

Molecular structures of ruthenium half-sandwich complexes with primary and secondary phosphines: $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2(\text{PR}_3)]$ $[p\text{-cymene} = 1\text{-Me-4-Pr}^i\text{C}_6\text{H}_4$; $\text{PR}_3 = \text{PH}_2\text{Fc}$, $\text{PH}_2\text{CH}_2\text{Fc}$, $\text{PH}(\text{CH}_2\text{Fc})_2$; $\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)]$

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Abstract

A series of air-stable half-sandwich complexes of general formula $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2(\text{PR}_3)]$ [$p\text{-cymene} = 1\text{-Me-4-Pr}^i\text{C}_6\text{H}_4$; $\text{PR}_3 = \text{PH}_2\text{Fc}$ (**1**), $\text{PH}(\text{CH}_2\text{Fc})_2$ (**3**); $\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)$] were synthesized from $[(p\text{-cymene})\text{RuCl}_2]_2$ and the corresponding phosphine and fully characterized by IR and NMR (¹H, ¹³C, ³¹P) spectroscopy. Molecular structures of $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2(\text{PR}_3)]$ [$\text{PR}_3 = \text{PH}_2\text{Fc}$ (**1**), $\text{PH}_2\text{CH}_2\text{Fc}$ (**2**), $\text{PH}(\text{CH}_2\text{Fc})_2$ (**3**)] are reported.

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1. Introduction

With respect to organometallic complexes incorporating phosphines, the majority of studies have included only tertiary mono-, bi-, or polydentate phosphines [1]. Not surprisingly, primary and secondary phosphine complexes have received much less attention, due to the toxicity and high reactivity of the free phosphines (some are even pyrophoric). This lack of attention has prompted the development of primary and secondary phosphines that are more air-stable and hence easier to use [2–7]. Interest in these phosphines has arisen from the possibility of post-coordination modification of the P–H bond, which allows for chemical flexibility in the

synthesis of new and intriguing transition-metal phosphine complexes. Developments in this area have included the use of bulky aryl groups [5,6] and aminoalkyl substituents [7]. Another recent development in the stabilization of primary phosphines was the use of the ferrocenylmethyl fragment by Henderson and co-workers [4], who showed the phosphine $\text{PH}_2\text{CH}_2\text{Fc}$ [$\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)$] to be indefinitely air-stable, as well as having the ability to coordinate to molybdenum carbonyls or $(p\text{-cymene})\text{RuCl}_2$ ($p\text{-cymene} = 1\text{-Me-4-Pr}^i\text{C}_6\text{H}_4$) without alteration of the PH_2 group, while P–H activation occurred in the reaction with $\text{Ru}_3(\text{CO})_{12}$, which gave two products with capping phosphinidene ligands [3]. We have recently extended this chemistry to the secondary ferrocenyl-phosphine $\text{PH}(\text{CH}_2\text{Fc})_2$ [8], and have shown that the phosphines PH_2Fc , $\text{PH}_2\text{CH}_2\text{Fc}$, and $\text{PH}(\text{CH}_2\text{Fc})_2$ (= L) react with transition metal complexes with reactive M–X bonds (X = halide) without loss of HX but with

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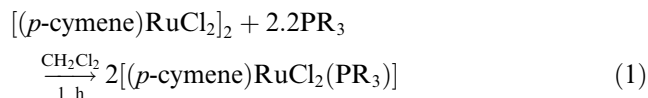
clean formation of the corresponding phosphine complexes, such as $[\text{Cp}^{\text{R}}\text{TaCl}_4\text{L}]$ ($\text{Cp}^{\text{R}} = \text{C}_5\text{H}_4\text{Me}$, C_5Me_5) [9], $[\text{Ml}_2(\text{CO})_3\text{L}_2]$ and $[\text{Ml}_2(\text{CO})_2\text{L}_3]$ ($\text{M} = \text{Mo}$, W) [10–12].

We have now extended these studies to organometallic ruthenium(II) complexes. Examples of ruthenium complexes incorporating these versatile primary and secondary phosphine ligands can be found in the literature. Most often primary and secondary phosphines are employed as capping or bridging ligands in clusters and bimetallic systems [13–15]. These functions are achieved due to the reactivity of the P–H bond in these ligands towards deprotonation reagents (e.g., KOBu^t or $\text{LiN}(\text{SiMe}_3)_2$). Complexes that have been synthesized from primary and secondary phosphines while attempting to maintain their P–H functionality are typically rather air- and/or moisture-sensitive and are uncommon in the literature. Reid et al. [16,17] synthesized complexes of the formula $[\text{RuX}_2(\text{PR}_3)_4]$ ($\text{X} = \text{Br}$, Cl ; $\text{PR}_3 = \text{PH}_2\text{Ph}$, PPh_2). Other groups have successfully prepared half-sandwich complexes, such as $[\text{Cp}^*\text{RuCl}(\text{PPh}_2)_2]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) [18], $[(p\text{-cymene})\text{RuCl}_2(\text{L})]$ ($\text{L} = \text{PPh}_2$ [19], $\text{P}(\text{CH}_2\text{Fc})(\text{CH}_2\text{OH})_2$ [20], $\text{PPh}_2(\text{CH}_2\text{Fc})$ [21]). The only examples of half-sandwich complexes incorporating primary phosphines are, to the best of our knowledge, $[(p\text{-cymene})\text{RuCl}_2(\text{PH}_2\text{CH}_2\text{Fc})]$ [3] and $[(p\text{-cymene})\text{RuCl}_2(\text{PH}_2\text{Mes}^*)]$ [22] ($\text{Mes}^* = 2,4,6\text{-Bu}_3\text{C}_6\text{H}_2$). In response to this lack of examples, a series of monophosphine half-sandwich complexes were synthesized by employing the ruthenium moiety $[(p\text{-cymene})\text{RuCl}_2]$ and the ferrocenylphosphines PH_2Fc , $\text{PH}_2\text{CH}_2\text{Fc}$, and $\text{PH}(\text{CH}_2\text{Fc})_2$.

2. Results and discussion

2.1. Synthesis and reactivity of complexes 1–3

The title compounds of general formula $[(p\text{-cymene})\text{RuCl}_2(\text{PR}_3)]$ [$\text{PR}_3 = \text{PH}_2\text{Fc}$ (**1**), $\text{PH}_2\text{CH}_2\text{Fc}$ (**2**) [3], $\text{PH}(\text{CH}_2\text{Fc})_2$ (**3**)] were obtained in more than 90% yield as orange powders from $[(p\text{-cymene})\text{RuCl}_2]_2$ and the corresponding phosphine (Eq. (1)) in a similar manner to a procedure published by Nolan and Serron [23] for compounds of general formula $[(p\text{-cymene})\text{RuCl}_2(\text{PR}_3)]$, where PR_3 is a tertiary phosphine.



For **2** and **3**, the reaction proceeded smoothly in dichloromethane over 1 h. Compound **2** was previously prepared and characterized by elemental analysis and NMR (^1H , ^{13}C , ^{31}P) spectroscopy [3]. In the case of PH_2Fc , the reaction required more forcing conditions.

In dichloromethane, only approximately 10% of **1** was formed after 3 d at room temperature. However, in refluxing THF (a coordinating solvent) **1** formed almost quantitatively within 1 h. It is not clear whether the decreased reactivity is due to an electronic effect, such as a lack of σ -donating ability, or a steric one. From an electronic standpoint, one can imagine that increased delocalization of the lone pair on the phosphorus atom into the cyclopentadienyl ring would decrease the relative Lewis basicity of the phosphine. If this is true, rehybridization of the phosphine may occur, tending more towards sp^2 rather than sp^3 hybridization. The rehybridization would lead to an increased Tolman's cone angle [24] and hence a greater steric effect. Thus, the lowered reactivity is most likely due to a combination of both electronic and steric factors, as shown previously by Nolan and Serron [23] for this particular ruthenium system.

^1H and ^{31}P NMR spectra indicate that the P–H functionality is maintained upon coordination for **1–3** [3], which was also observed for other transition-metal halide complexes incorporating primary and secondary phosphines [3,9–12,25–29]. Even after exposure to moist air for several months, no decomposition was observed by NMR spectroscopy for **1–3** in the solid state. The free phosphines themselves are just as air-stable, with the exception of PH_2Fc , which is slightly air-sensitive. The difference in stability of PH_2Fc and **1** is most likely due to the participation of the lone pair of electrons of the phosphine in σ coordination, which prevents reaction of the lone pair of electrons with atmospheric oxygen. Dichloromethane solutions of **1–3** display low air-sensitivity.

2.2. Spectroscopic data for complexes 1–3

Table 1 lists selected spectroscopic data for **1–3** and their respective free phosphines. As indicated by the ^{31}P NMR data, a shift to low field by more than 100 ppm for the primary phosphines and more than 70 ppm for the secondary phosphine, as well as a rather pronounced increase in the P–H coupling constant by ca. 150 to 190 Hz, is observed on coordination to the ruthenium center. The increase in P–H coupling could be assumed to signify strengthening of the P–H bond. However, this assump-

Table 1
Selected spectroscopic data for compounds **1–3** and their respective free phosphines

Compound	$\nu_{\text{P-H}}$ (cm^{-1}) ^a	$\delta(^{31}\text{P})$, ppm ^b	$^1J_{\text{P-H}}$ (Hz)	Ref.
1	2340	−27.6	394	This work
2	2338	−27.7	359	[3]
3	2376	24.7	351	This work
PH_2Fc	2259	−143.3	203	[39]
$\text{PH}_2\text{CH}_2\text{Fc}$	2285	−129.1	194	[3]
$\text{PH}(\text{CH}_2\text{Fc})_2$	2285	−53.3	196	[8]

^a FTIR data obtained on KBr pellets.

^b NMR data obtained in CDCl_3 .

tion is contradicted by the literature, as evidence seems to indicate that on coordination the P–H bond of a primary or secondary phosphine is significantly weakened. This is demonstrated by the formation of bridged phosphanido and phosphinidene species for some systems when attempting to incorporate primary or secondary phosphines. Examples of this reactivity include $[\text{Ru}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-PCH}_2\text{R})]$ [3], $(\text{Me}_2\text{Al})_4[(\mu\text{-PH})_2(\text{C}_6\text{H}_4)_2]$ [25], and $[\{\text{PtCl}(\text{PPh}_2)(\text{PHPh}_2)\}_2]$ [28]. Interestingly, an increase in coupling between two atoms has been observed when electron density is withdrawn from a system. For example, methane has a C–H coupling constant, $^1J_{\text{C-H}}$, of 125 Hz by ^{13}C NMR [30]. As each hydrogen atom is subsequently replaced with a fluorine atom, following the formula $\text{CH}_n\text{F}_{4-n}$, the C–H coupling for the remaining hydrogen atoms increases: $n = 3$, $^1J_{\text{C-H}} = 149$ Hz; $n = 2$, $^1J_{\text{C-H}} = 185$ Hz; $n = 1$, $^1J_{\text{C-H}} = 239$ Hz. This seems to indicate that as electron density is drawn

to the substituents, enhanced element–H coupling occurs.

The FTIR data presented in Table 1 support a stronger P–H bond on coordination. The P–H stretching frequency increases by ca. 80–90 cm^{-1} on coordination to ruthenium, which would seem to indicate an increase in the bond order of the P–H bond. Most likely, however, this is due to an increased ionic component of the P–H bond. Considering the very small difference in electronegativity of phosphorus (2.06) [31] and hydrogen (2.20) [31], the P–H bond may be thought of as non-polar and covalent. Metal coordination acts to withdraw electron density from the system without drastic rehybridization, causing a change in the polarization of the P–H bond. This polarization would result in a greater partial negative charge at the phosphorus and a partial positive charge at the hydrogen atom and thus increase the ionic component of the bond. The result is a bond

Table 2
Crystal data and structure refinement for 1–3

	1	2	3
Empirical formula	$\text{C}_{20}\text{H}_{25}\text{Cl}_2\text{FePRu} \cdot \text{CH}_2\text{Cl}_2$	$\text{C}_{21}\text{H}_{27}\text{Cl}_2\text{FePRu}$	$\text{C}_{32}\text{H}_{37}\text{Cl}_2\text{Fe}_2\text{PRu} \cdot 0.5\text{CH}_2\text{Cl}_2$
Formula weight	609.12	538.22	778.72
Temperature	213(2) K	210(2) K	213(2) K
Wavelength	71.073 pm	71.073 pm	71.073 pm
Crystal system	Tetragonal	Triclinic	Monoclinic
Space group	$I4_1/a$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions			
<i>a</i> (pm)	2497.8(5)	607.88(6)	616.21(7)
<i>b</i> (pm)	2497.8(5)	1894.58(18)	2822.0(3)
<i>c</i> (pm)	1702.2(4)	2036.04(19)	1868.7(2)
α (°)	90	111.254(2)	90
β (°)	90	94.886(2)	90.021(2)
γ (°)	90	94.111(2)	90
Volume (nm ³)	10.62(1)	2.1641(4)	3.2495(6)
<i>Z</i>	16	4	4
<i>D</i> _(calc) (Mg/m ³)	1.524	1.652	1.592
Absorption coefficient (mm ⁻¹)	1.583	1.692	1.657
<i>F</i> (000)	4896	1088	1580
Crystal size (mm ³)	0.20 × 0.20 × 0.20	0.20 × 0.08 × 0.05	0.50 × 0.10 × 0.08
Theta range for data collection (°)	2.18–26.37	1.86–26.37	1.81–29.26
Index ranges	–31 ≤ <i>h</i> ≤ 27, –31 ≤ <i>k</i> ≤ 31, –21 ≤ <i>l</i> ≤ 15	–5 ≤ <i>h</i> ≤ 7, –22 ≤ <i>k</i> ≤ 23, –25 ≤ <i>l</i> ≤ 23	–8 ≤ <i>h</i> ≤ 8, –38 ≤ <i>k</i> ≤ 23, –24 ≤ <i>l</i> ≤ 25
Reflections collected	29 507	12 229	21 104
Independent reflections	5431 [<i>R</i> (int) = 0.0490]	8640 [<i>R</i> (int) = 0.0414]	7987 [<i>R</i> (int) = 0.0577]
Completeness to θ (max)	99.9%	97.4%	89.9%
Absorption correction	SADABS	SADABS	SADABS
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5431/9/263	8640/12/491	7987/15/389
Goodness-of-fit on <i>F</i> ²	1.111	1.061	1.117
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]			
<i>R</i> ₁	0.0628	0.0751	0.0569
<i>wR</i> ₂	0.1596	0.1288	0.0837
<i>R</i> indices (all data)			
<i>R</i> ₁	0.0857	0.1355	0.0796
<i>wR</i> ₂	0.1705	0.1475	0.0888
Largest diff. peak and hole (e Å ⁻³)	1.137 and –0.895	2.202 and –0.831	0.596 and –0.822

that is strong versus homolytic cleavage but weaker versus heterolytic cleavage.

2.3. Structural data for 1–3

X-ray quality orange needles were obtained for **1–3** by slow vapor diffusion employing an Et₂O/CH₂Cl₂ solvent system. Table 2 contains the crystallographic data and structure refinement parameters for **1–3**. Both **1** and **3** contain molecules of dichloromethane within their crystal lattices, 1 and 0.5 equiv, respectively. Compound **2** has two independent molecules in the asymmetric unit.

All three complexes display the “three-legged piano stool” conformation expected for such complexes (see Figs. 1–3). Many analogous structures have been reported in the literature, most of which have tertiary phosphines [32–37] with the exception of [(*p*-cymene)RuCl₂(PPh₂)] [19]. Table 3 contains selected bond distances and bond angles for **1–3**.

The Cl–Ru–Cl bond angles for the title compounds are on par with the majority of structures identified previously, being approximately 88° in all cases. Of note are the decreased average Cl–Ru–P bond angles for these complexes. Compounds **1–3** display slightly more acute angles, 78.76(6)° to 83.77(9)°, as opposed to the average angle of 86.0° for analogous complexes with tertiary phosphines. The secondary phosphine complex [(*p*-cymene)RuCl₂(PPh₂)] [19] also displays a more acute average P–Ru–Cl angle of 82.08(2)°. Ideally, the sum of all three L–M–L angles should equal 270° with each L–M–L angle being 90°, i.e., an octahedral complex in which the arene occupies one face of the structure. In the case of the above-mentioned tertiary analogues, the sum of the L–M–L angles is on average around 260°, most likely due to the larger arene (versus cyclopentadienyl ligand) combined with the bulk of the substituents on the ring itself. Compounds **1–3** exhibit a

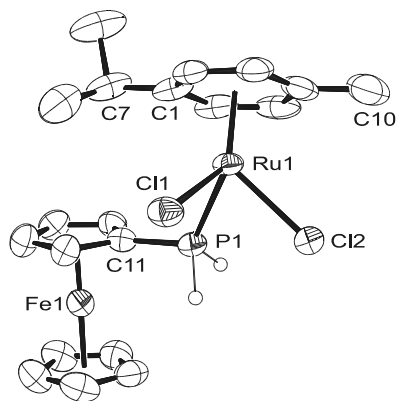


Fig. 1. Perspective ORTEP view of [(*p*-cymene)RuCl₂(PH₂Fc)] (**1**) [44]. Thermal ellipsoids at 50% probability. Hydrogen atoms (other than PH) omitted for clarity.

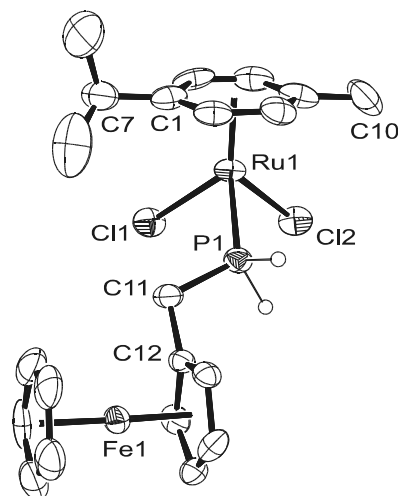


Fig. 2. Perspective ORTEP view of [(*p*-cymene)RuCl₂(PH₂CH₂Fc)] (**2**) [44]. Thermal ellipsoids at 50% probability. Hydrogen atoms (other than PH) omitted for clarity. Only one of the two independent molecules is shown.

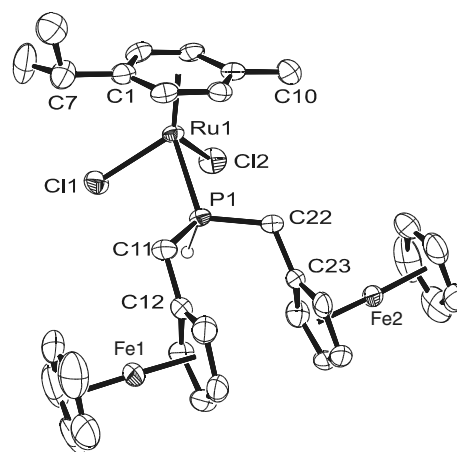


Fig. 3. Perspective ORTEP view of [(*p*-cymene)RuCl₂{PH(CH₂Fc)₂}] (**3**) [44]. Thermal ellipsoids at 50% probability. Hydrogen atoms (other than PH) omitted for clarity.

sum of 250.6° to 254.4°, even more distorted from ideal geometry than the tertiary analogues.

All three complexes **1–3** have slightly shorter Ru–P bonds (2.296(2)–2.312(2) Å) versus the 2.34–2.37 Å bond lengths observed in similar complexes containing tertiary phosphines. This is most likely due to steric rather than electronic effects, considering the lack of proper σ* orbitals on the phosphine for backbonding with ruthenium. Again, the complex [(*p*-cymene)RuCl₂(PPh₂)] displays similar structural characteristics to the presented compounds, with a Ru–P bond length of 2.316(1) Å [19]. The average Ru–Cl bond lengths of about 2.41 Å for all three complexes are consistent with those of other complexes found in the literature, as is the Ru–Cnt (Cnt = centroid) distance of around 1.69–1.70 Å. The P–H bond lengths of **1–3**

Table 3
Selected interatomic bond lengths (Å) and angles (°) for complexes 1–3

Distances and angles	1	2 ^a	3
Ru–Cnt ^b	1.697	1.690	1.692
Ru–Cl1	2.410(3)	2.415(2)	2.414(2)
Ru–Cl2	2.417(2)	2.410(2)	2.407(2)
Ru–P	2.312(2)	2.310(1)	2.296(2)
P–H1	1.32(4)	1.43(5)	1.27(6)
P–H2	1.32(4)	–	1.29(6)
P–C11	1.818(9)	1.815(5)	1.786(6)
P–C22	–	1.810(5)	–
Cl1–Ru–Cl2	88.0(1)	89.77(5)	88.75(5)
Cnt–Ru–Cl1	128.88	129.62	128.29
Cnt–Ru–Cl2	126.92	125.54	129.17
Cnt–Ru–P	130.78	132.78	131.63
P–Ru–Cl1	82.63(9)	80.87(5)	83.10(6)
P–Ru–Cl2	83.77(9)	81.89(5)	78.76(6)
Ru–P–H1	115(4)	108(2)	118(2)
Ru–P–H2	115(4)	–	123(3)
Ru–P–C11	120.0(3)	116.7(2)	120.0(2)
Ru–P–C22	–	113.5(2)	–
H1–P–C11	105(4)	101(2)	105(3)
H2–P–C11	103(4)	–	98(3)
H1–P–H2	96(5)	–	86(4)
H1–P–C22	–	104(2)	–
C11–P–C22	–	111.9(3)	–

^a Average of both independent molecules for compound 2.

^b Cnt = centroid of the *p*-cymene six-membered ring.

(1.27(6)–1.43(5) Å) are only slightly larger than that of [(*p*-cymene)RuCl₂(PPh₂)] (1.25(2) Å) [19].

The torsion angles associated with the orientation of the phosphine in each compound are intriguing. Compound 2 has a C–P–Ru–Cnt torsion angle of 84.1° (average of both independent molecules), where C is the CH₂ group of the ferrocenylmethyl fragment. One would expect that the bulkiest substituent bound to the phosphine, barring electronic effects, would take up an orientation *trans* to the arene ring. This does not seem to be true in this case. In fact, the average torsion angle for the hydrogen *trans* to the arene for both orientations of 2, H₂–P–Ru–Cnt, is only 151.4°, which is almost a 30° deviation from the typical orientation seen in tertiary phosphine analogues. Most likely the observed abnormal orientation is an effect of crystal packing, although the exact reason is not certain. The lack of other bulky substituents on the phosphine may account for this preference of orientation, given that the compound [(*p*-cymene)RuCl₂(PPh₂CH₂Fc)] [21] has the ferrocenylmethyl fragment in the expected *trans* orientation.

Compound 3 displays what appears to be a more symmetrical orientation, in which the single hydrogen atom on the phosphine is located *trans* to the arene ligand (torsion angle 176.7°). Of interest is the orientation of the two ferrocenylmethyl groups on the phosphine with respect to one another. The substituted cyclopentadienyl rings of the ferrocene moieties appear to be in a

“stacked” conformation, as opposed to a more staggered arrangement. The interatomic distance of the two rings is ca. 3.5 Å, seemingly too far for any true through-space interactions.

Compound 1, like 2, appears to have the bulkiest substituent on the phosphine, i.e., the ferrocenyl fragment, in a *cis* rather than *trans* orientation, with a C–P–Ru–Cnt torsion angle of 53.9°. For the hydrogen atom that is in the *trans* position a H–P–Ru–Cnt torsion angle of 175.4° is observed, which is close to ideal 180°. Again, this unexpected orientation is most likely due to packing and lack of other bulky substituents on the phosphine.

3. Experimental

3.1. General

All manipulations were carried out under a nitrogen or argon atmosphere by employing standard Schlenk and glovebox techniques. Elemental analyses (C, H) were performed by Desert Analytics (Tucson, AZ) under nitrogen. ¹H (400 MHz), ¹³C{¹H} (100.6 MHz), and ³¹P (162 MHz) NMR spectra were obtained in CDCl₃ at 25 °C on an AVANCE DRX 400 spectrometer: internal reference solvent and TMS (¹H, ¹³C), external reference 85% H₃PO₄ (³¹P). FTIR spectra were obtained on KBr pellets on a Perkin–Elmer System 2000 in the range of 350–4000 cm^{−1}.

3.2. Materials

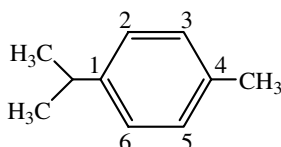
RuCl₃·*x*H₂O was used as received from Umicore AG & Co KG. [{(*p*-cymene)RuCl₂}₂] [38], [(*p*-cymene)RuCl₂(PH₂CH₂Fc)] [3], and the phosphines (PH₂Fc [39], PH₂CH₂Fc [2], and PH(CH₂Fc)₂ [8]) were prepared according to the literature procedures. Tetrahydrofuran (Aldrich), dichloromethane (Aldrich), and CDCl₃ (Cambridge Isotopes) were freshly distilled and degassed prior to use.

3.3. Synthesis of [(*p*-cymene)RuCl₂(PH₂Fc)] (1)

A solution of [{(*p*-cymene)RuCl₂}₂] (200 mg, 0.326 mmol) and PH₂Fc (284 mg, 0.718 mmol) in tetrahydrofuran (50 mL) was refluxed for 1 h. Then all volatile substances were removed under reduced pressure to produce an orange solid. The solid was washed with anhydrous diethyl ether and dried in vacuo to yield an orange product (320 mg, 94% yield). Orange needles of 1 were obtained by slow vapor diffusion employing an Et₂O/CH₂Cl₂ solvent system. Mp: 166–170 °C (decomp.). ¹H NMR: δ 1.16 (d, 6H, ³J_{H–H} = 7 Hz,

CH(CH₃)₂, 2.08 (s, 3H, CH₃), 2.66 (sep, 1H, ³J_{H-H} = 7 Hz, CH(CH₃)₂), 4.24 (s, 5H, C₅H₅), 4.59 (br s, 2H, *m*-H in C₅H₄), 4.63 (br s, 2H, *o*-H in C₅H₄), 5.69 (d, 2H, ¹J_{H-P} = 392 Hz, PH₂), 5.21 (d, 2H, ³J_{H-H} = 5 Hz, CH^{3,5} in *p*-cymene), 5.32 (d, 2H, ³J_{H-H} = 5 Hz, CH^{2,6} in *p*-cymene). ¹³C{¹H} NMR: δ 18.52 (s, CH₃), 22.17 (s, CH(CH₃)₂), 30.76 (s, CH(CH₃)₂), 71.47 (d, ³J_{C-P} = 8 Hz, *m*-C in C₅H₄), 72.19 (s, ²J_{C-P} = 11 Hz, *o*-C in C₅H₄), 70.66 (s, C₅H₅), 77.23 (obscured by solvent peak, *ipso*-C in C₅H₄), 85.95 (d, *J*_{C-P} = 4 Hz, C^{3,5} in *p*-cymene), 86.74 (d, *J*_{C-P} = 5 Hz, C^{2,6} in *p*-cymene), 100.81 (d, *J*_{C-P} = 2 Hz, C⁴ in *p*-cymene), 105.25 (d, *J*_{C-P} = 2 Hz, C¹ in *p*-cymene). ³¹P NMR: δ -27.6 (t, ¹J_{P-H} = 394 Hz). Anal. Calc. for C₂₀H₂₅Cl₂FePRu: C, 45.82, H, 4.82. Found: C, 46.08, H, 5.07.

Numbering scheme for *p*-cymene:



3.4. Synthesis of [(*p*-cymene)RuCl₂{PH(CH₂Fc)₂}] (3)

A solution of [(*p*-cymene)RuCl₂]₂ (200 mg, 0.326 mmol) and PH(CH₂Fc)₂ (308 mg, 0.718 mmol) in dichloromethane (50 mL) was stirred for 1 h at room temperature, after which the volatile substances were removed under reduced pressure to produce an orange solid. The solid was washed with anhydrous diethyl ether and dried in vacuo to yield an orange product (430 mg, 90% yield). Orange needles of **3** were obtained by slow vapor diffusion employing a Et₂O/CH₂Cl₂ solvent system. Mp: 203–210 °C (decomp.). ¹H NMR: δ 1.19 (d, 6H, ³J_{H-H} = 7 Hz, CH(CH₃)₂), 2.03 (s, 3H, CH₃), 2.67 (sep, 1H, ³J_{H-H} = 7 Hz, CH(CH₃)₂), 2.90 (ddd, 2H, ²J_{H-H} = 15 Hz, ³J_{H-H} = 6 Hz, ²J_{H-P} = 10 Hz, PH(CH₂Fc)₂), 3.22 (ddd, 2H, ²J_{H-H} = 15 Hz, ³J_{H-H} = 4 Hz, ²J_{H-P} = 4 Hz, PH(CH₂Fc)₂), 4.11 (s, 5H, C₅H₅), 4.18 (br s, 2H, *m*-H in C₅H₄), 4.23 (br s, 2H, *o*-H in C₅H₄), 4.72 (d of m, 1H, ¹J_{H-P} = 349 Hz, PH), 4.94 (d, 2H, ³J_{H-H} = 5 Hz, CH^{3,5} in *p*-cymene), 5.10 (d, 2H, ³J_{H-H} = 5 Hz, CH^{2,6} in *p*-cymene). ¹³C{¹H} NMR: δ 18.28 (s, CH₃), 22.44 (d, ¹J_{C-P} = 25 Hz, PH(CH₂Fc)), 27.25 (s, CH(CH₃)₂), 30.61 (s, CH(CH₃)₂), 67.94 (s, *m*-C in C₅H₄), 68.19 (s, *m*-C in C₅H₄), 69.13 (s, *o*-C in C₅H₄), 69.25 (s, *o*-C in C₅H₄), 69.13 (s, C₅H₅), 83.29 (d, ²J_{C-P} = 3 Hz, *ipso*-C in C₅H₄), 85.49 (d, *J*_{C-P} = 4 Hz, C^{3,5} in *p*-cymene), 85.54 (d, *J*_{C-P} = 3 Hz, C^{2,6} in *p*-cymene), 101.06 (d, *J*_{C-P} = 3 Hz, C⁴ in *p*-cymene), 106.77 (d, *J*_{C-P} = 3 Hz, C¹ in *p*-cymene). ³¹P NMR: δ 24.7 (d of m, ¹J_{P-H} = 351 Hz). Anal. Calc. for C₃₂H₃₇Cl₂Fe₂PRu · 0.3H₂O (water identified by ¹H NMR): C, 51.77, H, 5.07. Found: C, 51.49, H, 5.35.

3.5. Data collection and structural refinement of **1–3**

Data were collected on a Siemens CCD (SMART) [40] diffractometer (λ(Mo Kα) = 0.71073 Å). Data reduction was performed with SAINT [41] including the program SADABS [42] for empirical absorption correction. The structures were solved by direct methods and refined using the program SHELX97 [43]. Fe, Ru, Cl, P, and C atoms were refined anisotropically, whereas all hydrogen atoms were calculated on idealized positions except the H atoms attached to phosphorus, which were calculated by difference maps and refined isotropically. Compound **3** was found to be a merohedric twin (twin matrix 100 0-10 00-1). Crystallographic data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for material should quote the full literature citation and the references CCDC 259760 (**1**), 259759 (**2**), 259761 (**3**).

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Appendix A. Supplementary data

Details of the IR spectra are available as electronic supplement. Supplementary data associated with this article can be found, in the online version, at [10.1016/j.jorganchem.2005.02.006](https://doi.org/10.1016/j.jorganchem.2005.02.006).

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