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# Synthesis and structural studies of Ti–Ru polymetallic systems

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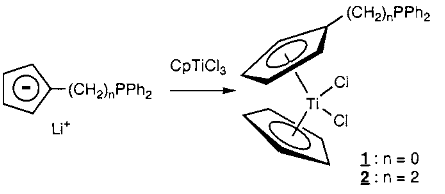
**Abstract**

The reaction of the titanocene monophosphines **1** and **2** with the dimer [($p$-cymene)$RuCl_2$]$_2$ give the heterobimetallic compounds ($p$-cymene)[($\eta^5$-$C_5H_4$)($\mu$-$\eta^5$:$\eta^1$-$C_5H_4PPh_2$)$TiCl_2$]$RuCl_2$ and ($p$-cymene)[($\eta^5$-$C_5H_4$)($\mu$-$\eta^5$:$\eta^1$-$C_5H_4CH_2CH_2PPh_2$)$TiCl_2$]$RuCl_2$, respectively. Both structures have been confirmed by X-ray diffraction. By using same procedure, the synthesis of a trimetallic complex Ru–Ti–Ru has been achieved. © 2000 Elsevier Science S.A. All rights reserved.

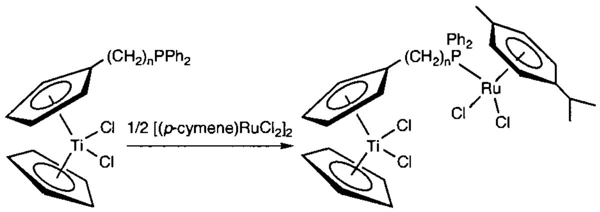
*Keywords:* Titanocene; Ruthenium; Heterobimetallic complexes

## 1. Introduction

Numerous studies have been directed towards the synthesis of early–late heterobimetallic complexes [1]. Surprisingly, only few reports have been reported about their catalytic behavior [2]. However, their potential in homogeneous catalysis remains fantastic. Indeed, a cooperative work by the two metal centers in the complex would lead to new catalytic systems with unique reactivity [3]. We have therefore concentrated our efforts on the synthesis and study of heterobimetallic complexes in which both metal fragments are already well-known in catalysis field. Titanocenes are of considerable interest as cocatalysts for the polymerisation of α-olefins [4]. The catalytic performance of $RuCl_2$(arene) complexes has been demonstrated in many kind of reactions [5]. In attempts to examine such type of catalytic activity we studied the complexation of bent titanocene metalloligands with the dimer [($p$-cymene)$RuCl_2$]$_2$.



Scheme 1.



**3** : n = 0 (85 % yield)
**4** : n = 2 (90 % yield)

Scheme 2.

The use of heterodifunctional ligands as $^-C_5H_4(CH_2)_nPPh_2$ is a very convenient method to link dissimilar transition metals, and in this way, allowed the access to many polymetallic systems [6]. The metal fragments are held together through the bridging ligand with or without a direct metal–metal bond. Here we report the synthesis of two Ti–Ru bimetallic and one Ru–Ti–Ru trimetallic complexes by using this strategy.

## 2. Discussion and results

Previous studies in our laboratory gave rise to a straightforward access to bent titanocene mono and diphosphines [6a,b]. The monophosphines **1** and **2** were prepared according to an earlier method involving the

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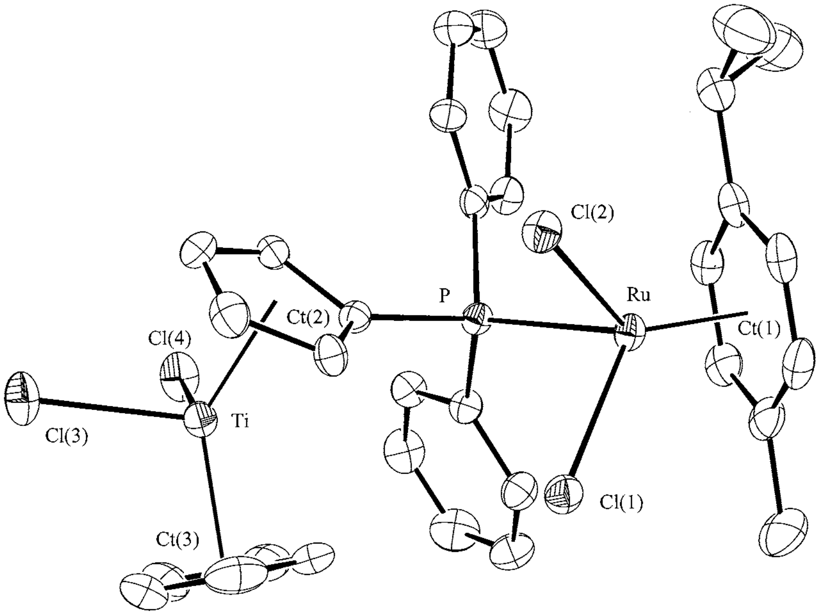


Fig. 1. An ORTEP [8] view of the compound **3** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and solvate molecules are omitted for clarity.

reaction of the lithium (diphenylphosphino)- or ((diphenylphosphino)ethyl) cyclopentadienide with $CpTiCl_3$ (Scheme 1) [6a].

The $^1H$-NMR and $^{31}P$-NMR chemical shifts of these two phosphines are consistent with the phosphine ligands not coordinated to a metal atom. Both are stable under argon and can be handled easily. Despite these two ligands are made of bent titanocene and diphenylphosphine entities, the coordinative ability of both phosphorus atoms might be different. Indeed, the phosphorus atom in **2** will be in a less hindered environment than in **1**. Moreover, the alkyl bridge might prevent any electron attractive effect of the titanium center on the phosphorus atom.

Organic phosphines can easily cleave the chloride bridges of the dimer $[(p\text{-cymene})RuCl_2]_2$ to lead to $(p\text{-cymene})RuCl_2PR_3$ complexes [7]. On the basis of this result we carried out experiments by using the metallophosphines **1** and **2** with the dimer $[(p\text{-cymene})RuCl_2]_2$ in benzene. The bimetallic complexes **3** and **4** were obtained with high yields after 4 h at room temperature (Scheme 2).

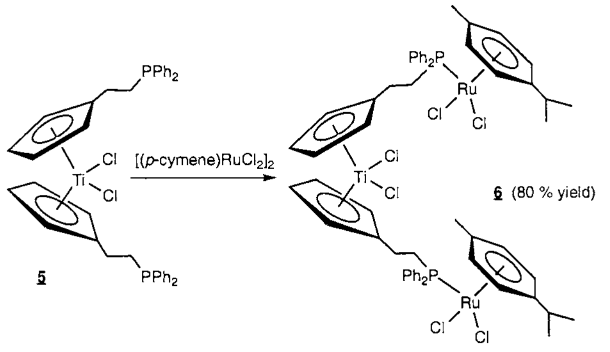
The characterisation of **3** and **4** was based upon elemental analysis, $^1H$-NMR and $^{31}P$-NMR spectroscopic data. The $^{31}P$-NMR chemical shifts of **3** and **4** of 15.1 and 21.3 ppm correspond to a downfield shift of 31 and 39 ppm relatively to free ligands. The $^1H$-NMR spectra of **3** and **4** displays 0.2–0.5 ppm upfield shift of the *p*-cymene protons resonances compared to the ruthenium dimer precursor. A downfield shift of the diphenylphosphine *ortho*-protons was observed. These results are indicative of the coordination of the phosphorus atoms to the ruthenium metal.

Single crystals of **3** and **4**, suitable for X-ray diffraction, were obtained by layering technique. ORTEP views of the compounds **3** and **4** are respectively shown in Figs. 1 and 2. The Crystallographic Parameters are reported in Table 1 and the bond distances and angles in Table 2.

Both structures consist in two fragments: a dichloro titanocene moiety and a $(p\text{-cymene})RuCl_2$ moiety. The linkage is achieved either by a direct bonding of the phosphorus atom to one carbon atom of a Cp ring for **3** or by an ethylene spacer between the Cp ring and the phosphorus atom for **4**.

The geometries of the $CpCp'TiCl_2$ fragments are typically tetrahedral in both structures with similar structural parameters. These two titanocene moities show only a difference in the position of the substituents held by the cyclopentadienyl ring: in **4**, the uncluttered methylene substituent is located in the open side of the bent metallocene and lies above the $TiCl_2$ fragment, the dihedral angle between the Ct(3)–Ct(2)–C(12) plane and the Ct(2)–TiCt(3) one is only 8°. In contrast, for the compound **3**, the bulky $PPh_2$ substituent is rotated from the previous bisecting position leading to a dihedral angle defined as above equal to 144°. While in **3** the carbon atom attached to the Cp ring lies in the Cp plane, in the compound **4**, the phosphorus atom lies 0.39 Å above this plane.

In both structures, the arene ruthenium moities present a three-legged piano stool structure with structural parameters similar to those observed for 19 $(\eta^6\text{-arene})RuCl_2(PPh_2R)$ structures (among these, three include both ferrocene and $(\eta^6\text{-arene})RuCl_2$ linked by a diphenyl phosphido bridge [9]). In these complexes the



Scheme 3.

mean Ru–Cl and Ru–P distances are equal to 2.41(1) and 2.35(2) Å, respectively.

These results prompted us to use the same strategy for the preparation of trimetallic complexes. The organometallic diphosphine **5** [6a] reacts with the dimer $[(p\text{-cymene})RuCl_2]_2$ to give the trimetallic complex **6** isolated as a brick powder in 80% yield (Scheme 3). The $^1$H-NMR and $^{31}$P-NMR spectra of **6** display almost the same chemical shifts as **4**. The $^{31}$P-NMR spectrum of **6** exhibits only one singlet at +21.6 ppm. The $^1$H-NMR shows an upfield shift of the *p*-cymene protons resonances compared to the ruthenium dimer precursor as well as a downfield shift of the diphenylphosphine *ortho*-protons relatively to **5**. These results are in agreement with the suggested structure **6**.

Our attempts to prepare a cationic ruthenium (II) complex via removal of a chloride by $NH_4PF_6$ in order to obtain a structure involving chelation by the two phosphorus atoms of the ligand **5** led to oligomeric mixtures as judged by their NMR spectra. The crystallographic structure of **4** might explain this result. Indeed, the flexibility of the alkyl bridge allowed the ruthenium center to lie away from the titanium atom. The two phosphorus atoms are probably located far one each other, so as to permit coordination with the ruthenium atoms. These results are closely similar to those obtained by Graham et al. for titane–rhodium and titane–palladium complexes [6f].

## 3. Conclusion

We report the preparation of two heterobimetallic complexes containing both titanocene and ruthenium(arene) fragments. These syntheses involve the preparation of titanocene monophosphines followed by the coordination of the phosphorus group to the ruthenium atom. The targeted heterobimetallic complexes have been obtained with good yields. Similar strategy allowed us to synthesize a Ru–Ti–Ru trimetallic complex with good yield. Studies about the catalytic activity of these new heteropolymetallic systems are currently in progress.

## 4. Experimental

NMR spectra were recorded on a BRUKER AC200 (200.135 MHz for $^1$H, 81.004 MHz for $^{31}$P) spectrometer. Elemental analysis was performed on a FISON EA 1108 within the laboratory. The cyclopentadienyl phosphine ligands $Li[C_5H_4(CH_2)_nPPh_2]$ were prepared according to the literature method [10]. The phosphine **5** has been recently synthesized according to a modified procedure [6e].

### 4.1. Complex *1*

A 0.77g (2.7 mmol) sample of $Li[C_5H_4PPh_2]$ in 10 ml of THF was added to 0.6 g of $CpTiCl_3$ (2.7 mmol) in 15 ml of THF. After stirring for four hours at room temperature (r.t.), the solvent was removed in vacuo. The red residue was extracted with $CH_2Cl_2$, filtered through celite, and precipitated by the addition of

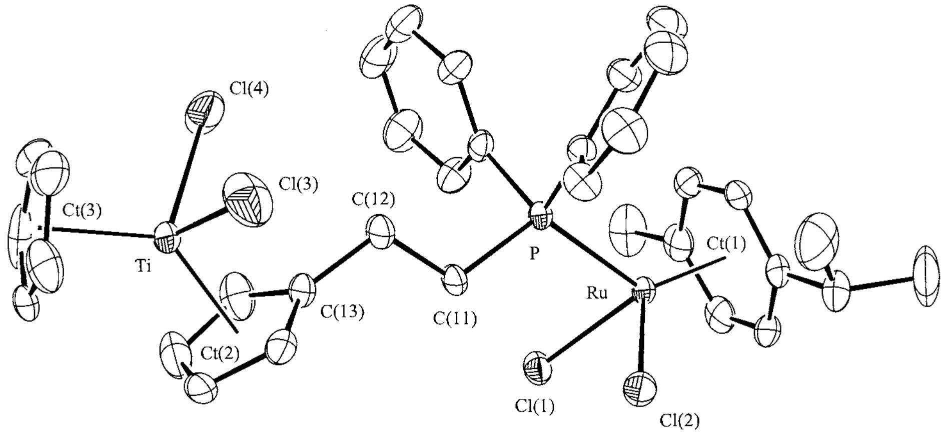


Fig. 2. An ORTEP view of the compound **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and the toluene solvate molecule are omitted for clarity.

Table 1
Crystal data and structure refinement for **3** and **4**

| Compound | **3** | **4** |
|---|---|---|
| Empirical formula | $C_{32}H_{33}Cl_4PRuTi\cdot 2(CHCl_3)\cdot 0.5(C_6H_{14})$ | $C_{34}H_{37}Cl_4PRuTi\cdot C_7H_8$ |
| Formula weight | 1021.15 | 859.51 |
| $T$ (K) | 293(2) | 293(2) |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions | | |
| $a$ (Å) | 10.567(1) | 10.792(2) |
| $b$ (Å) | 13.038(1) | 12.915(2) |
| $c$ (Å) | 16.035(2) | 15.314(2) |
| $\alpha$ (°) | 101.05(1) | 83.09(1) |
| $\beta$ (°) | 92.43(1) | 70.92(1) |
| $\gamma$ (°) | 91.82(1) | 81.31(1) |
| $V$ (Å$^3$) | 2164.5(4) | 1988.3(5) |
| $Z$ | 2 | 2 |
| $F$(000) | 1030 | 880 |
| $D_{calc}$ (g cm$^{-3}$) | 1.567 | 1.436 |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| $\mu$ (mm$^{-1}$) | 1.214 | 0.918 |
| Crystal size (mm$^3$) | $0.36\times 0.28\times 0.25$ | $0.30\times 0.30\times 0.22$ |
| $\sin(\theta)/\lambda_{max}$ (Å$^{-1}$) | 0.59 | 0.62 |
| Index ranges | $h$: $-12$; 12<br>$k$: 0; 15<br>$l$: $-18$; 18 | $h$: 0; 13<br>$k$: $-15$; 16<br>$l$: $-18$; 19 |
| Decay (%) | 65 | 0 |
| Absorption correction | psi-scan 84–93% | psi-scan 94–98% |
| RC, Reflections collected | 7675 | 8511 |
| IRC, independent RC | 7316 [$R_{int}=0.0342$] | 8063 [$R_{int}=0.0137$] |
| IRCGT = IRC and [$I>2\sigma(I)$] | 4886 | 6423 |
| Refinement method | Full-matrix L.S. on $F^2$ | Full-matrix L.S. on $F^2$ |
| Data/restraints/parameters | 7316/0/466 | 8063/6/380 |
| $R$ for IRCGT | $R_1$[a] $=0.0435$, $wR_2$[b] $=0.108$ | $R_1$[a] $=0.0408$, $wR_2$[b] $=0.1082$ |
| $R$ for IRC | $R_1$[a] $=0.1086$, $wR_2$[b] $=0.129$ | $R_1$[a] $=0.0632$, $wR_2$[b] $=0.1205$ |
| Goodness-of-fit [c] | 1.036 | 1.014 |
| Largest $\Delta\rho$ (e Å$^{-3}$) | 0.756 and $-0.639$ | 1.219 and $-0.979$ |

[a] $R_1=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$.

[b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]^{1/2}$ where $w=1/[\sigma^2(F_o^2)+(0.069*P)^2+1.98P]$ for **3** and $w=1/[\sigma^2(F_o^2)+(0.0654*P)^2+2.22P]$ for **4** where $P=(\max(F_o^2,0)+2*F_c^2)/3$.

[c] Goodness-of-fit $=[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$.

Table 2
Selected bond distances (Å) and angles (°)

| | | | |
|---|---|---|---|
| Molecule **3** | | | |
| Ru–Ct(1) | 1.71 | Ti–Ct(2) | 2.07 |
| Ru–P | 2.3701(13) | Ti–Ct(3) | 2.06 |
| Ru–Cl(1) | 2.4208(13) | Ti–Cl(3) | 2.366(2) |
| Ru–Cl(2) | 2.4037(13) | Ti–Cl(4) | 2.329(2) |
| P–C(11) | 1.834(5) | | |
| Ct(1)–Ru–P | 129.0 | Ct(2)–Ti–Ct(3) | 131.9 |
| Ct(1)–Ru–Cl(1) | 125.7 | Ct(2)–Ti–Cl(3) | 106.0 |
| Ct(1)–Ru–Cl(2) | 125.3 | Ct(2)–Ti–Cl(4) | 107.4 |
| P–Ru–Cl(1) | 88.94(4) | Ct(3)–Ti–Cl(3) | 105.3 |
| P–Ru–Cl(2) | 86.55(4) | Ct(3)–Ti–Cl(4) | 106.3 |
| Cl(1)–Ru–Cl(2) | 88.47(5) | Cl(3)–Ti–Cl(4) | 93.39(6) |
| Molecule **4** | | | |
| Ru–Ct(1) | 1.70 | Ti–Ct(2) | 2.06 |
| Ru–P | 2.3504(8) | Ti–Ct(3) | 2.07 (2.05)[a] |
| Ru–Cl(1) | 2.419(1) | Ti–Cl(3) | 2.370(2) |
| Ru–Cl(2) | 2.422(1) | Ti–Cl(4) | 2.324(2) |
| P–C(11) | 1.829(3) | | |
| Ct(1)–Ru–P | 129.3 | Cl(4)–Ti–Cl(3) | 95.26(8) |
| Ct(1)–Ru–Cl(1) | 125.8 | Ct(2)–Ti–Ct(3) | 131.2 (133.7)[a] |
| Ct(1)–Ru–Cl(2) | 126.7 | Ct(2)–Ti–Cl(3) | 104.3 |
| P–Ru–Cl(1) | 87.93(3) | Ct(2)–Ti–Cl(4) | 106.2 |
| P–Ru–Cl(2) | 86.98(3) | Ct(3)–Ti–Cl(3) | 109.3 (103.2)[a] |
| Cl(1)–Ru–Cl(2) | 87.63(4) | Ct(3)–Ti–Cl(4) | 104.9 (107.6)[a] |

[a] Distance and angle values in brackets reference to the second centroid of the desordered cyclopentadienyl ring.

hexane. The solution was then placed in a freezer ($-20$°C) overnight. The solvent was removed by filtration and the red residue was dried under vaccuum (75% yield).

$^{31}P\{^1H\}$-NMR (81.004 MHz, $CDCl_3$) $\delta$ $-16.45$ (s, $PPh_2$). $^1H$-NMR (200.135 MHz, $CDCl_3$) $\delta$ 6.46 (s, 5H, Cp), 6.58–6.66 (m, 4H, $CpPPh_2$), 7.32–7.42 (m, 10H, Ph). Anal. Calc. for $C_{22}H_{19}Cl_2PTi$ (433.1521): C, 61.00; H, 4.42. Found: C, 60.55; H, 4.26%.

### 4.2. Complex **2**

This compound was obtained following the above procedure but with $Li[C_5H_4CH_2CH_2PPh_2]$ (85% yield). $^{31}P\{^1H\}$-NMR (81.004 MHz, $CDCl_3$) $\delta$ $-18.08$ (s, $PPh_2$). $^1H$-NMR (200.135 MHz, $CDCl_3$) $\delta$ 2.38 (t, 2H, $CH_2$, $J=7.9$ Hz), 2.87 (dt, 2H, $CH_2$, $J=9.7$, $J=7.9$ Hz), 6.30–6.40 (m, 4H, Cp), 7.26–7.46 (m, 10H, Ph). Anal. Calc. for $C_{24}H_{23}Cl_2PTi$ (461.2057): C, 62.50; H, 5.03. Found: C, 61.60; H, 5.03%. The relatively low percentage of carbon can be attributed to the presence of LiCl.

### 4.3. Complex **5**

A solution of 0.98 g (3.47 mmol) of $Li[C_5H_4CH_2CH_2PPh_2]$ in 15 ml of THF was added to 0.58 g (1.7 mmol) of $TiCl_4(THF)_2$ in 10 ml of THF. After stirring for 2 h at reflux, the solution was concentrated and fractionated through 10 cm of Sephadex (LH-20) to afford a red solution. Removal of the solvent gave **5** (50% yield) as red powder. $^{31}P\{^1H\}$-NMR (81.004 MHz, $CDCl_3$) $\delta$ $-18.27$ (s, $PPh_2$). $^1H$-NMR (200.135 MHz, $CDCl_3$) $\delta$ 2.31 (t, 2H, $CH_2$,

$J=7.9$ Hz), 2.96 (dt, 2H, $CH_2$, $J=10.0$, $J=7.9$ Hz), 6.25–6.30 (m, 8H, Cp), 7.28–7.41 (m, 20H, Ph). Anal. Calc. for $C_{38}H_{36}Cl_2P_2Ti$ (673.4364): C, 67.77; H, 5.39. Found: C, 67.01; H, 5.1%. The relatively low percentage of carbon can be attributed to the presence of LiCl.

### 4.4. Complex **3**

A 25 ml Schlenk flask was charged under argon with **1** (0.4 g, 0.92 mmol), $[(p\text{-cymene})RuCl_2]_2$ (0.28 g, 0.46 mmol) and degassed benzene. The mixture was stirred at r.t. for 4 h during which time a brick precipitate slowly formed. The solvent was removed by filtration and the red residue was dried under vaccuum (85% yield). $^{31}P\{^1H\}$-NMR (81.004 MHz, $CDCl_3$) $\delta$ 15.07 (s, $PPh_2$). $^1H$-NMR (200.135 MHz, $CDCl_3$) $\delta$ 1.04 (d, 6H, isopropyl $CH_3$, $J=7.0$ Hz), 1.69 (s, 3H, $CH_3$ *p*-cymene), 2.45 (hept, 1H, CH isopropyl, $J=7.0$ Hz), 5.13 (s apparent, 4H, =CH *p*-cymene), 6.10 (s, 5H, Cp), 6.28–6.32 (m, 2H, Cp), 7.45–7.52 (m, 8H, *m,p*-Ph + Cp), 7.84–7.94 (m, 4H, *o*-Ph). Anal. Calc. for $C_{32}H_{33}Cl_4PRuTi$ (739.3487): C, 51.98; H, 4.50. Found: C, 52.22; H, 4.58%.

#### 4.4.1. X-ray analysis of **3**

Crystals suitable for the X-ray structure analysis were obtained by layering *n*-hexane onto a saturated chloroform solution of **3** at r.t. A dark red crystal ($0.36\times0.28\times0.25$ $mm^3$) was mounted in a capillary with the mother liquor on an Enraf–Nonius CAD4 diffractometer. A total of 7675 reflections (7316 unique) were collected up to $\sin(\theta)/\lambda=0.59$ Å$^{-1}$ at r.t. The data were corrected for Lorentz and polarization effects [11] and for absorption (psi-scan method) [12]. A 65% decay was linearly corrected. The structure was solved via a Patterson search program [13] and refined (space group $P\bar{1}$) with full-matrix least squares methods based on $|F^2|$. Except for one carbon atom of a disordered solvate molecule (see below) all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in their calculated positions and refined with a riding model. The asymmetric unit contains one molecule of the complex, two chloroform molecules and 1/2 hexane molecule located on an inversion center. One of the chloroform molecule is disordered and occupies two positions with occupation factors $m_1=0.68$ and $m_2=0.32$. Two chlorine atoms are shared by the two molecules and then refined with an occupation factor $m=1$. The carbon atom with the smaller multiplicity was refined isotropically. The finals agreement indices are $wR_2=0.129$ for all data and $R_1=0.0435$ for 4886 intensities with $I>2\sigma(I)$. Final difference electron density: $\Delta\rho=0.756$ and $-0.639$ e Å$^{-3}$. Crystal data are reported in Table 1.

### 4.5. Complex **4**

Under the above experimental conditions, 90% of **4** was isolated as a brick powder, $^{31}P\{^1H\}$-NMR (81.004 MHz, $CDCl_3$) $\delta$ 21.28 (s, $PPh_2$). $^1H$-NMR (200.135 MHz, $CDCl_3$) $\delta$ 0.82 (d, 6H, isopropyl $CH_3$, $J=6,8$ Hz), 1.89 (s, 3H, $CH_3$ *p*-cymene), 2.35–2.60 (m, 3H, $CH_2$ + CH isopropyl), 2.68–2.82 (m, 2H, $CH_2$), 5.08 (d, 2H, =CH *p*-cymene, $J=6.2$ Hz), 5.27 (d, 2H, =CH *p*-cymene, $J=6.2$ Hz), 6.18–6.21 (m, 2H, Cp), 6.31–6.34 (m, 2H, Cp), 6.48 (s, 5H, Cp), 7.43–7.50 (m, 6H, *m,p*-Ph), 7.81–7.91 (m, 4H, *o*-Ph). Anal. Calc. for $C_{34}H_{37}Cl_4PRuTi$ (767.4023): C, 53.22; H, 4.86. Found: C, 52.88; H, 4.96%.

#### 4.5.1. X-ray analysis of **4**

Crystals for the X-ray structure analysis were obtained by layering toluene onto a saturated chloroform solution of **4** at r.t. A red crystal ($0.30\times0.30\times0.22$ $mm^3$) was mounted on an Enraf–Nonius CAD4 diffractometer. A total of 8511 reflections (8063 unique) were collected up to $\sin(\theta)/\lambda=0.62$ Å$^{-1}$ at r.t. The data were corrected for Lorentz and polarization effects [11] and for absorption (psi-scan method) [12]. No decay was observed. The structure was solved via a Patterson search program [13] and refined (space group $P\bar{1}$) with full-matrix least squares methods based on $|F^2|$. Except the carbon atoms of the toluene solvate molecule (see below) all non-hydrogen atoms were refined with anisotropic thermal parameters. The methyl hydrogen atoms of the disordered toluene solvate molecule were not included in the model while the others were included in their calculated positions and refined with a riding model. The terminal cyclopentadienyl ring of the complex is desordered and occupies two positions with refined occupation factors $m_1=0.53$ and $m_2=0.47$. The rings are rotated with respect to each other and their centroids are shifted by 0.22 Å. The toluene solvate molecule is also desordered over two positions and the refinement led to the occupations factors $m_1=0.56$ and $m_2=0.44$. The carbon atoms of the solvate were left isotropic and only two thermal parameters were refined: one for the phenyl carbon atoms and one for the methyl groups. The finals agreement indices are $wR_2=0.121$ for all data and $R_1=0.0408$ for 6423 intensities with $I>2\sigma(I)$. Final difference electron density: $\Delta\rho=1.219$ (close to Cl(3)) and $-0.979$ e Å$^{-3}$. Crystal data are reported in Table 1.

### 4.6. Complex **6**

Metallodiphosphine **5** (0.48 g, 0.75 mmol), and 0.46 g (0.75 mmol) of $[(p\text{-cymene})RuCl_2]_2$ were dissolved under an inert atmosphere of argon in degassed $CH_2Cl_2$. After stirring for 4 h, the solvent was evaporated and the resulting red solid was purified by recrystallisation from chloroform/hexane (60% yield).$^{31}P\{^1H\}$-NMR (81,004 MHz, $CDCl_3$) $\delta$ 21.60 (s, $PPh_2$). $^1H$-NMR (200.135 MHz, $CDCl_3$) $\delta$ 0.80 (d, 12H, isopropyl $CH_3$, $J = 7.1$ Hz), 1.87 (s, 6H, $CH_3$ *p*-cymene), 2.30–2.47 (m, 4H, $CH_2$), 2.51 (hept, 2H, CH isopropyl, $J = 7.1$ Hz), 2.63–2.84 (m, 4H, $CH_2$), 5.00 (d, 4H, =CH *p*-cymene, $J = 5.9$ Hz), 5.24 (d, 4H, =CH *p*-cymene, $J = 5.9$ Hz), 5.99–6.02 (m, 4H, Cp), 6.16–6.19 (m, 4H, Cp), 7.43–7.47 (m, 12H, *m,p*-Ph), 7.80–7.92 (m, 8H, *o*-Ph). Anal. Calc. for $C_{58}H_{64}Cl_6P_2Ru_2Ti$ (1285.8296): C, 54.18; H, 5.02. Found: C, 53.74; H, 5.16%.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 140519 for the compounds **3** and CCDC no. 140520 for the compounds **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.aac.uk or www: http://www.ccdc.cam.ac.uk).

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