ELSEVIER

Inorganica Chimica Acta 229 (1995) 87–93

Inorganica Chimica Acta

Neutral and anionic halide complexes of ruthenium(IV) ☆

Jonathan W. Steed, Derek A. Tocher *

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

Received 15 April 1994

Abstract

Treatment of the ruthenium(IV) complex [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (**3a**) with [PPh_4]Cl in CH_2Cl_2 at room temperature results in the immediate formation of an orange solution of the anionic trichloro complex [PPh_4][Ru(η^3:η^3-$C_{10}H_{16}$)Cl_3] (**4a**) in which the chloride ligands adopt a meridional type arrangement. Complex **4a** has been characterised by spectroscopic means and by X-ray crystallography. The equatorial Ru–Cl distance is found to be significantly longer than the axial Ru–Cl bond lengths (2.418(1) av. versus 2.458(1) Å). The bromo analogue [PPh_4][Ru(η^3:η^3-$C_{10}H_{16}$)Br_3] (**4b**) is formed along with the bromo analogue of **3a**, [{Ru(η^3:η^3-$C_{10}H_{16}$)Br(μ-Br)}$_2$] (**3b**), by reaction of **4a** with LiBr in acetone. Complex **3b** has been synthesized more simply by reaction of **3a** with LiBr, whilst pre-treatment of **3a** with Ag[BF_4] followed by addition of LiI gives the iodo complex [{Ru(η^3:η^3-$C_{10}H_{16}$)I(μ-I)}$_2$] (**3c**). The reactions of **3b** and **3c** with a number of Lewis bases have been investigated by a series of NMR experiments and are similar to, although slower than, those of **3a**. The new anionic complex has also been used to form mixed valence and mixed metal chloro-bridged binuclear species, one of which, [(η^3:η^3-$C_{10}H_{16}$)ClRu(μ-Cl)$_2$RhCl(η^5-C_5Me_5)] (**10**), has been characterised by X-ray crystallography.

Keywords: Crystal structures; Ruthenium complexes; Bis(allyl) ligand complexes; Halide complexes

1. Introduction

Anionic transition metal complexes are relatively uncommon but are of significant importance as synthons. Significant examples include the salts of chloroplatinic and chloropalladic acid [MCl_4]$^-$ (M = Pd, Pt) [1] or Na_2[Fe(CO)$_4$] which is of use in the functionalisation of organo halogen compounds [2].

In ruthenium chemistry, reaction of [{Ru(nbd)(CO)Cl_2}$_n$] (nbd = norbornadiene, $n \geq 2$) with MCl (M = Cs or benzyl(triphenyl)phosphonium) in acidified acetone over several days gives the anionic complex M[Ru(nbd)(CO)Cl_3] (**1**) [3]. As with many related (diene)rhodium(I) compounds [4], the olefin ligand may be replaced with a range of two electron nucleophiles to give anionic complexes of the form M[Ru(CO)Cl_3L_2] (L = Me_2S, DMSO, CH_2=CHCN) or neutral compounds [Ru(nbd)(CO)Cl_2L'] (L' = $AsPh_3$, $SbPh_3$, NC_5H_5) [5]. A similar reaction of [{Ru(η^6-C_6H_6)Cl(μ-Cl)}$_2$] with CsCl in acidified ethanol also results in an anionic complex Cs[Ru(η^6-C_6H_6)Cl_3] (**2**). The low lability of the arene ligand in **2** means that, in contrast to **1**, complex **2** is not a useful synthetic precursor to anionic trichloro compounds and forms only neutral products arising from displacement of chloride upon reaction with Lewis bases.

We now report the synthesis, X-ray crystal structure and reactions of a new trichloride anion of ruthenium in the +4 oxidation state, and related compounds. In contrast to **1** and **2** the chloride ligands adopt a meridional geometry.

2. Experimental

2.1. Materials and instrumentation

IR spectra were recorded on a PE983 spectrometer between 4000 and 180 cm^{-1} as KBr disks or nujol mulls. NMR spectra were recorded on a Varian VXR400 spectrometer at UCL and microanalyses were carried out by the departmental service. All manipulations were carried out under nitrogen with degassed solvents using conventional Schlenk line techniques, although no significant air sensitivity of the products was noted.

[{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] was prepared by published literature methods [6–8]. Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey

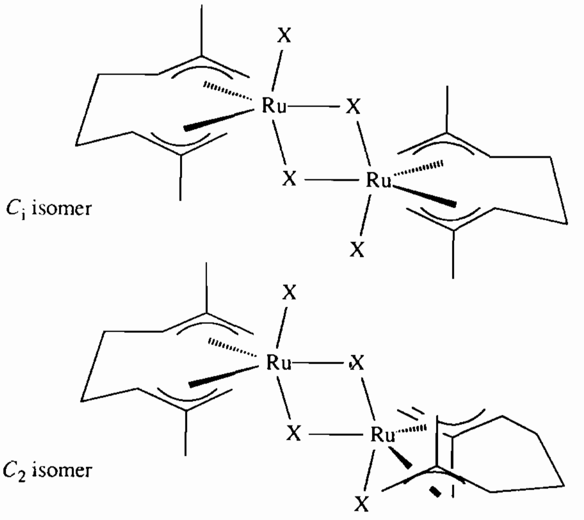
---

☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

* Corresponding author.

SSDI 0020-1693(94)04231-J

plc and was purified before use by repeated dissolution in water and boiling to dryness. All other reagents and materials were obtained from the usual commercial sources.



3a (X = Cl)
3b (X = Br)
3c (X = I)

2.2. *Preparations*

2.2.1. *[{Ru(η³:η³-C₁₀H₁₆)Br(μ-Br)}₂] (3b)*

The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.10 g, 0.16 mmol) was stirred in acetone (10 cm³) with LiBr (0.4 g, excess) for 4 h resulting in an orange–brown solution from which the product gradually deposited as a purple precipitate. The precipitate was isolated by filtration, washed with acetone and recrystallised from CH_2Cl_2 (100 cm³) to give the product as an orange–brown powder. Yield 0.08 g, 0.10 mmol, 63%. *Anal.* Found: C, 30.15; H, 3.85; Br, 40.20. Calc. for $C_{20}H_{32}Br_4Ru_2$: C, 30.25; H, 4.05; Br, 40.25%. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 5.91 (s, 1H), 5.59 (s, 1H), 5.40 (s, 1H), 5.23 (s, 1H), 5.14 (s, 1H), 4.89 (s, 1H), 4.86 (s, 1H), 4.62 (s, 1H) terminal allyl; 4.88 (m, 1H), 4.84 (m, 1H), 4.47 (m, 1H), 4.39 (m, 1H) internal allyl; 2.49 (m, 8H) $-CH_2CH_2-$; 2.55 (s, 3H), 2.48 (s, 6H), 2.45 (s, 3H) Me.

2.2.2. *[{Ru(η³:η³-C₁₀H₁₆)I(μ-I)}₂] (3c)*

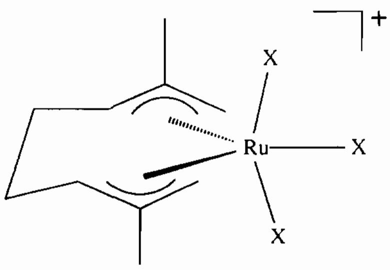
The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.12 g, 0.19 mmol) was stirred in acetone (10 cm³) with $Ag[BF_4]$ (0.15 g, 0.79 mmol). The mixture was filtered through Celite to remove AgCl and LiI (0.36 g, excess) added resulting in an immediate colour change to deep brown and the formation of a yellow–brown precipitate. After stirring for 2 h the resulting suspension was filtered and the residue recrystallised from CH_2Cl_2. Yield 0.09 g, 0.093 mmol, 49%. *Anal.* Found: C, 24.10; H, 3.05. Calc. for $C_{20}H_{32}I_4Ru_2$: C, 24.45; H, 3.30%. ^1H NMR (ppm): δ 5.71 (s, 1H), 5.44 (s, 1H), 5.42 (s, 1H), 5.20 (s, 1H), 5.13 (s, 1H), 5.08 (s, 1H), 4.96 (s, 1H), 4.71 (s, 1H) terminal allyl; 5.03 (m, 2H), 4.32 (m, 1H), 4.27 (m, 1H) internal allyl; 2.50 (m, 4H), 2.20 (m, 4H) $-CH_2CH_2-$; 2.85 (s, 3H), 2.82 (s, 6H), 2.78 (s, 3H) Me.

2.2.3. *[PPh₄][Ru(η³:η³-C₁₀H₁₆)Cl₃] (4a)*

The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.065 g, 0.11 mmol) was stirred in CH_2Cl_2 (10 cm³) with $[PPh_4]Cl$ (0.078 g, 0.21 mmol) for 30 min resulting in a rapid colour change from purple to orange. Removal of the solvent in vacuo followed by addition of hexane (5 cm³) to the resulting oil resulted in the formation of the product as orange–red crystals which were isolated by filtration and dried under vacuum. Yield 0.11 g, 0.16 mmol, 73%. *Anal.* Found: C, 59.05; H, 5.50; Cl, 16.40. Calc. for $C_{34}H_{36}Cl_3PRu$: C, 59.80; H, 5.30; Cl, 15.55%. ^1H NMR (ppm): δ 5.10 (s, 2H), 4.67 (s, 2H) terminal allyl; 4.97 (m, br, 2H) internal allyl; 2.83 (m, 2H), 2.23 (m, 2H) $-CH_2CH_2-$; 2.31 (s, 6H) methyl; 7.91 (m, 4H), 7.77 (m, 8H), 7.60 (m, 8H) $[PPh_4]^+$.

2.2.4. *[PPh₄][Ru(η³:η³-C₁₀H₁₆)Br₃] (4b)*

The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.085 g, 0.14 mmol) was stirred in acetone (10 cm³) with $[PPh_4]Cl$ (0.10 g, 0.28 mmol) and LiBr (0.2 g, excess) for 30 min resulting in an orange–brown solution. The acetone was removed in vacuo and the resulting brownish purple residue extracted into CH_2Cl_2 (10 cm³). Evaporation of the solvent resulted in a deep brown oil from which the product (a 2:1 mixture of **3b** and **4b** by ^1H NMR) was deposited as a deep purple powder on standing for 72 h. The solid products were isolated by filtration and dried under vacuum. Yield 0.12 g. Complex **4b** was not isolated in pure form because of its tendency to convert into **3b** in solution. ^1H NMR (ppm) for **4b**: δ 5.14 (s, 2H), 4.86 (s, 2H) terminal allyl; 5.27 (m, br, 2H) internal allyl; 2.78 (m, 2H), 2.29 (m, 2H) $-CH_2CH_2-$; 2.53 (s, 6H) Me; 7.91 (m, 4H), 7.78 (m, 8H), 7.59 (m, 8H) $[PPh_4]^+$.



4a (X = Cl)
4b (X = Br)

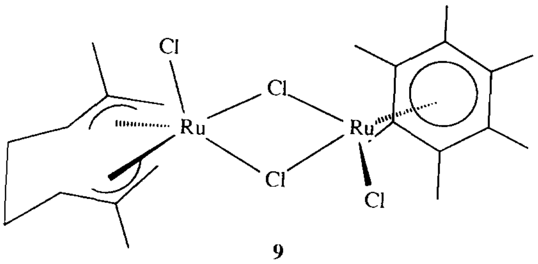
2.2.5. *[(η³:η³-C₁₀H₁₆)ClRu(μ-Cl)₂RuCl(η⁶-C₆Me₆)] (9)*

$[\{Ru(\eta^6\text{-}C_6Me_6)Cl(\mu\text{-}Cl)\}_2]$ (0.14 g, 0.21 mmol) was stirred in acetone (5 cm³) with $Ag[BF_4]$ (0.08 g, 0.42

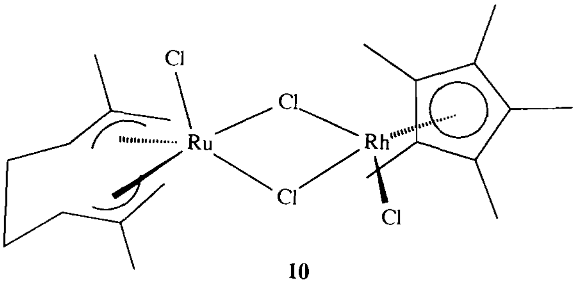
mmol) for 20 min. The mixture was filtered through Celite and an acetone (5 cm^3) solution of $[PPh_4][Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_3]$ (**4a**) (0.28 g, 0.56 mmol) added to the filtrate at 0 °C resulting in a rapid colour change from orange to red. The solvent was immediately removed in vacuo resulting in a ~6:1:1 mixture of **9**, **3a** and $[\{Ru(\eta^6\text{-}C_6Me_6)Cl(\mu\text{-}Cl)\}_2]$, respectively, as well as contaminating $[PPh_4][BF_4]$. The lability of the chloride bridges in **9** made purification impractical. ^1H NMR (ppm) for **9**: δ 6.67 (s, 1H), 5.55 (s, 1H), 5.04 (s, 1H), 4.83 (s, 1H) terminal allyl; 4.83 (m, 1H), 4.56 (m, 1H) internal allyl; 2.71 (m, 2H), 2.51 (m, 2H) $-CH_2CH_2-$; 2.32 (s, 3H), 2.26 (s, 3H) Me; 2.03 (s, 18H) C_6Me_6.

2.2.6. $[(\eta^3:\eta^3\text{-}C_{10}H_{16})ClRu(\mu\text{-}Cl)_2RhCl(\eta^5\text{-}C_5Me_5)]$ (10)

$[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (0.06 g, 0.10 mmol) was stirred in acetone (5 cm^3) with $Ag[BF_4]$ (0.04 g, 0.20 mmol) for 20 min. The mixture was filtered through Celite and an acetone (5 cm^3) solution of $[PPh_4][Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_3]$ (**4a**) (0.15 g, 0.30 mmol) added to the filtrate as described for **9**. Removal of the solvent gave a ~4:1:1 mixture of **10**, **3a** and $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$, respectively, as well as contaminating $[PPh_4][BF_4]$. The lability of the chloride bridges in **10** made purification impractical. ^1H NMR (ppm) for **10**: δ 6.71 (s, 1H), 5.53 (s, 1H), 5.02 (s, 1H), 4.66 (s, 1H) terminal allyl; 4.99 (m, 1H), 4.63 (m, 1H) internal allyl; 2.78 (m, 2H), 2.49 (m, 2H) $-CH_2CH_2-$; 2.38 (s, 3H), 2.34 (s, 3H) Me; 1.68 (s, 18H) C_5Me_5.



9



10

2.3. Reactions of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})X(\mu\text{-}X)\}_2]$ (X = Br (3b), I (3c)) followed by ^1H NMR spectroscopy

To a solution of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})X(\mu\text{-}X)\}_2]$ (~0.01 g) in $CDCl_3$ was added a small excess of (i) DMSO, (ii) acetonitrile and (iii) pyrazene (**3b** only).

(i) For **3b** the solution was observed to change gradually from brownish orange to yellow. ^1H NMR (ppm): δ 4.67 (s, 2H), 4.36 (s, 2H) terminal allyl; 5.44 (m, 2H) internal allyl; 3.06 (m, 2H), 2.72 (m, 2H) $-CH_2CH_2-$; 2.53 (s, 6H) Me; 2.02 (s, 6H) DMSO. In the case of **3c** no reaction was observed.

(ii) For **3b** the solution was observed to change gradually from brownish orange to yellow. ^1H NMR (ppm) MeCN axial: δ 5.19 (s, 1H), 5.04 (s, 1H), 4.82 (s, 1H), 3.83 (s, 1H) terminal allyl; 5.42 (dd, 1H, ^3J = 11.1 and 4.5), 4.34 (dd, 1H, ^3J = 11.1 and 4.5) internal allyl; 3.17 (m, 1H), 2.97 (m, 1H), 2.49 (m, 2H) $-CH_2CH_2-$; 2.66 (s, 3H), 2.26 (s, 3H) Me; 2.37 (s, 3H) CH_3CN; MeCN equatorial: 5.01 (s, 2H), 4.78 (s, 2H) terminal allyl; 5.28 (m, 2H) internal allyl; 2.86 (m, 2H), 2.49 (m, 2H) $-CH_2CH_2-$; 2.60 (s, 6H) Me; 2.01 (s, 3H) CH_3CN. In the case of **3c** a gradual colour change from deep yellow–brown to orange–red was observed over ~24 h. ^1H NMR (ppm) MeCN axial: δ 5.11 (s, 1H), 4.89 (s, 1H), 4.53 (s, 1H), 3.49 (s, 1H) terminal allyl; 5.78 (m, 1H), 4.16 (m, 1H) internal allyl; 3.16 (m, 1H), 2.92 (m, 1H), 2.38 (m, 2H) $-CH_2CH_2-$; 2.91 (s, 3H), 2.19 (s, 3H) Me; ~1.9 (s, 3H) CH_3CN; MeCN equatorial: 5.07 (s, 2H), 3.30 (s, 2H) terminal allyl; 4.87 (m, 2H) internal allyl; 3.46 (m, 2H), 2.58 (m, 2H) $-CH_2CH_2-$; 2.14 (s, 6H) Me; 2.31 (s, 3H) CH_3CN.

(iii) The solution was observed to change gradually from brownish orange to yellow. Initially a mixture of **3b** and two diastereomeric forms of **7** were observed. Further addition of pyrazene resulted in the observation of only one isomer of **7**. ^1H NMR (ppm) most stable diastereoisomer: δ 4.77 (s, 4H), 4.72 (s, 4H) terminal allyl; 5.57 (m, 4H) internal allyl; 2.94 (m, 4H), 2.49 (m, 4H) $-CH_2CH_2-$; 2.67 (s, 12H) Me; 9.39 (s, 4H) $N_2C_4H_4$; less stable diastereoisomer: 4.76 (s, 4H), 4.69 (s, 4H) terminal allyl; 5.57 (m, 4H) internal allyl; 2.94 (m, 4H), 2.49 (m, 4H) $-CH_2CH_2-$; 2.66 (s, 12H) Me; 9.26 (s, 4H) $N_2C_4H_4$.

2.4. X-ray crystallography

2.4.1. $[PPh_4][Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_3]$ (4a)

Crystal data. $C_{34}H_{36}Cl_3PRu$, M = 683.09 g mol^{-1}, monoclinic, space group $P2_1/a$, $a = 13.261(2)$, $b = 15.312(2)$, $c = 16.614(2)$ Å, $\beta = 112.90(1)°$, $U = 3108$ Å^3 (by least-squares refinement of diffractometer angles for 33 automatically centred reflections in the range $19 \leq 2\theta \leq 28°$, $\lambda = 0.71073$ Å), $Z = 4$, F(000) = 1400, $D_c = 1.46$ g cm^{-3}, μ(Mo Kα) = 8.27 cm^{-1}. Deep orange block 0.6×0.3×0.2 mm.

The ω–2θ technique was used to collect a total of 5939 data (5462 unique) in the range $5 \leq 2\theta \leq 50°$ on a Nicolet R3mV diffractometer equipped with graphite monochromated Mo Kα radiation. Three standards monitored every 97 reflections showed no appreciable change in intensity throughout the data collection. Data were corrected for Lorentz and polarisation effects and for absorption based on additional azimuthal scan data. Omission of intensities of $I \leqslant 3\sigma(I)$ gave 3989 observed data which were employed in the analysis. The structure was solved by a combination of conventional direct methods and difference-Fourier techniques. From systematically absent data the space group was unequivocally identified as $P2_1/a$, the asymmetric unit contained one complete anionic molecule and one tetraphenylphosphonium cation. All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in idealised positions and allowed to ride on the atoms to which they were attached (C–H 0.96 Å, U_{iso} 0.08 Å^2). The final cycle of full-matrix least-squares refinement included 352 parameters (weighting scheme applied: $w^{-1} = \sigma^2(F) + 0.000177F^2$) and the largest shift to error ratio was 0.002, $R = 0.0396$, $R_w = 0.0402$. The largest residual peak was 0.47 e Å^{-3} and no intermolecular short contacts were observed.

2.4.2. *[(η^3:η^3-$C_{10}H_{16}$)ClRu(μ-Cl)$_2$RhCl(η^5-C_5Me_5)] (10·$CHCl_3$)*

Crystal data. $C_{20.5}H_{31.5}Cl_{5.5}RhRu$, $M = 676.98$ g mol^{-1}, monoclinic, space group $P2_1/c$, $a = 8.022(3)$, $b = 13.913(4)$, $c = 26.049(11)$ Å, $\beta = 95.44(3)°$, $U = 2894$ Å^3 (by least-squares refinement of diffractometer angles for 26 automatically centred reflections in the range $11 \leqslant 2\theta \leqslant 22°$, $\lambda = 0.71073$ Å), $Z = 4$, $F(000) = 1344$, $D_c = 1.55$ g cm^{-3}, μ(Mo Kα) = 15.93 cm^{-1}. Deep red needle $0.55 \times 0.1 \times 0.1$ mm.

The ω–2θ technique was used to collect a total of 5666 data (5043 unique) in the range $5 \leqslant 2\theta \leqslant 50°$ on a Nicolet R3mV diffractometer equipped with graphite monochromated Mo Kα radiation. Three standards monitored every 97 reflections showed no appreciable change in intensity throughout the data collection however profiling scans through a selection of strong peaks showed these to be unusually broad. Data were corrected for Lorentz and polarisation effects and for absorption based on additional azimuthal scan data. Omission of intensities of $I \leqslant 3\sigma(I)$ gave 2047 observed data which were employed in the analysis. From systematically absent data the space group was unequivocally identified as $P2_1/c$. The structure was solved by a combination of conventional direct methods and difference-Fourier techniques. The asymmetric unit contained one binuclear molecule. In the latter stages of refinement it was apparent that there were chloroform molecules within the lattice. The crystallographically unique of chloroform of crystallisation was best modelled with an occupancy of 50%. Only the transition metal ions and the chloride ligands were refined anisotropically. All remaining non-hydrogen atoms were refined isotropically while hydrogen atoms were placed in idealised positions and allowed to ride on the atoms to which they were attached (C–H 0.96 Å, U_{iso} 0.08 Å^2). The final cycle of full-matrix least-squares refinement included 151 parameters (weighting scheme applied: $w^{-1} = \sigma^2(F) + 0.00006F^2$) and the largest shift to error ratio was 0.068, $R = 0.0973$, $R_w = 0.0979$. The largest residual peak was 1.5 e Å^{-3} (close to the chloroform solvate molecule). The poor quality of the final refinement is a consequence of the combination of the broad peak profiles and the low proportion of observed data, together with the presence of the poorly defined lattice solvent molecule. Preliminary examination of several other crystals of this compound reveal that these problems are not confined to the sample used in the reported measurement.

All calculations were carried out using the SHELXTL PLUS program package [9] on a Micro Vax II computer. Fractional atomic coordinates and equivalent isotropic displacement factors are listed in Tables 1 and 3 and selected bond lengths and angles in Tables 2 and 4.

3. Results and discussion

Reaction of the ruthenium(IV) dichloride dimer [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (**3a**) [6,7,10] which contains the bis(allyl) 2,7-dimethylocta-2,6-diene-1,8-diyl ligand, with two mole equivalents of [PPh_4]Cl in dichloromethane at room temperature results in an instantaneous colour change from purple to orange. Removal of the solvent results in the isolation of the anionic complex [PPh_4][Ru(η^3:η^3-$C_{10}H_{16}$)Cl_3] (**4a**). This rapid reaction contrasts to the formation of both **1** and **2** (which are only formed under acidic conditions over periods of days), and may be attributable to the more electrophilic nature of the Ru(IV) centre. The bis(allyl) ligand in compounds derived from **3a** has been shown to be a very sensitive NMR probe to the coordination geometry about the metal centre, which is invariably described as a trigonal bipyramid, with the two allylic functionalities occupying two of the equatorial coordination sites [10,11]. In the case of **4a** the observation of two singlet signals for the terminal allyl protons (δ 5.10 and 4.67 ppm) and one methyl resonance (δ 2.31 ppm) indicates that the compound is monomeric and that the two axial sites are equivalent, hence the chloride ligands occupy both the axial, and the remaining equatorial coordination sites and lie in a plane with the Ru(IV) centre in a relatively sterically crowded meridional arrangement.

Attempts to synthesise the corresponding caesium salt of **4a**, Cs[Ru(η^3:η^3-$C_{10}H_{16}$)Cl_3], from reaction of **3a** in ethanol or acetone with CsCl/HCl resulted in the formation of an insoluble orange precipitate over a period of ~2 h. The ^{1}H NMR spectrum of this material in DMSO-d$_6$, indicated that the bis(allyl) ligand had been displaced and no further attempts at characterisation were made.

Table 1
Atomic coordinates ($\times 10^4$) for $[PPh_4][Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_3]$ (**4a**)

	x	*y*	*z*
Ru(1)	1307(1)	5697(1)	8516(1)
Cl(1)	2415(1)	4516(1)	9373(1)
Cl(2)	848(1)	4686(1)	7275(1)
Cl(3)	107(1)	6715(1)	7461(1)
P(1)	6792(1)	3788(1)	6264(1)
C(1)	2526(4)	6120(4)	7973(3)
C(2)	2957(4)	6364(3)	8857(3)
C(3)	2269(5)	6879(3)	9117(3)
C(4)	2466(5)	7079(3)	10063(3)
C(5)	1398(5)	6879(3)	10142(4)
C(6)	1062(4)	5978(3)	9742(3)
C(7)	20(4)	5777(3)	9110(3)
C(8)	−63(5)	4970(3)	8693(3)
C(9)	4027(4)	6009(4)	9465(4)
C(10)	−927(5)	6398(4)	8829(4)
C(11)	6585(3)	4598(3)	6961(3)
C(12)	6287(4)	5436(3)	6661(3)
C(13)	6033(4)	6043(3)	7171(3)
C(14)	6086(4)	5806(3)	7976(3)
C(15)	6402(5)	4978(3)	8291(3)
C(16)	6649(4)	4372(3)	7783(3)
C(21)	7253(4)	4317(3)	5510(3)
C(22)	6704(5)	4208(3)	4614(3)
C(23)	7107(7)	4597(4)	4057(4)
C(24)	8053(7)	5059(5)	4364(5)
C(25)	8584(5)	5182(4)	5244(5)
C(26)	8185(4)	4829(3)	5822(3)
C(31)	5514(4)	3255(3)	5674(3)
C(32)	5465(4)	2562(3)	5119(3)
C(33)	4485(5)	2201(3)	4606(3)
C(34)	3541(5)	2511(4)	4658(3)
C(35)	3579(4)	3180(3)	5220(4)
C(36)	4562(4)	3554(3)	5720(3)
C(41)	7753(3)	2992(3)	6912(3)
C(42)	8864(4)	3149(3)	7198(3)
C(43)	9597(4)	2572(3)	7765(3)
C(44)	9224(4)	1838(3)	8037(3)
C(45)	8130(4)	1677(3)	7755(3)
C(46)	7384(4)	2244(3)	7186(3)

Table 2
Selected bond lengths (Å) and angles (°) for $[PPh_4][Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_3]$ (**4a**)

Bond lengths			
Ru–Cl(1)	2.415(1)	Ru–Cl(2)	2.458(1)
Ru–Cl(3)	2.421(1)	Ru–C(1)	2.232(6)
Ru–C(2)	2.278(5)	Ru–C(3)	2.215(5)
Ru–C(6)	2.225(6)	Ru–C(7)	2.282(6)
Ru–C(8)	2.246(6)	C(1)–C(2)	1.404(7)
C(2)–C(3)	1.396(9)	C(3)–C(4)	1.521(8)
C(4)–C(5)	1.503(10)	C(5)–C(6)	1.521(7)
C(6)–C(7)	1.406(6)	C(7)–C(8)	1.400(7)
P(1)–C	1.789(5) av.		
Bond angles			
Cl(1)–Ru–Cl(2)	85.3(1)	Cl(2)–Ru–Cl(3)	85.4(1)
Cl(1)–Ru–Cl(3)	170.7(1)	Cl(1)–Ru(1)–C(2)	83.3(1)
Cl(1)–Ru(1)–C(7)	99.9(1)		

Table 3
Atomic coordinates ($\times 10^4$) for $[(\eta^3:\eta^3\text{-}C_{10}H_{16})ClRu(\mu\text{-}Cl)_2RhCl(\eta^5\text{-}C_5Me_5)]$ (**10**)

	x	*y*	*z*
Ru(1)	1169(3)	8545(1)	1136(1)
Rh(1)	1356(3)	7339(1)	2432(1)
Cl(1)	−678(11)	9838(5)	855(3)
Cl(2)	2674(10)	7236(5)	1615(3)
Cl(3)	−240(9)	8615(4)	1950(2)
Cl(4)	3486(10)	8487(5)	2770(3)
C(1)	2691(27)	9592(14)	1575(7)
C(2)	3647(39)	9269(19)	1164(11)
C(3)	2923(40)	9261(22)	683(11)
C(4)	3678(51)	8721(29)	226(14)
C(5)	2267(50)	8066(26)	7(13)
C(6)	1460(39)	7635(23)	455(11)
C(7)	−113(45)	7706(24)	482(12)
C(8)	−837(39)	7447(20)	959(10)
C(9)	5235(40)	8770(22)	1316(11)
C(10)	−1297(55)	8256(31)	40(15)
C(11)	−869(43)	6571(22)	2636(12)
C(12)	123(40)	5984(20)	2394(10)
C(13)	1776(35)	5903(17)	2670(10)
C(14)	2014(44)	6390(22)	3113(12)
C(15)	228(40)	6888(20)	3080(11)
C(16)	−2469(69)	6909(36)	2530(19)
C(17)	−444(62)	5424(34)	1979(16)
C(18)	3052(47)	5288(25)	2503(13)
C(19)	3232(43)	6472(24)	3504(12)
C(20)	−51(63)	7505(33)	3539(17)
Cl(51)	4822(30)	5509(16)	1084(8)
Cl(52)	4307(37)	3573(19)	684(10)
Cl(53)	7296(36)	4534(19)	654(10)
C(51)	5463(119)	4440(67)	966(40)

Table 4
Selected bond lengths (Å) and angles (°) for $[(\eta^3:\eta^3\text{-}C_{10}H_{16})ClRu(\mu\text{-}Cl)_2RhCl(\eta^5\text{-}C_5Me_5)]$ (**10**)

Bond lengths			
Ru(1)–Cl(1)	2.400(8)	Ru(1)–Cl(2)	2.459(7)
Ru(1)–Cl(3)	2.496(7)	Rh(1)–Cl(2)	2.470(8)
Rh(1)–Cl(3)	2.464(6)	Rh(1)–Cl(4)	2.441(7)
Bond angles			
Cl(1)–Ru(1)–Cl(2)	165.7(3)	Cl(1)–Ru(1)–Cl(3)	85.0(3)
Cl(2)–Ru(1)–Cl(3)	80.7(2)	Cl(2)–Rh(1)–Cl(3)	81.1(2)
Cl(2)–Rh(1)–Cl(4)	90.4(2)	Cl(3)–Rh(1)–Cl(4)	91.4(2)
Ru(1)–Cl(2)–Rh(1)	99.5(3)	Ru(1)–Cl(3)–Rh(1)	98.6(2)

The geometry of **4a** was confirmed by a single crystal X-ray structure determination. The crystal structure of the anion is shown in Fig. 1 and is, in general, similar to that observed for the neutral compound $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(PF_3)]$ [12]. The complex may be thought of as being based on a distorted trigonal bipyramidal geometry, as in all previous structure determinations. The axial sites are occupied by chlorides with a 'normal' bond length to ruthenium, Ru–Cl av. 2.418(1) Å. The remaining equatorial site, occupied by the third chloride has a significantly longer bond, Ru–Cl(2) 2.458(1) Å.

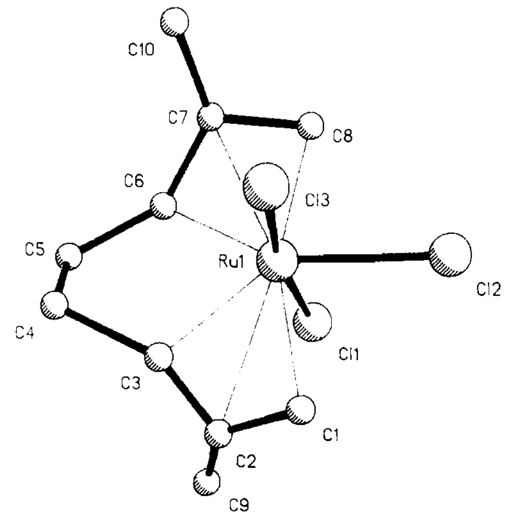


Fig. 1. Crystal structure of the anion of $[PPh_4][Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_3]$ (**4a**) showing the atom numbering scheme adopted.

The equatorial chloride ligand probably competes for the same metal orbitals as the strongly *trans* influencing allyl ligands and hence is less strongly bound. The angle Cl(1)–Ru–Cl(3) of 170.7(1)° is typical of the distortion from the ideal 180° invariably observed in these systems and, as expected, is almost identical to the analogous angle for the pyrazene bridged binuclear adduct $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-}N_2C_4H_4)]$ (170.2(1)° [13]), although this parameter may vary considerably in the case of compound in which the axial substituents form part of a chelate ring [11].

Reaction of **4a** in acetone with LiBr gave a mixture of the analogous bromo complex $[PPh_4][Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Br_3]$ (**4b**) and a compound displaying eight terminal allyl signals in its ^{1}H NMR spectrum, in a similar pattern to those observed for **3a**. Like **4a**, complex **4b** exhibits a very simple ^{1}H NMR spectrum implying that the axial sites of the metal ion are equivalent. The second product was synthesised independently by reaction of **3a** with LiBr in acetone and shown to be the dibromide dimer $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Br(\mu\text{-}Br)\}_2]$ (**3b**). Like **3a**, compound **3b** exists as two diastereoisomers, occurring in almost equimolar proportions. In contrast, in the case of **3a** the diastereoisomer of C_2 symmetry is somewhat more stable; $K_{20} = [C_2]/[C_i] = 1.25$ [7]. For completeness the reaction of **3a** with lithium iodide was also examined. Addition of LiI to an acetone suspension of **3a** resulted in the rapid formation of a deep brown solution from which a dark yellow solid precipitated. This material was shown to consist of a mixture of halide bridged complexes. Treatment of **3a** with $Ag[BF_4]$, to remove chloride, followed by addition of LiI gave the iodo-bridged complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})I(\mu\text{-}I)\}_2]$ (**3c**) cleanly. Unlike **3a** and **3b** which are respectively pink and deep purple in colour when in the form of powders, complex **3c** is a dark yellow and is soluble in acetone and diethyl ether, as well as CH_2Cl_2. Like **3a** and **3b**, complex **3c** also exists as two diastereoisomers, as clearly demonstrated by ^{1}H NMR spectroscopy (see Section 2).

The reactions of **3b** and **3c** with Lewis bases have been examined by ^{1}H NMR spectroscopy. In common with **3a**, compound **3b** reacts in $CDCl_3$ with ligands L (L = DMSO-d_6 (**na**), MeCN-d_3 (**nb**)) to give simple bridge cleaved adducts $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Br_2(L)]$ **5a** and **5b**. In the case of complex **5a** the DMSO ligand occupies an equatorial site on the metal ion. In the acetonitrile complex **5b**, the isomer with the MeCN occupying one of the equatorial coordination sites co-exists in equilibrium with the corresponding axially coordinated isomer, $K = [ax]/[eq.] = 5.4$ (in a ~10:1 mixture of chloroform:MeCN at 293 K). This compares to values for K for the analogous chloro compound of up to 14 in pure acetonitrile solution, and down to 1.7 in a 9:1 mixture of chloroform and MeCN [7].

Addition of DMSO to a $CDCl_3$ solution of **3c** gave no reaction. Cleavage of the iodide bridges in **3c** is likely to be slow and the DMSO molecule may well be too bulky to coordinate the small Ru(IV) centre in the presence of two large iodide anions. Addition of MeCN to an NMR tube containing **3c** resulted in a sluggish reaction which had gone to completion after ~1 day. As observed for **3a** and **3b** the resulting spectrum was consistent with the presence of a mixture of axial and equatorial mononuclear solvates ($K = [ax.]/[eq.] = 2.9$).

Reaction of the bromo complex **3b** with pyrazene in $CDCl_3$ resulted initially in an ^{1}H NMR spectrum similar to that of the diastereomeric pair of complexes $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\}_2(\mu\text{-}N_2C_4H_4)]$ (**6**) [13,14], indicating that the bromo analogue $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Br_2\}_2(\mu\text{-}N_2C_4H_4)]$ (**7**) also exists as two diastereoisomers, as a consequence of the chirality of the '$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})$' fragment (e.g. $N_2C_4H_4$ signals, **6**: δ 9.32 and 9.24 ppm [14], cf. **7**: 9.39 and 9.26 ppm). In the case of **6** at room temperature (20 °C) the two diastereomeric forms are in equilibrium, $K_{20} = [C_2]/[C_i] = 1.14$. The corresponding ratio for **7** observed upon running the ^{1}H NMR spectrum immediately after addition of the pyrazene is 1.36. Startlingly however, addition of more pyrazene and re-recording the spectrum after several hours results in the observation of *only a single diastereoisomer*. In the case of **6** and **3b** one diastereomeric form is marginally more stable in solution. It is clear that in the more sterically crowded bromo complex **7** the effect is greatly enhanced such as to completely destabilise one isomer.

Reaction of **3b** with $[PPh_4]Cl$ resulted in the formation of a complex mixture of the anionic complex $[PPh_4][Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Br_2Cl]$ (**4c**) and several mixed halide binuclear compounds.

Attempts were made to use the anionic complex **4a** to form mixed valence and mixed metal chloride bridged compounds analogous to the thiolate species $[(\eta^3:\eta^3\text{-}C_{10}H_{16})ClRu(\mu\text{-}Cl)(\mu\text{-}SEt)MCl(L)]$ (M = Ru, L = C_6H_6 (**8a**), C_6Me_6 (**8b**); M = Rh, L = C_5Me_5 (**8c**)) [15] which we have found may be readily synthesised by reaction of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(SHEt)]$ with the appropriate Ru(II) or Rh(III) dimer [16].

Slow addition of an acetone solution of **4a**, at 0 °C, to a solution of $[Ru(\eta^6\text{-}C_6Me_6)Cl(solv)_2]^+$ (generated by action of $Ag[BF_4]$ upon $[\{Ru(\eta^6\text{-}C_6Me_6)Cl(\mu\text{-}Cl)\}_2]$) resulted in the formation of the mixed valence binuclear species $[(\eta^3:\eta^3\text{-}C_{10}H_{16})ClRu(\mu\text{-}Cl)_2RuCl(\eta^6\text{-}C_6Me_6)]$ (**9**). Unlike complexes of type **3**, this complex does not exhibit diastereoisomerism (four terminal allyl resonances only) as the Ru(II) centre is not chiral. In a similar way the mixed metal Ru(IV)/Rh(III) complex $[(\eta^3:\eta^3\text{-}C_{10}H_{16})ClRu(\mu\text{-}Cl)_2RhCl(\eta^5\text{-}C_5Me_5)]$ (**10**) was also prepared. Unlike the thiolato bridges in complexes of type **8**, the chloride bridges in **9** and **10** are labile, resulting in scrambling of the two termini of the molecules in solution to give equilibrium mixtures containing approximately statistical distributions of the **3a**, **9** or **10**, and the appropriate Ru(II) or Rh(III) dichloride dimers. As a result of his scrambling process, in the case of the preparation of **9** we were unable to recrystallise the complex to remove contaminating $[PPh_4][BF_4]$, which is formed as a side product. Slow crystallisation (hexane/chloroform liquid diffusion) of a mixture of **3a**, **10** and $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ resulted in the isolation of deep red needle-like crystals. Dissolution of these crystals in $CDCl_3$ and running their ^1H NMR spectrum demonstrated a 2:1:1 mixture of **10**, **3a** and $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ as before. However, a single crystal X-ray structure determination revealed the crystal to consist solely of **10** (as the chloroform solvate), Fig. 2. The structure is not a high quality one (see Section 2) and does not justify detailed discussion. Nevertheless there are a few points worth mentioning. The two axial Ru–Cl bonds deviate from linearity to a greater extent (165.7(3)°) than in **4a**. While the $M\text{–}Cl_{(terminal)}$ bond on the ruthenium ion is significantly shorter than the $M\text{–}Cl_{(bridge)}$ ones that distinction is not made for the bonds to rhodium. This contrasts [17] with the situation found for $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ where the bonds to the axial chloride ligands are significantly shorter. The angles at the bridging chlorides are obtuse consistent with no direct bonding between the metals (Ru...Rh 3.76 Å).

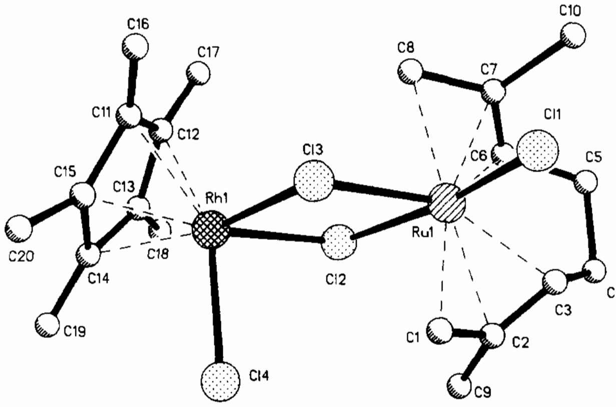


Fig. 2. Crystal structure of $[(\eta^3:\eta^3\text{-}C_{10}H_{16})ClRu(\mu\text{-}Cl)_2RhCl(\eta^5\text{-}C_5Me_5)]$ (**10**) showing the atom numbering scheme adopted.

Acknowledgements

We thank Johnson Matthey plc for generous loans of ruthenium trichloride and the SERC for a studentship (to J.W.S.) and for provision of the X-ray equipment.

References

[1] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 3rd edn., 1972, p. 1032.
[2] Ch. Elschenbroich and A. Saltzer, *Organometallics*, VCH, Weinheim, Germany, 1989, p. 236.
[3] T.A. Stephenson, E.S. Switkes and L. Ruiz-Ramirez, *J. Chem. Soc., Dalton Trans.*, (1973) 2112.
[4] R.R. Schrock and J.A. Osborn, *J. Am. Chem. Soc., 93* (1971) 2397; L.M. Haines, *Inorg. Chem., 10* (1971) 1685, and refs. therein.
[5] L. Ruiz-Ramirez and T.A. Stephenson, *J. Chem. Soc., Dalton Trans.*, (1974) 1640.
[6] L. Porri, M.C. Gallazzi, A. Colombo and G. Allegra, *Tetrahedron Lett., 47* (1965) 4187.
[7] D.N. Cox and R. Roulet, *Inorg. Chem., 29* (1990) 1360.
[8] J.G. Toerien and P.H. van Rooyen, *J. Chem. Soc., Dalton Trans.*, (1991) 1563.
[9] G.M. Sheldrick, *SHELXTL PLUS*, an integrated system for refining and displaying crystal structures from diffraction data, University of Göttingen, Germany, 1986.
[10] A. Colombo and G. Allegra, *Acta Crystallogr., Sect. B, 27* (1971) 1653.
[11] J.W. Steed and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1992) 2765.
[12] P.B. Hitchcock, J.F. Nixon and J. Sinclair, *J. Organomet. Chem., 86* (1975) C34.
[13] J.W. Steed and D.A. Tocher, *J. Organomet. Chem., 412* (1991) C34.
[14] J.W. Steed and D.A. Tocher, *Polyhedron, 11* (1992) 2729.
[15] G. Belchem, J.W. Steed and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1994) 1949.
[16] G. Belchem, J.W. Steed and D.A. Tocher, *J. Organomet. Chem., 460* (1993) C30.
[17] M.R. Churchill, S.A. Julis and F.J. Rotella, *Inorg. Chem., 16* (1977) 1137.