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Synthesis of (4*S*,5*S*)-*trans*-4-(cyclopentadiene-1-methyl)-5-diphenylphosphine-2,2-dimethyl-1,3-dioxolane and the ferrocene derivative; *trans*-[Fe{ η-$C_5H_4CH_2[\overline{CHOC(CH_3)_2OCH}]CH_2PPh_2$ }$_2$]

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Abstract

The syntheses of the chiral cyclopentadiene compound (4*S*,5*S*)-*trans*-4-(cyclopentadiene-1-methyl)-5-diphenylphosphine-2,2-dimethyl-1,3-dioxolane (**4**) and of the related ferrocenylphosphine derivative *trans*-[Fe{ η-$C_5H_4CH_2[\overline{CHOC(CH_3)_2OCH}]CH_2PPh_2$ }$_2$] (**5**) are described.

A large number of chiral chelating phosphine ligands are known [1], such as Kagan's DIOP (**3**) [2]. However there are few examples of chelate ligands in which there is a cyclopentadienyl group which is coupled to a two-electron ligand at the end of an hydrocarbon chain; an example is [η-$C_5H_4(CH_2)_4AsPh_2$] [3,4]. Up to now there have been no chiral compounds in this class. We report here the synthesis of a novel chelating chiral ligand, η-C_5H_4(chiral unit)-PR_2.

Results and discussion

Treatment of the previously described ditosylate (**1**) [5] with one equivalent of $NaPPh_2$ in THF under reflux for 6 h gave a mixture of the optically active compounds **2** and **3**, which were separated by column chromatography, in 27.5 and 8% yields, respectively. Treatment of **2** with one equivalent of $Na^+C_5H_5^-$ in THF under reflux for 4 h gave the compound **4**, as a mixture of the 2 and 3 isomers, in 47% yield. The addition of n-BuLi (one equivalent) to **4** is assumed to produce the lithium salt, since the product mixture reacts with $FeCl_2$ to give the chiral ferrocenyl derivative **5** in 70% yield.

The compounds **2**, **4**, and **5** have been characterised by micro-analysis, mass spectra, ^{13}C and ^{31}P NMR spectra, and, in the cases of **4** and **5**, by [^1H–^1H] COSY 2-dimensional NMR experiments, the results of which are summarised in the Tables

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Table 1

^{1}H NMR data for compound **4** in $CDCl_3$

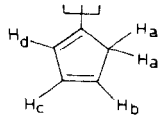
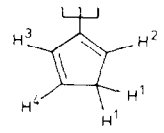
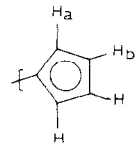
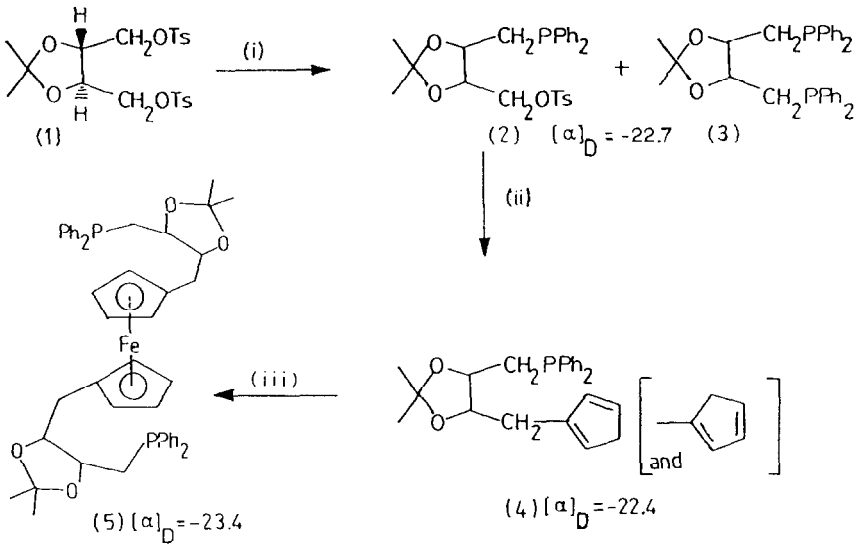
δ (ppm)	Assignment	
1.37(s), 1.42(s)	$4CH_3$	
3.78(m)	$2CHCH_2PPh_2$	
4.05(m)	2CH	
2.29(m)	$2CH_2PPh_2$	
2.71(m)	$2CH_2$	
2.7(m)	$2H_a$,$2H^1$	
6.4(m)	H_b,H_c,H^3	
6.0(m)	H_d	
6.1(m)	H^2	
6.3(m)	H^4	
7.33(m), 7.41(m)	2Ph	

Table 2

^{1}H NMR data for compound **5** in $CDCl_3$

δ (ppm)	Assignment	
1.3(s), 1.4(s)	$2CH_3$	
3.70(m)	$CHCH_2PPh_2$	
3.86(m)	CH	
2.16(m)	CH_2PPh_2	
2.60(m)	CH	
7.32(m), 7.39(m)	2Ph	
3.87(m)	$2H_a$	
3.94(m)	$2H_b$	



Scheme 1. For clarity hydrogens at the chiral centers are omitted after the first indication. (i) $NaPPh_2$ in THF at reflux for 6 h (27%). (ii) NaCp in THF at reflux for 4 h (58%). (iii) n-BuLi (1/1) in diethyl ether, at r.t. for 30 min, then $FeCl_2$ in THF at r.t., for 1 h (70%).

1 and 2. On the basis of the data we propose the structures for **4** and **5** shown in Scheme 1.

Compound **5** is related to a group of functionalised ferrocenyl phosphines that have been utilised in asymmetric synthesis [6], although these suffer from the disadvantage of requiring resolution during their preparation. In addition, compound **2** can be regarded as a potential intermediate for the synthesis of a series of chiral chelate ligands of the type *trans*-η-(polyene)-$CH_2[\overline{CHOC(CH_3)_2OCH}]CH_2L$.

Experimental

All reactions were carried out under dry nitrogen by standard Schlenk techniques. Subsequent manipulations were carried out in air. Tetrahydrofuran was dried over sodium benzophenone ketyl and distilled. Preparative column chromatography was performed with alumina (grade 3). (*R*,*R*)-(−)-1,4-Di-tosyl-2,3-isopropylidene-L-threitol (**1**) was prepared by the published procedure [5].

Preparation of 2

Sodium diphenylphosphide (10.9 g, 53 mmol) in THF (50 cm^3) was added dropwise during 20 min to a stirred solution of the ditosylate **1** (20 g, 42 mmol) in THF (50 cm^3). The mixture was refluxed for 6 h, then added to ice/water, and the product extracted into diethyl ether. The extract was dried over magnesium sulphate and transferred onto an alumina column. Elution with 10% ethyl acetate in petroleum ether (b.p. 40–60 °C) gave compound **3** 1.7 g (8%), closely followed by compound **2** 5.7 g (28%). Compound **3** was characterised by analysis and comparison of its ^1H NMR spectrum with published data. **3**: Analysis, found: C, 64.0; H, 6.1. $C_{26}H_{29}O_5PS$ calc: C, 64.4; H, 6.0%. ^1H NMR (250 MHz, $CDCl_3$, chemical shift in δ, ppm), 1.26 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 2.43 (s, 3H, CH_3-tolyl), 2.37 (m, 2H, CH_2-P), 3.93 (m, 1H, CH), 4.02 (m, 1H, CH), 4.14 (m, 2H, CH_2-O), 7.40 (m, 10H, 2Ph) and 7.35, 7.77 (d, 4H, tolyl).

Preparation of 4

A solution of sodium cyclopentadienide (3.2 g, 36 mmol) in THF (50 cm^3) was added dropwise to a stirred solution of **2** (3.5 g, 8 mmol) in THF (75 cm^3). The mixture was refluxed for 4 h then added to water. The product was extracted into diethyl ether (2 × 100 cm^3) and the extract was dried over magnesium sulphate then transferred to an alumina column. Elution with 10% ethyl acetate in petroleum ether (b.p. 40–60 °C) followed by rigorous removal of solvent at reduced pressure gave compound **4**, 1.7 g (58%). ^{31}P NMR data (101.1 MHz, $CDCl_3$, chemical shift in δ, ppm), −26.3, −26.63. Analysis, found: C, 77.2; H, 7.76. $C_{24}H_{27}O_2P$ calc: C, 76.2; H, 7.2%. *m/e* data, M^+ (378).

Preparation of the lithium salt of 4

A hexane solution of n-BuLi (0.35 cm^3, 1.6 *M*, 0.6 mmol) was added dropwise, with stirring, to a cooled solution (−20 °C) of **4** (214 mg, 5.7 mmol) in diethyl ether (10 cm^3). The mixture was stirred for 30 min then allowed to warm to r.t. The solvent was removed under reduced pressure and the resulting pale yellow solid used as such for further reactions.

Preparation of **5**

A solution of the lithium salt (1.5 mmol) in THF (50 cm^3) at 0 °C was added during 20 min to a stirred solution of $FeCl_2$ (50 cm^3, 140 mg) in THF (50 cm^3). After 1 h the solvent was removed from the yellow solution and the residue chromatographed on alumina. Elution with 10% ethyl acetate in petroleum ether (b.p. 40–60 °C) yielded **5** (415 mg, 70%). ^{31}P NMR data (101.1 MHz, $CDCl_3$ chemical shift in δ, ppm), −26.2. *m/e* data, M^+ (810, FAB).

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