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Synthesis and crystal structures of two isomers of $[Ru_4(CO)_9(\mu_3\text{-}C_{15}H_{20})]$

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Two isomeric clusters **1** and **2** of formula $[Ru_4(CO)_9(C_{15}H_{20})]$ have been isolated from the reaction of $[Ru_3(CO)_{12}]$ and 1,3,5-triisopropenylbenzene $C_{15}H_{18}$ and their crystal structures determined. It would appear that two hydrogen atoms have been transferred to a different carbon atom of $C_{15}H_{18}$ in each case, generating the two different molecular structures.

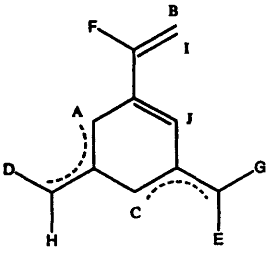
Arene cluster chemistry has emerged as an important area of modern organometallic chemistry and clusters of nuclearities from three to eight are now known in which one or more arene ligands are present.[1] Much of the current interest arises from the analogy between the interaction of arenes with polynuclear metal complexes and that with metal surfaces.[2] As a result of a detailed study of the interaction of various arene ligands with ruthenium and osmium clusters it has been established that, in general, aromatic rings show a preference towards two basic bonding modes: *viz* terminal (η^6) or face capping (μ_3-$\eta^2:\eta^2:\eta^2$). We are now expanding the chemistry of these arene clusters by employing substituted arenes carrying unsaturated side chains such as isopropenyl groups. Earlier we reported[3] on the molecular clusters obtained by treating isopropenylbenzene or 1,3-diisopropenylbenzene with $[Ru_3(CO)_{12}]$. In this paper we report the preparation and the structural characterization of the two isomeric tetrahedral clusters of formula $Ru_4(CO)_9(C_{15}H_{20})$ containing the $C_{15}H_{20}$ ligand in a face-capping mode, which have been prepared from a similar reaction with 1,3,5-triisopropenylbenzene. In this case the products are dominated by ligand hydrogenation.

Results and Discussion

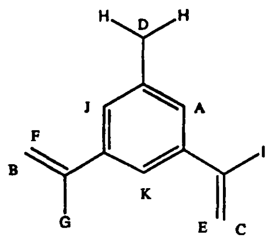
The reaction of $[Ru_3(CO)_{12}]$ with 1,3,5-triisopropenylbenzene in octane under reflux for 3 h results in a dark brown solution. Separation of the products from this solution may be achieved by thin-layer chromatography on silica, eluting with a solution of 30% dichloromethane–hexane. Several products may be isolated, the majority in low yield. However, the main red band containing $[Ru_4(CO)_9(C_{15}H_{20})]$ in reasonable yield was eluted with dichloromethane. A second separation of this band with a solution of 10% methanol–hexane gave two components containing the isomeric clusters **1** and **2** respectively.

The mass spectrum of compound **1** contains a parent ion at *m/z* 857 and that for **2** at *m/z* 856 (calc. 856), respectively. These are followed by a series of peaks corresponding to the loss of carbonyl ligands which is typical for clusters of this type. The ^1H NMR spectra of **1** and **2** recorded in $CDCl_3$ have been fully assigned by a series of nuclear Overhauser effect (NOE)–decoupling experiments. For **1** ten signals are observed for the total of twenty protons. The three ring protons may be assigned to resonances at δ 3.57(A), 2.22(C) and −0.28(J). Two other signals at δ 3.22(B) and 1.42(I) with an integral of 1 H are associated with the CH_2 group. Finally the set of five singlet resonances at δ 2.09(D), 2.00(E), 1.65(F), 1.50(G) and 1.21(H) may be assigned to the remaining methyl groups.

For compound **2** a total of eleven resonances are observed in the range δ 5.43–0.21 (labelled A–K). The two pendant arms lie parallel to the ring plane and their directions are fixed. The resonance at δ 5.43(A) is higher than usual for a CH group of a μ_3-bonded ring $\{[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$, δ 4.56$\}$.[4] However, the other two CH resonances occur at very low frequencies δ 0.59(J) and 0.21(K). A strong shift of this kind has been observed for similar compounds.[3] The signals at δ 3.35(B), 2.97(C), 1.94(E) and 1.66(F) may be attributed to CH_2 protons, while the remaining singlet resonances at δ 1.52(G) and 1.31(I) arise from the methyl groups. The isopropyl group is represented in the signals at δ 2.40(D) and 1.44(H).



Ligand in **1**



Ligand in **2**

Molecular structures in the solid state

Crystals of compounds **1** and **2** suitable for single-crystal X-ray analysis were grown from a CH_2Cl_2–hexane solution by cooling. The molecular structures are shown in Figs. 1–4. Relevant structural parameters for the two molecules are listed in Tables 1–3. In each of the two structures the ligand formally contributes ten electrons to the metal cluster unit. Thus, the total electron count for the tetrahedral species is 60, in keeping with the total number of valence electrons typically associated with tetrahedral transition-metal cluster species.

Compound 1. The four metal atoms form a regular tetrahedron with no bridging carbonyls. The organic ligand which is placed on one tetrahedral face is disordered because the molecule lies on a three-fold axis of the unit cell. The occupancy for C(4a) is $\frac{1}{3}$ and for C(4b) it is $\frac{2}{3}$. The ligand is $\eta^2:\eta^2:\eta^3:\eta^3$-co-ordinated to the triangular face of the cluster. The double bond is rotated out of the arene plane towards the metal side with an angle of 15.9°. The methyl groups are also out of the ring plane and are bent towards the other side of the ligand. In the crystal packing, two molecules are aligned such that there is direct interaction between the arene ligands. The distance between these arene planes is with 3.35 Å which is significantly shorter than the van der Waals interaction. The molecules are twisted against each other at 60° presumably to give the minimum interaction between the side arms.

Compound 2. The four ruthenium atoms form a nearly regular tetrahedron [2.822(1) Å average, shortest Ru(1)–Ru(4) 2.6874(7), longest Ru(1)–Ru(3) 2.8705(7) Å] with one

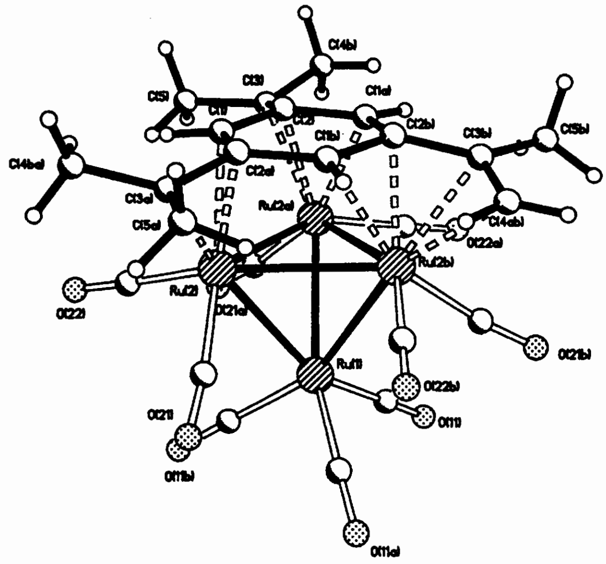


Fig. 1 Molecular structure of $[Ru_4(CO)_9(C_{15}H_{20})]$ 1. The C atoms of the CO ligands bear the same number as the corresponding O atoms

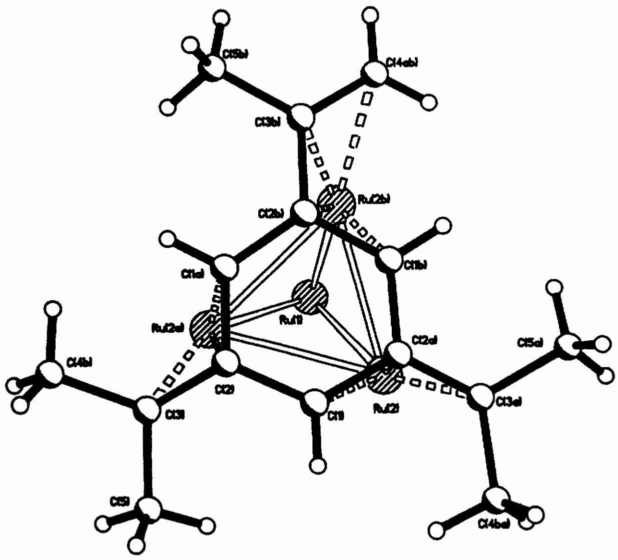


Fig. 2 Molecular structure of $[Ru_4(CO)_9(C_{15}H_{20})]$ 1 without CO ligands

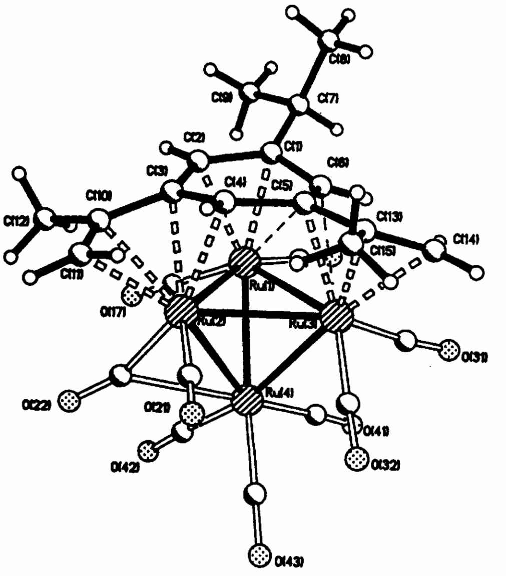


Fig. 3 Molecular structure of $[Ru_4(CO)_9(C_{15}H_{20})]$ 2. The C atoms of the CO ligands bear the same number as the corresponding O atoms

semibridging carbonyl ligand. The ruthenium triangle does not sit centrally under the six-membered ring as observed in **1**, which is clearly apparent from the top view of the molecule shown in Fig. 4. Cluster **2** has a very similar structure to that of the compound $[Ru_4(CO)_9(C_{12}H_{14})]$ [3] except that one hydrogen is replaced by an isopropyl group. This has a dramatic influence on the structure in the solid state. The three metals no longer sit under the centre of the three aromatic double bonds and Ru(1) especially is turned nearer to carbon atom C(1) [2.203(5) Å]. This produces a weak interaction with carbon atom C(6) [2.448(5) Å] so that it may be viewed as a mixture of η^2 and η^3 co-ordination to Ru(1). Similar behaviour is observed for Ru(3) and C(6) [2.510(5) Å]. As a further result, the six-membered ring is even more twisted than in the compound $[Ru_4(CO)_9(C_{12}H_{14})]$ which contains two CO bridges. The electronic state of the π system of the ligand is illustrated in Scheme 1.

The allylic co-ordination of arene ligands to a metal triangle is unusual and has not been observed previously. It may be caused by the need to restrict the π system in order to maximize overlap with the ruthenium metal orbitals. The original 1,3,5-triisopropenylbenzene is too large to fit neatly over the triruthenium face and thus able to donate all twelve electrons to the cluster core, even by deformation and loss of planarity of the ring. Reducing the ligand to a ten-electron donor permits a smaller π system. Thus, there exist two bonding possibilities. In the first the π bonding is centralized (leading to compound **1**) and in the second it is concentrated on one side of the ligand (leading to **2**).

The difference between the two ligand bonding modes is that the two additional hydrogens (compared to the arene $C_{15}H_{18}$)

Table 1 Selected bond lengths (Å) for compound **1**

Ru(1)–Ru(2)	2.7561(11)	C(1)–C(2a)	1.425(11)
Ru(2)–Ru(2a)	2.8592(14)	C(1)–C(2)	1.434(11)
Ru(2)–C(2a)	2.143(7)	C(2)–C(3)	1.426(11)
Ru(2)–C(3a)	2.262(8)	C(3)–C(4a)	1.34(3)
Ru(2)–C(1)	2.305(7)	C(3)–C(4b)	1.53(2)
Ru(2b)–C(4ab)	2.49(3)	C(3)–C(5)	1.509(11)

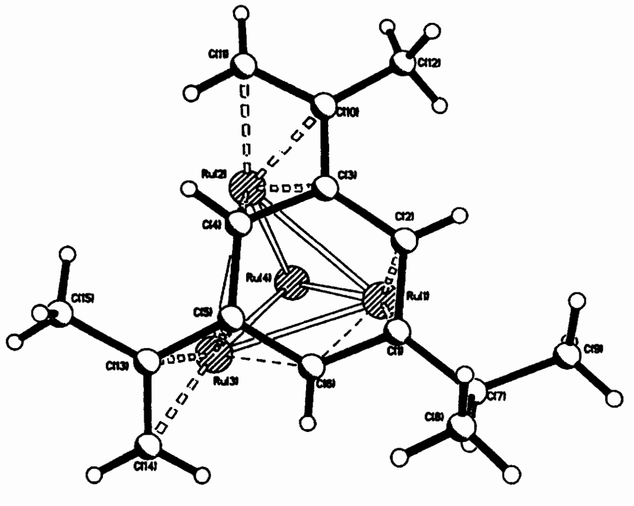
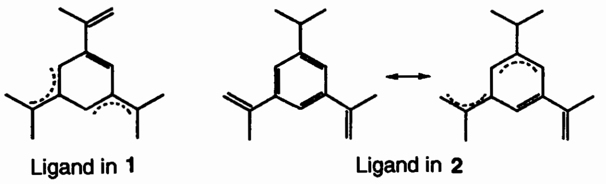


Fig. 4 Molecular structure of $[Ru_4(CO)_9(C_{15}H_{20})]$ 2 without CO ligands



Scheme 1 Proposal electronic π system of the ligands in compounds **1** and **2**

have been transferred to different carbon atoms within the C_{15} framework. By forming compound **1** the two hydrogens have been transferred to two CH_2 groups of different side arms, whereas by creating **2** both hydrogen atoms have been added to the same double bond. In a separate experiment it has been shown that $[Ru_4H_2(CO)_{13}]$ does not react with the same proligand to give either **1** or **2** and therefore is not a potential intermediate in this reaction. In contrast to the reactions involving isopropenylbenzene or 1,3-diisopropenylbenzene, no related trinuclear precursors to either **1** or **2** have been found in the reaction mixture. The source of hydrogen for the observed reductions is almost certainly 1,3,5-triisopropenylbenzene and products containing various dehydrogenated forms of this arene have also been found.[5]

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

Ru(1)–Ru(4)	2.6874(7)	C(1)–C(2)	1.402(7)
Ru(1)–Ru(2)	2.8606(8)	C(1)–C(6)	1.426(8)
Ru(1)–Ru(3)	2.8705(7)	C(1)–C(7)	1.516(7)
Ru(2)–Ru(3)	2.8030(8)	C(2)–C(3)	1.461(7)
Ru(2)–Ru(4)	2.8484(8)	C(3)–C(10)	1.426(8)
Ru(3)–Ru(4)	2.7993(10)	C(3)–C(4)	1.457(8)
		C(4)–C(5)	1.452(7)
Ru(1)–C(1)	2.203(5)	C(5)–C(6)	1.430(7)
Ru(1)–C(2)	2.238(5)	C(5)–C(13)	1.443(7)
Ru(1)–C(6)	2.448(5)	C(7)–C(8)	1.461(8)
Ru(2)–C(4)	2.198(5)	C(7)–C(9)	1.511(8)
Ru(2)–C(3)	2.227(5)	C(10)–C(11)	1.410(8)
Ru(2)–C(10)	2.233(5)	C(10)–C(12)	1.497(8)
Ru(2)–C(11)	2.259(5)	C(13)–C(14)	1.402(8)
Ru(3)–C(13)	2.210(5)	C(13)–C(15)	1.510(8)
Ru(3)–C(5)	2.225(5)		
Ru(3)–C(6)	2.510(5)		
C(2)–C(1)–C(6)	116.2(5)	C(1)–C(6)–C(5)	123.5(5)
C(2)–C(1)–C(7)	123.4(5)	C(8)–C(7)–C(9)	113.0(5)
C(6)–C(1)–C(7)	119.6(5)	C(8)–C(7)–C(1)	111.9(5)
C(1)–C(2)–C(3)	120.2(5)	C(9)–C(7)–C(1)	114.9(5)
C(10)–C(3)–C(4)	114.8(5)	C(11)–C(10)–C(3)	117.8(5)
C(10)–C(3)–C(2)	125.1(5)	C(11)–C(10)–C(12)	119.9(5)
C(4)–C(3)–C(2)	119.9(5)	C(3)–C(10)–C(12)	122.2(5)
C(5)–C(4)–C(3)	117.2(5)	C(14)–C(13)–C(5)	117.9(5)
C(6)–C(5)–C(13)	120.4(5)	C(14)–C(13)–C(15)	121.1(5)
C(6)–C(5)–C(4)	117.2(5)	C(5)–C(13)–C(15)	120.9(5)
C(13)–C(5)–C(4)	121.9(5)		

Conclusion

In this work we have established that 1,3,5-triisopropenylbenzene undergoes reaction with $[Ru_3(CO)_{12}]$ to produce compounds directly related to those from analogous reactions of the same carbonyl with the mono- and di-(isopropenyl)benzene ligand. Significantly, the major products of this reaction are those which contain hydrogenated forms of the ligand, and of special note is the difference in the nature of the products obtained from ruthenium and osmium.

Experimental

General procedures and materials

Reactions were carried out using octane (Aldrich Chemicals) and nitrogen gas was passed over the top of the condenser. The work-up to the products was carried out using standard laboratory-grade solvents. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform instrument, mass spectra by positive fast atom bombardment on a Kratos MS50TC, calibrated with CsI and ^1H NMR spectra using a Bruker AM360 spectrometer referenced to internal $SiMe_4$.

The cluster $[Ru_3(CO)_{12}]$ was prepared according to the literature method.[6] 1,3,5-Triisopropenylbenzene was prepared *via* bromination and HBr elimination from 1,3,5-triisopropylbenzene:[7] $\delta_H(CDCl_3)$ 7.50 (3 H, s), 5.42 (3 H, m), 5.15 (3 H, dq, *J* 1.4) and 2.20 (9 H, dd, *J* 1.4 + 0.7 Hz).

Thermolysis of $[Ru_3(CO)_{12}]$ with 1,3,5-triisopropenylbenzene in octane

Triruthenium dodecacarbonyl, $[Ru_3(CO)_{12}]$ (400 mg, 0.626 mmol), was refluxed in octane with an excess of 1,3,5-triisopropenylbenzene (0.5 cm³) for 3 h. The reaction was followed by IR spectroscopy and spot TLC. On completion the solvent was removed *in vacuo* and the reaction mixture subjected to TLC using hexane–dichloromethane (7:3) as solvent. Beside other products, a red band was observed at the bottom half of the plate; which contained compounds **1** and **2**. This was extracted with CH_2Cl_2 and chromatographed again using hexane–methanol (9:1). Two bands were found: the first contained 4.7 mg (1.2%) of **1**, the second 21.1 mg (5.5%) of **2**.

Table 3 Crystal data and structure refinement for $[Ru_4(CO)_9(C_{15}H_{20})]$ **1** and **2***

	1	2
Crystal system	Rhombohedral	Monoclinic
Space group	*R*3*c*	*P*2$_1$/*n*
a/Å	16.189(2)	14.341(3)
b/Å	16.189(2)	12.063(2)
c/Å	34.052(7)	14.593(3)
β/°		90.30(3)
U/Å³	7729(2)	2524.5(9)
Z	12	4
D_c/g cm^{-3}	2.209	2.254
μ/mm^{-1}	2.351	2.399
F(000)	4944	1648
Crystal size/mm	0.19 x 0.27 x 0.16	0.64 x 0.60 x 0.51
θ Range for data collection/°	2.52–25.04	2.61–24.05
hkl Ranges	−16 to 16, 0–19, 0–40	−16 to 16, 0–13, 0–16
Reflections collected	2867	4133
Independent reflections (R_{int})	1526 (0.0437)	3986 (0.0186)
Maximum, and minimum transmission	0.693, 0.585	0.195, 0.143
Data, restraints, parameters	1525, 0, 118	3979, 0, 334
Goodness of fit on F^2	1.052	1.112
Final *R*1, wR_2 indices [$I > 2\sigma(I)$]	0.0503	0.0315
	0.1033	0.0745
(all data)	0.0774	0.0374
	0.1140	0.0916
Largest difference peak and hole/e Å^{-3}	2.108, −1.080	1.981, −1.087

* Details in common: $C_{24}H_{20}O_9Ru_4$; *M* 856.68; Mo-Kα radiation, λ = 0.710 73 Å.

Compound **1**: δ_H[250 MHz, $CDCl_3$ all coupling constants assign to *J*(HH)] 3.57 (1 H, dd, *J* 2, H_A), 3.22 (1 H, d, *J* 2.2, H_B), 2.22 (1 H, dd, *J* 2, H_C), 2.09 (3 H, s, H_D), 2.00 (3 H, s, H_E), 1.65 (3 H, s, H_F), 1.50 (3 H, s, H_G), 1.21 (3 H, s, H_H), 1.42 (1 H, d, *J* 2.2, H_I) and −0.28 (1 H, dd, *J* 2 Hz, H_J); mass spectrum (FAB) *m*/*z* 857 (M^+, calc. 856) (Found: C, 33.35; H, 1.95. $C_{24}H_{20}O_9Ru_4$ requires C, 33.65; H, 2.35%); IR (CH_2Cl_2) $\tilde{\nu}$/cm^{-1} 2060s, 2000vs, 1964w and 1933w. Compound **2**: δ_H(250 MHz, $CDCl_3$) 5.43 (1 H, d, *J* 1.7, H_A), 3.35 (1 H, d, *J* 2.3, H_B), 2.97 (1 H, d, *J* 2.3, H_C), 2.40 (1 H, spt, *J* 7, H_D), 1.94 (1 H, d, *J* 2.3, H_E), 1.66 (1 H, d, *J* 2.3, H_F), 1.52 (3 H, s, H_G), 1.44 (6 H, d, *J* 7, H_H), 1.31 (3 H, s, H_I), 0.59 (1 H, t, *J* 1.7, H_J) and 0.21 (1 H, d, *J* 1.7 Hz, H_K); mass spectrum (FAB) *m*/*z* 856 (M^+, calc. 856) (Found: C, 33.4; H, 2.05. $C_{24}H_{20}O_9Ru_4$ requires C, 33.65; H, 2.35%); IR (CH_2Cl_2) $\tilde{\nu}$/cm^{-1} 2060s, 2000vs, 1965w, 1923w and 1900w.

Crystallography

Crystal data and details of measurements for compounds **1** and **2** are summarized in Table 3. The diffraction intensities were collected at 150.0(2) K on a Stöe four-circle diffractometer, equipped with an Oxford Cryosystems low-temperature device. The intensities were reduced to F_o^2 and an absorption correction based on ψ-scan data was applied. The structures were solved by direct methods, followed by Fourier difference and full-matrix least-squares refinements using the computer programs SHELXS 86 and SHELXL 93.[8] In **2** all non-H atoms were allowed to refine with anisotropic displacement parameters. In **1** the arene ligand is disordered about the crystallographic three-fold axis on which the molecule lies. The disorder was modelled with atoms C(4a) and C(4b) having occupancies $\frac{1}{3}$ and $\frac{2}{3}$, respectively. All atoms with the exception of C(4a) were refined with anisotropic displacement parameters. The H atoms in both structures were placed in idealized positions and allowed to ride on their respective C atoms.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/191.

Acknowledgements

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