Redox Activation of the Hexanuclear Ruthenium Cluster $[Ru_6C(CO)_{16}]^{2-}$ using Oxidative Addition

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The dianion $[Ru_6C(CO)_{16}]^{2-}$ (**1**) reacts with ligands L [= CO, $P(OMe)_3$, PPh_3, or PPh_2Me] in the presence of $[Fe(\eta^5\text{-}C_5H_5)_2]BF_4$, $FeCl_3$ or electrochemically to yield the corresponding $[Ru_6C(CO)_{16}L]$ derivatives; with the disubstituted alkynes PhCCEt or EtCCMe, the dianion (**1**) gives the alkyne substituted clusters $[Ru_6C(CO)_{15}(PhCCEt)]$ and $[Ru_6C(CO)_{15}(EtCCMe)]$ as the respective products at room temperature; and with C_5Me_5H or $C_6H_5(CH_3)$ the compounds $[Ru_6C(CO)_{14}(\mu\text{-}H)(\eta^5\text{-}C_5Me_5)]$ and $[Ru_6C(CO)_{14}\{\eta^6\text{-}C_6H_5(CH_3)\}]$ are obtained.

The approach employed in studying controlled synthesis in osmium/ruthenium carbonyl cluster chemistry has been the utilisation of stable intermediates that allow the displacement of ligand groups under mild conditions. The ready preparation of $[M_3(CO)_{11}(NCMe)]$ and $[M_3(CO)_{10}(NCMe)_2]$ (M = Ru or Os) by trimethylamine *N*-oxide oxidation of the carbonyl groups in acetonitrile has led to an extensive chemistry of these clusters.[1,2] More recently this approach has been extended to $[Os_4H_4(CO)_{12}]$, $[Os_5(CO)_{16}]$, $[Os_6(CO)_{18}]$, and even $[Os_7(CO)_{21}]$ clusters.[3–6] Our attempts to extend this technique to high nuclearity ruthenium clusters have so far proved unsuccessful.

Previous studies by Bruce *et al.*[7] demonstrated the use of electrochemically stimulated substitution reactions of trinuclear ruthenium clusters. Our recent studies on the redox chemistry of the decaosmium carbido cluster $[Os_{10}C(CO)_{24}]^{2-}$[8] have shown that it can exist in five different oxidation states, and prompted us to investigate the hexanuclear ruthenium carbido cluster $[Ru_6C(CO)_{16}]^{2-}$.[9]

We report in this paper an alternative technique to activate a high nuclearity ruthenium cluster, $[Ru_6C(CO)_{16}]^{2-}$, by the use of either electrochemical or chemical oxidative addition. A preliminary account of part of this work has been published.[10]

Results and Discussion

Previous work by Ansell and Bradley[9] with $[Ru_6C(CO)_{16}]^{2-}$ (**1**) and tropylium bromide led to the isolation of $[Ru_6C(CO)_{14}(C_{14}H_{14})]$ in high yield. The incoming ligand was the organic redox product, bitropenyl ($C_{14}H_{14}$,bi-2,4,6-cycloheptatrien-1-yl). This initial observation led us to believe that the oxidation (both chemical or electrochemical) of (**1**) under CO to $[Ru_6C(CO)_{17}]$ should occur in high yield, and this was indeed found to be the case.[10,11]

The dianion $[Ru_6C(CO)_{16}]^{2-}$ (**1**) shows an irreversible two-electron oxidation wave in dichloromethane at $E_p = +0.48$ V *vs.* a Ag–AgCl reference electrode, and associated with this wave is a consequent reduction at $E_p = -0.47$ V, *i.e.* the reduction wave of the oxidised product. Ferrocene was used as a one-electron standard, since it is known to be oxidised reversibly to a stable monocation. Quantitative oxidation of (**1**) at a platinum gauze electrode in CH_2Cl_2 at the above potential yields $[Ru_6C(CO)_{17}]$ in poor yield. The formation of $[Ru_6C(CO)_{17}]$ in this redox reaction may be attributed to the scavenging of carbon monoxide by the electron deficient '$[Ru_6C(CO)_{16}]$'. If however the controlled bulk electrolysis is performed under a steady stream of carbon monoxide, the desired product $[Ru_6C(CO)_{17}]$ is obtained in near quantitative yield as the oxidative addition product [see Figure 1(*a*)]. Oxidation at a platinum gauze at +0.50 V consumed 1.9 ± 0.2 electrons as the solution went from orange to red. Cyclic voltammograms after bulk electrolysis [Figure 1(*b*)] were the reverse of those prior to electrolysis. Reduction of this solution of $[Ru_6C(CO)_{17}]$ at −0.50 V consumed 1.9 ± 0.2 electrons and re-established the original cyclic voltammogram of $[Ru_6C(CO)_{16}]^{2-}$ (**1**).

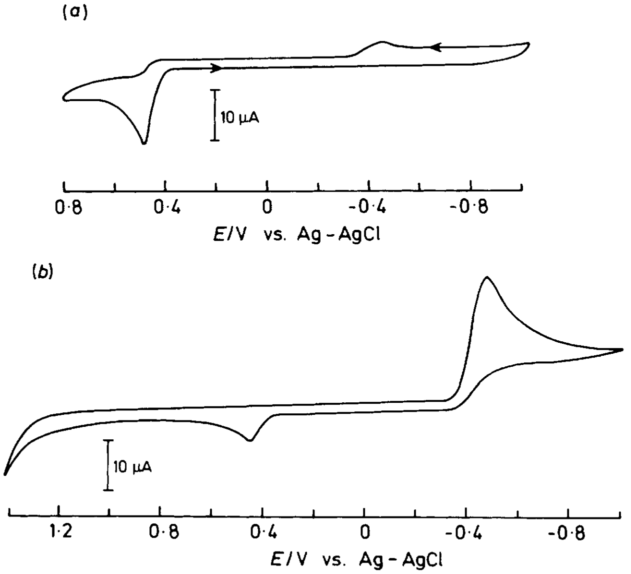
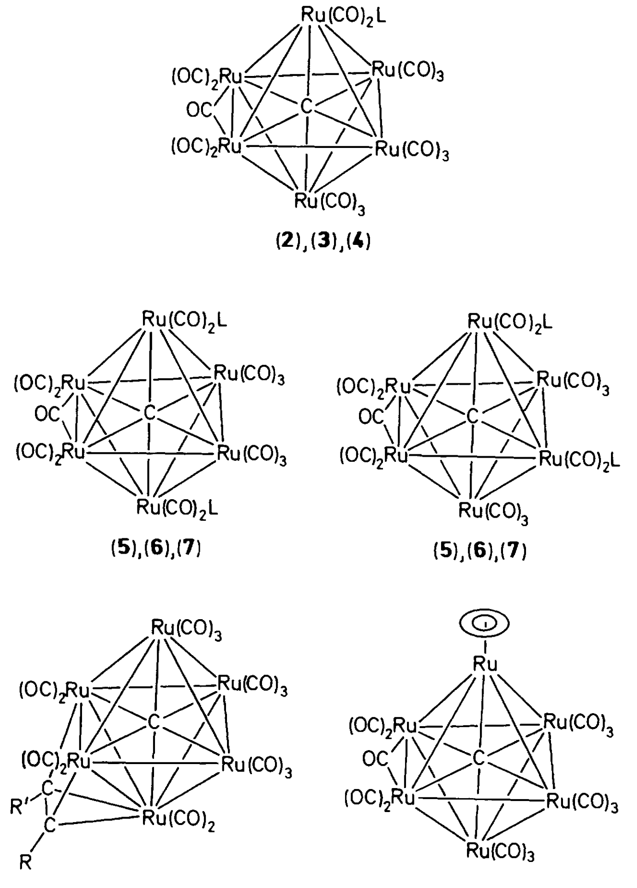


Figure 1. (*a*) Cyclic voltammogram of 2.34×10^{-5} mol dm^{-3} $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ (**1**) in 0.2 mol dm^{-3} NBu_4BF_4–CH_2Cl_2 at a platinum electrode. Scan rate 100 mV s^{-1} (at room temperature). (*b*) Cyclic voltammogram of 4.57×10^{-5} mol dm^{-3} $[Ru_6C(CO)_{17}]$ in 0.2 mol dm^{-3} NBu_4BF_4–CH_2Cl_2 at a platinum electrode. Scan rate 100 mV s^{-1} (at room temperature)

Likewise the neutral cluster $[Ru_6C(CO)_{17}]$ shows an irreversible two-electron reduction at $E_p = -0.46$ V *vs.* a Ag–AgCl reference electrode, and also associated with this reduction step is an oxidation wave at $E_p = +0.45$ V, *i.e.* the oxidation wave of the reduced product $[Ru_6C(CO)_{16}]^{2-}$ (**1**). The reduction of this cluster to the dianion (**1**) at a platinum gauze electrode in CH_2Cl_2 under a constant stream of argon gas occurs in quantitative yield [see Figure 1(*b*)]. No paramagnetic species could be detected by e.s.r. during the formation of the dianion (**1**). On the same electrochemical scale the $[Fe(\eta^5\text{-}C_5H_5)_2]$–$[Fe(\eta^5\text{-}C_5H_5)_2]^+$ couple is +0.54 V as is $FeCl_3$ [see equation (1)].[12] These simple experiments demonstrate that the wave observed at −0.46 V is due to a two-electron process resulting in the formation of $[Ru_6C(CO)_{16}]^{2-}$ (**1**), which



(2),**(3)**,**(4)**

(5),**(6)**,**(7)**

(5),**(6)**,**(7)**

(8),**(9)**

(10),**(11)**

Figure 2. Proposed structures for compounds (**2**)—(**11**), where L = P(OMe)$_3$ (**2**) and (**5**), PPh$_3$ (**3**) and (**6**), PPh$_2$Me (**4**) and (**7**), PhCCEt (**8**), or EtCCMe (**9**). The doughnut denotes an η^5-C_5Me_5 ring attached to (**10**), and an η^6-$C_6H_5(CH_3)$ ring attached to (**11**)

can be anodically oxidised back to the starting material. These results are consistent with the previously established stability of both the neutral and dianionic forms of the hexanuclear ruthenium cluster.[9,11]

$$[Ru_6C(CO)_{16}]^{2-} \underset{+2e^-,-CO}{\overset{-2e^-,+CO}{\rightleftarrows}} [Ru_6C(CO)_{17}] \qquad (1)$$

Thus an alternative method of synthesis using either chemical or electrochemical oxidation of ruthenium cluster dianions in the presence of the ligand is possible at room temperature, resulting in a higher and more selective yield of the desired product. The chemical oxidation routes were preferred to the electrochemical oxidation as preparative methods, since isolation of the products from electrochemical solutions is hindered by the presence of an excess of base electrolyte.

Reaction of (**1**) *with Donor Ligands*.—The clusters (**2**)—(**11**) (Figure 2) have been characterised by i.r., ^1H n.m.r., electron-impact mass spectrometry and satisfactory microanalysis (see Table 1). All of the derivatives had clear molecular ions consistent with their formulations, and the mass spectra showed the stepwise loss of the required number of carbonyl groups. The i.r. spectra indicated the presence of terminal and bridging carbonyls and no resonances in the metal hydride region were observed in the ^1H n.m.r. spectra of (**2**)—(**9**) and (**11**).

Treatment of (**1**) with donor ligands such as P(OMe)$_3$, PPh$_3$, or PPh$_2$Me in the presence of [Fe(η^5-$C_5H_5)_2$]BF$_4$ results in the formation of the known compounds [Ru$_6$C(CO)$_{16}${P(OMe)$_3$}] (**2**), [Ru$_6$C(CO)$_{16}$(PPh$_3$)] (**3**), and the new compound [Ru$_6$C(CO)$_{16}$(PPh$_2$Me)] (**4**) in excellent yield, with very little of the disubstituted complexes [Ru$_6$C(CO)$_{15}$(PR$_3$)$_2$] [PR$_3$ = P(OMe)$_3$ (**5**), PPh$_3$ (**6**), and PPh$_2$Me (**7**)] being formed.[13] As previously observed by Evans and co-workers,[13] the phosphine and phosphite derivatives (**2**)—(**7**) undergo fluxional behaviour in solution, with *cis* and *trans* isomers observed for (**5**)—(**7**). These derivatives may also be prepared by controlled potential electrolysis of (**1**) at +0.50 V in the presence of the required ligand using a platinum electrode in CH$_2$Cl$_2$, followed by chromatographic separation of the products.

This procedure shows distinct advantages over the thermal reactions of [Ru$_6$C(CO)$_{17}$] with PR$_3$.[13,14] The structure of a related compound has been previously undertaken by *X*-ray crystallography and shown to consist of a Ru$_6$ octahedron with a terminal PPh$_2$Et group.[13]

The reaction of (**1**) with PhCCEt or EtCCMe in the presence of [Fe(η^5-$C_5H_5)_2$]BF$_4$ at room temperature results in the formation of the new compounds, [Ru$_6$C(CO)$_{15}$(PhCCEt)] (**8**) and [Ru$_6$C(CO)$_{15}$(EtCCMe)] (**9**) in high yields. These reactions probably proceed *via* an electron deficient ruthenium cluster, with a vacant co-ordination site, *i.e.* '[Ru$_6$C(CO)$_{16}$]'. In this respect the chemistry is similar to that of the activated trinuclear clusters [Ru$_3$(CO)$_{12-x}$(NCMe)$_x$] (x = 1 or 2) where the intermediates 'Ru$_3$(CO)$_{11/10}$' are stabilised in solution by the MeCN groups.[2]

The acetylene groups may act as four-electron donors in these clusters; a related cluster, [Ru$_6$C(CO)$_{15}$(PhCCMe)] has been recently characterised by *X*-ray crystallography and the acetylene ligand was found to bond in a μ_3-η mode.[15]

Cyclic alkenes or aromatic rings such as pentamethylcyclopentadiene and toluene react with (**1**) in moderate yield at room temperature to produce the clusters [Ru$_6$C(CO)$_{14}$(μ-H)(η^5-C_5Me_5)] (**10**) and [Ru$_6$C(CO)$_{14}${η^6-$C_6H_5(CH_3)$}] (**11**). The ^1H n.m.r. spectra of these two compounds show singlet resonances for the organic rings, suggesting η^5 and η^6 co-ordination to apical ruthenium atoms. In [Ru$_6$C(CO)$_{14}$(μ-H)(η^5-C_5Me_5)] it seems likely that the hydride ligand which has migrated from the C_5Me_5H during the reaction is in an edge-bridging mode. The competing mechanism in the formation of (**10**) and (**11**) is the formation of [Ru$_6$C(CO)$_{17}$] by CO scavenging, thereby lowering the yields to 50—60% overall.

Similar hexanuclear ruthenium clusters with benzene and toluene have been previously prepared under fairly harsh conditions in *ca.* 5% yield.[16,17] The organic ligands were found to be bonded to one apical ruthenium atom in an η^6 bonding mode. We are presently attempting to extend this technique of oxidative addition to [Ru$_4$(H)C(CO)$_{12}$]$^-$, [Ru$_5$N(CO)$_{14}$]$^-$, and [Ru$_6$N(CO)$_{16}$]$^-$ clusters using a variety of oxidising agents.

Experimental

All reactions were carried out under nitrogen using dry degassed solvents. Infrared spectra were recorded on a Perkin-Elmer PE 983 spectrometer. ^1H N.m.r. spectra were recorded on Bruker WM 250 and WH 400 instruments using CD$_2$Cl$_2$ as the internal reference. Electron-impact mass spectrometry was run on a N.E.I. MS 12 spectrometer using tris(perfluoroheptyl)-*s*-triazine as calibrant.

Electrochemical apparatus and techniques are as described previously.[11] For the cyclic voltammetry experiments the effects of solution resistance were minimized by using 10^{-4}—10^{-5} mol dm^{-3} solutions of the samples and small electrodes so that peak currents were generally below 10 μA. Scan rates were varied between 20 and 500 mV s^{-1} with 100 mV s^{-1} as the standard scan rate. All potentials quoted are *vs.* Ag–AgCl(aq) unless otherwise

Table. Spectroscopic data for the clusters (**2**)—(**11**)

Cluster	I.r. data[a]/cm^{-1}	*M/z*[b]	^{1}H N.m.r.[c]
(**2**)	2 086w, 2 057m, 2 046s, 2 031s, 2 020m (sh), 2 003w, 1 985w, 1 845vw	1 190	3.77 [d, 9 H, Me, *J*(PH) 12]
(**3**)	2 084m, 2 056vs, 2 045ms, 2 029vs, 2 003m, 1 984m, 1 844w	1 328	7.41 (m, Ph)
(**4**)	2 083m, 2 055vs, 2 046s, 2 030vs, 2 019m (sh), 2 004w, 1 985w, 1 846vw	1 256	7.41 (m, 10 H, Ph) 2.07 [d, 3 H, Me, *J*(PH) 10]
(**5**)	2 072w, 2 048vw, 2 032s (sh), 2 020vs, 1 878w, 1 864vw, 1 840w	1 316	3.68 [d, 18 H, Me, *J*(PH) 12] 3.75 [d, 18 H, Me, *J*(PH) 12] ratio 1:2
(**6**)	2 069w (sh), 2 064w, 2 046s, 2 018s br, 1 998w, 1 987w, 1 845w br	*d*	7.38 (m, Ph)
(**7**)	2 070w (sh), 2 064w, 2 046s, 2 028s, 2 019vs, 1 992w, 1 983w, 1 970w (sh), 1 950vw, 1 860vw, 1 839vw	*d*	7.41 (m, Ph) 2.12 [d, 6 H, Me, *J*(PH) 10] 2.05 [d, 6 H, Me, *J*(PH) 10] ratio 2:1
(**8**)	2 088w, 2 043vs, 2 036s (sh), 2 019m, 2 012m, 1 983w, 1 963vw (sh)	1 174	7.36 (m, Ph), 3.09 (q, 2 H, CH_2), 1.58 (t, 3 H, CH_3)
(**9**)	2 088w, 2 045vs, 2 038s (sh), 2 020m (sh), 2 014m (sh), 1 986w, 1 962vw (sh)	1 114	3.40 (s, 3 H, Me), 3.11 (q, 2 H, CH_2), 1.60 (t, 3 H, CH_2CH_3)
(**10**)	2 097w, 2 071s, 2 058vs, 2 046m, 2 028s, 2 016m (sh), 1 993m, 1 980m, 1 952vw, 1 792vw	1 163	2.17 (s, 15 H, C_5Me_5) −22.64 (s, Ru–H–Ru)
(**11**)	2 080s, 2 037s (sh), 2 030s, 2 012w, 2 000m, 1 986m, 1 975m, 1 829w br	1 201	5.47 (s, 5 H, C_6H_5) 1.19 (s, 3 H, CH_3)

[a] ν(CO) (CH_2Cl_2). [b] Using ^{102}Ru. [c] ^{1}H N.m.r. spectroscopic data for the complexes in CD_2Cl_2, *J* in Hz. [d] Molecular ions not observed, instead peak due to [$Ru_6C(CO)_{17}$] observed.

indicated and are uncompensated for solution resistance and the effects of liquid junction potentials. With the use of this reference the $E_{\frac{1}{2}}$ value for [Fe(η^5-C_5H_5)$_2$]–[Fe(η^5-C_5H_5)$_2$]$^+$ was +0.54 V in CH_2Cl_2.

Microanalyses were performed in the University Chemical Laboratory, Cambridge. Thin layer chromatography plates were bought from Merck and consisted of 20 × 20 cm plates 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.[18]

Preparation of [$Ru_6C(CO)_{16}${P(OMe)$_3$}] (**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 P(OMe)$_3$ (1 drop, large excess) added to the solution. The oxidant [Fe(η^5-C_5H_5)$_2$]BF_4 (30 mg, 0.111 mmol) was added as a solid and the reaction monitored by i.r. spectroscopy and 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 by thin layer chromatography using CH_2Cl_2–hexane (1:4) to yield a yellow band at R_f 0.1 (ferrocene) and the phosphite derivative [$Ru_6C(CO)_{16}${P(OMe)$_3$}] (**2**) as a brown band at R_f 0.4, closely followed by a trace amount of [$Ru_6C(CO)_{15}${P(OMe)$_3$}$_2$] (**5**) at R_f 0.55. Black crystals of [$Ru_6C(CO)_{16}${P(OMe)$_3$}] (**2**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 24 h at 20 °C (yield 47 mg, 89%) and were characterised by i.r. spectroscopy, ^{1}H n.m.r. and mass spectroscopy (Table).

Preparation of [$Ru_6C(CO)_{16}$(PPh$_3$)] (**3**).—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 PPh$_3$ (11 mg, 0.060 mmol) added to the solution. The oxidant [Fe(η^5-C_5H_5)$_2$]BF_4 (38 mg, 0.111 mmol) was added as a solid and the reaction monitored by i.r. spectroscopy and was complete after 5 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 by thin layer chromatography using CH_2Cl_2–hexane (1:4) to yield a yellow band at R_f 0.1 (ferrocene) and the phosphine derivative [$Ru_6C(CO)_{16}$(PPh$_3$)] (**3**) as a brown band at R_f 0.35, closely followed by a trace amount of [$Ru_6C(CO)_{15}$(PPh$_3$)$_2$] (**6**). Black crystals of [$Ru_6C(CO)_{16}$(PPh$_3$)] (**3**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 24 h at 20 °C (yield 56 mg, 91%) and were characterised by i.r. spectroscopy, ^{1}H n.m.r., and mass spectroscopy (Table).

Preparation of [$Ru_6C(CO)_{16}$(PPh$_2$Me)] (**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 PPh$_2$Me (8 μl, 0.061 mmol) added to the solution. The oxidant [Fe(η^5-C_5H_5)$_2$]BF_4 (30 mg, 0.111 mmol) was added as a solid and the reaction monitored by i.r. spectroscopy and 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 by thin layer chromatography using CH_2Cl_2–hexane (1:4) to yield a yellow band at R_f 0.1 (ferrocene) and the cluster [$Ru_6C(CO)_{16}$(PPh$_2$Me)] (**4**) as a brown band at R_f 0.45, closely followed by a small amount of the disubstituted cluster [$Ru_6C(CO)_{15}$(PPh$_2$Me)$_2$] (**7**). Black crystals of [$Ru_6C(CO)_{16}$(PPh$_2$Me)] (**4**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 24 h at 0 °C (yield 51 mg, 88%) and were characterised by i.r. spectroscopy, ^{1}H n.m.r., mass spectroscopy (Table), and microanalysis (Found: C, 28.50; H, 1.05. Calc. for $C_{30}H_{13}O_{15}PRu_6$: C, 28.30; H, 1.00%).

Preparation of [$Ru_6C(CO)_{15}$(PhCCEt)] (**8**).—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 PhCCEt (8 μl, 0.0604 mmol) added at 0 °C to the solution. The oxidant [Fe(η^5-C_5H_5)$_2$]BF_4 (30 mg, 0.111 mmol) was added as a solid and the reaction monitored by i.r. spectroscopy and 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 by thin layer chromatography using CH_2Cl_2–hexane (1:4) to yield a yellow band at R_f 0.1 (ferrocene) and the alkyne cluster $[Ru_6C(CO)_{15}(PhCCEt)]$ (**8**) as a brown band at R_f 0.4. Black crystals of $[Ru_6C(CO)_{15}(PhCCEt)]$ (**8**) 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. spectroscopy, ^1H n.m.r., mass spectroscopy (Table 1), and microanalysis (Found: C, 26.85; H, 0.95. Calc. for $C_{26}H_{10}O_{15}Ru_6$: C, 26.55; H, 0.85%).

Preparation of $[Ru_6C(CO)_{15}(EtCCMe)]$ (**9**).—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 EtCCMe (7 μl, 0.0604 mmol) added at 0 °C to the solution. The oxidant $[Fe(\eta^5-C_5H_5)_2]BF_4$ (30 mg, 0.111 mmol) was added as a solid and the reaction monitored by i.r. spectroscopy and 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 by thin layer chromatography using CH_2Cl_2–hexane (1:4) to yield a yellow band at R_f 0.1 (ferrocene) and the alkyne cluster $[Ru_6C(CO)_{15}(EtCCMe)]$ (**9**) as a brown band at R_f 0.4. Black crystals of $[Ru_6C(CO)_{15}(EtCCMe)]$ (**9**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 24 h at 0 °C (yield 44 mg, 85%) and were characterised by i.r. spectroscopy, ^1H n.m.r., mass spectroscopy (Table), and microanalysis (Found: C, 23.00; H, 0.85. Calc. for $C_{21}H_8O_{15}Ru_6$: C, 22.65; H, 0.70%).

Preparation of $[Ru_6C(CO)_{14}(\mu-H)(\eta^5-C_5Me_5)]$ (**10**).—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 C_5Me_5H (1 drop, excess) added at 0 °C to the solution, through which a slow nitrogen gas purge was passed. The oxidant $[Fe(\eta^5-C_5H_5)_2]BF_4$ (30 mg, 0.111 mmol) was added as a solid and the reaction monitored by i.r. spectroscopy and 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 by thin layer chromatography using CH_2Cl_2–hexane (1:1) to yield a yellow band at R_f 0.1 (ferrocene), closely followed by an orange band of $[Ru_6C(CO)_{17}]$ R_f 0.2 (34%), and then the cluster $[Ru_6C(CO)_{14}(\mu-H)(\eta^5-C_5Me_5)]$ (**10**) as a yellow-orange band at R_f 0.3, and one other low yield (10%) unidentified brown band at R_f 0.55. Orange crystals of $[Ru_6C(CO)_{14}(\mu-H)(\eta^5-C_5Me_5)]$ (**10**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 12 h at 0 °C (yield 28 mg, 51%) and were characterised by i.r. spectroscopy, ^1H n.m.r., mass spectroscopy (Table), and microanalysis (Found: C, 26.05; H, 1.35. Calc. for $C_{25}H_{15}O_{15}Ru_6$: C, 25.70; H, 1.30%).

Preparation of $[Ru_6C(CO)_{14}\{\eta^6-C_6H_5(CH_3)\}]$ (**11**).—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 toluene (1 drop, excess) added at 0 °C to the solution, through which a nitrogen gas purge was slowly passed. The oxidant $[Fe(\eta^5-C_5H_5)_2]BF_4$ (30 mg, 0.111 mmol) was added as a solid and the reaction monitored by i.r. spectroscopy and 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 by thin layer chromatography using CH_2Cl_2–hexane to yield a yellow band at R_f 0.1 (ferrocene), closely followed by an orange band of $[Ru_6C(CO)_{17}]$ R_f 0.2 (30%), and then the cluster $[Ru_6C(CO)_{14}\{\eta^6-C_6H_5(CH_3)\}]$ (**11**) as a brown band at R_f 0.25. Dark brown crystals of $[Ru_6C(CO)_{14}\{\eta^6-C_6H_5(CH_3)\}]$ (**11**) were obtained by slow diffusion of a layered CH_2Cl_2–hexane solution under N_2 over 24 h at 0 °C (yield 31 mg, 57%), and were characterised by i.r. spectroscopy, ^1H n.m.r., mass spectroscopy (Table), and microanalysis (Found: C, 23.80; H, 0.85. Calc. for $C_{22}H_8O_{15}Ru_6$: C, 23.45; H, 0.70%).

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