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Phosphinosulphoxide rhodium complexes. Synthesis, crystal structure, and catalytic chemistry of [(2,3,5,6-η)-bicyclo[2.2.1]-hepta-2,5-diene][*P*,*O*-diphenyl(phenylsulphinylmethyl)-phosphine]rhodium(I)trifluoromethanesulphonate and asymmetric analogues

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Abstract

α-Phosphinosulphoxides are readily accessible by the reaction of α-lithioalkyl-sulphoxides with Ph_2PCl, and are stable towards internal oxygen transfer when pure. The compound $Ph_2PCH_2S(O)Ph$ thus prepared was shown to form a cationic rhodium bicyclo[2,2,1]hepta-2,5-diene complex in which the phosphine and sulphoxide form a chelating entity; the structure was confirmed by an X-ray diffraction study. Crystals of the phosphinosulphoxide complex (thf adduct) $C_{27}H_{25}F_3O_4S_2PRh$; C_4H_8O are monoclinic, $P2_1/c$, $a = 10.462$, $b = 16.500$, $c = 18.690$ Å, $\beta = 104.50°$, $Z = 4$, $D_c = 1.47$ g cm^{-3}, $R = 0.041$, $R_\omega = 0.046$ for 4809 unique observed reflections ($I > 3\ \sigma(I)$). An optically active analogue was prepared from (*R*)-*p*-tolyl methyl sulphoxide, and the rhodium complexes were evaluated for catalytic effectiveness in homogeneous hydrogenation. It was demonstrated that 2/1 ligand/rhodium complexes are present under turnover conditions.

Introduction

Chelate complexes in which one ligating atom is phosphorus and the second nitrogen or oxygen have been less thoroughly investigated than their biphosphine counterparts. For P,N chelates, application in catalysis is well established, a conspicuous example being the asymmetric cross-coupling reaction of Kumada and Hayashi, for which the most successful ligands are β-aminoethyl phosphines derived from bulky amino-acids [1]. Aminoalkylferrocenylphosphines are of comparable

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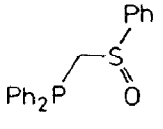
effectiveness [2], and related ligands have been used in hydrogenation [3]. For P,O chelates, the most striking example is nickel-catalysed oligomerisation of terminal olefins, for which Keim has utilised β-enoxyphosphine complexes [4]. More recently the $SnCl_2$-promoted platinum-complex catalysed hydrogenation of terminal olefins involving complexes containing employing β-ketophosphines has been reported [5]; structural studies indicate that a P,O-chelate is formed.

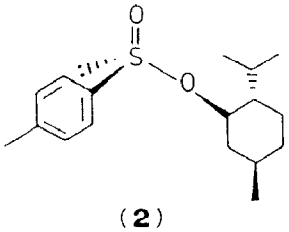
Results and discussion

The objectives of current work were to prepare α-phosphinosulphoxides, study their ligating properties, and examine catalysis by their complexes. Since sulphoxides are readily obtained optically pure, the new ligands could find application in asymmetric catalysis. At the outset it was not clear how stable α-phosphinosulphoxides would be, since internal oxygen transfer is strongly exothermic [6*]. The kinetic barrier is substantial, temperatures of 225 °C being required before appreciable reaction occurs between trialkylphosphines and DMSO [7]. We confirmed that PhS(O)Me and Ph_2PMe or $PhPMe_2$ reacted only to a small extent over a protracted period at 53 °C in solution. Vedejs and co-workers [8] have prepared a series of α-phosphinosulphoxides as intermediates in the synthesis of thiol esters. They indicated that the former are rather unstable, tending to decompose on chromatography or crystallisation with partial oxygen transfer to phosphorus, and purification at that stage was not recommended. Given this caveat, we synthesised the possible by-products Ph_2PCH_2SPh, $Ph_2P(O)CH_2Ph$, and $Ph_23P(O)CH_2S(O)Ph$ [9] so that the target ligand could be identified more readily.

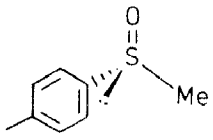
The preparation proved to be quite straightforward. Methyl phenyl sulphoxide was deprotonated in thf at −78 °C by use of 1.1 equivalents of MeLi. The pale yellow solution was treated with 1.1 equivalents of Ph_2PCl and stirred for 2 h. Work-up gave a mixture of two components which were separated by flash-column chromatography. The faster running material proved to be pure phosphinosulphoxide (**1**), although the yields were consistently in the 20–30% range. The colourless



(**1**)



(**2**)



(**3**)

oil solidified on drying in vacuo for several days, giving a stable white powder which was fully characterised. It was then shown that treatment of a thf solution of compound **1** with a few crystals of iodine promoted oxygen-transfer and the isomer $PhSCH_2P(O)Ph_2$ was formed cleanly.

Following Herbrandson and Dickerson [10], and Solladie [11], optically pure *S*-(−)menthyl *p*-toluenesulphinate (**2**) was prepared and converted into *R*-(+)-*p*-tolyl methyl sulphoxide (**3**) by reaction with MeMgBr in Et_2O at −30 °C, in 60%

* Reference number with asterisk indicates a note in the list of references.

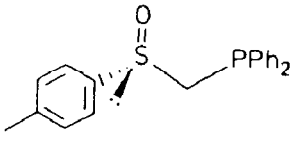
yield [12]. The optical rotation of purified product ($[\alpha]_D^{20}$ 149.7° (*c* 1.07 in Me_2CO)) agreed closely with values reported by Oae [13] and by Kagan [14], the latter for material of carefully authenticated optical purity; it thus appears that the higher values reported by Solladie [11] and by Corey [12] are incorrect. In keeping with this, a sample of **3** analysed by using Kagan's chiral NMR shift reagent [15] was optically pure within the limits of detection.

Sulphoxide **3** may be deprotonated without racemisation by employing $LiNiPr_2$ [16] and this procedure was followed. Reaction of the resulting anion with Ph_2PCl in thf at −78°C for 2 h followed by aqueous work-up gave the desired phosphinosulphoxide **4** as a white powder in 23% yield, and this was fully characterised. The NMR method [15] indicated that it was optically pure.

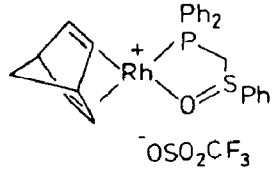
Rhodium complexes of phosphinosulphoxides

Several methods are available for synthesis of cationic diene rhodium complexes, developed largely for their application in homogeneous hydrogenation [17]. Of these, the reaction of phosphinosulphoxide (**2**) with $(C_7H_8)_2RhBF_4$ in thf at −78°C followed by precipitation with Et_2O proved to be the most successful but yields of the desired product **5** were variable, and never more than 75%. This prompted us to develop a new method, starting from the rhodium acetylacetonate [18]. A yellow solution of C_7H_8Rh acac in thf was treated at ambient temperature with one equivalent of $Me_3SiOSO_2CF_3$, followed by one equivalent of ligand **1**. After 20 min at room temperature the sample was added to vigorously stirred hexane, to give a precipitate of analytically pure **5** (as its triflate salt) in 91% yield. The related cyclooctadiene complex **6**, and the corresponding norbornadiene complex 7 of optically active phosphinosulphoxide **4** were prepared in this manner, all as stable crystalline solids.

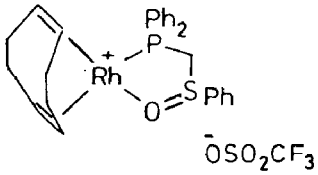
For the cyclooctadiene complex **6** the ^1H NMR spectrum is as expected, with HC=CH *trans* to phosphorus giving a broad singlet at 5.73 ppm and HC=CH *trans*



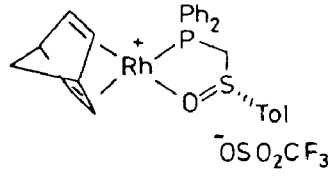
(4)



(5)



(6)



(7)

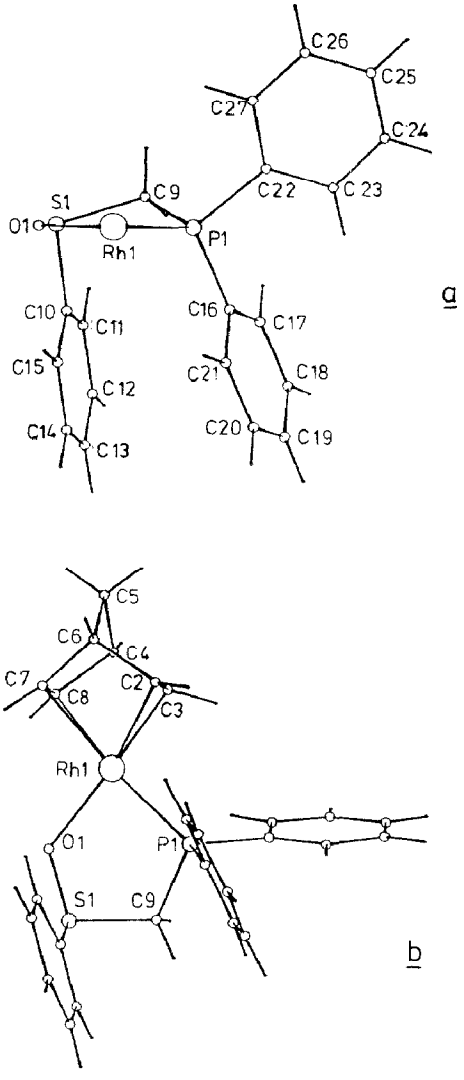


Fig. 1. The X-ray crystal structure of complex **5** (a) viewed approximately into the Rh-chelate ring and (b) from above the plane of the chelate ring. The norbornadiene is omitted from the first view for clarity.

Table 1

X-ray crystal structure of compound **5**. Summarised crystal data.

Formula $C_{27}H_{25}F_3O_4PRhS_2$; C_4H_8O, M = 738.5 (666.4)	
Crystal dimensions	0.44×0.63×0.53 mm
Bounding faces	{011} {100}
Space group $P2_1/c$, monoclinic, orange-red blocks	
a 10.462 Å	
b 16.500 Å	β 104.05°
c 18.690 Å	
Z = 4	D 1.47 g cm^{-3} U = 3130(1)
λ(Mo-(K_α) 0.71069 Å; T 290 K; μ(Mo-K_α) 7.0 cm^{-1}	
6863 collected reflections, 4809 considered observed ($I/\sigma(I) \geq 3$)	
R = 0.041, R_ω = 0.046.	

to sulphoxide oxygen exhibiting diastereotopic splitting at 3.68 and 3.26 ppm [19]. The spectrum of corresponding norbornadiene complex **5** was more complex, and the olefinic protons were identified only as a broad envelope centred at 4–5 ppm. Although this indicates the existence of some intramolecular dynamic process (the

Table 2

Final atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($Å^2 \times 10^3$) with estimated standard deviations in parentheses, for compound **5**

	x	y	z	U^a
Rh	811.9(3)	6240.3(2)	6917.7(1)	35(1)
P	2122(1)	6299.0(6)	6116.0(5)	34(1)
S(1)	2626(1)	7821.1(6)	6910.4(5)	42(1)
S(2)	3233(1)	1592(1)	3538.8(7)	69(1)
O(1)	1585(3)	7408(2)	7233(1)	44(1)
O(2)	2097(3)	1785(2)	2982(2)	90(2)
O(3)	2993(4)	951(2)	4006(3)	91(2)
O(4)	4434(4)	1519(3)	3327(2)	91(2)
F(1)	4547(3)	2370(2)	4685(2)	92(1)
F(2)	3715(3)	3128(2)	3764(2)	97(1)
F(3)	2459(3)	2638(2)	4396(2)	112(2)
C(1)	3508(3)	2470(2)	4120(2)	28(1)
C(2)	−432(4)	5246(2)	6572(2)	48(1)
C(3)	652(4)	5001(2)	7126(2)	46(1)
C(4)	235(4)	5070(2)	7859(2)	51(1)
C(5)	−1221(4)	4823(3)	7594(3)	63(2)
C(6)	−1524(4)	5451(3)	6960(3)	54(2)
C(7)	−962(4)	6218(2)	7386(2)	47(1)
C(8)	98(4)	5983(3)	7922(2)	46(1)
C(9)	3358(3)	7018(2)	6488(2)	41(1)
C(10)	1756(4)	8335(2)	6091(2)	41(1)
C(11)	2456(5)	8758(3)	5685(3)	58(2)
C(12)	1766(5)	9151(3)	5042(3)	70(2)
C(13)	425(5)	9108(3)	4835(3)	66(2)
C(14)	−261(5)	8697(3)	5257(3)	65(2)
C(15)	402(4)	8305(3)	5895(2)	50(1)
C(16)	1380(4)	6505(2)	5163(2)	37(1)
C(17)	2106(4)	6781(2)	4686(2)	48(1)
C(18)	1494(5)	6976(3)	3964(2)	59(2)
C(19)	176(5)	6910(3)	3719(2)	61(2)
C(20)	−579(4)	6650(3)	4182(2)	58(2)
C(21)	21(4)	6446(3)	4915(2)	48(2)
C(22)	3167(4)	5358(2)	6076(2)	41(1)
C(23)	3262(4)	4998(3)	5424(2)	55(2)
C(24)	4063(5)	4320(3)	5439(3)	77(2)
C(25)	4748(5)	4002(3)	6092(3)	79(2)
C(26)	4674(5)	4362(3)	6740(3)	85(2)
C(27)	3864(5)	5019(3)	6737(3)	68(2)
O(100)	4554(4)	8116(3)	3230(2)	103(2)
C(101)	4156(6)	8697(4)	3664(3)	89(3)
C(102)	5240(9)	9241(4)	3938(4)	128(4)
C(103)	6281(8)	8935(7)	3666(7)	194(7)
C(104)	5934(7)	8143(6)	3369(5)	133(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 3

X-ray crystal structure of compound **5**. (a) Bond lengths, (b) bond angles, (c) selected torsion angles.

(a) Bond lengths (Å)			
Rh–P	2.263(1)	Rh–O(1)	2.117(3)
Rh–C(2)	2.096(4)	Rh–C(3)	2.096(4)
Rh–C(7)	2.237(5)	Rh–C(8)	2.224(5)
P–C(9)	1.848(4)	P–C(16)	1.819(3)
P–C(22)	1.819(4)	S(1)–O(1)	1.528(3)
S(1)–C(9)	1.806(4)	S(1)–C(10)	1.794(3)
S(2)–O(2)	1.413(3)	S(2)–O(3)	1.432(5)
S(2)–O(4)	1.411(4)	S(2)–C(1)	1.792(4)
F(1)–C(1)	1.328(4)	F(2)–C(1)	1.318(5)
F(3)–C(1)	1.347(5)	C(2)–H(2)	1.032(44)
C(2)–C(3)	1.397(5)	C(2)–C(6)	1.532(7)
C(3)–H(3)	1.885(47)	C(3)–C(4)	1.538(6)
C(4)–C(5)	1.538(6)	C(4)–C(8)	1.520(6)
C(5)–C(6)	1.549(6)	C(6)–C(7)	1.533(6)
C(7)–H(7)	0.997(43)	C(7)–C(8)	1.358(5)
C(8)–H(8)	0.919(42)	C(10)–C(11)	1.366(7)
C(10)–C(15)	1.375(5)	C(11)–C(12)	1.402(6)
C(12)–C(13)	1.364(7)	C(13)–C(14)	1.369(8)
C(14)–C(15)	1.385(6)	C(16)–C(17)	1.382(6)
C(16)–C(21)	1.388(5)	C(17)–C(18)	1.384(5)
C(18)–C(19)	1.348(7)	C(19)–C(20)	1.372(7)
C(20)–C(21)	1.402(6)	C(22)–C(23)	1.380(6)
C(22)–C(27)	1.389(6)	C(23)–C(24)	1.394(7)
C(24)–C(25)	1.361(7)	C(25)–C(26)	1.367(6)
C(26)–C(27)	1.375(8)	O(100)–C(101)	1.383(8)
O(100)–C(104)	1.404(8)	C(101)–C(102)	1.439(10)
C(102)–C(103)	1.403(14)	C(103)–C(104)	1.431(14)
(b) Bond angles (°)			
P–Rh–O(1)	86.6(1)	P–Rh–C(2)	102.7(1)
O(1)–Rh–C(2)	164.7(1)	P–Rh–C(3)	101.8(1)
O(1)–Rh–C(3)	151.4(1)	C(2)–Rh–C(3)	38.9(1)
P–Rh–C(7)	162.3(1)	O(1)–Rh–C(7)	101.7(1)
C(2)–Rh–C(7)	66.1(2)	C(3)–Rh–C(7)	78.4(2)
P–Rh–C(8)	159.9(1)	O(1)–Rh–C(8)	97.0(1)
C(2)–Rh–C(8)	78.5(2)	C(3)–Rh–C(8)	66.3(2)
C(7)–Rh–C(8)	35.4(1)	Rh–P–C(9)	103.1(1)
Rh–P–C(16)	117.6(1)	C(9)–P–C(16)	106.6(2)
C(16)–P–C(22)	106.0(2)	O(1)–S(1)–C(9)	105.3(2)
O(1)–S(1)–C(10)	106.6(2)	C(9)–S(1)–C(10)	98.9(2)
O(2)–S(2)–O(3)	112.0(2)	O(2)–S(2)–O(4)	117.3(2)
O(3)–S(2)–O(4)	114.1(3)	O(2)–S(2)–C(1)	104.3(2)
O(3)–S(2)–C(1)	104.7(2)	O(4)–S(2)–C(1)	102.5(2)
Rh–O(1)–S(1)	123.8(2)	S(2)–C(1)–F(1)	111.2(3)
S(2)–C(1)–F(2)	112.5(3)	F(1)–C(1)–F(2)	107.5(3)
S(2)–C(1)–F(3)	111.2(2)	F(1)–C(1)–F(3)	107.8(3)
F(2)–C(1)–F(3)	106.4(3)	Rh–C(2)–H(2)	114.6(25)
Rh–C(2)–C(3)	70.5(2)	H(2)–C(2)–C(3)	125.6(24)
Rh–C(2)–C(6)	99.2(3)	H(2)–C(2)–C(6)	124.6(24)
C(3)–C(2)–C(6)	106.1(4)	Rh–C(3)–C(2)	70.5(2)
Rh–C(3)–H(3)	112.9(24)	C(2)–C(3)–H(3)	120.4(21)
Rh–C(3)–C(4)	98.4(2)	C(2)–C(3)–C(4)	106.5(4)
H(3)–C(3)–C(4)	129.6(22)	C(3)–C(4)–C(5)	99.6(3)
C(3)–C(4)–C(8)	101.3(3)	C(5)–C(4)–C(8)	100.5(3)

Table 3 (continued)

(b) Bond angles (°)			
C(4)–C(5)–C(6)	94.1(3)	C(2)–C(6)–C(5)	100.2(3)
C(2)–C(6)–C(7)	101.1(3)	C(5)–C(6)–C(7)	100.0(3)
Rh–C(7)–C(6)	93.4(3)	Rh–C(7)–H(7)	100.6(26)
C(6)–C(7)–H(7)	133.1(22)	Rh–C(7)–C(8)	71.8(3)
C(6)–C(7)–C(8)	106.8(3)	H(7)–C(7)–C(8)	120.0(21)
Rh–C(8)–C(4)	93.8(3)	Rh–C(8)–C(7)	72.8(3)
C(4)–C(8)–C(7)	107.5(3)	Rh–C(8)–H(8)	104.6(34)
C(4)–C(8)–H(8)	124.9(28)	C(7)–C(8)–H(8)	127.5(28)
P–C(9)–S(1)	110.4(2)	S(1)–C(10)–C(11)	119.1(3)
S(1)–C(10)–C(15)	119.1(3)	C(11)–C(10)–C(15)	121.8(4)
C(10)–C(11)–C(12)	118.6(4)	C(11)–C(12)–C(13)	120.0(5)
C(12)–C(13)–C(14)	120.6(4)	C(13)–C(14)–C(15)	120.3(4)
C(10)–C(15)–C(14)	118.7(4)	P–C(16)–C(17)	123.0(3)
P–C(16)–C(21)	118.0(3)	C(17)–C(16)–C(21)	119.0(3)
C(16)–C(17)–C(18)	120.6(4)	C(17)–C(18)–C(19)	120.3(5)
C(18)–C(19)–C(20)	120.6(4)	C(19)–C(20)–C(21)	120.0(4)
C(16)–C(21)–C(20)	119.3(4)	P–C(22)–C(23)	123.3(3)
P–C(22)–C(27)	118.2(3)	C(23)–C(22)–C(27)	118.4(4)
C(22)–C(23)–C(24)	119.9(4)	C(23)–C(24)–C(25)	120.7(5)
C(24)–C(25)–C(26)	119.7(5)	C(25)–C(26)–C(27)	120.4(5)
C(22)–C(27)–C(26)	120.8(5)	C(101)–O(100)–C(104)	108.1(5)
O(100)–C(101)–C(102)	108.5(6)	C(101)–C(102)–C(103)	105.1(7)
C(102)–C(103)–C(104)	108.9(8)	O(100)–C(104)–C(103)	104.7(7)
(c) Selected torsion angles (°)			
O(1)–Rh–P–C(9)	19.3		
P–Rh–O(1)–S(1)	−1.4		
Rh–P–C(9)–S(1)	−33.2		
C(9)–S(1)–O(1)–Rh	−17.8		
O(1)–S(1)–C(9)–P	32.9		
Rh–P–C(16)–C(17)	157.9		
Rh–P–C(16)–C(21)	−20.9		
Rh–P–C(22)–C(23)	133.5		
Rh–P–C(22)–C(27)	−43.9		

^{31}P spectrum is sharp at room temperature, $\delta(CH_2Cl_2)$ 46.8 ppm J(PRh) 181 Hz) it was not studied further since full structural identification was achieved by an X-ray diffraction study.

Crystals of complex **5** containing 1 molecule of thf were grown from thf/Et_2O and solved in the monoclinic space group $P2/c$ by conventional means. Two views of the cation structure are displayed in Fig. 1, indicating that the oxygen rather than sulphur is chelated, with the *S*-phenyl ring occupying a pseudo-axial site. The chelate is significantly non-planar, its conformation being best described as a distorted envelope with CH_2 canted by 0.6 Å out of the plane of the other four atoms. The PPh_2 entity is disposed in edge-face array, like the majority of 5-ring chelate complexes derived from optically active biphosphines [20]. This results in Rh–P–C_{ar}–C_{ar} torsion angles of −21° (edge) and −44° (face). One *ortho* aryl hydrogen (H(21)) interacts weakly with rhodium [21]. The *S*-phenyl and *endo* P-phenyl rings are in approximately parallel planes at a distance of ca. 3.3 Å, eliciting a favourable stacking interaction [22]. There is a strong and differentiated

trans-effect evident in the olefin–rhodium bond lengths (Table 2). For C(7) and C(8) *trans* to P the average bond length is 2.243 Å whereas for C(2) and C(3) *trans* to oxygen the bond length is 2.096 Å. In keeping with this, there is a significant difference in the C=C bond lengths of coordinated olefin, with C(2)–C(3) at 1.397 Å, and C(7)–C(8) at 1.358 Å. This presents a very clear example of electronic effects that are evident in related structure determinations where one double-bond of an rhodium coordinated chelating olefin is *trans* to Cl and the other *trans* to P [23]. The olefinic group placed *trans* to the electronegative atom involves a shorter (and presumably stronger) bond to rhodium, the C–C distance is greater because of increased back-bonding [23]. Crystal data are presented in Tables 1–3.

Catalytic hydrogenation

At the outset of this work, the intention was to develop new catalysts for asymmetric synthesis. For hydrogenation, this is most effective when the reactant carries a polar group capable of binding to the metal during the course of the catalytic cycle [24]. Hence complexes **5** and **6** were employed in a brief survey of

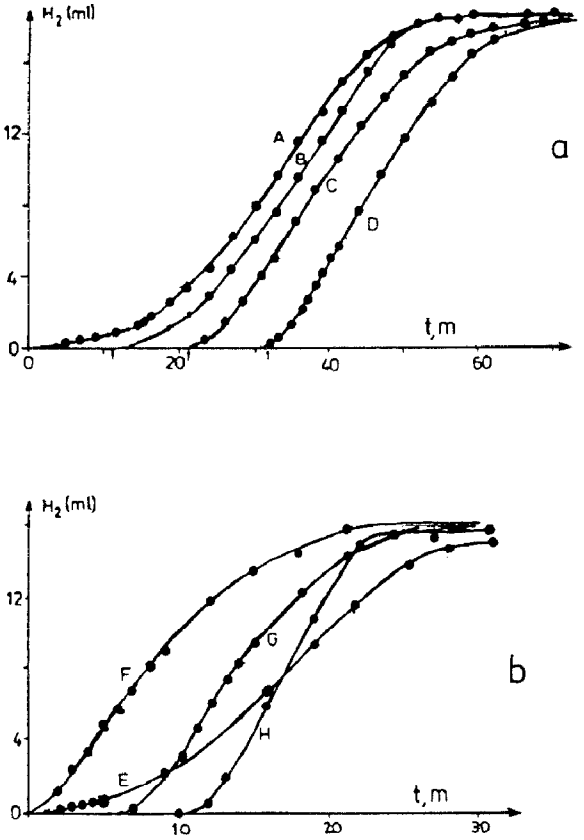


Fig. 2. Induction periods in hydrogenation with rhodium phosphinosulphoxide complexes. (a) Reduction of styrene; in A H_2 is present from the outset whilst in B, C, and D it is added 10, 21 and 31 minutes respectively after the onset of stirring. (b) Reduction of 1-decene; in E H_2 is present from the outset whilst in B, C and D it is added 2, 5 and 10 minutes after the onset of stirring. Conditions: <1 mmol olefin, 1 mol% complex **5**, MeOH.

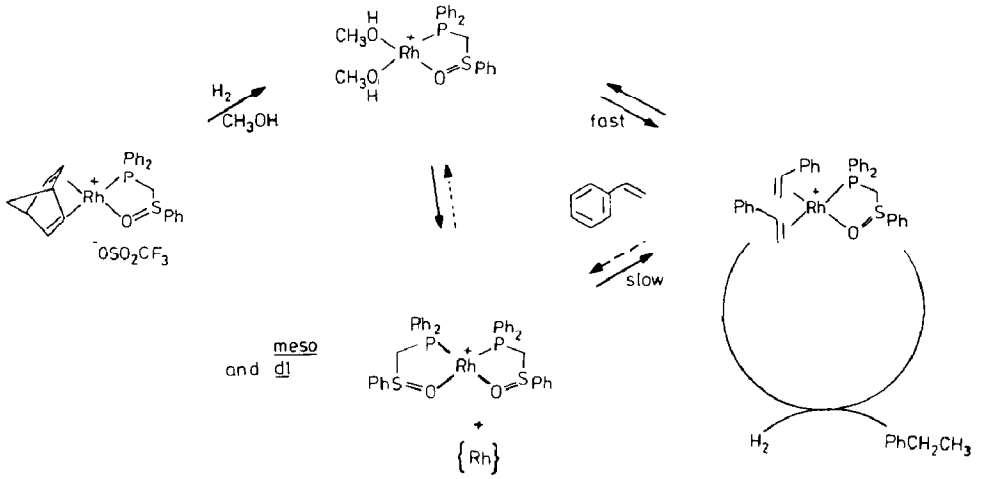


Fig. 3. Hydrogenation and disproportionation of rhodium phosphinosulphoxide complexes.

hydrogenations. It was immediately apparent that the most effective reaction occurs with hex-1-ene and styrene; polar functional groups suppress catalytic reactivity. For these simple olefins reduction occurs cleanly, with little evidence of the competing olefin isomerisation which is a problem with many phosphine or biphosphine-based cationic rhodium complexes.

It was noted that the rate of hydrogenation was time-dependent in the case of styrene, with a slow initial phase followed by a longer, linear, more rapid phase of gas uptake. When addition of the olefin to the catalyst solution is delayed, then the slow initial period is reduced (Fig. 2). This demonstrates that formation of the catalytically active species is rather slow. Similar behaviour was observed for hydrogenation of dec-1-ene, but the non-linear period was shorter and the rate-difference less marked.

These observations led us to carry out an NMR study of the reaction intermediates. When the optically active sulphoxide complex **7** was dissolved in MeOH and agitated under H_2 for 15 min at 20 °C, a single species was observed in the ^{31}P NMR spectrum, with parameters (δ 71.3 ppm, J(RhP) 204 Hz) characteristic of an intermediate with a P–Rh–O *trans*-ligation [25]. Under similar conditions the ^1H NMR spectrum of the product of hydrogenation of complex **7** in CD_3OD showed, inter alia, an AB quartet due to S–CH_2 (δ 5.00, 4.28 ppm. J(HCH′) 14, J(PCH′) 5 Hz). Traces of a second compound were apparent. The corresponding racemic sulphoxide complex **5** gave two products in comparable proportions on hydrogenation in CH_3OH (δ 70.4 ppm J(RhP) 202 Hz, and δ 71.1 ppm, J(RhP) 204 Hz). Similarly, when the reaction was monitored by ^1H NMR spectroscopy in CD_3OD then two S-CH_2 residues were observed, one similar to that from the sample above and a second (δ 4.63, 4.48 ppm; J(HCH′) 14, J(PCH′) 4 Hz) of comparable intensity corresponding to the trace impurity observed earlier. An essentially identical ^{31}P NMR spectrum was observed when bis(norbornadiene)Rh^+ BF_4^- was treated in CH_3OH with two equivalents of the racemic phosphinosulphoxide **1**. The two related compounds produced are therefore the *meso* and *dl* diastereomers of complex **8**. Although attempts to isolate and characterise this mixture were unsuc-

cessful, the FAB mass spectrum showed the expected peak at m/z 751. Results are consistent with the chemical transformations depicted in Fig. 3.

In summary, these experiments demonstrate the feasibility of forming chelate complexes from β-phosphinosulphoxides. Although the rhodium complexes prepared here possess catalytic reactivity in hydrogenation, their application is complicated by a disproportionation reaction; the resulting bis-ligand complex may be the catalytically active species.

Experimental section

Solvents were freshly distilled from standard drying agents [26]. All reactions were carried out by use of vacuum-line techniques in Schlenk tubes under an inert atmosphere. Melting-points were determined using a Reichert–Koffler block and are corrected. Optical rotations were recorded on a Perkin–Elmer 241 polarimeter, Microanalyses were performed in our laboratory by Mrs. V. Lamburn.

Infrared spectra were recorded using Perkin–Elmer 781 and 1750 spectrometers. Mass spectra were recorded on Varian CH7, ZAB 1F and VG Micromass 16F spectrometers. NMR spectra were recorded at 300 MHz (^{1}H) on a Bruker WH-300 machine, and ^{31}P spectra at 101.2 MHz on a Bruker AM 250 machine.

Diphenyl(phenylthiomethyl)phosphine

Prepared by Sanger's method [9a], m.p. 86–87 °C δ(H) (300 MHz; $CDCl_3$) 3.55 (2 H, d, J(PCH) 4 Hz, CH_2) and 7.22–7.52 (15 H, m, Ph); δ(P) (101 MHz; CH_2Cl_2) −22.0 (s); m/z (EI): 308 (M^+, 18%), 262 ($C_{18}H_{15}P^+$, 41), 199 ($C_{13}H_{12}P^+$, 92), 183 ($C_{12}H_8P^+$, 32), 121 ($C_78H_6P^+$, 100), 77 ($C_6H_5^+$, 42) and 51 ($C_4H_3^+$, 35).

Diphenyl(phenylthiomethyl)phosphine oxide

This was prepared as described by Grayson and Warren [9b] as white crystals (3.68 g, 67.2%), m.p. 105–107 °C (lit. [72] 106–107 °C); ν_{max} (KBr disc) 1185 cm^{-1} (P=O); δ(H) (300 MHz; $CDCl_3$) 3.73 (2 H, d, J 10 Hz, CH_2) and 7.15–7.85 (15 H, m, Ph); δ(P) (101 MHz; CH_2Cl_2) 23.5 (s); m/z (EI) 324 (M^+, 17%), 215 ($C_{13}H_{12}OP^+$, 29), 201 ($C_{12}H_{10}OP^+$, 100), 183 ($C_{12}H_8P^+$, 12), 123 ($C_6H_4OP^+$, 19), 110 ($C_6H_7P^+$, 20), 77 ($C_6H_5^+$, 60) and 51 ($C_4H_3^+$, 42).

Diphenyl(phenylsulphinylmethyl)phosphine oxide

Diphenyl(phenylthiomethyl)phosphine oxide (628 mg, 1.93 mmol), was added in one portion to a solution of sodium periodate (435 mg, 2.03 mmol, 1.05 equiv.) in a mixture of H_2O (25 ml) and THF (10 ml) at 0 °C. The suspension was allowed to warm to room temperature (1.5 h) and stirred at ambient temperature until the reaction was complete as indicated by TLC (93 h), and CH_2Cl_2 (15 ml) then added to the mixture. The layers were separated and the aqueous fraction was saturated with NaCl and extracted with CH_2Cl_2 (2 × 10 ml). The combined organic extracts were washed with saturated aqueous NaCl solution (15 ml) then dried (Na_2SO_4), filtered, evaporated and dried in vacuo to give diphenyl(phenylsulphinyl)phosphine oxide (518 mg, 69%), m.p. 151–152 °C (Found: C, 66.8; H, 5.05; P, 8.9; S, 9.3: $C_{19}H_{17}O_2PS$ calcd.: C, 67.04; H, 5.03; P, 9.10; S, 9.42%); ν_{max} (KBr disc) 1196 (P=O) and 1040 cm^{-1} (S=O); δ(H) (300 MHz; $CDCl_3$) 3.70 (1 H, dd, J(HCH′) 6.75 Hz, C*H*H′), 3.90 (1 H, dd, J(PCH) 5.25 Hz, J(HCH′) 6.75 Hz, CH*H*′) and

7.32–7.82 (15 H, m, Ph); δ(P) (101 MHz, THF) 19.3 (s); *m/z* (DCI/NH_3) 341 ($M^+ + 1$, 100%), 325 ($C_{19}H_{18}OPS^+$, 74), 217 ($C_{13}H_{14}OP^+$, 71), 203 ($C_{12}H_{12}OP^+$, 23) and 201 ($C_6H_{10}OP^+$, 10).

Diphenyl(phenylsulphinylmethyl)phosphine

Methyl phenyl sulphoxide was prepared Drabowicz, Midura, and Mikolajczyk's method [27], m.p. 31°C (lit. [27] 28–30°C). Methyllithium (1.24 *M* in Et_2O, 4.43 ml, 5.49 mmol, 1.1 equiv.) dropwise during 20 min to a colourless solution of the sulphoxide (0.700 g. 4.99 mmol) in thf (20 ml) at −78°C. The pale yellow solution was stirred at −78°C for 1 h and a precooled solution of chlorodiphenylphosphine (1.21 g, 0.99 ml, 5.49 mmol, 1.1 equiv.) in thf (30 ml) then added dropwise during 15 min. The pale yellow solution was stirred under argon at −78°C for 2 h and then allowed to warm to room temperature during 20 min. Degassed CH_2Cl_2 (10 ml) and saturated aqueous NH_4Cl solution (10 ml) were added and the layers separated. The aqueous fraction was extracted with CH_2Cl_2 (10 ml) and the organic extracts combined and evaporated to leave a crude cream liquid (3.04 g). TLC with 60% EtOAc in light petroleum (b.p. 30–40°C) as eluent, showed two main spots (both of which were UV and I_2 positive) at R_f 0.43 and 0.35, in addition to material with a longer retention time. The mixture was purified by flash column chromatography (16 × 13 cm of packed silica, degassed 40% EtOAc in light petroleum (b.p. 30–40°C) eluent, 15 ml fractions, pressure applied using a N_2 cylinder). Fractions 23–36 contained only the product and were evaporated to give a colourless oil. This solidified when kept under vacuum for several days, to give diphenyl[(phenylsulphinyl)methyl phosphine as a white powder (400 mg, 25%) m.p. 72–73°C, (Found: C, 70.2; H, 5.50; P, 9.4; S, 10.2. $C_{19}H_{17}OPS$ calc.: C, 70.35; H, 5.28; P, 9.55; S, 9.88%); ν_{max} (KBr disc) 1040 cm^{-1} (S=O); δ(H) (300 MHz; $CDCl_3$) 3.67 (1 H, dd, *J*(HCH) 1.4 Hz, C*H*H′) 3.77 (1 H, dd, *J*(HCH′) 13.2 Hz, *J*(PCH) 1.2 Hz, CH*H*′), 7.30–7.49 (13 H, m, Ph) and 7.67 (2 H, m, Ph); δ_P (101 MHz, CH_2Cl_2) −32.8 (s); *m/z* (DCI/NH_3) 523 ($M^+ + 199$, combination ion, 26%), 325 ($M^+ + 1$, 100) and 199 ($C_{13}H_{12}P^+$, 56).

Addition of a few crystals of I_2 to a solution of the product in CH_2Cl_2 caused isomerisation to diphenyl(phenylthiomethyl)phosphine oxide; δ(P) (101 MHz; CH_2Cl) 23.9 (s).

R-(+)-Diphenyl(4-methylphenylsulphinylmethyl)phosphine

R-(+)-Methyl *p*-tolyl sulphoxide was prepared from *S*-(−)menthyl *p*-toluenesulphinate [11] and MeMgBr in Et_2O/thf at −30°C [12]. A colourless solution of (*R*)-(+)-methyl *p*-tolyl sulphoxide (700 mg, 4.54 mmol) in thf (5 ml) was added dropwise during 10 min to a solution of LDA (4.77 mmol, 1.05 equiv.) in THF (5 ml) cooled to −78°C. The resultant yellow solution was stirred at −78°C under argon for 45 min and a solution of $ClPPh_2$ (1.05 g, 0.86 ml, 4.77 mmol, 1.05 equiv.) in thf (10 ml), cooled to −78°C, was then added during 15 min. The yellow solution was stirred −78°C for 100 min then warmed to room temperature and reduced in volume to ca. 7 ml, and CH_2Cl_2 (3 ml) and saturated aqueous NH_4Cl solution (5 ml) were then added. The layers were separated and the aqueous fraction extracted with CH_2Cl_2 (10 ml). The combined organic extracts were evaporated to dryness and the mixture purified by anaerobic flash column chromatography (18 × 4 cm of packed silica, degassed 40% EtOAc in light petroleum (b.p. 30–40°C)

eluent, 15 ml fractions, pressure applied using a N_2 cylinder). Fractions 39–58 contained product and were evaporated and kept in vacuo for several days to give (*R*)-(+)-diphenyl{[(4-methylphenyl)sulphinyl]methyl}phosphine as a white powder (356 mg, 23.1%), m.p. 91–92°C, (Found: C, 70.6; H, 5.9; P, 8.9; S, 9.1. $C_{20}H_{19}OPS$ calc.: C, 70.98; H, 5.66; P, 8.9; S, 9.1%); $[\alpha]_D^{20}$ +64.4 (*c* 1.0 in MeOH); ν_{max} (KBr disc) 1048 cm^{-1} (S=O); δ(H) (300 MHz; $CDCl_3$) 2.39 (3 H, s, CH_3), 3.66 (1H, dd, *J*(HCH′) 13 Hz, *J*(PCH) 2 Hz, C*H*H′), 3.78 (1 H, dd, *J*(HCH′) 13 Hz, *J*(PCH) 1 Hz, CH*H*′), 7.21-7.45 (12 H, m, Ar) and 7.55 (2 H, d, *J* 9 Hz, Ar); δ_P (101 MHz; CH_2Cl_2) −33.1 (s); *m/z* (EI) 338 (M^+, 9%), 199 ($C_{13}H_{12}P^+$, 84), 183 ($C_8H_8OPS^+$, 16), 137 ($C_7H_5OS^+$, 11), 121 ($C_7H_6P^+$, 100), 91 ($C_7H_7^+$, 24) 77 ($C_6H_5^+$, 26), 65 ($C_5H_3^+$, 13) and 51 ($C_4H_3^+$, 13).

Addition of a few crystals of I_2 to a solution of the product in CH_2Cl_2 caused isomerisation to diphenyl[(4-methylphenyl)thiomethyl] phosphine oxide, $Ph_2P(O)$-CH_2STol, δ(P) (101 MHz; CH_2Cl_2) 23.9 (s).

Addition of Kagan's shift reagent (16.9 mg, 500 μmol) to a solution of product (16.9 mg, 500 μmol) in $CDCl_3$ (500 μl) did not cause splitting of AB quartets due to the diastereomeric methylene protons, indicating that the product was optically pure. In confirmation, ^1H NMR analysis of a mixture of equimolar (500 mmol) amounts of shift reagent and achiral phosphinosulphoxide in $CDCl_3$ (500 μl) showed doubling of the resonances due to the methylene protons.

[(2,3,5,6-η)-(Bicyclo[2.2.1]hepta-2,5-diene][P,O-diphenyl(phenylsulphinylmethyl)phosphine]rhodium(I) tetrafluoroborate

A colourless solution of $Ph_2CH_2S(O)Ph$ (59.1 mg, 182 μmol) in THF (1 ml), precooled to −78°C, was added dropwise to a solution of $(nbd)_2RhBF_4$ [28] (68.1 mg, 182 μmol) in THF (2 ml) precooled to −78°C. The resultant golden-brown solution was stirred at −78°C for 1.5 h and then transferred by cannula to vigorously stirred Et_2O (40 ml) precooled to 0°C. Solvent was removed by filtration and the yellow precipitate washed with Et_2O (15 ml). The product was dried in vacuo and obtained as a dull orange powder (82.9 mg, 75.1%), m.p. > 190°C, δ(H) (300 MHz; $CDCl_3$) 1.63 (2H, s, H(7) of diene), 4.13 (2H, s, H(1), H(4) of diene), 4.38 (1H, dd, *J*(HCH) 16 Hz, *J*(PCH) 2 Hz, PC*H*H′), 4.68 (1 H, dd, *J*(HCH) 16 Hz, *J*(PCH) 9 Hz, CH*H*′) and 7.17–7.67 (15 H, m, Ph); δ(P) (101 MHz; CH_2Cl_2) 44.8 (d, *J*(RhP) 181 Hz); *m/z* (FAB) 519 (M^+).

[(2,3,5,6-η)-(Bicyclo[2.2.1]hepta-2,5-diene][P,O-diphenyl(phenylsulphinylmethyl)phosphine]rhodium(I) trifluoromethanesulphonate

$Me_3SiOSO_2CF_3$ (89.4 mg, 77.7 μl, 402 μmol) was added to a yellow solution of (nbd)Rh(acac) (118 mg, 402 μmol) in THF (5 ml). The yellow-orange solution was stirred under argon for 5 min and solid $Ph_2CH_2S(O)Ph$ (131 mg, 402 μmol) then added in one portion. The solution colour changed briefly to orange before a yellow precipitate separated, to leave an orange mother-liquor. The suspension was stirred at ambient temperature for 1 h and then added to vigorously-agitated hexane (50 ml). Most of the liquid was removed by cannula and further hexane (10 ml) then added. The precipitate was filtered off and dried, to give [(2,3,5,6-η)-(bicyclo[2.2.1]hepta-1,5-diene][*P,O*-diphenyl(phenylsulphinylmethyl)phosphine]rhodium(I) trifluoromethanesulphonate as a dull orange powder (244 mg, 91%), m.p. 96–97°C, (Found: C, 48.7; H, 4.35; P, 4.7; S, 10.0. $C_{27}H_{25}F_3O_4PRhS_2$ calcd.: C,

48.51; H, 3.77; P, 4.63; S, 9.59%); ν_{max} (KBr disc) 3068(w), 2940(w), 1695(m), 1641(m), 1588(m), 1572(m), 1478(m), 1462(m), 1433(m), 1278(m), 1249(s), 1223(s) 1.158(s), 1141(m), 1101(m), 1076(m), 998(m) 808(m), 755(m), 712(m), 696(m) and 638(s) cm^{-1}; δ(H) (300 MHz; $CDCl_3$) 1.63 (2 H, s, H(7) of diene), 4.14 (2 H, br s, H(1), H(4) of diene), 4.37 (1 H, dd, J(HCH) 15 Hz, J(PCH) 3 Hz, PC*H*H′), 4.52 (1 H, dd, J(HCH) 15 Hz, J(PCH) 9 Hz, PCH*H*′) and 7.18–7.69 (15 H, m, Ph); δ(P) (101 MHz; CH_2Cl_2) 46.8 (d, J(RhP) 181 Hz); m/z (FAB) 519 (M^+). Recrystallisation of complex **5** from THF/Et_2O gave orange-red blocks, suitable for X-ray analysis (vide infra).

[(1,2,5,6-η)-(Cycloocta-1,5-diene[*P*,*O*-diphenyl(phenylsulphinylmethyl)phosphine]rhodium(I) trifluoromethanesulphonate was prepared in the same manner in 58% yield as a yellow-orange powder, m.p. 63–67°C, ν_{max} (KBr disc) 3056(w), 2916(w), 2.868(w), 2826(w), 1436(m), 1267(br, s), 1221(m), 11433(br, m), 1096(m), 1058(s), 942(m), 746(m), 689(m) and 633 cm^{-1} (s); δ(H) (300 MHz; $CDCl_3$) 1.60–2.73 (8 H, m, CH_2 of diene), 3.26 (1 H, br s, =CH *trans* to O), 3.689 (1 H, br s, =CH′ *trans* to O), 4.59 (1 H, dd, J(HCH) 15 Hz, J(PCH) 10 Hz, PC*H*H′), 4.73 (1 H, dd, J(HCH) 15 Hz, J(PCH) 3 Hz, PCH*H*′), 5.73 (2 H, br s, =CH *trans* to P) and 7.19–7.71 (15 H, m, Ph); δ(P) (101 MHz; CH_2Cl_2) 51.6 (d, J(RhP) 165 Hz; m/z (FAB) 535 (M^+).

[(1,2,5,6-η)bicyclo[2.2.1]hepta-2,5-diene][*P*,*O*-diphenyl-(*R*)-4-methylphenylsulphinylmethyl)phosphine]rhodium(I) trifluoromethanesulphonate was prepared by the same method in 94% yield as an orange powder, m.p. 56–58°C; ν_{max} (KBr disc) 3056(w), 2950(w), 2920(w), 2844(w), 1433(m), 1278(br, s), 1257(br, s), 1222(m), 1157(br,m), 1098(m), 1028(s), 742(m), 691(m), and 638 cm^{-1} (s); δ(H) (300 MHz; CD_2Cl_2) 1.57 (2 H, s, H(7) of diene), 2.30 (3 H, s, CH_3), 4.07 (2 H, s, H(1), H(4) of diene), 4.19 (2 H, d, J(PCH) 6 Hz, PCH_2) and 7.17–7.67 (14 H, m, Ar); δ(P) (101 MHz; CH_2Cl_2) 435.9 (d, J(RhP) 181 Hz); m/z (FAB) 533 (M^+).

Attempted synthesis of bis[P,O-diphenyl(R)-4-methylphenylsulphinylmethyl)phosphine]-rhodium trifluoromethanesulphonate

A solution of the ligand (10.1 mg, 31.1 μmol) in THF (0.5 ml), precooled to −78°C, was added dropwise to a deep-red solution of (norbornadiene)rhodium-(ligand) complex (20.8 mg, 31.1 μmol) in THF (0.5 ml) at −78°C. The orange solution was stirred at this temperature for 20 min, allowed to warm to room temperature during 10 min, and then transferred to an 8 mm NMR tube. The ^{31}P NMR spectrum of the mixture showed a major signal at 69.4 ppm (d, J(RhP) 204 Hz) and small signals from impurities at 19.1(s) and 30.5(s) ppm.

General procedure for hydrogenation of alkenes

The following description is representative: a yellow solution of complex (7.7 mg, 12.7 μmol, 1 mol%) and dec-1-ene (240 μl, 178 mg, 1.27 mmol) in THF (6 ml) was cooled to −78°C then evacuated and saturated with hydrogen three times. The yellow-orange solution was allowed to warm to room temperature under a positive pressure of hydrogen. The mixture was connected to a calibrated burette, stirring begun, and the rate of hydrogen uptake monitored. After the required amount of hydrogen had been absorbed the mixture was added to an excess (30 ml) of ether, and the resulting precipitate filtered off, and the filtrate evaporated to dryness. No starting material was detected by ^1H NMR spectroscopy or GLC.

X-ray procedure

Data were collected with a Syntex P2 four-circle diffractometer. Maximum 20–50°, with approximately half the possible reflections in the 50–55° range, scan range ±0.85° (2θ) around the $K_{\alpha 1}$–$K_{\alpha 2}$ angles, scan speed 5–9° min^{-1} depending on the intensity of a 2s pre-scan; backgrounds measured at each end of the scan for 0.25 of the scan time. *hkl* ranges: −12 to 12°, 0 to 21°, 0 to 24°. Three standard reflections were monitored every 200 reflections and showed slight changes during data collection; data were rescaled to correct for this. The density was measured by flotation. Unit cell dimensions and standard deviations were obtained by least squares fit to 15 reflections ($28° < 2\theta > 30°$).

Reflections were processed using profile analysis to give 6863 unique reflections ($R_{int} = 0.020$); 4809 considered observed ($I/\sigma(I) > 3.0$) and used in refinement; these were collected for Lorentz, polarisation and absorption effects, the last with ABSCOR [28]; maximum and minimum transmission factors 0.81 and 0.76. Crystal dimensions $0.4 \times 0.63 \times 0.53$ mm with bounding faces {011} {100}. Systematic absences $h0l$, $l \neq 2n$, $0k0$, $k \neq 2n$, indicating space group $P2_1/c$.

Heavy atoms were located by the Patterson interpretation section of SHELXTL and the light atoms were then found on successive Fourier syntheses, including one molecule of solvent THF. Anisotropic temperature factors were used for all non-H atoms. Hydrogen atoms were given fixed isotropic temperature factors, $U = 0.07$ Å^2 inserted at calculated positions and not refined apart from H(2), H(3), H(7) and H(8). Final refinement was on F by cascaded least squares methods; largest positive and negative peaks on a final difference Fourier synthesis were of height +0.7 and −0.8 el. Å^{-3}.

A weighting scheme of the form $w = 1/(\sigma^2(F) + g^{F2})$ with $g = 0.0006$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.041$, $R_w = 0.046$. The maximum shift error in the final cycle was 0.07 computing was with SHELXTL [29] on a Data General DG 30, apart from absorption correction on a Burroughs B 6700. Scattering factors in the analytical form and anomalous dispersion factors were taken from International Tables (1974) [30]. Final atomic coordinates are shown in Table 2 and bond lengths and angles in Table 3a,b. Tables of thermal parameters and lists of observed and calculated structure factors are available from the authors.

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