a phosphorus single-atom bridge, from the reaction of indenyllithium with dichlorophenylphosphine. A number of different isomers were isolated and characterized by n.m.r. spectroscopy and X-ray crystallography.

Experimental

General Procedures

All reactions were carried out under an atmosphere of dry argon or nitrogen. N.m.r. spectra were recorded on an AC300 Bruker spectrometer. Solvents were purified by conventional methods. Indene and dichlorophenylphosphine (Aldrich) were used as received. (1*H*-Inden-1-yl)lithium was prepared by reaction of butyllithium and indene in hexanes.

*Di(1*H*-inden-3-yl)phenylphosphine (1)*

A solution of $C_6H_5PCl_2$ (1·40 g, 7·8 mmol) dissolved in tetrahydrofuran (10 ml) was added dropwise to a stirred solution of LiC_9H_7 (2·0 g, 16·4 mmol) in tetrahydrofuran (40 ml) cooled at −78°C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure. Toluene (20 ml) and hexane (20 ml) were added and the reaction mixture was filtered over a Celite plug. The toluene/hexane was removed under reduced pressure to yield (1) as an air-sensitive pale yellow oil (2·44 g, 7·2 mmol, 92%). Attempts to obtain an analytically pure sample of (1) were not successful. ^{1}H n.m.r. δ (C_6D_6) 2·96, CH_2; 6·16, dt, J 3·3, 2·0 Hz, P–C=CH; 6·98, m, 7H; 7·17, d, J 7·5 Hz, 2H; 7·52, m, 4H. ^{13}C n.m.r. δ (C_6D_6) 39·9, d, J 5·7 Hz; 121·8, d, J 5·3 Hz; 123·9; 125·3; 125·6; 128·7; 128·8; 129·2; 134·4, d, J 129·6 Hz; 140·7, d, J 11·2 Hz; 141·6; 144·3; 146·3, d, J 21·6 Hz. ^{31}P n.m.r. δ (C_6D_6) −41·3.

*Di(1*H*-inden-3-yl)phenylphosphine Sulfide (2)*

A solution of $C_6H_5PCl_2$ (1·79 g, 10 mmol) dissolved in tetrahydrofuran (20 ml) was added dropwise to a stirred solution of LiC_9H_7 (2·44 g, 20 mmol) in tetrahydrofuran (30 ml) cooled at −78°C. The reaction mixture was allowed to warm to room temperature, stirred overnight and then quenched with a few drops of glacial acetic acid. Freshly sublimed sulfur (0·32 g, 10 mmol) was added and the reaction mixture stirred overnight. The solvent was removed under reduced pressure and the crude product was extracted once with toluene (40 ml). The product was purified by chromatography (silica gel-60; ethyl acetate/hexanes, 1 : 2) to yield the pure sulfide (2) (2·75 g, 7·4 mmol, 74%) (Found: C, 77·5; H, 5·3; S, 8·7. $C_{24}H_{19}PS$ requires C, 77·8; H, 5·2; S, 8·7%). ^{1}H n.m.r. δ ($CDCl_3$) [n.m.r. assignments are in accord with the numbering shown in Diagram (A)] 3·56, br, H 3; 6·87, dt, J_{P-H} 10·9, J_{H-H} 1·9 Hz, 2H, H 2; 7·22, m, 4H, H 6/H 7; 7·47, m, 3H, H 12/H 13; 7·49, m, 2H, H 5; 7·71, m, 2H, H 8; 7·95, dd, J 14·4, 7·9 Hz, 2H, H 11. ^{13}C n.m.r. δ ($CDCl_3$) 39·8, d, J 13·9 Hz, C 3; 123·2,

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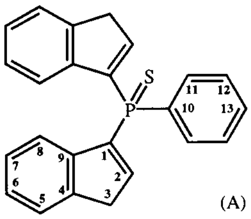
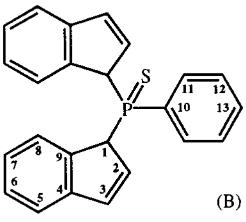
C 8; 123·9, C 5; 125·7, C 6; 126·5, C 7; 128·6, d, J 13·3 Hz, C 12; 131·0, d, J 88·2 Hz, C 10; 131·9, d, J 11·4 Hz, C 11; 131·9, d, J 3·3 Hz, C 13; 137·3, d, J 88·4 Hz, C 1; 142·1, d, J 13·4 Hz, C 9; 144·2, d, J 10·2 Hz, C 4; 146·7, d, J 9·7 Hz, C 2. ^{31}P n.m.r. δ (CDCl$_3$) 20·6.



(A)



(B)

*Di(1*H*-inden-1-yl)phenylphosphine Sulfide (3)*

A solution of C$_6$H$_5$PCl$_2$ (1·79 g, 10 mmol) dissolved in toluene (20 ml) was added dropwise to a stirred suspension of LiC$_9$H$_7$ (2·44 g, 20 mmol) in toluene (30 ml) cooled at −78°C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with a few drops of glacial acetic acid. Freshly sublimed sulfur (0·32 g, 10 mmol) was added, the reaction mixture stirred overnight, filtered and the solvent removed under reduced pressure. The product was purified by chromatography (silica gel-60; ethyl acetate/hexanes, 1 : 2) to yield (3) (3·37 g, 9·1 mmol, 91%) as a *mixture* of (±) and two *meso* isomers (Found: C, 77·1; H, 5·2; S, 8·5. C$_{24}$H$_{19}$PS requires C, 77·8; H, 5·2; S, 8·7%). Pure (±)-(3) can be obtained by recrystallization from hot ethanol.

(±)-(3): ^{1}H n.m.r. δ (CDCl$_3$) [n.m.r. assignments are in accord with the numbering shown in Diagram (B)] 4·81, d, $J_{\text{P-H}}$ 19·7 Hz, P–CH; 4·76, d, $J_{\text{P-H}}$ 21·8 Hz, P–CH; 6·40, m, 1H, P–CH–CH=C**H**; 6·75, m, 1H, P–CH–CH=C**H**; 7·01, m, 2H, P–CH–C**H**=CH; 7·25, m, 10H; 7·56, dd, J 12·4, 7·2 Hz, 2H, H 11; 8·02, d, J 6·2 Hz, H 8. ^{13}C n.m.r. δ (CDCl$_3$) 54·5, d, J 41·7 Hz, C 1; 55·0, d, 42·2 Hz, C 1′; 121·6, C 8; 122·0, C 8′; 124·1, C 5; 124·6, C 5′; 125·5, C 6, C 6′; 127·4, C 7; 127·6, d, J 5·5 Hz, C 12; 127·9, C 7′; 129·5, d, J 5·9 Hz, C 3; 130·6, d, J 5·9 Hz, C 3′; 131·4, d, J 8·8 Hz, C 11; 131·7, d, J 2 Hz, C 13; 135·5, d, J 9·4 Hz, C 2; 135·8, d, J 8·8 Hz, C 2′; 139·5, C 9; 144·6, C 4. ^{31}P n.m.r. δ (CDCl$_3$) 51·0.

meso-(3) (two isomers): ^{1}H n.m.r. δ (CDCl$_3$) 4·76, d, $J_{\text{P-H}}$ 20·8 Hz, P–CH. ^{13}C n.m.r. δ (CDCl$_3$) 54·8, d, J 42·6 Hz. ^{31}P n.m.r. δ (CDCl$_3$) 51·2, 52·2.

X-Ray Structure Determination of (2) and (3) (C$_{24}$H$_{19}$PS)

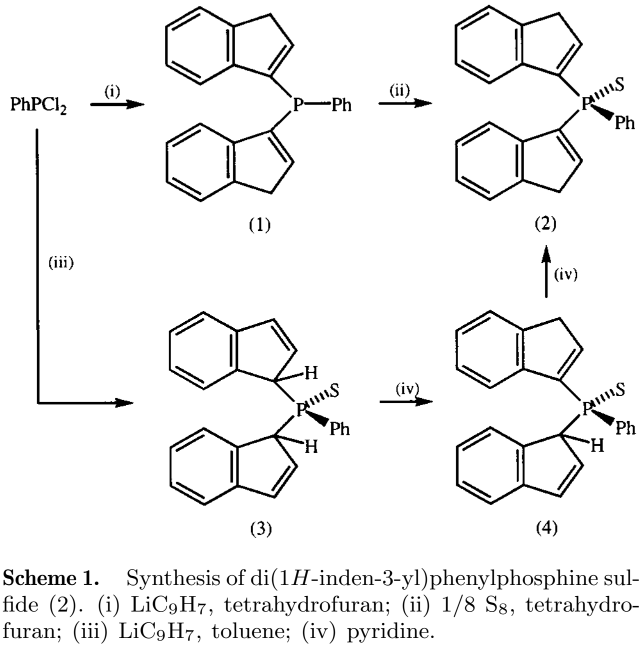
Suitable crystals of (2) and (3) were obtained by recrystallization from hot ethanol. Most crystallographic details are provided in Table 1. Both (2) and (3) have formula weight 370·4 and crystallized with four molecules/cell in the monoclinic space group $P2_1/n$. The crystals were mounted on a glass fibre under a nitrogen cold stream. All data were collected with ω scans at 168 K by using graphite-monochromatized Mo Kα radiation (λ 0·71073 Å) on a Siemens P 3 diffractometer.[20] The structures were solved by direct methods with SHELXS-90.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms in (2) were located from difference Fourier maps and fully refined. For (3) the hydrogens were included in idealized positions with fixed thermal parameters. Final refinement was done by full-matrix least-squares refinement with SHELXL-96.[22]

Results and Discussion

The reaction of dichlorophenylphosphine with 2 equiv. of indenyllithium in tetrahydrofuran proceeds smoothly and produces a high yield of di(1*H*-inden-3-yl)-phenylphosphine (1) as is depicted in Scheme 1. It was not possible to isolate compound (1) because it appears to be extremely air-sensitive and thermally unstable. An analogous compound, di(cyclopentadienyl)phenyl phosphine, was also reported to be very unstable.[13,15] Because of this instability compound (1) was further purified by reacting it with sulfur to form the corresponding phosphine sulfides which are air-stable compounds (see below). Compound (1) displays one signal in its ^{31}P n.m.r. spectrum at −41·3 ppm indicat-

Table 1. Crystallographic data and data collection parameters for (2) and (3)

	(2)	(3)
a (Å)	14·329(4)	9·521(5)
b (Å)	7·0936(10)	16·223(8)
c (Å)	19·405(5)	12·930(6)
β (deg)	99·18(2)	107·41(3)
Volume (Å^3)	1947·1(8)	1905·7(16)
No. of reflections used for cell determination	42	24
θ range (deg)	4·7–12·5	2·2–8·6
D_{calc} (g/cm^3)	1·264	1·291
Crystal size (mm^3)	0·65×0·3×0·3	0·35×0·1×0·1
Crystal colour	pale yellow	orange
Absorption coefficient (mm^{-1})	0·253	0·258
θ collection range (deg)	2·13–29·99	2·07–23·50
h range	0–16	0–10
k range	0–9	0–18
l range	−27–26	−14–13
Reflections collected	4549	3005
Independent reflections	4284	2817
R_{int}	0·048	0·184
Absorption (empirical) max., min. transmission	0·98, 0·84	none
Number of parameters	311	230
Goodness of fit on F^2	1·003	0·984
No. observed data $I > 2\sigma(I)$	2422	923
R_1 (observed)	0·060	0·105
wR_2	0·133	0·122
$\Delta\rho$ (max.) (e Å^{-3})	0·427	0·338
$\Delta\rho$ (min.) (e Å^{-3})	−0·227	−0·353



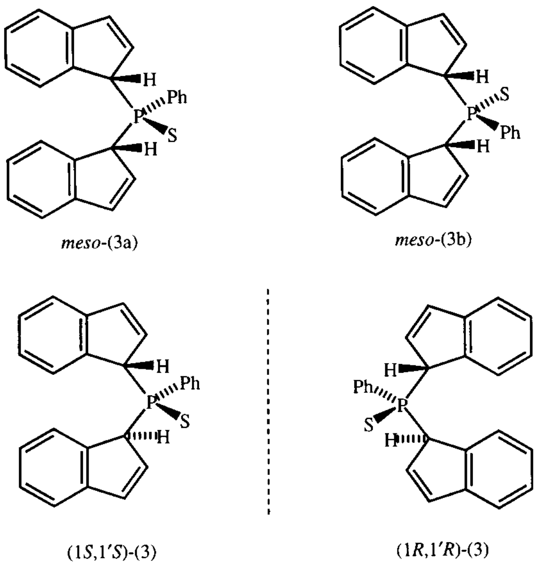
Scheme 1. Synthesis of di(1*H*-inden-3-yl)phenylphosphine sulfide (2). (i) LiC$_9$H$_7$, tetrahydrofuran; (ii) 1/8 S$_8$, tetrahydrofuran; (iii) LiC$_9$H$_7$, toluene; (iv) pyridine.

ing that only one isomer is present. This is consistent with the proposed structure and is further supported by the ^{1}H and ^{13}C n.m.r. spectra of (1). The signals for the protons of the five-membered ring of the indenyl moiety appear at 2·96 (CH_2) and 6·16 ppm (C=CH). The latter signal is a doublet of triplets with small coupling constants of 3·3 and 2·0 Hz ($^3J_{\mathrm{P-H}}$ and $^3J_{\mathrm{H-H}}$ respectively).

Compound (1) reacts with 1 equiv. of sulfur to yield di(1*H*-inden-3-yl)phenylphosphine sulfide (2). This compound was purified by column chromatography on silica gel. Compound (2) has a ^{31}P n.m.r. chemical shift of 20·6 ppm, and the ^{1}H and ^{13}C n.m.r. spectra are consistent with the proposed structure. The proton signals of the five-membered ring appear at 3·56 (CH_2) and 6·87 ppm (C=CH), the latter again as a doublet of triplets with a larger $^3J_{\mathrm{P-H}}$ coupling constant of 10·9 Hz when compared to (1).

When the same reaction sequence was carried out in toluene instead of tetrahydrofuran, a mixture of isomers of di(1*H*-inden-1-yl)phenylphosphine sulfide (3) was isolated instead of compound (2). Because the intermediate phosphine (1), observed as the product of the reaction in tetrahydrofuran, was found to be unstable, no attempt was made to isolate or identify the mixture of intermediate phosphines when the reaction was carried out in toluene. Instead, the crude product was converted into the phosphine sulfide (3) in a one-pot synthesis. The phosphorus atom in compound (3) is a pseudo asymmetric centre. It is not asymmetric when the carbon atoms directly connected to phosphorus are both of *R* (or *S*) configuration, but it is asymmetric when one of them is *R* and the other is *S*, resulting in two *meso* isomers and one racemic (±) pair (see Fig. 1).

The ^{31}P n.m.r. spectrum of the crude reaction product shows three signals at 51·0, 51·2 and 52·2 ppm consistent with the formation of three isomers. The racemic (±) isomer crystallized preferentially when the crude reaction product was recrystallized from hot ethanol and this allowed us to assign the (±) and both *meso* signals in the ^{31}P n.m.r. spectrum. (±)-(3) has a ^{31}P n.m.r. chemical shift of 51·0 ppm and the signals at 51·2 and 52·2 ppm were assigned to the two *meso*-(3) isomers. In (±)-(3) the two indenyl moieties are not identical and this results in an almost doubling up of all ^{1}H and ^{13}C n.m.r. signals, most of which could be assigned by a combination of ^{1}H–^{1}H and ^{1}H–^{13}C COSY experiments. The ^{1}H and ^{13}C n.m.r. signals of the *meso*-(3) compounds were more difficult to assign, mainly because it was not possible to isolate pure samples of *meso*-(3). However, it appears that both isomers have identical ^{1}H and ^{13}C n.m.r. signals for the more readily identified proton and carbon atoms in the five-membered ring of the indenyl moiety (see Experimental).



meso-(3a) *meso*-(3b)

(1*S*,1′*S*)-(3) (1*R*,1′*R*)-(3)

Fig. 1. Stereoisomers of di(1*H*-inden-1-yl)phenylphosphine sulfide (3).

The existence of *meso* and (±) isomers was described recently for a di(1*H*-inden-1-yl)dimethylsilane.[23] These silanes undergo interconversion of the *meso* and (±) isomers and this could be readily monitored by variable-temperature n.m.r. experiments. When a pure sample of (±)-(3), dissolved in $CDCl_3$, was heated at 60°C for several hours the formation of only a very small amount of the *meso*-(3) isomers was observed. The *meso*/(±) interconversion of (3) therefore takes place at a much lower rate than the analogous di(indenyl)silane. Interestingly, we did observe the appearance of two new signals at 35·3 and 35·0 ppm, chemical shifts which are halfway between (2) and (3). We assign these signals to the two isomers of (1*H*-inden-1-yl)(1*H*-inden-3-yl)phenylphosphine sulfide (4). These are the intermediate products for the complete isomerization of (3) into (2). Indenyl double-bond rearrangements of this type are reported to occur only at elevated temperature[23] or by base catalysis.[24,25] The addition of pyridine to an n.m.r. sample of (3) very readily isomerizes this to (2), while the intermediate signals assigned to (4) could also be observed. We thus established that compound (3) readily isomerizes to the more stable isomer (2) in the presence of a base. The observed solvent effect in the synthesis of (2) and (3) may have its origins in the fact that the use of tetrahydrofuran is likely to lead to solvent-separated ion pairs of indenyllithium whereas toluene will lead to contact ion pairs. This fact may contribute to a rapid isomerization of (1*H*-inden-1-yl)phosphine to (1*H*-inden-3-yl)phosphine in tetrahydrofuran, catalysed by indenyllithium, whereas this isomerization does not take place, or only very slowly, in toluene.

Structures of (2) and (±)-(3)

Both compounds (2) and (±)-(3) crystallize from hot ethanol. Each crystal contains independent molecules packed with only van der Waals contacts between them: the closest intermolecular contacts involve indenyl protons at 2·51 and 2·13 Å for (2) and (3) respectively.

Table 2. Selected bond distances (Å) for (2) and (3)

Atoms	(2)		(3)	
	C(1)–C(9)	C(11)–C(19)	C(1)–C(9)	C(11)–C(19)
P(1)–S(1)	1·954(1)		1·934(4)	
P(1)–C(20)	1·821(4)		1·804(10)	
P(1)–C(1)	1·786(3)	1·787(3)	1·820(10)	1·831(10)
C(1)–C(2)	1·344(5)	1·332(5)	1·534(13)	1·514(13)
C(1)–C(9)	1·473(4)	1·476(4)	1·463(14)	1·483(12)
C(2)–C(3)	1·500(5)	1·495(5)	1·307(13)	1·305(12)
C(3)–C(4)	1·501(5)	1·502(5)	1·472(14)	1·465(13)
C(4)–C(5)	1·377(5)	1·383(5)	1·381(14)	1·372(12)
C(4)–C(9)	1·403(4)	1·394(4)	1·409(13)	1·414(12)
C(5)–C(6)	1·374(6)	1·376(5)	1·371(14)	1·383(13)
C(6)–C(7)	1·377(6)	1·382(5)	1·365(13)	1·414(13)
C(7)–C(8)	1·386(5)	1·391(5)	1·381(13)	1·383(12)
C(8)–C(9)	1·373(5)	1·387(5)	1·397(13)	1·359(12)

Table 3. Selected bond angles (deg) for (2) and (3)

Atoms	(2)		(3)	
	C(1)–C(9)	C(11)–C(19)	C(1)–C(9)	C(11)–C(19)
S(1)–P(1)–C(20)	114·5(1)		114·7(4)	
C(11)–P(1)–C(20)	105·6(2)		108·4(5)	
C(1)–P(1)–C(20)	103·1(2)		102·5(5)	
C(11)–P(1)–S(1)	113·4(1)		111·6(4)	
C(1)–P(1)–S(1)	113·3(1)		114·9(4)	
C(1)–P(1)–C(11)	106·1(2)		103·7(5)	
C(9)–C(1)–C(2)	109·1(3)	108·8(3)	101·6(9)	102·0(9)
C(9)–C(1)–P(1)	124·2(2)	125·6(2)	114·6(8)	114·4(8)
C(2)–C(1)–P(1)	126·8(3)	125·6(3)	110·7(8)	117·5(8)
C(2)–C(3)–C(4)	103·0(3)	102·5(3)	111(1)	110(1)
C(1)–C(2)–C(3)	110·9(3)	111·6(3)	111(1)	112(1)
C(3)–C(4)–C(5)	131·5(3)	130·9(5)	131(1)	132(1)
C(3)–C(4)–C(9)	108·8(3)	109·0(3)	106(1)	107(1)
C(4)–C(5)–C(6)	119·4(4)	119·2(4)	117(1)	120(1)
C(5)–C(6)–C(7)	120·5(4)	121·0(4)	122(1)	119(1)
C(6)–C(7)–C(8)	121·4(4)	120·6(4)	121(1)	120(1)
C(8)–C(9)–C(1)	130·7(3)	131·1(3)	132(1)	132(1)
C(8)–C(9)–C(4)	121·2(3)	120·9(3)	197(1)	119(1)
C(7)–C(8)–C(9)	117·9(4)	118·3(4)	120(1)	121(1)
C(4)–C(9)–C(1)	108·1(3)	108·0(3)	111(1)	110(9)

Table 4. Selected dihedral angles for (2) and (3)

Atoms	(2)	(3)
C(11)–P(1)–C(1)–C(2)	0·0(4)	−57(1)
C(20)–P(1)–C(1)–C(2)	−110·7(3)	−170(1)
S(1)–P(1)–C(1)–C(2)	125·0(3)	65(1)
C(11)–P(1)–C(1)–C(9)	179·3(3)	−171(1)
C(20)–P(1)–C(1)–C(9)	68·6(3)	76(1)
S(1)–P(1)–C(1)–C(9)	−55·7(3)	−49(1)
P(1)–C(1)–C(2)–C(3)	178·6(3)	−119(1)
P(1)–C(1)–C(9)–C(8)	1·8(5)	−64(2)
P(1)–C(1)–C(9)–C(4)	−178·5(2)	117(1)
C(1)–P(1)–C(11)–C(12)	−109·6(3)	−43(1)
C(20)–P(1)–C(11)–C(12)	−0·6(3)	65(1)
S(1)–P(1)–C(11)–C(12)	125·5(3)	−168(1)
C(1)–P(1)–C(11)–C(19)	73·7(3)	−163(1)
C(20)–P(1)–C(11)–C(19)	−177·4(3)	−54(1)
S(1)–P(1)–C(11)–C(19)	−51·3(3)	73(1)
P(1)–C(11)–C(12)–C(13)	−177·4(3)	−125(1)
P(1)–C(11)–C(19)–C(18)	−1·74(5)	−55(2)
P(1)–C(11)–C(19)–C(14)	177·2(2)	127(1)
C(1)–P(1)–C(20)–C(25)	−150·5(3)	−115(1)
C(11)–P(1)–C(20)–C(25)	98·4(3)	136(1)
S(1)–P(1)-C(20)–C(25)	−27·0(3)	10(1)
C(1)–P(1)–C(20)–C(21)	30·4(3)	59(1)
C(11)–P(1)–C(20)–C(21)	−80·6(3)	−50(1)
S(1)–P(1)–C(20)–C(21)	154·0(3)	−175(1)

Table 5. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for (2)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	10^4x	10^4y	10^4z	10^3U_{eq}
S(1)	651(1)	12190(1)	8912(1)	43(1)
P(1)	656(1)	9497(1)	8702(1)	29(1)
C(1)	1189(2)	8952(4)	7955(2)	28(1)
C(2)	1906(3)	7745(5)	7927(2)	38(1)
C(3)	2140(3)	7635(6)	7202(2)	49(1)
C(4)	1450(2)	8985(5)	6801(2)	35(1)
C(5)	1321(3)	9548(5)	6113(2)	45(1)
C(6)	634(3)	10855(6)	5881(2)	54(1)
C(7)	81(3)	11603(7)	6332(2)	54(1)
C(8)	205(3)	11083(6)	7029(2)	43(1)
C(9)	890(2)	9773(4)	7257(2)	31(1)
C(11)	1268(2)	8115(4)	9402(2)	29(1)
C(12)	912(3)	6641(5)	9698(2)	35(1)
C(13)	1601(3)	5864(6)	10289(2)	40(1)
C(14)	2438(2)	7144(5)	10301(2)	33(1)
C(15)	3298(3)	7191(6)	10742(2)	42(1)
C(16)	3947(3)	8559(6)	10646(2)	46(1)
C(17)	3751(3)	9874(6)	10117(2)	42(1)
C(18)	2889(3)	9849(5)	9670(2)	37(1)
C(19)	2235(2)	8476(4)	9770(2)	29(1)
C(20)	−514(2)	8443(5)	8491(2)	32(1)
C(21)	−651(3)	6837(6)	8073(2)	49(1)
C(22)	−1543(3)	6078(7)	7904(2)	63(1)
C(23)	−2294(3)	6878(7)	8161(2)	57(1)
C(24)	−2145(3)	8419(7)	8587(3)	55(1)
C(25)	−1261(3)	9225(6)	8755(2)	45(1)

Table 6. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for (3)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	10^4x	10^4y	10^4z	10^3U_{eq}
S(1)	2730(3)	2914(2)	3547(3)	49(1)
P(1)	1971(3)	4023(2)	3510(2)	33(1)
C(1)	1002(12)	4233(6)	4500(8)	40(3)
C(2)	2056(11)	4175(7)	5657(8)	45(3)
C(3)	1630(12)	3601(6)	6205(9)	49(4)
C(4)	251(13)	3219(7)	5543(10)	43(3)
C(5)	−635(13)	2625(7)	5793(10)	51(4)
C(6)	−1902(13)	2417(7)	5003(10)	56(4)
C(7)	−2291(12)	2782(7)	4007(9)	43(3)
C(8)	−1424(12)	3388(7)	3758(8)	43(3)
C(9)	−114(12)	3622(6)	4531(9)	33(3)
C(11)	3452(10)	4789(6)	3821(8)	33(3)
C(12)	3066(11)	5661(6)	4050(8)	35(3)
C(13)	3442(11)	6192(6)	3422(8)	38(3)
C(14)	4125(11)	5766(6)	2697(8)	26(3)
C(15)	4717(11)	6052(6)	1919(8)	38(3)
C(16)	5379(10)	5506(7)	1387(9)	39(3)
C(17)	5404(10)	4659(7)	1642(9)	40(3)
C(18)	4772(10)	4382(6)	2412(8)	33(3)
C(19)	4135(11)	4916(6)	2943(8)	25(3)
C(20)	628(11)	4306(6)	2250(8)	30(3)
C(21)	54(11)	5104(7)	2071(8)	42(3)
C(22)	−1021(12)	5298(7)	1104(9)	55(4)
C(23)	−1522(12)	4720(7)	371(10)	54(4)
C(24)	−1056(11)	3920(7)	513(8)	54(4)
C(25)	47(11)	3714(7)	1474(8)	51(4)

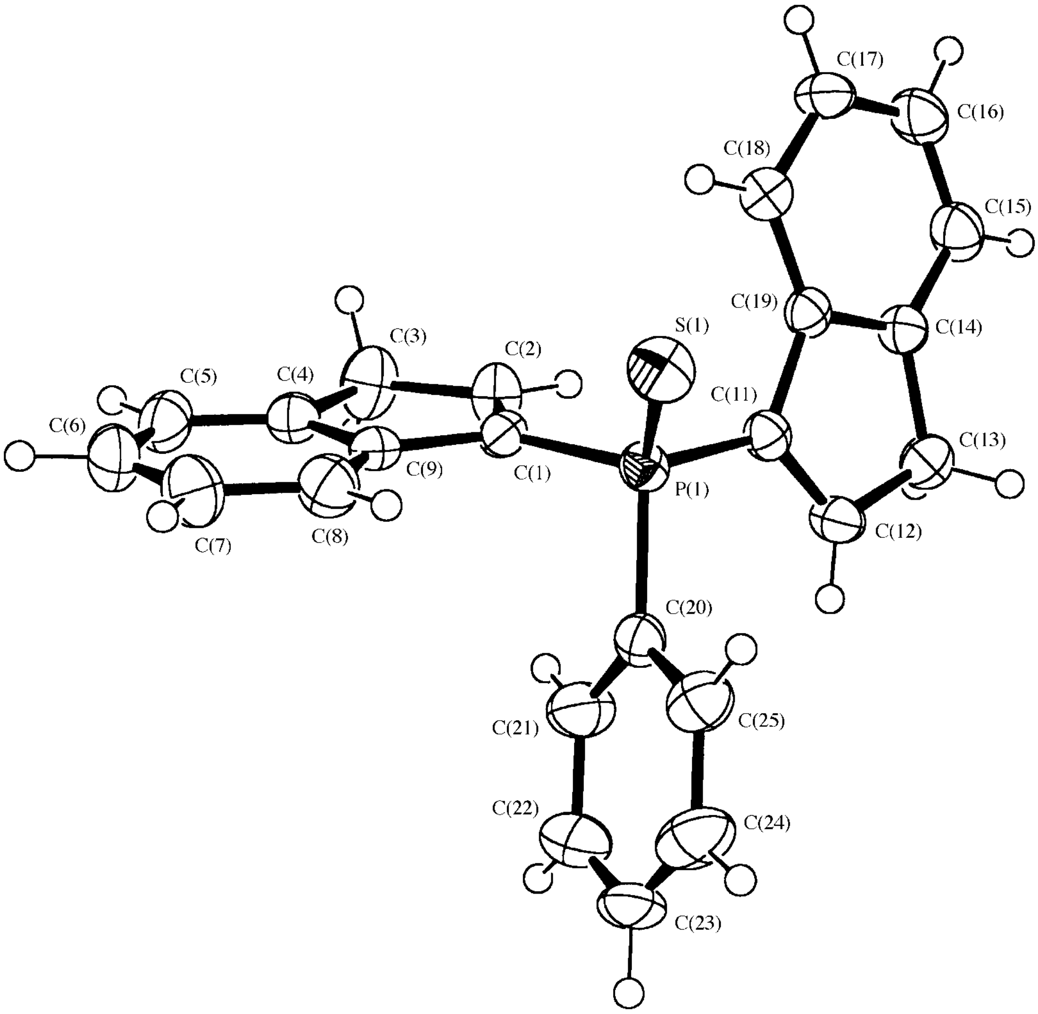


Fig. 2. View of the molecular structure of di(1*H*-inden-3-yl)phenylphosphine sulfide (2), with the non-hydrogen atom labelling scheme. In Figs 2 and 3 the thermal ellipsoids are scaled to 50% probability,[26] and the hydrogen atoms have arbitrary radii.

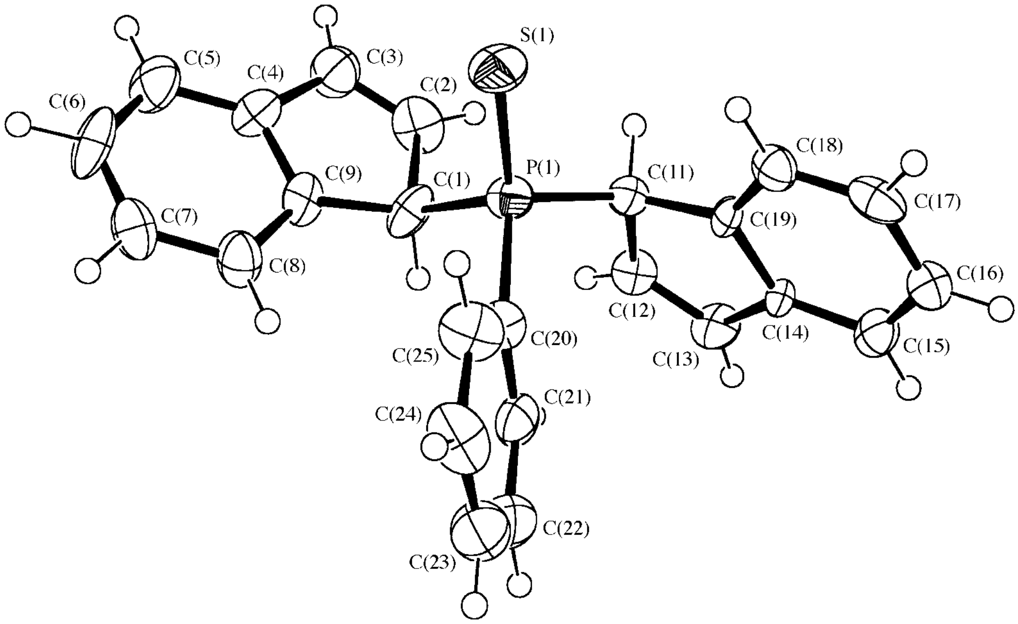


Fig. 3. View of the molecular structure of di(1*H*-inden-1-yl)phenylphosphine sulfide (3), with the non-hydrogen atom labelling scheme.

A summary of the crystal data, selected bond lengths and angles, and atomic positional parameters are listed in Tables 1–6.* The ORTEP diagrams of (2) and (±)-(3) with the adopted numbering scheme are shown in Figs 2 and 3.[26] For compound (±)-(3) only the *R,R* isomer is shown.

Although the crystals of (±)-(3) were of poorer quality (several twins were rejected in the prescreening), the dimensions are self-consistent as shown in Tables 2–4. Likewise, the inden-3-yl rings in (2) are identical. Both indenyl geometries are similar to those reported previously.[14] Only the P–S bond length in (±)-(3), at 1·934(4) Å, is barely significantly smaller than the P–S bond length of 1·954(1) Å in (2) and in other phosphine sulfides (e.g. mean 1·950(2)[27] and 1·947(1) Å[28]). The P–C(indenyl) bond lengths (mean 1·787(3) and 1·83(1) Å for (2) and (3) respectively) are significantly different but both these values lie within ranges observed previously.[29] The phosphorus atom in (2) has an almost regular tetrahedral geometry as expected for four-coordinate P^V. The angles about the phosphorus atom range from 103·1(2) for C(20)–P(1)–C(1) to 113·3(1)° for C(1)–P(1)–S(1) with the bulky sulfide atom apparently causing the distortions from the 109·5° tetrahedral angle. The same pattern is found for the phosphorus atom in (3) for which the angles range from 102·5(5) to 114·9(4)°. The indenyl and phenyl rings in (2) are planar with root mean square deviations of 0·007, 0·010 and 0·008 Å respectively. The phosphorus atom lies just outside these planes by 0·030(4), 0·089(4) and 0·033(5) Å. Within the poorer structural resolution, the phenyl and indenyl rings in (3) are also planar. In this case, the phosphorus is close to planar to the phenyl ring (0·063(13) Å) but 1·488(8) and 1·329(8) Å from the indenyl ring planes.

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* Further data (bond lengths and angles, anisotropic displacement parameters, hydrogen atom parameters, and structure factors) are available, until 31 December 2003, from the Australian Journal of Chemistry, P.O. Box 1139, Collingwood, Vic. 3066.