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Inorganica Chimica Acta 295 (1999) 18-24

Inorganica Chimica Acta

# Coordination chemistry and X-ray crystal structure of (ferrocenylmethyl)diphenylphosphine, $FcCH_2PPh_2$ [ $Fc = (\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)$ ]

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Received 26 March 1999; accepted 18 June 1999

#### Abstract

The known ferrocenyl-phosphine  $FcCH_2PPh_2$  has been synthesised by a new route, involving reaction of the hydroxymethylphosphine  $Ph_2PCH_2OH$  (generated in situ by reaction of air-stable  $[Ph_2P(CH_2OH)_2]Cl$  and KOH) with  $[FcCH_2NMe_3]I$ . An X-ray crystal structure determination has been carried out on the product. Reaction of  $FcCH_2PPh_2$  with 0.5 molar equivalent of  $[RuCl_2(\eta^6-p-cymene)]_2$  gave the ruthenium-phosphine complex  $[RuCl_2(\eta^6-p-cymene)(FcCH_2PPh_2)]$  by a chloride bridge-splitting reaction. The product was also fully characterised, including an X-ray crystal structure. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Ferrocene complexes; Ruthenium complexes; Phosphine complexes

# 1. Introduction

Phosphine ligands containing ferrocene groups continue to attract substantial interest for their coordination chemistry, with a particularly large amount of work devoted to catalysis using ferrocene-phosphine complexes [1]. While most research has centred on ferrocenylphosphine ligands with a direct phosphoruscyclopentadienyl link, relatively little work has been done with ligands where the phosphine is separated from the ferrocenyl moiety by a carbon spacer [2,3]. The main exceptions to this generalisation are the wellknown Josiphos-type ligands 1 [4] and the TRAP-type ligands 2 [5].

The earliest reported and one of the simplest compounds of this type of ferrocenyl-phosphine is  $FcCH_2PPh_2$  (3), originally prepared by reduction of the ylide  $FcCH = PPh_3$  with  $LiAlH_4$  [6]. A later synthesis involved the reaction of diphenylphosphine (Ph<sub>2</sub>PH) with either [FcCH<sub>2</sub>NMe<sub>3</sub>]I or FcCH<sub>2</sub>OH in aqueous



2, R = alkyl or aryl

solution for 18 or 24 h, respectively [7]. It was also shown that  $(FcCH_2)_2PPh$  could be synthesised by reaction of phenylphosphine and  $[FcCH_2NMe_3]I$  under the same reaction conditions. The phosphine oxide,  $FcCH_2P(O)Ph_2$  (4) [7,8] and sulfide  $FcCH_2P(S)Ph_2$ derivatives of 3 have also been prepared [9]. However, as far as we are aware, no metal complexes of 3 have been reported. A stannyl-substituted analogue of 3 has also been prepared, as shown in Scheme 1 [10]. Surprisingly, in view of the vast amount of literature concerning the ligand dppf (5), the analogous compound 1,1'-bis(diphenylphosphinomethyl)ferrocene (dpmf) (6a) was not synthesised until 1994 (by reaction of Fe( $\eta^5$ - $C_5H_4CH_2Cl)_2$  with LiPPh<sub>2</sub>), along with a dinuclear

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Scheme 1.

palladium complex [11]. More recently, ruthenium(II) [12,13] and rhodium(III) [13] complexes of dpmf have been prepared. The tetramethyl analogue of dpmf (**6b**) has also been prepared [3]. Together, these constitute only a very small number of studies of what appears to be very flexible ligands.



We recently reported the synthesis of  $FcCH_2P$ -( $CH_2OH$ )<sub>2</sub>, by alkylation of  $P(CH_2OH)_3$  with the ferrocenylalkylating agent [14] [ $FcCH_2NMe_3$ ]I, followed by treatment with base, to convert the intermediate  $FcCH_2P(CH_2OH)_3^+$  cation into the product [15]. We therefore reasoned that the analogous reaction of [ $FcCH_2NMe_3$ ]I with  $Ph_2PCH_2OH$  should lead to the phosphine  $FcCH_2PPh_2$  (3), and the results of these studies are described in this paper.  $Ph_2PCH_2OH$  can be considered as a protected, and relatively air-stable form of  $Ph_2PH$ , which is air-sensitive and is liable to spontaneously ignite in air [16].

#### 2. Results and discussion

# 2.1. Synthesis and characterisation of $FcCH_2PPh_2$ (3)

The known phosphine **3** was synthesised by overnight reflux of a methanolic solution of the readily-prepared ferrocene-ammonium salt  $[FcCH_2NMe_3]I$  and Ph<sub>2</sub>PCH<sub>2</sub>OH (Scheme 2). The Ph<sub>2</sub>PCH<sub>2</sub>OH was generated in situ by the reaction of the air-stable phosphonium salt  $[Ph_2P(CH_2OH)_2]CI$  with slightly less than 1 molar equivalent of KOH. Excess triethylamine was



Scheme 2.

added, and after extraction of the product followed by column chromatography,  $FcCH_2PPh_2$  was isolated in moderate yield as an air-stable orange crystalline solid. Electrospray mass spectrometry (ESMS) of **3** gave the  $[M]^+$  ion, through oxidation of the ferrocene moiety, as found for other neutral ferrocene compounds [17].  $FcCH_2PPh_2$  (and a wide range of other ferrocenyl-phosphines) has been previously characterised as a silver adduct by ESMS [18].

Reaction of **3** with hydrogen peroxide gave the known phosphine oxide derivative **4** [7,8]. Additionally, quaternary phosphonium salts  $[FcCH_2PPh_2R]^+I^-$  (7, R = Me; **8**, R = Et) were prepared by reaction of **3** with MeI or EtI. The compounds were characterised by ESMS; this technique has been previously used in the analysis of phosphonium salts [19]. The expected phosphonium cations were observed as the base peak in the positive-ion ES spectra at low cone voltages (e.g. 30 V). At the higher cone voltage of 60 V both cations underwent fragmentation, yielding the stable  $FcCH_2^+$  ion at m/z 199, as the base peak in both cases, with the parent phosphonium ion at ca. 60% intensity. Other  $FcCH_2X$  compounds have been found to undergo comparable fragmentation in their ES spectra [17].

An X-ray crystal structure determination has been carried out on 3; Fig. 1 shows the molecular structure together with the atom numbering scheme, while Table 1 gives selected bond lengths and angles. Overall, the



Fig. 1. ORTEP diagram of the molecular structure of  $FcCH_2PPh_2$  (3), with the atom numbering scheme. Hydrogen atoms are displayed as small open circles. Thermal ellipsoids are at the 50% probability level.

100.99(14)

P(1)-C(1)-C(11)

Table 1					
Selected bond lengths (Å) and bond angles (°) for FcCH <sub>2</sub> PPh <sub>2</sub> (3)					
Bond lengths					
P(1)-C(1)	1.860(3)	C-C for Cp rings			
P(1) - C(31)	1.840(3)	· -			
P(1) - C(41)	1.837(3)	C-C for Ph rings			
C(1)–C(11)	1.500(4)	-			
Bond angles					
C(1) - P(1) - C(31)	100.34(13)	C(31) - P(1) - C(41)			

structure shows no unusual features, with intermolecular bond lengths and angles being within their normal ranges. The cyclopentadienyl rings adopt an eclipsed conformation, and the phosphorus atom is directed away from the ferrocene unit, as observed in other FcCH<sub>2</sub>P structures. The Fc–C (1.500(4) Å) and C–P (C(1)–P 1.860(3) Å) bond distances of **3** are similar to those of other ferrocenylmethylphosphines, for example FcCH<sub>2</sub>P(CH<sub>2</sub>OH)<sub>2</sub> (Fc–C 1.489(6), P–C 1.858(4) Å) [15].

# 2.2. Synthesis and characterisation of $[RuCl_2(\eta^6-p-cymene)(FcCH_2PPh_2)]$ (9)

Distance of Fe(1) out of substituted Cp ring

Angle between planes of Ph rings

Distance of Fe(1) out of unsubstituted Cp ring

Arene ruthenium complexes are of interest as catalyst precursors in a range of organic syntheses [20], and accordingly we have synthesised the *p*-cymene ruthenium complex of **3**. Reaction of the chloride-bridged dimeric complex [RuCl<sub>2</sub>( $\eta^6$ -*p*-cymene)]<sub>2</sub> with 2 molar equivalents of **3** gave the expected complex [RuCl<sub>2</sub>( $\eta^6$ -*p*cymene)(FcCH<sub>2</sub>PPh<sub>2</sub>)] (**9**), by a standard halide bridgesplitting reaction [12]. The product was readily purified by recrystallisation to give a dichloromethane solvate, and satisfactory microanalytical and spectroscopic data were obtained. The positive-ion electrospray mass spectrum of **9** showed the expected [M - Cl + MeCN]<sup>+</sup> ion at m/z 696; such behaviour is typical for transition metal phosphine halide complexes [21].

Crystals of 9 suitable for X-ray analysis were obtained by vapour diffusion of petroleum spirits into a dichloromethane solution of the complex. A number of structures have been reported for compounds analogous to 9 [12,22]. The structure of 9 contains three independent molecules in the asymmetric unit along with three molecules of dichloromethane. One of the independent molecules (molecule 1) is shown in Fig. 2, while selected bond lengths and angles for all three independent molecules are given in Table 2. The three molecules differ mainly in small changes in conformation as indicated by the torsion angles given in Table 2. All three independent molecules share some common characteris-

respect to conformation. tics with The geometry about Ru(1) is a piano-stool conformation, i.e. the coordination is *pseudo*-octahedral with the  $\eta^6$ cymene ligand occupying one facial site. This geometry is somewhat distorted, so that the bond angles between the chloride and phosphorus atoms at the ruthenium centre are between 84 and 89°, slightly lower than the idealised 90°. In addition, the Ru(1) and ferrocene group adopts an *anti* configuration about the P(1)-C(1)bond, and there is a staggered arrangement of substituents about the Ru(1)-P(1) bond. The Ru-P and Ru-Cl bond lengths (average for the three independent molecules 2.3494(18) and 2.4114(18) Å) are comparable with those of other  $\eta^6$ -arene ruthenium phosphine dichloride complexes, which are around 2.34 and 2.40 Å [12].

av

av.

range

range

1.413(5)

1.388(4)

103.02(12)

1.6475(15) 1.6486(17)

111.6(2)

56.9(1)

1.382(6)-1.437(6)

1.378(5)-1.399(4)

No notable sources of disorder were observed in the structure — only in the unsubstituted cyclopentadienyl ring of molecule 1 were the ellipsoids elongated. However, the refinement values such as  $R_1$  and GOF are relatively poor. This is probably accounted for by the



Fig. 2. ORTEP diagram of one of the independent molecules (molecule 1) of  $[RuCl_2(\eta^6\text{-}p\text{-}cymene)(FcCH_2PPh_2)]$  (9). All hydrogen atoms have been omitted for clarity. Thermal ellipsoids are at the 50% probability level.

C(1)-P(1)-C(41)

Table 2 Selected bond lengths (Å) and bond angles (°) for  $[RuCl_2(\eta^6-p-cymene)(FcCH_2PPh_2)]$  (9)

		Molecule 1	Molecule 2	Molecule 3
Bond lengths				
Ru(1)-Cl(1)		2.4031(18)	2.4109(18)	2.4113(17)
Ru(1)-Cl(2)		2.4182(17)	2.4137(17)	2.4112(18)
Ru(1)-P(1)		2.3507(18)	2.3483(18)	2.3494(18)
P(1)-C(1)		1.854(6)	1.843(7)	1.850(7)
P(1)-C(31)		1.820(7)	1.824(7)	1.827(7)
P(1)-C(41)		1.820(7)	1.823(7)	1.821(7)
C(1)–C(11)		1.492(9)	1.493(9)	1.493(10)
C(51)-C(2)		1.494(11)	1.510(11)	1.504(11)
C(54) - C(3)		1.512(10)	1.515(11)	1.518(10)
C(3) - C(4)		1.506(12)	1.502(13)	1.502(13)
C(3)–C(5)		1.525(11)	1.526(12)	1.545(12)
C–C for Cp rings	Range	1.325(18)-1.441(10)	1.384(13)-1.423(9)	1.381(14)-1.434(12)
	Average	1.386(15)	1.405(12)	1.405(13)
C-C for Ph rings	Range	1.369(12)-1.404(9)	1.372(10)-1.404(9)	1.371(13)-1.405(10)
	Average	1.385(11)	1.386(11)	1.387(11)
C–C for cymene	Range	1.378(11)-1.436(12)	1.389(11)-1.436(10)	1.384(11)-1.436(10)
	Average	1.412(11)	1.415(11)	1.412(11)
Distance of Ru(1) out of plane of cymene ring		1.7020(40)	1.7022(40)	1.6942(40)
Distance of Fe(1) out of planes of Cp rings (average)		1.6464(52)	1.6577(44)	1.6484(48)
Bond angles				
P(1)-Ru(1)-Cl(1)		84.99(6)	84.67(6)	86.81(6)
P(1)-Ru(1)-Cl(2)		86.97(6)	86.95(6)	85.35(6)
Cl(1)-Ru(1)-Cl(2)		87.78(7)	88.56(7)	88.60(7)
Ru(1) - P(1) - C(1)		115.8(2)	115.2(2)	114.5(2)
Ru(1) - P(1) - C(31)		114.6(2)	116.3(2)	115.6(2)
Ru(1) - P(1) - C(41)		112.1(2)	110.6(2)	112.0(2)
P(1)-C(1)-C(11)		113.2(5)	113.6(5)	113.6(5)
C(54) - C(3) - C(4)		114.8(7)	113.8(8)	114.0(7)
C(54) - C(3) - C(5)		109.7(7)	108.5(8)	109.2(7)
C(4) - C(3) - C(5)		110.6(7)	111.4(8)	110.2(8)
Torsion angles				
Ru(1) - P(1) - C(1) - C(11)		164.7(4)	161.4(4)	164.8(4)
P(1)-Ru(1)-C(51)-C(2)		62.4(10)	58.1(9)	61.7(9)
P(1)-C(1)-C(11)-C(12)		-94.2(7)	-97.7(7)	-100.55(8)
C(11)-C(1)-P(1)-C(41)		-71.1(5)	-76.2(6)	-71.7(6)
C(11)-C(1)-P(1)-C(31)		39.9(5)	34.6(6)	38.7(6)
C(4)-C(3)-C(54)-C(55)		-9.0(10)	-20.8(12)	-12.5(7)
C(5)-C(3)-C(54)-C(55)		116.3(8)	103.8(9)	111.2(9)
Angle between planes of Ph rings		51.03	54.51	52.01

exceptionally long unit cell b axis, which is about 61 Å in length, which made complete resolution of the diffraction pattern difficult.

### 3. Experimental

General experimental details were as described in a previous paper from these laboratories [15]. Petroleum spirits refers to the fraction of boiling point  $60-80^{\circ}$ C except where otherwise stated. The compounds [FcCH<sub>2</sub>NMe<sub>3</sub>]I [23], [Ph<sub>2</sub>P(CH<sub>2</sub>OH)<sub>2</sub>]Cl [24] and [RuCl<sub>2</sub>( $\eta^{6}$ -*p*-cymene)]<sub>2</sub> [25] were prepared by literature

procedures. NMR spectra were recorded in CDCl<sub>3</sub> solution. Scheme 3 depicts the labelling scheme used in assignment of ferrocenyl NMR signals.



Scheme 3. Atom labelling used in NMR assignments of the cyclopentadienyl rings.

# 3.1. Synthesis of FcCH<sub>2</sub>PPh<sub>2</sub> (3)

A solution of [Ph<sub>2</sub>P(CH<sub>2</sub>OH)<sub>2</sub>]Cl (2.006 g, 7.09 mmol) in methanol (30 ml) was purged and placed under a nitrogen atmosphere, then KOH (0.359 g, 6.39 mmol) was added. The solution was stirred under nitrogen for 2 h, generating a solution of Ph<sub>2</sub>PCH<sub>2</sub>OH. The Ph<sub>2</sub>PCH<sub>2</sub>OH was added to a solution of [FcCH<sub>2</sub>NMe<sub>3</sub>]I (2.002 g, 5.23 mmol) in methanol (40 ml) under nitrogen, and the resulting mixture refluxed under nitrogen for 18 h. Most of the solvent was removed under reduced pressure, and a mixture of water (40 ml), diethyl ether (40 ml) and triethylamine (30 ml) added. This mixture was stirred for 4 h, and the organic layer isolated and filtered before washing with water  $(3 \times 20)$ ml). Removal of solvent under reduced pressure gave an orange oil. This was purified by tlc on silica, with dichloromethane used to charge the plate and 10% diethyl ether in petroleum spirits used as the eluting solvent. The desired product ran with an  $R_{\rm f}$  of 0.73, and after removal from the plate and drying under vacuum, 3 was isolated as an orange oil which slowly crystallised (0.505 g, 25%). M.p. 80-84°C. Found: C, 72.1; H, 5.4%.  $C_{23}H_{21}FeP$  requires: C, 71.9; H, 5.5%. IR (cm<sup>-1</sup>): 1583(w), 1480(w), 1469(w), 1432(m), 1305(w), 1182(w), 1102(m), 1023(m), 999(m), 924(w), 840(w), 816(s), 741(s), 695(s), 479(s). ESMS (positive-ion, cone voltage 20 V), m/z 384  $[M]^+$ . <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta$  - 11.8 (s). <sup>1</sup>H NMR:  $\delta$  3.16 (FcCH<sub>2</sub>P, s, 2H), 3.92 (C<sub>B</sub>-H, unres. t, 2H), 3.98 (C<sub>A</sub>-H, t, J 2, 2H), 4.10 (C<sub>D</sub>-H, s, 5H), 7.31–7.42 (Ph, m, 10H).  ${}^{13}C{}^{1}H{}: \delta$  30.29 (FcCH<sub>2</sub>P, d, J 14), 67.42 (C<sub>A</sub>, s), 68.84 (C<sub>D</sub>, s), 69.23 (C<sub>B</sub>, d, J 4), 84.33 (C<sub>C</sub>, d, J 17), 128.35-138.85 (m, Ph).

# 3.2. Synthesis of $FcCH_2P(O)Ph_2$ (4)

FcCH<sub>2</sub>PPh<sub>2</sub> (3) (0.100 g, 0.260 mmol) was placed in a flask with hydrogen peroxide (0.190 g, 6%, 0.335 mmol), water (5 ml), methanol (35 ml) and dichloromethane (10 ml). The solution was stirred for 1 h before most of the solvent was removed under reduced pressure without heating. Once the product had largely precipitated out of solution, diethyl ether was added and the organic layer was separated and washed with water  $(3 \times 10 \text{ ml})$ . Solvent was removed under reduced pressure, giving the crude product as a yellow powder in quantitative yield. Recrystallisation by vapour diffusion spirits (b.p. 40–60°C) petroleum into of а dichloromethane solution at 4°C gave 4 as a brown powder (0.086 g, 83%). M.p. 203-205°C (decomp.) lit.: 207-209°C [7]. Found: C, 68.4; H, 5.1%. C<sub>23</sub>H<sub>21</sub>FeOP requires: C, 69.0; H, 5.3%. IR (cm<sup>-1</sup>): 1437(m), 1385(w), 1208(w), 1183(s), 1121(m), 1101(m), 1071(w), 1001(w), 928(w), 821(m), 744(s), 726(s), 696(s), 604(w), 537(s), 508(m), 490(s). ESMS (positive-ion, cone voltage 100 V): m/z 801  $[2M + H]^+$ , 401  $[M + H]^+$ , 335  $[M - Cp]^+$ , 199  $[FcCH_2]^+$ . <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta$  29.0 (s). <sup>1</sup>H NMR:  $\delta$  3.42 (FcCH<sub>2</sub>P, d, J 13, 2H), 4.01 (C<sub>A</sub>-H and C<sub>B</sub>-H, s, 4H), 4.08 (C<sub>D</sub>-H, s, 5H), 7.39–7.70 (Ph, m, 10H). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  33.38 (FcCH<sub>2</sub>P, d, J 67), 68.02 (C<sub>A</sub>, s), 68.90 (C<sub>D</sub>, s), 69.85 (C<sub>B</sub>, s), 77.77 (C<sub>C</sub>, d, J 3), 128.43–133.06 (Ph, m).

#### 3.3. Synthesis of phosphonium salts 7 and 8

A small quantity (ca. 30 mg) of  $FcCH_2PPh_2$  (3) was dissolved in dichloromethane (2 ml) and an excess of either MeI or EtI was added, and the reaction mixture was allowed to stand overnight. The solvent was evaporated, the residue washed with diethyl ether (5 ml), and then recrystallised by diffusion of diethyl ether into a dichloromethane solution. The resulting orange crystals were air-dried.

7: ESMS (positive-ion, cone voltage 30 V): m/z 399 (100%), [FcCH<sub>2</sub>PPh<sub>2</sub>Me]<sup>+</sup>.

8: ESMS (positive-ion, cone voltage 30 V): m/z 413 (100%), [FcCH<sub>2</sub>PPh<sub>2</sub>Et]<sup>+</sup>.

# 3.4. Synthesis of $[RuCl_2(\eta^6-p-cymene)(FcCH_2PPh_2)]$ (9)

The complex  $[RuCl_2(\eta^6-p-cymene)]_2$  (0.037 g, 0.0609 mmol) was dissolved in dichloromethane (10 ml), which was placed under a nitrogen atmosphere before addition of  $FcCH_2PPh_2$  (3) (0.047 g, 0.122 mmol). The mixture was refluxed for 15 min and the solvent removed under reduced pressure to give the crude product as a dark oil in quantitative yield. Recrystallisation by vapour diffusion of petroleum spirits (b.p. 30-40°C) into a dichloromethane solution at 4°C yielded the product as large dark-purple crystals suitable for X-ray crystallography (0.070 g, 84%). M.p. ~ 200°C (decomp.). Found: C, 52.6; H, 4.7%. C<sub>33</sub>H<sub>35</sub>Cl<sub>2</sub>FePRu. CH<sub>2</sub>Cl<sub>2</sub> requires: C, 52.6; H, 4.8%. IR (cm<sup>-1</sup>): 3053(m), 2963(m), 1481(m), 1409(m), 1469(m), 1433(s), 1386(m), 1319(w), 1276(w), 1237(w), 1196(m), 1160(w), 1103(s), 1057(m), 1026(m), 1000(m), 926(m), 821(s), 750(s), 728(s), 696(s), 663(m), 597(m), 483(w). ESMS (positive-ion, cone voltage 60 V): m/z 696  $[M - Cl + MeCN]^+$ , 384  $[FcCH_2PPh_2]^+$ . <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta$  28.8 (s). <sup>1</sup>H NMR:  $\delta$  0.86 [CH(CH<sub>3</sub>)<sub>2</sub>, d, J 7, 6H], 1.82 (CH<sub>3</sub>, s, 3H), 2.50, [CH(CH<sub>3</sub>)<sub>2</sub>, hept., J 7, 1H], 3.32 (FcCH<sub>2</sub>P, s, 2H), 3.63 (C<sub>A</sub>-H, d, J 7, 2H), 3.70 (C<sub>B</sub>-H, d, J 2, 2H), 3.99 (C<sub>D</sub>-H, s, 5H), 5.08 [CH<sub>3</sub>C(CH)<sub>2</sub>, d, J 6, 2H], 5.22 [(CH<sub>3</sub>)<sub>2</sub>CHC(CH)<sub>2</sub>, d, J 6, 2H], 7.32–7.71 (Ph, m, 10H). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 17.30 (CH<sub>3</sub>, s), 21.48 [CH(CH<sub>3</sub>)<sub>2</sub>, s], 25.36 (FcCH<sub>2</sub>P, d, J 22), 30.00 [CH(CH<sub>3</sub>)<sub>2</sub>, s], 67.04 (C<sub>A</sub>, s), 68.75 (C<sub>D</sub>, s), 70.05 (C<sub>B</sub>, s), 80.72 (C<sub>C</sub>, d, J 9), 85.61 [CH<sub>3</sub>C(CH)<sub>2</sub>, d, J 5], 90.08 [(CH<sub>3</sub>)<sub>2</sub>CHC(CH)<sub>2</sub>, d, J 4], 94.09 [CH<sub>3</sub>C(CH)<sub>2</sub>, s], 108.40 [(CH<sub>3</sub>)<sub>2</sub>CHC(CH)<sub>2</sub>, s], 127.79-133.95 (Ph, m).

Table 3 Crystallographic data for  $FcCH_2PPh_2$  (3) and  $[RuCl_2(\eta^6-p-cymene)-(FcCH_2PPh_2)]$  (9)

	3	9
Empirical formula	C <sub>23</sub> H <sub>21</sub> FeP	C <sub>34</sub> H <sub>35</sub> Cl <sub>2</sub> FePRu·CH <sub>2</sub> Cl <sub>2</sub>
Formula weight	384.22	775.33
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/n$
Unit cell dimensions		
a (Å)	10.3723(7)	10.6555(6)
b (Å)	8.2245(10)	60.958(3)
c (Å)	10.9666(8)	15.5291(8)
β (°)	104.755(5)	94.517(1)
$V(Å^3)$	904.68(14)	10 055.4(9)
$D_{\text{cale.}}$ (g cm <sup>-3</sup> )	1.410	1.536
Z	2	12
F(000)	400	4728
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.92	1.11
Temperature (°C)	-115	-70
Crystal size (mm)	0.8(0.4(0.2	0.39(0.28(0.22
$\theta$ Range (°)	$2.03 < \theta < 30.00$	$2.34 < \theta < 26.41$
Total reflections	2963	49 849
Unique reflections	2822	19 138
R <sub>int</sub>	0.0254	0.0378
$T_{\min}$	0.298	0.665
T <sub>max</sub>	0.377	0.834
$R_1 (I > 2\sigma(I))$	0.0342	0.0790
$wR_2$ (all data)	0.0792 <sup>a</sup>	0.1543 <sup>ь</sup>
GOF	1.092	1.259
Electron density		
Max. (e Å <sup>-3</sup> )	0.407	1.495
Min. (e Å <sup>-3</sup> )	-0.226	-1.566
Flack x-parameter	-0.02(2)	_
Solution and refinement	SHELXS-86 [26]	SHELXS-97 [28]
programs	SHELXL-93 [27]	SHELXL-97 [28]

<sup>a</sup>  $w = [\sigma^2(F_o^2) + (0.0425P)^2 + 0.10P]^{-1}$  where  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ .

<sup>b</sup>  $w = [\sigma^2(F_o^2) + (0.0000P)^2 + 80.12P]^{-1}$  where  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ .

# 3.5. Crystal structure determinations of $FcCH_2PPh_2$ (3) and $[RuCl_2(\eta^6-p-cymene)(FcCH_2PPh_2)]$ (9)

Crystallographic data for the two compounds are given in Table 3.

#### 3.5.1. Compound 3

Crystals suitable for X-ray structure analysis were obtained serendipitously by recrystallisation from a mixture of water, diethyl ether and petroleum spirits. Data were collected by  $\omega$  scans on a Nicolet R3 diffractometer and were corrected for absorption based on a series of  $\psi$  scans. The structure was solved by direct methods and developed routinely. Full-matrix leastsquares refinement was based on  $F^2$ , with all non-hydrogen atoms anisotropic. Hydrogen atoms were included in calculated positions with isotropic temperature factors 1.2 times the  $U_{iso}$  of the atom to which they are bonded.

#### 3.5.2. Compound 9

The data collection for this structure, on a Siemens SMART CCD diffractometer, nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different  $\phi$  angle for the crystal and each exposure covered 0.3° in  $\omega$ . The crystal-to-detector distance was 5.0 cm. In hindsight it appears that a longer crystal-to-detector distance would have been desirable in order to avoid the problems of low resolution of spots in the k direction due to the exceptionally long b axis of the unit cell. The data set was corrected empirically for absorption using SADABS [29]. The structure was solved by Patterson methods and developed routinely. Full-matrix least-squares refinement was based on  $F^2$ .

All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions with isotropic temperature factors 1.2 times that of the  $U_{iso}$  of the atom to which they are bonded. Hydrogen atom positions for the methyl functionalities C(2), C(4) and C(5) of the three independent molecules were calculated by positioning of the methyl group such that the conformation obtained gave the best fit to the electron density distribution observed. Many of the large residual peaks in the electron density map are located near the dichloromethane molecules of crystallisation.

#### 4. Supplementary material

Tables of full bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC), and can be obtained from the authors on request.

#### Acknowledgements

The authors thank the University of Waikato and the New Zealand Lottery Grants Board for financial support of this work. The authors also thank Professor Ward Robinson (University of Canterbury) and Associate Professor Cliff Rickard (University of Auckland) for collection of the X-ray data sets, and also Wendy Jackson and Amu Upreti for technical assistance. NJG thanks the University of Waikato and the William Georgetti Trust for scholarships.

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