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The synthesis, structural characterisation and variable temperature ^{1}H NMR study of the bis-toluene hexaruthenium carbidocarbonyl cluster $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5Me)]$ *

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Abstract

The synthesis, chemical characterisation and single crystal X-ray structural study of the bis-toluene hexaruthenium carbidocarbonyl cluster $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5Me)]$ is reported. A variable temperature ^{1}H n.m.r. study reveals that in solution the complex exists in two isomeric forms, one of them, that observed in the solid state and the other the *trans*-$[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)_2]$ isomer. Interchange of the toluene ligand between the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ and η^6 co-ordination mode if confirmed by deuterum labelling experiments involving $C_6D_5CD_3$.

1. Introduction

The bis-benzene cluster $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **(1a)** has been known for some time [1]. It and the related species $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ were the first reported examples in organometallic cluster chemistry of benzene coordinated symmetrically over a trimetal face. Since that initial report, the chemistry of both species has been developed extensively, as has that of the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ benzene ligand in other cluster systems. The bis-benzene cluster is of considerable interest because the two benzene ligands adopt different bonding modes to the central cluster unit, *i.e.* one is in the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ face-capping mode, and the other in the more commonly found η^6 terminal coordination mode. More recently, it has been found that two further isomeric forms of this complex exist. Heating the bis-benzene complex **1a** in nonane yields *trans*-$[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2]$ **(1c)**, in which the metal core is sandwiched between two benzene groups [2a]. In contrast, on standing at low temperature, *cis*-$[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2]$ **(1b)** is produced [2b]; in this complex the two terminal benzene ligands are bonded to ruthenium atoms adjacent to each other within the octahedral metal framework. These complexes are illustrated in Scheme 1.

Other related bis-arene Ru_6C clusters in which two different arene moieties are present have also been prepared. In these systems the two arenes adopt different coordination modes. For example, it has been found that for the range of mixed arene-benzene complexes $[Ru_6C(CO)_{11}(\eta^6\text{-arene})(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **(2a–2c)** (where arene = C_6H_5Me, $C_6H_4Me_2$ and

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* Dedicated to Professor M.F. Lappert on the occasion of his 65th birthday.

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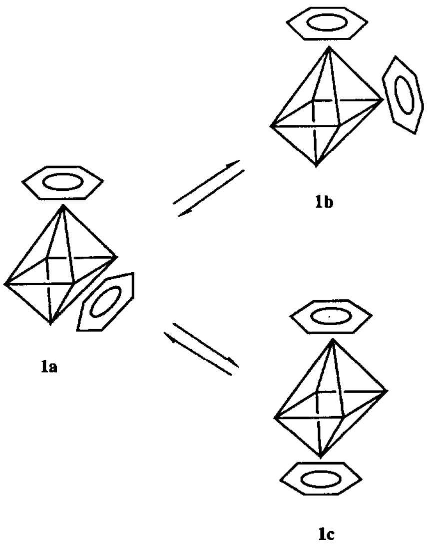
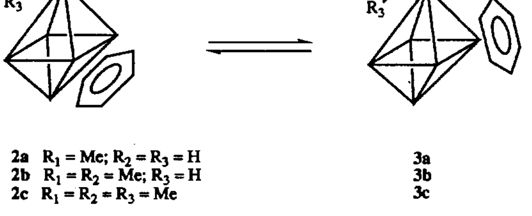


Scheme 1. The three isomers of $[Ru_6C(CO)_{11}(C_6H_6)_2]$.

$1,3,5\text{-}C_6H_3Me_3$) [2b] the arene always adopts an η^6 bonding mode, whereas the benzene displays μ_3-$\eta^2:\eta^2:\eta^2$ co-ordination. During a prolonged period the benzene ligand undergoes migration at low temperatures to yield the *cis*-$[Ru_6C(CO)_{11}(\eta^6\text{-arene})(\eta^6\text{-}C_6H_6)]$ derivatives for all these arenebenzene species, as shown in Scheme 2. In contrast, the bis-mesitylene complex $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)_2]$ (**3**) is obtained in the trans-form, and has not been observed to undergo any transformations from its sandwichtype structure [3].

These complexes **1–3** raise some fundamental questions in respect of the factors that govern the co-ordination mode preferred by a particular arene. While electronic and steric effects can be reasonably expected to control the bonding type, it is not easy to assess their relative contribution. Hence, a study of the bis-toluene cluster was carried out in order to increase the understanding of such factors.



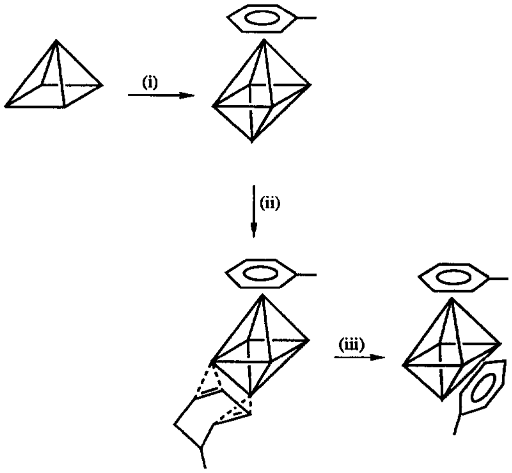
2a $R_1 = Me; R_2 = R_3 = H$ **3a**
2b $R_1 = R_2 = Me; R_3 = H$ **3b**
2c $R_1 = R_2 = R_3 = Me$ **3c**

Scheme 2. Interconversion of the mixed hexaruthenium arene-benzene complexes **2a–2c**.

2. Results and discussion

2.1. *Synthesis and chemical characterisation*

The synthesis of the bis-toluene complex involves the separate addition of each toluene ligand, in a sequence similar to that employed for the preparation of arene-benzene complexes $[Ru_6C(CO)_{11}(\eta^6\text{-arene})(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (**1a**, **2a–2c**). Scheme 3 illustrates this reaction pathway. Ionic coupling between the dianionic cluster $[Ru_5C(CO)_{14}]^{2-}$ and the ruthenium toluene dication $[Ru(\eta^6\text{-}C_6H_5Me)(MeCN)_3]^{2+}$ yields the known complex $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$, prepared by heating $[Ru_3(CO)_{12}]$ in toluene [4]. Spectroscopic data for this product are in good agreement with those reported earlier. The dropwise addition of two molecular equivalents of trimethylamine-N-oxide (Me_3NO) in dichloromethane to a solution of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ in dichloromethane/dihydrotoluene (dihydrotoluene = 1-methylcyclohexa-2,5-diene) yields a series of inseparable isomers of formula $[Ru_6C(CO)_{12}(C_6H_5Me)(C_6H_7Me)]$ (**4**). Formulation of this complex is based on the mass spectrum, which shows a strong molecular ion peak at 1140 amu (calc. = 1141 amu). The ^1H NMR spectrum of the reaction mixture is extremely complicated and has not been fully resolved. However, there appear to be at least four major isomers present. A comparison of the carbonyl stretching frequencies in the infrared spectrum of this isomeric mixture with those of the arene-cyclohexadiene compounds $[Ru_6C(CO)_{11}(\eta^6\text{-arene})(\mu_2\text{-}\eta^2:\eta^2\text{-}C_6H_8)]$ (where arene = C_6H_6, C_6H_5Me,



Scheme 3. Synthesis of $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}\eta^2:\eta^{2\prime}:\eta^2\text{-}C_6H_5Me)]$. Reagents and conditions: (i) addition of $[Ru(\eta^6\text{-}C_6H_5Me)(MeCN)_3]^{2+}$ to a refluxing solution of $[Ru_5C(CO)_{14}]^{2-}$ in CH_2Cl_2, (ii) Me_3NO added dropwise to a solution of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ in CH_2Cl_2 (−78°C–RT) (iii) Me_3NO added dropwise to a solution of $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_2\text{-}\eta^2:\eta^2\text{-}C_6H_7Me)]$.

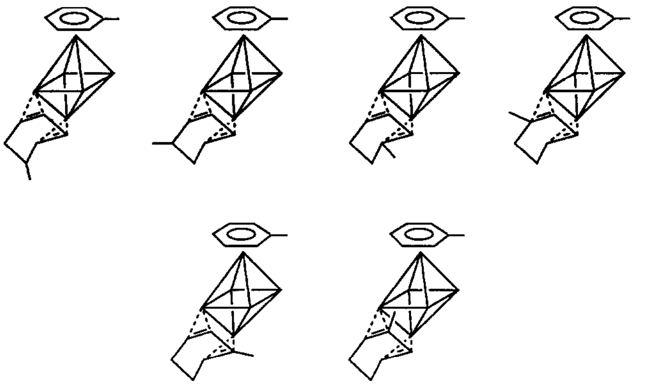


Fig. 1. The proposed isomeric forms of [$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_2\text{-}\eta^2:\eta^2\text{-}C_6H_7Me)$].

$C_6H_4Me_2$ and $C_6H_3Me_3$) [2b] shows that the same gross features are present. The profiles of the spectrum in the ν_{CO} region are almost identical, and the bands affect at similar wavenumbers. On this basis we believe that the structures of these isomers and that of the arenecyclohexadiene compounds **4** are essentially similar. Thus, the more precise formulation [$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_2\text{-}\eta^2:\eta^2\text{-}C_6H_7Me)$] can be given with reasonable confidence, with isomers arising from the potential arrangement of the double bonds of the diene (initially in the 1,4-form) and hence the position of the methyl group relative to co-ordination. Figure 1 shows these possible isomeric derivatives.

Reaction of [$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_2\text{-}\eta^2:\eta^2\text{-}C_6H_7Me)$] with a further molecular equivalent of Me_3NO in dichloromethane results in the formal dehydrogenation of the C_6H_7Me ring to yield the bis-toluene cluster [$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)_2$] (**5a**). The parent peak in the mass spectrum of this compound is at 1111 amu, correct for the proposed formulation. The ^1H NMR spectrum of **5a** is shown in Fig. 2. The signals are labelled A–H, and those at δ 5.73, 5.49, 5.02 and 2.32 ppm may be attributed to an η^6 toluene ligand, while those at lower frequency, at δ 4.36, 4.18, 3.76 and 2.21 ppm, are from the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ bonded toluene. This difference in chemical shift is comparable with that observed for the analogous bis-benzene complex [$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2C_6H_6)$] [1], which exhibits singlets at δ 5.54 and 4.14 ppm for the protons of the terminal and face-capping benzene ligands, respectively. It is noteworthy that for both toluene rings the signals are similar. In each case the signals arising from the methyl groups are singlets of relative

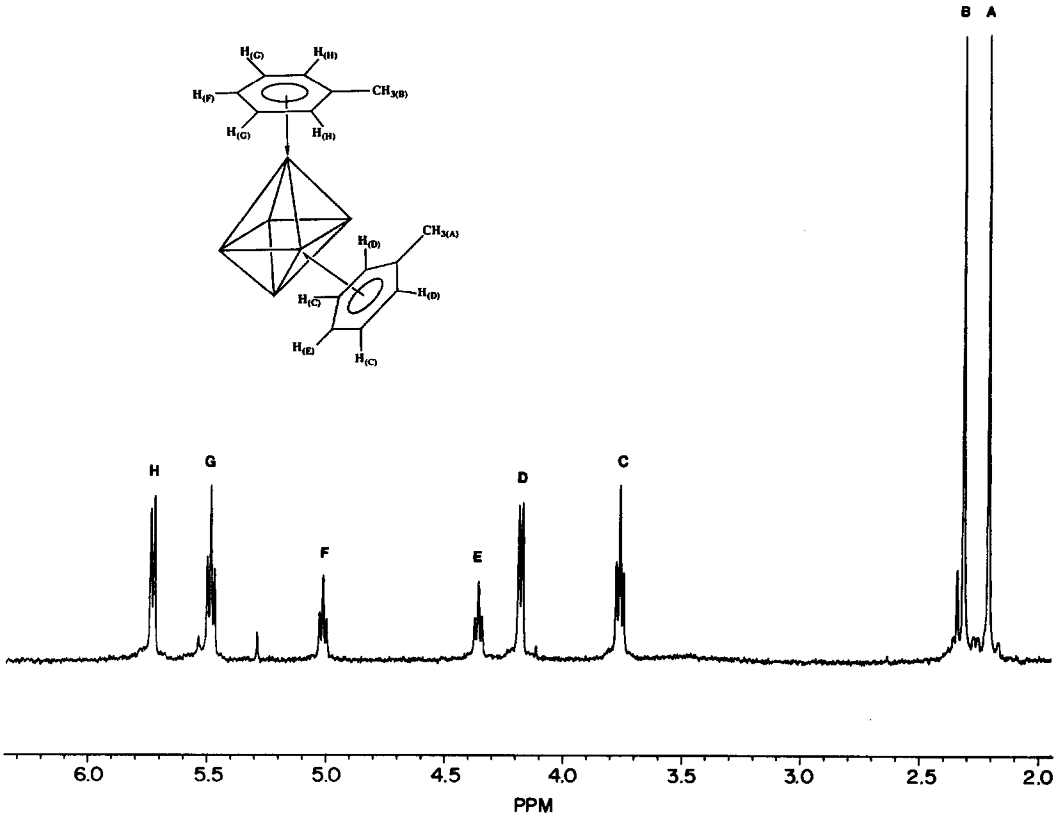


Fig. 2. The ^1H NMR spectrum of [$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5Me)$] and the diagram showing the assignment of protons, labelled A–H.

intensity three. The *ortho*-proton signals are doublets of relative intensity two, while the signals of the *meta*- and *para*-protons are both triplets of relative intensities two and one, respectively. All coupling constants are of the order of 6 Hz. The signal assignment shown in Fig. 2 was confirmed by a homonuclear COSY experiment. The bis-toluene complex can therefore be described by the formula $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5Me)]$. To reiterate, the mean chemical shift of the μ_3-$\eta^2:\eta^2:\eta^2$ toluene group is at a significantly lower frequency than that observed for the η^6 ligand, and even more so relative to that for free toluene, these being centred at δ 5.41, 4.10, and 7.42 ppm, respectively. This change may be taken to indicate a reduction in ring current on moving from anuncoordinated, through a η^6-coordinated to a μ_3-$\eta^2:\eta^2:\eta^2$ co-ordinated moiety, and with increase in the olefinic nature of the ring. This feature is also apparent from the X-ray structure (see below), in which the methyl group shows a considerably larger out-of-plane bending away from the cluster surface than is observed for the η^6 ligand. This feature may be attributed to an increase in the p-character of the substituted ring carbon from sp^2 to sp^3, a feature that has been examined in some detail for the triosmium cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ [5].

2.2. *X-Ray structure of* $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5Me)]$ *(5a)*

The solid state molecular structure of **5a** was determined by single crystal X-ray diffraction. The molecular structure is shown in Fig. 3, together with the labelling scheme. Relevant bond distances and angles are listed in Table 1.

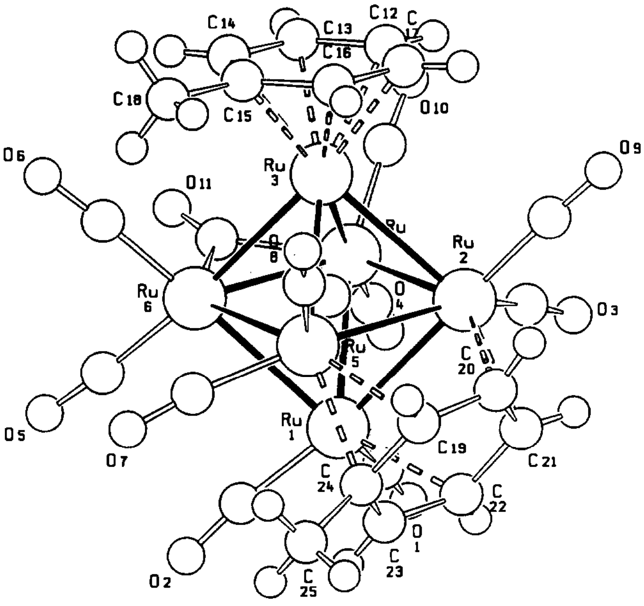


Fig. 3. The molecular structure of **5a** in the solid state. The C-atoms of the CO-groups bear the same labelling as the corresponding O-atoms.

TABLE 1. Selected bond lengths (Å) and angles (deg) for **5a**

Ru(1)–Ru(5)	2.824(1)	Ru(3)–C(17)	2.22(1)
Ru(1)–Ru(2)	2.824(1)	Ru(3)–C(13)	2.23(1)
Ru(1)–Ru(6)	2.904(1)	Ru(3)–C(16)	2.23(1)
Ru(1)–Ru(4)	2.919(1)	Ru(3)–C(14)	2.25(1)
Ru(2)–Ru(4)	2.880(1)	Ru(3)–C(15)	2.28(1)
Ru(2)–Ru(3)	2.883(1)	Ru(5)–C(19)	2.24(1)
Ru(2)–Ru(5)	2.929(1)	Ru(5)–C(24)	2.30(1)
Ru(3)–Ru(5)	2.866(1)	Ru(6)–C(10)	1.86(1)
Ru(3)–Ru(4)	2.875(1)	C(1)–O(1)	1.16(1)
Ru(3)–Ru(6)	2.883(1)	C(2)–O(2)	1.14(1)
Ru(4)–Ru(6)	2.813(1)	C(3)–O(3)	1.15(1)
Ru(5)–Ru(6)	3.014(1)	C(4)–O(4)	1.14(1)
Ru(1)–C	2.08(1)	C(5)–O(5)	1.15(1)
Ru(2)–C	2.05(1)	C(6)–O(6)	1.13(1)
Ru(3)–C	1.93(1)	C(7)–O(7)	1.12(1)
Ru(4)–C	2.09(1)	C(8)–O(8)	1.15(1)
Ru(5)–C	2.03(1)	C(9)–O(9)	1.14(1)
Ru(6)–C	2.08(1)	C(10)–O(10)	1.15(1)
Ru(1)–C(2)	1.87(1)	C(11)–O(11)	1.17(1)
Ru(1)–C(1)	1.89(1)	C(12)–C(17)	1.39(1)
Ru(2)–C(3)	1.88(1)	C(12)–C(13)	1.40(1)
Ru(2)–C(4)	1.89(1)	C(13)–C(14)	1.38(1)
Ru(3)–C(12)	2.19(1)	C(14)–C(15)	1.41(1)
Ru(4)–C(5)	1.87(1)	C(15)–C(16)	1.43(1)
Ru(4)–C(6)	1.87(1)	C(15)–C(18)	1.50(1)
Ru(4)–C(11)	2.04(1)	C(16)–C(17)	1.40(1)
Ru(5)–C(8)	1.89(1)	C(19)–C(24)	1.39(1)
Ru(5)–C(7)	1.89(1)	C(19)–C(20)	1.43(1)
Ru(6)–C(9)	1.90(1)	C(20)–C(21)	1.41(1)
Ru(6)–C(11)	2.05(1)	C(21)–C(22)	1.44(1)
Ru(1)–C(23)	2.26(1)	C(22)–C(23)	1.39(1)
Ru(1)–C(22)	2.31(1)	C(23)–C(24)	1.46(1)
Ru(2)–C(21)	2.20(1)	C(24)–C(25)	1.51(1)
Ru(2)–C(20)	2.34(1)		
O(1)–C(1)–Ru(1)	174(1)	O(7)–C(7)–Ru(5)	172(1)
O(2)–C(2)–Ru(1)	174(1)	O(8)–C(8)–Ru(5)	176(1)
O(3)–C(3)–Ru(2)	170(1)	O(9)–C(9)–Ru(6)	176(1)
O(4)–C(4)–Ru(2)	177(1)	O(10)–C(10)–Ru(6)	176(1)
O(5)–C(5)–Ru(4)	178(1)	O(11)–C(11)–Ru(4)	138(1)
O(6)–C(6)–Ru(4)	177(1)	O(11)–C(11)–Ru(6)	135(1)

The structure of **5a** is closely related to that of the bis-benzene derivatives $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$, and those of the mixed arenes $[Ru_6C(CO)_{11})(\eta^6\text{-arene})(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (arene $= C_6H_5Me$, $C_6H_4Me_2$) previously reported [1,2b]. All these species share a common feature: one arene is apically bound (η^6-coordination mode) while benzene is bound in facial mode (μ_3-coordination). Compound **5a** is novel in that the facial ligand is not benzene but toluene, thus providing the first example of a facial-apical isomer in which both ligands are methyl-substituted benzenes. The CO-ligand distribution is that common to most bis-arene derivatives of $Ru_6C(CO)_{17}$, *viz*. one bridging CO spanns the edge opposite to the facial ligand, while the remaining ten CO's are terminally bound and show different degrees of bending. As can be seen from Fig. 3, the presence of a methyl group on the facial ligand appears to give rise to steric interaction to the extent that the Me-group is bent out-of-plane with respect to the plane defined by the C_6-ring. This out-of-plane bending may also be due (at least in part) to electronic influences. Within this molecule, the elevation of the methyl group above the plane of the face-capping ring is 0.6 Å, while that of the terminal ring displays no out-of-plane bonding.

The C–C bond lengths within the facial ligand alternate in length, with the short bonds [average 1.40(1) Å] interacting directly with the underlying Ru-atoms, and the long bonds [average 1.44(1) Å] parallel to the Ru–Ru bonds. Similar bond length distribution was previously observed in the arene cluster $[Ru_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ [6], and in several other derivatives containing facial ligands for which the diffraction data were of reasonably high quality [2b,7]. In the present case it is interesting to observe this pattern for a toluene ligand, whose symmetry differs from that of benzene. The Ru–C distances in the apical and facial ligands do not differ appreciably in their mean values [2.23(1) *vs*. 2.28(1) Å, respectively], although the Ru–C(facial) distances alternate in length [2.24(1) *vs*. 2.32(1) Å], reflecting the rather strained steric situation of the ligand. C–C bond lengths average 1.42(1) Å in the apical ligand.

Ru–Ru bond lengths range from 2.814(1) to 3.014(1) Å, the shortest bond corresponding to the CO-bridged edge. As previously observed in most arene derivatives of $Ru_6C(CO)_{17}$ the C(carbide) atom is not located in the middle of the octahedral cavity, but is displaced towards the Ru-atom carrying the η^6-bound ligand [Ru(3)–C 1.925(7) *vs*. a range of 2.031(7)–2.086(7) Å for the remaining distances].

2.3. Variable temperature and toluene-d_8 ^1H NMR spectroscopy

Figure 4 shows the series of ^1H NMR spectra recorded in the range 295–385 K at regular intervals. The most notable feature is that as the temperature is raised more signals appear around those stemming from the η^6 toluene ligand, for both the aromatic and methyl resonances. This complexity may be attributed to the presence of two isomers of $[Ru_6C(CO)_{11}(C_6H_5Me)_2]$. One is similar to that observed in the solid state (**5a**), and dominates at lower temperature, while the other is thought to be *trans*-$[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)_2]$. (**5b**), and is derived by migration of the

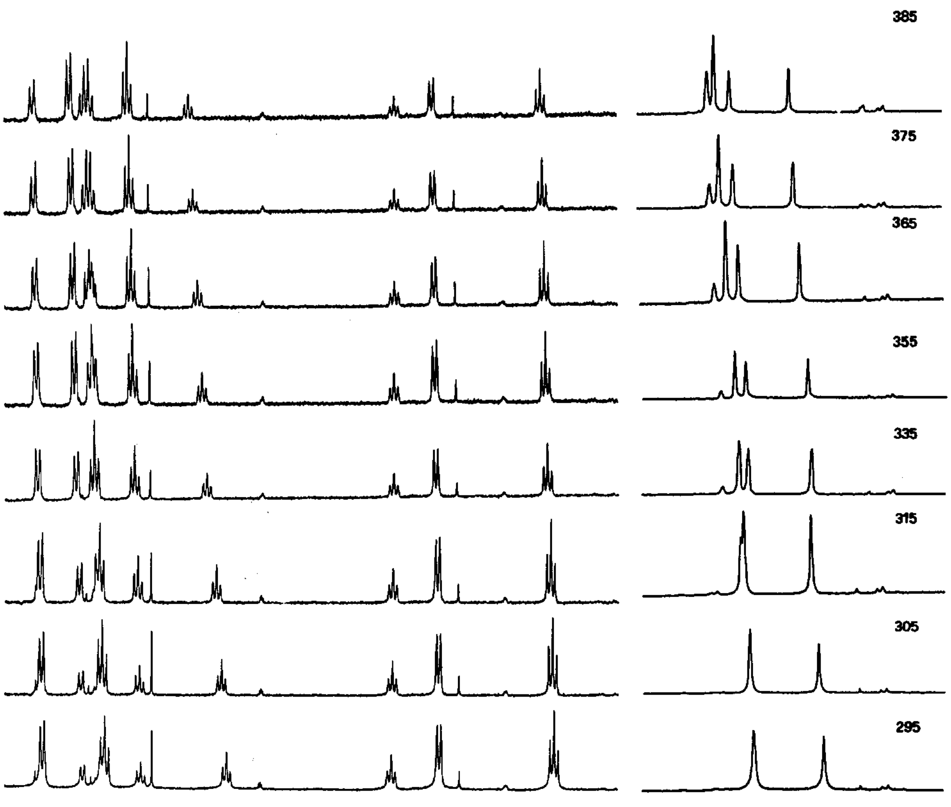


Fig. 4. The variable temperature ^1H NMR of **5**, recorded between 295 and 385 K.

μ_3-$\eta^2:\eta^2:\eta^2$-C_6H_5Me ligand to an η^6 site. This second isomeric form is similar to that of **3**, with the two toluene groups attached to ruthenium atoms at opposite ends of the octahedral framework. The *trans*- (as opposed to the *cis*-) formulation is proposed because heating of the analogous bis-benzene complex $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **1a** yields *trans*-$[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2]$ **1c**. For the bis-toluene cluster the amount of trans-isomer increases with temperature, *i.e.* the equilibrium is displaced to the right hand side of eqn. (1).

$$\underset{\textbf{5a}}{[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_5Me)]} \leftrightarrow \underset{\textbf{5b}}{[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)_2]} \qquad (1)$$

At 295 K, signals at δ 5.58, 5.50, 5.35 and 2.32 ppm may be attributed to the two chemically equivalent η^6 moieties. Although the signals at δ 5.50 and 2.32 ppm overlap others, they are resolved as the temperature increases. The singlet at δ 2.35 ppm arises from the presence of free toluene generated by decomposition of the compound during heating.

As the temperature is raised the signals attributed to isomer **5b** increase in intensity, while the resonances assigned to isomer **5a** all decrease in intensity. At 295 K the ratio of **5a**/**5b** is estimated to be 9:1. The ratio changes to 1:1 at 385 K. When the sample is recooled to 295 K the ratio of **5a**/**5b** returns to approximately 8:1, approximately the same value observed initially for the non-crystalline sample. Saturation transfer experiments showed no exchange between the μ_3-$\eta^2:\eta^2:\eta^2$ and η^6 toluene groups, even with a 30 s mixing time. Hence, the NMR data are not suitable for thermodynamic calculations, since the exchange process is slow, and equilibrium had not been reached when the spectra were recorded.

In a separate experiment a solution of compound **5** in $C_6D_5CD_3$ was kept for several weeks at room temperature. No appreciable exchange of bonded toluene with toluene-d_8 was observed during this period, indicating that the interconversion takes place by a non-dissociative mechanism. In an additional experiment the mixed complex $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6D_5CD_3)(\mu_3\text{-}\eta^2:\eta^{2\prime}:\eta^2\text{-}C_6H_5Me)]$ was prepared by a route similar to that shown in Scheme 3. Monitoring of the ^1H NMR spectrum of this compound revealed scrambling of the toluene ligand between the two potential sites. These observations are consistent with a unimolecular process.

3. Experimental details

3.1. General synthetic and spectroscopic details

All reactions were carried out with the exclusion of air using solvents freshly distilled under dry nitrogen. Subsequent work-up of products was carried out without precautions to exclude air, with standard laboratory grade solvents. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR in CH_2Cl_2 using NaCl cells. Positive fast atom bombardment mass spectra were obtained with a Kratos MS50TC spectrometer, with CsI as calibrant. ^1H NMR spectra were recorded in $CDCl_3$ (variable temperature, in tetrachloroethane-d_4) using Bruker WP250 and AM360 instruments referenced to internal TMS. Products were separated by chromatography on silica gel. $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ was prepared according to the literature procedure [2b]. Dihydrotoluene (1-methylcyclohexa-2,5-diene) and toluene-d_8 were purchased from Aldrich Chemicals and used without further purification. Trimethylamine-N-oxide (Me_3NO) was sublimed prior to reaction.

3.2. Reaction of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ with dihydrotoluene and 2 molar equivalents of Me_3NO

To a solution of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ (90 mg) in dichloromethane (30 ml) containing an excess of dihydrotoluene (2 ml) was added a solution of Me_3NO (2.1 mol. equiv.) in dichloromethane (5 ml). The mixture was stirred for 25 min, after which IR spectroscopy indicated complete consumption of the starting material. The solvent was removed *in vacuo* and the products separated by TLC with dichloromethane/hexane (40:60) as eluent. The major brown band was characterised as $[Ru_6C(CO)_{12}(C_6H_5Me)(C_6H_7Me)]$ (23 mg). The minor red band was characterised as $[Ru_6C(CO)_{11}(C_6H_5Me)_2]$ (5 mg).

Spectroscopic data for $[Ru_6C(CO)_{12}(C_6H_5Me)(C_6H_7Me)]$: IR ($CH_2Cl_2$): (CO) 2037 (m), 1999 (vs), 1949 (w), 1795 (w, br) cm^{-1}; positive FAB MS: $M^+ =$ 1137 (calc. = 1135) amu.

Spectroscopic data for $[Ru_6C(CO)_{11}(C_6H_5Me)_2]$: IR ($CH_2Cl_2$): (CO) 2037 (m), 1999 (vs), 1949 (w), 1795 (w, br) cm^{-1}; positive FAB MS: $M^+ = 1105$ (calc. = 1105) amu.

3.3. Reaction of $[Ru_6C(CO)_{12}(C_6H_5Me)(C_6H_7Me)]$ with 1 molar equivalent Me_3NO

To a solution of $[Ru_6C(CO)_{12}(C_6H_5Me)(C_6H_7Me)]$ (20 mg) in dichloromethane (20 ml) was added dropwise a solution of Me_3NO (3 mg, 1.1 mol. equiv.) in dichloromethane (3 ml). The mixture was stirred for a further 15 min, after which IR spectroscopy that reaction was complete. The solvent was removed *in vacuo* and the products separated by tlc with dichloromethane/hexane (40:60) as eluent. The brown and red bands were eluted and characterised spectroscopically as the starting material $[Ru_6C(CO)_{12}(C_6H_5Me)(C_6H_7Me)]$ (7 mg) and $[Ru_6C(CO)_{12}(C_6H_5Me)_2]$ (5 mg).

3.4. *Thermolysis of [$Ru_3C(CO)_{12}$] with toluene-d_8 in octane*

A solution of [$Ru_3C(CO)_{12}$] (500 mg) in octane (20 ml) and toluene-d_8 was heated under reflux for 4 h. IR spectroscopy indicated complete consumption of the starting material. The solvent was removed *in vacuo* and the products isolated by column chromatography with dichloromethane/hexane (40:60) as eluent. The major, brown, product was characterised as [$Ru_6C(CO)_{14}(\eta^6\text{-}C_6D_5CD_3)$] (110 mg).

Spectroscopic data for [$Ru_6C(CO)_{14}(\eta^6\text{-}C_6D_5CD_3)$]: IR ($CH_2Cl_2$): (CO) 2076 (m), 2025 (vs), 1816 (w, br) cm^{-1}; positive FAB MS: $M^+ = 1111$ (calc. = 1111) amu.

Preparation of the bis-toluene complex from [$Ru_6C(CO)_{14}(\eta^6\text{-}C_6D_5CD_3)$] follows the procedure outlined for [$Ru_6C(CO)_{14}(\eta^6\text{-}C_6D_5CD_3)$] (above).

3.5. *X-Ray structure determination of* **5a**

Diffraction data for compound **5a** were collected at room temperature in the ω–2θ scan mode on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo-Kα radiation, λ = 0.71069 Å). Crystal data and measurements details are summarized in Table 2. The structure was solved by direct methods followed by Fourier difference synthesis and subsequent least-squares refinement. For all calculations the SHELX86 [8] and SHELX92 [9] programs were used. All non-H atoms were treated anisotropically. Hydrogen atoms were added in calculated positions ($C_{sp^2} - H = 0.93$, $C_{sp^3} - H = 0.96$ Å) and refined 'riding' on their respective C atoms. Fractional atomic coordinates are reported in Table 3.

Additional material is available from the Cambridge Crystallographic Data Centre and comprises H-atom

TABLE 2. Crystal data and details for measurements for **5a**

	5a
Formula	$C_{26}H_{16}O_{11}Ru_6$
Mol. Wt.	1144
Crystal size (mm)	0.12×0.15×0.10
System	triclinic
Space group	$P\bar{1}$
a (Å)	10.156(2)
b (Å)	17.286(4)
c (Å)	9.421(3)
α (°)	93.92(2)
β (°)	111.69(2)
γ (°)	79.71(2)
U (Å^3)	1512
Z	2
F (000)	1080
D_{calcd} (g cm^{-3})	2.51
λ (MoKα) (Å)	0.71069
μ (MoKα) (cm^{-1})	30.41
θ-range (°)	3–25
Scan mode	$\omega - 2\theta$
Octants explored ($h_{min}h_{max}$, $k_{min}k_{max}$, $l_{min}l_{max}$)	−12 12, −20 20, 0 11
Measured reflections	5635
Observed reflections	5284 [R(int) = 0.054]
Unique observed reflections [$I_o > 2\sigma(I_o)$]	3252
No. of refined parameters	396
GOF on F^2	1.02
Final R indices [$I > \sigma(I)$] R_1 (on F), wR_2 (on F^2)	0.031, 0.075
Final R indices (all data)] R_1 (on F), wR_2 (on F^2)	0.084, 0.092

TABLE 3. Fractional atomic coordinates (×10^4) for **5a**

Atom	x	y	z
Ru(1)	7731(1)	3155(1)	1860(1)
Ru(2)	5384(1)	3375(1)	2853(1)
Ru(3)	5797(1)	1700(1)	3259(1)
Ru(4)	5313(1)	2326(1)	326(1)
Ru(5)	8191(1)	2508(1)	4710(1)
Ru(6)	8018(1)	1457(1)	1981(1)
C	6728(8)	2394(4)	2578(8)
C(1)	7022(10)	3686(5)	−29(10)
O(1)	6688(9)	4042(4)	−1145(8)
C(2)	9520(12)	2868(5)	1665(12)
O(2)	10601(9)	2764(4)	1515(12)
C(3)	4124(10)	3828(5)	980(10)
O(3)	3369(8)	4209(4)	−49(8)
C(4)	3899(9)	3535(5)	3645(10)
O(4)	2983(8)	3669(5)	4091(8)
C(5)	4913(10)	2732(5)	−1603(10)
O(5)	4628(9)	2974(5)	−2805(7)
C(6)	3528(11)	1993(6)	−468(10)
O(6)	2423(8)	1820(5)	−951(8)
C(7)	10043(10)	1946(5)	4973(9)
O(7)	11202(7)	1681(4)	5237(8)
C(8)	8253(10)	2161(6)	6595(10)
O(8)	8343(8)	1980(5)	7778(7)
C(9)	9513(10)	1200(5)	1193(10)
O(9)	10376(8)	1006(4)	681(8)
C(10)	8422(9)	406(5)	2548(10)
O(10)	8707(8)	−255(4)	2829(9)
C(11)	6459(10)	1300(5)	−101(9)
O(11)	6312(8)	816(4)	−1048(7)
C(12)	3622(9)	1478(5)	2785(11)
C(13)	4344(10)	820(5)	2261(10)
C(14)	5620(10)	421(5)	3268(10)
C(15)	6243(9)	651(5)	4801(10)
C(16)	5462(9)	1318(5)	5294(10)
C(17)	4154(9)	1712(5)	4300(11)
C(18)	7619(10)	220(5)	5892(11)
C(19)	8136(10)	3703(5)	5795(10)
C(20)	6697(10)	4071(5)	4975(10)
C(21)	6343(11)	4449(5)	3574(11)
C(22)	7445(13)	4384(5)	2934(11)
C(23)	8826(11)	3991(5)	3695(10)
C(24)	9200(10)	3633(5)	5178(10)
C(25)	10758(10)	3543(6)	6221(12)

coordinates, thermal parameters and remaining bond lengths and angles.

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