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Half-sandwich complexes of ruthenium, rhodium and iridium with a chiral bisphosphine monoselenide

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Abstract

Monoselenation of the chiral bisphosphine (*S*)-(+)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyldi-*t*-butylphosphine gives the first enantiomerically pure chiral bisphosphine monoselenide prepared from a commercially available chiral bisphosphine. This bisphosphine monoselenide ligand is an effective chelating ligand that utilizes a [P,Se] donor set when forming chelates with half-sandwich complexes of ruthenium(II), rhodium(III) and iridium(III). These complexes have been characterised spectroscopically and, in some cases, crystallographically. The chirality of the ligand influences and controls the metal-centred chirality yielding one of two possible chelate complexes with high diastereoselectivity.

Keywords: Bisphosphine monoselenide; Chiral metal complexes; Heterobidentate ligands

1. Introduction

There has been much interest recently in the co-ordination chemistry of bisphosphine monoxide ligands (BPMOs) [1–8]. The co-ordination of such heterobidentate ligands to [(arene)MX] fragments gives rise to half-sandwich complexes that are chiral at the metal centre, such that the use of chiral BPMOs leads to the formation of diastereomeric complexes [9–11]. The use of chiral BPMOs has been advanced by the publication of an excellent general route to such ligands from commercial chiral bisphosphines [12,13].

Bisphosphines may also be monoxidised by other chalcogens, and there is an extensive literature relating to the preparation and co-ordination chemistry of phosphine sulfides and selenides [8,14]. There are few examples, however, of chiral bisphosphine monosulfides and selenides analogous to the chiral BPMOs [15,16]. As part of a continuing program of research in this area, we report the first synthesis of a chiral bisphosphine monoselenide prepared by direct selenation of a commercially available chiral bisphosphine along with some of its monodentate and chelate complexes.

2. Experimental

2.1. General procedures

The synthesis of **1**–**7** was carried out under an atmosphere of dry nitrogen. All reagents were obtained commercially and used as received except $[CyRuCl_2]_2$ [17] and $[Cp^*MCl_2]_2$ (M = Rh, Ir) [18] which were prepared by literature methods. Solvents were dried and distilled prior to use. The ^1H- and ^{31}P-NMR spectra were measured using a GE Omega 500 or Bruker AM250 spectrometer. Chemical shifts are reported relative to the residual protio peaks of the deuterated solvent (^1H) or external 85% H_3PO_4 (^{31}P). Coupling constants are given in Hz.

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2.2. Preparation of (S)-(+)-1-[(R)-2-(diphenylphosphino)ferrocenyl]ethyldi-t-butylphosphine monoselenide (1)

To a solution of (*S*)-(+)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyldi-*t*-butylphosphine (500 mg, 0.92 mmol) in 25 ml of THF was added selenium (72 mg, 0.92 mmol). The mixture was stirred for 4 h, after which a clear orange solution was formed. The solvent was removed under reduced pressure and the residue extracted with 2 ml of methylene chloride. The extract was filtered through Celite and Et_2O added to the filtrate until precipitation was complete. The yellow-orange microcrystalline product was collected, washed with Et_2O and dried under vacuum. Yield: 548 mg, 96%. ^{1}H-NMR (CD_2Cl_2, 293 K, δ), 8.01–7.20 (m, 10H, arom), 4.48 (m, 1H, Cp–H), 4.42 (m, 1H, Cp–H), 4.35 (m, 1H, Cp–H), 3.72 (s, 5H, Cp–H), 2.13 (dd, 3H, J = 15 and 8 Hz, C(H)CH_3), 2.05 (dq, 1H, J = 15 and 8 Hz, C(H)CH$_3$), 1.44 (d, 9H, J = 14 Hz, Bu^t), 1.02 (d, 9H, J = 14 Hz, Bu^t). ^{31}P{^{1}H} δ 88.0, ^1J(^{77}Se–^{31}P) = 699, P(V); δ −28.0, P(III). Anal. calc. for $C_{32}H_{40}FeP_2Se$: C, 61.80; H, 6.50. Found C, 61.75; H, 6.45%.

2.3. Preparation of (η^5-Cp*)Rh(κ^1-1-P)Cl$_2$ (2)

To a solution of [(η^5-Cp*)RhCl$_2$]$_2$ (100 mg, 0.16 mmol) in 25 ml of CH_2Cl_2 was added **1** (198 mg, 0.32 mmol). The reaction was stirred for 2 h during which time the solution developed a red colour. The solvent was removed under reduced pressure, the deep red solid residue extracted into 2 ml of CH_2Cl_2 and filtered through a Celite plug. Et_2O was added until precipitation of the brown microcrystalline solid was complete, and the product collected by filtration. Yield: 232 mg, 78%. ^{1}H-NMR (CD_2Cl_2, 293 K, δ), 7.93–7.26 (m,10H, arom), 4.51 (m, 1H, Cp–H), 4.39 (m, 1H, Cp–H), 4.28 (m, 1H, Cp–H), 3.64 (s, 5H, Cp–H), 2.54 (dq, 1H, J = 15 and 8 Hz, C(H)CH$_3$), 2.05 (dd, 3H, J = 15 and 8 Hz, C(H)CH_3), 1.57 (s, 15H, Cp*), 1.45 (d, 9H, J = 14 Hz, Bu^t), 0.90 (d, 9H, J = 14 Hz, Bu^t). ^{31}P{^{1}H} δ 89.0, ^1J (^{77}Se–^{31}P) = 696, P(V); δ 17.1 ^1J (^{103}Rh–^{31}P) = 140 Hz, P(III). Anal. calc. for $C_{42}H_{55}Cl_2FeP_2RhSe$: C, 54.15; H, 5.95. Found C, 54.15; H, 5.90%.

2.4. Preparation of (η^5-Cp*)Ir(κ^1-1-P)Cl$_2$ (3)

To a solution of [(η^5-Cp*)IrCl$_2$]$_2$ (127 mg, 0.16 mmol) in 25 ml of CH_2Cl_2 was added **1** (198 mg, 0.32 mmol). The reaction was stirred for 2 h during which time the solution turned orange-yellow. The solvent was removed under reduced pressure, the yellow solid residue extracted into 2 ml of CH_2Cl_2 and this solution was filtered through a Celite plug. Et_2O was added until precipitation of the yellow microcrystalline solid was complete, and the product collected by filtration. Yield: 299 mg, 92%. ^{1}H-NMR ($CDCl_3$, 293 K, δ), 8.20–7.05 (m, 10H, arom), 4.72 (m, 2H, Cp–H), 4.62 (m, 1H, Cp–H), 4.26 (s, 5H, Cp–H), 2.60 (m, 1H, C(H)CH$_3$), 1.55 (dd, 3H, J = 15 and 6 Hz, C(H)CH_3), 1.47 (d, 9H, J = 15 Hz, Bu^t), 1.23 (d, 15H, 2.5, Cp*), 0.98 (d, 9H, J = 15 Hz, Bu^t). ^{31}P{^{1}H} δ 85.8, ^1J (^{77}Se–^{31}P) = 603 Hz, P(V), δ −13.1, P(III). Anal. calc. for $C_{42}H_{55}Cl_2FeIrP_2Se$: C, 49.45; H, 5.45. Found C, 49.35; H, 5.50%.

2.5. Preparation of (η^6-Cy)Ru(κ^1-1-P)Cl$_2$ (4)

To a solution of [(η^6-Cy)RuCl$_2$]$_2$ (100 mg, 0.16 mmol) in 25 ml of CH_2Cl_2 was added **1** (198 mg, 0.32 mmol). The reaction was stirred for 2 h during which time the solution developed a deep red colour. The solvent was removed under reduced pressure, the deep red residue extracted into 2 ml of CH_2Cl_2 and this solution was filtered through a Celite plug. Et_2O was added until precipitation of the red microcrystalline solid was complete, and the product collected by filtration. Yield: 258 mg, 86%. ^{1}H-NMR ($CDCl_3$, 293 K, δ), 8.20–7.05 (m, 10H, arom), 5.47 (d, 1H, 5.5, Cy–H), 5.39 (d, 1H, 5.5, Cy–H), 4.92 (m, 2H, Cp–H), 4.88 (d, 1H, 5.5, Cy–H), 4.64 (m, 1H, Cp–H), 4.49 (d, 1H, J = 5.5 Hz, Cy–H), 4.26 (5H, s, Cp–H), 2.62 (1H, sept, J = 7 Hz, CH(CH$_3$)$_2$), 2.52 (1H, m, C(H)CH$_3$), 1.90 (3H, s, Cy–CH_3), 1.55 (3H, dd, J = 6.2 Hz, C(H)CH_3), 1.43 (9H, d, J = 15 Hz, Bu^t), 1.18 (3H, d, J = 7 Hz, CH_3C(H)CH$_3$), 1.10 (3H, d, J = 7 Hz, CH_3C(H)CH$_3$), 0.82 (9H, d, J = 15 Hz, Bu^t). ^{31}P{^{1}H} δ 86.7, ^1J (^{77}Se–^{31}P) = 694 Hz, P(V); δ 11.1, P(III). Anal. calc. for $C_{42}H_{45}Cl_2FeP_2RuSe$: C, 54.35; H, 5.90. Found C, 54.30; H, 5.80%.

2.6. Preparation of [(η^5-Cp*)Rh(κ^2-1-P, Se)Cl]SbF$_6$ (5)

To a solution of **2** (100 mg, 0.11 mmol) in 25 ml of CH_2Cl_2 was added $NaSbF_6$ (28 mg, 0.11 mmol). The reaction was stirred for 2 h during which time the solution colour darkened. The solvent was removed under reduced pressure, the red-brown solid residue was extracted into 2 ml of CH_2Cl_2 and this solution was filtered through a Celite plug. Et_2O was added until precipitation of the red microcrystalline solid was complete, and the product was collected by filtration. Yield: 106 mg, 85%. ^{1}H-NMR (CD_2Cl_2, 293 K, δ), 8.50 (br, 1H, arom), 7.91–7.55 (m, 9H, arom), 5.48 (dq, 1H, J = 16 and 6.5 Hz, C(H)CH3), 4.52 (br, 1H, Cp–H), 4.39 (br, 1H, Cp–H), 4.27 (br, 1H, Cp–H), 3.64 (s, 5H, Cp–H), 2.05 (dd, 1H, J = 16 and 6.5 Hz, C(H)CH$_3$), 1.58 (d, 9H, J = 15 Hz, Bu^t), 1.57 (s, 15H, Cp*), 1.40 (d, 9H, J = 15 Hz, Bu^t). ^{31}P{^{1}H} δ 86.4, ^1J (^{77}Se–^{31}P) = 605 Hz, P(V), δ 35.6, ^1J (^{103}Rh–^{31}P) = 137 Hz, P(III). Anal. calc. for $C_{42}H_{55}Cl_2F_6FeP_2RhSbSe$: C, 44.45; H, 4.90. Found C, 44.40; H, 4.85%.

2.7. Preparation of [(η^5-Cp*)Ir(κ^2-1-P, Se)Cl]SbF_6 (6)

To a solution of **3** (150 mg, 0.148 mmol) in 25 ml of CH_2Cl_2 was added $NaSbF_6$ (39 mg, 0.15 mmol). The reaction was stirred for 2 h during which time the solution lightened in colour. The solvent was removed under reduced pressure, the yellow solid residue extracted into 2 ml of CH_2Cl_2 and this solution was filtered through a Celite plug. Et_2O was added until precipitation of the yellow microcrystalline solid was complete, and the product collected by filtration. Yield: 142 mg, 78%. ^{1}H-NMR ($CDCl_3$, 293 K), 8.60 (br, 1H, arom), 7.62–7.26 (m, 9H, arom), 5.65 (dq, 1H, $J = 18.5$ and 7 Hz, C(H)CH_3), 4.58 (br, 2H, Cp–H), 4.52 (br, 1H, Cp–H), 3.68 (s, 5H, Cp–H), 2.09 (dd, 3H, $J = 16$ and 7 Hz, C(H)CH_3), 1.58 (d, 9H, $J = 15$ Hz, Bu^t), 1.42 (d, 9H, $J = 15$ Hz, Bu^t), 1.38 (s, 15H, Cp*). ^{31}P{^{1}H} δ 81.2, ^1J (^{77}Se–^{31}P) = 643 Hz, P(V), δ −3.7, P(III). Anal. calc. for $C_{42}H_{55}Cl_2F_6FeIrP_2SbSe$: C, 41.20; H, 4.55. Found C, 41.10; H, 4.40%.

2.8. Preparation of [(η^6-Cy)Ru(κ^2-1-P, Se)Cl]SbF_6 (7)

To a solution of **4** (100 mg, 0.11 mmol) in 25 ml of CH_2Cl_2 was added $NaSbF_6$ (28 mg, 0.11 mmol). The reaction was stirred for 2 h during which time the solution colour darkened. The solvent was removed under reduced pressure, the deep red-brown solid residue was extracted into 2 ml of CH_2Cl_2 and this solution was filtered through a Celite plug. Et_2O was added until precipitation of the red microcrystalline solid was complete, and the product collected by filtration. Yield: 106 mg, 85%. ^{1}H-NMR (CD_2Cl_3, 293 K, δ), 8.50 (1H, br, arom), 7.81–7.30 (m, 9H, arom), 5.62 (d, 1H, $J = 6$ Hz, Cy–H), 5.50 (d, 1H, $J = 6$ Hz, Cy–H), 5.45 (dq, 1H, $J = 15$ and 7.5 Hz, C(H)CH_3), 5.38 (d, 1H, $J = 6$ Hz, Cy–H), 5.24 (d, 1H, $J = 6$ Hz, Cy–H), 4.61 (br, 1H, Cp–H), 4.48 (br, 1H, Cp–H), 4.38 (br, 1H, Cp–H), 4.26 (s, 5H, Cp–H), 2.61 (hept, 1H, $J = 7$ Hz, CH(CH_3)$_2$), 1.96 (dd, 1H, $J = 7.5$ and 6 Hz, C(H)CH_3), 1.92 (s, 3H, CyCH_3), 1.66 (d, 9H, $J = 15$ Hz, Bu^t), 1.42 (d, 9H, $J = 15$ Hz, Bu^t), 1.11 (d, 3H, $J = 7$ Hz, CH_3C(H)CH_3), 0.67 (d, 3H, $J = 7$ Hz, CH_3C(H)CH_3). ^{31}P{^{1}H} δ 82.9, ^1J (^{77}Se–^{31}P) = 565 Hz, P(V), δ 28.8 P(III). Anal. calc. for $C_{42}H_{54}Cl_2F_6FeP_2RuSbSe$: C, 44.65; H, 4.80. Found C, 44.85; H, 4.80%.

2.9. X-ray structure determination of 3, 6′, and 7

Data were collected on a Nonius KappaCCD (Mo–K_α radiation) and corrected for absorption (SORTAV) [19]. The structure was solved by direct methods (SIR92) [20] and refined on F for all reflections using the TEXSAN crystallographic software package of Molecular Structure Corporation [21]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Relevant crystal and data parameters are presented in Table 1. Selected bond distances and angles are shown in Table 2.

The structure of compound **3** was determined at room temperature. Preparation of the perchlorate analogue of **6** [22] allowed a structure determination of **6′** which was performed at −90 °C. The perchlorate ion showed a disorder which was modeled with two rigid groups of tetrahedra of oxygen atoms. To obtain crystals suitable for crystallography, a sample of **7** was recrystallized from $CHCl_3$. The structure of **7** was determined at −90 °C but was complicated by having a monoclinic cell with a β angle near 90°; however, merging of 'equivalent' reflections in an orthorhombic system gave a $R_{int} = 51\%$ indicating that a monoclinic cell was indeed correct. The structure has two independent molecules in the unit cell and it also contains one independent $CHCl_3$ molecule. The absolute configurations were established by reference to the known absolute configuration of the ligand. This was confirmed in each case by observing increased R factors from anomalous dispersion when the coordinates were inverted: **3** corr. $R = 0.043$, $R_w = 0.049$; inv. $R = 0.060$, $R_w = 0.072$. **6′** corr. $R = 0.043$, $R_w = 0.046$; inv. $R = 0.078$, $R_w = 0.098$; **7** corr. $R = 0.036$, $R_w = 0.040$; inv. $R = 0.046$, $R_w = 0.054$.

3. Results and discussion

The interaction of (*S*)-(+)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyldi-*t*-butylphosphine with elemental selenium in a 1:1 mole ratio in THF gives the bisphosphine monoselenide **1**. The progress of the rapid reaction can be followed conveniently by the disappearance from the reaction mixture of the solid selenium. The product **1** is obtained in excellent yield and there is no evidence of the formation of either the other possible bisphosphine monoselenide or of the diselenide. The selectivity in the selenation presumably arises from the relative ease of oxidation of alkyl compared to aryl phosphines and the control of stoichiometry in the reaction, respectively.

Two equivalents of **1** react with [(arene)$MCl_2]_2$ in dichloromethane solution to give complexes of general formula (arene)M(κ^1**1**-*P*)Cl_2 (arene = Cp*, M = Rh **2**, Ir **3**; arene = cymene, M = Ru **4**), Scheme 1. Complexation is accompanied by a significant downfield shift of the ^{31}P{^{1}H} resonance associated with the P(III) terminus of the ligand indicating that initial co-ordination is through this phosphorus. This is expected, since the relative basicity of the free phosphine is greater than that of the phosphine selenide. The structure of complex **3** comprising monodentate **1** is shown in Fig. 1, with

Table 1
Crystallographic data for **3**, **6′** and **7**

	3	**6′**	**7**
Color, shape	orange, prism	orange, prism	red, plate
Empirical formula	$C_{42}H_{55}Cl_2FeIrP_2Se$	$C_{42}H_{55}Cl_2FeIrO_4P_2Se$	$C_{42}H_{54}ClF_6FeP_2RuSbSe.0.5CHCl_3$
Formula weight	1019.78	1083.77	1137.55
Radiation (Å)		Mo–K_α (monochr.) 0.71069	
Temperature (K)	296	183	183
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)
Unit cell dimensions			
a (Å)	9.4472(3)	10.6837(3)	11.7844(2)
b (Å)	22.5444(6)	13.5050(3)	20.0041(3)
c (Å)	19.2039(2)	29.1398(5)	19.7714(3)
β (°)	108.812(2)	90	90.0736(10)
V (Å^3)	2057.15(9)	4204.4(2)	4660.8(1)
Z	2	4	4
D_{calc} (g cm^{-3})	1.646	1.712	1.692
μ (cm^{-1})	7.14	46.25	22.48
Crystal size (mm)	0.12 × 0.12 × 0.24	0.07 × 0.12 × 0.24	0.04 × 0.14 × 0.17
Reflections, collected, unique	16897, 8896	14717, 5395	39930, 20249
R_{int}	0.072	0.076	0.051
Reflections observed [$I > 3\sigma(I)$]	3969	4345	7950
Parameters, constr	441, 0	462, 0	1026, 0
R [a], R_w [b], Goodness-of-fit	0.043, 0.049, 1.38	0.043, 0.046, 1.38	0.036, 0.040, 0.97
Resid. density (e Å^{-3})	−1.41 < 0.97	−1.30 < 1.92	−0.59 < 0.55

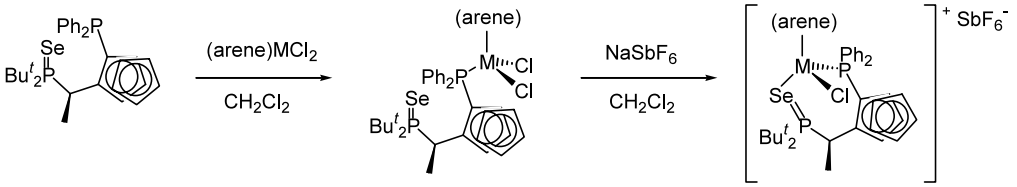
[a] $R = \Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$, for all $I > 3\sigma(I)$.
[b] $R_w = [\Sigma[w(|F_o|-|F_c|)^2]/\Sigma[w(F_o)^2]]^{1/2}$.

Table 2
Selected bond lengths and angles for complexes **3**, **6′**, and **7**

	3	**6′**	**7**	
Bond lengths (Å)				
M–Se(1)		2.526(1)	2.542 (1)	2.561(1)
M–P	2.359(3)	2.316(3)	2.346(2)	2.349(2)
M–Cl(1)	2.407(3)	2.420(2)	2.407(2)	2.349(2)
M–Cl(2)	2.382(3)			
P–Se	2.131(3)	2.179(3)	2.172(2)	2.185(2)
Bond angles (°)				
P–M–Se		88.87(7)	81.75(6)	82.76(6)
P–M–Cl(1)	93.2(1)	90.65(9)	85.91(8)	86.03(7)
P–M–Cl(2)	86.8(1)			
Cl(1)–M–Cl(2)	89.9(1)			
Se–M–Cl		104.13(7)	103.01(6)	104.20(5)
M–Se–P		116.84(8)	117.43(7)	116.37(7)

structure determination details given in Table 1 and metrical parameters in Table 2. The complexes comprising monodentate **1** are all quite stable, showing no propensity to form chelate complexes without prior abstraction of a chloro ligand.

Treatment of the monodentate complexes **2**–**4** with sodium hexafluoroantimonate in dichloromethane solution leads rapidly to the abstraction of a chloride from the complexes with concomitant chelation of **1**, giving the cationic complexes **5**–**7**, Scheme 1. In each case, chelation of **1** leads to the formation of a seven-membered metallacyclic ring illustrated in Scheme 1 and Figs. 2 and 3, the structures of the cations in **6′** and **7**. This chelation also gives rise to a new chiral centre at the pseudotetrahedral metal centre in each case, and therefore the possibility of diastereomers [23]. The cations in **6′** and **7** were both found by crystallography



arene = Cp*, M = Rh, **2**
arene = Cp*, M = Ir, **3**
arene = Cy, M = Ru, **4**

arene = Cp*, M = Rh, **5**
arene = Cp*, M = Ir, **6**
arene = Cy, M = Ru, **7**

Scheme 1.

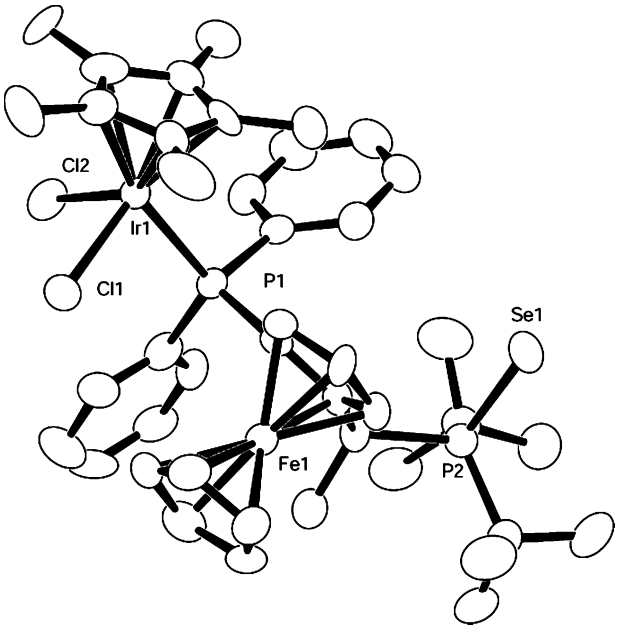


Fig. 1. ORTEP drawing of **3** with 50% probability ellipsoids.

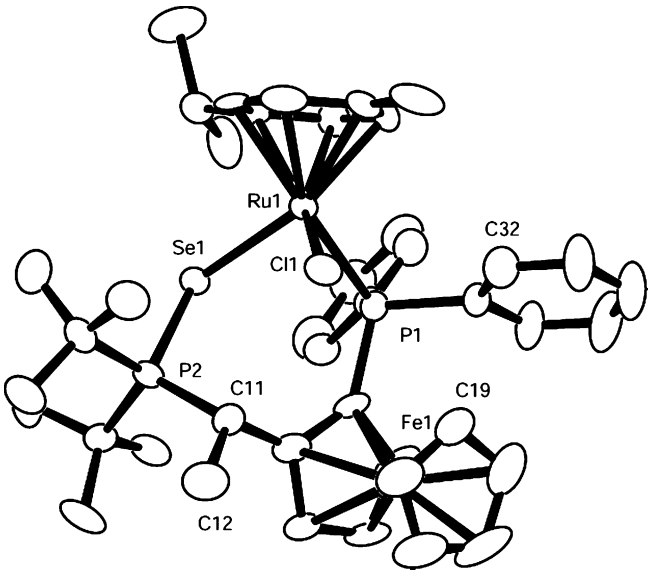


Fig. 3. ORTEP drawing of **7** with 50% probability ellipsoids. Only one of the two similar molecules in the unit cells is shown.

to have uniquely the (*R*)-configuration at the metal centre in the crystal. It would appear that the dominant steric interaction is that of the ferrocenyl moiety with the arene ligand and this presumably gives rise to a thermodynamic preference for the (*R*)-configuration at the metal in the crystal.

Inspection of the room temperature solution ^{1}H-NMR spectra of the chelated complexes suggests the presence of a single diastereomer in solution in each case. However, some of the resonances appear broad at room temperature and this raises the possibility of the existence of a conformational or configurational equilibrium. The peaks due to the diphenylphosphino protons show appreciable broadening at room temperature in the spectra of **5** and **6** while the remainder of the resonances are sharp. In each case, the broad aromatic resonance becomes sharp at temperatures around 250 K and so this may be attributable to conformational interconversion of the phenyl groups on the phosphine. The advent of high field NMR spectrometers and larger chemical shift differences for diastereomeric conformations or rotamers can lead to these relatively low barrier processes producing broadening in the spectra at low temperatures [24,25]. In our case, this effect appears to be associated with a restricted rotation of one of the two diphenylphosphino phenyl rings arising from a close approach of the proton in the ortho position of one of these phenyl rings and a proton of the unsubstituted Cp ring of the ferrocenyl moiety. From the structure of **6′**, a value for this C–C separation (C19–C32) in the solid state is 3.42(2) Å and the separation $C_{ferrocenyl}$–H C_{phenyl} is 2.57 Å. There is a similar situation in the ruthenium cation, **7**. For the molecule shown in Fig. 3 the C19–C32 distance is 3.38(2) Å and the (C19)H–C32 separation is 2.71(1) Å. The analogous distances for the second molecule in the cell are 3.48(1) and 2.62(1) Å. For **6′** there is also a relatively close contact between a methyl of the Cp* and the other phenyl ring (3.43 Å) that could also hinder its rotation.

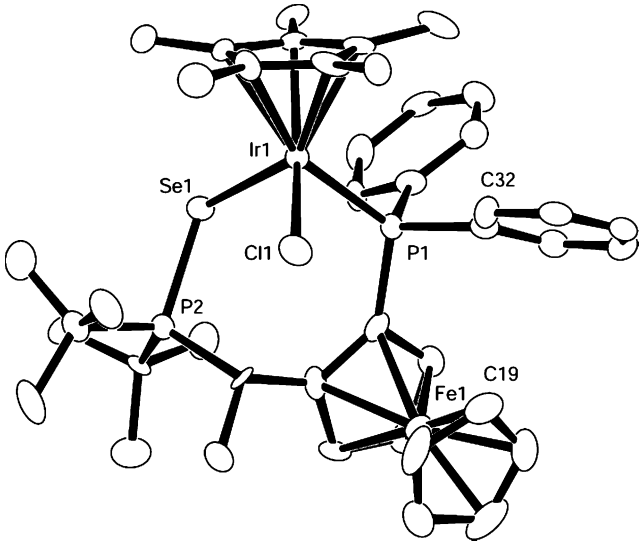


Fig. 2. ORTEP drawing of **6′** with 50% probability ellipsoids.

The ^{1}H-NMR spectrum of **7** in $CDCl_3$ at room temperature shows similar behavior with respect to the aromatic resonances. However, on lowering the temperature a second set of resonances is seen indicating the presence in solution of a second species. A similar spectrum is also seen at room temperature in CD_2Cl_2 solution, indicating that the nature of the solvent can influence the position of the conformational equilibrium

in the same way that temperature can. Similar ruthenium half-sandwich complexes with asymmetric chelating ligands have been reported to exhibit configurational instability owing to epimerization at the metal centre [26–31]. In this case, however, it is not clear whether the second species present is an epimer of **7** differing in configuration at the metal centre or just a different conformer. An epimerisation at the ruthenium centre would lead to a closer approach of the ferrocenyl moiety to the η^6-cymene ligand, leading to a large degree of steric conflict. An alternative interpretation of the results is that there are two conformational isomers present, for example, arising from a restricted rotation of the η^6-cymene ligand with respect to the rest of the ligand set. If the two orientations of the polyhapto ligand could not interconvert rapidly at this temperature then there would be two different conformers present and therefore two ^{1}H-NMR spectra would be observed. There is an example in the literature of a related complex, (η^6-Cy)Ru(κ^2-pfc-*P,O*)Cl (pfc is the anion of (S_p)-2-(diphenylphosphino)ferrocenecarboxylic acid) which undergoes a spontaneous epimerization upon crystallization to give a single diasteromeric product [32]. In the room temperature ^{1}H-NMR spectrum of the diastereomerically pure compound, broad resonances of the η^6-cymene ligand are observed, suggesting that here too the interconversion of the two orientations of the polyhapto ligand is impeded by the sterically demanding ferrocene-derived ligand [32]. Two comformational isomers may also be observed by NMR owing to differing conformations of the chelate rings. Such an observation has been made in the NMR spectra of palladium complexes of JOSIPHOS that exhibit two ring conformations at room temperature [33].

In the case of the rhodium and iridium complexes **5** and **6** there is no sign of any new species detectable by ^{1}H-NMR produced in solution to temperatures of 183 K, indicating a more rapid conformational interconversion in these complexes over this temperature range. The only significant change seen in the spectra is the broadening of the resonances associated with the *t*-butyl groups of the ligand in the lower temperature spectra. This is most probably due to the slowing of the rotation about the P–$C_{t\text{-butyl}}$ bond at these temperatures, an observation previously made for a number of P(Bu^t)$_2$R complexes of transition metals [34]. As there seems to be no configurational rearrangement of these two complexes over this temperature range, it seems that epimerization is not a facile process for these particular complexes. This indirectly supports the argument that the isomerization seen in the case of **7** may not be an epimerization but is more likely a conformational interconversion, although no definitive statements can be made from the data at hand.

4. Conclusion

Monoxidation of commercial chiral bisphosphines can be successfully carried out using chalcogens other than oxygen to give new heterobidentate chelating ligands that have both steric and electronic asymmetry. The ease with which the stoichiometry and site specificity of this oxidation can be controlled and the stability and binding diastereoselectivity of the resulting ligands suggests that such ligands may be a fruitful area of study.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 203303–203305 for compounds **3**, **6′** and **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. (Fax: +44-1223-336033. e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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