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Journal of Organometallic Chemistry 690 (2005) 2285–2290
Journal of Organometallic Chemistry
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Synthesis and X-ray crystal structure of [2-(phosphinomethyl)ferrocenyl]diphenylphosphine

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Received 19 January 2005; revised 25 February 2005; accepted 28 February 2005
Available online 14 April 2005

Abstract

[2-(Phosphinomethyl)ferrocenyl]diphenylphosphine **2**, is an air stable primary phosphine bearing a 1,2-disubstituted ferrocene framework, which has been prepared by reduction of the corresponding phosphonate. Confirmation of its structure has been obtained by X-ray single-crystals diffraction analysis. Despite its high stability toward oxidation, phosphine **2** still displays a normal coordinative behaviour toward $[(p\text{-cymene})RuCl_2]_2$. The expected (*p*-cymene)$RuCl_2$(phosphine) complex is formed by coordination of the primary phosphine function, while the conceivably competitive complexation of the PPh_2 group was not observed.
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Keywords: Ferrocenyl derivative; Diphosphine; Primary phosphine

1. Introduction

Primary phosphines are highly useful intermediates in organophosphorus chemistry, owing to the reactive character of the P–H bond. They are however also typically air-sensitive, often pyrophoric and, thus, difficult compounds to handle. Recent work from Henderson and co-workers [1–3] pointed out the availability of especially 'user-friendly' primary phosphines which incorporate ferrocenyl groups, i.e., ferrocenylmethyl- and ferrocenylethylphosphines **1**. These primary phosphines are remarkably air stable, both in solution and in the solid state. Albeit the origin of the exceptionally high air-stability can't be explained to date, the synthetic utility of **1** was easily anticipated (see Scheme 1).

Based on the pioneering work above, we envisioned the synthesis of the analogous primary phosphine **2** which bears an additional diphenylphosphino function on the cyclopentadienyl moiety. If the 'user-friendly' physical properties of **1** would be retained in diphosphine **2**, this compound could represent a highly convenient synthon to produce new ferrocenyl-based diphosphines with planar chirality.

Ferrocenyl-based diphosphines with planar chirality constitute a well known, efficient class of chiral auxiliaries for transition metal catalysed reactions [4]. Togni's Josiphos [5] is the lead-compound in this series, however a variety of other diphosphines bearing chiral, 1,2-disubstituted ferrocene moieties and, possibly, an additional chiral carbon centre, have been prepared [6] since the initial work of Hayashi et al. [7]. Several synthetic approaches have been applied to their synthesis, however, as far as we are aware, the use of primary phosphines, such as **2**, as synthetic intermediates has never been considered before.

We report hereafter on a synthetic approach to racemic and enantio-enriched **2**, as well as on its structural characterization by X-ray diffraction.

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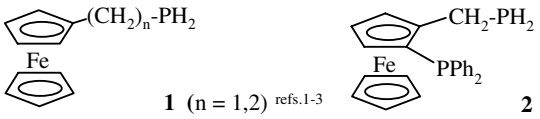
0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.02.034



Scheme 1.

2. Results and discussion

For the synthesis of the target diphosphine **2**, the known oxide **4** [8] and sulphide **5** [7] of [2-(*N*,*N*-dimethylaminomethyl)ferrocenyl]diphenylphosphine **3** [7,9], have been considered as suitable starting materials. Conversion of their nitrogen functions into trimethylammonium iodide functions should create leaving groups to be displaced then by a suitable phosphorus reagent. An analogous procedure had been applied to the synthesis of **1**, by using tris(hydroxymethyl)phosphine as the nucleophile [1] (See Schemes 2 and 3).

While nitrogen methylation of the trivalent phosphine **3**, is hampered by the potentially concurrent alkylation of phosphorus, it can be suitably performed on both the phosphine oxide and sulphide to afford **6** and **7**, respectively. Starting from **6**, the reaction with tris(hydroxymethyl)phosphine in refluxing methanol, according to the Henderson procedure [10,11], did not afford the expected bis(hydroxymethyl)phosphino derivative, mainly due to the low reactivity of the starting material. Different approaches were then considered, where the ammonium iodide function would serve as a leaving group in Michaelis–Becker or Arbuzov-like reactions with sodium diethylphosphite and trimethylphosphite, respectively. The last reaction led successfully to the desired phosphonates **8** and **9** in 57% and 20% yields, respectively.

The use of ammonium iodides in Arbuzov-like reactions [12] has been applied previously to the synthesis of diethyl ferrocenylmethylphosphonate [13], a ferrocene derivative closely related to **8** or **9**.

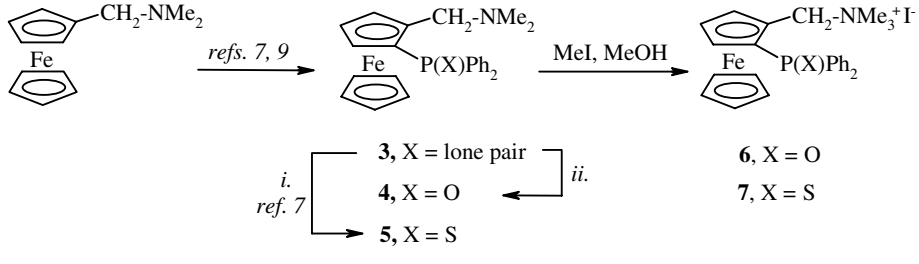
Reduction of both the phosphonate and phosphine oxide functions of **8** has been performed in a single step by using a trichlorosilane–triethylamine mixture, in benzene or toluene, by heating at 120 °C in a sealed tube. The final diphosphine **2** [^{31}P NMR δ −23 and −127 ppm, $^{1}J_{P-H}$ = 196 Hz] is a stable compound which has been purified by column chromatography and stored in air without noticeable oxidation.

Crystals of **2** have been grown from pentane, which were suitable for X-ray crystal structure determination. ORTEP drawing of **2** is reported in Fig. 1. Selected bond angles and distances are given in Table 1.

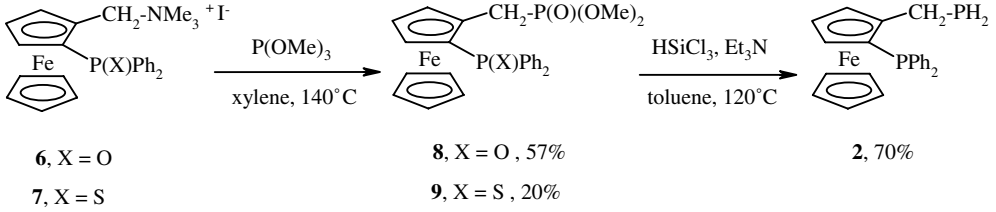
The geometry of diphosphine **2** is similar to that of the ferrocenylmethylphosphine **1** [1], with the phosphino group pointing away from the ferrocene fragment. Bond angles and distances for the PH_2CH_2Cp moiety are fully comparable with those of **1**, despite the additional PPh_2 group in *ortho*-position. The X-ray data and ORTEP drawing above show, once more, that stabilisation of primary ferrocenylmethylphosphines cannot be assigned to interactions of the PH_2 function with the iron centre, neither to a particularly high steric hindrance.

The coordinative behaviour of **2** has been checked by reaction with the ruthenium dimer, $[(p\text{-cymene})RuCl_2]_2$ [14]. Of the two phosphorus atoms, the PH_2 group displayed the higher coordinating ability toward ruthenium, as complex **10** is formed exclusively, as shown in Scheme 4.

Compound **10** is an orange-red, air stable solid. ^{31}P NMR data are diagnostic of the exclusive complexation of the PH_2 fragment, with an almost unchanged chemi-



Scheme 2.



Scheme 3.

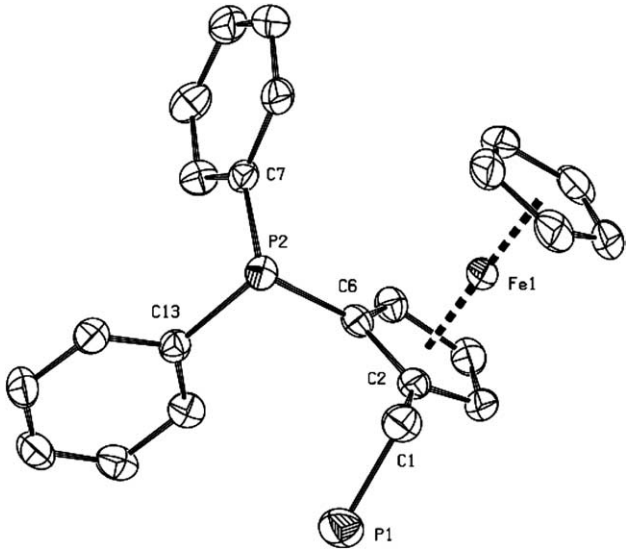


Fig. 1. ORTEP drawing of diphosphine **2**.

Table 1
Selected bond lengths (Å) and angles (°) for diphosphine **2**

C(1)–P(1)	1.851(3)	Fe–C(6)	2.043(2)
C(2)–C(1)	1.492(4)	Fe–C(3)	2.035(2)
C(6)–P(2)	1.820(2)	P(1)–C(1)–C(2)	115.5(2)
C(2)–C(6)	1.447(3)	C(1)–C(2)–C(6)	126.7(2)
P(2)–C(13)	1.830(3)	C(2)–C(6)–P(2)	123.6(2)
Fe–C(2)	2.051(3)	C(6)–P(2)–C(13)	101.6(1)

cal shift for the PPh_2 unit [δ −25 ppm] and a considerably large $\Delta\delta$ value [106 ppm] for the PH_2 group [δ −21 ppm], with respect to the uncomplexed diphosphine **2**. The two enantiotopic P–H bonds display two different $^1J_{H-P}$ couplings of 385 and 348 Hz, respectively, as well as separate ^{1}H NMR signals for the corresponding protons at δ 4.26 and 4.48 ppm, respectively.

Thus, the efficient synthetic approach to the primary phosphine **2** reported herein, affords a new 'user-friendly' ligand as well as a valuable precursor for ferrocene-based diphosphines.

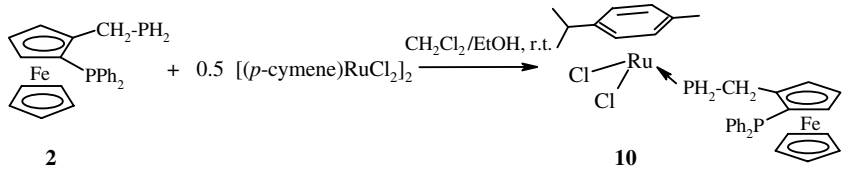
Finally, we wished to check if the synthetic approach defined above would be suitable for the synthesis of enantiomerically pure **2** through stereospecific transformations of a chiral starting material. Thus, the known phosphine sulphides (*R*)- and (*S*)-**5** have been prepared separately through the reported resolution method, which implies fractional crystallisation with dibenzoyltartaric acid [7]. (*R*)-**5** was then converted into the corresponding oxide (*R*)-**4** by reaction with oxone [15] (see Scheme 5).

The next step, the Arbuzov-like reaction of the ammonium salt **6** with trimethylphosphite, causes partial racemisation and, consequently, phosphonate **8** was obtained in only 46% enantiomeric excess (measured by HPLC on Daicel OD-H column). Racemisation has been barely noticed for ferrocenes bearing planar chirality, including ferrocenylphosphines [16]. Racemisation, e.g., coordination of iron by the other face of the Cp, may take place by either an intermolecular exchange process via triple-decker sandwich intermediates, or via a dissociative process [*a*], or again via η^1 coordination of the Cp ring followed by 1,5-proton shift [*b*]. The last two mechanisms are shown in Scheme 6 hereafter.

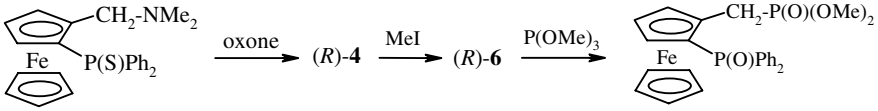
Both a dissociative process and slippage of the Cp ring from η^5- to η^1-coordination are plausibly promoted, in the experimental conditions of the Arbuzov reaction, by temporary complexation of trimethylphosphite (L = $P(OMe)_3$). An haptotropic shift of the Cp ligand of a ferrocene derivative, in the presence of trimethylphosphite, has been documented recently [17].

The observed partial racemisation process prevents application of the synthetic method above to the synthesis of an enantiomerically pure diphosphine **2**.

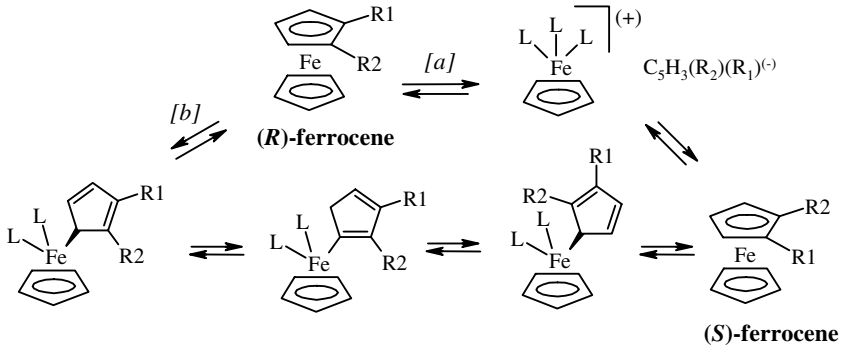
Other approaches to enantiomerically pure **2** are being considered. These include resolution of racemic



Scheme 4.



Scheme 5.



Scheme 6. Intramolecular racemisation processes for chiral ferrocenes.

2 or even resolution of phosphonate **8**, given that reduction of **8** in the reported conditions, proved to be stereospecific. Also, the use of more suitable precursors, allowing the synthesis of **8** in milder conditions, is under investigation.

3. Experimental

The [2-(*N*,*N*-dimethylaminomethyl)ferrocenyl]diphenylphosphine **3** and [2-(*N*,*N*-dimethylamino-methyl)-ferrocenyl]diphenylphosphine sulfide **5** have been prepared according to Hayashi et al. [7]. All experiments were performed under an inert atmosphere. NMR spectra were recorded on either a Bruker AM 200 or an AM 400 spectrometer.

*3.1. [2-(N,N-dimethylaminomethyl)ferrocenyl]diphenylphosphine oxide (**4**)*

*From **3***. To a suspension of phosphine **3** (7.7 g, 16 mmol) in methanol (130 mL) at 0 °C, was added dropwise 2.1 mL of 30% hydrogen peroxide. After 30 min at room temperature, aqueous sodium sulfite was added to decompose the excess hydrogen peroxide. After evaporation of methanol, the reaction mixture was extracted with dichloromethane. The extract was washed with water, dried over anhydrous magnesium sulphate and then evaporated. Purification of the residue by column chromatography on basic alumina (ether/methanol, 99:1) gave the corresponding oxide **4** in 91% yield (7.1 g).

From (*R*)-***5***. (*R*)-[2-(*N*,*N*-dimethylaminomethyl)ferrocenyl]diphenylphosphine sulfide **5** [7] (2.4 g, 5.2 mmol, $[\alpha]_D = -47$ ($c = 0.5$, $CHCl_3$), e.e. = 94%, based on the $[\alpha]_D$ value) was dissolved in a THF/MeOH 1:1 mixture (100 mL). Then 50 mL of a 0.2-M buffered solution (pH 6–7) of oxone® were added slowly at 0 °C. After 20 min stirring at room temperature, the mixture was hydrolysed with aqueous sodium thiosulfate and extracted with chloroform. The organic extracts were dried over $MgSO_4$ and solvents were removed to afford the crude oxide **4** which was purified as above. (*R*)-**4** was obtained in 80% yield (1.8 g); $[\alpha]_D = -104$ ($c = 0.2$, $CHCl_3$). A 10% amount of (2-formylferrocenyl)diphenylphosphine oxide [^{31}P NMR ($CDCl_3$) δ 29.0; ^{1}H NMR ($CDCl_3$) δ 4.24 (br s, 1H), 4.41 (s, 5H, Cp), 4.78 (br s, 1H), 5.24 (br s, 1H), 7.3–7.9 (m, 10h, Ph), 10.4 (1H, CHO); ^{13}C NMR (50 MHz) δ 194.3 (s, CHO) ppm] was formed as side-product when addition of oxone was performed at room temperature.

4: Orange-red solid. Spectral data are in agreement with the reported data [8]. ^{31}P NMR ($CDCl_3$) δ 29.7; ^{1}H NMR ($CDCl_3$) δ 1.94 (s, 6H, NMe_2), 3.36 (*A*B, $J = 13.4$ Hz, 1H, CH_2), 3.64 (A*B*, 1H, CH_2), 3.92 (br s, 1H), 4.20 (s, 5H, Cp), 4.33 (br s, 1H), 4.62 (br s, 1H), 7.3–7.9 (m, 10h, Ph) ppm. Anal. Calc. for $C_{25}H_{26}FeNP$: C, 67.74; H, 5.91; N, 3.16. Found: C, 67.62, H, 5.96; N, 3.20%.

*3.2. Trimethyl[(2-diphenylphosphinyl)ferrocenylmethyl] ammonium iodide (**6**)*

To a solution of amine **4** (6.5 g, 14.6 mmol) in methanol (15 mL), an excess methyl iodide (2.7 mL, 44 mmol) was added at room temperature. The solution was heated for 10 min at about 60 °C and then cooled to room temperature. 130 mL of ether were added with stirring. The ammonium salt **6** separates as an orange oil which crystallizes on standing (7.3 g, 85% yield). ^{31}P NMR ($CDCl_3$) δ 30.8; ^{1}H NMR ($CDCl_3$) δ 3.10 (s, 9H, NMe_3), 4.16 (s, 5H, Cp), 4.35 (br s, 1H), 4.72 (br s, 1H), 5.23 (*A*B, $J = 12.7$ Hz, 1H, CH_2), 5.30 (br s, 1H), 5.45 (A*B*, 1H, CH_2), 7.4–7.8 (m, 10h, Ph) ppm. The crude ammonium salt was used without further purification.

3.3. Trimethyl[(2-diphenylthiophosphinyl)ferrocenylmethyl]ammonium iodide (7)

It was prepared by the same procedure as for **6**, in 70% yield. ^{31}P NMR ($CDCl_3$) δ 41.4; ^{1}H NMR ($CDCl_3$) δ 3.06 (s, 9H, NMe_3), 4.18 (br s, 1H), 4.36 (s, 5H, Cp),

4.68 (br s, 1H), 5.33 (br s, 1H), 5.41 (*A*B, J = 13.2 Hz, 1H, CH_2), 5.92 (A*B*, 1H, CH_2), 7.4–7.9 (m, 10h, Ph) ppm. The crude ammonium salt was used without further purification.

3.4. Dimethyl [2-(diphenylphosphinyl)ferrocenyl]-methyl phosphonate (**8**)

A solution containing the ammonium salt **6** (4.0 g, 6.8 mmol) and trimethylphosphite (4 mL) in xylene (10 mL) was heated at 145 °C for 2.5 h, solvent and excess $P(OMe)_3$ were removed by distillation under vacuum. The residue was taken up in dichloromethane and purified by chromatography on alumina with ether/methanol 95:5 as the eluent. 2.0 g of **8** were obtained (57% yield). ^{31}P NMR ($CDCl_3$) δ 29.6 and 30.9 ppm; ^1H NMR (CD_2Cl_2) 400 MHz, δ 3.06 (dd, $J = 20.7$ Hz, $J = 15.7$ Hz, 1H, CH_2), 3.30 (d, $^3J_{H-P} = 10.9$ Hz, 3H, OMe), 3.45 (d, $^3J_{H-P} = 10.9$ Hz, 3H, OMe), 3.74 (dd, $J = 19.0$ Hz, $J = 15.7$ Hz, 1H, CH_2), 4.00 (br m, 1H), 4.11 (s, 5H, Cp), 4.43 (q, $J = 2.4$ Hz, 1H), 4.72 (br s, 1H), 7.4–7.9 (m, 10h, Ph); ^{13}C NMR (50 MHz, selected data) δ 24.8 (d, $^1J_{PC} = 138.6$ Hz, PCH_2), 51.8 (d, $^2J_{PC} = 6.8$ Hz, OCH_3), 52.3 (d, $^2J_{PC} = 6.8$ Hz, OCH_3), 70.6 (s, Cp), 70.7 (dd, $^1J_{PC} = 114.0$ Hz, $^3J_{PC} = 6.0$ Hz, PC), 71.9 (d, $J_{PC} = 11.0$ Hz, CH), 72.6 (d, $J_{PC} = 14.4$ Hz, CH), 73.4 (dd, $J_{PC} = 9.6$ Hz, $J_{PC} = 2.4$ Hz, CH), 82.9 (d, $J_{PC} = 10.0$ Hz, $J_{PC} = 4.0$ Hz, C), 134.9 (d, $J_{PC} = 105.5$ Hz, C_{ipso}), 133.8 (d, $J_{PC} = 106.3$ Hz, C_{ipso}) ppm. Mass spectrum: *m*/*z* 508 (M, 95%), 443 (M – Cp, 100%). Anal. Calc. for $C_{25}H_{26}FeO_4P_2$: C, 59.08; H, 5.16. Found: C, 58.99; H, 5.20%.

When starting from the ammonium iodide of (*R*)-**4** above, phosphonate (*R*)-**8** was obtained with an enantiomeric excess of 46%. The enantiomeric excess was determined by HPLC analysis: Chiracel OD-H, hexane/*i*PrOH 85:15, $t_1 = 12.6$ min (major), $t_2 = 17.4$ min. $[\alpha]_D = -34$ ($c = 0.2$, $CHCl_3$).

3.5. Dimethyl [2-(diphenylthiophosphinyl)ferrocenyl]-methylphosphonate (**9**)

The same procedure as for **8**, afforded **9** in 20% yield. ^{31}P NMR ($CDCl_3$) δ 29.7 and 42.5; ^1H NMR ($CDCl_3$) 400 MHz, δ 3.25 (t, $J = 18$ Hz, 1H, CH_2), 3.33 (d, $^3J_{H-P} = 10.1$ Hz, 3H, OMe), 3.51 (d, $^3J_{H-P} = 10.2$ Hz, 3H, OMe), 3.76 (br s, 1H), 4.02 (t, $J = 17.3$ Hz, 1H, CH_2), 4.24 (s, 5H, Cp), 4.34 (br s, 1H), 4.83 (br s, 1H), 7.3–7.8 (m, 10h, Ph); ^{13}C NMR (100 MHz, selected data) δ 24.8 (d, $^1J_{PC} = 138$ Hz, PCH_2), 51.9 (d, $^2J_{PC} = 6$ Hz, OCH_3), 52.5 (d, $^2J_{PC} = 6$ Hz, OCH_3), 69.8 (d, $J_{PC} = 9.8$ Hz, CH), 71.2 (s, Cp), 73.0 (dd, $^1J_{PC} = 89.5$ Hz, $^3J_{PC} = 6$ Hz, PC), 74.1 (d, $J_{PC} = 12$ Hz, CH), 74.5 (d, $J_{PC} = 2$ Hz, CH), 82.9 (d, $J_{PC} = 13$ Hz, C), 133.4 (d, $J_{PC} = 86$ Hz, C_{ipso}), 134.7 (d, $J_{PC} = 87$ Hz, C_{ipso}) ppm. Mass spectrum: *m*/*z* 524 (M, 34%), 459 (M – Cp, 100%).

3.6. [2-(phosphinomethyl)ferrocenyl]diphenyl-phosphine (**2**)

A toluene solution of phosphonate **8** (1.0 g, 2.0 mmol) was added to a solution of trichlorosilane (4.0 mL, 40 mmol) in toluene (20 mL) at 0 °C. An excess triethylamine (4.5 mL, 32 mmol) was then added. The mixture was then heated in a sealed glass tube at 120 °C for 5 h. After cooling to room temperature, hydrolysis was performed by slow addition of an aqueous NaOH solution (20% weight). After extraction with dichloromethane, the combined organic layer were washed with water and dried over magnesium sulphate. Purification was performed by column chromatography on alumina with cyclohexane–ether 94:6 as the eluent. Yield 70% (0.51 g, orange-red solid). The enantiomeric excess was determined by HPLC analysis: Chiracel OJ, hexane/*i*-PrOH 98:2, $t_1 = 6.3$ min (major), $t_2 = 9.8$ min. E.e. = 45%, $[\alpha]_D = -54$ ($c = 0.2$, $CHCl_3$).

^{31}P NMR ($CDCl_3$) δ −127.5 ($J_{H-P} = 196$ Hz) and −22.9 ($J_{P-P} = 1.6$ Hz); ^1H NMR ($CDCl_3$) 400 MHz, δ 2.71 (dm, $J_{H-P} = 197.2$ Hz, 2H, PH_2), 2.7–2.9 (m, 2H, CH_2), 3.73 (br, 1H), 4.00 (s, 5H, Cp), 4.25 (t, $J = 2.4$ Hz, 1H), 4.18 (q, $J = 2.0$ Hz, 1H, CH), 7.2–7.6 (m, 10h, Ph); ^{13}C NMR (100 MHz, C_6D_6), δ 13.8 (dd, $J_{PC} = 12.0$ Hz, $J_{PC} = 10.2$ Hz, PCH_2), 69.3 (s, CH), 70.1 (s, Cp), 70.7 (t, $J_{PC} = 3.8$ Hz, CH), 71.0 (d, $J_{PC} = 3.9$ Hz, CH), 75.7 (dd, $J_{PC} = 7.6$ Hz, $J_{PC} = 1.5$ Hz, C), 95.0 (dd, $J_{PC} = 25.8$ Hz, $J_{PC} = 3.8$ Hz, PC), 138.4 (d, $J_{PC} = 9.5$ Hz, C_{ipso}), 140.6 (d, $J_{PC} = 10.6$ Hz, C_{ipso}) ppm. Mass spectrum (C.I.): *m*/*z* 417 (M + 1). Anal. Calc. for $C_{23}H_{22}FeP_2$: C, 66.37; H, 5.33. Found: C, 66.35; H, 5.65%.

3.7. [(*p*-cymene)$RuCl_2$(**2**)] complex (**10**)

A solution containing diphosphine **2** (83 mg, 0.2 mmol) and $[(p\text{-cymene})RuCl_2]_2$ (61 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL) – EtOH (1.5 mL) was stirred at room temperature for 2.5 h. During this time a red solid precipitates which was recovered by filtration.

^{31}P NMR ($CDCl_3$) δ −25.5 ($J_{H-P} = 196$ Hz, PH_2) and −21.1; ^1H NMR ($CDCl_3$) 400 MHz, δ 1.00 (d, $J = 6.9$ Hz, 3H, CH*Me*), 1.04 (d, $J = 6.9$ Hz, 3H, CH*Me*), 2.07 (s, 3H, Me), 2.36 (m, 1H, C*H*Me_2) 3.33 (m, 2H, CH_2), 3.88 (m, 1H), 3.98 (s, 5H, Cp), 4.26 (dm, $J_{H-P} = 385$ Hz, 1H, PH_2), 4.35 (t, $J = 2.5$ Hz, 1H), 4.45 (br s, 1H, CH), 4.48 (dm, $J_{H-P} = 348$ Hz, 1H, PH_2), 5.09 (d, $J_{H-P} = 5.8$ Hz, 1H, CH), 5.20 (d, $J_{H-P} = 5.9$ Hz, 1H, CH), 5.25 (d, $J_{H-P} = 5.3$ Hz, 1H,

CH), 5.28 (d, J_{H-P} = 5.0 Hz, 1H, CH), 7.3–7.6 (m, 10h, Ph) ppm.

Crystal data for **2**

Molecular formula	$C_{23}H_{22}FeP_2$
Molecular weight	416.2
Crystal habit	Orange plate
Crystal size (mm)	$0.22 \times 0.18 \times 0.12$
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	23.028(10)
b (Å)	8.4680(10)
c (Å)	23.0340(10)
α (°)	90.00
β (°)	116.4100(10)
γ (°)	90.00
V (Å^3)	4022.9(5)
Z	8
D (g cm^{-3})	1.374
F(0 0 0)	1728
μ(cm^{-1})	0.912
Diffractometer	KappaCCD
X-ray source	Mo Kα
λ (Å)	0.71069
T (K)	150.0(1)
Reflections measured	14272
Unique data	8928
R_{int}	0.0247
Reflection used	7220
Refinement type	Fsqd
Hydrogen atoms	Mixed
Parameters refined	482
Reflections/parameter	14
wR_2	0.0831
R_1	0.0358
GoF	0.976
Difference peak/hole (e Å^{-3})	0.728(0.060)/−0.422(0.060)

Appendix A. Supplementary data

Crystallographic data for the structural analysis of compound **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 264508. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. Fax. +44(1223)336-033 or Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.02.034.

References

[1] N.J. Goodwin, W. Henderson, B.K. Nicholson, Chem. Commun. (1997) 31.
[2] N.J. Goodwin, W. Henderson, B.K. Nicholson, J. Fawcett, D.R. Russell, J. Chem. Soc., Dalton Trans. (1999) 1785.
[3] W. Henderson, S.R. Alley, J. Organomet. Chem. 636 (2002) 120.
[4] For a recent update of their catalytic applications see: T.J. Colacot, Chem. Rev. 103 (2003) 3101.
[5] A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, J. Am. Chem. Soc. 116 (1994) 4062.
[6] (a) Representative examples: M. Sawamura, A. Yamauchi, T. Takegawa, Y. Ito, J. Chem. Soc., Chem. Commun. (1991) 874;
(b) M. Sawamura, H. Hamashima, Y. Ito, Tetrahedron: Asymmetry 2 (1991) 593;
(c) Riant, G. Argouarch, D. Guillaneux, O. Samuel, H.B. Kagan, J. Org. Chem. 63 (1998) 3511;
(d) J.J. Almena Perea, A. Börner, P. Knochel, Tetrahedron Lett. 39 (1998) 8073;
(e) T. Ireland, G. Grossheimann, C. Wieser-Jeunesse, P. Knochel, Angew. Chem., Int. Ed. 38 (1999) 3212;
(f) W. Zhang, T. Shimanuki, T. Kida, Y. Nakatsuji, I. Ikeda, J. Org. Chem. 54 (1999) 6247;
(g) T. Sturm, W. Weissensteiner, F. Spindler, Adv. Synth. Catal. 345 (2003) 160;
(h) P. Barbaro, C. Bianchini, G. Giambastiani, D. Masi, S.L. Parisel, A. Togni, Synthesis (2004) 345.
[7] T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto, M. Kumada, Bull. Chem. Soc. Jpn. 53 (1980) 1138.
[8] Y. Miyake, A. Yamauchi, Y. Nishibayashi, S. Uemura, Bull. Chem. Soc. Jpn. 76 (2003) 381.
[9] G. Marr, T. Hunt, J. Chem. Soc. (C) (1969) 1070.
[10] N.J. Goodwin, W. Henderson, J.K. Sarfo, Chem. Commun. (1996) 1551.
[11] N.J. Goodwin, W. Henderson, B.K. Nicholson, J.K. Sarfo, J. Fawcett, D.R. Russel, J. Chem. Soc., Dalton Trans. (1997) 4377.
[12] (a) Selected examples: J. Szmuszkovicz, J. Am. Chem. Soc. 80 (1958) 3782;
(b) S. Hirai, R.G. Harvey, E.V. Jensen, Tetrahedron 22 (1966) 1625;
(c) H. Gross, H. Seibt, I. Keitel, J. Prakt. Chem. 317 (1979) 890;
(d) M. Mikolajczyk, P. Graczyk, M.W. Wieczorek, G. Bujacz, Tetrahedron Lett. 29 (1988) 6801;
(e) J-W. Weener, J.P.G. Versleijen, A. Meetsma, W. Ten Hoeve, A.M. Van Leusen, Eur. J. Org. Chem. (1998) 1511.
[13] V.I. Boev, Zh. Obshch. Khim. 48 (1978) 1594.
[14] For representative examples of ruthenium complexes of primary phosphines see ref. [2] J.F. van der Maelen Uria, S. Garcia-Granda, J.A. Cabeza, I. de Rio, Acta Crystallogr. Sect. C 50 (1994) 1064.
[15] L.A. Wozniak, W.J. Stec, Tetrahedron Lett. 40 (1999) 2537.
[16] (a) M. Tsukazaki, M. Tinkl, A. Roglans, B.J. Chapell, N.J. Taylor, V. Snieckus, J. Am. Chem. Soc. 118 (1996) 685;
(b) R.S. Laufer, U. Veith, N.J. Taylor, V. Snieckus, Org. Lett. 2 (2000) 629;
(c) O.J. Curnow, G.M. Fern, Organometallics 21 (2002) 2827;
(d) O.J. Curnow, G.M. Fern, M.L. Hamilton, A. Zahl, R. van Eldik, Organometallics 23 (2004) 906, and references therein.
[17] T. Mizuta, Y. Imamura, K. Miyoshi, J. Am. Chem. Soc. 125 (2003) 2068.