Synthesis, Crystal Structure and Nuclear Magnetic Resonance Spectral Study of the (+)-(*R*,*R*,*R**,*S**)- and (−)-(*S*,*S*,*R**,*S**)-Enantiomers of the Chiral Diphosphine [$C_6H_4(PPhCH_2CHO)_2CMe_2$]-1,2†

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Treatment of the dilithiodiphosphide [Li(tmen)]$_2$[$C_6H_4(PPh)_2$-1,2] (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) with (−)-(*R*,*R*)- or (+)-(*S*,*S*)-$Me_2C(OCHCH_2OSO_2C_6H_4Me$-*p*)$_2$ afforded the enantiomeric chiral diphosphine (+)-(*R*,*R*,*R**,*S**)- or (−)-(*S*,*S*,*R**,*S**)-[$C_6H_4(PPhCH_2CHO)_2CMe_2$]-1,2, respectively. Their crystal structures have been determined which show them to be isostructural; hence they are enantiomers rather than diastereoisomers. Thus the original chirality of $Me_2C(OCHCH_2OSO_2C_6H_4Me$-*p*)$_2$ induces a preferred chirality at the P atoms of the product diphosphines. A ^1H and ^{31}P NMR spectral study of (+)-(*R*,*R*,*R**,*S**)-[$C_6H_4(PPhCH_2CHO)_2CMe_2$]-1,2 has been carried out, involving selective decoupling and nuclear Overhauser experiments, Karplus curves for both $^3J_{HH}$ and $^2J_{PH}$ couplings and ring current shielding effects. This allows assignments to be made of the ^{31}P and non-aromatic ^1H signals, and demonstrates that the structure determined by X-ray crystallography in the solid state is not significantly changed in solution.

Tertiary phosphines have a central role in the co-ordination chemistry of the later transition metals. They are often components of important homogeneous catalysts, especially with noble metals. Bis(tertiary phosphines) are a significant sub-class, and optically active variants are valuable as chiral auxiliaries in several enantioselective organic reactions. The archetypal example is (*R*,*R*)- or (*S*,*S*)-$(Ph_2PCH_2CHO)_2CMe_2$, (−)- or (+)-diop, in which the centres of chirality are remote from the phosphorus atoms. Alternatively, in another class, illustrated by $XCH_2CH_2CH_2X$ [X = P(Ph)C_6H_4OMe-*o*], (+)- or (−)-dipamp, it is the phosphorus centres which are chiral.

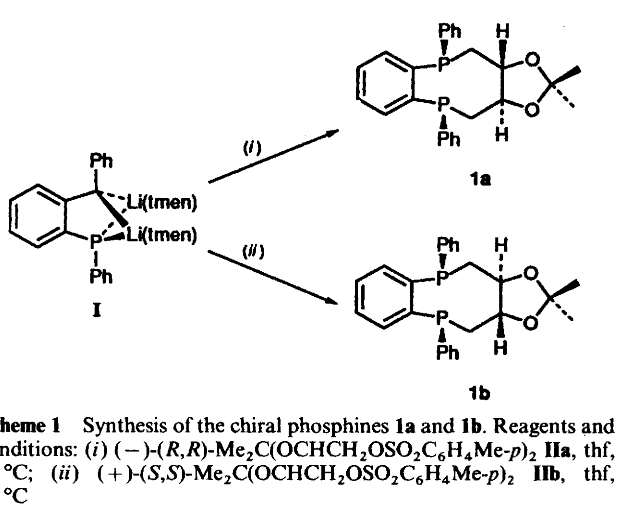
Our objective was to synthesise a ligand in which the diphosphine has the phosphorus atoms at the junctions of a fused bicyclic skeleton. Moreover we sought to combine the chiral features of diop with those of a dipamp analogue.

The synthesis and some reactions of [Li(tmen)]$_2$[$C_6H_4(PR)_2$-1,2] (R = Ph **I**,[1,2] H[3] or $SiMe_3$;[4] tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) have previously been reported. We now describe the reaction of **I** with (−)-(*R*,*R*)- or (+)-(*S*,*S*)-$Me_2C(OCHCH_2OSO_2C_6H_4Me$-*p*)$_2$,[5] **IIa** and **IIb** respectively, leading to the novel chiral diphosphines **1a** and **1b**, respectively. Additionally we discuss the assignment of the ^1H and ^{31}P NMR spectra of **1a** based on selective decoupling experiments, homo- and hetero-nuclear coupling constants and ring current effects. It is shown that these data are consistent with the solution state structure being the same as that in the crystal, as determined by X-ray crystallography.

Results and Discussion

Reactions of [Li(tmen)]$_2$[$C_6H_4(PPh)_2$-1,2] **I** *with* **IIa** *and* **IIb**.—Treatment of the bis(tosylate) **IIa** with **I** in tetrahydrofuran (thf) at room temperature stereospecifically gave, as the only product, the diphosphine (+)-(*R*,*R*,*R**,*S**)-[$C_6H_4(PPhCH_2CHO)_2CMe_2$]-1,2 **1a** [step (*i*) in Scheme 1], as established by examination of the ^{31}P-{^1H} NMR spectrum of the crude reaction mixture. Compound **1a** was separated as colourless crystals in *ca.* 75% yield by extraction of the oily residue, obtained after removal of volatiles from the reaction mixture, with hot hexane. The enantiomeric bis(tosylate) **IIb** reacted likewise with **I** in thf at ambient temperature and gave compound **1b**, the enantiomer of **1a** [step (*ii*) in Scheme 1]; hence **1a** and **1b** gave identical NMR spectra. The ^{31}P-{^1H} NMR spectrum of a mixture of **1a** and **1b** showed only one set of AB quartets. Compounds **1a** and **1b** have essentially identical melting points but opposite optical rotations (Table 1). Thus, in these reactions, the chirality of the carbon atoms in the starting materials **IIa** and **IIb** induces a preferred chirality at the second chiral centres, the chiral phosphorus atoms of **1a** and **1b**.

X-Ray Crystallographic Studies.—The molecular structure of compound **1a** is shown in Fig. 1. The crystal data and refinement parameters for compounds **1a** and **1b**, selected intramolecular bond distances and angles, torsion angles, and atomic coordinates are given in Tables 2–5, respectively. It is



Scheme 1 Synthesis of the chiral phosphines **1a** and **1b**. Reagents and conditions: (*i*) (−)-(*R*,*R*)-$Me_2C(OCHCH_2OSO_2C_6H_4Me$-*p*)$_2$ **IIa**, thf, 25 °C; (*ii*) (+)-(*S*,*S*)-$Me_2C(OCHCH_2OSO_2C_6H_4Me$-*p*)$_2$ **IIb**, thf, 25 °C

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Yields, melting points, optical rotations (°) and analytical data for the colourless chiral diphosphines **1a** and **1b**

Compound	Yield[a] (%)	M.p.[b]/°C	α(589.3 nm, *T*, *c*,[c] s[d])	*T*/°C	Analysis[e] (%) C	H	P
1a	74	156–157	+26.1 (0.550, $CDCl_3$)	27	71.5 (71.4)	6.4 (6.2)	13.6 (14.7)
1b	52	154–155	−22.5 (0.323, $CDCl_3$)	29	70.6 (71.4)	6.2 (6.2)	

[a] Not optimised. [b] Measured in a sealed capillary under an atmosphere of argon. [c] g 100 cm^{-3}. [d] Solvent. [e] Calculated values in parentheses.

Table 2 Crystal data and refinement parameters for compounds **1a** and **1b**[a]

	1a	**1b**[b]
Formula	$C_{25}H_{26}O_2P_2$	$C_{25}H_{26}O_2P_2$
M	420.4	420.4
Crystal system	Triclinic	Triclinic
a/Å	8.483(4)	8.429(5)
b/Å	10.124(3)	10.120(0)
c/Å	14.371(3)	14.349(6)
α/°	73.58(2)	73.613(1)
β/°	89.83(3)	89.978(4)
γ/°	70.68(3)	70.857(3)
U/Å^3	1111.6	1102.2
Z	2	2
D_c/g cm^{-3}	1.26	1.26
Space group	$P\bar{1}$	$P\bar{1}$
F(000)	222	222
μ(Mo-Kα)/cm^{-1}	2.1	2.1
λ/Å	0.710 69	0.710 69
$2\theta_{max}$/°	50	
Unique reflections measured	3879	
Reflections used in refinement [$I > \sigma(I)$]	3133	
R	0.046	
R'	0.057	

[a] Using single crystals mounted in sealed capillaries. [b] As **1b** and **1a** (inevitably) had identical cell constants, refinement of this structure was not carried out.

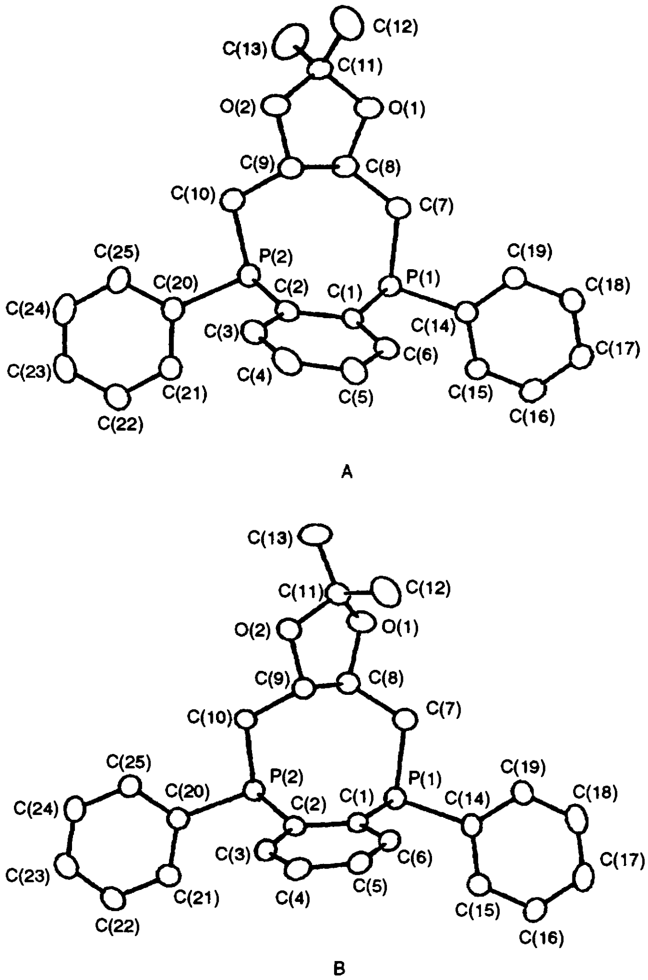


Fig. 1 Molecular structure and the atom numbering scheme for compound **1a**

noteworthy that the unit cell of **1a** contains two molecules having slightly different conformations, as shown in Fig. 2. In each molecule, the two phenyl groups are on the same side of the $C_6H_4P_2$-1,2 moiety, the chiral organic framework is on the other side and the lone-pairs on the phosphorus atoms are almost coplanar with that moiety. This is a rather rigid fused bicyclic structure, and hence it is not unreasonable that in solution there should be no change in its conformation.

NMR Spectroscopic Studies of Compounds **1a** *and* **1b**.—Compounds **1a** and **1b** were characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopy. The data for **1a** are presented in Tables 6 (^1H and ^{31}P) and 7 (^{13}C); **1b** was shown to be spectroscopically equivalent to **1a**.

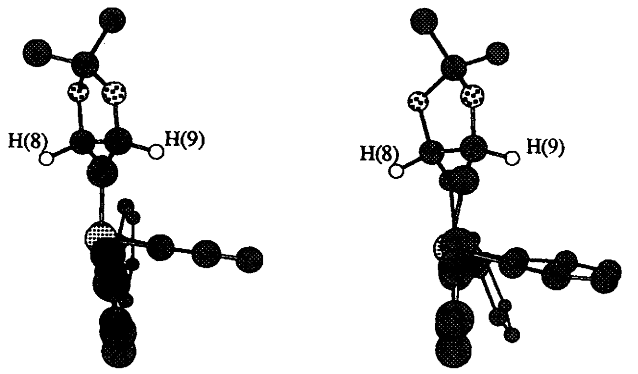
The observed ^1H NMR spectrum of compound **1a** may be compared with that of its analogue (*R*,*R*)-(Ph_2PCH_2-$CHO)_2CMe_2$, (*R*,*R*)-diop.[5] The main difference between the two spectra is that in **1a** (*i*) each of the six methine and methylene protons is magnetically distinct, and (*ii*) the two methine protons have both been considerably shifted from their value of δ 3.92 in (*R*,*R*)-diop, one to high frequency and the other to low. From an electronic viewpoint, the protons in the non-aromatic region are in very similar environments in the two compounds, so the difference must arise from the high rigidity introduced into **1a** by the formation of the eight-membered ring. A significant structural feature (see Fig. 2) is that H(9), one of the methine protons, is pointing towards the aromatic ring whilst the other, H(8), points away. Hence H(9) is expected to show significant shielding due to the ring current effect, the size of which can be estimated by measuring the position of H(9) with respect to the centre of the ring from the crystal structure, and applying the equations of Johnson and Bovey.[8] The shift calculated by this procedure is −0.7 to −0.9 ppm which is in reasonable agreement with the observed value of −0.65 ppm. The calculated shift for H(8) is +0.14 to +0.17 ppm, whereas the observed shift is +0.88 ppm; the discrepancy is attributed to the additional deshielding effect of the phosphorus lone-pairs which are in close proximity to H(8).

Having established the position of the two methine protons, the methylene protons were assigned by selective decoupling of each methine multiplet. To distinguish between the protons in each methylene group, the relevant coupling constants were compared to two Karplus curves; the first for three-bond proton–proton vicinal coupling,[6] and the second, relating $^2J_{PH}$ to the dihedral angle between the CH bond and the phosphorus lone-pair.[7]

The related dihedral and torsion angle data are listed in

Table 3 Selected intramolecular bond distances (Å) and angles (°) for the diphosphine **1a** with estimated standard deviations in parentheses

	A	B		A	B
P(1)–C(1)	1.865(4)	1.853(4)	P(1)–C(7)	1.860(5)	1.858(6)
P(1)–C(14)	1.838(5)	1.843(4)	P(2)–C(2)	1.829(5)	1.853(4)
P(2)–C(10)	1.856(7)	1.851(5)	P(2)–C(20)	1.839(4)	1.840(5)
O(1)–C(8)	1.427(6)	1.428(7)	O(1)–C(11)	1.425(7)	1.430(7)
O(2)–C(9)	1.421(7)	1.415(6)	O(2)–C(11)	1.411(5)	1.403(6)
C(1)–C(2)	1.425(6)	1.397(5)	C(1)–C(6)	1.378(6)	1.416(6)
C(2)–C(3)	1.417(6)	1.396(6)	C(3)–C(4)	1.362(8)	1.402(7)
C(4)–C(5)	1.382(7)	1.374(7)	C(5)–C(6)	1.408(7)	1.377(7)
C(7)–C(8)	1.504(8)	1.525(6)	C(8)–C(9)	1.568(7)	1.527(6)
C(9)–C(10)	1.521(6)	1.526(7)	C(11)–C(12)	1.484(10)	1.526(9)
C(11)–C(13)	1.482(10)	1.500(8)	C(14)–C(15)	1.393(8)	1.377(7)
C(14)–C(19)	1.390(5)	1.384(8)	C(15)–C(16)	1.388(7)	1.401(7)
C(16)–C(17)	1.367(6)	1.363(9)	C(17)–C(18)	1.373(9)	1.355(9)
C(18)–C(19)	1.388(8)	1.390(7)	C(20)–C(21)	1.388(8)	1.382(8)
C(20)–C(25)	1.365(8)	1.390(5)	C(21)–C(22)	1.366(7)	1.383(7)
C(22)–C(23)	1.368(9)	1.374(6)	C(23)–C(24)	1.365(10)	1.371(9)
C(24)–C(25)	1.398(7)	1.391(8)			
C(1)–P(1)–C(7)	99.6(2)	103.5(2)	C(1)–P(1)–C(14)	101.7(2)	101.2(2)
C(7)–P(1)–C(14)	100.4(2)	101.3(2)	C(2)–P(2)–C(10)	100.7(2)	96.9(2)
C(2)–P(2)–C(20)	102.1(2)	104.2(2)	C(10)–P(2)–C(20)	102.0(2)	100.9(2)
C(8)–O(1)–C(11)	108.2(3)	108.8(4)	C(9)–O(2)–C(11)	110.2(4)	107.8(3)
P(1)–C(1)–C(2)	117.1(3)	118.1(3)	P(1)–C(1)–C(6)	123.1(3)	123.6(3)
C(2)–C(1)–C(6)	119.8(4)	118.2(4)	P(2)–C(2)–C(1)	118.1(3)	117.7(3)
P(2)–C(2)–C(3)	123.2(3)	122.4(3)	C(1)–C(2)–C(3)	118.6(4)	119.5(4)
C(2)–C(3)–C(4)	120.5(4)	120.9(4)	C(3)–C(4)–C(5)	120.9(5)	119.8(4)
C(4)–C(5)–C(6)	120.1(5)	119.8(4)	C(1)–C(6)–C(5)	120.1(4)	121.7(4)
P(1)–C(7)–C(8)	118.3(3)	114.6(4)	O(1)–C(8)–C(7)	105.1(3)	110.6(4)
O(1)–C(8)–C(9)	102.2(4)	104.0(4)	C(7)–C(8)–C(9)	116.5(4)	115.4(4)
O(2)–C(9)–C(8)	104.3(4)	104.8(4)	O(2)–C(9)–C(10)	108.0(4)	107.5(3)
C(8)–C(9)–C(10)	117.3(5)	115.4(4)	P(2)–C(10)–C(9)	112.4(4)	114.8(3)
O(1)–C(11)–C(2)	107.0(4)	104.8(4)	O(1)–C(11)–C(12)	106.2(5)	109.8(4)
O(1)–C(11)–C(13)	112.1(6)	108.5(5)	O(2)–C(11)–C(12)	110.7(5)	111.0(5)
O(2)–C(11)–C(13)	108.6(4)	109.6(4)	C(12)–C(11)–C(13)	112.1(6)	112.8(6)
P(1)–C(14)–C(15)	117.0(3)	117.4(4)	P(1)–C(14)–C(19)	125.6(4)	125.1(3)
C(15)–C(14)–C(19)	117.2(4)	117.1(4)	C(14)–C(15)–C(16)	121.3(4)	121.5(6)
C(15)–C(16)–C(17)	120.4(5)	120.7(6)	C(16)–C(17)–C(18)	119.4(5)	118.0(5)
C(17)–C(18)–C(19)	120.5(4)	122.3(6)	C(14)–C(19)–C(18)	121.1(5)	120.4(5)
P(2)–C(20)–C(21)	116.7(4)	117.1(3)	P(2)–C(20)–C(25)	126.1(4)	124.1(4)
C(21)–C(20)–C(25)	116.7(4)	118.6(4)	C(20)–C(21)–C(22)	122.4(6)	120.2(4)
C(21)–C(22)–C(23)	120.0(6)	121.0(5)	C(22)–C(23)–C(24)	119.3(5)	119.5(5)
C(23)–C(24)–C(25)	120.0(7)	120.0(4)	C(20)–C(25)–C(24)	121.4(6)	120.7(5)



A B

Fig. 2 Two different solid-state conformations of the diphosphine **1a** (from molecular structure)

Table 4. When four atoms are involved, the dihedral angles are taken as the absolute values of the torsion angles taken from the X-ray data. As far as the lone-pair of the phosphorus is concerned, the dihedral angle between this and the C–H bond was calculated on the assumption that the dihedral angles between the lone-pair and the two P–C(aromatic) bonds are equal. Table 5 lists the observed shifts and coupling data.

A nuclear Overhauser effect study was carried out; each of

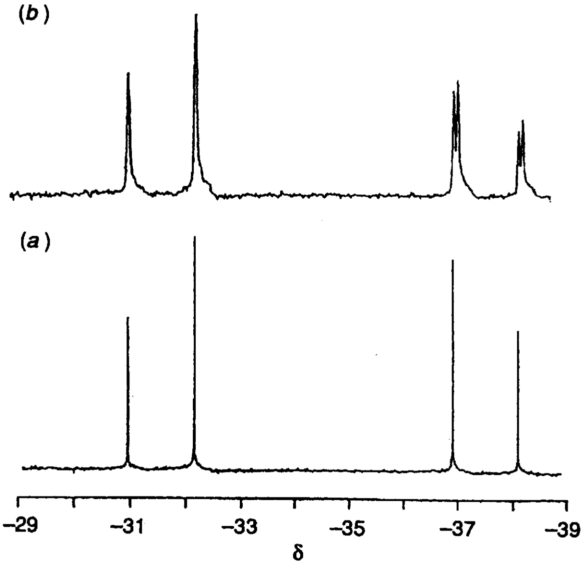


Fig. 3 Phosphorus-31 NMR spectra of **1a**: (*a*) $^{31}P-\{^{1}H\}$ and (*b*) ^{31}P (with selective irradiation of the aromatic region of the proton spectrum)

Table 4 Torsion and average dihedral angles (°) of the diphosphine **1a**

	Torsion angle[a]/°			Average dihedral angle/°
	A	B		
H(7A)–C(7)–C(8)–H(8)	80	80	H(7A)–H(8)	80(95)
H(7B)–C(7)–C(8)–H(8)	−164	−164	H(7B)–H(8)	164(150)
C(1)–P(1)–C(7)–H(7A)	153	163		
C(1)–P(1)–C(7)–H(7B)	35	46		
C(14)–P(1)–C(7)–H(7A)	49	58		
C(14)–P(1)–C(7)–H(7B)	−69	−59		
H(7A)–C(7)–P(1)–lp[b]	−163[b]	−174[b]	H(7B)–lp	169 (148)
H(7B)–C(7)–P(1)–lp[b]	78[b]	70[b]	H(7A)–lp	74(65 or 85)
H(8)–C(8)–C(9)–H(9)	131	121	H(8)–H(9)	126 (120)
H(9)–C(9)–C(10)–H(10A)	56	53	H(9)–H(10A)	55 (55)
H(9)–C(9)–C(10)–H(10B)	175	169	H(9)–H(10B)	172 (156)
C(2)–P(2)–C(10)–H(10A)	−66	−59		
C(2)–P(2)–C(10)–H(10B)	177	−177		
C(20)–P(2)–C(10)–H(10A)	39	47		
C(20)–P(2)–C(10)–H(10B)	−78	−71		
H(10A)–C(10)–P(2)–lp[b]	−166[b]	−174[b]	H(10A)–lp	170 (155)
H(10B)–C(10)–P(2)–lp[b]	49[b]	56[b]	H(10A)–lp	53 (45)

[a] X-Ray structural data. [b] lp = Lone-pair electrons. Values calculated on the assumption that the dihedral angles between the lone-pair and the two P–C(aromatic) bonds are equal. The numbers in parentheses represent the dihedral angles as calculated from the observed *J* coupling according to refs. 6 and 7.

Table 5 Atomic coordinates for the diphosphine **1a**

	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
P(1)	0.3381	0.2747	0.1251	−0.5424(2)	−0.0863(1)	−0.3324(1)
P(2)	0.5677(2)	0.1321(1)	0.3235(1)	−0.3398(1)	−0.2738(1)	−0.1271(1)
O(1)	0.2729(5)	0.6322(4)	0.2182(3)	−0.3264(5)	−0.4980(4)	−0.3629(2)
O(2)	0.5195(5)	0.5477(4)	0.3149(3)	−0.3763(5)	−0.6125(3)	−0.2136(2)
C(1)	0.5700(5)	0.2048(4)	0.1207(3)	−0.6609(5)	−0.1232(4)	−0.2252(3)
C(2)	0.6721(5)	0.1455(4)	0.2114(3)	−0.5710(5)	−0.1896(4)	−0.1331(3)
C(3)	0.8489(6)	0.1022(5)	0.2105(4)	−0.6577(6)	−0.2056(4)	−0.0503(3)
C(4)	0.9193(6)	0.1152(5)	0.1245(4)	−0.8334(6)	−0.1613(5)	−0.0585(3)
C(5)	0.8205(6)	0.1679(5)	0.0367(4)	−0.9219(6)	−0.1029(5)	−0.1492(4)
C(6)	0.6444(6)	0.2138(4)	0.0348(3)	−0.8379(5)	−0.0836(4)	−0.2313(3)
C(7)	0.3106(6)	0.4609(5)	0.1335(3)	−0.5057(7)	−0.2490(5)	−0.3761(3)
C(8)	0.3346(6)	0.4778(5)	0.2326(4)	−0.3710(6)	−0.3884(5)	−0.3137(3)
C(9)	0.5205(6)	0.4326(5)	0.2765(4)	−0.4224(6)	−0.4636(4)	−0.2165(3)
C(10)	0.5915(7)	0.2885(5)	0.3577(4)	−0.3341(6)	−0.4586(4)	−0.1259(3)
C(11)	0.3625(6)	0.6620(5)	0.2890(4)	−0.3761(7)	−0.6180(5)	−0.3101(3)
C(12)	0.3842(10)	0.8041(8)	0.2400(7)	−0.5512(8)	−0.5974(7)	−0.3513(5)
C(13)	0.2745(11)	0.6652(10)	0.3780(5)	−0.2460(10)	−0.7579(6)	−0.3149(5)
C(14)	0.2607(5)	0.3199(4)	−0.0034(3)	−0.7105(6)	0.0539(4)	−0.4240(3)
C(15)	0.2537(6)	0.2046(5)	−0.0359(4)	−0.7948(9)	0.1827(5)	−0.4035(4)
C(16)	0.1829(7)	0.2295(5)	−0.1290(4)	−0.9153(10)	0.3000(6)	−0.4719(4)
C(17)	0.1173(7)	0.3689(5)	−0.1910(4)	−0.9479(8)	0.2919(6)	−0.5625(4)
C(18)	0.1251(7)	0.4843(5)	−0.1613(4)	−0.8625(9)	0.1666(7)	−0.5836(4)
C(19)	0.1960(6)	0.4604(5)	−0.0684(4)	−0.7449(8)	0.0478(6)	−0.5164(4)
C(20)	0.7245(6)	−0.0259(5)	0.4113(3)	−0.2663(5)	−0.3084(4)	0.0008(3)
C(21)	0.7557(7)	−0.1618(6)	0.3968(4)	−0.2688(6)	−0.1884(5)	0.0293(3)
C(22)	0.8588(9)	−0.2890(6)	0.4612(4)	−0.2064(7)	−0.2073(5)	0.1227(4)
C(23)	0.9376(7)	−0.2851(6)	0.5427(4)	−0.1357(6)	−0.3450(6)	0.1877(4)
C(24)	0.9049(10)	−0.1542(7)	0.5615(5)	−0.1294(6)	−0.4654(6)	0.1599(4)
C(25)	0.7978(9)	−0.0251(6)	0.4955(4)	−0.1957(6)	−0.4474(5)	0.0669(4)

the two methyl signals was irradiated in turn. Irradiation of the low-frequency methyl produced enhancements of 2.9% in H(9) and 0.8% in H(7A), whilst irradiation of the high-frequency methyl produced enhancements of 5.1% in H(8) and 1.5% in H(10B). Hence, we assign the low-frequency methyl to H(11) and the high frequency to H(12); these results are consistent with the proposition that the structure is identical to that found in the crystal.

The ^{31}P-{^{1}H} NMR spectrum of the diphosphine **1a**, Fig. 3(*a*), shows an AB quartet coupling pattern, due to two non-equivalent phosphorus atoms with a chemical shift difference of 5.5 ppm and $^{3}J_{PP} = 175.6$ Hz. Fig.3(*b*) shows the ^{31}P spectrum with selective irradiation of the aromatic region of the proton spectrum. It is noted that the upfield part of the AB quartet then showed an additional splitting, this being the 12.6 Hz coupling to H(10B), already observed in the proton spectrum. These data are consistent with the Karplus curve of Albrand *et al.*,[7] showing that the vicinal angle must be between 40 and 50° to produce a coupling of this size; inspection of Table 6 shows that only for the P(2)–H(10B) pair is this condition fulfilled,

Table 6 Selected chemical shifts and coupling constants (observed and calculated[a]) for compound **1a**

		J/Hz							
Spin	δ[b]	P(1)	P(2)	H(7B)	H(7A)	H(8)	H(9)	H(10A)	H(10B)
P(1)	−31.8	—	175.6	4.3(2[c])	2.0(0[c])	2.4	—	—	0.7
P(2)	−37.3		—	—	2.0	—	1.4	3.1 (2[c])	12.6 (10[c])
H(7B)	2.23			—	12.4	11.3 (15.3[d])	—	—	—
H(7A)	2.64				—	2.6 (3.3[d])	—	—	—
H(8)	4.80					—	7.4 (9.2[d])	—	—
H(9)	3.28						—	5.2 (5.3[d])	10.4 (15.7[d])
H(10A)	2.67							—	11.5
H(10B)	2.12								—
H(11)	1.28								
H(12)	1.34								

[a] Calculated values in parentheses. [b] For ^{1}H referred to residual protonated solvent relative to $SiMe_4$, T = 298 K, frequency = 360 MHz or for ^{31}P relative to external H_3PO_4, T = 298 K, frequency = 101.256 MHz. [c] Calculated according to ref. 7. [d] Calculated according to ref. 6.

Table 7 Carbon-13 NMR spectroscopic data and assignments for the diphosphines **1a** and **1b**

	δ*	
Assignment	**1a**	**1b**
$C(CH_3)_2$	26.9 (s) 27.3 (s)	27.1 (s) 27.2 (s)
PCH_2	33.5 (d, $^{1}J_{PC}$ 16) 36.0 (d, $^{1}J_{PC}$ 16)	33.1 (d, $^{1}J_{PC}$ 16) 35.6 (d, $^{1}J_{PC}$ 15)
PCH_2CH	79.5 (d, $^{2}J_{PC}$ 10) 80.5 (dd, $^{2}J_{PC}$ 8, $^{3}J_{PC}$ 29)	79.4 (d, $^{2}J_{PC}$ 11) 80.5 (dd, $^{2}J_{PC}$ 8, $^{3}J_{PC}$ 29)
$C(CH_3)_2$	107.9 (s)	108.4(s)
Aromatics	124–137 (m)	129–148 (m)
Solvent	[$^{2}H_8$]toluene	$CDCl_3$

* Referred to solvent relative to $SiMe_4$, T = 298 K, frequency = 90.570 MHz; J in Hz.

all the other pairs being expected to give much smaller couplings. We therefore assign the upfield part of the AB quartet to P(2).

A similar comparison of the experimental $^{3}J_{HH}$ couplings with those calculated from the Karplus curve[6] and the X-ray data show reasonable agreement. The main discrepancy lies in the H(7B)–H(8) and H(10B)–H(9) couplings, which are significantly smaller than calculated, suggesting some distortion of the ring structure between the solid and the solution. This is consistent with the calculation of dihedral angles from the J couplings, which are listed in Table 4; these show that distortion could be as much as 20° in some cases. The enantiomers **1a** and **1b** are interesting from the point of view of having chirality at both carbon and phosphorus centres. Their potential as ligands for transition metals will be discussed in a subsequent paper.

Experimental

General Procedures and Instruments.—All experiments were performed under an atmosphere of pure argon, unless otherwise stated, in an efficient fume-cupboard. The solvents used were of reagent grade or better, and were freshly distilled under dry dinitrogen or pure argon and freeze–thaw degassed prior to use. The drying agents were sodium–potassium alloy (n-hexane, toluene or thf) and phosphorus(v) oxide ($CHCl_3$ and CH_2Cl_2). The deuteriated solvents used were dried and freeze–thaw degassed prior to use; the drying agents were sodium–potassium alloy ([$^{2}H_8$]toluene) and activated 3 Å molecular sieves ($CDCl_3$).

Microanalyses were performed in this University or by Butterworth Laboratories Ltd., Teddington, Middlesex.

The melting points were determined under an atmosphere of argon in sealed capillaries on an electrothermal apparatus and are uncorrected. The optical rotations were recorded using a standard cell with a 10 cm pass on a Perkin-Elmer 241 polarimeter. The NMR spectra were recorded using Bruker WP80, AC250 or WM360 instruments.

The starting materials $[Li(tmen)]_2[C_6H_4(PPh)_2\text{-}1,2]$ **I**[1] and (−)-(R,R)- or (+)-(S,S)-$Me_2C(OCHCH_2OSO_2C_6H_4Me\text{-}p)_2$ **IIa** or **IIb**[5] were prepared by literature methods.

Synthesis of (+)-(R,R,R*,S*)-$[C_6H_4(PPhCH_2CHO)_2CMe_2]\text{-}1,2$ **1a**.—A solution of (−)-(R,R)-$Me_2C(OCHCH_2OSO_2C_6H_4Me\text{-}p)_2$ **IIa** (2.38 g, 5.06 mmol) in thf (50 cm^3) was added dropwise to an orange solution of **I** (2.72 g, 5.05 mmol) in thf (150 cm^3) at 25 °C. Colour changes from orange to deep red and then to pale yellow were observed. The resulting mixture was stirred for 18 h. After the removal of the volatiles *in vacuo*, a pale yellow gum remained, which was extracted with hot $n\text{-}C_6H_{14}$ (3 × 100 cm^3). The combined extracts were filtered, concentrated and set aside at 25 °C for 48 h to give colourless crystals of the compound **1a** (1.58 g, 3.76 mmol, 74%).

Synthesis of (−)-(S,S,R*,S*)-$[C_6H_4(PPhCH_2CHO)_2CMe_2]\text{-}1,2$ **1b**.—The same procedure as above was performed with a solution of (+)-(S,S)-$Me_2C(OCHCH_2OSO_2C_6H_4Me\text{-}p)_2$ **IIb** (0.70 g, 1.49 mmol) in thf (15 cm^3), and a solution of **I** (0.80 g, 1.49 mmol) in thf (50 cm^3), and (for extraction) hot $n\text{-}C_6H_{14}$ (3 × 50 cm^3). Colourless crystals of the compound **1b** (0.33 g, 0.79 mmol, 52%) were obtained.

X-Ray Crystallography.—Data were collected using a crystal (*ca.* 1.0 × 0.4 × 0.3 mm) sealed in a capillary under argon, on an Enraf-Nonius CAD4 diffractometer at room temperature in the θ–2θ mode with $\Delta\theta = (0.8 + 0.35 \tan\theta)°$ and a maximum scan time of 1 min. A total of 3879 unique reflections were measured for $2 < \theta < 25°$ and $+h \pm k \pm l$, and 3133 reflections with $I > \sigma(I)$ where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/Lp$, were used in the refinement. No correction was made for absorption.

The structure was solved by direct methods using MULTAN[9] and non-hydrogen atoms refined anisotropically by full-matrix least squares. Hydrogen atoms were held fixed at calculated positions with $B_{iso} = 1.3\ B_{eq}$ for the atom to which they are bonded. The weighting scheme was $w = 1/\sigma^2(F)$. Programs from the Enraf-Nonius SDP-Plus package were run on a MicroVax computer. A refinement of the η parameter[10] confirmed the absolute configuration known on chemical grounds.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank Dr. W.-P. Leung for his assistance (to P. Y.) in the early stages of this work and the Chinese Government, British Council for a scholarship awarded to P. Y. and the SERC for other support.

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Received 9*th January* 1995; *Paper* 5/00121H