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# Cationic half-sandwich ruthenium(II) complexes with cyclopentadienyl–phosphine ligands

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Dedicated to Professor Pierre Braunstein.

**Abstract**

The reaction of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2]_2$ (**1**) with the Cp-linked phosphine ligands $L_n$ ($C_5H_5$–$CH_2CHRPR'_2$; R = H, R′ = Ph, $n$ = 1; R = Ph, R′ = Ph, $n$ = 2), in a 5:1 mixture of acetonitrile–ethanol and in the presence of $Li_2CO_3$ and $KPF_6$ affords the cationic half-sandwich ruthenium(II) complexes $[\{\eta^5\text{-}C_5H_4$–$CH_2CHRPR'_2\text{-}\kappa P\}Ru(CH_3CN)_2]\cdot[PF_6]$ (**4**) and (**5**). Both complexes have been characterized in the solid state by an X-ray structure analysis. In contrast, the reaction between **1** and $L_3$ (R = Ph, R′ = *o*-xylyl) affords the cationic sandwich compound $[\{\eta^5:\eta^6\text{-}C_5H_4$–$CH_2CHPhPR'_2\}Ru]\cdot[PF_6]$ (**7**), in which one arene substituent of the phosphine is $\eta^6$-coordinated to the metal and the phosphorus remains pendant. Treatment of **5** with tertiary phosphines ($PR''_3$, R″ = i-Pr, Ph, Cy) affords a mixture of the diastereomers $[L_2Ru(CH_3CN)PR''_3]^+$. The diastereoselectivity observed depends on the steric bulkiness of the phosphines and on the reaction conditions.


*Keywords:* Ruthenium; Cyclopentadienyl; Phosphane; Optically active metal complexes; Chiral ligands; X-ray crystallography

## 1. Introduction

Chelating ligands containing both a cyclopentadienyl and a heteroatom have received considerable attention in recent years. A special attraction of these ligand is the possibility to vary its three structural components independently, namely the cyclopentadienyl ring, the spacer and the heteroatom and its substituents. The heteroatom can be a hard nucleophile such as oxygen and nitrogen, but also a soft nucleophile such as phosphorus, arsenic or sulfur. Both classes of bidentate ligands and their metal complexes have recently been reviewed [1,2].

The increased interest in these ligands is in part due to their application as so-called 'constraint-geometry' catalysts (CGC) in industrial Ziegler–Natta catalysis [3]. Among the possible heteroatoms, phosphorus is most prominent in view of the general importance of phosphine ligands in organometallic chemistry and homogeneous catalysis. A cyclopentadienyl–phosphine ligand, connected by an appropriate linker, acts as a 6+2 electron ligand and forms a stable chelate ring with both early and late transition metals [2]. There was, however, still a lack of suitable methods to prepare such ligands by a general and flexible route. We have recently reported such a route [4,5] by extending the method of Kauffmann for ring-opening substituted spiro [2,4]hepta-4,6-dienes [6] to include also optically active spacers.

Half-sandwich complexes of ruthenium have been employed in homogeneous catalysis with considerable success, especially by Trost for C–C bond formation [7]. The catalysts employed were compounds such as $CpRu(PPh_3)_2Cl$, $CpRu(COD)Cl$ or $[CpRu(CH_3CN)_3]^+$. . Kirchner has shown that substitution of one $CH_3CN$ ligand in the latter compound to form $[CpRu(CH_3CN)PPh_3]^+$ also gave a very active catalyst for redox isomerization and C–C bond coupling [8,9]. Various attempts have been made to link the Cp and phosphorus moieties in such compounds through a

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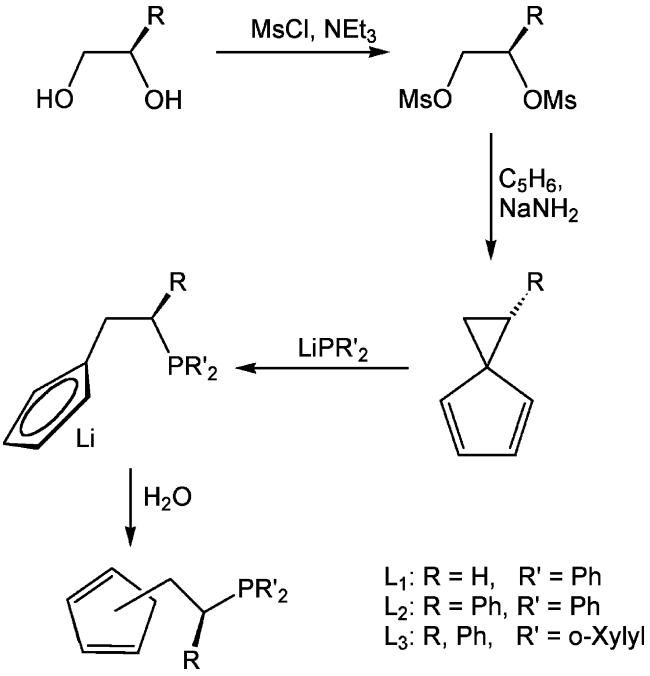
spacer [2]. In almost all cases, these complexes contain a $PPh_3$ ligand, as the synthesis, starting from $RuCl_2(PPh_3)_3$, gives no alternate choice. Only in one case, a bis(acetonitrile) complex could be isolated by Takahashi in which the linker connects through an ester group at the cyclopentadienyl ligand [10].

Additionally, chirality introduced into systems in which phosphorus is coordinated to the metal may assist in controlling the stereochemistry of reactions at the metal center, ultimately leading to an increase in stereoselection in stoichiometric and catalytic reactions. This may be dependent on the spatial proximity of the stereogenic center(s) to the metal, the rigidity of the chelate ring as well as the shape of the chiral 'pocket' created by it.

In some cases, the highly selective formation of a new stereogenic center at ruthenium has been observed with such ligands [11–13]. This has prompted us to find a new route to prepare $(\eta^5\text{-}CpCH_2CHRPR'_2\text{-}\kappa P)Ru(CH_3CN)_2]^+$ with both chiral and achiral linkers to compare its reactivity with that of previously prepared compounds without linker.




Scheme 1.

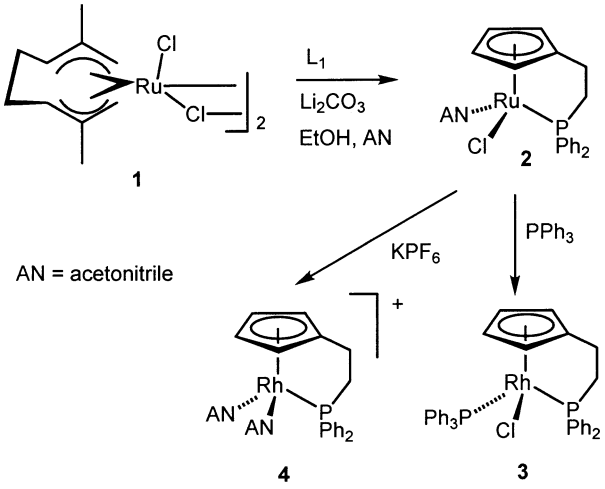
## 2. Results and discussion

### 2.1. Synthesis of the ligands

The synthesis of $L_1$ ($C_5H_5$–$CH_2CH_2PPh_2$) has been previously reported [14]. The synthesis of the chiral cyclopentadienyl–phosphine ligands $L_n$ ($C_5H_5$–$CH_2CHPhPR'_2$, $R' = Ph$, $n = 2$; $R' = o$-xylyl, $n = 3$) starts from optically active vicinal diols [5,6] and is shown in Scheme 1. Treatment of 1-Phenyl-1,2-ethanediol [15] with methanesulfonyl chloride affords the bismethanesulfonate ester in quantitative yield. Displacement of the methanesulfonate groups by cyclopentadiene in presence of excess $NaNH_2$ affords the spiroannulated diene with inversion of the configuration at the chiral carbon. The ring opening reaction with $LiPR'_2$ ($R' = Ph$, $o$-xylyl) proceeds with complete regioselectivity at the substituted carbon atom of the cyclopropane ring, bringing the stereogenic center close to the phosphorus atom. The lithium salts of the ligands are then converted by quenching with water to the corresponding dienes, obtained as a mixture of two regioisomers.

### 2.2. Complexes with $L_1$

The reaction of $[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})Cl_2]_2$ (**1**) with the Cp-linked phosphine ligand $L_1$ in a 1:2 ratio in a mixture of acetonitrile and ethanol at room temperature and in presence of $Li_2CO_3$, afforded the neutral complex $[\{\eta^5\text{-}C_5H_4$–$CH_2CH_2PPh_2\text{-}\kappa P\}Ru(CH_3CN)Cl]$ (**2**) (Scheme 2). The ligand acts as a heterobidentate chelating ligand




Scheme 2.

forming a five-membered ring. Compound **1** has already been shown to be a useful reagent in organoruthenium chemistry, since it can effectively be used to provide in situ sources of $Ru^{2+}$ ions [16,17]. The 2,7-dimethyloctadienediyl ligand is eliminated by reductive coupling leading to 1,6-dimethyl-1,5-cyclooctadiene, which was detected spectroscopically. This accounts both for its lability and for the formal Ru(IV)/Ru(II) reduction. There is spectroscopic evidence that in acetonitrile solution **2** is in equilibrium with the cationic species $[L_1Ru(CH_3CN)_2]$ [Cl] (**4**·[Cl]): a freshly prepared sample of **2** shows one signal in the $^{31}P$ NMR spectrum at about 64 ppm. Another signal slowly appears at about 69 ppm, but upon addition of LiCl, it disappears again. Un-

fortunately, **2** is not stable in the solid state to allow a complete characterization. Therefore, it was converted into **3** by reaction with triphenylphosphine. This compound has been previously synthesized in 41% yield from $RuCl_2(PPh_3)_3$ and $L_1$ [14]. As **3** crystallized in a different space group than reported before [14], we have performed an X-ray structure analysis to confirm its composition. The result is shown in Fig. 1.

The chloride ligand in **2** can easily be scavenged by metathesis with $KPF_6$ in acetonitrile solution, affording the cationic bis(acetonitrile) complex **4**·[$PF_6$]. A more direct synthesis of **4** consists in the reaction of **1** with $L_1$ in an acetonitrile–ethanol mixture, in the presence of $Li_2CO_3$ and $KPF_6$. The phosphorus atom coordinated to the metal resonates at low field (69.5 ppm, $CD_3CN$). The large downfield shift is characteristic for the formation of a five-membered chelate ring [18]. The coordinated acetonitrile ligands give rise to a doublet at 2.1 ppm with a long range coupling ($^5J$) with phosphorus of 1.2 Hz. Easy replacement of the acetonitrile ligands with $CD_3CN$ is confirmed by means of $^1H$ NMR, suggesting that they are substitutionally labile. The mass spectrum shows the molecular ion at $m/z$ 461. Compound **4**·[$PF_6$] has also been characterized in the solid state by X-ray analysis (Fig. 2).

### 2.3. Complexes with $L_2$

With the same procedure used to synthesize **4**·[$PF_6$], the chiral cationic ruthenium compound **5** was formed in 77% yield from **1** and the ligand $L_2$ (Scheme 3). The phosphorus is here even more deshielded than in **4**, giving rise to a singlet at 88.7 ppm. Due to the asymmetry of the molecule, the acetonitrile ligands are no longer equivalent, giving rise to two signals, one at 1.63 ppm and the other at 2.12, both split into a doublet due to the coupling with phosphorus ($^5J_{HP} = 1.4$ and 1.1 Hz, respectively).

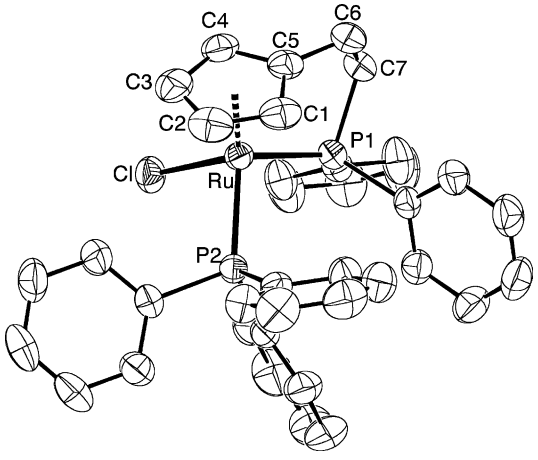



Fig. 1. PLATON view of compound **3** with 50% displacement ellipsoid probability, H-atoms omitted.

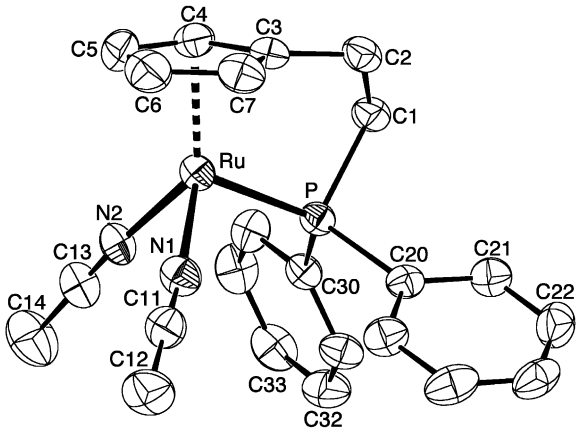
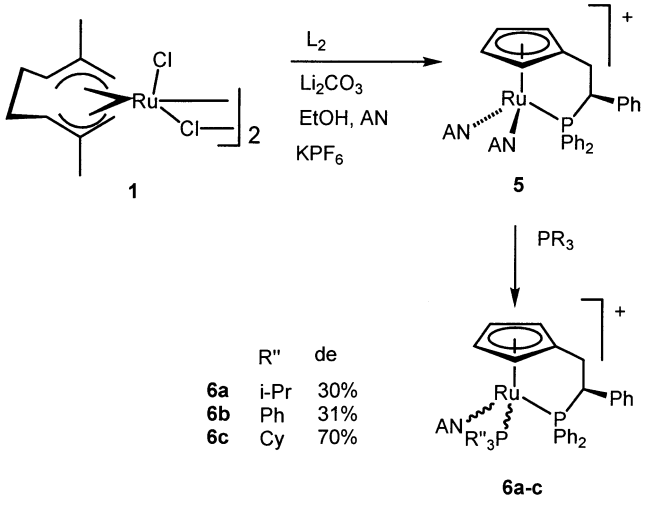



Fig. 2. PLATON view of the complex cation **4** with 50% displacement ellipsoid probability, H-atoms omitted.




Scheme 3.

Compound **5**·[$PF_6$] has also been characterized in the solid state by X-ray analysis (Fig. 3). There is a remarkable similarity in the relative conformation of the three phenyl groups compared with the analogous

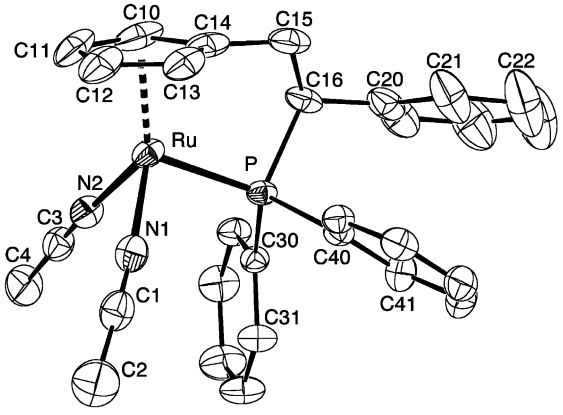



Fig. 3. PLATON view of the complex cation **5** with 50% displacement ellipsoid probability, H-atoms omitted.

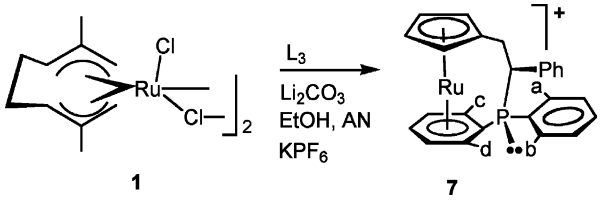
rhodium complexes prepared by us previously [4,5], which represents the most stable conformation and is not caused by crystal packing effects.

In order to determine how the chirality in the linker can control the induction of metal-centered chirality, we have reacted **5**·[$PF_6$] with tertiary phosphines with different steric properties. The reactions, carried out in $CH_2Cl_2$ solution at room temperature with an equimolar amount of the phosphines, afforded the cationic species **6a**–**c** in quantitative yield as a mixture of the two diastereomers. It was found that the selectivity depends on the steric bulkiness of the phosphine with similar results for P(i-Pr)$_3$ and $PPh_3$ (de = 30 and 31%, respectively). The de values were derived from the ratio of the two diastereomers measured by $^1H$ and $^{31}P$ NMR. A higher value (de = 71%) was observed with the bulky $PCy_3$ ligand. These results are somewhat lower than those reported by Takahashi [11]. This may possibly be due to the fact that Takahashi's ligands exhibit planar chirality as they are derived from an unsymmetrically substituted cyclopentadienyl. Another possible explanation could be inferred from the observation that the ratio between the two diastereomers changes slowly at room temperature. The reaction is under kinetic control, that is, the acetonitrile ligand that easily dissociates is most probably the one close to the phenyl substituents of the linker (as shown by the X-ray analysis, the $N_1$–Ru bond is longer than the $N_2$–Ru bond), but as this is also the most hindered side of the molecule, the incoming phosphine is not prone to replace it. Indeed, if the reaction is carried out under thermodynamic control, in a 20:1 mixture of $CH_2Cl_2$–$CH_3CN$ under reflux for 24 h, the de observed is much higher (63% for **6b**).

### 2.4. Complex with $L_3$

A different behavior was observed with the ligand $L_3$. The reaction was carried out under the same experimental conditions used to synthesize **4** and **5**, but instead of the expected complex, the sandwich compound **7** was formed in quantitative yield (Scheme 4).

The methyl groups of the xylyl substituents shield the phosphorus atom, preventing, due to their steric hindrance, the coordination to the metal. The metal therefore binds to one xylyl of the phosphine instead. This is not surprising, as the high arenophilicity of ruthenium is well known. Due to the coordination of one xylyl group, the phosphorus atom now becomes a stereogenic center, and only one diastereomer is detectable by analysis of the $^1H$ and $^{31}P$ spectra. Due to the asymmetry of the molecule, the four methyl groups (**a**–**d**, see Scheme 4), resonate at different frequencies. They could be easily assigned by means of NOE-difference experiments: **a** and **b** are strongly shielded (0.71 and 1.51 ppm, respectively, $CD_3CN$), probably due to anisotropic effect of the aromatic ring current of the phenyl substituents in the linker. In contrast, the methyl groups of the metal-coordinated xylyl, **c** and **d**, are deshielded (2.91 and 3.26 ppm, respectively), probably due to anisotropic effects of the metal.




1 7

Scheme 4.

### 2.5. Conclusion

In conclusion, we have shown a simple method to obtain cationic ruthenium(II) compounds with cyclopentadienyl-linked phosphines. In contrast to the Takahashi method [10], our ligands are easily prepared starting from readily available chiral diols; in addition, the ligand backbone can be systematically varied. Due to the lability of the acetonitrile ligands, we anticipate that they could be active species in catalytic or stoichiometric reactions. We are currently investigating their possible application.

## 3. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and deoxygenated by standard methods. NMR spectra were recorded on a Varian Mercury 200 (200 MHz, $^1H$; 50 MHz, $^{13}C$; 81 MHz, $^{31}P$) and a Varian Unity 500 (500 MHz, $^1H$; 125 MHz, $^{13}C$; 202 MHz, $^{31}P$) at ambient temperature. Chemical shifts ($\delta$) are given in ppm relative to the residual solvent signal ($^1H$ and $^{13}C$) or to external $H_3PO_4$ ($^{31}P$). IR spectra were recorded on a Perkin–Elmer FT IR Model 1720 × spectrometer. Mass spectra were obtained with a Finnigan MAT 95 spectrometer. Elemental analyses were obtained on a Carlo Erba Strumentazione element analyzer, Model 1106. Methanesulfonyl chloride (Fluka), $NaNH_2$, $MgSO_4$ (Merck), Li-n-Bu (2.5 M in hexane, Aldrich), $HPPh_2$, P(i-Pr)$_3$, $PPh_3$, $PCy_3$ (Strem), $Li_2CO_3$, $KPF_6$ (Merck) and $KBF_4$ (Aldrich) were used as purchased. Alumina (Merck) was deactivated with water (10%). 1-Phenyl-1,2-ethanediol [15], HP(*o*-xylyl)$_3$ [19], **1** [17], $L_1$ [14], $L_2$ [5,6] were prepared by published procedures.

### 3.1. Syntheses

#### 3.1.1. Synthesis of **2**

A flask was charged with **1** (0.86 g, 1.4 mmol), $Li_2CO_3$ (0.52 g, 7 mmol) and a 5:1 mixture of acetonitrile–ethanol (50 ml). The ligand $L_1$ (0.78 g, 2.8 mmol), dissolved in acetonitrile (3 ml), was added and the mixture stirred at room temperature for 16 h. The yellow solution obtained was filtered over celite and evaporated to dryness. The solid was dissolved in acetonitrile and filtered through a short pad of alumina. After evaporation of the solvent a yellow solid was obtained (0.83 g, 65%). The compound is not stable in the solid state nor in the presence of chlorinated solvents. In acetonitrile solution, it slowly converts to **4**·[Cl].

#### 3.1.2. Synthesis of **3**

Freshly prepared **2** (0.28 g, 0.61 mmol) was dissolved in acetonitrile (10 ml). Triphenylphosphine (0.16 g, 0.61 mmol) was added and the solution stirred for 3 h. Then the solution was concentrated to about 1 ml and diethyl ether was added dropwise affording a yellow–orange solid (0.55 g, 81%). $^1$H NMR ($CD_2Cl_2$): $\delta$ 1.94–2.09 (m, $CH_2P$, 2H), 2.58 (m, Cp, 1H), 2.97 (m, $CH_2$, 1H), 3.12 (m, $CH_2$, 1H), 4.59 (m, Cp, 1H), 4.98 (m, Cp, 1H), 5.06 (m, Cp, 1H), 6.87–7.40 (m, aromatics, 23H), 7.94 (m, aromatics, 2H). $^{31}$P{H} NMR ($CD_2Cl_2$): $\delta$ 44.75 (d, $PPh_3$, $J_{PP} = 37.1$ Hz), 53.6 (d, $PPh_2$, $J_{PP} = 37.1$ Hz). FAB mass (*m*/*z*): 676 [$(M)^+$], 641 [$(M-Cl)^+$], 414 [$(M-PPh_3)^+$], 379 [$(M-PPh_3-Cl)^+$]. *Anal.* Calc. for $C_{37}H_{33}ClP_2Ru+CH_3CN$: C, 65.30; H, 5.07; N, 1.95. Found: C, 64.90; H, 5.10; N, 1.75%.

#### 3.1.3. Synthesis of **4**·[$PF_6$]

A flask was charged with **1** (1.0 g, 1.6 mmol), $Li_2CO_3$ (0.60 g, 8 mmol), $KPF_6$ (0.55 g, 3.2 mmol) and a 5:1 mixture of acetonitrile–ethanol (80 ml). The ligand $L_1$ (0.89 g, 3.2 mmol), dissolved in acetonitrile (5 ml), was added and the mixture stirred under reflux for 8 h. The resulting yellow solution was filtered through a short pad of alumina. The product was obtained by slow crystallization at $-35$ °C as yellow crystals (1.9 g, 75%), m.p. = 138 °C. $^1$H NMR ($CD_2Cl_2$): $\delta$ 2.08 (d, $CH_3CN$, $J_{HP} = 1.2$ Hz, 6H), 2.1–2.3 (m, $CH_2P$, 2H), 3.0–3.2 (m, $CH_2Cp$, 2H), 4.17 (m, Cp, 2H), 5.19 (m, Cp, 2H), 7.4–7.6 (m, aromatics, 10 H). $^{31}$P{H} NMR ($CD_2Cl_2$): $\delta$ $-144.3$ (m, $PF_6$, $J_{PF} = 710$ Hz), 67.0 (s, $PPh_2$). FAB mass (*m*/*z*): 461 [$(M)^+$], 420 [$(M-CH_3CN)^+$], 379 [$(M-2CH_3CN)^+$], 145 [$(PF_6)^-$]. *Anal.* Calc. for $C_{23}H_{24}F_6N_2P_2Rh$: C, 45.49; H, 3.98; F, 18.76. Found: C, 45.18; H, 4.03; F, 18.92%.

#### 3.1.4. Synthesis of **5**·[$PF_6$]

The title compound was prepared from **1** and $L_2$ following the procedure as for **4**·[$PF_6$] on a 1 g scale. Yield 0.85 g, 77%, m.p. = 147 °C. Compound **5**·[$BF_4$] was prepared according to the same procedure except that $KBF_4$ instead of $KPF_6$ was used. $^1$H NMR ($CD_2Cl_2$): $\delta$ 1.63 (d, $J_{HP} = 1.4$ Hz, $CH_3CN$, 3H), 2.12 (d, $J_{HP} = 1.1$ Hz, $CH_3CN$, 3H), 2.30–2.62 (m, $CH_2$, 2H), 4.09 (m, Cp, 1H), 4.41 (m, Cp, 1H), 4.66 (m, CH, 1H), 5.13 (m, Cp, 1H), 6.48–7.45 (m, aromatics, 15H). $^{13}$C{H} NMR ($CD_2Cl_2$): $\delta$ 1.85, 3.0, 28.4 (d, $J_{CP} = 8.7$ Hz, $CH_2$), 58.5 (s, Cp), 59.9 (d, $J_{CP} = 24.7$ Hz, CH), 65.7 (s, Cp), 80.9 (d, $J_{CP} = 7.7$ Hz, Cp), 88.2 (d, $J_{CP} = 5.4$ Hz, Cp), 103.1 (d, $J_{CP} = 3.9$ Hz, Cp), 124.3, 126.0, 126.2 (d, $J_{CP} = 3.4$ Hz), 127.18, 127.19, 127.24, 127.27, 127.32, 127.9 (d, $J_{CP} = 14.9$ Hz), 128.7 (d, $J_{CP} = 3.6$ Hz), 130.2, 130.4 (d, $J_{CP} = 4.4$ Hz), 130.7 (d, $J_{CP} = 14.1$ Hz), 135.1 (d, $J_{CP} = 18.6$ Hz), 135.4 (d, $J_{CP} = 14.1$ Hz). $^{31}$P{H} NMR ($CD_2Cl_2$): $\delta$ $-143.6$ (m, $PF_6$, $J_{PF} = 709$ Hz), 88.65 (s, $PPh_2$). FAB mass (*m*/*z*): 536 [$(M)^+$], 495 [$(M-CH_3CN)^+$], 454 [$(M-2CH_3CN)^+$], 145 [$(PF_6)^-$]. IR (Nujol): 2280, 2251, 1601, 1585, 838, 698 cm$^{-1}$. $[\alpha]^D = +22.7°$ ($c = 1$, $CHCl_3$). *Anal.* Calc. For $C_{29}H_{28}F_6N_2P_2Ru+1/2(CH_3CN)$: C, 51.32; H, 4.24; N, 4.99. Found: C, 51.38; H, 4.20; N, 4.97%.

#### 3.1.5. Synthesis of **6a–c**·[$BF_4$]

The title compounds were prepared in quantitative yield following this procedure: **5**·[$BF_4$] (0.1 g, 0.16 mmol) was dissolved in $CH_2Cl_2$ (10 ml), the phosphine (0.16 mmol) was added and the solution stirred at room temperature until all phosphine had reacted. The solution was concentrated to 1 ml and diethyl ether was added dropwise, the solid was filtered and collected. The de was determined by $^1$H and $^{31}$P NMR.

Compound **6a**·[$BF_4$]: de = 30%. $^{31}$P{H} NMR ($CD_2Cl_2$): $\delta$ (major) 53.3 (d, P(i-Pr)$_3$, $J_{PP} = 24.7$ Hz), 85.1 (d, $PPh_2$, $J_{PP} = 24.7$ Hz); (minor) 52.3 (d, P(i-Pr)$_3$, $J_{PP} = 27.1$ Hz), 75.7 (d, $PPh_2$, $J_{PP} = 27.1$ Hz). IR (Nujol): 2273, 1056, 698 cm$^{-1}$. *Anal.* Calc. For $C_{36}H_{46}BF_4NP_2Ru$: C, 58.21; H, 6.26; N, 1.89. Found: C, 58.57; H, 6.41; N, 1.59%.

Compound **6b**·[$BF_4$]: de = 31% $^{31}$P{H} NMR ($CD_2Cl_2$): $\delta$ (major) 48.9 (d, $PPh_3$, $J_{PP} = 27.1$ Hz), 87.9 (d, $PPh_2$, $J_{PP} = 27.1$ Hz); (minor) 49.7 (d, $PPh_3$, $J_{pp} = 29.7$ Hz), 79.8 (d, $PPh_2$, $J_{PP} = 29.7$ Hz). IR (Nujol): 2267, 1055, 696 cm$^{-1}$. *Anal.* Calc. For $C_{45}H_{40}BF_4NP_2Ru$: C, 63.98; H, 4.78; N, 1.66. Found: C, 63.58; H, 5.03; N, 1.65%.

Compound **6c**·[$BF_4$]: de = 71% $^{31}$P{H} NMR ($CD_2Cl_2$): $\delta$ (major) 44.8 (d, $PCy_3$, $J_{PP} = 24.7$ Hz), 86.0 (d,$PPh_2$, $J_{PP} = 24.7$ Hz); (minor) 45.2 (d, $PCy_3$, $J_{PP} = 24.9$ Hz), 76.0 (d, $PPh_2$, $J_{PP} = 24.9$ Hz). IR (Nujol): 2272, 1056, 698 cm$^{-1}$. *Anal.* Calc. For $C_{45}H_{58}BF_4NP_2Ru$: C, 62.63; H, 6.79; N, 1.62. Found: C, 62.42; H, 6.54; N, 1.53%.

### 3.1.6. Synthesis of $L_3$

The ligand was prepared following a procedure similar to that used to synthesize $L_2$ [2]. (*S*)-1-phenyl-spiro-[2,4]hepta-4,6-diene (1.75 g, 10.4 mmol) was added dropwise at −78 °C to a solution of LiP(*o*-xylyl)$_2$ in THF, prepared in situ by addition of n-BuLi (4.2 ml of a 2.5 M solution) to a solution of HP(*o*-xylyl)$_2$ (2.5 g, 10.3 mmol). The solution was stirred for 2 h at −78 °C and then it was allowed to reach ambient temperature overnight. The solvent was evaporated and the oil obtained was washed several times with hexane. It was then dissolved in THF, water (10 ml) was added and the organic phase was separated, dried over $MgSO_4$, filtered and evaporated. The product was obtained as a pale yellow air sensitive oil. Yield 3.8 g, 90%. $^1$H NMR ($CD_2Cl_2$): $\delta$ 2.30 (s, $CH_3$, 6H), 2.49 (s, $CH_3$, 6H), 2.4–2.6 (m, $CH_2$, 2H), 4.62 (m, CH, 1H), 5.8–6.3 (m, Cp, 4H), 6.7–7.3 (m, aromatics, 11H). $^{31}$P{H} NMR ($CD_2Cl_2$): $\delta$ −6.36 (s), −5.93 (s).

### 3.1.7. Synthesis of 7·[$PF_6$]

The title compound was prepared in quantitative yield from **1** and $L_3$ following the same procedure used for **4**·[$PF_6$]. M.p. = 135–140 °C. $^1$H NMR ($CD_3CN$): $\delta$ 0.71 (s, $CH_3$, 3H), 1.51 (s, $CH_3$, 3H), 2.40–2.80 (m, $CH_2$, 2H), 2.91 (s, $CH_3$, 3H), 3.26 (s, $CH_3$, 3H), 4.15 (m, Cp, 1H), 4.41 (m, Cp, 1H), 5.10 (m, Cp, 1H), 5.20 (m, Cp, 1H), 6.50–7.25 (m, aromatics, 11H). $^{13}$C{H} NMR ($CD_3CN$): $\delta$ 23.5 (d, $J_{CP}$ = 9.5 Hz, $CH_3$), 23.8 (d, $J_{CP}$ = 13.4 Hz, $CH_3$), 24.1 (s, $CH_3$), 25.6 (s, $CH_3$), 35.5 (d, $J_{CP}$ = 13.4 Hz, $CH_2$), 59.9 (s, Cp), 63.1 (d, $J_{CP}$ = 18.2 Hz, CH), 69.6 (s, Cp), 83.7 (d, $J_{CP}$ = 7.7 Hz, Cp), 86.2 (d, $J_{CP}$ = 4.8 Hz, Cp), 102.4 (s, Cp), 127.8, 128.5, 128.9, 130.1, 130.4 (d, $J_{CP}$ = 6.7 Hz), 130.6 (d, $J_{CP}$ = 7.7 Hz), 130.8 (d, $J_{CP}$ = 7.7 Hz), 130.9 (d, $J_{CP}$ = 4.8 Hz), 137.6, 138.4, 139.8 (d, $J_{CP}$ = 11.4 Hz), 140.1 (d, $J_{CP}$ = 8.7 Hz), 144.1 (d, $J_{CP}$ = 17.2 Hz), 145.1. $^{31}$P{H} NMR ($CD_3CN$): $\delta$ −143.5 (m, $PF_6$, $J_{PF}$ = 694.5 Hz), 61.76 (s, $PAr_2$). *Anal.* Calc. For $C_{25}H_{21}F_6P_2Ru$: C, 50.18; H, 3.53; F, 19.05. Found: C, 50.27; H, 3.58; F, 19.21%.

### 3.2. Crystal structure determination

X-ray structure determinations of **3**, **4**·[$PF_6$] and **5**·[$PF_6$]: geometry and intensity data were collected with Mo Kα radiation on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator. A summary of crystal data, data collection parameters and convergence results is compiled in Table 1. An empirical absorption correction based on azimuthal scans [20] was performed in the case of **4** whereas the platelet-like crystal of **5** was face-indexed and absorption correction was made by Gaussian integration [21]. The structures were solved by direct methods [22] and refined on intensities [23]. In the full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic displacement parameters. Hydrogen atoms were treated as riding in idealized positions. The crystal structure of **3** as an acetonitrile solvate was also determined, but is not documented here in detail as the solvent-free structure had already been communicated by Williams et al. [14].

Table 1
Crystal data, data collection parameters, and convergence results for **4** and **5**

| | **4** | **5** |
|---|---|---|
| Molecular formula | $C_{23}H_{24}F_6N_2P_2Ru$ | $C_{29}H_{28}F_6N_2P_2Ru$ |
| Formula weight | 605.47 | 681.57 |
| Crystal system | monoclinic | orthorhombic |
| Space group (no) | $P2_1/c$ (14) | $P2_12_12_1$ (19) |
| $a$ (Å) | 14.798(3) | 10.727(4) |
| $b$ (Å) | 7.6680(14) | 13.3307(19) |
| $c$ (Å) | 21.427(3) | 20.470(3) |
| $\beta$ (°) | 91.23(2) | |
| $U$ (Å$^3$) | 2430.8(7) | 2927.2(12) |
| Z | 4 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.65 | 1.51 |
| $\mu$ (cm$^{-1}$) | 8.21 | 6.73 |
| $\theta_{max}$ (°) | 26.0 | 27.0 |
| Temperature (K) | 228 | 213 |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| Crystal dimensions (mm$^3$) | 0.4 × 0.4 × 0.09 | 0.3 × 0.3 × 0.05 |
| Absorption correction | empirical $\Psi$ | numerical |
| Number of reflections | 9863 | 32 740 |
| Independent reflections | 4779 | 6366 |
| Number of vars. | 309 | 363 |
| $R$ [a] | 0.0407 | 0.0350 |
| $wR_2$ [b] | 0.1030 | 0.0618 |
| Goodness-of-fit [c] | 1.047 | 1.057 |
| Res el dens (e Å$^{-3}$) | 0.81 (close to Ru) | 0.37 |
| Flack parameter | | −0.05(2) |

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ based on data $I > 2\sigma(I)$.
[b] $wR_2 = [\Sigma\, w(F_o^2-F_c^2)^2/\Sigma\, wF_o^2]^{1/2}$ based on all data.
[c] GOF = $[\Sigma\, w(F_o^2-F_c^2)^2/(\text{obs}-\text{var})]^{1/2}$.

## 4. Supplementary material

Further details on the structure determinations are available from the Cambridge Crystallographic Data Center, CCDC Nos.188173 (for **3**), 188174 (for **4**) and 188175 (for **5**) 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; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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