Synthesis of a Series of Hexanuclear Ruthenium Carbido Cluster Alkynes under Mild Conditions: *X*-Ray Structure Analyses of the Complexes $[Ru_6C(CO)_{15}(\mu_3\text{-}\eta^2\text{-}PhCCH)]$ and $[Ru_6C(CO)_{15}(\mu_3\text{-}\eta^2\text{-}PhCCMe)]$ †

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The reaction of $[Ru_6C(CO)_{16}]^{2-}$ (**1**) with alkynes in the presence of $[Fe(cp)_2]BF_4$ (cp = η^5-C_5H_5) or $FeCl_3$ gives the alkyne cluster derivatives $[Ru_6C(CO)_{15}(\mu_3\text{-}\eta^2\text{-}RCCR')]$ [R = R′ = H (**2**), Me (**3**), Et (**4**), or Ph (**5**); R ≠ R′, H and Ph (**6**), Me and Ph (**7**)] as the respective major products at room temperature. Prolonged heating of the cluster $[Ru_6C(CO)_{15}(\mu_3\text{-}\eta^2\text{-}PhCCH)]$ (**6**) in toluene over 3 d converts it into $[Ru_6C(CO)_{15}(\mu\text{-}H)(CCPh)]$ (**8**), with hydride migration from the organo-fragment to a ruthenium metal centre. The structure of complexes (**6**) and (**7**) have been established by *X*-ray diffraction studies which show the alkyne ligands bonding to triangular ruthenium faces in a μ_3-η^2 mode.

The analogy between the chemistry of alkyne- or alkene-substituted cluster complexes and the chemisorption of such organic molecules on a metal surface is well known.[1] An understanding of the interaction of an alkyne with a transition-metal cluster may provide some insight into the nature of the interaction occurring between an unsaturated organic molecule and a metal surface. The chemistry of alkyne derivatives of M_3 and M_4 (M = Fe, Ru, or Os) clusters is now well established,[2,3] and for trinuclear ruthenium clusters the use of the activated cluster $[Ru_3(CO)_{12-n}(NCMe)_n]$ (n = 1 or 2)[4] containing the labile acetonitrile ligand has considerably simplified the production of specific cluster complexes under mild reaction conditions.[5]

Progress in the area of organo higher-nuclearity clusters has until recently been restricted due to the forcing conditions required, and many early Ru_6 organo complexes were products of $[Ru_3(CO)_{12}]$ aggregation reactions.[6] Ansell and Bradley[7] were able to isolate $[Ru_6C(CO)_{14}(C_{14}H_{14})]$ in high yield by the direct reaction of $[Ru_6C(CO)_{16}]^{2-}$ (**1**) and tropylium bromide $[C_7H_7]Br$. The incoming ligand bitropyl ($C_{14}H_{14}$) is a product of the simple redox reaction between $[Ru_6C(CO)_{16}]^{2-}$ (**1**) and tropylium. More recently Hayward and Shapley[8] have shown that the oxidation of (**1**) under CO to $[Ru_6C(CO)_{17}]$ occurs in high yield. It has now been found that this approach is widely applicable for the synthesis of a range of substituted complexes of (**1**).[9]

Results and Discussion

We have previously shown that the electrochemical two-electron oxidation of $[Ru_6C(CO)_{16}]^{2-}$ (**1**) under a carbon monoxide atmosphere at a platinum electrode occurs at +0.5 V (*vs.* Ag–AgCl) and on the same scale the couples $[Fe(cp)_2]/[Fe(cp)_2]BF_4$ (cp = η^5-C_5H_5) and $FeCl_2$–$FeCl_3$ occur at similar values of +0.53 V.[10] This provides the basis for an alternative method of synthesis using either chemical or electrochemical oxidation of ruthenium cluster dianions in the presence of the ligand at room temperature, which results in a higher and more selective yield of the product desired.

The reactions of $[Ru_6C(CO)_{16}]^{2-}$ (**1**) with alkynes in the presence of 2 equivalents of either of the oxidants $[Fe(cp)_2]BF_4$ or $FeCl_3$ results in the formation of products of general formula $[Ru_6C(CO)_{15}(RCCR')]$. All of the products were isolated from the reaction mixtures in high yield, by the use of chromatography. The clusters (**2**)—(**7**) have been characterised by i.r., ^{1}H n.m.r., electron-impact mass spectrometry (Table 1), and satisfactory microanalysis. The derivatives all had clear molecular ions consistent with the formulation $[Ru_6C(CO)_{15}(RCCR')]$, and the mass spectra showed the stepwise loss of 15 carbonyl groups. The i.r. spectra (Table 1) indicated the presence of only terminal carbonyl ligands, and no resonances in the metal hydride region were observed in the ^{1}H n.m.r. spectra. The nature of the bonding of the organic fragments and the overall molecular geometries of (**6**) and (**7**) were established by single-crystal *X*-ray structure analysis. Selected bond lengths and angles are in Table 2.

In the structures of (**6**) and (**7**) shown in Figures 1 and 2 the six ruthenium atoms adopt a slightly distorted octahedral geometry [Ru–Ru 2.764—2.980(2) for (**6**) and 2.782—2.991(1) for (**7**)], with the interstitial carbon atom lying close to the geometric centre in each [Ru–C 2.015(14)—2.073(15) for (**6**) and 1.992(13)—2.098(11) Å for (**7**)] and mean Ru–C(carbido) distances of 2.045(25) in (**6**) and 2.045(42) in (**7**), which are shorter than that in $[Ru_6C(CO)_{16}]^{2-}$ (**1**).[11] The organo ligand is bonded to the triangular face Ru(1), Ru(2), Ru(3), the co-ordination of each metal being completed by carbonyl ligands, with three carbonyls on each of the three remaining ruthenium atoms.

In structures (**6**) and (**7**) both carbon atoms of the alkyne group bond to Ru(3) [Ru(3)–C(1) 2.264(11) (**6**) and 2.181(11) (**7**), Ru(3)–C(2) 2.174(11) (**6**) and 2.201(11) (**7**)], in addition each bonds to one other ruthenium atom of the triangular face [Ru(1)–C(1) 2.095(13) (**6**) and 2.069(8) (**7**); Ru(2)–C(2) 2.076(13) (**6**) and 2.078(9) Å (**7**)].

The alkynic C(1)–C(2) bond lies nearly parallel to the Ru(1)–Ru(2) edge of the two clusters (Figures 1 and 2), and in both cases a reduction in the formal C–C bond order upon co-

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† μ_6-Carbido-1,1,2,2,2,3,3,3,4,4,5,5,6,6,6-pentadecacarbonyl-μ_3-[phenylvinylene-C^1(Ru^{1,4})C^2(Ru^{1,5})]- and -μ_3-[methyl(phenyl)vinylene-C^1(Ru^{1,4})C^2(Ru^{1,5})]-*octahedro*-hexaruthenium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Selected spectroscopic data for complexes (**2**)—(**8**)

Complex	I.r.[a] ν(CO)/cm^{-1}	m/z[b]	^{1}H N.m.r.[c] (δ)
(**2**)	2 089w, 2 046vs, 2 039s, 2 025m, 2 018m, 1 995w, 1 987w, 1 973vw	1 070	9.09 (s, 2 H)
(**3**)	2 087w, 2 042vs, 2 035s (sh), 2 020m, 2 011m, 1 988w, 1 960w (sh)	1 098	3 02 (s, 6 H)
(**4**)	2 088w, 2 043vs, 2 036s (sh), 2 019m, 2 010m, 1 982w (sh), 1 963vw (sh)	1 126	3.12 (q, 3 H), 1.57 (t, 2 H)
(**5**)	2 088w, 2 045vs, 2 038s (sh), 2 018m (sh), 2 014m, 1 986w, 1 962vw (sh)	1 222	7.42 (m, Ph)
(**6**)	2 088w, 2 044vs, 2 039s (sh), 2 019m (sh), 2 014m, 1 988w, 1 963vw (sh)	1 146	10.17 (s, 1 H), 7.41 (m, Ph)
(**7**)	2 088w, 2 046vs, 2 037s (sh), 2 022m, 2 015m (sh), 1 982w, 1 964vw	1 160	7.38 (m, Ph), 3.40 (s, 3 H)
(**8**)	2 096w, 2 051vs, 2 039s (sh), 2 028m, 2 016m, 1 994w (sh)	1 146	7.36 (m, Ph), −17.04 (s, Ru–H–Ru)

[a] In CH_2Cl_2. [b] Using ^{102}Ru. [c] In CD_2Cl_2, J in Hz.

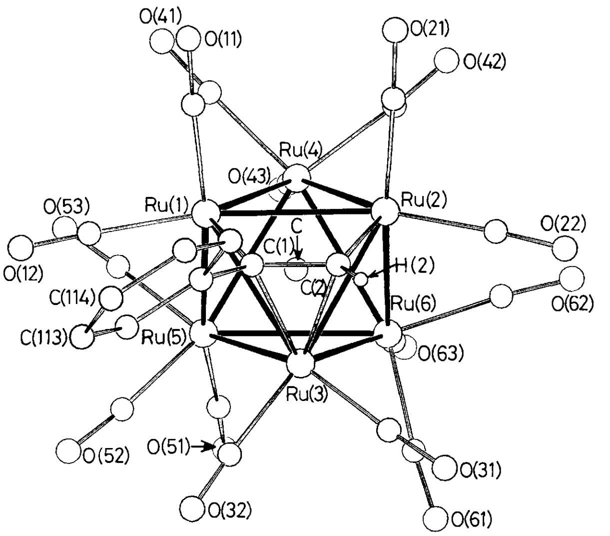

Figure 1. The structure of $[Ru_6C(CO)_{15}(\mu_3\text{-}\eta^2\text{-PhCCH})]$ (**6**). The carbonyl carbon atoms have the same number as the corresponding oxygen atoms

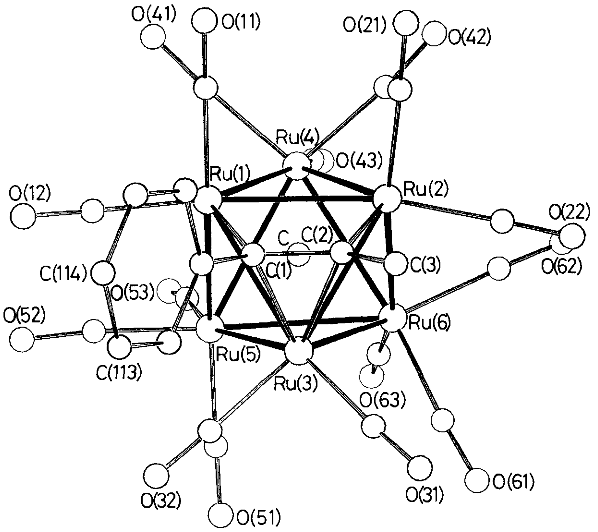

Figure 2. The structure of $[Ru_6C(CO)_{15}(\mu_3\text{-}\eta^2\text{-PhCCMe})]$ (**7**). The carbonyl carbon atoms have the same number as the corresponding oxygen atoms

ordination of the alkyne is indicated by the C(1)–C(2) bond lengths of 1.365(17) in (**6**) and 1.395(13) in (**7**). The interaction of the alkyne with metal atoms Ru(1) and Ru(2) in both structures may be formally described as σ bonding in character, with that to Ru(3) being π bonding (Figures 1 and 2). This 'parallel' μ_3-η^2 mode of bonding is more widely observed in clusters containing alkyne ligands than the alternative perpendicular μ_3-η^2 mode.[12] Formally in (**6**) and (**7**) the alkyne ligand is contributing a total of four electrons to the overall polyhedral count of the cluster giving a total of 86 electrons, as expected for octahedral clusters.

The alkyne clusters (**2**)—(**5**) and (**7**) were found to be stable to extremes of heat, *e.g.* (**3**) was heated under reflux in toluene for 4 d and recovered in near-quantitative yield. In contrast the cluster $[Ru_6C(CO)_{15}(\mu_3\text{-}\eta^2\text{-PhCCH})]$ (**6**) on heating in toluene at 60 °C for 3 d is converted into the new cluster $[Ru_6C(CO)_{15}(\mu\text{-H})(CCPh)]$ (**8**). The mass spectrum shows a clear molecular ion and the ^{1}H n.m.r. spectrum of (**8**) in CD_2Cl_2 is consistent with the presence of a metal hydride. It appears that there has been a transfer of a hydrogen atom from the organo fragment to the metal core. We attribute this thermal stability to the presence of the interstitial carbido atom in these hexanuclear ruthenium clusters. The corresponding Os_6 and Os_7 alkyne-based clusters have been found to undergo major skeletal rearrangements on prolonged heating.[13,14]

Experimental

All reactions were carried out under nitrogen using dry degassed solvents. Infrared spectra were recorded on a Perkin-Elmer PE 983 spectrometer, ^{1}H n.m.r. spectra on Bruker WM 250 and WH 400 instruments using CD_2Cl_2 as the internal reference. Electron-impact mass spectroscopy was performed on a N.E.I. MS 12 spectrometer using tris(perfluoroheptyl)-s-triazine as calibrant. Microanalyses were performed in the University Chemical Laboratory, Cambridge. Thin-layer chromatography plates (20 x 20 cm) were bought from Merck and were coated with a 0.25-mm layer of silica gel. The cluster $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ was prepared by the literature method.[11]

Preparations.—$[Ru_6C(CO)_{15}(HCCH)]$ (**2**). The salt $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ (100 mg, 0.0467 mmol) was dissolved in CH_2Cl_2 (freeze-thaw degassed) (15 cm^3) and HCCH bubbled through the solution for 10 min. The oxidant $[Fe(cp)_2]BF_4$ (30 mg, 0.111 mmol) was then added as a solid and the reaction monitored by i.r. spectroscopy. It was complete after 15 min with a change in colour from red to black. The reaction mixture was then filtered through a sintered funnel and reduced in volume. The resulting solution was then separated on thin silica plates using 20% CH_2Cl_2–80% hexane to yield a yellow band at r.f. 0.1 (ferrocene) and the alkyne cluster $[Ru_6C(CO)_{15}(HCCH)]$ (**2**) as a brown band at r.f. 0.4. Black crystals of (**2**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 24 h at 0 °C (yield 16 mg, 27%), and were characterised by i.r. ^{1}H n.m.r., mass spectroscopy (Table 1), and microanalysis (Found: C, 20.35; H, 0.20. Calc. for $C_{18}H_2O_{15}Ru_6$: C, 20.20; H, 0.20%).

Table 2. Selected bond lengths (Å) and angles (°) for complexes (**6**) and (**7**)

	(**6**)	(**7**)		(**6**)	(**7**)
Ru(1)–Ru(2)	2.837(2)	2.815(1)	Ru(3)–C(2)	2.174(11)	2.201(11)
Ru(1)–Ru(3)	2.815(2)	2.791(1)	Ru(4)–Ru(5)	2.874(2)	2.915(1)
Ru(1)–Ru(4)	2.980(2)	2.989(1)	Ru(4)–Ru(6)	2.857(2)	2.836(1)
Ru(1)–Ru(5)	2.863(1)	2.952(1)	Ru(4)–C(41)	1.946(20)	1.916(11)
Ru(1)–C(11)	1.894(15)	1.883(13)	Ru(4)–C(42)	1.925(16)	1.894(12)
Ru(1)–C(12)	1.895(15)	1.882(12)	Ru(4)–C(43)	1.930(16)	1.908(17)
Ru(1)–C(1)	2.095(13)	2.069(8)	Ru(5)–Ru(6)	2.912(2)	2.870(1)
Ru(2)–Ru(3)	2.764(2)	2.782(1)	Ru(5)–C(51)	1.902(14)	1.910(13)
Ru(2)–Ru(4)	2.963(2)	2.991(1)	Ru(5)–C(52)	1.908(19)	1.876(17)
Ru(2)–Ru(6)	2.934(1)	2.885(1)	Ru(5)–C(53)	1.880(18)	1.902(11)
Ru(2)–C(21)	1.892(16)	1.904(13)	Ru(6)–C(61)	1.913(19)	1.929(12)
Ru(2)–C(22)	1.871(17)	1.888(10)	Ru(6)–C(62)	1.893(16)	1.890(13)
Ru(2)–C(2)	2.076(13)	2.078(9)	Ru(6)–C(63)	1.862(21)	1.880(14)
Ru(3)–Ru(5)	2.969(2)	2.880(1)	C(1)–C(2)	1.365(17)	1.395(13)
Ru(3)–Ru(6)	2.930(2)	2.974(1)	C(1)–C(111)	1.475(13)	1.504(12)
Ru(3)–C(31)	1.864(17)	1.906(9)	C(2)–C(3)		1.519(13)
Ru(3)–C(32)	1.915(15)	1.902(12)	Cl(1)–C(S)		1.61(6)
Ru(3)–C(1)	2.264(11)	2.181(11)	Cl(2)–C(S)		1.97(6)
Ru–Carbide	2.015—2.073	1.992—2.098			
Ru(3)–Ru(1)–Ru(2)	58.6(1)	59.5(1)	C(32)–Ru(3)–Ru(1)	110.5(5)	102.1(3)
Ru(4)–Ru(1)–Ru(2)	61.2(1)	62.0(1)	C(32)–Ru(3)–Ru(2)	165.8(4)	162.7(3)
Ru(4)–Ru(1)–Ru(3)	90.1(1)	90.7(1)	C(32)–Ru(3)–Ru(5)	94.3(4)	81.1(3)
Ru(5)–Ru(1)–Ru(2)	91.3(1)	89.6(1)	C(32)–Ru(3)–Ru(6)	131.6(4)	126.4(3)
Ru(5)–Ru(1)–Ru(3)	63.0(1)	60.1(1)	C(41)–Ru(4)–Ru(1)	73.9(5)	76.1(3)
Ru(5)–Ru(1)–Ru(4)	58.9(1)	58.8(1)	C(41)–Ru(4)–Ru(2)	113.0(5)	117.7(3)
Ru(3)–Ru(2)–Ru(1)	60.3(1)	59.8(1)	C(41)–Ru(4)–Ru(5)	102.7(5)	102.6(4)
Ru(4)–Ru(2)–Ru(1)	61.8(1)	61.9(1)	C(41)–Ru(4)–Ru(6)	161.3(5)	161.5(4)
Ru(4)–Ru(2)–Ru(3)	91.5(1)	90.9(1)	C(42)–Ru(4)–Ru(1)	121.3(5)	109.5(4)
Ru(6)–Ru(2)–Ru(1)	90.1(1)	91.5(1)	C(42)–Ru(4)–Ru(2)	75.4(6)	68.7(3)
Ru(6)–Ru(2)–Ru(3)	61.8(1)	63.3(1)	C(42)–Ru(4)–Ru(5)	157.1(6)	154.1(3)
Ru(6)–Ru(2)–Ru(4)	58.0(1)	57.7(1)	C(42)–Ru(4)–Ru(6)	96.4(6)	98.4(3)
Ru(2)–Ru(3)–Ru(1)	61.1(1)	60.7(1)	C(43)–Ru(4)–Ru(1)	144.5(4)	157.9(5)
Ru(5)–Ru(3)–Ru(1)	59.3(1)	62.7(1)	C(43)–Ru(4)–Ru(2)	152.1(5)	143.4(4)
Ru(5)–Ru(3)–Ru(2)	90.6(1)	91.7(1)	C(43)–Ru(4)–Ru(5)	93.8(5)	104.4(6)
Ru(6)–Ru(3)–Ru(1)	90.6(1)	90.1(1)	C(43)–Ru(4)–Ru(6)	96.7(6)	96.2(5)
Ru(6)–Ru(3)–Ru(2)	61.9(1)	60.1(1)	C(51)–Ru(5)–Ru(1)	171.2(5)	143.2(3)
Ru(6)–Ru(3)–Ru(5)	59.2(1)	58.7(1)	C(51)–Ru(5)–Ru(3)	119.5(6)	90.4(3)
Ru(2)–Ru(4)–Ru(1)	57.0(1)	56.2(1)	C(51)–Ru(5)–Ru(4)	110.1(5)	143.7(4)
Ru(5)–Ru(4)–Ru(1)	58.5(1)	60.0(1)	C(51)–Ru(5)–Ru(6)	81.8(5)	90.1(4)
Ru(5)–Ru(4)–Ru(2)	88.6(1)	86.9(1)	C(52)–Ru(5)–Ru(1)	97.5(4)	81.0(6)
Ru(6)–Ru(4)–Ru(1)	88.8(1)	88.9(1)	C(52)–Ru(5)–Ru(3)	85.4(5)	106.1(4)
Ru(6)–Ru(4)–Ru(2)	60.5(1)	59.3(1)	C(52)–Ru(5)–Ru(4)	158.7(5)	120.8(5)
Ru(6)–Ru(4)–Ru(5)	61.1(1)	59.8(1)	C(52)–Ru(5)–Ru(6)	132.6(6)	167.8(5)
Ru(3)–Ru(5)–Ru(1)	57.7(1)	57.2(1)	C(53)–Ru(5)–Ru(1)	88.3(4)	121.9(4)
Ru(4)–Ru(5)–Ru(1)	62.6(1)	61.3(1)	C(53)–Ru(5)–Ru(3)	145.1(4)	161.1(4)
Ru(4)–Ru(5)–Ru(3)	89.2(1)	90.5(1)	C(53)–Ru(5)–Ru(4)	80.7(5)	74.8(4)
Ru(6)–Ru(5)–Ru(1)	90.1(1)	89.0(1)	C(53)–Ru(5)–Ru(6)	135.0(5)	99.4(4)
Ru(6)–Ru(5)–Ru(3)	59.7(1)	62.3(1)	C(61)–Ru(6)–Ru(2)	120.2(4)	107.4(4)
Ru(6)–Ru(5)–Ru(4)	59.2(1)	58.7(1)	C(61)–Ru(6)–Ru(3)	78.2(5)	76.5(4)
Ru(3)–Ru(6)–Ru(2)	56.3(1)	56.7(1)	C(61)–Ru(6)–Ru(4)	162.1(5)	166.6(4)
Ru(4)–Ru(6)–Ru(2)	61.5(1)	63.0(1)	C(61)–Ru(6)–Ru(5)	102.4(5)	111.2(4)
Ru(4)–Ru(6)–Ru(3)	90.3(1)	90.2(1)	C(62)–Ru(6)–Ru(2)	76.9(4)	85.1(4)
Ru(5)–Ru(6)–Ru(2)	88.5(1)	89.8(1)	C(62)–Ru(6)–Ru(3)	117.1(5)	132.9(4)
Ru(5)–Ru(6)–Ru(3)	61.1(1)	59.0(1)	C(62)–Ru(6)–Ru(4)	102.7(6)	96.0(4)
Ru(5)–Ru(6)–Ru(4)	59.7(1)	61.4(1)	C(62)–Ru(6)–Ru(5)	161.4(5)	156.4(3)
C(11)–Ru(1)–Ru(2)	95.7(5)	90.6(3)	C(63)–Ru(6)–Ru(2)	142.6(8)	156.0(4)
C(11)–Ru(1)–Ru(3)	140.7(6)	140.0(3)	C(63)–Ru(6)–Ru(3)	151.7(6)	134.0(4)
C(11)–Ru(1)–Ru(4)	103.1(5)	98.0(4)	C(63)–Ru(6)–Ru(4)	87.8(8)	93.6(3)
C(11)–Ru(1)–Ru(5)	153.9(6)	153.0(3)	C(63)–Ru(6)–Ru(5)	94.1(7)	83.1(3)
C(12)–Ru(1)–Ru(2)	168.0(6)	164.2(3)	Ru(3)–C(1)–Ru(1)	80.4(4)	82.0(4)
C(12)–Ru(1)–Ru(3)	111.3(5)	112.5(3)	C(2)–C(1)–Ru(1)	108.2(9)	110.2(6)
C(12)–Ru(1)–Ru(4)	128.1(4)	133.7(3)	C(2)–C(1)–Ru(3)	68.5(7)	72.2(6)
C(12)–Ru(1)–Ru(5)	88.7(4)	97.8(4)	C(111)–C(1)–Ru(1)	125.3(8)	124.1(6)
C(21)–Ru(2)–Ru(1)	94.3(5)	96.4(3)	C(111)–C(1)–Ru(3)	127.9(8)	130.7(7)
C(21)–Ru(2)–Ru(3)	143.8(5)	141.3(3)	C(111)–C(1)–C(2)	125(1)	121.8(7)
C(21)–Ru(2)–Ru(4)	98.6(6)	104.6(3)	Ru(3)–C(2)–Ru(2)	81.1(4)	81.0(3)
C(21)–Ru(2)–Ru(6)	150.0(5)	153.7(3)	C(1)–C(2)–Ru(2)	113(1)	109.8(6)

Table 2 (*continued*)

	(6)	(7)		(6)	(7)
C(22)–Ru(2)–Ru(1)	158.8(5)	165.4(3)	C(1)–C(2)–Ru(3)	75.7(7)	70.7(6)
C(22)–Ru(2)–Ru(3)	105.5(5)	107.4(3)	C(3)–C(2)–Ru(2)		123.6(7)
C(22)–Ru(2)–Ru(4)	138.0(5)	128.9(3)	C(3)–C(2)–Ru(3)		128.7(7)
C(22)–Ru(2)–Ru(6)	96.6(4)	88.3(4)	C(3)–C(2)–C(1)		124.4(9)
C(31)–Ru(3)–Ru(1)	155.4(4)	155.3(4)	C(112)–C(111)–C(1)	123.4(7)	122.1(8)
C(31)–Ru(3)–Ru(2)	99.7(4)	106.8(4)	C(116)–C(111)–C(1)	116.6(7)	117.9(8)
C(31)–Ru(3)–Ru(5)	141.2(4)	141.9(4)	Cl(2)–C(S)–Cl(1)		106(3)
C(31)–Ru(3)–Ru(6)	93.1(4)	101.9(4)			

Table 3. Fractional atomic co-ordinates for complexes (**6**) and (**7**)

	(6)			(7)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ru(1)	−0.347 80(12)	0.317 26(6)	0.049 07(6)	−0.340 26(4)	−0.169 29(8)	0.063 42(8)
Ru(2)	−0.319 18(12)	0.162 52(6)	−0.000 65(6)	−0.182 20(4)	−0.072 17(8)	0.077 53(8)
Ru(3)	−0.111 41(12)	0.275 84(6)	0.007 83(6)	−0.231 52(4)	−0.120 32(8)	0.330 74(8)
Ru(4)	−0.273 23(12)	0.184 85(7)	0.158 68(6)	−0.252 76(5)	−0.357 48(8)	−0.116 74(8)
Ru(5)	−0.065 82(12)	0.307 21(6)	0.166 20(6)	−0.299 79(5)	−0.398 29(8)	0.156 63(8)
Ru(6)	−0.029 55(12)	0.148 02(6)	0.118 14(6)	−0.140 53(4)	−0.301 12(8)	0.154 24(8)
C(11)	−0.554 8(16)	0.317 6(10)	0.010 6(9)	−0.368 5(6)	−0.086 0(11)	−0.083 6(11)
O(11)	−0.678 4(12)	0.315 5(7)	−0.012 7(8)	−0.385 7(5)	−0.033 1(9)	−0.170 0(9)
C(12)	−0.348 6(17)	0.427 1(9)	0.068 1(8)	−0.442 6(6)	−0.188 2(11)	0.096 5(12)
O(12)	−0.345 5(13)	0.492 0(6)	0.079 1(6)	−0.504 9(5)	−0.195 4(11)	0.115 7(12)
C(21)	−0.522 4(17)	0.141 8(9)	−0.037 8(9)	−0.197 5(6)	0.031 6(11)	−0.056 3(12)
O(21)	−0.643 5(12)	0.130 4(8)	−0.056 1(7)	−0.208 5(5)	0.094 5(9)	−0.137 3(10)
C(22)	−0.293 8(17)	0.082 8(9)	−0.061 9(8)	−0.076 6(6)	0.014 3(10)	0.140 0(11)
O(22)	−0.271 5(13)	0.034 3(7)	−0.100 1(7)	−0.012 9(4)	0.069 5(9)	0.180 8(10)
C(31)	−0.021 7(16)	0.227 6(8)	−0.050 9(7)	−0.155 4(6)	−0.011 2(11)	0.506 3(11)
O(31)	0.028 7(13)	0.196 0(6)	−0.088 1(6)	−0.109 2(5)	0.055 5(9)	0.606 6(9)
C(32)	−0.008 5(15)	0.368 5(8)	−0.002 3(7)	−0.294 9(6)	−0.161 2(10)	0.466 0(11)
O(32)	0.052 8(12)	0.420 2(6)	−0.012 1(6)	−0.334 1(5)	−0.186 7(9)	0.542 8(10)
C(41)	−0.431 1(20)	0.243 0(8)	0.173 1(9)	−0.350 1(6)	−0.389 8(10)	−0.252 8(12)
O(41)	−0.516 5(13)	0.272 1(7)	0.188 6(7)	−0.405 8(5)	−0.416 9(8)	−0.342 5(10)
C(42)	−0.367 5(18)	0.083 4(9)	0.133 2(10)	−0.192 2(6)	−0.266 4(11)	−0.222 1(11)
O(42)	−0.425 6(15)	0.026 6(7)	0.122 4(7)	−0.159 6(5)	−0.230 8(9)	−0.304 9(8)
C(43)	−0.181 1(18)	0.157 9(8)	0.262 9(9)	−0.228 8(9)	−0.525 5(17)	−0.223 1(18)
O(43)	−0.124 6(13)	0.145 6(7)	0.323 3(6)	−0.213 6(7)	−0.628 3(14)	−0.279 4(15)
C(51)	0.118 0(17)	0.283 5(9)	0.242 1(9)	−0.268 3(7)	−0.452 1(11)	0.330 8(12)
O(51)	0.224 6(14)	0.271 5(9)	0.288 7(8)	−0.249 1(6)	−0.487 1(8)	0.430 9(9)
C(52)	0.005 9(19)	0.407 8(11)	0.150 6(9)	−0.404 5(9)	−0.422 7(16)	0.172 8(17)
O(52)	0.044 6(16)	0.470 6(7)	0.145 6(7)	−0.467 6(8)	−0.447 6(13)	0.188 4(15)
C(53)	−0.148 6(17)	0.350 5(10)	0.231 2(8)	−0.315 3(6)	−0.574 8(12)	0.013 5(12)
O(53)	−0.195 3(14)	0.378 5(8)	0.271 9(7)	−0.325 9(6)	−0.686 3(8)	−0.056 6(10)
C(61)	0.142 9(18)	0.158 1(9)	0.095 5(9)	−0.078 7(7)	−0.233 6(12)	0.358 8(14)
O(61)	0.249 5(12)	0.156 7(7)	0.085 0(7)	−0.037 5(5)	−0.202 6(10)	0.473 4(9)
C(62)	−0.071 0(17)	0.043 4(9)	0.081 6(9)	−0.053 2(6)	−0.268 1(13)	0.066 2(14)
O(62)	−0.084 3(15)	−0.022 0(6)	0.064 0(8)	−0.000 5(5)	−0.255 1(11)	0.013 8(13)
C(63)	0.065 8(24)	0.110 6(12)	0.214 8(12)	−0.135 0(6)	−0.483 6(13)	0.118 9(14)
O(63)	0.126 5(19)	0.082 0(10)	0.271 2(10)	−0.129 8(6)	−0.594 6(9)	0.097 7(12)
C	−0.194 4(16)	0.232 1(8)	0.084 2(8)	−0.242 2(7)	−0.237 7(12)	0.101 3(13)
C(1)	−0.338 5(13)	0.322 5(7)	−0.057 5(6)	−0.299 5(5)	0.007 3(9)	0.246 1(10)
C(2)	−0.321 0(14)	0.247 4(7)	−0.078 7(7)	−0.221 6(5)	0.057 5(9)	0.251 7(10)
C(111)	−0.379 3(9)	0.391 6(4)	−0.107 6(4)	−0.350 5(4)	0.096 5(7)	0.321 5(8)
C(112)	−0.318 6(9)	0.466 6(4)	−0.087 2(4)	−0.366 5(4)	0.101 3(7)	0.465 3(8)
C(113)	−0.364 3(9)	0.529 2(4)	−0.137 6(4)	−0.416 0(4)	0.182 5(7)	0.528 6(8)
C(114)	−0.470 7(9)	0.516 9(4)	−0.208 3(4)	−0.449 6(4)	0.259 0(7)	0.448 1(8)
C(115)	−0.531 4(9)	0.441 9(4)	−0.228 7(4)	−0.433 6(4)	0.254 2(7)	0.304 4(8)
C(116)	−0.485 7(9)	0.379 2(4)	−0.178 4(4)	−0.384 1(4)	0.172 9(7)	0.241 1(8)
C(3)				−0.179 4(6)	0.202 1(11)	0.338 8(12)
C(S)				−0.020 1(31)	−0.429 3(52)	−0.359 3(59)
Cl(1)				−0.054 6(5)	−0.552 8(10)	−0.303 2(13)
Cl(2)				0.023 1(8)	−0.509 3(13)	−0.540 8(16)

[Ru$_6$C(CO)$_{15}$(MeCCMe)] (**3**). The salt [N(PPh$_3$)$_2$]$_2$[Ru$_6$C(CO)$_{16}$] (100 mg, 0.0467 mmol) was dissolved in CH$_2$Cl$_2$ (freeze-thaw degassed) (15 cm^3) and MeCCMe (5 μl, 0.060 mmol) added at 0 °C to the solution. The oxidant [Fe(cp)$_2$]BF$_4$ (38 mg, 0.111 mmol) was then added as a solid and the reaction monitored by i.r. spectroscopy. It was complete after 15 min with a change in colour from red to black. The reaction mixture was then filtered through a sintered funnel and reduced in volume. The resulting solution was separated on thin silica plates using 20% CH_2Cl_2–80% hexane to yield a yellow band at R_f 0.1 (ferrocene) and the alkyne cluster [$Ru_6C(CO)_{15}$(MeCCMe)] (**3**) as a brown band at R_f 0.4. Black crystals of (**3**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 24 h at 0 °C (yield 45 mg, 89%), and were characterised by i.r., ^1H n.m.r., mass spectroscopy (Table 1), and microanalysis (Found: C, 22.20; H, 0.65. Calc for $C_{20}H_6O_{15}Ru_6$: C, 21.85; H, 0.55%).

[$Ru_6C(CO)_{15}$(EtCCEt)] (**4**). The salt [$N(PPh_3)_2]_2[Ru_6C(CO)_{16}$] (100 mg, 0.0467 mmol) was dissolved in CH_2Cl_2 (freeze-thaw degassed) (15 cm^3) and EtCCEt (5 μl, 0.061 mmol) added at 0 °C to the solution. The oxidant [$Fe(cp)_2]BF_4$ (30 mg, 0.111 mmol) was then added as a solid and the reaction monitored by i.r. spectroscopy. It was complete after 15 min with a change in colour from red to black. The reaction mixture was then filtered through a sintered funnel and reduced in volume. The resulting solution was separated on thin silica plates using 20% CH_2Cl_2–80% hexane to yield a yellow band at r.f. 0.1 (ferrocene) and the alkyne cluster [$Ru_6C(CO)_{15}$(EtCCEt)] (**4**) as a brown band at R_f 0.4. Black crystals of (**4**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 24 h at 0 °C (yield 48 mg, 90%), and were characterised by i.r., ^1H n.m.r., mass spectroscopy (Table 1), and microanalysis (Found: C, 23.50; H, 1.00. Calc. for $C_{22}H_{10}O_{15}Ru_6$: C, 23.45; H, 0.90%).

[$Ru_6C(CO)_{15}$(PhCCPh)] (**5**). The salt [$N(PPh_3)_2]_2[Ru_6C(CO)_{16}$] (100 mg, 0.0467 mmol) was dissolved in CH_2Cl_2 (freeze-thaw degassed) (15 cm^3) and PhCCPh (10 mg, 0.0562 mmol) added at 0 °C to the solution. The oxidant [$Fe(cp)_2]BF_4$ (30 mg, 0.111 mmol) was then added as a solid and the reaction monitored by i.r. spectroscopy. It was complete after 15 min with a change in colour from red to black. The reaction mixture was then filtered through a sintered funnel and reduced in volume. The resulting solution was separated on thin silica plates using 20% CH_2Cl_2–80% hexane to yield a yellow band at R_f 0.1 (ferrocene) and the alkyne cluster [$Ru_6C(CO)_{15}$(PhCCPh)] (**5**) as a brown band at R_f 0.4. Black crystals of (**5**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 24 h at 0 °C (yield 54 mg, 94%), and were characterised by i.r., ^1H n.m.r., mass spectroscopy (Table 1), and microanalysis (Found: C, 29.65; H, 0.95. Calc. for $C_{30}H_{10}O_{15}Ru_6$: C, 29.45; H, 0.80%).

[$Ru_6C(CO)_{15}$(PhCCH)] (**6**). The salt [$N(PPh_3)_2]_2[Ru_6C(CO)_{16}$] (100 mg, 0.0467 mmol) was dissolved in CH_2Cl_2 (freeze-thaw degassed) (15 cm^3) and PhCCH (7 μl, 0.060 mmol) added at 0 °C to the solution. The oxidant [$Fe(cp)_2]BF_4$ (30 mg, 0.111 mmol) was then added as a solid and the reaction monitored by i.r. spectroscopy. It was complete after 15 min with a change in colour from red to black. The reaction mixture was then filtered through a sintered funnel and reduced in volume. The resulting solution was then separated on thin silica plates using 20% CH_2Cl_2–80% hexane to yield a yellow band at R_f 0.1 (ferrocene) and the alkyne cluster [$Ru_6C(CO)_{15}$(PhCCH) (**6**) as a brown band at R_f 0.4. Black crystals of (**6**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 24 h at 0 °C (yield 50 mg, 92%), and were characterised by i.r., ^1H n.m.r., mass spectroscopy (Table 1), and microanalysis (Found: C, 25.25; H, 0.70. Calc. for $C_{24}H_6O_{15}Ru_6$: C, 25.15; H, 0.55%).

[$Ru_6C(CO)_{15}$(PhCCMe)] (**7**). The salt [$N(PPh_3)_2]_2[Ru_6C(CO)_{16}$] (100 mg, 0.0467 mmol) was dissolved in CH_2Cl_2 (freeze-thaw degassed) (15 cm^3) and PhCCMe (7 μl, 0.0604 mmol) added at 0 °C to the solution. The oxidant [$Fe(cp)_2]BF_4$ (30 mg, 0.111 mmol) was then added as a solid and the reaction monitored by i.r. spectroscopy. It was complete after 15 min with a change in colour from red to black. The reaction mixture was then filtered through a sintered funnel and reduced in volume. The resulting solution was separated on thin silica plates using 20% CH_2Cl_2–80% hexane to yield a yellow band at R_f 0.1 (ferrocene) and the alkyne cluster [$Ru_6C(CO)_{15}$(PhCCMe)] (**7**) as a brown band at R_f 0.4. Black crystals of (**7**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 24 h at 0 °C (yield 50 mg, 91%), and were characterised by i.r., ^1H n.m.r., mass spectroscopy (Table 1), and microanalysis (Found: C, 26.05; H, 0.85. Calc. for $C_{25}H_8O_{15}Ru_6$: C, 25.85; H, 0.70%).

[$Ru_6C(CO)_{15}$(μ-H)(CCPh)] (**8**). The cluster [$Ru_6C(CO)_{15}$(PhCCH)] (100 mg, 0.0873 mmol) was dissolved in toluene (freeze-thaw degassed) (15 cm^3) and heated at 60 °C for 3 d. The reaction was monitored by i.r. spectroscopy and was complete after this time with a change in colour from brown to black. The reaction mixture was then filtered through a sintered funnel and reduced in volume. The resulting solution was separated on thin silica plates using 40% CH_2Cl_2–60% hexane to yield a red-brown band of [$Ru_6C(CO)_{15}$(μ-H)(CCPh)] (**8**) at R_f 0.5. Black crystals of (**8**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 24 h at 0 °C (yield 82 mg, 82%), and were characterised by i.r., ^1H n.m.r., mass spectroscopy (Table 1), and microanalysis (Found: C, 25.40; H, 0.75. Calc. for $C_{24}H_6O_{15}Ru_6$: C, 25.15; H, 0.55%).

X-Ray Structure Analyses.—Crystal data for complex (**6**), $C_{24}H_6O_{15}Ru_6$, M = 1 140.30, monoclinic, space group $P2_1/c$, a = 9.853(2), b = 16.911(3), c = 19.312(4) Å, β = 111.79(2)°, U = 2 987.93 Å^3, Z = 4, D_c = 2.534 g cm^{-3}, F(000) = 2 136, μ(Mo-K_α) = 27.51 cm^{-1}.

Crystal data for complex (**7**)·0.5 CH_2Cl_2, $C_{25.5}H_9Cl_2O_{15}Ru_6$, M = 1 197, triclinic, space group $P\bar{1}$ (no. 2), a = 17.809(3), b = 10.567(2), c = 9.310(2) Å, α = 106.99(2), β = 98.135(2), γ = 98.824(2)°, U = 1 623.23 Å^3, Z = 2, D_c = 2.449 g cm^{-3}, F(000) = 1 126, μ(Mo-K_α) = 28.2 cm^{-1}.

Data collection. Crystals of sizes 0.38 × 0.26 × 0.18 mm for (**6**) and 0.25 × 0.20 × 0.18 mm for (**7**) were used for data collection using a Philips PW1100 diffractometer in the θ range 3—25°, as described previously,[15] with scan widths of 0.80° for (**6**) and 0.90° for (**7**). Equivalent reflections for (**6**) and for (**7**) were merged to give 3 033 and 4 037 data respectively with $I/\sigma(I) \geqslant 3.0$.

Structure solution and refinement.[16] The co-ordinates of the six ruthenium atoms in each structure were deduced from a Patterson synthesis, and the remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. Absorption corrections were applied to the data using the method of Walker and Stuart.[17] For both structures the metal atoms and the atoms of the carbonyl ligands were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement, in which weights of $w = 1/\sigma^2(F_o)$ were assigned to the individual reflections. Refinement converged at R = 0.0487 and R' = 0.0483 for (**6**) and R = 0.0460 and R' = 0.0469 for (**7**).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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