Syntheses and *X*-Ray Crystal Structures of $[Ru_4(CO)_{12}(MeC{=}CMe)]$ and $[Ru_6C(CO)_{15}(MeCH{=}CH{-}CH{=}CHMe)]$, Products of the Reaction of Ethylene with $[Ru_3(CO)_{12}]$

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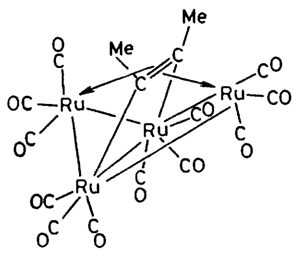
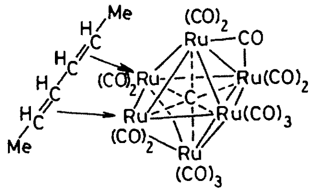
Summary The reaction of ethylene with $[Ru_3(CO)_{12}]$ yields, amongst others, the products $[Ru_4(CO)_{12}(MeC{=}CMe)]$ (**1**) and $[Ru_6C(CO)_{15}(MeCH{=}CH{-}CH{=}CHMe)]$ (**2**), both of which have been characterised by single-crystal *X*-ray analysis; (**2**) contains a novel six carbon-atom chain co-ordinated across an edge of the octahedral cluster.

THE structural characterisation of organic ligands on transition metal carbonyl clusters is of interest in catalytic chemistry.[1] Previous reports have described the synthesis of hexanuclear organo-osmium derivatives from the reaction of $[Os_6(CO)_{18}]$ with ethylene[2] and diphenylacetylene.[3] Although $[Ru_3(CO)_{12}]$ reacts with ethylene to produce moderate yields of $[Ru_6C(CO)_{17}]$,[4] we now report the characterisation of two minor products from this reaction, both of which contain unsaturated organic ligands. The clusters $[Ru_4(CO)_{12}(MeC{=}CMe)]$ (**1**) [i.r. ν_{CO} ($CHCl_3$) 2090vw, 2064s, 2036sh, 2032vs, and 2004 mbr cm^{-1}; ^1H n.m.r. τ ($CDCl_3$) 6.81(s); and *m/e* (AEI MS12) 794] and $[Ru_6C(CO)_{15}(MeCH{=}CH{-}CH{=}CHMe)]$ (**2**) [i.r. ν_{CO} ($CHCl_3$) 2081m, 2042s, 2027sbr, 1980mw, and 1830w cm^{-1}; ^1H n.m.r. τ ($CDCl_3$) *ca.* 2·35(m) and *ca.* 5·7(m); and *m/e* (AEI MS12) 1120] were separated from the reaction mixture by t.l.c. and characterised using i.r., ^1H n.m.r., and mass spectroscopic data. The nature of the organic units and the overall molecular geometries of (**1**) and (**2**) were established by single-crystal *X*-ray analyses following crystallisation from CH_2Cl_2–MeOH.†



(1)



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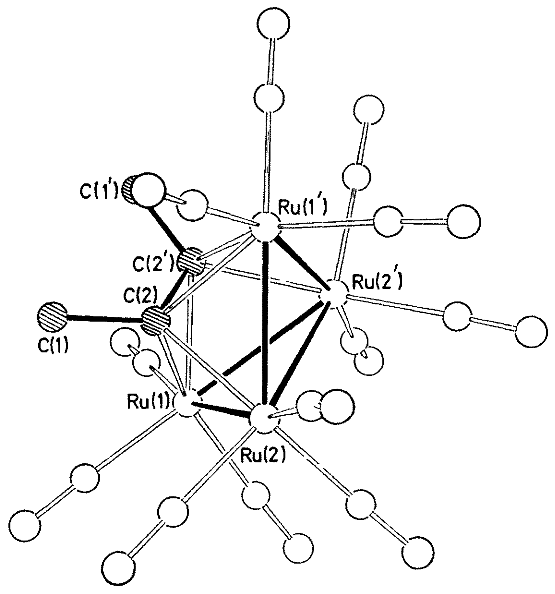

FIGURE 1. The structure of $[Ru_4(CO)_{12}(MeC{=}CMe)]$ (**1**). Principal bond lengths are Ru(1)–Ru(2) 2·728, Ru(1)–Ru(2′) 2·710, Ru(2)–Ru(2′) 2·880, Ru(1)–C(2) 2·24, Ru(1)–C(2′) 2·27, Ru(2)–C(2) 2·16, C(2)–C(2′) 1·45, Ru–CO (mean) 1·91, and C–O (mean) 1·14 Å. Maximum e.s.d.'s Ru-Ru 0·001 and Ru-C and C–C 0·01 Å. The angle C(1)–C(2)–C(2′) is 123·8(2)°. The dihedral angle between the Ru(1)Ru(2)Ru(2′) and Ru(1′)(Ru(2)Ru(2′) planes is 63·1°.

The structure of (**1**) is shown in Figure 1, together with some important bond parameters. The four Ru atoms adopt a 'butterfly' configuration and the olefinic fragment lies over the metal skeleton with the ethylenic C–C bond parallel to the Ru–Ru 'hinge' bond. A crystallographic C_2 axis bisects the Ru(2)–Ru(2′) and C(2)–C(2′) bonds. The organic fragment is π-bound to the two 'wing-tip' metal atoms and is σ-bound to the two 'hinge' atoms to form a distorted octahedral core. A similar mode of bonding of the organic fragment has been observed in other ruthenium clusters.[5,6] The ethylenic bonds in all these complexes lie in the range

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† *Crystal data:* (**1**) $C_{16}H_6O_{12}Ru_4$, $M = 794{\cdot}61$, orthorhombic, *Pnna*, $a = 13{\cdot}118(3)$, $b = 13{\cdot}457(4)$, $c = 12{\cdot}169(4)$ Å, $U = 2148{\cdot}2$ Å^3, $Z = 4$, $D_c = 2{\cdot}46$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 27{\cdot}4$ cm^{-1}; $F > 3\sigma(F)$, $2\theta_{max}$ 55°; R 0·030 for 2349 reflections measured on a Stoe 4-circle diffractometer. (**2**) $C_{22}H_{10}O_{15}Ru_6$, $M = 1120{\cdot}90$, monoclinic, $P2_1/c$, $a = 10{\cdot}592(3)$, $b = 32{\cdot}953(8)$, $c = 16{\cdot}746(5)$ Å, $\beta = 96{\cdot}34(2)°$, $U = 5809{\cdot}3$ Å^3, $Z = 8$, $D_c = 2{\cdot}56$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 28{\cdot}4$ cm^{-1}; $I > 3\sigma(I)$, $2\theta_{max}$ 50°, R 0·042 for 7887 reflections measured on a Philips PW1100 diffractometer. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

1·43—1·46 Å and are considered to have formal double-bond character. The C(2)—C(1) bond is single and the twelve carbonyl groups are terminal.

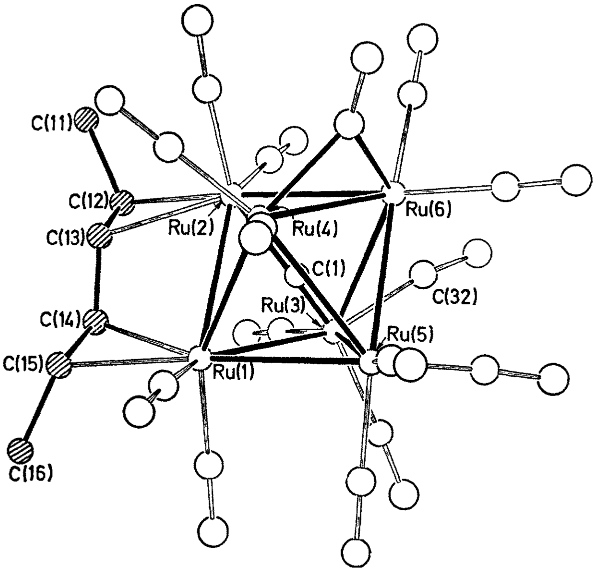

FIGURE 2. The structure of $[Ru_6C(CO)_{15}(MeCH{=}CH{-}CH{=}CHMe)]$ (**2**). [There are two independent molecules in the asymmetric unit of (**2**). The bond lengths for the second molecule, in which the organo-ligand is disordered, are not given.] Principal bond lengths are Ru(1)–Ru(2) 2·982(1), Ru(1)–Ru(3) 2·913, Ru(1)–Ru(4) 2·911, Ru(1)–Ru(5) 2·881, Ru(2)–Ru(3) 2·895, Ru(2)–Ru(4) 2·943, Ru(2)–Ru(6) 2·842, Ru(3)–Ru(5) 2·829, Ru(3)–Ru(6) 2·964, Ru(4)–Ru(5) 2·966, Ru(4)–Ru(6) 2·842, Ru(5)–Ru(6) 2·915, Ru(2)–C(12) 2·31, Ru(2)–C(13) 2·31, Ru(1)–C(14) 2·27, Ru(1)–C(15) 2·30, Ru–C(1) (mean) 2·06, C(11)–C(12) 1·51, C(12)–C(13) 1·37, C(13)–C(14) 1·42, C(14)–C(15) 1·34, C(15)–C(16) 1·49, Ru–CO (mean) 1·89, and C–O (mean) 1·16 Å. Maximum e.s.d.'s are Ru–Ru 0·001, Ru–C 0·01, and C–C 0·02 Å. The C–C–C angles are 123—129°.

The most interesting feature of the structure of (**2**), shown in Figure 2, is the observation for the first time of a six carbon-atom chain bonded to a hexa-metal cluster compound. Integration of the ^{1}H n.m.r. spectrum is consistent with the assignment of the low-field multiplet to the four (C–H) protons and the remaining multiplet to the methyl groups of the hexadiene ligand. The overall structure of (**2**) is related to that of $[Ru_6C(CO)_{17}]$[7] by replacement of two carbonyl ligands on adjacent metal atoms with the *trans, trans*-hexa-2,4-diene molecules; the μ_2-carbonyl ligand is retained and there is also an incipient carbonyl bridge [Ru(3)–C(32) 1·879(11), Ru(6)–C(32) 2·692(11) Å, Ru(3)–C(32)–O(32) 162·4(9)°]. Since the carbon atom at the centre of the Ru_6 octahedron contributes 4 electrons to the skeletal cluster-bonding, it reduces the number of carbonyl ligands required by two compared with a non-carbido-cluster. Clearly the presence of this interstitital carbon atom in (**2**) is important in allowing the accommodation of the bulky six carbon-atom chain among the close-packed carbonyl ligands on the cluster surface. It is significant that although the first interstitial carbido-cluster to be characterised was the arene complex $[Ru_6C(CO)_{14}(Me_3C_6H_3)]$,[8] no arene derivatives have so far been obtained for octahedral Os_6 carbonyl clusters, which show no tendency to incorporate interstitial atoms.

The isolation of (**1**) and (**2**) indicates that oligomerisation of ethylene has occurred in the reaction with $[Ru_3(CO)_{12}]$ and such compounds may be important intermediates in the catalytic polymerisation of small organic molecules by transition metal clusters.

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