

The preparation of mixed ligand ruthenocenes containing bulky cyclopentadienyl ligands. Crystal structures of pentaphenylruthenocene, $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{H}_5)]$, pentaparatolylruthenocene, $[\text{Ru}\{\eta^5\text{-C}_5(p\text{-MeC}_6\text{H}_4)_5\}(\eta^5\text{-C}_5\text{H}_5)]$ and pentaphenylpentamethylruthenocene, $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{Me}_5)]^1$

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Abstract

The preparations of the mixed ligand ruthenocenes $[\text{Ru}(\eta^5\text{-C}_5\text{R}_5)(\eta^5\text{-C}_5\text{H}_5)]$ [$\text{R}_5 = \text{Ph}_5$ (**1**), Ph_4H (**2**) and $(p\text{-MeC}_6\text{H}_4)_5$ (**3**)] and $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{Me}_5)]$ (**4**) are reported. The molecular structures of **1** (*Pbca*, $a = 14.234(3)$, $b = 20.276(3)$, $c = 20.625(4)$ Å, $P\bar{1}$, $a = 19.319(7)$, $b = 21.007(7)$, $c = 10.436(3)$ Å, $\alpha = 103.76^\circ$, $\beta = 95.07(3)^\circ$, $\gamma = 112.59(2)^\circ$) and **4**· H_2O (*P* $\bar{1}$, $a = 12.145(2)$, $b = 12.696(4)$, $c = 14.281(2)$ Å, $\alpha = 80.41(2)^\circ$, $\beta = 66.43(1)^\circ$, $\gamma = 62.80(2)^\circ$) were determined by single crystal X-ray diffraction studies; the cyclopentadienyl rings in each structure are almost parallel and nearly eclipsed. For **1**, **2** and **3**, two oxidative processes, but no reductive electrochemical processes, were observed. The precipitated product from the reaction of $\text{Ru}_3(\text{CO})_{12}$, $\text{C}_5\text{Ph}_5\text{Br}$ and Zn in xylenes yielded, after subsequent reaction with NaBPh_4 , $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)\{\eta^6\text{-C}_6\text{H}_4(\text{CH}_3)_2\}]^+\text{BPh}_4^-$ (**5**). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Cyclopentadienyl; Crystal structure

1. Introduction

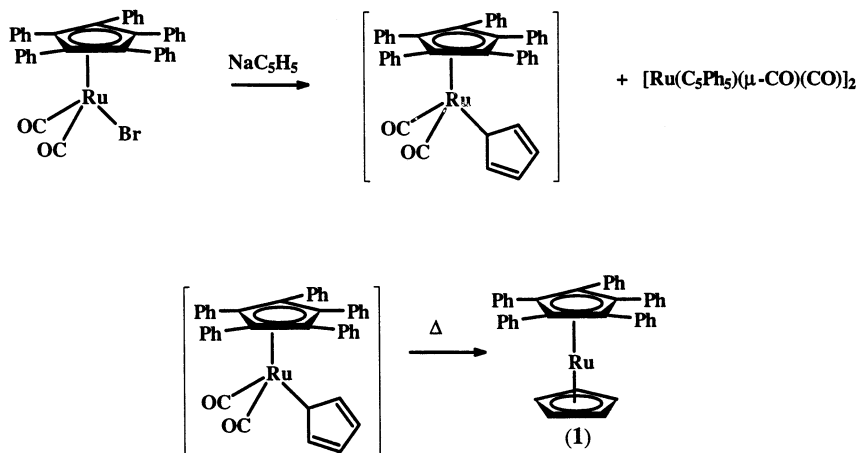
Interest in bulky cyclopentadienyl ligands stems from their ability to confer unique steric, electronic and stability properties on their metal complexes. The syntheses and characterisation of decaphenylmetallocenes of chromium [1,2], molybdenum [3], iron [1,4–6], cobalt [2], and nickel [1,7] have been described. Unfortunately, although these species are air-stable, the development of their chemistries is limited by their very low solubilities. The solubilities can be improved by the introduction of appropriate substituents on the phenyl rings [8],

or by oxidation to the corresponding metallocenium salts, several of which have been structurally characterised [2,4,5]. Alternatively, the few reported pentarylmetallocenes are generally more soluble.

Although we, and others, have described the chemistry of iron sandwich derivatives of the pentaphenylcyclopentadienyl ligand, the authenticated chemistry of ruthenium and osmium derivatives has been limited to half sandwich compounds. Thus, the ruthenium compounds $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\text{LX}]^n$ ($n = 0, 1$; $\text{L} = \text{CO}$, PR_3 , C_2H_4 , $\text{MeC}\equiv\text{CMe}$; $\text{X} = \text{Br}$, R , COMe , $\text{MeC}=\text{CMe}_2$) [9–11], and the dimeric $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\mu\text{-CO})(\text{CO})_2]$ [9] have been adequately characterised, with structural characterisation being reported for the compounds $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ [10] and $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PPh}_3)\text{Br}]$ [11]. The starting material for much of this chemistry is $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$, prepared from the reaction of $\text{Ru}_3(\text{CO})_{12}$ with $\text{C}_5\text{Ph}_5\text{Br}$ in toluene. A series of osmium compounds of the type

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¹ Dedicated to Professor Michael Bruce on the occasion of his 60th birthday in recognition of his outstanding contributions to organometallic and inorganic chemistry. Professor Bruce is thanked by one of the authors (PAH) for the guidance and encouragement given to him as a PhD student.



[Os(η^5 -C₅Ph₅)(CO)LX] has also been recently reported [12]. The possible existence of the mixed sandwich compounds, [Ru(η^5 -C₅Ph₅)(η^5 -C₅R₅)] (R = H, Me), has been briefly noted, but the formulation of these compounds has not been established [13].

We report here the syntheses and characterisation of the mixed sandwich compounds of ruthenium, [Ru(η^5 -C₅Ar₅)(η^5 -C₅R₅)] (R = H, Ar₅ = Ph₅ (**1**), Ph₄H (**2**), (*p*-MeC₆H₄)₅ (**3**); R = Me, Ar₅ = Ph₅ (**4**)) and of [Ru(η^5 -C₅Ph₅)(η^6 -Me₂C₆H₄)]BPh₄ (**5**).

2. Results and discussion

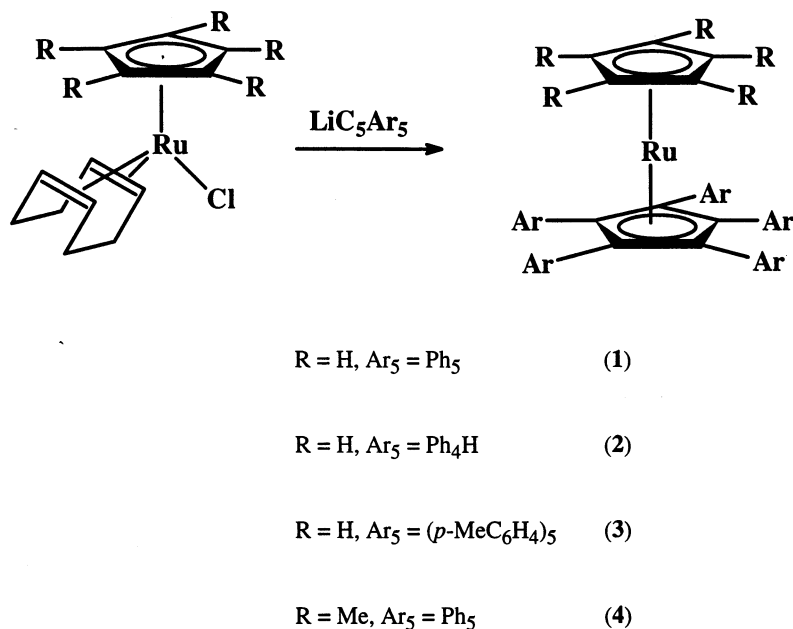
2.1. Syntheses

Pale yellow, crystalline [Ru(η^5 -C₅Ph₅)(η^5 -C₅H₅)] (**1**) was initially prepared in low yield by the thermolysis of the product of the reaction between [Ru(η^5 -C₅Ph₅)(CO)₂Br] and cyclopentadienylsodium. During the course of the reaction, a precipitate formed which has been identified by IR spectroscopy as the known compound [Ru(η^5 -C₅Ph₅)(μ -CO)(CO)]₂ (Scheme 1) [9]. Complex **1** is probably formed via the intermediary of [Ru(η^5 -C₅Ph₅)(η^1 -C₅H₅)(CO)₂], as postulated for the synthesis of [Fe(η^5 -C₅Ph₅)(η^5 -C₅H₅)] from [Fe(η^5 -C₅Ph₅)(CO)₂Br] and cyclopentadienyl sodium [14] and established for the synthesis of [Fe{(η^5 -C₅(*p*-MeC₆H₄)₅)}(η^5 -C₅H₅)] from [Fe{(C₅(*p*-MeC₆H₄)₅)}(CO)₂Br] and cyclopentadienylsodium in which [Fe{(η^5 -C₅(*p*-MeC₆H₄)₅)(η^1 -C₅H₅)}(CO)₂] was isolated [8]. Compound **1** was obtained as an air-stable solid after purification on a silica gel column followed by crystallisation from dichloromethane/*n*-hexane, and was characterised by elemental analysis and mass, IR and ¹H- and ¹³C-NMR spectroscopies, cyclic voltammetry and single crystal X-ray diffraction. The pale yellow colour

is consistent with the previous observation [15] that ruthenocene derivatives are usually white to pale or bright yellow when other chromophores are absent. An alternative preparative method (as used [16] in the synthesis of [Ru(η^5 -C₅H₅)(η^5 -C₅Me₅)] involved the reaction of pentaphenylcyclopentadienyllithium with a THF solution of [Ru(η^5 -C₅H₅)(COD)Cl] (COD = η^4 -1,5-C₈H₁₂). In both reactions the yield of **1** was low. An analogous reaction of [Ru(η^5 -C₅H₅)(COD)Cl] with the less sterically demanding ligand (C₅Ph₄H)[−] produced a pale yellow solid, [Ru(η^5 -C₅Ph₄H)(η^5 -C₅H₅)] (**2**), in a much higher yield (58%). Compound **2** was characterised as above. The symmetrical complex, [Ru(η^5 -C₅Ph₄H)₂], has been prepared previously by the reaction between KC₅Ph₄H and [Ru(η^4 -COD)Cl₂]_{*n*} or [Ru(*p*-cymene)Cl₂]_{*n*} in refluxing diglyme [17].

The reaction of penta-*p*-tolylcyclopentadienyllithium with a THF solution of [Ru(η^5 -C₅H₅)(COD)Cl] yielded small amounts of very pale yellow to colourless crystals of [Ru{(η^5 -C₅(*p*-MeC₆H₄)₅)}(η^5 -C₅H₅)] (**3**). It was isolated as an air-stable solid after purification on a silica gel column and crystallisation from *n*-hexane, and was characterised by elemental analysis, mass, IR and ¹H- and ¹³C-NMR spectroscopies, cyclic voltammetry and single crystal X-ray diffraction.

Similarly, very pale yellow to colourless crystals of [Ru(η^5 -C₅Ph₅)(η^5 -C₅Me₅)] (**4**) were isolated in very low yield from the reaction of Li(C₅Ph₅) with [Ru(η^5 -C₅Me₅)(COD)Cl] in THF followed by column chromatography and a number of recrystallisations from dichloromethane/*n*-hexane to remove HC₅Ph₅ (Scheme 2). Compound **4** was characterised by mass, IR and ¹H-NMR spectroscopies and by single crystal X-ray diffraction. Attempts to improve the yield of **4** by using alternative synthetic strategies have not so far proven successful.



Scheme 2.

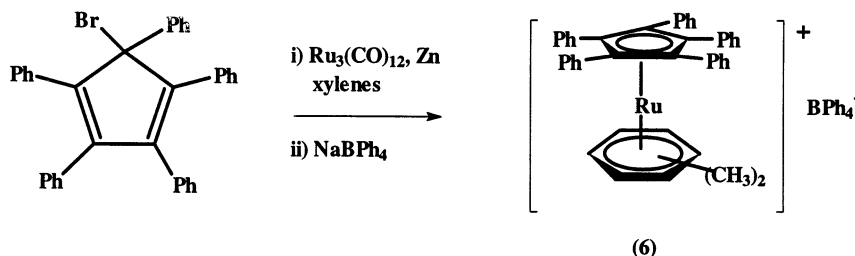
The pentaphenylcyclopentadienyl and penta-*p*-tolylcyclopentadienyl derivatives were all obtained in low yields as soluble monomeric solids. A characteristic of the reactions was that copious amounts of the ligand precursor, $\text{C}_5\text{Ar}_5\text{H}$, were always produced in syntheses using LiC_5Ar_5 as starting material. This contaminant has a similar colour and spectroscopic properties to the mixed sandwich products, from which it can be difficult to separate. Isolation of pure ruthenocene derivatives, therefore, can be non-trivial. Although $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_4\text{H})(\eta^5\text{-C}_5\text{H}_5)]$ could be prepared in significantly higher yields, the low yields of the C_5Ar_5 derivatives do not seem to be due to steric interference, since $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{H}_5)]$ was prepared in 58% yield [14]. For example, in the reaction of $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ with NaC_5Ph_5 , a significant product (obtained in variable yields) is the stable, insoluble dimer, $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\mu\text{-CO})(\text{CO})_2]$. The analogous dimer is obtained in the iron system, but is much less stable and so the iron mixed sandwich is the major product. In the syntheses using $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{COD})\text{Cl}]$, other product(s) decompose during the chromatographic separation.

It has been shown previously that the reaction of $\text{Fe}(\text{CO})_5$ (one equivalent), zinc dust (two equivalents) and bromopentaphenylcyclopentadiene (two equivalents) in refluxing benzene followed by column chromatography yields $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)\{\eta^6\text{-C}_6\text{H}_5\text{C}_5\text{Ph}_4\}]$ with $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ and $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^6\text{-C}_6\text{H}_6)]^+$ as minor by-products [18]. Dark blue $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)\{\eta^6\text{-C}_6\text{H}_5\text{C}_5\text{Ph}_4\}]$ is a linkage isomer of pink/purple decaphenylferrocene, $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)_2]$, to which it can be converted by heating in refluxing xylene.

In an attempt to prepare $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)_2]$ in a similar manner, a mixture of $\text{Ru}_3(\text{CO})_{12}$, bromopentaphenylcyclopentadiene and zinc dust was heated in refluxing xylenes. A grey solid precipitated from the crude reaction mixture. The major product in the supernatant, as identified by IR spectroscopy, was $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$. A pale coloured precipitate was obtained after purification and crystallisation of the grey solid. Further purification of the precipitate afforded a pale yellow solid, identified as $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)\{\eta^6\text{-C}_6\text{H}_4(\text{CH}_3)_2\}]\text{X}$ (X = unidentified anion) by mass, IR and ^1H -NMR spectra. A white tetraphenylborate salt (**5**) was made by reacting $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)\{\eta^6\text{-C}_6\text{H}_4(\text{CH}_3)_2\}]\text{X}$ with sodium tetraphenylborate (Scheme 3). This salt was isolated in ca. 50% overall yield (from $\text{Ru}_3(\text{CO})_{12}$) and was characterised by elemental analysis and mass, IR and ^1H -NMR spectroscopies. The cation is analogous to the known $[\text{Ru}(\eta^5\text{-C}_5\text{R}_5)\{\eta^6\text{-C}_6\text{R}'_6\}]^+$ species [19,20].

2.2. X-ray crystallography

The structures of **1**, **3** and **4** were determined by single crystal X-ray diffraction. Compounds **3** and **4** crystallise in the triclinic space group $P\bar{1}$ (No. 2), compound **1** in the orthorhombic space group $Pbca$ (No. 61) (**1**). Compound **3** is only the second structurally characterised complex containing the penta-*p*-tolylcyclopentadienyl ligand. Its asymmetric unit contains two crystallographically independent molecules. Figs. 1–3 show the molecules viewed side-on and along the normals to the C_5Ar_5 planes. Selected structural parameters are collected in Tables 1–3 and



Scheme 3.

the crystallographic parameters are summarised in Table 4. No intermolecular contacts of significance were observed in the solids; the closest intermolecular non-bonding approach between molecules being 3.430(8) Å (**1**), 3.35(2) Å (**3**) and 3.39(1) Å (**4**).

The C₅ rings of all compounds are not significantly distorted from co-planarity. The maximum deviation of the C₅ carbon atoms from the C₅R₅ rings are: **1** 0.010 Å, R = C₆H₅; 0.005 Å, R = H; **3** 0.019 Å (0.016 Å), R = C₆H₅; 0.004 Å (0.005 Å), R = H for the two molecules in the unit cell; and **4** 0.006 Å, R = C₆H₅; 0.003 Å, R = Me.

The two C₅ rings of each complex are almost parallel (the angle between the normals to the rings 0.72°, 0.30(0.96)° and 0.68° for **1**, **3** (both molecules) and **4**, respectively), and are nearly eclipsed in the solid state, as is usual for most ruthenocene derivatives [15]. All C–C bond distances are normal within statistical significance [average 1.436 Å (C₅Ph₅), 1.402 Å (C₅H₅) for **1**; 1.45(1.43) Å (η⁵-C₅(*p*-MeC₆H₄)₅), 1.41(1.41) Å (C₅H₅) for **3**; and 1.439 Å (C₅Ph₅), 1.419 Å (C₅Me₅) for **4**]. Those of the C₅Ph₅[−] ligands are similar to those in [Ru(η⁵-C₅Ph₅)(CO)₂Br] (1.441 Å average) [10] and [Ru(η⁵-C₅Ph₅)(CO)(PPh₃)Br] (1.42 Å average) [11], which are the only other structurally characterised Ru(C₅Ph₅) complexes. The C–C bond distances of the (η⁵-C₅(*p*-MeC₆H₄)₅) ligand are similar to those in [Fe(η⁵-C₅(*p*-MeC₆H₄)₅)(η⁵-C₅H₅)] [8]. The bond angles in the C₅ ring are normal for the C₅ rings of cyclopentadienyl and substituted cyclopentadienyl derivatives.

The *ipso*-carbon atoms of each of the arene rings of the C₅Ar₅ ligands are displaced slightly from the C₅ plane by between 0.003 and 0.176 Å (**1**), 0.021(0.061) and 0.144(0.187) Å (**3**) and 0.129 and 0.200 Å (**4**), with the average distances being 0.096 Å (**1**), 0.077(0.129) Å (**3**) and 0.159 Å (**4**). These *ipso*-carbon atoms and the ruthenium atom are on opposite sides of the C₅ plane, similar to the orientations seen in other pentaarylcyclopentadienyl compounds. The aryl rings are all also planar to within 0.011 Å (**1**), 0.021(0.018) Å (**3**) and 0.012 Å (**4**) with normal dimensions and are canted at between 49.6 and 59.0° (**1**), 46.8(47.2) and 53.0(57.5)° (**3**) and 48.2 and 53.0° (**4**) to the C₅ ring of the C₅Ar₅ ligand in the usual paddlewheel arrangement, with an average deviation of the phenyl rings from co-planarity

with the C₅ rings of 54.0° (**1**), 50.4(54.3)° (**3**) and 50.2° (**4**). The methyl groups of the C₅Me₅ ligand are displaced from the C₅ plane by between 0.095 and 0.147 Å, with the average displacement being 0.127 Å. The methyl substituents and the ruthenium atom are on opposite sides of the C₅ plane.

The Ru–(C₅Ar₅ ring centroid) distances are 1.796 Å (**1**), 1.779(1.795) Å (**3**) and 1.818 Å (**4**); the Ru–(C₅H₅ ring centroid) distances are 1.824 Å (**1**), 1.810(1.817) Å (**3**) and the Ru–(C₅Me₅ ring centroid) distance is 1.836 Å (**4**). Therefore, the separations between the C₅ ligand planes are 3.620 Å (**1**), 3.589(3.612) Å (**3**) and 3.654 Å (**4**). These values can be compared with those obtained at 293 K for [Ru(η⁵-C₅Me₅)(η⁵-C₅H₅)] [1.792 Å (Ru–C₅Me₅) and 1.829 Å (Ru–C₅H₅) and separation between planes of 3.621 Å] [21], for [Ru(η⁵-C₅H₅)₂] [ca. 3.63 Å, (X-ray) [22] ca. 3.68(1) Å (electron diffraction)] [23,24], [Ru(η⁵-C₅Me₅)₂] [3.60(1) Å] [16,25] and for [Ru(η⁵-C₅Ph₄H)₂] [3.664(2) Å] [17].

The structures of **1**, **3** and **4** provide comparisons of the effects of substituting the C₅Ph₅ ligand by the C₅(*p*-MeC₆H₄)₅ ligand and of the C₅H₅ ligand by the C₅Me₅ ligand in these sterically demanding systems. The only other structural comparison between the C₅Ph₅ and the C₅(*p*-MeC₆H₄)₅ ligands is that involving the analogous iron compounds [8,14]. The presence of a solute molecule in **4** complicates the comparison of the lattice parameters somewhat, however, the unit cell volume of [Ru{(η⁵-C₅(*p*-MeC₆H₄)₅)}(η⁵-C₅H₅)] **3**, is substantially less than that of [Ru(η⁵-C₅Ph₅)(η⁵-C₅H₅)] **1**.

As might be expected on steric grounds, the substitution of the C₅H₅ ligand by the bulkier C₅Me₅ ligand leads to increases in both the Ru–C₅Ph₅ and Ru–C₅R₅ (R = H, Me) distances.

The C₅Ph₅ and C₅(*p*-MeC₆H₄)₅ ligands are expected to make near equivalent steric demands at the metal centre. However, the substitution of the C₅Ph₅ ligand by the C₅(*p*-MeC₆H₄)₅ ligand results in a decrease in both the Ru–C₅Ar₅ and Ru–C₅H₅ distances. These effects, although small, are significant. A similar effect was observed in the structures of the corresponding iron compounds, [Fe(η⁵-C₅Ar₅)(η⁵-C₅H₅)] (Ar = Ph, *p*-MeC₆H₄) [8,14]. The structural effect is small but is observed in both the ruthenium and iron chemistries.

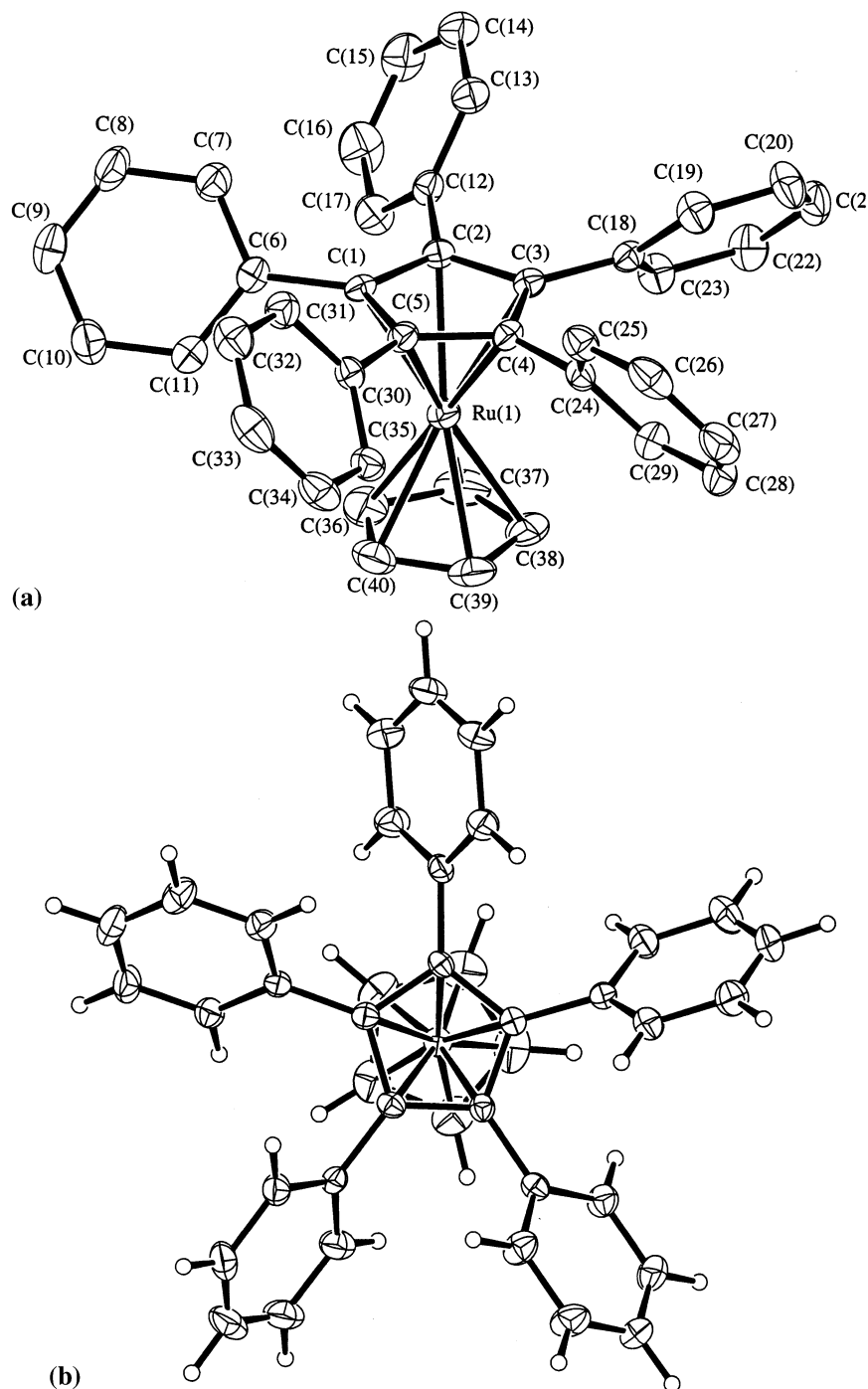


Fig. 1. ORTEP [39] (25% probability) illustration of the molecular structure of $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{H}_5)]$, **1**. View (a) showing the numbering of the non-hydrogen atoms, view (b) along the normal to the C_5Ph_5 plane, including the hydrogen atoms.

The difference between the C_5Ph_5 and $\text{C}_5(p\text{-MeC}_6\text{H}_4)_5$ ligands is thus suggested to be electronic in origin, with the $\text{C}_5(p\text{-MeC}_6\text{H}_4)_5$ ligand acting as a slightly better electron donor.

2.3. Cyclic voltammetry

Cyclic voltammetric studies should establish if the

$\text{C}_5(p\text{-MeC}_6\text{H}_4)_5$ ligand is a better electron donor than the C_5Ph_5 ligand. However, the comparison can be complicated if the electron transfer processes involved are not reversible. The reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{H}_5)]$ is not simple—the C_5Ph_5 ligand exists in both the $\eta^5\text{-C}_5\text{Ph}_5$ and $\text{C}_5\{\eta^6\text{-C}_6\text{H}_5\}\text{Ph}_4$ configurations [14]. Fortunately, an opportunity for such a comparison exists in the electrochemistry of the present compounds

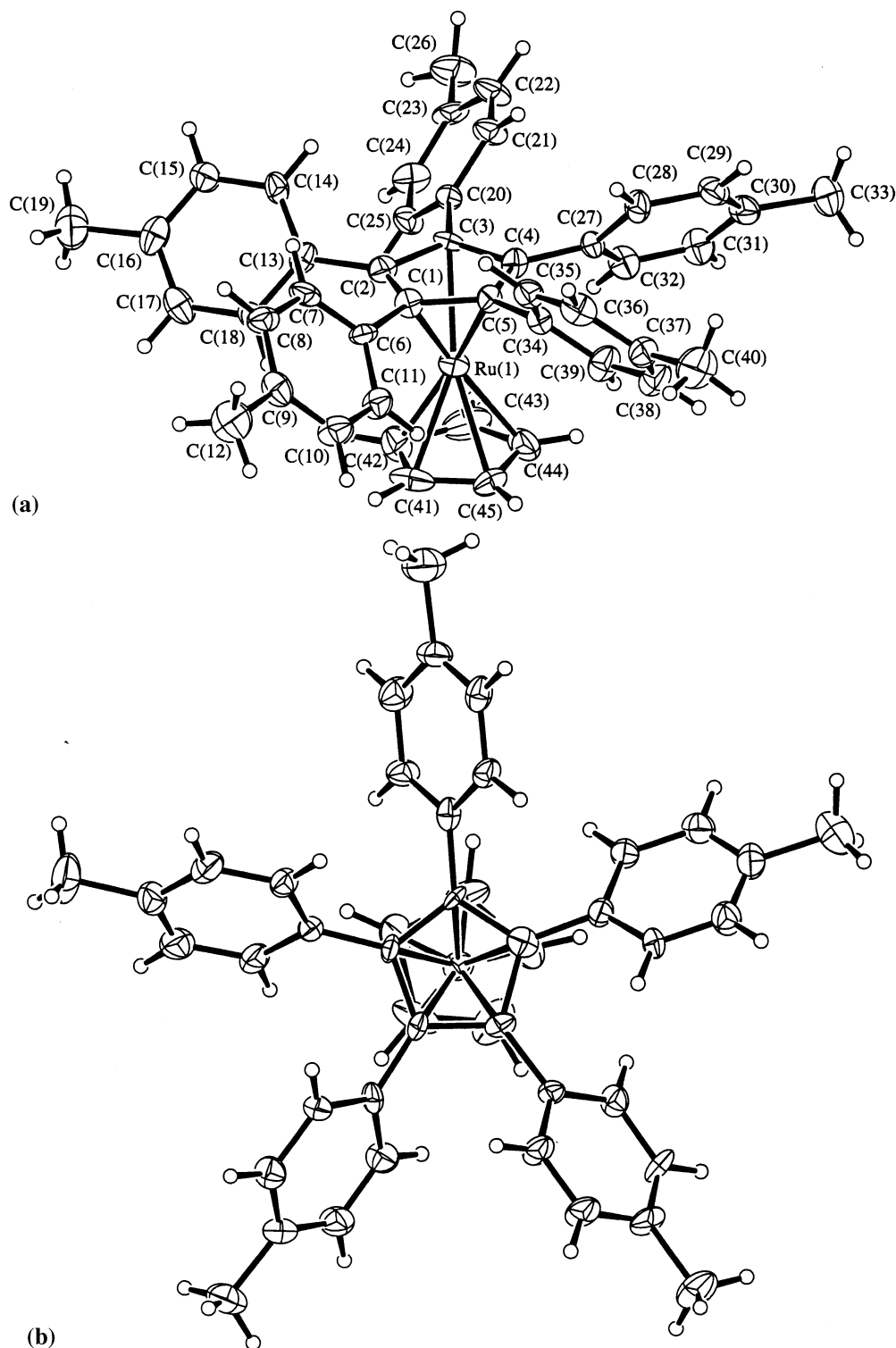


Fig. 2. ORTEP [39] (25% probability) illustration of the molecular structure of $[\text{Ru}\{\eta^5\text{-C}_5(p\text{-MeC}_6\text{H}_4)_5\}(\eta^5\text{-C}_5\text{H}_5)]$, **3**. View (a) showing the numbering of the non-hydrogen atoms, view (b) along the normal to the C_5Ar_5 plane, including the hydrogen atoms.

for which reversible oxidations are observed.

The only electron transfer process observed for ruthenocene at a platinum electrode at r.t. is an irreversible two-electron oxidation [26]. A reduction of ruthenocene has been observed only at -50°C [15].

Decamethylruthenocene undergoes a reversible one-electron oxidation at a platinum electrode at 0.57 V (versus $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{+/0}$ in dichloromethane) to the monocation, $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)_2]^+$ [27]. A second, irreversible, oxidation is observed at 1.27 V (versus

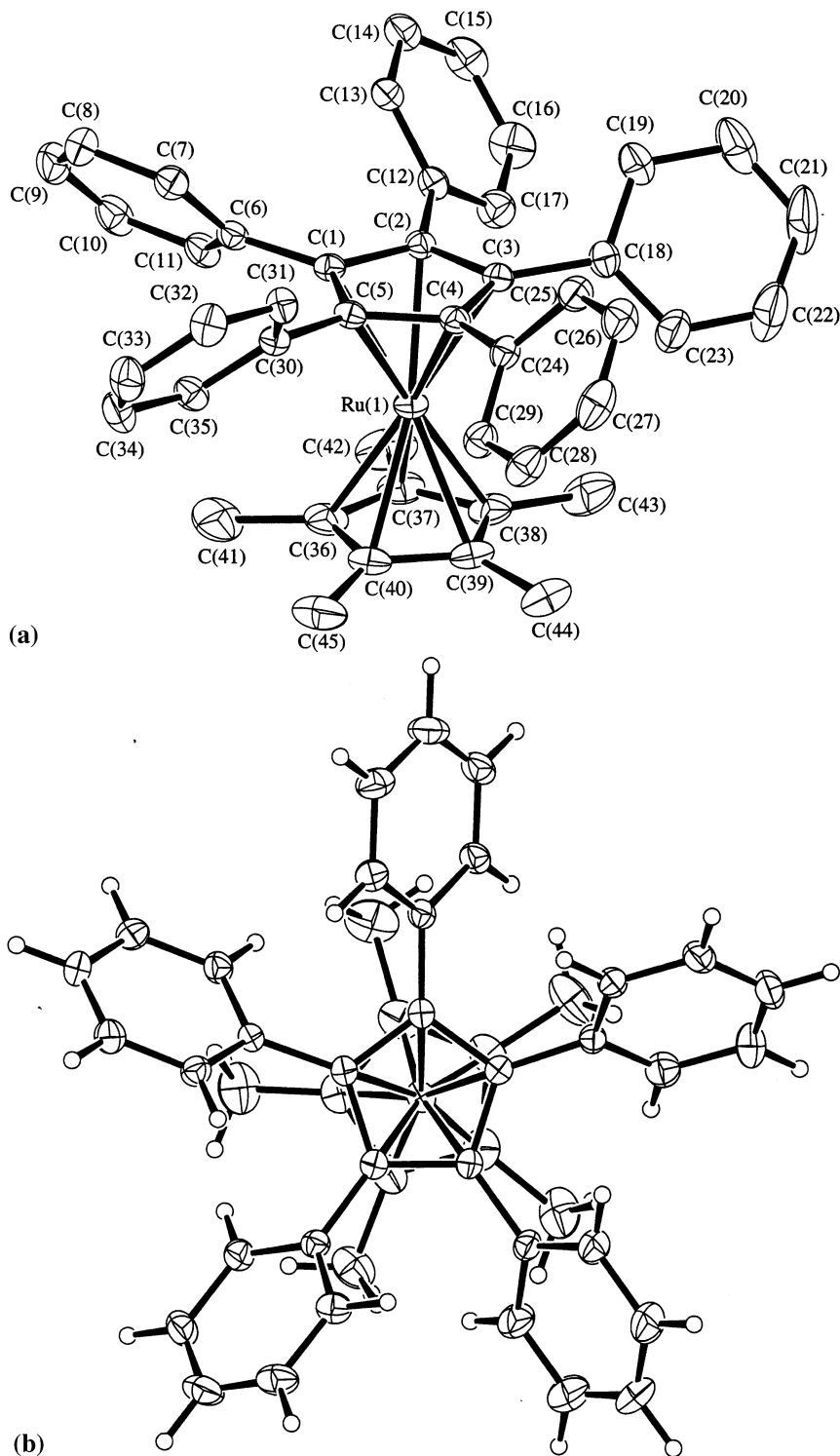


Fig. 3. ORTEP [39] (25% probability) illustration of the molecular structure of [Ru(η⁵-C₅Ph₅)(η⁵-C₅Me₅)] **4**. View (a) showing the numbering of the non-hydrogen atoms, view (b) along the normal to the C₅Ph₅ plane, including the hydrogen atoms.

[Fe(C₅Me₅)₂]^{+ / 0} in dichloromethane). The cation can be generated chemically by oxidation with AgBF₄ and is stable in solution for a short time at r.t. [27]. In the present work performed at r.t., no reductive processes were observed in preliminary cyclic voltammetric stud-

ies at platinum and glassy carbon electrodes for [Ru(η⁵-C₅Ph₅)(η⁵-C₅H₅)] **1**, [Ru(η⁵-C₅Ph₄H)(η⁵-C₅H₅)] **2**, and [Ru(η⁵-C₅(*p*-MeC₆H₄)₅)(η⁵-C₅H₅)] **3**. However, all compounds undergo overall two-electron oxidations to form unstable dications. The three compounds differed

from each other and from ruthenocene in the stabilities of the monocations, $[\text{Ru}(\eta^5\text{-C}_5\text{R}_5)(\eta^5\text{-C}_5\text{H}_5)]^+$ ($\text{R}_5 = \text{Ph}_5, \text{Ph}_4\text{H}, p\text{-MeC}_6\text{H}_4)_5$). Thus, at low scan rates, the pentaaryl compounds **1** and **3** were oxidised in two consecutive one-electron steps, whereas oxidation of the tetraaryl derivative **2** was an irreversible two-electron process. At a scan rate of 100 mV s^{-1} , the first oxidations of **1** and **3** showed signs of reversibility. As the scan rate was increased, the two anodic peaks separated in each case and the oxidations to the monocations were seen to be clearly reversible. The oxidation of **2**, however, appeared to be irreversible at scan rates below 1 V s^{-1} . These results indicate that the monocations of the penta-*p*-tolylcyclopentadienyl and pentaphenylcyclopentadienyl compounds are stabilised to a greater extent than is that of tetraphenylruthenocene. This is presumably due to the increased steric bulk around the cyclopentadienyl ring, which slows the subsequent chemical reactions. The peak potentials of the observed processes and the E_f potentials of the reversible couples are collected in Table 5, where the values are compared

Table 1

Selected bond lengths (Å) and bond angles (°) for $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{H}_5)]$ (**1**)

Bond lengths			
Ru(1)–C(1)	2.165(4)	Ru(1)–C(3)	2.176(4)
Ru(1)–C(2)	2.173(4)	Ru(1)–C(5)	2.181(4)
Ru(1)–C(4)	2.167(5)	Ru(1)–C(37)	2.181(5)
Ru(1)–C(36)	2.190(6)	Ru(1)–C(39)	2.176(5)
Ru(1)–C(38)	2.168(5)	Ru(1)–C(40)	2.180(5)
Bond angles			
C(1)–Ru(1)–C(2)	38.7(2)	C(2)–Ru(1)–C(3)	38.5(2)
C(3)–Ru(1)–C(4)	38.5(2)	C(4)–Ru(1)–C(5)	38.7(2)
C(5)–Ru(1)–C(1)	38.6(2)	C(1)–Ru(1)–C(3)	64.8(2)
C(2)–Ru(1)–C(4)	64.5(2)	C(3)–Ru(1)–C(5)	64.5(2)
C(4)–Ru(1)–C(1)	64.9(2)	C(5)–Ru(1)–C(2)	64.5(2)
C(36)–Ru(1)–C(37)	38.2(2)	C(37)–Ru(1)–C(38)	38.0(2)
C(38)–Ru(1)–C(39)	37.3(2)	C(39)–Ru(1)–C(40)	37.1(2)
C(40)–Ru(1)–C(36)	37.1(2)	C(36)–Ru(1)–C(38)	63.0(2)
C(37)–Ru(1)–C(39)	62.9(2)	C(38)–Ru(1)–C(40)	62.4(2)
C(39)–Ru(1)–C(36)	62.2(2)	C(40)–Ru(1)–C(37)	63.0(2)
C(1)–Ru(1)–C(36)	114.0(2)	C(3)–Ru(1)–C(36)	150.6(2)
C(1)–Ru(1)–C(37)	135.1(2)	C(3)–Ru(1)–C(37)	119.9(2)
C(1)–Ru(1)–C(38)	172.0(2)	C(3)–Ru(1)–C(38)	113.7(2)
C(1)–Ru(1)–C(39)	149.3(2)	C(3)–Ru(1)–C(39)	134.7(2)
C(1)–Ru(1)–C(40)	120.3(2)	C(3)–Ru(1)–C(40)	170.6(2)
C(2)–Ru(1)–C(36)	121.1(2)	C(4)–Ru(1)–C(36)	170.6(2)
C(2)–Ru(1)–C(37)	114.0(2)	C(4)–Ru(1)–C(37)	149.1(2)
C(2)–Ru(1)–C(38)	135.2(2)	C(4)–Ru(1)–C(38)	119.3(2)
C(2)–Ru(1)–C(39)	171.3(2)	C(4)–Ru(1)–C(39)	113.4(2)
C(2)–Ru(1)–C(40)	150.3(2)	C(4)–Ru(1)–C(40)	134.4(2)
C(5)–Ru(1)–C(36)	134.6(2)	C(5)–Ru(1)–C(39)	119.8(2)
C(5)–Ru(1)–C(37)	171.7(2)	C(5)–Ru(1)–C(40)	113.8(2)
C(5)–Ru(1)–C(38)	148.8(2)		

Table 2

Selected bond lengths (Å) and bond angles (°) for $[\text{Ru}(\eta^5\text{-C}_5(p\text{-MeC}_6\text{H}_4)_5)(\eta^5\text{-C}_5\text{H}_5)]$ (**3**)

Molecule A			
Bond lengths			
Ru(1)–C(1)	2.15(1)	Ru(1)–C(3)	2.18(1)
Ru(1)–C(2)	2.15(1)	Ru(1)–C(5)	2.17(1)
Ru(1)–C(4)	2.15(1)	Ru(1)–C(43)	2.16(1)
Ru(1)–C(41)	2.17(1)	Ru(1)–C(44)	2.15(1)
Ru(1)–C(42)	2.19(1)	Ru(1)–C(45)	2.18(1)
Bond angles			
C(1)–Ru(1)–C(2)	38.4(4)	C(2)–Ru(1)–C(3)	40.1(4)
C(3)–Ru(1)–C(4)	39.3(4)	C(4)–Ru(1)–C(5)	38.5(4)
C(5)–Ru(1)–C(1)	38.8(4)	C(1)–Ru(1)–C(3)	65.4(5)
C(2)–Ru(1)–C(4)	66.3(5)	C(3)–Ru(1)–C(5)	65.1(5)
C(4)–Ru(1)–C(1)	65.2(5)	C(5)–Ru(1)–C(2)	65.2(5)
C(41)–Ru(1)–C(42)	37.4(5)	C(42)–Ru(1)–C(43)	37.7(6)
C(43)–Ru(1)–C(44)	36.8(5)	C(44)–Ru(1)–C(45)	39.8(5)
C(45)–Ru(1)–C(41)	37.7(5)	C(41)–Ru(1)–C(43)	62.2(6)
C(42)–Ru(1)–C(44)	63.4(5)	C(43)–Ru(1)–C(45)	63.6(6)
C(44)–Ru(1)–C(41)	63.6(5)	C(45)–Ru(1)–C(42)	63.8(5)
C(1)–Ru(1)–C(41)	112.6(5)	C(3)–Ru(1)–C(41)	155.7(8)
C(1)–Ru(1)–C(42)	128.8(7)	C(3)–Ru(1)–C(42)	123.2(7)
C(1)–Ru(1)–C(43)	164.1(9)	C(3)–Ru(1)–C(43)	112.5(6)
C(1)–Ru(1)–C(44)	157.1(9)	C(3)–Ru(1)–C(44)	128.0(7)
C(1)–Ru(1)–C(45)	122.7(6)	C(3)–Ru(1)–C(45)	164.7(7)
C(2)–Ru(1)–C(41)	122.6(7)	C(4)–Ru(1)–C(41)	164.3(8)
C(2)–Ru(1)–C(42)	111.3(6)	C(4)–Ru(1)–C(42)	156.3(8)
C(2)–Ru(1)–C(43)	129.5(8)	C(4)–Ru(1)–C(43)	124.1(8)
C(2)–Ru(1)–C(44)	163.7(9)	C(4)–Ru(1)–C(44)	111.8(5)
C(2)–Ru(1)–C(45)	154.1(7)	C(4)–Ru(1)–C(45)	128.9(7)
C(5)–Ru(1)–C(41)	129.9(7)	C(5)–Ru(1)–C(44)	124.3(7)
C(5)–Ru(1)–C(42)	164.1(8)	C(5)–Ru(1)–C(45)	111.9(6)
C(5)–Ru(1)–C(43)	156(1)		
Molecule B			
Bond lengths			
Ru(2)–C(46)	2.19(1)	Ru(2)–C(86)	2.17(1)
Ru(2)–C(47)	2.20(1)	Ru(2)–C(87)	2.18(2)
Ru(2)–C(48)	2.17(1)	Ru(2)–C(88)	2.18(2)
Ru(2)–C(49)	2.13(1)	Ru(2)–C(89)	2.18(1)
Ru(2)–C(50)	2.15(1)	Ru(2)–C(90)	2.17(1)
Bond angles			
C(46)–Ru(2)–C(47)	38.7(4)	C(47)–Ru(2)–C(48)	38.3(4)
C(48)–Ru(2)–C(49)	38.6(4)	C(49)–Ru(2)–C(50)	37.8(4)
C(50)–Ru(2)–C(46)	39.3(4)	C(46)–Ru(2)–C(48)	63.9(5)
C(47)–Ru(2)–C(49)	65.4(5)	C(48)–Ru(2)–C(50)	63.5(4)
C(49)–Ru(2)–C(46)	65.0(5)	C(50)–Ru(2)–C(47)	65.0(4)
C(86)–Ru(2)–C(87)	37.4(5)	C(87)–Ru(2)–C(88)	36.8(6)
C(88)–Ru(2)–C(89)	38.2(6)	C(89)–Ru(2)–C(90)	39.0(6)
C(90)–Ru(2)–C(86)	37.6(5)	C(86)–Ru(2)–C(88)	62.7(7)
C(87)–Ru(2)–C(89)	62.8(6)	C(88)–Ru(2)–C(90)	64.1(6)
C(89)–Ru(2)–C(86)	63.5(5)	C(90)–Ru(2)–C(87)	62.9(6)
C(46)–Ru(2)–C(86)	112.7(6)	C(48)–Ru(2)–C(86)	155.7(8)
C(46)–Ru(2)–C(87)	129.0(7)	C(48)–Ru(2)–C(87)	123.9(7)
C(46)–Ru(2)–C(88)	162.4(9)	C(48)–Ru(2)–C(88)	112.5(6)
C(46)–Ru(2)–C(89)	157.7(9)	C(48)–Ru(2)–C(89)	129.1(8)
C(46)–Ru(2)–C(90)	124.0(8)	C(48)–Ru(2)–C(90)	165.1(9)
C(47)–Ru(2)–C(86)	123.3(7)	C(49)–Ru(2)–C(86)	164.7(8)
C(47)–Ru(2)–C(87)	111.8(6)	C(49)–Ru(2)–C(87)	156.0(8)
C(47)–Ru(2)–C(88)	127.4(7)	C(49)–Ru(2)–C(88)	124.1(9)
C(47)–Ru(2)–C(89)	162.7(9)	C(49)–Ru(2)–C(89)	112.3(6)
C(47)–Ru(2)–C(90)	155.7(9)	C(49)–Ru(2)–C(90)	129.7(7)
C(50)–Ru(2)–C(86)	130.8(7)	C(50)–Ru(2)–C(89)	124.6(7)
C(50)–Ru(2)–C(87)	165.2(8)	C(50)–Ru(2)–C(90)	113.5(5)
C(50)–Ru(2)–C(88)	157(1)		

with data for ruthenocene obtained in the present work under the same conditions.

With regard to variations in the central metal atom, $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)_2]$ has been shown to be harder to oxidise (by 0.57 V) than $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2]$ [27]. Similarly, $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{H}_5)]$ is harder to oxidise (by 0.486 V) than is $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{H}_5)]$.

A more complete description of the electrochemistry with full simulations will be reported later.

These results indicate that the addition of phenyl and *p*-tolyl substituents onto the cyclopentadienyl ring causes an increase in oxidation potentials. Compound **3** is easier to oxidise than **1** and **2** due to the greater electron donating nature of the *p*-tolyl substituent, which promotes oxidation. The tetraphenylcyclopentadienyl derivative (**2**) is easier to oxidise than the pentaphenylcyclopentadienyl derivative (**1**) perhaps because of the change in the angles between the phenyl groups and the C_5 ring, which results in a change in the electronic coupling of the phenyl substituents to the C_5 core. However, the tetraphenylruthenocenium cation appears to be more reactive than the pentaphenylruthenocenium cation.

The observation that $[\text{Ru}\{(\eta^5\text{-C}_5(p\text{-MeC}_6\text{H}_4)_5)\}(\eta^5\text{-C}_5\text{H}_5)]$ is easier to oxidise than is $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{H}_5)]$

(i.e. the $\text{C}_5(p\text{-MeC}_6\text{H}_4)_5$ ligand being the better electron donor) is consistent with the structural results.

It is somewhat surprising that the electronic effects of the methyl substituent on the arene ring should be observable at the metal centre. The methyl substituent is remote from the metal. Furthermore, in these compounds, the aryl groups are canted at some 55° to the C_5 rings, rather than the two rings being coplanar as required for optimal transmission of any electronic effects. However, the simplicity of the solution NMR spectra suggest that there is free rotation of the aryl rings.

3. Conclusion

This study provides the first fully characterised examples of ruthenocenes containing the bulky pentaphenyl- and penta-*p*-tolyl-cyclopentadienyl ligands. As expected, the pentaparatolylcyclopentadienyl compound has the greatest solubility, being soluble in hexane. Structural and cyclic voltammetric studies indicate that the pentaparatolylcyclopentadienyl ligand is a better electron donating ligand than is the pentaphenylcyclopentadienyl ligand.

4. Experimental

4.1. Instrumentation

Elemental analyses (C, H) were performed by either the Australian National University or University of Sydney Microanalytical Service. The melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. FTIR spectra were recorded on a Digilab FTS40 spectrometer. ^1H - and ^{13}C -NMR spectra were recorded on a Bruker AC200F (^1H -NMR 200.13 MHz, ^{13}C -NMR 50.33 MHz) spectrometer. The spectra were referenced internally to TMS or to residual solvent resonances (CD_2Cl_2 , ^1H δ 5.30 ppm, ^{13}C δ 53.8 ppm). Electron impact mass spectra were obtained using a Kratos MS 9 geometry mass spectrometer with a direct insertion probe, a 280°C source temperature, 70 eV ionisation voltage and 4 kV acceleration voltage.

Electrochemical experiments were performed using a BAS 100B electrochemical analyser and BAS 100W version 2.0 software. A three-electrode system was used, in which the working electrode was either a 3 mm glassy carbon disc electrode or a 1.2 mm platinum disc electrode. Both electrodes were polished with an alumina suspension (0.04 μm grade) before each cyclic voltammogram was recorded. The auxiliary electrode was a platinum wire (0.5 mm diameter, 5 cm length) and a $\text{Ag}/\text{AgCl}/\text{NaCl}(\text{sat.})$ electrode was used as the

Table 3

Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$) for $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{Me}_5)]$ (**4**)

Bond lengths			
Ru(1)–C(2)	2.189(5)	Ru(1)–C(1)	2.196(5)
Ru(1)–C(4)	2.201(5)	Ru(1)–C(3)	2.190(5)
Ru(1)–C(36)	2.191(6)	Ru(1)–C(5)	2.181(5)
Ru(1)–C(38)	2.196(6)	Ru(1)–C(37)	2.202(6)
Ru(1)–C(40)	2.201(6)	Ru(1)–C(39)	2.198(6)
Bond angles			
C(1)–Ru(1)–C(2)	38.1(2)	C(2)–Ru(1)–C(3)	38.8(2)
C(3)–Ru(1)–C(4)	37.9(2)	C(4)–Ru(1)–C(5)	38.6(2)
C(5)–Ru(1)–C(1)	38.3(2)	C(1)–Ru(1)–C(3)	64.3(2)
C(2)–Ru(1)–C(4)	64.2(2)	C(3)–Ru(1)–C(5)	64.0(2)
C(4)–Ru(1)–C(1)	64.4(2)	C(5)–Ru(1)–C(2)	64.0(2)
C(36)–Ru(1)–C(37)	37.8(2)	C(37)–Ru(1)–C(38)	37.2(2)
C(38)–Ru(1)–C(39)	38.1(2)	C(39)–Ru(1)–C(40)	37.5(2)
C(40)–Ru(1)–C(36)	37.8(2)	C(36)–Ru(1)–C(38)	62.5(3)
C(37)–Ru(1)–C(39)	63.2(2)	C(38)–Ru(1)–C(40)	62.9(2)
C(39)–Ru(1)–C(36)	62.9(2)	C(40)–Ru(1)–C(37)	63.3(2)
C(1)–Ru(1)–C(36)	113.7(2)	C(3)–Ru(1)–C(36)	168.7(2)
C(1)–Ru(1)–C(37)	122.5(2)	C(3)–Ru(1)–C(37)	132.7(2)
C(1)–Ru(1)–C(38)	153.1(2)	C(3)–Ru(1)–C(38)	113.7(2)
C(1)–Ru(1)–C(39)	167.4(2)	C(3)–Ru(1)–C(39)	121.6(2)
C(1)–Ru(1)–C(40)	132.2(2)	C(3)–Ru(1)–C(40)	151.9(2)
C(2)–Ru(1)–C(36)	132.7(2)	C(4)–Ru(1)–C(36)	152.7(2)
C(2)–Ru(1)–C(37)	113.8(2)	C(4)–Ru(1)–C(37)	167.6(2)
C(2)–Ru(1)–C(38)	122.6(2)	C(4)–Ru(1)–C(38)	132.1(2)
C(2)–Ru(1)–C(39)	153.3(2)	C(4)–Ru(1)–C(39)	112.4(2)
C(2)–Ru(1)–C(40)	168.1(2)	C(4)–Ru(1)–C(40)	121.3(2)
C(5)–Ru(1)–C(36)	122.1(2)	C(5)–Ru(1)–C(39)	131.5(2)
C(5)–Ru(1)–C(37)	153.2(2)	C(5)–Ru(1)–C(40)	112.8(2)
C(5)–Ru(1)–C(38)	167.8(2)		

Table 4
Crystallographic data and refinement details for **1**, **3** and **4**·H₂O

Compound	1	3	4 ·H ₂ O
Molecular formula	C ₄₀ H ₃₀ Ru	C ₄₅ H ₄₀ Ru	C ₄₅ H ₄₀ ORu
<i>M</i>	611.76	681.88	697.88
Crystal colour, shape	Colourless, blade	Colourless, blade	Colourless, blade
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	<i>Pbca</i> (No. 61)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	14.234(3)	19.319(7)	12.145(2)
<i>b</i> (Å)	20.276(3)	21.007(7)	12.696(4)
<i>c</i> (Å)	20.625(4)	10.436(3)	14.281(2)
α (°)	90.0000	103.76(3)	80.41(2)
β (°)	90.0000	95.07(3)	66.43(1)
γ (°)	90.0000	112.59(2)	62.80(2)
<i>U</i> (Å ³)	5952(1)	3721(2)	1794.8(8)
<i>Z</i>	8	4	2
<i>D</i> _{calc} (g cm ^{−3})	1.365	1.217	1.291
μ (Mo–K α) (cm ^{−1}) (λ (Å))	5.54 (0.71069)	—	4.70 (0.71069)
μ (Cu–K α) (cm ^{−1}) (λ (Å))	—	36.13 (1.54178)	—
<i>F</i> (000)	2512.00	1416.00	724.00
Crystal dimensions (mm)	0.50 × 0.22 × 0.05	0.40 × 0.32 × 0.05	0.28 × 0.20 × 0.05
2 θ _{max} (°)	49.9	130.2	54.9
<i>hkl</i> range	0, 16; 0, 24; 0, 24	0, 20; −23, 22; −12, 12	−14, 15; −16, 16; 0, 18
No. of reflections collected	5791	10198	8833
No. of unique reflections, <i>R</i> _{merge}	5781	9782, 0.040	8230, 0.025
No. of observed data used	2898 (<i>I</i> > 2.50(σ))	3633 (<i>I</i> > 3.00(σ))	5404 (<i>I</i> > 3.00(σ))
<i>R</i> ; <i>R</i> _w ^a	0.036; 0.031	0.050; 0.062	0.050; 0.057
Final electron density difference features (max, min) (e Å ^{−3})	0.30, −0.39	0.60, −0.43	0.97, −0.46

^a $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_w = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o))$.

reference electrode. The electroactive species were examined as ca. 0.1 mM solutions in dichloromethane and the supporting electrolyte was ca. 0.1 M tetrabutylammonium perchlorate (Fluka). All samples were degassed with high purity argon (BOC) for 5–10 min prior to use. The argon was passed through a H₂O/O₂ removal assembly which consisted of an indicating moisture trap (5 Å molecular sieves with Dryerite, Activon, RDMT400D), a high capacity coiled O₂ trap (Alltech, 4003) and an indicating O₂ trap (Alltech, 4004). All potentials are quoted relative to the ferrocenium/ferrocene redox couple, which was observed at +470 mV versus the Ag/AgCl/NaCl(sat.) electrode.

4.2. General reaction conditions

All manipulations were performed at atmospheric pressure under an atmosphere of dinitrogen by using conventional Schlenk techniques, but no special precautions were taken to exclude oxygen during work-up. THF (Merck) was predried over sodium wire and distilled from sodium benzophenone ketyl. *n*-Hexane (BDH) was distilled from sodium wire. Dichloromethane (Ajax) and methanol (Biolab) were distilled from calcium hydride. Xylenes (Ajax) was distilled from sodium.

4.3. Starting materials

Ru(η^5 -C₅Ph₅)(CO)₂Br [9], Ru(η^5 -C₅H₅)(COD)Cl [28], Ru(η^5 -C₅Me₅)(COD)Cl [29], HC₅Ph₅ [30] and HC₅(*p*-MeC₆H₄)₅ [8] were prepared as described previously. Cyclopentadienylsodium, butyllithium (2.5 M solution in hexanes), 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (90%) and sodium tetraphenylborate (Aldrich) and Ru₃(CO)₁₂ (Strem) were used as-received. Flash silica (240–400 mesh) was obtained from Merck.

4.4. Preparation of [Ru(η^5 -C₅Ph₅)(η^5 -C₅H₅)] (**1**)

4.4.1. From Ru(η^5 -C₅Ph₅)(CO)₂Br and NaCp

NaC₅H₅ (0.82 ml of a 2.0 M solution in THF, 1.64 mmol) was added at r.t. to a stirred solution of [Ru(η^5 -C₅Ph₅)(CO)₂Br] (0.686 g, 1.01 mmol) in THF (50 ml). After stirring for 18 h, the supernatant was filtered from a solid identified as [Ru(η^5 -C₅Ph₅)(μ -CO)(CO)]₂ (yield 0.132 g, 22%) by IR (KBr ν_{CO} 1962, 1779 cm^{−1}) and mass (*m/e* 1092 ([Ru₂(C₅Ph₅)₂−2H]⁺, 17%), 991 ([Ru(C₅Ph₅)₂−H]⁺, 100%), 546 ([Ru(C₅Ph₅)−H]⁺, 19%) spectroscopies. The solvent was removed in vacuo. The resultant solid was heated at 200°C for 5 h in vacuo. After CH₂Cl₂ (40 ml) was added and filtration by gravity, column chromatography was performed. Elu-

Table 5
Electrochemical data^a for [Ru(η^5 -C₅Ph₅)(η^5 -C₅H₅)] (1), [Ru(η^5 -C₅Ph₄H)(η^5 -C₅H₅)] (2), [Ru{(η^5 -C₅(*p*-MeC₆H₄)₅)}(η^5 -C₅H₅)] (3), [Ru(η^5 -C₅H₅)₂] and [Ru(η^5 -C₅Me₅)₂]^b

Compound	<i>E</i> _{p1a} (V)	<i>E</i> _{p2a} (V)	<i>E</i> _{p1c} (V)	<i>E</i> _{p3c} (V)	<i>E</i> _f (V)
[Ru(η^5 -C ₅ Ph ₅)(η^5 -C ₅ H ₅)] (1)	0.770	0.981	0.682	0.340	0.726
[Ru(η^5 -C ₅ Ph ₄ H)(η^5 -C ₅ H ₅)] (2)	0.830	—	0.510	0.150	0.670
[Ru{(η^5 -C ₅ (<i>p</i> -MeC ₆ H ₄) ₅)}(η^5 -C ₅ H ₅)] (3)	0.680	0.796	0.683	0.280	0.632
[Ru(η^5 -C ₅ H ₅) ₂]	0.490	—	—	0.250	—
[Ru(η^5 -C ₅ Me ₅) ₂] ^b	—	0.738	—	—	0.038

^a All data measured at r.t. at scan rates of 1 V s⁻¹ in dichloromethane/0.1 M tetrabutylammonium perchlorate vs. [Fe(η^5 -C₅H₅)₂]^{+ / 0}.

^b Data from [27], measured at r.t. at a scan rate of 20 mV s⁻¹ in dichloromethane. Potentials quoted in [27] vs. [Fe(η^5 -C₅Me₅)₂]^{+ / 0}; converted to potentials vs. [Fe(η^5 -C₅H₅)₂]^{+ / 0} using the data of [40].

tion with 30% CH₂Cl₂/70% *n*-hexane afforded, after evaporation to dryness and crystallisation of the solid from CH₂Cl₂/*n*-hexane, very pale yellow crystals of [Ru(η^5 -C₅Ph₅)(η^5 -C₅H₅)] (1) (127 mg, 21%) m.p. > 250°C (decomp.). (Found C, 78.8; H, 4.9. C₄₀H₃₀Ru requires C, 78.5; H, 4.9%). ¹H-NMR (CD₂Cl₂, 200.13 MHz): δ 7.07–6.95 (m, 25H, Ar-*H*), 4.73 (s, SH, C₅H₅) ppm. ¹³C-NMR (CD₂Cl₂, 50.33 MHz): δ 136.0 (*q* Ar-C), 133.0, 127.3, 126.5 (Ar-CH), 94.6 (C₅ of C₅Ar₅), 76.6 (C₅ of C₅H₅) ppm. MS-EI (*m/e*) 612 ([*M*]⁺, 100%). IR (KBr) $\nu_{\max}$ 3106 vw, 3093 vw, 3083 vw, 3056 w, 3044 (sh), 3028 vw, 3010 vw, 2988 vw, 1653 vw, 1601 w, 1576 vw, 1559 vw, 1540 vw, 1502 m, 1443 w, 1407 vw, 1176 vw, 1155 vw, 1102 vw, 1072 w, 1027 w, 999 vw, 919 vw, 840 vw, 829 vw, 810 w, 802 w, 784 w, 740 vs, 699 vs, 674 vw, 669 vw, 622 vw, 575 m, 556 m, 545 w, 415 w cm⁻¹. Elution with 50% CH₂Cl₂/50% *n*-hexane yielded, after evaporation to dryness and crystallisation of the solid from CH₂Cl₂/*n*-hexane, yellow–orange crystals of [Ru(η^5 -C₅Ph₅)(CO)₂Br] (72 mg, 10%) identified by comparison of its ν_{CO} (CH₂Cl₂) IR spectrum with that of an authentic sample [9].

4.4.2. From [Ru(η^5 -C₅H₅)(COD)Cl] and LiC₅Ph₅

A solution of Li(C₅Ph₅) [prepared from HC₅Ph₅ (605 mg, 1.35 mmol) and BuLi (0.56 ml of a 2.5 M solution in hexanes, 1.4 mmol)] in THF (15 ml) was added via a canula to a solution of [Ru(η^5 -C₅H₅)(COD)Cl] (350 mg, 1.13 mmol) in THF (25 ml). The reaction mixture was stirred for 18 h, the solvent was removed and the crude product was purified by column chromatography. Elution with 30% CH₂Cl₂/70% *n*-hexane afforded a pale yellow solution which, after evaporation to dryness and fractional crystallisation of the solid from CH₂Cl₂/*n*-hexane, initially gave HC₅Ph₅ (241 mg, 40%), identified by comparison of its KBr IR spectrum with that of an authentic sample. Subsequent crystallisation of the solid obtained from the filtrate from CH₂Cl₂/*n*-hexane yielded [Ru(η^5 -C₅Ph₅)(η^5 -C₅H₅)] (1) (84 mg, 12%) identified by comparison of its KBr IR spectrum with that of a sample prepared as in Section 4.4.1.

4.5. Preparation of [Ru(η^5 -C₅Ph₄H)(η^5 -C₅H₅)] (2)

A solution of Li(C₅Ph₄H) [prepared from HC₅Ph₄H (90%, 415 mg, 1.01 mmol) and BuLi (0.5 ml of a 2.5 M solution in hexanes, 1.25 mmol)] in THF (30 ml) was added via a canula to a solution of [Ru(η^5 -C₅H₅)(COD)Cl] (262 mg, 0.846 mmol) in THF (20 ml). The reaction mixture was stirred for 18 h, filtered, the solvent was removed and the crude product purified by column chromatography. Elution with 30% CH₂Cl₂/70% *n*-hexane initially afforded a pale yellow solution which, after evaporation to dryness and crystallisation of the solid from CH₂Cl₂/*n*-hexane, yielded HC₅Ph₄H (57 mg, 14%) identified by comparison of its KBr IR spectrum with that of an authentic sample. Further elution yielded, after evaporation to dryness and crystallisation of the solid from CH₂Cl₂/*n*-hexane, pale yellow [Ru(η^5 -C₅Ph₄H)(η^5 -C₅H₅)] (2) (261 mg, 58%) m.p. 181–184°C. (Found C, 76.5; H, 4.6. C₃₄H₂₆Ru requires C, 76.24; H, 4.89%). ¹H-NMR (CD₂Cl₂, 200.13 MHz): δ 7.24–7.05 (m, 20H, Ar-*H*), 5.36 (s, 1H, C₅Ph₄H), 4.61 (s, 5H, C₅H₅) ppm. ¹³C-NMR (CD₂Cl₂, 50.33 MHz): δ 137.5, 136.0 (*q* Ar-C), 133.2, 130.4, 127.8, 127.5, 126.7, 126.7 (Ar-CH), 95.6, 92.3 (C₅ of C₅Ar₅), 75.4, 73.0 (C₅ of C₅H₅) ppm. MS-EI (*m/e*) 536 ([*M*]⁺, 100%). IR (KBr) $\nu_{\max}$: 3108 vw, 3084 vw, 3057 w, 3030 vw, 1600 w, 1577 vw, 1507 w, 1501 w, 1448 w, 1407 w, 1178 vw, 1153 vw, 1101 w, 997 w, 919 vw, 914 vw, 814 w, 791 w, 764 s, 735 m, 698 vs, 634 w, 618 w, 567 w, 558 w, 544 w, 526 w, 483 w, 419 w cm⁻¹.

4.6. Preparation of [Ru{(η^5 -C₅(*p*-MeC₆H₄)₅)}(η^5 -C₅H₅)] (3)

A solution of Li[C₅(*p*-MeC₆H₄)₅] [prepared from HC₅(*p*-MeC₆H₄)₅ (650 mg, 1.26 mmol) and BuLi (0.46 ml of a 2.5 M solution in hexanes, 1.15 mmol)] in THF (15 ml) was added via a canula to a solution of [Ru(η^5 -C₅H₅)(COD)Cl] (341 mg, 1.10 mmol) in THF (30 ml).

The reaction mixture was stirred at r.t. overnight and filtered by canula. After evaporation to dryness, the residue was dissolved in CH_2Cl_2 (50 ml) and after filtration, and evaporation to dryness, the crude product was purified by column chromatography. Elution with 30% CH_2Cl_2 /70% *n*-hexane afforded a pale yellow solution which, after evaporation to dryness, was identified as $\text{HC}_5(p\text{-MeC}_6\text{H}_4)_5$ (267 mg, 41%) by comparison of its KBr IR spectrum with that of an authentic sample. Elution with 70% CH_2Cl_2 /30% *n*-hexane afforded, after evaporation to dryness and crystallisation of the solid from *n*-hexane, very pale yellow crystals of $[\text{Ru}\{\eta^5\text{-C}_5(p\text{-MeC}_6\text{H}_4)_5\}(\eta^5\text{-C}_5\text{H}_5)]$ (**3**) (40 mg, 5%) m.p. > 280°C. (Found C, 79.1; H, 6.3. $\text{C}_{45}\text{H}_{40}\text{Ru}$ requires C, 79.27; H, 5.91%). $^1\text{H-NMR}$ (CD_2Cl_2 , 200.13 MHz): δ 6.91–6.81 (AB quartet, $J(\text{HH}) = 8.1$ Hz, 20H, Ar-*H*), 4.68 (s, 5H, C_5H_5), 2.22 (s, 15H, CH_3) ppm. $^{13}\text{C-NMR}$ (CD_2Cl_2 , 50.33 MHz): δ 136.0, 133.2 (*q*Ar-*C*), 132.9, 128.0 (Ar-*CH*), 94.5 (C_5 of C_5Ar_5), 76.3 (C_5 of C_5H_5), 21.2, (CH_3) ppm. MS-EI (*m/e*) 682 ($[\text{M}]^+$, 100%). IR (KBr) ν_{max} : 3087 vw, 3055 vw, 3030 vw, 3014 w, 2988 vw, 2977 vw, 2954 vw, 2944 vw, 2920 w, 2864 vw, 1654 vw, 1559 vw, 1540 vw, 1520 vs, 1457 w, 1182 w, 1112 vw, 1102w, 1021 w, 998 vw, 840 w, 817 m, 811 m, 805 m, 747 m, 727 m, 700 vw, 679 vw, 643 vw, 566 w, 544 w, 526 vs, 451 vw, 416 w cm^{-1} .

4.7. Preparation of $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{Me}_5)]$ (**4**)

A solution of $\text{Li}(\text{C}_5\text{Ph}_5)$ [prepared from HC_5Ph_5 (901 mg, 2.02 mmol) and BuLi (0.85 ml of a 2.5 M solution in hexanes, 2.02 mmol)] in THF (50 ml) was added via a canula to a solution of $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{COD})\text{Cl}]$ (767 mg, 2.02 mmol) in THF (20 ml). The reaction mixture was stirred for 16 h and after filtration and evaporation to dryness, the crude product was purified by column chromatography. Elution with 25% CH_2Cl_2 /75% *n*-hexane afforded a pale yellow solution which, after evaporation to dryness and crystallisation of the solid from CH_2Cl_2 /*n*-hexane, gave HC_5Ph_5 (100 mg, 11%) identified by comparison of its KBr IR spectrum with that of an authentic sample. Repeated recrystallisations of the filtrate from CH_2Cl_2 /*n*-hexane and removal of more HC_5Ph_5 finally yielded very pale yellow crystals of $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\eta^5\text{-C}_5\text{Me}_5)]$ (**4**) (22 mg, 2%). $^1\text{H-NMR}$ (CD_2Cl_2 , 200.13 MHz): δ 7.57–6.80 (m, 25H, Ar-*H*), 1.67 (s, 15H, CH_3) ppm. MS-EI (*m/e*) 682 ($[\text{M}]^+$, 100%). IR (KBr) ν_{max} : 3079 vw, 3056 w, 3026 vw, 1653 w, 1601 w, 1576 w, 1559 w, 1540 w, 1506 m, 1489 w, 1443 w, 1407 w, 1102 vw, 1071 w, 1027 w, 999 w, 810 w, 802 w, 784 w, 740 s, 697 vs, 668 w, 575 m, 555 m, 545 w cm^{-1} .

4.8. Reaction of $\text{Ru}_3(\text{CO})_{12}$ with $\text{C}_5\text{Ph}_5\text{Br}$ in the presence of Zn

A mixture of $\text{Ru}_3(\text{CO})_{12}$ (250 mg, 0.391 mmol), $\text{C}_5\text{Ph}_5\text{Br}$ (1.20 g, 2.28 mmol) and Zn (150 mg, 2.29 mmol) in xylenes (150 ml) was heated at reflux for 42 h, to give a red–orange solution and pale coloured precipitate. After filtration via canula, the pale coloured precipitate was extracted with hot MeOH to give an orange–yellow filtrate and an insoluble grey material. Evaporation of the filtrate to dryness and crystallisation of the resultant solid from CH_2Cl_2 /*n*-hexane afforded a pale yellow solid which was collected on a sintered glass funnel and washed with *n*-hexane. The solid was identified as $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)\{\eta^6\text{-C}_6\text{H}_4(\text{CH}_3)_2\}]^+ \text{X}^-$ where X is an unidentified anion (520 mg) m.p. > 250°C (decomp.). (Found C, 57.3; H, 3.9%). $^1\text{H-NMR}$ (CD_2Cl_2 , 200.13 MHz): δ 7.27–6.85 (m, 25H, Ar-*H*), 6.42–6.05 (m, 4H, C_6H_4), 2.24, 2.23, 2.19 (3 × s, 6H, $\text{C}_6\text{H}_4(\text{CH}_3)_2$ mixture of isomers) ppm. MS-EI (*m/e*) 652 ($[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)\{\eta^6\text{-C}_6\text{H}_4(\text{CH}_3)_2\}\text{-H}]^+$, 15%), 545 ($[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)\text{-H}]^+$, 1%), 106 ($[\text{C}_6\text{H}_4(\text{CH}_3)_2]^+$, 44%), 91 ($[\text{C}_6\text{H}_4(\text{CH}_3)]^+$, 100%). IR (KBr) ν_{max} : 3110 vw, 3085 (sh), 3057 w, 3032 vw, 2973 vw, 1558 vw, 1540 w, 1506 w, 1505 (sh), 1457 w, 1445 w, 1417 w, 1410 w, 1408 (sh), 1403 (sh), 1076 vw, 1027 w, 801 vw, 783 vw, 740 s, 704 (sh), 700 vs, 575 m, 556 m, 551 w cm^{-1} .

A tetraphenylborate salt of the above compound was obtained by adding NaBPh_4 (70 mg, 0.205 mmol) to $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)\{\eta^6\text{-C}_6\text{H}_4(\text{CH}_3)_2\}]^+ \text{X}^-$ (150 mg) in CH_2Cl_2 /MeOH (25 ml/4 ml). After stirring for 15 min, evaporation to ca. 5 ml in vacuo precipitated a white solid, which was recrystallised from CH_2Cl_2 /*n*-hexane yielding $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)\{\eta^6\text{-C}_6\text{H}_4(\text{CH}_3)_2\}]^+ \text{BPh}_4^-$ (**5**) (110 mg, 50%) m.p. > 250°C (decomp.). (Found C, 81.7; H, 5.6. $\text{C}_{67}\text{H}_{55}\text{BRu}$ requires C, 82.79; H, 5.70%). $^1\text{H-NMR}$ (CD_2Cl_2 , 200.13 MHz): δ 7.31–6.79 (m, 45H, Ar-*H*), 5.87–5.71 (m, 4H, C_6H_4), 2.12, 2.08, 2.06 (3 × s, 6H, $\text{C}_6\text{H}_4(\text{CH}_3)_2$ mixture of isomers) ppm. MS-EI (*m/e*) 653 ($[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)\{\eta^6\text{-C}_6\text{H}_4(\text{CH}_3)_2\}]^+$, 3%), 242 ($[\text{BPh}_3]^+$, 18%), 164 ($[\text{BPh}_2\text{-H}]^+$, 100%), 78 (Ph^+ , 44%). IR (KBr) ν_{max} : 3112 vw, 3083 (sh), 3054 w, 3029 w, 3002 vw, 2983 vw, 1579 w, 1502 w, 1477 vw, 1457 vw, 1446 w, 1425 w, 1410 w, 1262 vw, 1254 (sh), 1223 vw, 1179 vw, 1157 vw, 1133 vw, 1075 vw, 1071 (sh), 1031 w, 1002 vw, 842 vw, 803 vw, 784 vw, 769 vw, 744 m, 735 s, 705 vs, 701 vs, 623 vw, 613 m, 575 m, 556 m, 549 w, 470 vw cm^{-1} .

4.9. X-ray structure determinations

For **1** and **4**, colourless blade-like (**1**) or approximately hexagonal plate-like (**4**) crystals (approximate dimensions of $0.50 \times 0.22 \times 0.05$ mm (**1**), $0.28 \times 0.20 \times 0.05$ mm (**4**)) were attached to thin glass fibres, and mounted on an Enraf-Nonius CAD4 diffractometer

employing graphite monochromated Mo–K α radiation. Cell constants were obtained from a least-squares refinement using the setting angles of 25 reflections in the range $19.00 < 2\theta < 24.22^\circ$ (**1**) or $16.66 < 2\theta < 24.02^\circ$ (**4**). Diffraction data were collected at a temperature of $21 \pm 1^\circ\text{C}$ using $\omega:4/3\theta$ scans to a maximum 2θ value of 49.9° (**1**) or 54.9° ($\omega:1/3\theta$ scans) (**4**). The intensities of three representative reflections measured every 60 min either (**1**) decreased by 2.1% and a linear correction factor was accordingly applied to the data, or (**4**) did not change significantly during the data collection. In both cases an analytical absorption correction was applied and the data were also corrected for Lorentz and polarisation effects.

For **3**, a colourless blade-like crystal (approximate dimensions, $0.40 \times 0.32 \times 0.05$ mm) was attached to a thin glass fibre, and mounted on a Rigaku AFC7R diffractometer employing graphite monochromated Cu–K α radiation from a rotating anode generator. Primitive triclinic cell constants were obtained from a least-squares refinement using the setting angles of 25 reflections in the ranges $18.80 < 2\theta < 27.87^\circ$. The unit cell volume of **3** suggested two complexes in the asymmetric unit. Diffraction data were collected at a temperature of $21 \pm 1^\circ\text{C}$ using $\omega-2\theta$ scans to a maximum 2θ value of 130.2° . The intensities of three representative reflections measured every 150 reflections did not change significantly during the data collection. An analytical absorption correction was applied and the data were also corrected for Lorentz and polarisation effects.

All calculations were undertaken with the teXsan [31] crystallographic software package. Neutral atom scattering factors were taken from Cromer and Waber [32]. Anomalous dispersion effects were included in F_{calc} [33] and the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [34]. The values for the mass attenuation coefficients were those of Creagh and Hubbell [35]. The structures were solved by direct methods (**1**) [36] (**3**, **4**) [37] and expanded using Fourier techniques [38]. The solution of **3** confirmed the presence of two crystallographically independent complexes in the asymmetric unit. In general, the non-hydrogen atoms were modelled anisotropically, the exception being the phenyl C(17) of **4** which was modelled isotropically. In the structure of **4**, two residual electron density peaks separated by $0.83 \text{ \AA}$ are assumed to be associated with the oxygen atom of a water molecule partially occupying each of the two sites. For all structures, hydrogen atoms were included in the models at calculated positions with group thermal parameters; no hydrogen atoms were included for the water molecule of **4**. Figures were produced using the program ORTEP [39].

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References

- [1] L.D. Field, T.W. Hambley, T. He, P.A. Humphrey, C.M. Lindall, A.F. Masters, *Aust. J. Chem.* 49 (1996) 889.
- [2] L.D. Field, T.W. Hambley, T. He, A.F. Masters, P. Turner, *Aust. J. Chem.* 50 (1998) in press.
- [3] W. Heubel, R. Merenyi, *J. Organomet. Chem.* 2 (1964) 213.
- [4] L.D. Field, C.M. Lindall, T. Maschmeyer, A.F. Masters, *Aust. J. Chem.* 47 (1994) 1127.
- [5] H. Schumann, A. Lentz, R. Weimann, J. Pickardt, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1731.
- [6] L.D. Field, G.J. Gainsford, T.W. Hambley, P.A. Humphrey, C.M. Lindall, A.F. Masters, T.G. St. Pierre, J. Webb, *Aust. J. Chem.* 48 (1995) 851.
- [7] A. Schott, H. Schott, G. Wilke, J. Brandt, H. Hoberg, E.G. Hoffmann, *Liebigs Ann. Chem.* (1973) 508.
- [8] L.D. Field, A.F. Masters, M. Gibson, D.R. Latimer, T.W. Hambley, I.E. Buys, *Inorg. Chem.* 32 (1993) 211.
- [9] N.G. Connelly, I. Manners, *J. Chem. Soc. Dalton Trans.* (1989) 283.
- [10] D.W. Slocum, M. Matusz, A. Clearfield, R. Peascoe, S. Duraj, *J. Macromol. Sci. Chem.* 27A (1990) 1405.
- [11] H. Adams, N.A. Bailey, A.F. Browning, J.A. Ramsden, C. White, *J. Organomet. Chem.* 387 (1990) 305.
- [12] L.D. Field, T.W. Hambley, P.A. Humphrey, A.F. Masters, P. Turner, *Polyhedron* (1998) in press.
- [13] D.W. Slocum, S. Duraj, M. Matusz, J.L. Cmarik, K.M. Simpson, D.A. Owen Jr., in: J.E. Sheats, C.A. Carraher Jr., C.V. Pittman (Eds.), *Metal Containing Polymeric Systems*, Plenum, New York, 1985, p. 59.
- [14] M.J. Aroney, I.E. Buys, G.D. Dennis, L.D. Field, T.W. Hambley, P.A. Lay, A.F. Masters, *Polyhedron* 12 (1993) 2051.
- [15] M.I. Bruce, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon, Oxford, 1995, p. 603.
- [16] M.O. Albers, D.C. Liles, D.J. Robinson, A. Shaver, E. Singleton, M.B. Wiege, J.C.A. Boeyens, D.C. Levendis, *Organometallics* 5 (1986) 2321.
- [17] R.J. Hoobler, J.V. Adams, M.A. Hutton, T.W. Francisco, B.S. Haggerty, A.L. Rheingold, M.P. Castellani, *J. Organomet. Chem.* 412 (1991) 157.
- [18] K.N. Brown, L.D. Field, P.A. Lay, C.M. Lindall, A.F. Masters, *J. Chem. Soc. Chem. Commun.* (1990) 408.
- [19] R.M. Moriarty, U.S. Gill, Y.-Y. Ku, *J. Organomet. Chem.* 350 (1988) 157.
- [20] H. Le Bozec, D. Touchard, P.H. Dixneuf, *Adv. Organomet. Chem.* 29 (1989) 163.
- [21] I.E. Zanin, M.Y. Antipin, Y.T. Struchkov, *Sov. Phys. Crystallogr.* 36 (1991) 225.
- [22] P. Seiler, J.D. Dunitz, *Acta Cryst.* B36 (1980) 2946.
- [23] A. Haarland, J.-E. Nilsson, *J. Chem. Soc. Chem. Commun.* (1968) 88.
- [24] A. Haarland, J.-E. Nilsson, *Acta Chem. Scand.* 22 (1968) 2653.
- [25] D.C. Liles, A. Shaver, E. Singleton, M.B. Wiege, *J. Organomet. Chem.* 286 (1985) 33.
- [26] S.P. Gubin, S.A. Smirnova, L.I. Denovich, A.A. Lubovich, *J. Organomet. Chem.* 30 (1971) 243.

- [27] U. Koelle, A. Salzer, *J. Organomet. Chem.* 1983 (1983) C27.
- [28] M. Albers, D.J. Robinson, A. Shaver, E. Singleton, *Organometallics* 5 (1986) 2197.
- [29] P.J. Fagan, W.S. Mahoney, J.C. Calabrese, I.D. Williams, *Organometallics* 9 (1986) 1843.
- [30] L.D. Field, K.M. Ho, C.M. Lindall, A.F. Masters, A.G. Webb, *Aust. J. Chem.* 43 (1990) 281.
- [31] TeXsan, Single Crystal Structure Analysis Software, Molecular Structure Corporation, 1993.
- [32] D.T. Cromer, J.T. Waber, in: J.A. Ibers, W.C. Hamilton (Eds.), *International Tables for X-Ray Crystallography*, Kynock Press, Birmingham, UK, 1974, p. 71.
- [33] J.A. Ibers, W.C. Hamilton, *Acta Crystallogr.* 17 (1964) 781.
- [34] D.C. Creagh, W.J. McAuley, in: A.J.C. Wilson (Ed.), *International Tables for Crystallography*, Kluwer, Boston, 1992, p. 219.
- [35] D.C. Creagh, J.H. Hubbell, in: A.J.C. Wilson (Ed.), *International Tables for Crystallography*, Kluwer, Boston, 1992, p. 200.
- [36] G.M. Sheldrick, *SHELXS-86*, Oxford University Press, Oxford, UK, 1985.
- [37] A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Cryst.* 26 (1993) 343.
- [38] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, *The DIRDIF-94 Program System*. Technical Report Crystallography Laboratory, University of Nijmegen, The Netherlands, DIRDIF-94 Nijmegen, 1994.
- [39] C.K. Johnson, *ORTEP: a Thermal Ellipsoid Plotting Program*, Report ORNL-5138, Oak Ridge National Laboratories, 1976.
- [40] I. Noviadri, K.N. Brown, D.S. Fleming, P.T. Gulyas, P.A. Lay, A.F. Masters, L. Phillips, *J. Phys. Chem.* (1997) submitted.