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The synthesis and characterisation of Ru_3, Ru_4 and Ru_6 clusters with styrene, 4-methylstyrene and 4-trifluoromethylstyrene†

Brian F. G. Johnson,*[a] Justin M. Matters,[a] Petra Escarpa Gaede,[b] Scott L. Ingham,[b] Nicholas Choi,[c] Mary McPartlin[c] and Mary-Ann Pearsall[c]

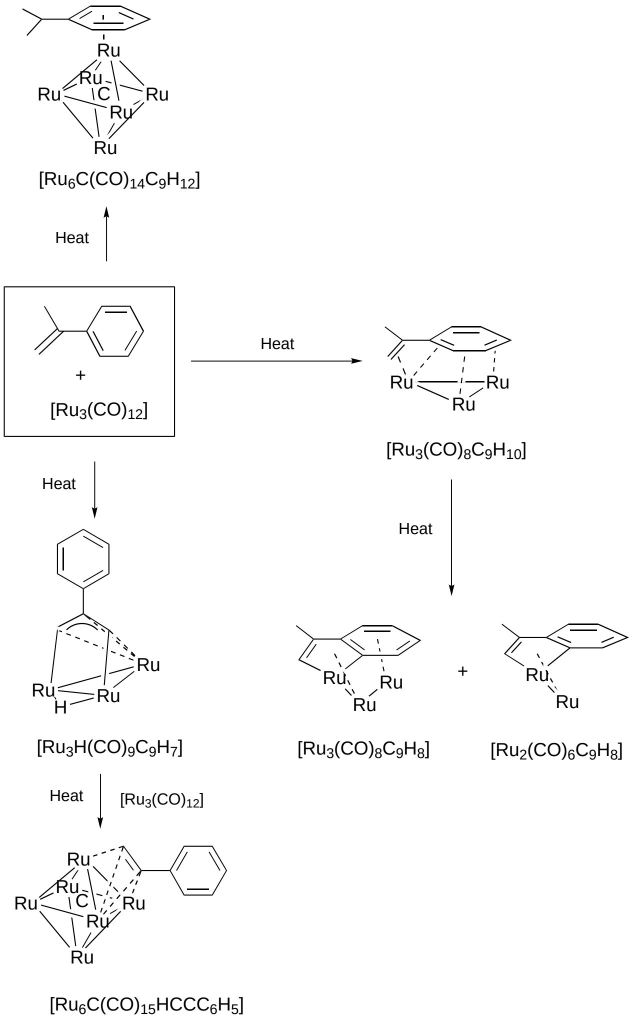
[a] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW*
[b] *University of Edinburgh, Department of Chemistry, Kings Buildings, West Mains Road, Edinburgh, UK EH9 3JJ*
[c] *University of North London, School of Applied Chemistry, 166–220 Holloway Road, London, UK N7 8DB*

The products of the thermolytic reaction of $[Ru_3(CO)_{12}]$ with styrene, 4-methylstyrene and 4-trifluoromethylstyrene respectively have been determined. In each case, compounds of the type $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}HCCC_6H_4R)]$ **1**, $[Ru_3(CO)_8\{\mu_3\text{-}\eta^6:\eta^2:\eta^1:\eta^1\text{-}HCC(H)C_6H_3R\}]$ **2** and $[Ru_6C(CO)_{14}(\eta^6\text{-}MeC_6H_4R)]$ **3** are observed (where R = H, Me or CF_3). The single-crystal structures of $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}HCCC_6H_5)]$ **1a**, $[Ru_3(CO)_8\{HCC(H)C_6H_3Me\}]$ **2b** and $[Ru_6C(CO)_{14}(\eta^6\text{-}1,4\text{-}Me_2C_6H_4)]$ **3b** have been determined. A fourth species $[Ru_6(CO)_{15}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}HCCC_6H_4R)(\eta^6\text{-}C_6H_4REt)]$ **4** is also reported, and a possible structure suggested.

The interaction of arene ligands with clusters has been an area of study for some years.[1] Clusters with arene ligands present are known to exist with nuclearities from three to eight, and there is interest in the analogy between arenes bound to metal clusters and the interaction of arenes with metal surfaces.[2] In general, arenes tend to co-ordinate in two main bonding modes; either terminal (η^6), or face capping ($\mu_3\text{-}\eta^2:\eta^2:\eta^2$). These bonding modes are known to undergo interconversion in some systems but the factors affecting the choice of bonding mode have been only partly elucidated.[1] We are interested in the effect of the additional functionality provided by unsaturated side-arms on the bonding mode of the arene group, and to this end we have prepared a variety of ruthenium clusters with unsaturated functional groups attached to the arene ligand including β-methylstyrene, isopropenylbenzene, diisopropenylbenzene and triisopropenylbenzene.

In this paper we wish to report the results of the thermolytic reaction of $[Ru_3(CO)_{12}]$ with an arene ring bearing a vinyl substituent. The vinyl functionality was selected because of its potential to form additional π bonds to the cluster. Related ligands with either an electron withdrawing (CF_3) or donating (CH_3) group *para* to the vinyl group were employed in order to investigate the possibility that favoured bonding modes could be altered by modifying the relative strengths of the π bonding of the vinyl and aryl functionalities to the cluster. We are able to report that both functionalities appear to be capable of binding to ruthenium clusters, and that one bonding mode is not significantly affected by the presence of either electron-donating or -withdrawing groups on the arene ring.

The interactions of isopropenylbenzene and diisopropenylbenzene have been reported previously.[3–5] These ligands display both η^6 and $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ as well as some more unusual bonding modes (see Scheme 1). In general, these ligands display reactivity which falls into one or more of four categories, *viz.* $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ co-ordination to a Ru_3 face, metallacycle formation, cluster build-up and finally allyl formation. Carbon–hydrogen bond activation together with the concomitant cleavage of a Ru–Ru bond was noted for $[Ru_3(CO)_8(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_9H_{10})]$ resulting in the loss of two hydrogen atoms and the formation of two Ru–C σ bonds to give $[Ru_3(CO)_8)(\mu_3\text{-}\eta^6:\eta^2:\eta^1:\eta^1\text{-}C_9H_8)]$.[5] Carbon–carbon bond cleavage was also noted in conjunction with cluster build-up to give $[Ru_6C(CO)_{15}(\mu_3\text{-}\eta^2:\eta^1:\eta^1\text{-}$



Scheme 1 The products of the reaction of isopropenylbenzene and $[Ru_3(CO)_{12}]$

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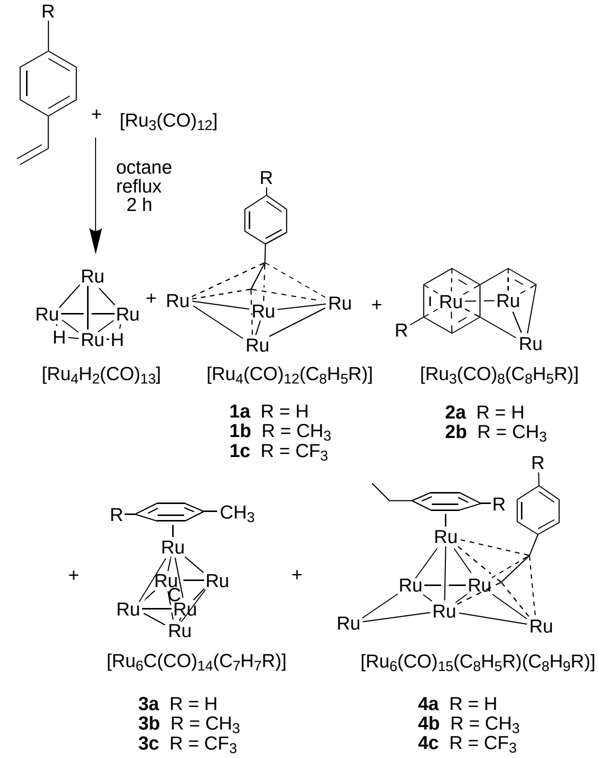
† This paper is dedicated to the memory of Sir Geoffrey Wilkinson FRS, a true friend.



Scheme 2 Products of the reaction of C_8H_7R with $[Ru_3(CO)_{12}]$

$C_8H_6)]$. Furthermore, an uncommon C−C bond cleavage was noted during cluster build-up from $[Ru_3H(CO)_9(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C_9H_7)]$ to give $[Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C_8H_6)]$[4] and another Ru_6C cluster $[Ru_6C(CO)_{14}(\eta^6\text{-}C_8H_6)]$ was also obtained. The mechanism of this bond cleavage has not been fully elucidated.[6]

In this paper we report that two of the four forms of reactivity observed for isopropenylbenzene and diisopropenylbenzene are also observed for styrene, 4-methylstyrene and 4-trifluoromethylstyrene, namely metallacycle formation and cluster build-up (see Scheme 2). Also, while allyl formation similar to that previously reported is not plausible for these species, analogous π donation from the vinyl unit would appear to be a feature of their reactivity. However, the styrene derivatives do not appear to be kinetically stable in the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ co-ordination mode on a Ru_3 face, so while the pathway to $[Ru_3(CO)_8\{\mu_3\text{-}\eta^6{:}\eta^2{:}\eta^1{:}\eta^1\text{-}HCC(H)C_6H_4\}]$ **2a** probably involves a $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ species similar to that shown in Scheme 1 for isopropenylbenzene, the subsequent Ru−Ru cleavage seems to occur readily, and only $[Ru_3(CO)_8\{\mu_3\text{-}\eta^6{:}\eta^2{:}\eta^1{:}\eta^1\text{-}HCC(H)C_6H_4\}]$ is observed. This change in stability in the absence of an α-methyl group is yet another example of the current unpredictability of bonding mode preference in cluster–arene systems.[1] Similar instability of the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ species has been observed in the analogous reaction with 4-phenylbutene.[6] No further reaction to produce a diruthenium product of type $[Ru_2(CO)_6(C_8H_5Me)]$ (see Scheme 1) was observed.

Cleavage of a carbon–carbon bond is also observed on a Ru_6 cluster. However, rather than the cleavage of a single bond, it would appear that the double bond between the exocyclic carbon atoms is preferentially broken and the resulting species doubly hydrogenated to give a methyl group. Whether the cleavage of this double bond takes place before, during or after cluster build-up has not been elucidated. Evidence is also presented for the production of a Ru_6 species with two differently co-ordinated arene ligands, and a possible structure suggested.

Some of the products found in this study have been previously reported. In particular $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}HCCC_6H_5)]$ has been observed previously as a product of a similar reaction,[7] while $[Ru_3(CO)_8(C_6H_5CHCH)]$ has been synthesised by the desulfurisation of thiophene.[8]

Table 1 Selected bond lengths (Å) and angles (°) for complex **1a** (molecule 1)

Ru(1)−C(1)	2.188(4)	C(1)−C(2)	1.451(6)
Ru(1)−C(2)	1.243(4)	C(2)−C(3)	1.494(6)
Ru(2)−C(1)	2.125(4)	C(3)−C(4)	1.385(7)
Ru(3)−C(2)	2.152(4)	C(3)−C(8)	1.383(6)
Ru(4)−C(1)	2.178(4)	C(4)−C(5)	1.381(7)
Ru(4)−C(2)	2.251(4)	C(5)−C(6)	1.374(8)
		C(6)−C(7)	1.356(9)
Ru(1)−Ru(2)	2.7130(5)	C(7)−C(8)	1.368(8)
Ru(1)−Ru(3)	2.7618(5)		
Ru(2)−Ru(3)	2.8369(5)		
Ru(2)−Ru(4)	2.7285(6)		
Ru(3)−Ru(4)	2.7240(5)		
Ru(1)−Ru(2)−Ru(3)	59.638(13)	C(1)−Ru(1)−Ru(3)	70.43(12)
Ru(1)−Ru(2)−Ru(4)	91.85(2)	C(1)−Ru(1)−C(2)	38.2(2)
Ru(1)−Ru(3)−Ru(2)	57.952(13)	C(1)−Ru(4)−Ru(2)	49.78(12)
Ru(2)−Ru(1)−Ru(3)	62.411(14)	C(1)−Ru(4)−Ru(3)	71.34(12)
Ru(3)−Ru(4)−Ru(2)	62.703(14)	C(1)−Ru(4)−C(2)	38.2(2)
Ru(4)−Ru(2)−Ru(3)	58.571(14)	C(2)−Ru(1)−Ru(2)	73.84(11)
Ru(4)−Ru(3)−Ru(1)	90.90(2)	C(2)−Ru(1)−Ru(3)	49.62(11)
Ru(4)−Ru(3)−Ru(2)	58.726(14)	C(2)−Ru(4)−Ru(2)	73.41(10)
C(1)−Ru(1)−Ru(2)	49.99(12)	C(2)−Ru(4)−Ru(3)	50.17(11)

Results and Discussion

The reaction of $Ru_3(CO)_{12}$ with styrene and its derivatives

The reaction of $[Ru_3(CO)_{12}]$ with styrene, 4-methylstyrene and 4-trifluoromethylstyrene in refluxing octane (127 °C) under a nitrogen atmosphere gave a mixture of products in low yields which were separated by TLC (Scheme 2). Three classes of compound were observed and identified as $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}HCCC_6H_4R)]$ **1**, $[Ru_3(CO)_8\{\mu_3\text{-}\eta^6{:}\eta^2{:}\eta^1{:}\eta^1\text{-}HCC(H)C_6H_3R\}]$ **2** (not observed for 4-trifluoromethylstyrene), and $[Ru_6C(CO)_{14}(\eta^6\text{-}MeC_6H_4R)]$ **3**; where R = H, Me or CF_3 respectively. A further class of compound has been tentatively identified as $[Ru_6(CO)_{15}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}HCCC_6H_4R)(\eta^6\text{-}EtC_6H_4R)]$ **4**. A further band was found to correspond to $[Ru_4H_2(CO)_{13}]$. Other products were present only in trace yields.

Repeating the reaction between $[Ru_3(CO)_{12}]$ and styrene at lower temperatures in either heptane (98) or cyclohexane (81 °C) under reflux over a longer time gave similar products to those found in octane. Heating at a higher temperature in nonane (151 °C) under reflux resulted in cluster breakdown, whilst in hexane (69 °C) no reaction was observed. In no case were the butterfly complexes α-$[Ru_4(CO)_9(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_8H_6)(\eta^6\text{-}C_8H_{10})]$ and β-$[Ru_4(CO)_9(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_8H_6)(\eta^6\text{-}C_8H_{10})]$ reported by previous researchers observed.[7]

The red tetranuclear cluster $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}HCCC_6H_5)]$ **1a** has been reported by previous workers.[7] The structure that they proposed has been confirmed by a single-crystal X-ray diffraction analysis (Fig. 1) (significant bond lengths and angles are given in Table 1). This shows the pseudo-octahedral form of the compound with the four ruthenium atoms in a butterfly arrangement and the two carbons of the alkynyl unit occupying the two remaining vertices of the octahedron. The C(1)−C(2) bond length of 1.451(6) Å is between that of a typical double bond (1.34 Å) and that of a typical single bond (1.54 Å). This lengthening of the C−C bond is consistent with the loss of electron density from the C−C π-bonding orbitals by donation to the four rutheniums and also by back donation from the 'hinge' ruthenium atoms (theoretical studies have shown that the 'wing-tip' ruthenium atoms do not back donate significantly[9]). The angle between the two triangular wings of the ruthenium butterfly in pseudo-octahedral **1a** is 113°; this compares with an angle of 115.5° in $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}PhCCPh)]$[10] and is of course far higher than the angle of 101° in pseudo-

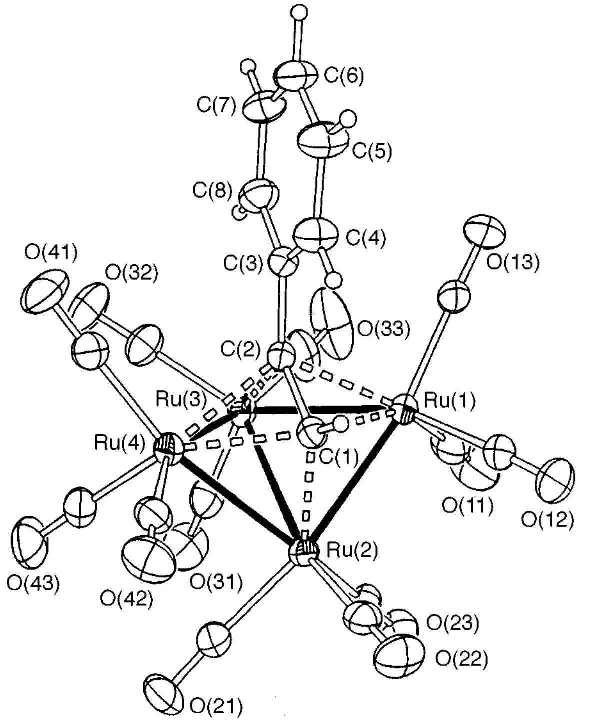


Fig. 1 Structure of $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^2:\eta^2:\eta^1:\eta^1\text{-}HCCC_6H_5)]$ **1a**

Table 2 Selected bond lengths (Å) and angles (°) for complex **2b**

Ru(1)–C(3)	2.356(5)	C(7)–C(8)	1.396(7)
Ru(1)–C(4)	2.277(5)	C(7)–C(6)	1.435(7)
Ru(1)–C(5)	2.276(5)	C(6)–C(5)	1.390(8)
Ru(1)–C(6)	2.281(5)	C(6)–C(9)	1.509(8)
Ru(1)–C(7)	2.274(5)	C(5)–C(4)	1.408(8)
Ru(1)–C(8)	2.355(4)	C(4)–C(3)	1.438(7)
Ru(2)–C(1)	2.237(5)	C(3)–C(8)	1.442(7)
Ru(2)–C(2)	2.249(5)	C(3)–C(2)	1.449(7)
Ru(3)–C(1)	2.060(5)	C(2)–C(1)	1.397(7)
Ru(3)–C(8)	2.096(5)		
Ru(1)–Ru(2)	2.9577(6)		
Ru(2)–Ru(3)	2.7838(6)		
Ru(1)–Ru(2)–Ru(3)	86.76(2)	C(3)–C(8)–Ru(1)	72.1(3)
Ru(3)–C(1)–Ru(2)	80.8(2)	C(2)–C(1)–Ru(3)	116.3(4)
Ru(3)–C(8)–Ru(1)	124.7(2)	C(3)–C(8)–Ru(3)	112.9(3)
C(1)–Ru(3)–C(8)	79.6(2)		

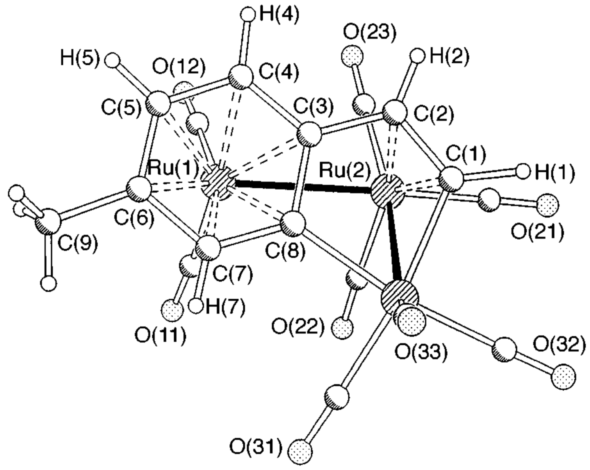


Fig. 2 Structure of $[Ru_3(CO)_8\{HCC(H)C_6H_3Me\}]$ **2b**

pentagonal bipyramidal $[Ru_5(\mu_3\text{-}H)(CO)_{14}(\mu_4\text{-}\eta^1:\eta^1:\eta^3:\eta^3\text{-}C_3H_2Ph)]$.

If the CH and CPh units are each regarded as donating three electrons the compound is a 62-electron species and corresponds to the observed butterfly arrangement with the four ruthenium atoms each formally possessing 18 valence electrons. Alternatively, by the application of Wade's rules, the compound can be seen to possess seven polyhedral skeletal electron pairs consistent with the octahedral structure observed for the Ru_4C_2 unit.

The tetranuclear cluster $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}HCCC_6H_4Me)]$ **1b** is a red solid which displays an IR spectrum very similar to that of **1a** with six peaks in the terminal region. The ^1H NMR spectrum of the compound in $CDCl_3$ displays a singlet at δ 10.16 due to the proton on the alkynyl unit, two singlets at δ 7.01 and 7.00 due to the two pairs of protons on the phenyl ring (while doublets would normally be expected for these signals, the signals are so similar in shift that the two protons they correspond to no longer obey the first-order approximation with respect to each other. This means they no longer constitute an AX system for coupling purposes, the system is instead an AB system in which the coupling between the two protons is not observed), and a singlet at δ 2.30 corresponding to the three methyl protons. The fast atom bombardment (FAB) mass spectrum indicated a mass of 857 (calc. 860) and peaks corresponding to the sequential loss of eight carbonyl ligands.

The related cluster $[Ru_4(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}HCCC_6H_4CF_3)(CO)_{12}]$ **1c** is also a red solid and displays an IR spectrum similar to that of **1a** with six peaks in the terminal region. The increase in frequency of the IR absorptions of **1c** compared to **1a** may be due to the electron-withdrawing nature of the trifluoromethyl group reducing electron donation towards the ruthenium atoms and thereby reducing the back donation to the carbonyls. The ^1H NMR spectrum of the compound in $CDCl_3$ displays the characteristic singlet at δ 10.31 due to the proton on the alkynyl unit, two signals at δ 7.49 and 7.23 due to the two pairs of protons on the phenyl ring. Once again, the change in NMR shifts (compared to **1a**) may be attributable to the electron-withdrawing effect of the trifluoromethyl group. The ^1H NMR signals corresponding to the ring protons are doublets of doublets suggesting a long-range coupling between hydrogens *meta* with respect to one another on the phenyl ring as well as the expected *ortho* coupling. Fast atom bombardment mass spectrometry indicated a mass of 917 (calc. 917) and the sequential loss of nine carbonyl ligands was observed.

The yellow triruthenium product $[Ru_3(CO)_8\{\mu_3\text{-}\eta^6:\eta^2:\eta^1:\eta^1\text{-}HCC(H)C_6H_4\}]$ **2a** has been obtained previously by the desulfurisation reaction of thiophene with $[Ru_3(CO)_{12}]$.[8] It has been shown that $[Ru_3(CO)_8(C_8H_6)]$ can be readily demetallated to give $[Ru_2(CO)_6(C_8H_6)]$ by applying 1 atm (101 325 Pa) of CO for 24 h. This species was not observed during the thermolytic reaction of styrene with $[Ru_3(CO)_{12}]$ but both $[Ru_3(CO)_8(C_6H_4\text{-}C(Me)CH)]$ and $[Ru_2(CO)_6(C_9H_8)]$ were observed in the analogous reaction between $[Ru_3(CO)_{12}]$ and isopropenylbenzene.[6]

The yellow trinuclear cluster $[Ru_3(CO)_8\{\mu_3\text{-}\eta^6:\eta^2:\eta^1:\eta^1\text{-}HCC(H)C_6H_3Me\}]$ **2b** has a similar IR spectrum to **2a** with absorptions at 2073s, 2041vs, 2009s, 1995s, 1970w and 1948w cm^{-1}. The ^1H NMR spectrum in $CDCl_3$ shows a doublet at δ 8.84 due to the proton H(1) and a doublet at δ 5.40 for the proton H(2). The proton H(7) displays a doublet at δ 5.17, the small splitting indicating that it is coupled to H(5) implying that the phenyl ring has retained its aromaticity. The proton H(5) causes a doublet of doublets at δ 5.97, and H(4) is represented by a doublet at δ 4.36. The protons of the methyl group are represented by a singlet at δ 2.54. The FAB mass spectrum indicated a mass of 641 (calc. 643) and the sequential loss of five carbonyl ligands.

The molecular structure of $[Ru_3(CO)_8\{HCC(H)C_6H_3Me\}]$ **2b** is illustrated in Fig. 2, and selected bond lengths and angles are listed in Table 2. One bond of the reactant Ru_3 triangle has been cleaved [Ru(1)···Ru(3) 3.9455(6) Å], leaving two Ru–Ru bonds virtually orthogonal to each other [Ru(1)–Ru(2)–Ru(3)

86.76(2)°], with significantly different lengths, Ru(1)–Ru(2) [2.9577(6) Å] being considerably longer than Ru(2)–Ru(3) [2.7838(6) Å]. The doubly dehydrogenated 4-methylstyrene ligand acts as a $\eta^6:\eta^2$ π donor with the benzene ring η^6 to Ru(1) [Ru–C 2.274(5)–2.356(5) Å] and C(1) and C(2) η^2 to Ru(2) [Ru(2)–C(1) 2.237(5), Ru(2)–C(2) 2.249(5) Å] and carbon atoms C(1) and C(8) forming σ bonds to Ru(3) [Ru(3)–C(1) 2.060(5), Ru(3)–C(8) 2.096(5) Å]. The MeC_6H_3CHCH fragment acts as a 10-electron donor to give a 50-electron cluster, in which 18e is achieved at each metal if the metal–metal bonds are of a donor/acceptor nature with donation from Ru(1) to Ru(2) and from Ru(2) to Ru(3). Ruthenium atom, Ru(3), and carbon atoms C(1), C(2), C(3) and C(8) form an almost planar five-membered ring [maximum deviation of 0.09 Å for Ru(3)] which is fused to the benzene ring, and it is possible to envisage the C_8H_5MeRu unit as a ruthenamethylindene system, which acts as an 8-electron donor to the remaining $Ru_2(CO)_5$ group; a similar co-ordination mode has been observed in related structures reported by other workers.[5,8]

The brown compound $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ **3a** has been prepared previously from the reaction of $[Ru_6C(CO)_{17}]$ with refluxing toluene.[11] In the IR spectrum peaks were observed at 2076s, 2032 (sh), 2025vs, 1999 (sh), 1983m, 1969 (sh) and 1813w cm^{-1}. At first this was thought to be the compound $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5CHCH_2)]$, but the mass spectrum indicated that carbon–carbon cleavage of the $C_6H_5CHCH_2$ had occurred followed by hydrogenation to the toluene derivative. The FAB mass spectrum shows a peak at *m/z* 1103 (calc. 1102) with the loss of up to eight carbonyl ligands. Similarly the ^1H NMR spectrum did not contain signals corresponding to a vinyl unit, showing instead two multiplets due to phenyl protons at δ 5.56 and 5.23, and a singlet due to methyl protons at δ 2.21. A single-crystal X-ray analysis confirmed that **3a** is the known cluster $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$. A ^1H NMR spectrum of the styrene used in the reaction indicated that toluene is not present in detectable levels and it would therefore appear that the double bond of the vinyl unit had been cleaved and the remaining CH group doubly hydrogenated. At present the mechanism for this double bond cleavage is unclear but it is a feature which has been observed in some of the styrene derivatives previously studied.[4,6]

The brown compound $[Ru_6C(CO)_{14}(1,4\text{-}Me_2C_6H_4)]$ **3b** has an IR spectrum similar to that of **3a** with four distinct peaks including both terminal and bridging carbonyl stretches. The ^1H NMR spectrum in $CDCl_3$ displays a singlet of relative intensity four at δ 5.56, and another singlet of relative intensity six at δ 2.10. Positive-ion FAB mass spectrometry indicated a molecular mass of 1118 (calc. 1117) with a sequential loss of five carbonyl ligands. Again it would appear that the double bond of the vinyl unit had been cleaved and the remaining CH group doubly hydrogenated. Compound **3b** was recrystallised from CH_2Cl_2, by vapour diffusion of pentane.

The crystal structure of **3b** (Fig. 3) indicates that the Ru_6 core is an octahedron as expected, and that there are two bridging carbonyl ligands situated equatorially, as predicted by analogy with $[Ru_6C(CO)_{14}(C_6H_5Me_2\text{-}1,3)]$, one of these carbonyls is fully bridging, while one is only semi-bridging (significant bond lengths and angles are given in Table 3). The phenyl ring of the ligand is bound η^6 to a single ruthenium atom. It is apparent that the double bond of the vinyl unit has been cleaved and doubly hydrogenated to give an additional second methyl group. As expected the methyl groups are bent out of the plane of the benzene ring away from the metal cluster (by 1.5°).

Table 3 Selected bond lengths (Å) for complex **3b**

Ru(1)–Ru(2)	2.8781(12)	Ru(5)–C	1.946(5)
Ru(1)–Ru(3)	2.8672(13)	Ru(6)–C	2.050(5)
Ru(1)–Ru(4)	2.926(2)		
Ru(1)–Ru(5)	2.9316(12)	Ru(5)–C(1)	2.285(6)
Ru(2)–Ru(4)	2.912(2)	Ru(5)–C(2)	2.263(6)
Ru(2)–Ru(5)	2.9111(13)	Ru(5)–C(3)	2.247(6)
Ru(2)–Ru(6)	2.9232(13)	Ru(5)–C(4)	2.277(6)
Ru(3)–Ru(4)	2.8892(12)	Ru(5)–C(5)	2.262(6)
Ru(3)–Ru(5)	2.893(2)	Ru(5)–C(6)	2.263(6)
Ru(3)–Ru(6)	3.0281(13)		
Ru(4)–Ru(6)	2.8737(12)	C(1)–C(2)	1.409(8)
Ru(5)–Ru(6)	2.860(2)	C(2)–C(3)	1.427(9)
		C(3)–C(4)	1.418(8)
Ru(1)–C	2.087(5)	C(4)–C(5)	1.427(9)
Ru(2)–C	2.077(5)	C(5)–C(6)	1.413(9)
Ru(3)–C	2.086(5)	C(6)–C(1)	1.421(9)
Ru(4)–C	2.116(5)	C(1)–C(7)	1.495(10)
		C(4)–C(8)	1.507(9)

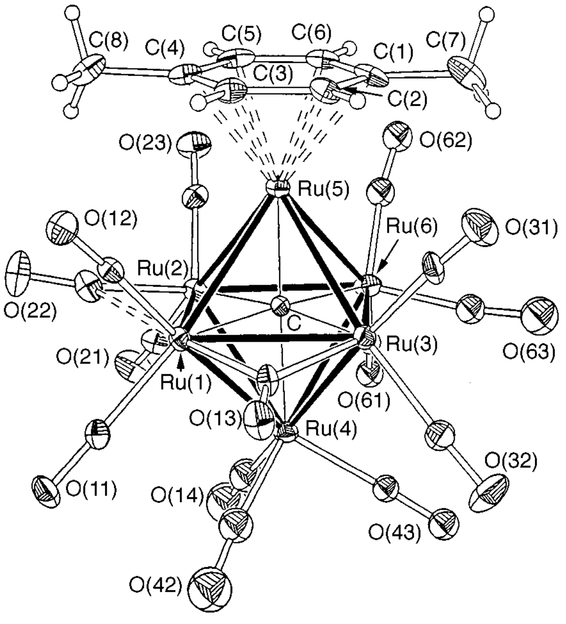


Fig. 3 Structure of $[Ru_6C(CO)_{14}(1,4\text{-}Me_2C_6H_4)]$ **3b**

Finally $[Ru_6C(CO)_{14}(C_6H_4Me\text{-}1\text{-}CF_3\text{-}4)]$ **3c** is also a brown solid with a carbonyl region IR spectrum similar to that of **3a**, with four distinct absorptions including one carbonyl bridging stretch. Once again the increase in frequency of the absorptions may be due to the electron-withdrawing nature of the trifluoromethyl group reducing the electron density on the ruthenium atoms and thereby reducing the back donation to the carbonyls, so that the C–O bonds are strengthened and their absorptions move to higher wavenumber. The ^1H NMR spectrum displays two doublets, each of integration 2 H, at δ 5.91 and 5.75 corresponding to the two distinct proton environments on the phenyl ring, and a singlet of integration 3 H at δ 2.10 for the methyl protons, which is in agreement with the identification of **3c** as $[Ru_6C(CO)_{14}(MeC_6H_4Me\text{-}1\text{-}CF_3\text{-}4)]$. The positive-ion FAB mass spectrum displays a parent ion peak at 1175 (calc. 1173) with the sequential loss of five carbonyl ligands.

Thus, three compounds containing the RC_6H_4Me (R = H, CH_3 or CF_3) ligand have been formed by the apparent cleavage of the vinylic double bond. The observation that the same chemistry occurs for all three precursor organic compounds $RC_6H_4CH{=}CH_2$ almost certainly precludes the inadvertent inclusion of RC_6H_4Me in any of the three starting materials, a point emphasised by the lack of C_6H_5Me in the styrene used to synthesise **3a** (see above).

The fourth product of the styrene reaction $[Ru_6(CO)_{15}\text{-}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}HCCC_6H_5)(\eta^6\text{-}C_6H_5Et)]$ **4a** is a purple oil product. It displays absorptions in the IR region at 2067s, 2041w, 2026s, 2012vs, 1995m, 1957m cm^{-1}, and the FAB mass spectrum showed a parent ion with a mass of 1230 (calc. 1232) and the loss of nine carbonyl ligands. The ^1H NMR spectrum in $CDCl_3$ displays a singlet at δ 9.93 due to the lone hydrogen of the alkynyl unit bound μ_4-η^1:η^1:η^2:η^2 in one hinge of the cluster and a multiplet at δ 7.11 due to the phenyl protons of the same ligand. Five signals of relative intensity 1:1:1:1:1 at δ 5.84, 5.73, 5.66, 5.10 and 4.36 correspond to the protons on the phenyl ring of the η^6-bound ligand. The inequivalence of the *ortho* and *meta* protons suggests that rotation of the ligand is hindered, possibly by the presence of the other styrene-derived ligand, though it may arise from the asymmetry of the molecule. This restricted rotation (or molecular asymmetry) is also apparent in the inequivalence of the two α-hydrogens of the hydrogenated vinyl unit which each show doublets of quartets at δ 2.07 and 1.88. The methyl protons of the hydrogenated vinyl unit give rise to a doublet of doublets at δ 1.10, which although apparently a triplet, is in fact a doublet of doublets with identical splitting constants.

Likewise $[Ru_6(CO)_{15}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}HCCC_6H_4Me)(\eta^6\text{-}C_6H_4Et\text{-}1\text{-}Me\text{-}4)]$ **4b** is a purple oily product. It likewise displays terminal carbonyl absorptions in the IR. The FAB mass spectrum shows a parent ion with a mass of 1258 (calc. 1260) and the sequential loss of five carbonyl ligands. The ^{1}H NMR spectrum in $CDCl_3$ displayed a singlet at δ 9.92 due to the lone hydrogen on the alkynyl unit in the hinge and a multiplet at δ 6.92 due to the phenyl protons of the same ligand. Four signals of integration 1 H at δ 5.11, δ 4.99, δ 4.91 and δ 4.81 correspond to the protons on the phenyl ring of the η^6-bound ligand. The two α-hydrogens of the hydrogenated vinyl unit which each show quartets at δ 2.47 and 2.46 (the absence of an observable coupling between these protons is for the same reasons as the failure to observe coupling in the case of **1b**). The methyl protons of the hydrogenated vinyl unit give rise to a pseudo-triplet at δ 1.10. The two *para* methyl units result in singlets at δ 2.27 and 2.24.

Finally $[Ru_6(CO)_{15}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}HCCC_6H_4CF_3)(\eta^6\text{-}C_6H_4\text{-}Et\text{-}1\text{-}CF_3\text{-}4)]$ **4c** is a purple oily product. It likewise displays terminal carbonyl absorptions in the IR region. The FAB mass spectrum showed a parent ion with a mass of 1368 (calc. 1368) and the sequential loss of five carbonyl ligands was observed. The ^{1}H NMR spectrum displays a singlet at δ 10.29 due to the lone hydrogen on the alkynyl unit in the hinge and multiplets at δ 7.67 and 7.11 due to the phenyl protons of that ligand. Four signals of relative intensity 1 H at δ 6.06, 5.49, 4.92 and 4.47 correspond to the protons on the phenyl ring of the η^6-bound ligand. The two α-hydrogens of the hydrogenated vinyl unit each show doublets of quartets at δ 2.92 and 2.66. The methyl protons of the hydrogenated vinyl unit give rise to a pseudo triplet at δ 1.32.

Conclusion

It is apparent that the lack of an α-methyl group on the vinyl functionality results in a marked change in the pattern of reactivity of styrene and its derivatives compared to that of isopropenylbenzene and diisopropenylbenzene. As well as the lack of possibility for allylic interaction, the kinetic stability of the μ_3-η^2:η^2:η^2-bonding mode appears to be markedly reduced. The lack of an α-methyl group also leads to a cleavage of the double bond of the vinyl unit during cluster build-up rather than the single bond cleavage observed when an α-methyl group is present. At present we have no views on how this cleavage occurs. The other anticipated product C_2H_4 has not been detected and no compounds containing CH_2 or a related moiety have been observed.

Experimental

All reactions were carried out using standard laboratory grade solvents under nitrogen unless otherwise noted. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform spectrometer. Positive ion mass spectra were obtained by fast atom bombardment on a Kratos MS50TC instrument. Proton NMR spectra were recorded using a Bruker AM360 or WM250 spectrometer referenced to $SiMe_4$.

The clusters $[Ru_3(CO)_{12}]$ and $[Ru_6C(CO)_{17}]$ were prepared according to literature methods.[12,13] Styrene, 4-methylstyrene and 4-trifluoromethylstyrene were purchased from Aldrich, and used as supplied.

Products were isolated by thin layer chromatography (TLC) using commercially prepared glass plates, precoated to 0.25 mm thickness with Merck Kieselgel 60G.

Reaction of $[Ru_3(CO)_{12}]$ with styrene in refluxing octane

In a typical reaction an excess of styrene (115 mg) in octane (20 cm^3) was added dropwise to a solution of $[Ru_3(CO)_{12}]$ (200 mg) in refluxing octane (100 cm^3) over a period of 20 min. Reflux was continued for 2 h. The solvent was removed *in vacuo* and the residue chromatographed using hexane–dichloromethane (7:3 v/v) as eluent. Some products were further purified by TLC using hexane–dichloromethane (9:1 v/v). Five significant products were observed of which four have been identified as $[Ru_4H_2(CO)_{13}]$ (<1%), $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}HCCC_6H_5)]$ **1a** (5%), $[Ru_3(CO)_8(C_8H_6)]$ **2a** (5%) and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ **3a** (2%). Another product **4a** was also obtained in similar yield (2%) and has been tentatively identified as $[Ru_6(CO)_{15}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}HCCC_6H_5)(\eta^6\text{-}C_6H_5Et)]$.

Spectroscopic data for $[Ru_4H_2(CO)_{13}]$. IR ν_{co} (CH_2Cl_2): 2078vs, 2068vs, 2052vs, 2032sh, 2020m, 1869w cm^{-1}.

Spectroscopic data for complex **1a**. IR ν_{co} (CH_2Cl_2): 2095vw, 2069vs, 2042 (sh), 2036vs, 2012s, 1971w cm^{-1}. Positive ion FAB mass spectrum: *m/z* 846 (calc. 846) loss of nine CO ligands observed. ^{1}H NMR ($CDCl_3$): δ 10.22 (s, 1 H), 7.20 (m, 5 H).

Spectroscopic data for complex **2a**. IR ν_{co} (CH_2Cl_2): 2074s, 2042vs, 2011vs, 1998s, 1972m, 1951w cm^{-1}. Positive ion FAB mass spectrum: *m/z* 631 (calc. 629) loss of eight CO ligands observed. ^{1}H NMR ($CDCl_3$): δ 8.91 (d, 6.3, 1 H), 6.37 (td, 5.9, 1.1, 1 H), 5.99 (td, 6.7, 1.3, 1 H), 5.46 (d, 6.3, 1 H), 5.13 (dd, 5.8, 1.2, 1 H), 4.46 (dd, 6.6, 1.0 Hz, 1 H).

Spectroscopic data for complex **3a**. IR ν_{co} (CH_2Cl_2): 2076s, 2032 (sh), 2025vs, 1999 (sh), 1983m, 1969 (sh), 1813w cm^{-1}. Positive ion FAB mass spectrum: *m/z* 1103 (calc. 1102) loss of eight CO ligands observed. ^{1}H NMR ($CDCl_3$): δ 5.56 (m, 3 H), 5.23 (m, 2 H), 2.21 (s, 3 H).

Spectroscopic data for complex **4a**. IR ν_{co} (CH_2Cl_2): 2067s, 2041w, 2026s, 2012vs, 1995m, 1957m. Positive ion FAB mass spectrum: *m/z* 1230 (calc. 1232) loss of nine CO ligands observed. ^{1}H NMR ($CDCl_3$): δ 9.93 (s, 1 H), 7.11 (m, 5 H), 5.84 (t, 5.3, 1 H), 5.73 (t, 5.5, 1 H), 5.66 (d, 5.6, 1 H), 5.10 (t, 5.5, 1 H), 4.36 (d, 6.3, 1 H), 2.07 (dq, 14.5, 7.3, 1 H), 1.88 (dq, 14.5, 7.2, 1 H), 1.10 (dd, 7.6, 7.6 Hz, 3 H).

Reaction of $[Ru_3(CO)_{12}]$ with styrene in refluxing heptane

An excess of styrene (115 mg) in heptane (20 cm^3) was added dropwise to a solution of $[Ru_3(CO)_{12}]$ (200 mg) in refluxing heptane (100 cm^3) over a period of 1 h . Reflux was continued for 2 h without precaution to exclude air. (The point at which monitoring of the reaction by spot TLC indicated optimum balance between remaining starting material and decomposition products had been achieved.) The solvent was removed *in vacuo* and the residue chromatographed using hexane–dichloromethane (7:3 v/v) as eluent. Some of the products were further purified by TLC using hexane–dichloromethane (9:1 v/v). Five significant products were observed of which five have been identified as $[Ru_4H_2(CO)_{13}]$ (<1%), $[Ru_4(CO)_{12}\text{-}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}HCCC_6H_5)]$ **1a** (6%), $[Ru_3(CO)_8(C_8H_6)]$ **2a** (1%), $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ **3a** (1%) and $[Ru_6(CO)_{15}\text{-}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}HCCC_6H_5)(\eta^6\text{-}C_6H_5Et)]$ **4a** (1%).

Reaction of $[Ru_3(CO)_{12}]$ with styrene in refluxing cyclohexane

In a typical reaction an excess of styrene (115 mg) in cyclohexane freshly distilled under N_2 (20 cm^3) was added dropwise to a solution under nitrogen of $[Ru_3(CO)_{12}]$ (200 mg) in refluxing cyclohexane freshly distilled under N_2 (100 cm^3) over a period of 20 min. Reflux was continued for 22 h. The solvent was removed *in vacuo* and the residue underwent column chromatography in air using cyclohexane, benzene, dichloromethane, acetone and methanol as eluents. Some of the products were further purified by TLC. Five products were observed in significant yield, of which five have been identified as $[Ru_4H_2(CO)_{13}]$ (1%), $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}HCCC_6H_5)]$ **1a** (5%), $[Ru_3(CO)_8(C_8H_6)]$ **2a** (3%), $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$ **3a** (1%) and $[Ru_6(CO)_{15}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}HCCC_6H_5)(\eta^6\text{-}C_6H_5\text{-}Et)]$ **4a** (2%). The butterfly complexes α-$[Ru_4(CO)_9(\mu_4\text{-}\eta^2:\eta^2:\eta^1:\eta^1\text{-}C_8H_6)(\eta^6\text{-}C_8H_{10})]$ and β-$[Ru_4(CO)_9(\mu_4\text{-}\eta^2:\eta^2:\eta^1:\eta^1\text{-}C_8H_6)(\eta^6\text{-}C_8H_{10})]$ reported by previous researchers were not observed.[12]

Reaction of $[Ru_3(CO)_{12}]$ with 4-methylstyrene in refluxing octane

In a typical reaction an excess of 4-methylstyrene (200 mg) in octane (20 cm^3) was added dropwise to a solution of $[Ru_3(CO)_{12}]$ (200 mg) in refluxing octane (100 cm^3) over a period of 20 min. Reflux was continued for 1 h. The solvent was removed *in vacuo* and the residue chromatographed using hexane–dichloromethane (7:3 v/v) as eluent. Some products were further purified by TLC using hexane–dichloromethane (9:1 v/v). Five significant products were observed of which four have been identified as $[Ru_4H_2(CO)_{13}]$ (1%), $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}HCCC_6H_4Me)]$ **1b** (5%), $[Ru_3(CO)_8(C_9H_8)]$ **2b** (6%) and $[Ru_6C(CO)_{14}(1,4\text{-}Me_2C_6H_4)]$ **3b** (<1%). Once again there is a product **4b** which has been tentatively identified as $[Ru_6(CO)_{15}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}HCCC_6H_4Me)(\eta^6\text{-}C_6H_4Et\text{-}1\text{-}Me\text{-}4)]$ (1%).

Spectroscopic data for complex **1b**. IR ν_{co} (CH_2Cl_2): 2095vw, 2069vs, 2043vs, 2035vs, 2012s, 1972w cm^{-1}. Positive ion FAB mass spectrum: *m/z* 857 (calc. 860) loss of eight CO ligands observed. ^1H NMR ($CDCl_3$): δ 10.16 (s, 1 H), 7.01 (s, 2 H), 7.00 (s, 2 H), 2.30 (s, 3 H).

Spectroscopic data for complex **2b**. IR ν_{co} (CH_2Cl_2): 2073s, 2041vs, 2009s, 1995s, 1970w, 1948w cm^{-1}. Positive ion FAB mass spectrum: *m/z* 641 (calc. 643) loss of five CO ligands observed. ^1H NMR ($CDCl_3$): δ 8.84 (d, 6.2, 1 H), 5.97 (dd, 6.7, 1.5, 1 H), 5.40 (d, 6.3, 1 H), 5.17 (d, 6.7, 1 H), 4.36 (d, 6.7 Hz, 1 H), 2.54 (s, 1 H).

Spectroscopic data for complex **3b**. IR ν_{co} (CH_2Cl_2): 2075s, 2028 (sh), 2024vs, 1996 (sh), 1982m, 1970 (sh), 1816w cm^{-1}. Positive ion FAB mass spectrum: *m/z* 1118 (calc. 1117) loss of five CO ligands observed. ^1H NMR ($CDCl_3$): δ 5.56 (s, 4 H), 2.10 (s, 6 H).

Spectroscopic data for complex **4b**. IR ν_{co} (CH_2Cl_2): 2066s, 2037w, 2024s, 2008vs, 1994m, 1955m. Positive ion FAB mass spectrum: *m/z* 1258 (calc. 1260) loss of five CO ligands observed. ^1H NMR ($CDCl_3$): δ 9.92 (s, 1 H), 6.92 (m, 5 H), 5.11 (d, 5.7, 1 H), 4.99 (d, 5.8, 1 H), 4.91 (d, 6.0, 1 H), 4.81 (t, 5.9, 1 H), 2.47 (q, 7.7, 1 H), 2.46 (q, 7.7, 1 H), 2.27 (s, 3 H), 2.24 (s, 3 H), 1.10 (dd, 7.6, 7.6 Hz, 3 H).

Reaction of $[Ru_3(CO)_{12}]$ with 4-trifluoromethylstyrene in refluxing octane

In a typical reaction an excess of 4-trifluoromethylstyrene (120 mg) in octane (20 cm^3) was added dropwise to a solution of $[Ru_3(CO)_{12}]$ (200 mg) in refluxing octane (100 cm^3) over a period of 20 min. Reflux was continued for 3 h. The solvent was removed *in vacuo* and the residue chromatographed using hexane–dichloromethane (7:3 v/v) as eluent. Some products were further purified by TLC using hexane–dichloromethane (9:1 v/v). Four significant products were observed of which three have been identified as $[Ru_4H_2(CO)_{13}]$, $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}HCCC_6H_4CF_3)]$ **1c** (1%) and $[Ru_6C(CO)_{14}(C_6H_4Me\text{-}1\text{-}CF_3\text{-}4)]$ **3c** (<1%). Once again a purple product **4c** was produced, which has been identified as $[Ru_6(CO)_{15}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}HCCC_6H_4CF_3)(\eta^6\text{-}C_6H_4Et\text{-}1\text{-}CF_3\text{-}4)]$. There was no evidence of the production of a 4-trifluoromethylstyrene analogue of **2**.

Spectroscopic data for complex **1c**. IR ν_{co} (CH_2Cl_2): 2097w, 2070vs, 2044vs, 2037vs, 2017s, 1978w cm^{-1}. Positive ion FAB mass spectrum: *m/z* 917 (calc. 917) loss of nine CO ligands observed. ^1H NMR ($CDCl_3$): δ 10.31 (s, 1 H), 7.49 (dd, 8, 1, 2 H), 7.23 (dd, 8, 1 Hz, 2 H).

Spectroscopic data for complex **3c**. IR ν_{co} (CH_2Cl_2): 2079s, 2067vw, 2061vw, 2037 (sh), 2029vs, 2011 (sh), 1989m, 1975 (sh), 1818w cm^{-1}. Positive ion FAB mass spectrum: *m/z* 1175 (calc. 1173) loss of five CO ligands observed. ^1H NMR ($CDCl_3$): δ 5.91 (d, 7, 2 H), 5.75 (d, 7 Hz, 2 H), 2.10 (s, 3 H).

Spectroscopic data for complex **4c**. IR ν_{co} (CH_2Cl_2): 2072m, 2041vs, 2027s, 2009s, 1987m, 1966w. Positive ion FAB mass spectrum: *m/z* 1368 (calc. 1368) loss of 5 CO ligands observed. ^1H NMR ($CDCl_3$): δ 10.29 (s, 1 H), 7.67 (m, 2 H), 7.11 (m, 2 H), 6.06 (s, 1 H), 5.49 (s, 1 H), 4.92 (s, 1 H), 4.47 (s, 1 H), 2.92 (dq, 15, 7.5, 1 H), 2.66 (dq, 15, 7.5 Hz, 1 H), 1.32 (m, 3 H).

Crystal-structure determination of compound 1a

Diffraction intensities for **1a** were collected on an Enraf-Nonius CAD4 diffractometer at 293 K (see Table 4). The data were corrected for Lorentz and polarisation factors. Absorption corrections were applied by the use of semiempirical ψ scans (maximum, minimum transmission coefficients 0.157, 0.110). The structure was solved by a combination of direct methods and Fourier techniques. Anisotropic thermal motion was assumed for all non-hydrogen atoms. Phenyl ring hydrogens were placed in calculated positions and refined using a riding model. The other hydrogens were placed in positions determined from a difference electron density Fourier synthesis and allowed to refine freely. Computations were performed with the SHELXTL PC[14] and SHELXL 93[15] programs.

Crystal-structure determination of compound 2b

Intensity data for **2b** were collected on a Siemens P4 diffractometer at 293 K with graphite-monochromated Mo-Kα radiation using 0–28 θ scans. The crystal data, data collection and refinement are summarised in Table 4. Three standard reflections measured after every 97 reflections showed no significant variation in intensity throughout data collection. The data were corrected for Lorentz and polarisation factors. Absorption corrections were applied by the use of semiempirical ψ scans (maximum, minimum transmission coefficients 0.821, 0.778). The structure was solved by direct methods and all non-hydrogen atoms were located from subsequent Fourier-difference syntheses. All the non-hydrogen atoms were assigned anisotropic displacement parameters and refined using full-matrix least squares on F^2. All hydrogen atoms were located directly from Fourier-difference maps, and were assigned a fixed isotropic displacement parameter of 0.08 Å^2, with the exception of the methyl group [C(9)] hydrogen atoms, which were placed in idealised positions and allowed to ride on the carbon atom (C−H 0.96 Å) and were assigned with isotropic displacement parameters equal to 1.5 × U_{eq} of C(9) [isotropic displacement parameter, U_{iso} for methyl group C(9) was 0.101 Å^2].

Crystal-structure determination of compound 3b

Diffraction intensities for **3b** were collected on a Stoe Stadi-4A diffractometer at 293 K (see Table 4). The data were corrected for Lorentz and polarisation factors. Absorption corrections were applied by the use of semiempirical ψ scans (maximum, minimum transmission coefficients 0.265, 0.155). The structure was solved by a combination of direct methods and Fourier techniques. Anisotropic thermal motion was assumed for

Table 4 Crystal-structure determination parameters for complexes **1a**, **2b** and **3b**

	1a	**2b**	**3b**
Formula	$C_{20}H_6O_{12}Ru_4$	$C_{17}H_8O_8Ru_3$	$C_{16}H_6O_8Ru_3$
M	842.53	643.44	629.4
T/K	293(2)	293(2)	293(2)
Lattice type	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$Pbca$	$P2_1/n$
Z	8	8	4
a/Å	20.163(2)	15.2963(8)	9.455(4)
b/Å	9.3342(7)	13.0615(12)	12.560(4)
c/Å	26.203(2)	18.9413(12)	14.808(7)
U/Å^3	4890.1(7)	3784.3(5)	1733
F(000)	3184	2448	1192
D_c/g cm^{-3}	2.289	2.259	2.413
λ(Mo-K$_\alpha$)/Å	0.71073	0.71073	0.71073
μ(Mo-K$_\alpha$)/mm^{-1}	2.484	2.406	2.624
Colour	Red	Yellow	Brown
Crystal size/mm	0.30 × 0.45 × 0.60	0.44 × 0.24 × 0.22	0.70 × 0.54 × 0.52
θ range/°	2.6–25.0	2.15–25.00	2.5–25
Index ranges h	0–23	−1 to 18	−20 to 18
k	0–11	−1 to 15	0–11
l	−31 to 30	−1 to 22	0–21
Measured reflections	8783	4173	5468
Independent reflections	8525	3330	3045
Absorption correction	Semiempirical ψ scans	Semiempirical ψ scans	Semiempirical ψ scans
Maximum and minimum transmission	0.157, 0.110	0.821, 0.778	0.265, 0.155
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data, restraints, parameters	8520, 0, 658	3326, 0, 254	4955, 0, 245
Goodness of fit on F^2, S	1.194	1.047	1.18
$R1$ final [$I > 2\sigma(I)$]	0.0275	0.0322	0.0322
$wR2$ final [$I > \sigma(I)$]	0.0658	0.0697	0.0711
$R1$ (all data)	0.0336	0.0439	0.0389
$wR2$ (all data)	0.0698	0.0767	0.0795
Weighting parameters x, y	0.0248, 6.4886	0.0238, 1.18	0.1000, 0.00
Largest difference peak, hole/e Å^{-3}	0.645, −0.390	0.442, −0.434	1.94, −1.31

$S = [\Sigma(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$, where n = number of reflections and p = total number of parameters. $R1 = \Sigma|F_o| + |F_c|/\Sigma|F_o|$. $wR2 = [w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{\frac{1}{2}}$. $w = 1/[\sigma(F_o)^2 + (xP)^2 + (yP)]$ where $P = [\max(F_o^2,0) + 2(F_c^2,0)]/3$.

all non-hydrogen atoms. Hydrogens were placed in calculated positions and refined using a riding model. Computations were performed with the SHELXTL PC and SHELXL 93 programs.

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