

Synthesis and structure of a chelating arene–ruthenium complex $[\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3-\eta^6\text{-C}_6\text{H}_5)]$

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Abstract

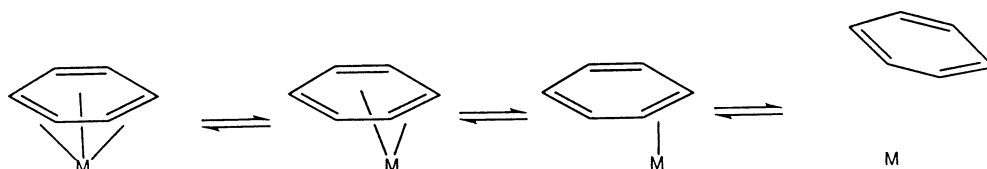
The synthesis of an arene–phosphine ligand, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Ph}$, has provided a route into a new chelating arene–phosphine–ruthenium complex, $[\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3-\eta^6\text{-C}_6\text{H}_5)]$ which has been structurally characterized. This complex can be made by thermolysis of $[(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ or electrochemically utilizing the formation of the labile seventeen-electron ruthenium(III) species $[(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]^+$ which can be converted in good yield into $[\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3-\eta^6\text{-C}_6\text{H}_5)]$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Arene–phosphine; Electrochemistry

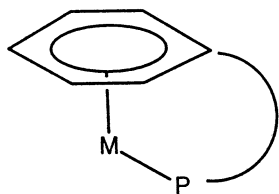
1. Introduction

The chemistry of arene–ruthenium complexes is rich and varied as a result of the strong arene–metal bond and the availability of reactive arene-containing compounds [1]. The complexes are finding increasing application in organic synthesis and catalysis, as catalysts, or catalyst precursors [2]. One of the critical reactions in such applications may involve progressive removal of the arene ligand from η^6 to η^4 , η^2 , and possibly involving complete loss of the arene ligand.

This reaction has been well documented for related complexes [3] but the complete loss of the ligand may be an unwanted side reaction. This report describes the results of an investigation into the possibility of increasing the robustness of these complexes towards arene substitution. An obvious way of stabilizing the arene–metal interaction is to ‘tie’ the arene group onto another ligand and hence capitalize on the chelate effect.



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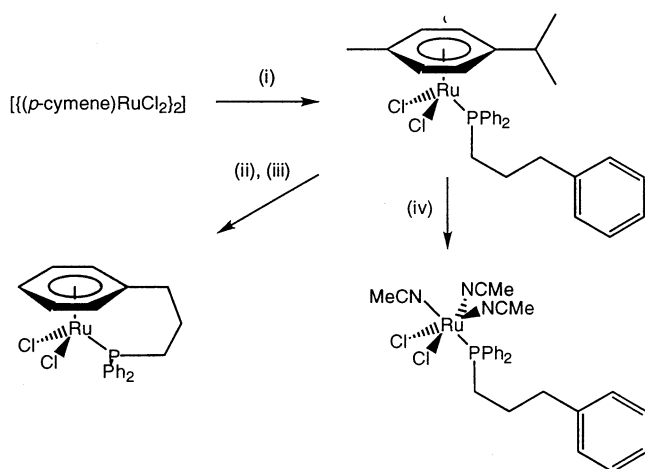
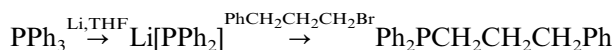


Examples of chelated cyclic polyene complexes have been previously reported for ruthenium, such as the cyclopentadiene derivative $[\text{RuCl}(\text{PPh}_3)(\text{PPh}_2(\text{CH}_2)_2-\eta^5\text{C}_5\text{H}_4)]$ [4] and further analogues include compounds containing a η^6 -arene ring linked to a sulphur atom [5]. For the purpose of this study we have examined adaptation of phosphine ligands, since they provide readily available starting materials and form robust ruthenium–arene complexes under mild conditions [6].

2. Results and discussion

2.1. Synthesis

The preparation of $\text{PPh}_2(\text{CH}_2)_3\text{Ph}$ (**1**) involved the cleavage of a phenyl ring from triphenylphosphine with lithium in THF giving a convenient source of the reactive lithium diphenylphosphide salt [7,8]. Selective protonation of the phenyllithium, produced simultaneously, was carried out by the addition of an equimolar amount of *t*-butylchloride to the reaction mixture [8]. (**1**) was formed, in 80% yield, by the reaction of this solution with an equivalent of 1-bromo-3-phenylpropane.



Scheme 1. Reaction conditions: (i) $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Ph}$, CH_2Cl_2 ; (ii) PhCl , 130°C , 18 h; (iii) Pt gauze working electrode, CH_2Cl_2 - $[\text{NBu}_4][\text{PF}_6]$ (0.1 mol dm^{-3}), $+1.5 \text{ V} \Rightarrow 0.0 \text{ V}$ (vs SCE), 298 K, N_2 (iv) Pt gauze working electrode, MeCN - $[\text{NH}_4][\text{PF}_6]$ (0.1 mol dm^{-3}), $+1.5 \text{ V} \Rightarrow 0.0 \text{ V}$ (vs SCE), 298 K, N_2 .

Table 1

Atomic co-ordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for (**3**)

	x	y	z	U(eq)
Ru(1)	6060(1)	6467(1)	6315(1)	29(1)
P(1)	5587(1)	8289(1)	7425(1)	32(1)
Cl(1)	4075(2)	5026(2)	7250(1)	55(1)
Cl(2)	3651(1)	8449(2)	5737(1)	42(1)
C(1)	8794(6)	5591(6)	6425(3)	42(1)
C(2)	8535(5)	7016(6)	5757(3)	36(1)
C(3)	7667(6)	6935(7)	5033(3)	42(1)
C(4)	7164(6)	5503(8)	4944(3)	50(1)
C(5)	7400(6)	4174(7)	5597(4)	47(1)
C(6)	8174(6)	4238(6)	6371(4)	46(1)
C(7)	9139(6)	8493(7)	5820(4)	47(1)
C(8)	8645(6)	9231(6)	6738(4)	47(1)
C(9)	6697(7)	9916(6)	7003(4)	44(1)
C(10)	6367(6)	7397(6)	8518(3)	38(1)
C(11)	6820(10)	5732(8)	8749(4)	69(2)
C(12)	7318(13)	5074(10)	9595(5)	91(3)
C(13)	7382(9)	6128(9)	10 211(4)	72(2)
C(14)	6945(8)	7781(9)	9990(4)	62(2)
C(15)	6418(7)	8437(7)	9137(4)	52(1)
C(20)	3392(6)	9417(6)	7840(3)	38(1)
C(21)	2340(7)	8553(7)	8403(4)	50(1)
C(22)	692(8)	9349(9)	8762(5)	65(2)
C(23)	71(8)	11 037(10)	8567(5)	71(2)
C(24)	1098(8)	11 887(8)	8007(5)	68(2)
C(25)	2762(7)	11 123(7)	7636(4)	50(1)

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The new ligand (**1**) was introduced to the co-ordination sphere of the ruthenium by careful addition of two equivalents of the phosphine to the dimer $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$ producing the complex $[(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ (**2**).

Thermal arene substitution was explored and reasonable yields of the complex $[\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\eta^6\text{-C}_6\text{H}_5)]$ (**3**) could be made by extended heating at 130°C in refluxing chlorobenzene. After 18 h the resulting brown product could be purified by chromatography to give a 50% yield of (**3**) as orange-red crystals Scheme 1.

2.2. Crystal structure of $[\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\eta^6\text{-C}_6\text{H}_5)]$ (**3**) (Table 1 and Table 2)

Crystals suitable for an X-ray crystal analysis were prepared by evaporation from CH_2Cl_2 -EtOH. The structure of the compound, shown in Fig. 1, is a pseudo-octahedral arene–ruthenium(II) complex.

The most noticeable feature of the structure is that the co-ordinated ring is pushed across the face of the metal so that free end of the ring is significantly lifted away from the ruthenium. The two carbon atoms involved, C(5) and C(6) are 2.241(4) and 2.246(5) $\text{\AA}$ from the ruthenium respectively compared with the other metal carbon distances which lie in the conventional 2.17–2.20 $\text{\AA}$ range. This distortion probably originates

from the steric constraints imposed by the link between the ring and the phosphorus atom and the *trans* influence of the phosphorus ligand.

An examination of the link between the co-ordinated ring and the phosphorus atom shows that the geometry about the carbon atoms involved, C(7), C(8) and C(9) is close to that expected for tetrahedral carbon and the stereochemistry is such that both the C(7)–C(8) and C(8)–C(9) adopt *gauche* conformations.

However the distortion in the structure is a signal that the control of the strain in the link between the ring and the phosphorus could be used to tune the $\eta^6\text{--}\eta^4$ shift of the ring and hence access to a vacant site on the metal.

The effect of the *trans* phosphorus ligands has been reported in related complexes lacking the link between ring and phosphorus, including $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{dippe})][\text{BPh}_4]$ [6] and $[(\eta^6\text{-arene})\text{RuCl}_2(\text{PPh}_2\text{Me})]$ [9] complexes. The Ru–Cl, Ru–P distances and the P–Ru–Cl angles in (3) are comparable to these analogues.

As would be expected for an octahedral geometry, three C–C bonds of the coordinated ring lie above the other three ligands. This results in a barely significant bond alternation around the ring. Interruption of conjugation in this way has been shown to be due to electronic effects within the molecule, rather than because of any crystallographic imposed symmetry effects [10]. The carbon atom C(7), linking the chelating arm to the $\eta^6\text{-C}_6\text{H}_5$ ring, was essentially in the same plane as the arene carbons C(1) and C(6). The angle subtended by these methylene groups suggests some strain, show-

ing a C(7)–C(8)–C(9) angle of 113.6° slightly larger than the ideal 109.5° for an sp^3 carbon.

Solution ^1H and ^{13}C NMR spectra provided structural information for solutions of (3). The asymmetry of the link between the co-ordinated ring and the phosphorus atom, revealed in the X-ray crystal structure, lowers the symmetry of the molecule from the ideal C_2 . However the ^1H spectrum of the co-ordinated ring contains three signals attributed to the coupling between *para*, *meta* and *ortho* positions giving two triplets and one doublet (vicinal coupling, $^3J_{\text{HH}} = 3\text{ Hz}$) of relative intensities 1:2:2, respectively. This apparent symmetry of the environment of the co-ordinated ring is likely to be due to the rapid twisting of the co-ordinated ring relative to the rest of the complex. The spectrum contains two peaks arising from the methylenes, which are accidentally coincident, forming a large multiplet.

2.3. Electrochemistry

Although the chemistry of arene–ruthenium complexes in the (II) and (O) oxidation states is very well developed, other possible higher oxidation states are less well explored. Paramagnetic organometallics are relatively uncommon but potentially important because of the higher kinetic lability that can be anticipated compared with their 18-electron counterparts. Acceleration of arene substitution in 17-electron half sandwich complexes is well established for chromium [11]. There are only a few isolated examples of organometallic complexes of ruthenium(III) known, most based on the pentamethylcyclopentadienyl (Cp^*) ligand [12].

The arene ligand is particularly suitable for forming paramagnetic compounds because the ligand only marginally stabilizes metal non-bonding d electrons by back-bonding to the arene, especially when the metal is in a positive oxidation state. This is reflected in the facile removal of electrons from arene clusters such as $[\text{Ru}_4\text{H}_4(\eta^6\text{-C}_6\text{H}_6)_4]^{2+}$ [13].

Electrochemical cyclovoltammetric studies have revealed quasi-reversible one-electron Ru(II)–Ru(III) redox behaviour associated a number of mononuclear arene–ruthenium species, such as the *nido*-carborane complex $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]$ [14] and a range of carbene [15], phosphine [16] and isocyanide [17] derivatives.

An electrochemical investigation of (2) revealed a quasi-reversible one-electron Ru(II)–Ru(III) redox couple in CH_2Cl_2 ($E_{1/2} = +1.25\text{ V vs SCE}$, $\Delta E = 90\text{ mV}$, $i_{\text{pa}}:i_{\text{pc}} = 0.91$), as illustrated in Fig. 2.

The reversibility of this redox process is solvent dependent and the addition of MeCN to the cell altered the nature of the observed Ru(II)–Ru(III) couple. Fig. 3 shows the cyclic voltammogram recorded during a multiscan experiment, where the initial redox couple

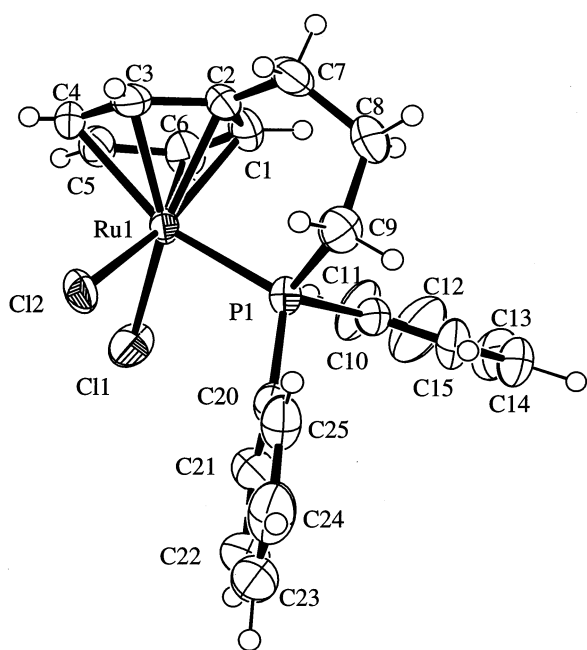


Fig. 1. ORTEP drawing of $[\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{-}\eta^6\text{-C}_6\text{H}_5)]$ (3) with 50% probability thermal ellipsoids.

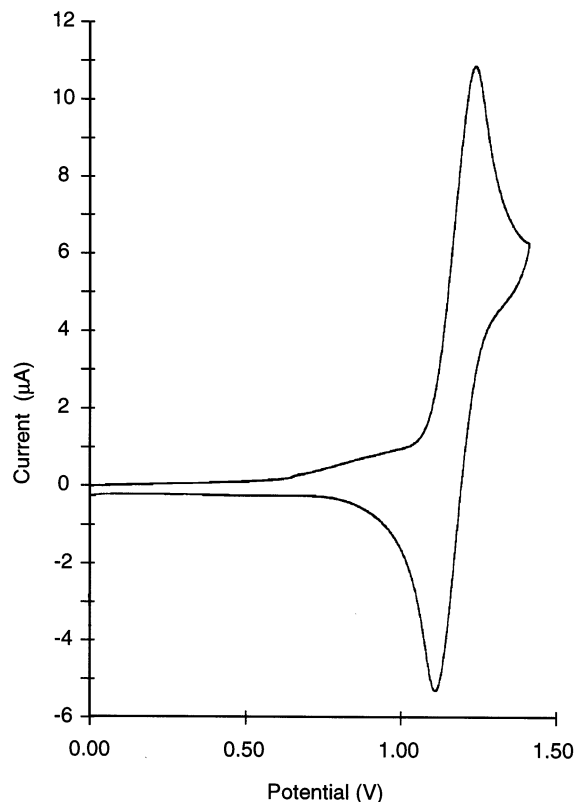


Fig. 2. Cyclic voltammogram recorded at a Pt bead working electrode (vs SCE) for $[(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ (**2**) (ca. 1 mmol dm^{-3}) in $\text{CH}_2\text{Cl}_2/[\text{NBu}_4][\text{PF}_6]$ (0.1 mol dm^{-3}) at 298 K, scan rate = 100 mV s^{-1} (ferrocene was used as an internal calibrant and i_p obeyed a linear relationship with the square root of the scan rate).

was irreversible and a new redox process emerged at a lower potential ($E_{1/2} = +0.56 \text{ V}$ vs SCE).

Controlled potential bulk electrolysis of (**2**) in MeCN, in which an exhaustive oxidation at $+1.5 \text{ V}$ was followed by subsequent reduction at 0.0 V , yielded a yellow product (Scheme 2). From NMR data the material isolated was identified as $[(\text{MeCN})_3\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ (**4**) resulting from arene substitution by MeCN via a kinetically labile Ru(III) intermediate, consistent with a typical electrochemical–chemical (EC) process. Attempts to synthesize (**4**) via thermal or photochemical methods have failed resulting in either decomposition or recovery of (**2**). This emphasizes the enhanced lability of the Ru(III) species compared with related Ru(II) complexes.

In the absence of MeCN, the controlled potential oxidation–reduction process provides an alternative route to the chelate $[\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{-}\eta^6\text{-C}_6\text{H}_5)]$ (**3**) leading to isolation of (**3**) in 75% yield. This method improves the synthetic route to the chelate complex.

Cyclovoltammetry of (**3**) shows a similar electrochemical behaviour to (**2**) ($E_{1/2} = +1.34 \text{ V}$ vs SCE, $\Delta E = 80 \text{ mV}$, $i_{pa}:i_{pc} = 0.94$) but in this case addition of

MeCN has no noticeable effect on the process, indicated that the chelating ring is no longer as easily substituted.

3. Experimental

All syntheses were carried out under a dry nitrogen atmosphere using conventional Schlenk techniques. Solvents were distilled from appropriate drying agents prior to use and were deoxygenated immediately before use. $[\{(p\text{-cymene})\text{RuCl}_2\}_2]$ was prepared by the literature method [18]. NMR spectra were recorded on a Bruker 250 MHz spectrometer.

3.1. 3-Phenylpropyldiphenylphosphine (**1**)

A suspension of triphenylphosphine (26.2 g, 0.1 mol) and strips of lithium metal (1.75 g, 0.25 mol) in dry THF (200 ml), was stirred rapidly for 1 h at 0°C under an atmosphere of dinitrogen. The solution became deep red and was allowed to reach room temperature whilst stirring for a further 30 min. The solution was then transferred to a clean dry flask away from any excess

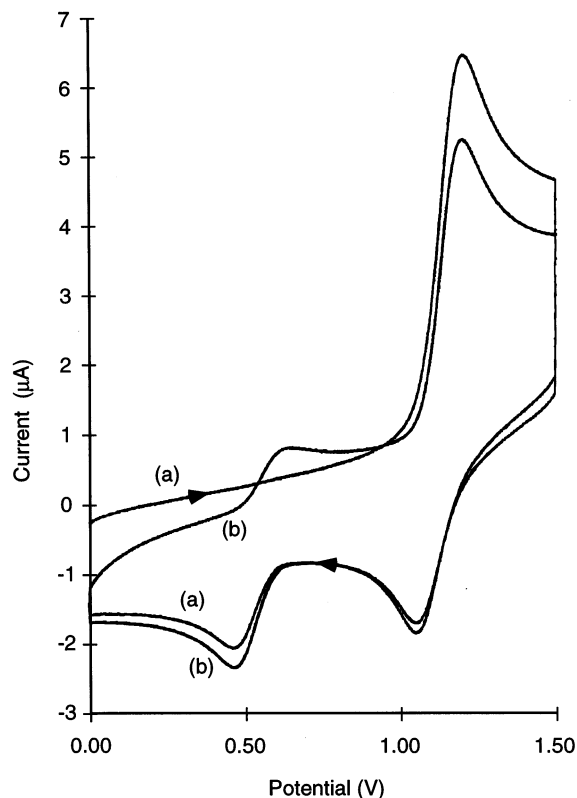
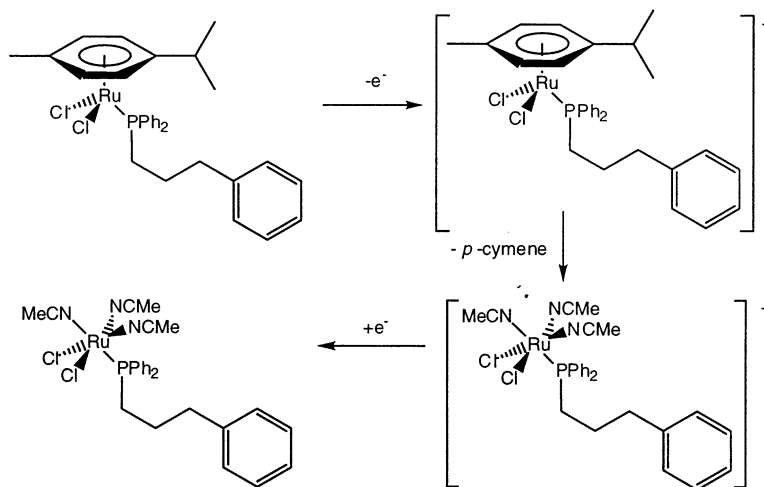


Fig. 3. Cyclovoltammogram of the first (a) and second (b) cycles recorded for $[(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ (**2**) upon addition of 2 ml of MeCN during a multiscan experiment where the potential was held at $+1.5 \text{ V}$ for 15 s during each sweep.



Scheme 2. The ECE mechanism proposed for the electrochemical preparation of $[(\text{MeCN})_3\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ (**4**).

lithium metal. A solution of *t*-butyl chloride (9.3 g, 11.05 ml, 0.1 mol) in THF (50 ml) was added dropwise with rapid stirring and cooling. The exothermic reaction was accompanied by gas evolution and partial discharge of colour. The reaction mixture was refluxed for 15 min and then cooled to room temperature. A solution of 1-bromo-3-phenylpropane (19.9 g, 14.7 ml, 0.1 mol) in THF (50 ml) was added dropwise with cooling and rapid stirring. The resulting yellow solution was refluxed for 30 min and then the solvent was removed under reduced pressure. The reaction mixture was purified by column chromatography on alumina using a mixture of dichloromethane-hexane as eluent. On removal of the solvent the phosphine was obtained as a colourless oil which slowly crystallized from cold diisopropyl ether to yield white crystals of $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Ph}$ yield 24.3 g, 80%. Anal. Found: C, 82.74; H, 7.14. $\text{C}_{21}\text{H}_{21}\text{P}$ requires C, 82.87; H, 6.95%. NMR (CDCl_3 , 250 MHz, 298 K): ^1H , δ 7.5–7.0 (m, 15H, Ph), 2.75 (t, 2H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 2.01 (t, 2H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.78 (quin, 2H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$); ^{13}C , δ 141.82–125.62 (Ph), 37.98 ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 27.82, 27.46, $^1J_{\text{CP}} = 31$ Hz ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 26.73 ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$); $^{31}\text{P}\{^1\text{H}\}$, δ –157.1.

3.2. $[(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ (**2**)

$\text{PPh}_2(\text{CH}_2)_3\text{Ph}$ (669 mg, 2.2 mmol) was added to a solution of $[(p\text{-cymene})\text{RuCl}_2]_2$ (612 mg, 1 mmol) in 50 ml of dichloromethane. The mixture was stirred for 1 h and the product crystallized from a mixture of dichloromethane-diisopropyl ether. Recrystallization from the same solvent combination gave $[(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ as red crystals. Yield 1.01 g, 83%. Anal. Found: C, 61.24; H, 5.91. $\text{C}_{31}\text{H}_{35}\text{Cl}_2\text{PRu}$ requires C, 60.98; H, 5.78%. NMR

(CDCl_3 , 250 MHz, 298 K): ^1H , δ 7.9–6.9 (m, 15H, Ph), 5.3–5.0 (dd, 4H, $\text{MeC}_6\text{H}_4\text{CHMe}_2$), 2.62 (t, 2H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 2.51 (sept, 1H, $\text{MeC}_6\text{H}_4\text{CHMe}_2$), 2.43 (t, 2H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.87 (s, 3H, $\text{MeC}_6\text{H}_4\text{CHMe}_2$), 1.32 (m, 2H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 0.73 (d, 6H, $\text{MeC}_6\text{H}_4\text{CHMe}_2$); ^{13}C , δ 141.8–126.91 (Ph), 97.98, 93.7, 90.46, 85.39 ($\text{MeC}_6\text{H}_4\text{CHMe}_2$), 36.92 ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 29.87 ($\text{MeC}_6\text{H}_4\text{CHMe}_2$), 25.52, 25.13, $^1J_{\text{CP}} = 34$ Hz ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 22.83 ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 21.05 ($\text{MeC}_6\text{H}_4\text{CHMe}_2$), 17 ($\text{MeC}_6\text{H}_4\text{CHMe}_2$); $^{31}\text{P}\{^1\text{H}\}$, δ –117.08.

3.3. $[\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\eta^6\text{-C}_6\text{H}_5)]$ (**3**)

(i) Thermolysis: A solution of $[(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ (305 mg, 0.5 mmol) in chlorobenzene (20 ml) was heated to 130°C for 18 h. The solvent was removed from the reaction mixture and the brown product purified by chromatography on alumina using dichloromethane as eluent. Recrystallization from dichloromethane-ethanol gave orange-red crystals. Yield 120 mg, 50%. Anal. Found: C, 52.79; H, 4.41. $\text{C}_{21}\text{H}_{21}\text{Cl}_2\text{PRu}$ requires C, 52.95; H, 4.44%. NMR (CDCl_3 , 250 MHz, 298 K): ^1H , δ 7.63–7.31 (m, 10H, Ph), 6.39 (t, 1H, *para* $\eta^6\text{-C}_6\text{H}_5$), 5.77 (t, 2H, *meta* $\eta^6\text{-C}_6\text{H}_5$), 5.16 (d, 2H, *ortho* $\eta^6\text{-C}_6\text{H}_5$), 2.57 (m, 4H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\eta^6\text{-C}_6\text{H}_5$), 2.18 (m, 2H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\eta^6\text{-C}_6\text{H}_5$); ^{13}C , δ 134.39–128.02 (Ph), 101.2 (*para* $\eta^6\text{-C}_6\text{H}_5$), 90.3 (*meta* $\eta^6\text{-C}_6\text{H}_5$), 89.17 (*ipso* $\eta^6\text{-C}_6\text{H}_5$), 84.67 (*ortho* $\eta^6\text{-C}_6\text{H}_5$), 30.79 ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\eta^6\text{-C}_6\text{H}_5$), 23.17, 22.67, $^1J_{\text{CP}} = 43$ Hz ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\eta^6\text{-C}_6\text{H}_5$), 20.45 ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\eta^6\text{-C}_6\text{H}_5$); $^{31}\text{P}\{^1\text{H}\}$, δ –117.45.

(ii) Electrolysis: A solution of $[(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ (305 mg, 0.5 mmol) in dichloromethane (15 ml) containing $[\text{NBu}_4][\text{PF}_6]$ (0.1 M) was electrolyzed at +1.5 V (vs

(ii) Electrolysis: A solution of $[(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ (305 mg, 0.5 mmol) in dichloromethane (15 ml) containing $[\text{NBu}_4][\text{PF}_6]$ (0.1 M) was electrolyzed at +1.5 V (vs SCE), using a two compartment bulk-electrolysis cell separated by Vycor porous glass with platinum gauze working and secondary electrodes, under a dinitrogen atmosphere at 298 K. The current fell exponentially during exhaustive-electrolysis (3 h) producing a brown-red solution. The potential was switched to 0.0 V (vs SCE) and the solution electrolyzed (1.5 h) forming a orange-red colour. This solution was removed from the cell and taken to dryness, washed with ethanol–methanol, 50:50, (3 × 50 ml) to remove supporting electrolyte and orange-red crystals were obtained as in Section 3.3(i). Yield 178 mg, 75%.

3.4. $[(\text{MeCN})_3\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ (**4**)

A solution of $[(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PPh}_2(\text{CH}_2)_3\text{Ph})]$ (305 mg, 0.5 mmol) in acetonitrile (15 ml) containing $[\text{NH}_4][\text{PF}_6]$ (0.1 M) was electrolyzed at +1.5 V (vs SCE) as in Section 3.3(ii) producing a brown-red solution. A subsequent electrolysis at 0.0 V (vs SCE) was carried out yielding a yellow solution, which was removed from the cell and take to dryness and the resulting yellow solid was washed with water (3 × 50 ml), to remove supporting electrolyte, and dried under vacuum. NMR (CD_3CN , 250 MHz, 298 K) ^1H , δ 7.56–7.01 (m, 15H, Ph), 2.61 (m, 2H, $\text{Ph}_2\text{PCH}_2\text{C-H}_2\text{CH}_2\text{Ph}$), 2.48 (m, 2H, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 2.06 (m, 2H $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.57 (s, 9H, $(\text{MeCN})_3\text{RuCl}_2$); ^{13}C , δ 142.73–126.88 (Ph), 125.14 ($(\text{MeCN})_3\text{RuCl}_2$), 37.4 ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 26.49, 26.19, $^1J_{\text{CP}} = 25$ Hz ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 26.01 ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 3.92 ($(\text{MeCN})_3\text{RuCl}_2$); $^{31}\text{P}\{^1\text{H}\}$, δ –93.68.

3.5. Crystal data and structure determination for (**3**)

$\text{C}_{21}\text{H}_{21}\text{Cl}_2\text{PRu}$, $M = 476.33$, triclinic, space group $P\bar{1}$, $a = 8.192(3)$, $b = 8.43(3)$, $c = 14.871(5)$ Å, $\alpha = 82.05(3)^\circ$, $\beta = 79.76(3)^\circ$, $\gamma = 73.68(2)^\circ$, $V = 965.6$ Å³, $Z = 2$, $D_c = 1.64$ g cm^{−3}, $\mu(\text{Mo-K}\alpha) = 1.172$ mm^{−1}, $F(000) = 480$, data were collected for 3360 reflections of which 3131 with $I > 3\sigma(I)$ were considered observed, $R = 0.043$, $wR_2 = 0.134$.

Cell dimensions and their standard deviations were obtained by least squares refinement of diffractometer setting angles for 12 centred reflections close to 13° in θ . Intensities of 3360 independent reflections ($2^\circ < \theta < 25^\circ$) were measured on a Hilger and Watts Y290 diffractometer in a ω - 2θ scan mode.

The structure analysis used 3131 reflections with $I < 3\sigma(I)$ after correction for Lorentz and polarization factors. No corrections were made for absorption. The

Table 2

Selected bond lengths [Å] and angles [°] for **3**

Intramolecular distances	
Ru(1)–C(6)	2.172(5)
Ru(1)–C(3)	2.171(4)
Ru(1)–C(1)	2.180(5)
Ru(1)–C(2)	2.199(4)
Ru(1)–C(4)	2.241(4)
Ru(1)–C(5)	2.246(5)
Ru(1)–P(1)	2.3187(13)
Ru(1)–Cl(2)	2.4039(14)
Ru(1)–Cl(1)	2.4271(14)
P(1)–C(20)	1.823(5)
P(1)–C(9)	1.833(5)
P(1)–C(10)	1.838(4)
C(1)–C(6)	1.389(7)
C(1)–C(2)	1.441(7)
C(2)–C(3)	1.411(6)
C(2)–C(7)	1.483(7)
C(3)–C(4)	1.410(8)
C(4)–C(5)	1.370(8)
C(5)–C(6)	1.424(7)
C(7)–C(8)	1.520(7)
C(8)–C(9)	1.536(7)
Intramolecular angles	
P(1)–Ru(1)–Cl(2)	84.26(5)
P(1)–Ru(1)–Cl(1)	90.67(5)
Cl(2)–Ru(1)–Cl(1)	88.79(6)
C(9)–P(1)–Ru(1)	110.0(2)
C(2)–C(7)–C(8)	116.4(4)
C(7)–C(8)–C(9)	113.4(4)
C(8)–C(9)–P(1)	113.2(3)

structure was solved using the program SHELXS86 [19] and refined with SHELXL93 [20] Fig. 1. was drawn with ORTEP3 [21]. Important bond lengths and angles are given in Table 2. The hydrogens were included in calculated positions and refined as riding atoms.

4. Supplementary Material

Tables of crystallographic data, including atomic coordinates and anisotropic thermal parameters, interatomic distances and angles and listings of calculated and observed structure factors are available. Ordering information is given on any masthead page.

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