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The preparation of mixed ligand ruthenocenes containing bulky cyclopentadienyl ligands. Crystal structures of pentaphenylruthenocene, [Ru(η^5-C_5Ph_5)(η^5-C_5H_5)], pentaparatolylruthenocene, [Ru{η^5-C_5(p-MeC_6H_4)$_5$}(η^5-C_5H_5)] and pentaphenylpentamethylruthenocene, [Ru(η^5-C_5Ph_5)(η^5-C_5Me_5)][1]

C.U. Beck, L.D. Field, T.W. Hambley, P.A. Humphrey *, A.F. Masters, P. Turner

School of Chemistry, The University of Sydney, Sydney, NSW 2006 Australia

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Abstract

The preparations of the mixed ligand ruthenocenes [Ru(η^5-C_5R_5)(η^5-C_5H_5)] [R_5 = Ph_5 (**1**), Ph_4H (**2**) and (p-MeC_6H_4)$_5$ (**3**)] and [Ru(η^5-C_5Ph_5)(η^5-C_5Me_5)] (**4**) are reported. The molecular structures of **1** (*Pbca*, $a = 14.234(3)$, $b = 20.276(3)$, $c = 20.625(4)$ Å), **3** ($P\bar{1}$, $a = 19.319(7)$, $b = 21.007(7)$, $c = 10.436(3)$ Å, $\alpha = 103.76$, $\beta = 95.07(3)$, $\gamma = 112.59(2)°$) and **4**·H_2O ($P\bar{1}$, $a = 12.145(2)$, $b = 12.696(4)$, $c = 14.281(2)$ Å, $\alpha = 80.41(2)$, $\beta = 66.43(1)$, $\gamma = 62.80(2)°$) 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 $Ru_3(CO)_{12}$, C_5Ph_5Br and Zn in xylenes yielded, after subsequent reaction with $NaBPh_4$, [Ru(η^5-C_5Ph_5){η^6-$C_6H_4(CH_3)_2$}]$^+$$BPh_4^-$ (**5**). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Cyclopentadienyl; Crystal structure

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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 [Ru(η^5-C_5Ph_5)(CO)LX]$^{n+}$ ($n = 0, 1$; L = CO, PR_3, C_2H_4, MeC≡CMe; X = Br, R, COMe, MeC = CMe_2) [9–11], and the dimeric [Ru(η^5-C_5Ph_5)(μ-CO)(CO)]$_2$ [9] have been adequately characterised, with structural characterisation being reported for the compounds [Ru(η^5-C_5Ph_5)$(CO)_2$Br] [10] and [Ru(η^5-C_5Ph_5)(CO)(PPh_3)Br] [11]. The starting material for much of this chemistry is [Ru(η^5-C_5Ph_5)$(CO)_2$Br], prepared from the reaction of $Ru_3(CO)_{12}$ with C_5Ph_5Br in toluene. A series of osmium compounds of the type

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* Corresponding author.

[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.

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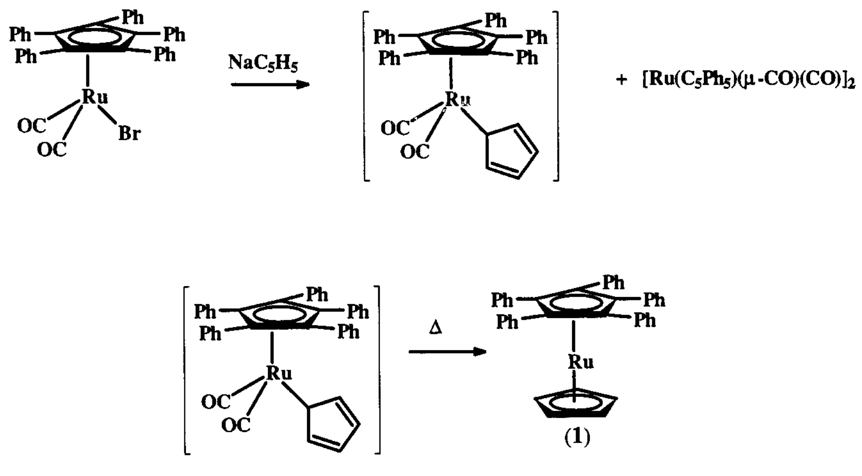


Scheme 1.

$[Os(\eta^5\text{-}C_5Ph_5)(CO)LX]$ has also been recently reported [12]. The possible existence of the mixed sandwich compounds, $[Ru(\eta^5\text{-}C_5Ph_5)(\eta^5\text{-}C_5R_5)]$ (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, $[Ru(\eta^5\text{-}C_5Ar_5)(\eta^5\text{-}C_5R_5)]$ (R = H, $Ar_5 = Ph_5$ (**1**), Ph_4H (**2**), $(p\text{-}MeC_6H_4)_5$ (**3**); R = Me, $Ar_5 = Ph_5$ (**4**)) and of $[Ru(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}Me_2C_6H_4)]BPh_4$ (**5**).

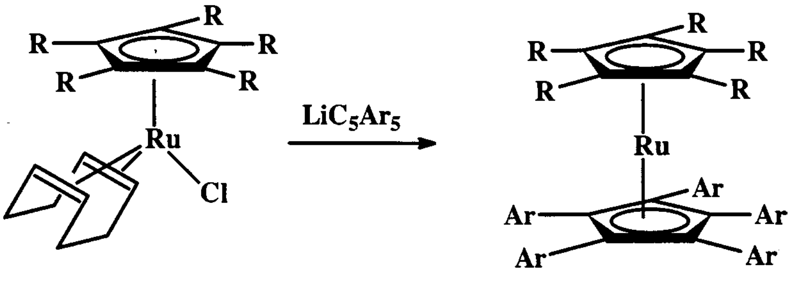
2. Results and discussion

2.1. Syntheses

Pale yellow, crystalline $[Ru(\eta^5\text{-}C_5Ph_5)(\eta^5\text{-}C_5H_5)]$ (**1**) was initially prepared in low yield by the thermolysis of the product of the reaction between $[Ru(\eta^5\text{-}C_5Ph_5)(CO)_2Br]$ and cyclopentadienylsodium. During the course of the reaction, a precipitate formed which has been identified by IR spectroscopy as the known compound $[Ru(\eta^5\text{-}C_5Ph_5)(\mu\text{-}CO)(CO)]_2$ (Scheme 1) [9]. Complex **1** is probably formed via the intermediary of $[Ru(\eta^5\text{-}C_5Ph_5)(\eta^1\text{-}C_5H_5)(CO)_2]$, as postulated for the synthesis of $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^5\text{-}C_5H_5)]$ from $[Fe(\eta^5\text{-}C_5Ph_5)(CO)_2Br]$ and cyclopentadienyl sodium [14] and established for the synthesis of $[Fe\{(\eta^5\text{-}C_5(p\text{-}MeC_6H_4)_5)\}(\eta^5\text{-}C_5H_5)]$ from $[Fe\{(C_5(p\text{-}MeC_6H_4)_5)\}(CO)_2Br]$ and cyclopentadienylsodium in which $[Fe\{(\eta^5\text{-}C_5(p\text{-}MeC_6H_4)_5)(\eta^1\text{-}C_5H_5)\}(CO)_2]$ 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 ^{13}C-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 $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]$) involved the reaction of pentaphenylcyclopentadienyllithium with a THF solution of $[Ru(\eta^5\text{-}C_5H_5)(COD)Cl]$ ($COD = \eta^4\text{-}1,5\text{-}C_8H_{12}$). In both reactions the yield of **1** was low. An analogous reaction of $[Ru(\eta^5\text{-}C_5H_5)(COD)Cl]$ with the less sterically demanding ligand $(C_5Ph_4H)^-$ produced a pale yellow solid, $[Ru(\eta^5\text{-}C_5Ph_4H)(\eta^5\text{-}C_5H_5)]$ (**2**), in a much higher yield (58%). Compound **2** was characterised as above. The symmetrical complex, $[Ru(\eta^5\text{-}C_5Ph_4H)_2]$, has been prepared previously by the reaction between KC_5Ph_4H and $[Ru(\eta^4\text{-}COD)Cl_2]_n$ or $[Ru(p\text{-}cymene)Cl_2]_n$ in refluxing diglyme [17].

The reaction of penta-*p*-tolylcyclopentadienyllithium with a THF solution of $[Ru(\eta^5\text{-}C_5H_5)(COD)Cl]$ yielded small amounts of very pale yellow to colourless crystals of $[Ru\{(\eta^5\text{-}C_5(p\text{-}MeC_6H_4)_5)\}(\eta^5\text{-}C_5H_5)]$ (**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 ^{13}C-NMR spectroscopies, cyclic voltammetry and single crystal X-ray diffraction.

Similarly, very pale yellow to colourless crystals of $[Ru(\eta^5\text{-}C_5Ph_5)(\eta^5\text{-}C_5Me_5)]$ (**4**) were isolated in very low yield from the reaction of $Li(C_5Ph_5)$ with $[Ru(\eta^5\text{-}C_5Me_5)(COD)Cl]$ in THF followed by column chromatography and a number of recrystallisations from dichloromethane/*n*-hexane to remove HC_5Ph_5 (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.



R = H, $Ar_5 = Ph_5$ **(1)**

R = H, $Ar_5 = Ph_4H$ **(2)**

R = H, $Ar_5 = (p\text{-}MeC_6H_4)_5$ **(3)**

R = Me, $Ar_5 = Ph_5$ **(4)**

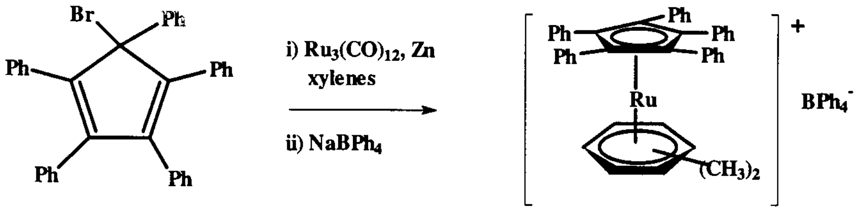
Scheme 2.

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, C_5Ar_5H, 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 $[Ru(\eta^5\text{-}C_5Ph_4H)(\eta^5\text{-}C_5H_5)]$ 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 $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^5\text{-}C_5H_5)]$ was prepared in 58% yield [14]. For example, in the reaction of $[Ru(\eta^5\text{-}C_5Ph_5)(CO)_2Br)]$ with NaC_5Ph_5, a significant product (obtained in variable yields) is the stable, insoluble dimer, $[Ru(\eta^5\text{-}C_5Ph_5)(\mu\text{-}CO)(CO)]_2$. 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 $[Ru(\eta^5\text{-}C_5H_5)(COD)Cl]$, other product(s) decompose during the chromatographic separation.

It has been shown previously that the reaction of $Fe(CO)_5$ (one equivalent), zinc dust (two equivalents) and bromopentaphenylcyclopentadiene (two equivalents) in refluxing benzene followed by column chromatography yields $[Fe(\eta^5\text{-}C_5Ph_5)\{(\eta^6\text{-}C_6H_5)C_5Ph_4\}]$ with $[Fe(\eta^5\text{-}C_5Ph_5)(CO)_2Br]$ and $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+$ as minor by-products [18]. Dark blue $[Fe(\eta^5\text{-}C_5Ph_5)\{(\eta^6\text{-}C_6H_5)C_5Ph_4\}]$ is a linkage isomer of pink/purple decaphenylferrocene, $[Fe(\eta^5\text{-}C_5Ph_5)_2]$, to which it can be converted by heating in refluxing xylenes. In an attempt to prepare $[Ru(\eta^5\text{-}C_5Ph_5)_2]$ in a similar manner, a mixture of $Ru_3(CO)_{12}$, 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 $[Ru(\eta^5\text{-}C_5Ph_5)(CO)_2Br]$. 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 $[Ru(\eta^5\text{-}C_5Ph_5)\{\eta^6\text{-}C_6H_4(CH_3)_2\}]X$ (X = unidentified anion) by mass, IR and ^1H-NMR spectra. A white tetraphenylborate salt (**5**) was made by reacting $[Ru(\eta^5\text{-}C_5Ph_5)\{\eta^6\text{-}C_6H_4(CH_3)_2\}]X$ with sodium tetraphenylborate (Scheme 3). This salt was isolated in ca. 50% overall yield (from $Ru_3(CO)_{12}$) and was characterised by elemental analysis and mass, IR and ^1H-NMR spectroscopies. The cation is analogous to the known $[Ru(\eta^5\text{-}C_5R_5)\{\eta^6\text{-}C_6R'_6\}]^+$ 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



(6)

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 C_5 rings of all compounds are not significantly distorted from co-planarity. The maximum deviation of the C_5 carbon atoms from the C_5R_5 rings are: **1** 0.010 Å, $R=C_6H_5$; 0.005 Å, R = H; **3** 0.019 Å (0.016 Å), $R=C_6H_5$; 0.004 Å (0.005 Å), R = H for the two molecules in the unit cell; and **4** 0.006 Å, $R=C_6H_5$; 0.003 Å, R = Me.

The two C_5 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 (C_5Ph_5), 1.402 Å (C_5H_5) for **1**; 1.45(1.43) Å (η^5-C_5(*p*-$MeC_6H_4)_5$), 1.41(1.41) Å (C_5H_5) for **3**; and 1.439 Å (C_5Ph_5), 1.419 Å (C_5Me_5) for **4**]. Those of the $C_5Ph_5{}^-$ ligands are similar to those in [Ru(η^5-C_5Ph_5)$(CO)_2$Br] (1.441 Å average) [10] and [Ru(η^5-C_5Ph_5)(CO)(PPh_3)Br] (1.42 Å average) [11], which are the only other structurally characterised Ru(C_5Ph_5) complexes. The C–C bond distances of the (η^5-C_5(*p*-$MeC_6H_4)_5$ ligand are similar to those in [Fe(η^5-C_5(*p*-$MeC_6H_4)_5$)(η^5-C_5H_5)] [8]. The bond angles in the C_5 ring are normal for the C_5 rings of cyclopentadienyl and substituted cyclopentadienyl derivatives.

The *ipso*-carbon atoms of each of the arene rings of the C_5Ar_5 ligands are displaced slightly from the C_5 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 C_5 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 C_5 ring of the C_5Ar_5 ligand in the usual paddlewheel arrangement, with an average deviation of the phenyl rings from co-planarity with the C_5 rings of 54.0° (**1**), 50.4(54.3)° (**3**) and 50.2° (**4**). The methyl groups of the C_5Me_5 ligand are displaced from the C_5 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 C_5 plane.

The Ru–(C_5Ar_5 ring centroid) distances are 1.796 Å (**1**), 1.779(1.795) Å (**3**) and 1.818 Å (**4**); the Ru–(C_5H_5 ring centroid) distances are 1.824 Å (**1**), 1.810(1.817) Å (**3**) and the Ru–(C_5Me_5 ring centroid) distance is 1.836 Å (**4**). Therefore, the separations between the C_5 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(η^5-C_5Me_5)(η^5-C_5H_5)] [1.792 Å (Ru–C_5Me_5) and 1.829 Å (Ru–C_5H_5) and separation between planes of 3.621 Å] [21], for [Ru(η^5-$C_5H_5)_2$] [ca. 3.63 Å, (X-ray) [22] ca. 3.68(1) Å (electron diffraction)] [23,24], [Ru(η^5-$C_5Me_5)_2$] [3.60(1) Å] [16,25] and for [Ru(η^5-$C_5Ph_4H)_2$] [3.664(2) Å] [17].

The structures of **1**, **3** and **4** provide comparisons of the effects of substituting the C_5Ph_5 ligand by the C_5(*p*-$MeC_6H_4)_5$ ligand and of the C_5H_5 ligand by the C_5Me_5 ligand in these sterically demanding systems. The only other structural comparison between the C_5Ph_5 and the C_5(*p*-$MeC_6H_4)_5$ 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{(η^5-C_5(*p*-$MeC_6H_4)_5$)}(η^5-C_5H_5)], **3**, is substantially less than that of [Ru(η^5-C_5Ph_5)(η^5-C_5H_5)], **1**.

As might be expected on steric grounds, the substitution of the C_5H_5 ligand by the bulkier C_5Me_5 ligand leads to increases in both the Ru–C_5Ph_5 and Ru–C_5R_5 (R = H, Me) distances.

The C_5Ph_5 and C_5(*p*-$MeC_6H_4)_5$ ligands are expected to make near equivalent steric demands at the metal centre. However, the substitution of the C_5Ph_5 ligand by the C_5(*p*-$MeC_6H_4)_5$ ligand results in a decrease in both the Ru–C_5Ar_5 and Ru–C_5H_5 distances. These effects, although small, are significant. A similar effect was observed in the structures of the corresponding iron compounds, [Fe(η^5-C_5Ar_5)(η^5-C_5H_5)] (Ar = Ph, *p*-MeC_6H_4) [8,14]. The structural effect is small but is observed in both the ruthenium and iron chemistries.

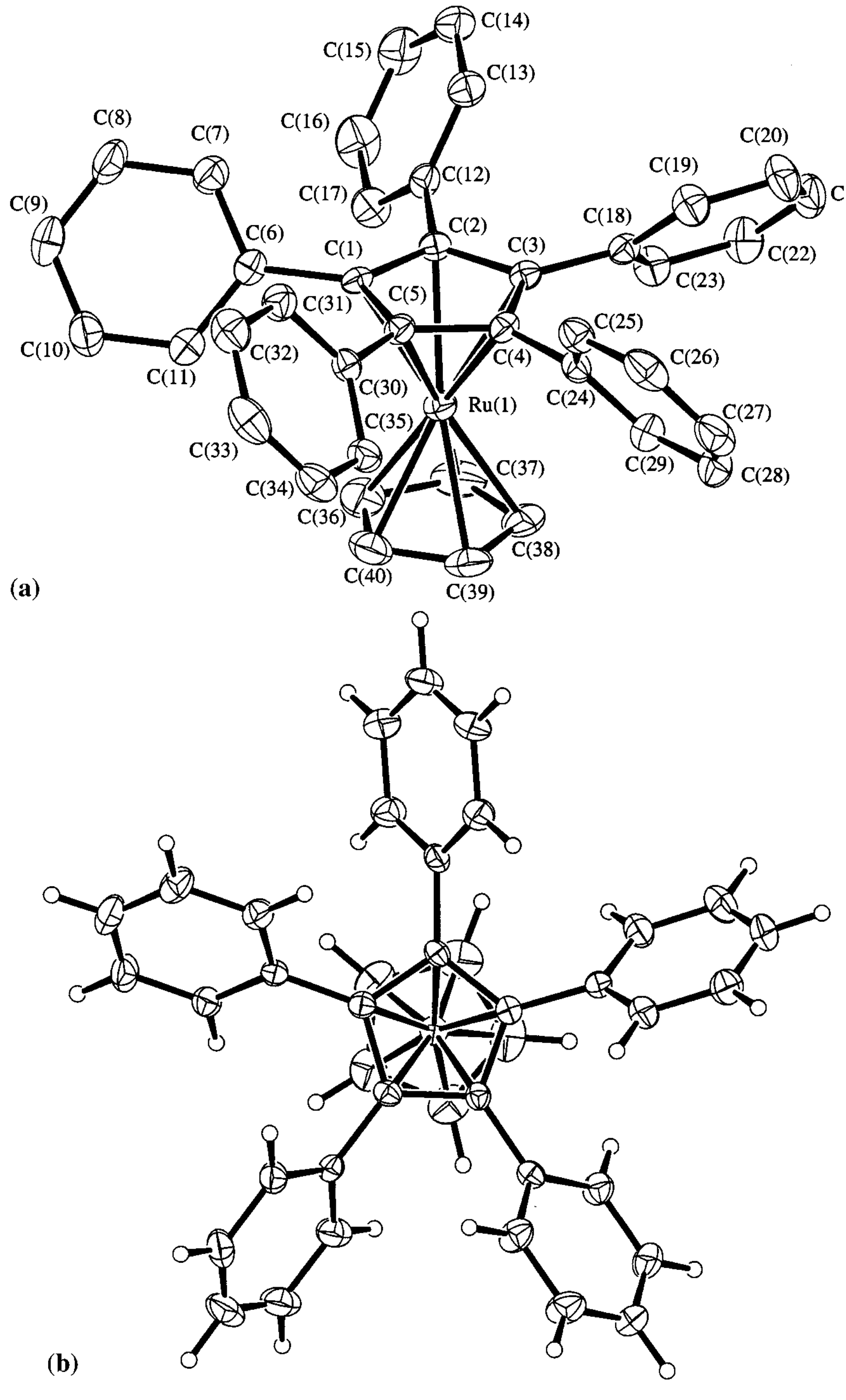


Fig. 1. ORTEP [39] (25% probability) illustration of the molecular structure of [Ru(η^5-C_5Ph_5)(η^5-C_5H_5)], **1**. View (a) showing the numbering of the non-hydrogen atoms, view (b) along the normal to the C_5Ph_5 plane, including the hydrogen atoms.

The difference between the C_5Ph_5 and $C_5(p\text{-}MeC_6H_4)_5$ ligands is thus suggested to be electronic in origin, with the $C_5(p\text{-}MeC_6H_4)_5$ ligand acting as a slightly better electron donor.

2.3. Cyclic voltammetry

Cyclic voltammetric studies should establish if the $C_5(p\text{-}MeC_6H_4)_5$ 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 [Fe(η^5-C_5Ph_5)(η^5-C_5H_5)] is not simple—the C_5Ph_5 ligand exists in both the η^5-C_5Ph_5 and $C_5\{(\eta^6\text{-}C_6H_5)Ph_4\}$ configurations [14]. Fortunately, an opportunity for such a comparison exists in the electrochemistry of the present compounds

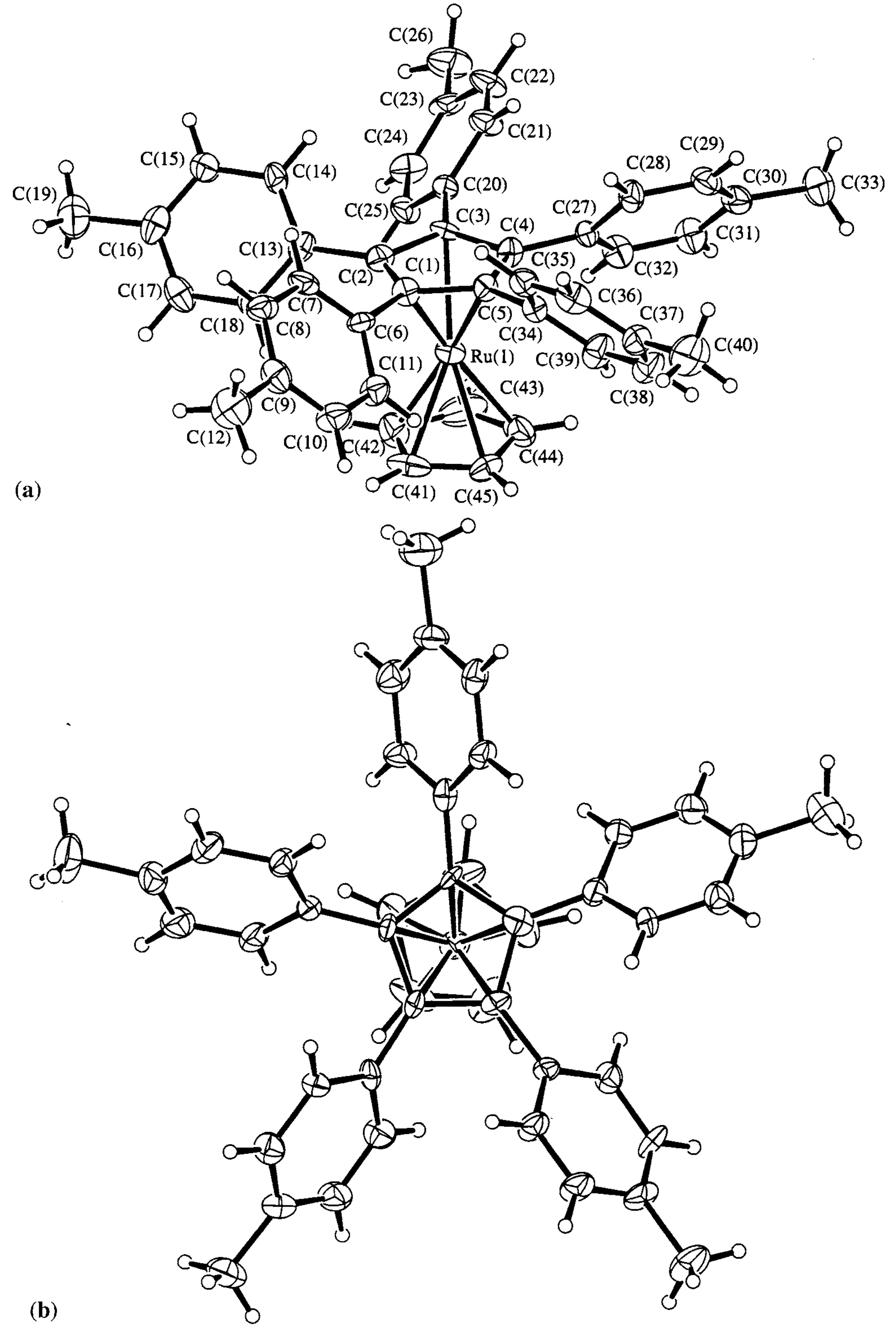


Fig. 2. ORTEP [39] (25% probability) illustration of the molecular structure of $[Ru\{\eta^5\text{-}C_5(p\text{-}MeC_6H_4)_5\}(\eta^5\text{-}C_5H_5)]$, **3**. View (a) showing the numbering of the non-hydrogen atoms, view (b) along the normal to the C_5Ar_5 plane, including the hydrogen atoms.

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 $[Fe(C_5Me_5)_2]^{+/0}$ in dichloromethane) to the monocation, $[Ru(\eta^5\text{-}C_5Me_5)_2]^+$ [27]. A second, irreversible, oxidation is observed at 1.27 V (versus

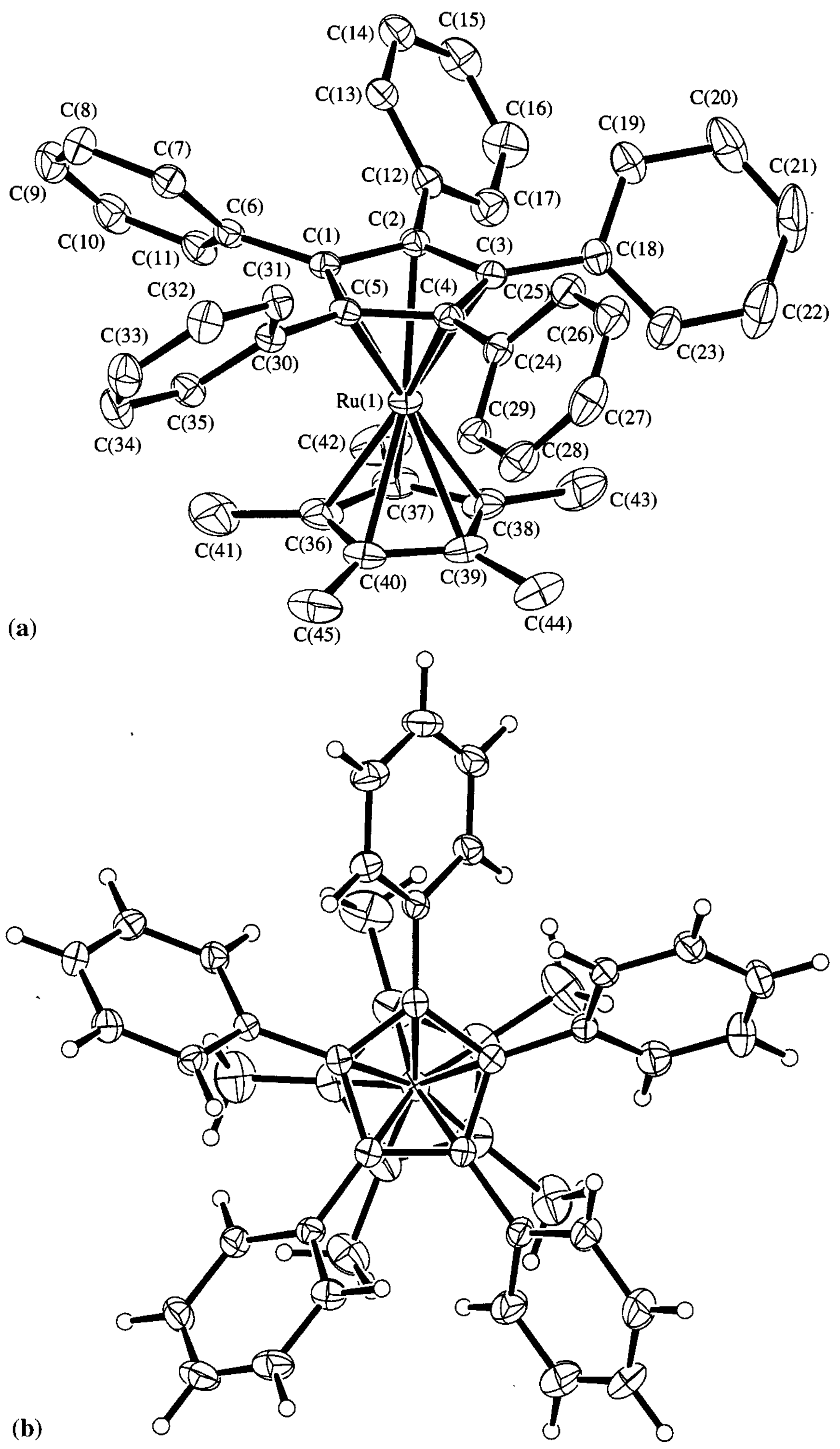


Fig. 3. ORTEP [39] (25% probability) illustration of the molecular structure of [Ru(η^5-C_5Ph_5)(η^5-C_5Me_5)], **4**. View (a) showing the numbering of the non-hydrogen atoms, view (b) along the normal to the C_5Ph_5 plane, including the hydrogen atoms.

$[Fe(C_5Me_5)_2]^{+/0}$ in dichloromethane). The cation can be generated chemically by oxidation with $AgBF_4$ 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 studies at platinum and glassy carbon electrodes for [Ru(η^5-C_5Ph_5)(η^5-C_5H_5)] **1**, [Ru(η^5-C_5Ph_4H)(η^5-C_5H_5)] **2**, and [Ru(η^5-C_5(p-MeC_6H_4)$_5$)(η^5-C_5H_5)] **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, $[Ru(\eta^5\text{-}C_5R_5)(\eta^5\text{-}C_5H_5)]^+$ ($R_5 = Ph_5$, Ph_4H, $p\text{-}MeC_6H_4)_5$). 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 $[Ru(\eta^5\text{-}C_5Ph_5)(\eta^5\text{-}C_5H_5)]$ (**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 $[Ru\{\eta^5\text{-}C_5(p\text{-}MeC_6H_4)_5\}(\eta^5\text{-}C_5H_5)]$ (**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, [Ru(η^5-C_5Me_5)$_2$] has been shown to be harder to oxidise (by 0.57 V) than [Fe(η^5-C_5Me_5)$_2$] [27]. Similarly, [Ru(η^5-C_5Ph_5)(η^5-C_5H_5)] is harder to oxidise (by 0.486 V) than is [Fe(η^5-C_5Ph_5)(η^5-C_5H_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 [Ru{(η^5-C_5(*p*-MeC_6H_4)$_5$)}(η^5-C_5H_5)] is easier to oxidise than is [Ru(η^5-C_5Ph_5)(η^5-C_5H_5)] (i.e. the C_5(*p*-MeC_6H_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.

Table 3
Selected bond lengths (Å) and bond angles (°) for [Ru(η^5-C_5Ph_5)(η^5-C_5Me_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)		

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. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC200F (^{1}H-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, ^{1}H 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 Ag/AgCl/NaCl(sat.) electrode was used as the

Table 4
Crystallographic data and refinement details for **1**, **3** and **4**·H_2O

Compound	**1**	**3**	**4**·H_2O
Molecular formula	$C_{40}H_{30}Ru$	$C_{45}H_{40}Ru$	$C_{45}H_{40}ORu$
M	611.76	681.88	697.88
Crystal colour, shape	Colourless, blade	Colourless, blade	Colourless, blade
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	14.234(3)	19.319(7)	12.145(2)
b (Å)	20.276(3)	21.007(7)	12.696(4)
c (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)
U (Å^3)	5952(1)	3721(2)	1794.8(8)
Z	8	4	2
D_{calc} (g cm^{-3})	1.365	1.217	1.291
μ(Mo–K$_\alpha$) (cm^{-1}) (λ (Å))	5.54 (0.71069)	—	4.70 (0.71069)
μ(Cu–K$_\alpha$) (cm^{-1}) (λ (Å))	—	36.13 (1.54178)	—
F(000)	2512.00	1416.00	724.00
Crystal dimensions (mm)	$0.50\times0.22\times0.05$	$0.40\times0.32\times0.05$	$0.28\times0.20\times0.05$
$2\theta_{max}$ (°)	49.9	130.2	54.9
hkl 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, R_{merge}	5781	9782, 0.040	8230, 0.025
No. of observed data used	2898 ($I>2.50(\sigma)I$)	3633 ($I>3.00(\sigma)I$)	5404 ($I>3.00(\sigma)I$)
R; R_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 H_2O/O_2 removal assembly which consisted of an indicating moisture trap (5 Å molecular sieves with Dryerite, Activon, RDMT400D), a high capacity coiled O_2 trap (Alltech, 4003) and an indicating O_2 trap (Alltech, 4004). All potentials are quoted relative to the ferrocinium/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-C_5Ph_5)(CO)$_2$Br [9], Ru(η^5-C_5H_5)(COD)Cl [28], Ru(η^5-C_5Me_5)(COD)Cl [29], HC_5Ph_5 [30] and HC_5(*p*-MeC_6H_4)$_5$ [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 $Ru_3(CO)_{12}$ (Strem) were used as-received. Flash silica (240–400 mesh) was obtained from Merck.

*4.4. Preparation of [Ru(η^5-C_5Ph_5)(η^5-C_5H_5)] (**1**)*

4.4.1. From Ru(η^5-C_5Ph_5)(CO)$_2$Br and NaCp

NaC_5H_5 (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-C_5Ph_5)(CO)$_2$Br] (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-C_5Ph_5)(μ-CO)(CO)]$_2$ (yield 0.132 g, 22%) by IR (KBr ν_{CO} 1962, 1779 cm^{-1}) and mass (*m*/*e* 1092 ([$Ru_2(C_5Ph_5)_2$–2H]$^+$, 17%), 991 ([Ru$(C_5Ph_5)_2$–H]$^+$, 100%), 546 ([Ru(C_5Ph_5)–H]$^+$, 19%) spectroscopies. The solvent was removed in vacuo. The resultant solid was heated at 200°C for 5 h in vacuo. After CH_2Cl_2 (40 ml) was added and filtration by gravity, column chromatography was performed. Elu-

Table 5
Electrochemical data[a] for [Ru(η^5-C_5Ph_5)(η^5-C_5H_5)] (**1**), [Ru(η^5-C_5Ph_4H)(η^5-C_5H_5)] (**2**), [Ru{(η^5-C_5(p-MeC_6H_4)$_5$)}(η^5-C_5H_5)] (**3**), [Ru(η^5-C_5H_5)$_2$] and [Ru(η^5-C_5Me_5)$_2$]

Compound	Ep_{1a} (V)	Ep_{2a} (V)	Ep_{1c} (V)	Ep_{3c} (V)	E_f (V)
[Ru(η^5-C_5Ph_5)(η^5-C_5H_5)] (**1**)	0.770	0.981	0.682	0.340	0.726
[Ru(η^5-C_5Ph_4H)(η^5-C_5H_5)] (**2**)	0.830	—	0.510	0.150	0.670
[Ru{(η^5-C_5(p-MeC_6H_4)$_5$)}(η^5-C_5H_5)] (**3**)	0.680	0.796	0.683	0.280	0.632
[Ru(η^5-C_5H_5)$_2$]	0.490	—	—	0.250	—
[Ru(η^5-C_5Me_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-C_5H_5)$_2$]$^{+/0}$.

[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-C_5Me_5)$_2$]$^{+/0}$; converted to potentials vs. [Fe(η^5-C_5H_5)$_2$]$^{+/0}$ using the data of [40].

tion with 30% CH_2Cl_2/70% n-hexane afforded, after evaporation to dryness and crystallisation of the solid from CH_2Cl_2/n-hexane, very pale yellow crystals of [Ru(η^5-C_5Ph_5)(η^5-C_5H_5)] (**1**) (127 mg, 21%) m.p. > 250°C (decomp.). (Found C, 78.8; H, 4.9. $C_{40}H_{30}Ru$ requires C, 78.5; H, 4.9%). ^{1}H-NMR (CD_2Cl_2, 200.13 MHz): δ 7.07–6.95 (m, 25H, Ar–*H*), 4.73 (s, SH, C_5H_5) ppm. ^{13}C-NMR (CD_2Cl_2, 50.33 MHz): δ 136.0 (qAr–*C*), 133.0, 127.3, 126.5 (Ar–*C*H), 94.6 (*C*$_5$ of C_5Ar_5), 76.6 (C_5 of *C*$_5H_5$) ppm. MS-EI (m/e) 612 ([M]$^+$, 100%). IR (KBr) ν_{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% CH_2Cl_2/50% n-hexane yielded, after evaporation to dryness and crystallisation of the solid from CH_2Cl_2/n-hexane, yellow–orange crystals of [Ru(η^5-C_5Ph_5)(CO)$_2$Br] (72 mg, 10%) identified by comparison of its ν_{CO} (CH_2Cl_2) IR spectrum with that of an authentic sample [9].

4.4.2. From [Ru(η^5-C_5H_5)(COD)Cl] and LiC$_5$Ph$_5$

A solution of Li(C_5Ph_5) [prepared from HC_5Ph_5 (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-C_5H_5)(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% CH_2Cl_2/70% n-hexane afforded a pale yellow solution which, after evaporation to dryness and fractional crystallisation of the solid from CH_2Cl_2/n-hexane, initially gave HC_5Ph_5 (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 CH_2Cl_2/n-hexane yielded [Ru(η^5-C_5Ph_5)(η^5-C_5H_5)] (**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-C_5Ph_4H)(η^5-C_5H_5)] (**2**)*

A solution of Li(C_5Ph_4H) [prepared from HC_5Ph_4H (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 addded via a canula to a solution of [Ru(η^5-C_5H_5)(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% CH_2Cl_2/70% n-hexane initially afforded a pale yellow solution which, after evaporation to dryness and crystallisation of the solid from CH_2Cl_2/n-hexane, yielded HC_5Ph_4H (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 CH_2Cl_2/n-hexane, pale yellow [Ru(η^5-C_5Ph_4H)(η^5-C_5H_5)] (**2**) (261 mg, 58%) m.p. 181–184°C. (Found C, 76.5; H, 4.6. $C_{34}H_{26}Ru$ requires C, 76.24; H, 4.89%). ^{1}H-NMR (CD_2Cl_2, 200.13 MHz): δ 7.24–7.05 (m, 20H, Ar–*H*), 5.36 (s, 1H, C_5Ph_4H), 4.61 (s, 5H, C_5*H*$_5$) ppm. ^{13}C-NMR (CD_2Cl_2, 50.33 MHz): δ 137.5, 136.0 (qAr–*C*), 133.2, 130.4, 127.8, 127.5, 126.7, 126.7 (Ar–*C*H), 95.6, 92.3 (*C*$_5$ of C_5Ar_5), 75.4, 73.0 (C_5 of *C*$_5H_5$) ppm. MS-EI (m/e) 536 ([M]$^+$, 100%). IR (KBr) ν_{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-C_5(p-MeC_6H_4)$_5$}(η^5-C_5H_5)] (3)

A solution of Li[C_5(p-MeC_6H_4)$_5$] [prepared from HC_5(p-MeC_6H_4)$_5$ (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-C_5H_5)(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 $HC_5(p\text{-}MeC_6H_4)_5$ (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 $[Ru\{\eta^5\text{-}C_5(p\text{-}MeC_6H_4)_5\}(\eta^5\text{-}C_5H_5)]$ (**3**) (40 mg, 5%) m.p. > 280°C. (Found C, 79.1; H, 6.3. $C_{45}H_{40}Ru$ requires C, 79.27; H, 5.91%). ^1H-NMR (CD_2Cl_2, 200.13 MHz): δ 6.91–6.81 (AB quartet, $J(HH) = 8.1$ Hz, 20H, Ar–*H*), 4.68 (s, 5H, C_5H_5), 2.22 (s, 15H, CH_3) ppm. ^{13}C-NMR (CD_2Cl_2, 50.33 MHz): δ 136.0, 133.2 (*q*Ar–*C*), 132.9, 128.0 (Ar–*C*H), 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 ([*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 $[Ru(\eta^5\text{-}C_5Ph_5)(\eta^5\text{-}C_5Me_5)]$ (**4**)

A solution of $Li(C_5Ph_5)$ [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 $[Ru(\eta^5\text{-}C_5Me_5)(COD)Cl]$ (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 $[Ru(\eta^5\text{-}C_5Ph_5)(\eta^5\text{-}C_5Me_5)]$ (**4**) (22 mg, 2%). ^1H-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 ([*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 $Ru_3(CO)_{12}$ with C_5Ph_5Br in the presence of Zn

A mixture of $Ru_3(CO)_{12}$ (250 mg, 0.391 mmol), C_5Ph_5Br (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 $[Ru(\eta^5\text{-}C_5Ph_5)\{\eta^6\text{-}C_6H_4(CH_3)_2\}]^+X^-$ where X is an unidentified anion (520 mg) m.p. > 250°C (decomp.). (Found C, 57.3; H, 3.9%). ^1H-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, $C_6H_4(CH_3)_2$ mixture of isomers) ppm. MS-EI (*m*/*e*) 652 ($[Ru(\eta^5\text{-}C_5Ph_5)\{\eta^6\text{-}C_6H_4(CH_3)_2\}\text{–}H]^+$, 15%), 545 ($[Ru(\eta^5\text{-}C_5Ph_5)\text{–}H]^+$, 1%), 106 ($[C_6H_4(CH_3)_2]^+$, 44%), 91 ($[C_6H_4(CH_3)]^+$, 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 $[Ru(\eta^5\text{-}C_5Ph_5)\{\eta^6\text{-}C_6H_4(CH_3)_2\}]^+X^-$ (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 $[Ru(\eta^5\text{-}C_5Ph_5)\{\eta^6\text{-}C_6H_4(CH_3)_2\}]^+BPh_4{}^-$ (**5**) (110 mg, 50%) m.p. > 250°C (decomp.). (Found C, 81.7; H, 5.6. $C_{67}H_{55}BRu$ requires C, 82.79; H, 5.70%). ^1H-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, $C_6H_4(CH_3)_2$ mixture of isomers) ppm. MS-EI (*m*/*e*) 653 ($[Ru(\eta^5\text{-}C_5Ph_5)\{\eta^6\text{-}C_6H_4(CH_3)_2\}]^+$, 3%), 242 ($[BPh_3)]^+$, 18%), 164 ($[BPh_2\text{–}H]^+$, 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 × 0.22 × 0.05 mm (**1**), 0.28 × 0.20 × 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 $19.00 < 2\theta < 24.22°$ (**1**) or $16.66 < 2\theta < 24.02°$ (**4**). Diffraction data were collected at a temperature of $21 \pm 1°C$ using ω:4/3θ scans to a maximum 2θ value of 49.9° (**1**) or 54.9° (ω:1/3θ 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 × 0.32 × 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 $18.80 < 2\theta < 27.87°$. The unit cell volume of **3** suggested two complexes in the asymmetric unit. Diffraction data were collected at a temperature of $21 \pm 1°C$ using ω-2θ 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 Fcalc [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 Å 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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