Bis(cyclopentadienyl) Clusters of Ruthenium: The Synthesis, Characterisation and Molecular Structures of $[Ru_5C(CO)_{10}(\eta^5\text{-}C_5H_5)_2]$ and $[Ru_6C(CO)_{12}(\eta^5\text{-}C_5H_5)_2]$†

Alexander J. Blake, Paul J. Dyson, Rosslyn C. Gash, Brian F. G. Johnson* and Peter Trickey
Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

Reaction of the hexanuclear cluster $[Ru_6C(CO)_{17}]$ with trimethylamine *N*-oxide in CH_2Cl_2 containing cyclopentadiene yielded a variety of products including $[Ru_6C(CO)_{12}(\eta^5\text{-}C_5H_5)_2]$ **1** and $[Ru_5C(CO)_{10}(\eta^5\text{-}C_5H_5)_2]$ **2** in moderate and modest yields, respectively. Compound **2** has also been isolated as a major product from a similar reaction of cyclopentadiene with $[Ru_5C(CO)_{15}]$ and as a minor product from the reaction of cyclopentadiene with $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$. The molecular structures of compounds **1** and **2** have been determined by X-ray diffraction, at 150 and 295 K, respectively.

The cyclopentadienyl (cp, C_5H_5) ligand has been used extensively throughout organometallic chemistry and has been shown to be extremely useful and versatile, exhibiting a wide range of bonding characteristics.[1] Metal clusters bearing the cp group are numerous, and include an elegant species, $[Ni_6(\eta^5\text{-}C_5H_5)_6]$ (prepared by the reduction of nickelocene) in which an octahedral Ni_6 unit is surrounded by a ligand shell consisting of six cp ligands.[2] Our interest in the cp ligand is different and is directed towards a comparison with six-member aromatic rings bonded to clusters, with respect to their structure and isomerisation.

We recently developed a convenient stepwise synthetic route to the bis(benzene) cluster $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$,[3] which was first reported in 1985.[4] This route involves the chemical removal of co-ordinated carbonyl ligands using trimethylamine *N*-oxide (Me_3NO), followed by reaction with cyclohexa-1,3-diene, resulting in the formation of the diene species $[Ru_6C(CO)_{15}(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)]$ and the benzene complex $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$. The former may be converted into the latter by the addition of further Me_3NO. By the same method, the bis(benzene) complex can be generated from $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$ *via* the formation of the two intermediate benzene–diene clusters $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)]$ and $[Ru_6(CO)_{11}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)]$. These are then readily converted to the desired product on treatment with additional Me_3NO. Two pentanuclear benzene–diene clusters of formula $[Ru_5C(CO)_{10}(C_6H_6)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)]$ (the benzene in η^6 and $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ bonding modes in the two isomers) can be prepared by a similar route.[5] Clearly, the C_6H_8 ligand is a useful precursor to benzene, undergoing dehydrogenation once co-ordinated to the metal cluster.

In studies on the isoelectronic mixed-metal cluster $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ we demonstrated that cyclopentadiene, C_5H_6, readily transforms to $\eta^5\text{-}C_5H_5$.[6] Treatment of this cluster with Me_3NO in CH_2Cl_2 containing excess of cyclopentadiene yields several products in low yield and $[Ru_5RhC(CO)_9(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)_2]$ in moderate yield. The ease with which two cp ligands are introduced onto the cluster framework compared with the C_6H_6 moiety must reflect the different donor–acceptor properties of the rings. To enhance our understanding of this we have examined the reactivity of cyclopentadiene with $[Ru_5C(CO)_{15}]$ and $[Ru_6C(CO)_{17}]$.

Results and Discussion

Using two molecular equivalents of the oxidative decarbonylation reagent Me_3NO as a 'chemical activator' the reaction of $[Ru_6C(CO)_{17}]$ with cyclopentadiene in dichloromethane results in the formation of several products. The products are readily separated by TLC on silica eluting with a dichloromethane–hexane mixture. The major product from the reaction has been characterised as $[Ru_6C(CO)_{12}(\eta^5\text{-}C_5H_5)_2]$ **1** by both spectroscopy and a single crystal X-ray diffraction analysis in the solid state. The ^1H NMR spectrum is very simple. A singlet resonance at δ 4.99 may be assigned to the chemically equivalent protons on the two cp groups. However, it is not possible to determine where the cp rings lie on the cluster, with the possibility of the rings being bonded to metals adjacent or *trans* to one another in the octahedral assembly. Suitable crystals for the low temperature (150 K) solid-state structural analysis were grown from a solution of dichloromethane–hexane at −25 °C. The molecular structure of compound **1** is shown in Fig. 1 accompanied by appropriate bond parameters in Table 1. The central metal unit consists of the familiar octahedral arrangement of ruthenium atoms encapsulating a C(carbide) atom, common to the parent cluster $[Ru_6C(CO)_{17}]$,[7] and many of its derivatives.[8] The metal–metal bond lengths lie in the range 2.846(2)–2.947(3) Å [mean = 2.878(3) Å] and the C(carbide) atom is slightly off-centered with respect to the middle of the octahedral cavity, lying nearest to Ru(6) [1.918(9) Å] which bears one of the cp ligands, while the mean value of the remaining five Ru–C(carbide) distances is 2.061(9) Å. Both the cp groups are co-ordinated to the cluster in terminal η^5 mode over metal atoms adjacent to one another within the octahedral metal frame. The carbonyl ligands display a range of bonding from essentially terminal groups through semi-bridging to bridging positions. One of the metal atoms, *i.e.* Ru(3), which carries a cp ligand also shares a bridging carbonyl group, the other ruthenium atom to which the cp ligand is bound, *viz.* Ru(6), is not involved with a symmetrically bridging carbonyl ligand, but carbonyl ligands on Ru(1), Ru(4) and Ru(5) bend towards it [Ru(6) ··· C(11) 3.12(1), Ru(6) ··· C(41) 3.23(1) and Ru(6) ··· C(52) 3.26(1) Å]. The reason for isolating this isomer, as opposed to a molecule in which the two cp moieties lie on opposite ruthenium atoms, is not easy to understand. With bis(benzene) analogues, both isomers have been observed, and it appears that they can be interconverted *via* the intermediacy of a face-capping benzene group. With the cyclopentadienyl cluster described above, no such isomerisation has been observed.

A second product from this reaction has also been identified

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

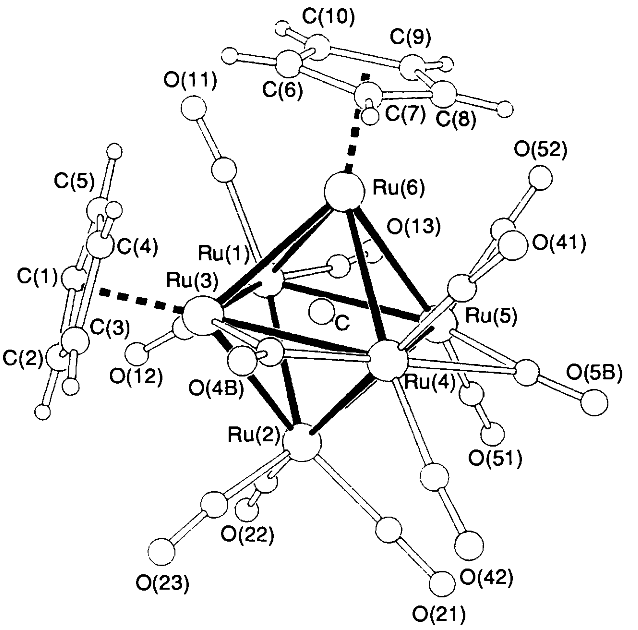

Fig. 1 The molecular structure of $[Ru_6C(CO)_{12}(\eta^5\text{-}C_5H_5)_2]$ **1** showing the atom-labelling scheme; the C atoms of the CO groups bear the same number as the corresponding O atoms

Table 1 Selected bond lengths (Å) for $[Ru_6C(CO)_{12}(\eta^5\text{-}C_5H_5)_2]$ **1**

Ru(1)–Ru(2)	2.893(2)	Ru(3)–C(4)	2.188(11)
Ru(1)–Ru(3)	2.947(3)	Ru(3)–C(5)	2.169(10)
Ru(1)–Ru(5)	2.901(3)	C(1)–C(2)	1.433(14)
Ru(1)–Ru(6)	2.890(3)	C(2)–C(3)	1.392(14)
Ru(2)–Ru(3)	2.871(3)	C(3)–C(4)	1.45(2)
Ru(2)–Ru(4)	2.878(3)	C(4)–C(5)	1.401(14)
Ru(2)–Ru(5)	2.850(3)	C(5)–C(1)	1.404(12)
Ru(3)–Ru(4)	2.858(3)	Ru(6)–C(6)	2.215(11)
Ru(3)–Ru(6)	2.857(3)	Ru(6)–C(7)	2.168(10)
Ru(4)–Ru(5)	2.857(3)	Ru(6)–C(8)	2.166(11)
Ru(4)–Ru(6)	2.846(2)	Ru(6)–C(9)	2.197(10)
Ru(5)–Ru(6)	2.886(3)	Ru(6)–C(10)	2.212(11)
Ru(1)–C	2.031(9)	C(6)–C(7)	1.41(2)
Ru(2)–C	2.117(9)	C(7)–C(8)	1.403(14)
Ru(3)–C	2.029(9)	C(8)–C(9)	1.42(2)
Ru(4)–C	2.076(9)	C(9)–C(10)	1.46(2)
Ru(5)–C	2.052(9)	C(10)–C(6)	1.41(2)
Ru(6)–C	1.918(9)	Ru(6) ··· C(11)	3.12(1)
Ru(3)–C(1)	2.214(11)	Ru(6) ··· C(41)	3.23(1)
Ru(3)–C(2)	2.220(10)	Ru(6) ··· C(52)	3.26(1)
Ru(3)–C(3)	2.196(10)		

as a minor product from a similar reaction involving the amine–oxide activation of $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ in the presence of cyclopentadiene. Once again, the ^1H NMR spectra consists of one singlet resonance at δ 5.12, and can be attributed to the ten protons on the cp rings. Since a pentaruthenium product was postulated, the parent cluster, $[Ru_5C(CO)_{15}]$, was treated with Me_3NO in the presence of cyclopentadiene, which afforded the same product in moderate yield. Clearly, as in the case of the hexaruthenium bis(cyclopentadienyl) cluster, more than one structural form can be envisaged, and in order to establish the precise location of the two cp rings on the cluster frame, an X-ray diffraction analysis was carried out at room temperature (295 K). It was not possible to collect data at a lower temperature as the crystals degraded visibly on cooling. A crystal for the analysis was grown from a solution of dichloromethane–hexane at −25 °C. The molecular structure of compound **2** is depicted in Fig. 2, with relevant distances listed in Table 2. The five ruthenium atoms constitute a square-based pyramidal arrangement in which the bond lengths vary from 2.7523(6) to 2.8374(6) Å [mean = 2.785(1) Å]. The C(carbide) atom lies closest to the metal atoms which carry the two η^5-C_5H_5 ligands [Ru(2) and Ru(4), 1.959(5) Å]. The shortening of these lengths has been observed in all the η^6-arene complexes based on the Ru_5C and Ru_6C cluster units. It has been ascribed to a compensatory effect to balance the electron density on the metal atom on changing from three carbonyl groups to the arene.[3,5a] This feature is also apparent in compound **1**, although to a lesser extent, possibly due to an enhanced compensatory effect of the non-linear carbonyl groups to the appropriate cyclopentadienyl-bearing metal atoms. The other two basal metals have intermediate metal–C(carbide) distances [Ru(1)–C 2.048(5) and Ru(5)–C 2.061(5) Å] while the apical ruthenium atom shows the longest bond with the C(carbide) atom of 2.141(5) Å. The two cp ligands lie on basal metal atoms *trans* to each other, these metal atoms each share a bridging carbonyl ligand with the apical metal atom, this latter metal also carrying two terminal carbonyls. The remaining two ruthenium atoms each bear three terminal carbonyl ligands. This ligand distribution yields a formal electron donation of six electrons to each ruthenium atom. The cp ligands are disordered over two sites with site-occupation factors in the ratio 6:4. This disorder is probably dynamic in nature, since the disc-like ring cannot easily be locked in place by the surrounding molecules in the crystal.[9]

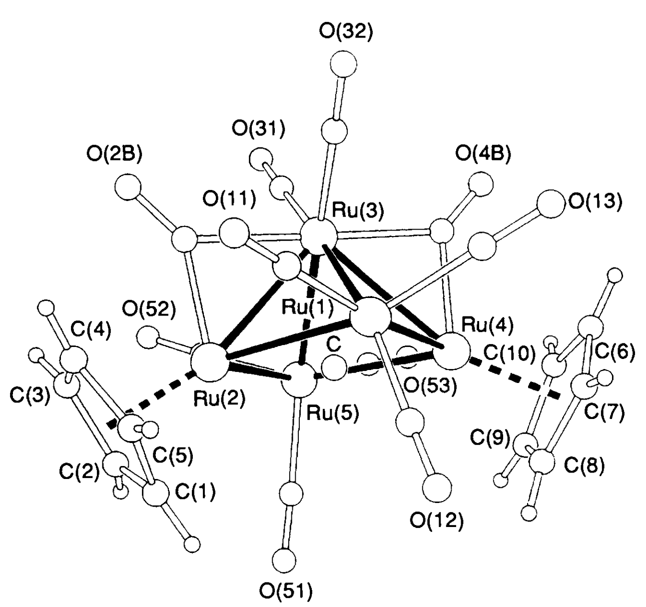

Fig. 2 The molecular structure of $[Ru_5C(CO)_{10}(\eta^5\text{-}C_5H_5)_2]$ **2** showing the atom-labelling scheme; the C atoms of the CO groups bear the same number as the corresponding O-atoms

Table 2 Selected bond lengths (Å) for $[Ru_6C(CO)_{12}(\eta^5\text{-}C_5H_5)_2]$ **2**

Ru(1)–Ru(2)	2.8374(6)	Ru(2)–C(1)	2.204(9)
Ru(1)–Ru(3)	2.7598(7)	Ru(2)–C(2)	2.206(9)
Ru(1)–Ru(4)	2.8104(7)	Ru(2)–C(3)	2.234(8)
Ru(2)–Ru(3)	2.771(2)	Ru(2)–C(4)	2.250(7)
Ru(2)–Ru(5)	2.816(2)	Ru(2)–C(5)	2.231(8)
Ru(3)–Ru(4)	2.7651(6)	C–C	1.426(9)
Ru(3)–Ru(5)	2.7523(6)	Ru(4)–C(6)	2.237(8)
Ru(4)–Ru(5)	2.821(2)	Ru(4)–C(7)	2.240(9)
Ru(1)–C	2.048(5)	Ru(4)–C(8)	2.234(9)
Ru(2)–C	1.959(5)	Ru(4)–C(9)	2.227(9)
Ru(3)–C	2.141(5)	Ru(4)–C(10)	2.228(9)
Ru(4)–C	1.959(5)	C–C	1.473(11)
Ru(5)–C	2.061(5)		

The chemical activation of the hexa- and penta-nuclear carbido clusters with Me_3NO towards reaction with cyclopentadiene is a far less systematic system than with cyclohexa-1,3-diene. Using this latter ligand, sequential substitution of the diene followed by dehydrogenation to benzene is possible, leading ultimately to the bis(benzene) cluster in the case of the hexaruthenium cluster,[3] and to benzene–diene derivatives of the pentaruthenium cluster.[5] With cyclopentadiene, many products are formed, as yet most are still uncharacterised, and although only two equivalents of Me_3NO are added, and hence only two carbonyl ligands should be removed, five are actually displaced for the substitution of two cp groups in the two clusters described above. Decapping of the hexaruthenium and mixed-metal Ru_5Rh clusters to yield Ru_5C species has not been observed when cyclohexa-1,3-diene is used. This decapping cannot be achieved when Me_3NO is used in the absence of cyclopentadiene and must therefore be induced by the cyclopentadienyl ligand. The ease by which two cp ligands are introduced into cluster systems compared to the difficulties associated with benzene can be rationalised from the point of view of both the electronic demands of the cluster units and also the differences between the cyclopentadienyl and benzene ligands. The former argument is based on the requirement of the cluster to have an even number of electrons formally donated by the surrounding ligands. Considering the metals as neutral, then cp must also be neutral, and is therefore a five-electron donor. Clearly, unless two cp moieties are introduced into the cluster systems ideal electron counts cannot be achieved. The latter hypothesis is in keeping with observations that demonstrate cp to be a more effective ligand than benzene, capable of accommodating the electron density on substitution of the CO groups more efficiently than benzene.

These reactions are not straightforward, *i.e.* the carbonyl ligands are not replaced according to the stoichiometry of the Me_3NO used, and alterations in metal cores can occur. Hence, it is not possible to speculate on the identities of the other species from the reactions of $[Ru_6C(CO)_{17}]$ and $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ with Me_3NO and cyclopentadiene, not yet fully characterised.

Experimental

All reactions were carried out using freshly distilled solvents under an atmosphere of nitrogen. Subsequent work-up of products was carried out using standard laboratory-grade solvents without precautions taken to exclude air. Infrared spectra were recorded on a Perkin-Elmer 1600 Fourier-Transform and ^1H NMR spectra on a Bruker WM200 spectrometer. Mass spectra were obtained by positive fast-atom bombardment on a Kratos MS50TC instrument. The clusters $[Ru_5C(CO)_{15}]$,[10] $[Ru_6C(CO)_{17}]$[11] and $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$[6] were prepared according to literature methods. Trimethylamine *N*-oxide (Me_3NO) and dicyclopentadiene were purchased from Aldrich and Me_3NO was dried then sublimed

Table 3 Crystallographic data and details of measurements for $[Ru_6C(CO)_{12}(\eta^5\text{-}C_5H_5)_2]$ **1** and $[Ru_5C(CO)_{10}(\eta^5\text{-}C_5H_5)_2]$ **2**

(*a*) Crystal data	**1**	**2**
Formula	$C_{23}H_{10}O_{12}Ru_6$	$C_{21}H_{10}O_{10}Ru_5$
M	1084.8	927.7
Crystal size/mm	0.35 × 0.15 × 0.05	0.39 × 0.31 × 0.11
Crystal colour, shape	Dark red triangular plate	Dark red tablet
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	9.256(6)	9.6474(15)
b/Å	9.954(8)	16.1853(15)
c/Å	15.576(15)	15.7329(17)
α/°	88.43(7)	
β/°	87.03(7)	93.467(13)
γ/°	66.66(6)	
U/Å^3	1316	2452
Z	2	4
$F(000)$	1016	1744
D_c/g cm^{-3}	2.738	2.513
μ/mm^{-1}	3.420	3.062
T/K	150	295
(*b*) Data collection *		
Measured reflections	3404	3317
Observed reflections $[I > 2\sigma(I)]$	2602	2668
(*c*) Structure refinement		
Number of refined parameters	316	282
Final R_1 for $I > 2\sigma(I)$ $(=\Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert)$	0.0368	0.0212
wR_2	0.1002	0.0541
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$		
S	1.093	1.161
Maximum, minimum Δρ/e Å^{-3}	1.06, −1.24	0.45, −0.44
Root-mean-square deviation from mean (Δρ = 0.00)/e Å^{-3}	0.22	0.12

* Graphite monochromator, Mo-Kα radiation (λ = 0.710 73 Å), ω–2θ scan mode, 2θ scan range 5–45°, 3 standard reflections measured.

Table 4 Fractional atomic coordinates (× 10^4) for compound **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Ru(1)	3 452(1)	8 560(1)	1 472(1)
Ru(2)	1 472(1)	6 935(1)	1 720(1)
Ru(3)	789(1)	9 481(1)	2 750(1)
Ru(4)	2 041(1)	6 641(1)	3 529(1)
Ru(5)	4 616(1)	5 694(1)	2 285(1)
Ru(6)	3 954(1)	8 275(1)	3 295(1)
C	2 781(10)	7 666(10)	2 526(6)
C(11)	4 180(12)	10 071(12)	1 657(6)
O(11)	4 594(9)	11 007(8)	1 678(5)
C(12)	2 475(13)	9 381(12)	422(8)
O(12)	1 879(10)	9 907(9)	−201(5)
C(13)	5 390(13)	7 354(12)	936(7)
O(13)	6 575(9)	6 799(8)	551(5)
C(21)	1 529(11)	5 021(11)	1 740(6)
O(21)	1 589(10)	3 843(8)	1 739(6)
C(22)	1 444(11)	6 960(10)	493(7)
O(22)	1 341(9)	6 914(10)	−228(5)
C(23)	−739(13)	7 939(11)	1 865(6)
O(23)	−2 083(9)	8 423(8)	1 914(5)
C(1)	101(12)	11 581(11)	2 036(7)
C(2)	−1 263(11)	11 245(11)	2 178(6)
C(5)	614(11)	11 710(11)	2 850(6)
C(3)	−1 558(12)	11 172(11)	3 060(6)
C(4)	−381(11)	11 486(11)	3 496(7)
C(41)	2 803(11)	6 342(10)	4 645(7)
O(41)	3 236(8)	6 112(7)	5 336(5)
C(42)	963(12)	5 374(11)	3 764(6)
O(42)	383(10)	4 589(10)	3 945(5)
C(4B)	183(12)	8 476(11)	3 883(7)
O(4B)	−792(8)	8 921(8)	4 419(5)
C(51)	5 122(11)	4 363(11)	1 365(7)
O(51)	5 435(9)	3 531(9)	811(5)
C(52)	6 742(12)	5 310(10)	2 538(7)
O(52)	7 994(9)	5 064(8)	2 669(6)
C(5B)	4 364(11)	4 292(11)	3 091(6)
O(5B)	4 579(8)	3 202(8)	3 422(5)
C(6)	3 888(12)	10 054(12)	4 141(7)
C(7)	4 022(11)	8 802(11)	4 630(6)
C(8)	5 448(12)	7 655(12)	4 386(7)
C(9)	6 239(12)	8 136(12)	3 715(7)
C(10)	5 227(12)	9 672(12)	3 572(7)

Table 5 Fractional atomic coordinates (× 10^4) for compound **2** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ru(1)	1088(1)	6793(1)	6766(1)
Ru(2)	775(1)	5447(1)	7894(1)
Ru(3)	−1153(1)	6717(1)	7773(1)
Ru(4)	−1574(1)	6414(1)	6048(1)
Ru(5)	−1971(1)	5159(1)	7253(1)
C	−323(5)	5864(3)	6896(3)
C(11)	2605(7)	7062(4)	7548(4)
O(11)	3527(5)	7228(3)	7997(3)
C(12)	2242(6)	6432(4)	5907(4)
O(12)	2926(5)	6235(4)	5384(3)
C(13)	732(6)	7853(4)	6253(4)
O(13)	488(5)	8474(3)	5941(3)
C(1)	2179(10)	4430(6)	7590(3)
C(2)	1213(7)	4133(4)	8165(7)
C(3)	1431(8)	4575(6)	8941(5)
C(4)	2531(8)	5144(4)	8846(4)
C(5)	2993(6)	5055(5)	8011(6)
C(1′)	2606(12)	4700(9)	7609(7)
C(2′)	1485(13)	4150(7)	7721(8)
C(3′)	1091(10)	4229(9)	8572(9)
C(4′)	1969(17)	4828(10)	8987(5)
C(5′)	2905(12)	5119(7)	8392(11)
C(2B)	144(6)	6188(4)	8798(4)
O(2B)	301(4)	6329(3)	9526(3)
C(31)	−2660(7)	6628(4)	8508(4)
O(31)	−3532(5)	6597(3)	8960(3)
C(32)	−468(6)	7793(4)	8089(4)
O(32)	−90(5)	8433(3)	8292(3)
C(6)	−2385(14)	7250(4)	5018(5)
C(7)	−1135(8)	6886(8)	4765(5)
C(8)	−1337(12)	6018(7)	4717(5)
C(9)	−2712(15)	5845(5)	4939(5)
C(10)	−3360(5)	6607(10)	5125(5)
C(6′)	−3274(19)	6869(21)	5101(13)
C(7′)	−2006(36)	7268(7)	4940(15)
C(8′)	−1035(12)	6651(23)	4733(13)
C(9′)	−1704(36)	5872(12)	4766(13)
C(10′)	−3088(29)	6006(17)	4993(12)
C(4B)	−2535(6)	7217(4)	6822(3)
O(4B)	−3427(5)	7699(3)	6771(3)
C(51)	−1722(6)	4132(4)	6693(4)
O(51)	−1513(5)	3524(3)	6378(3)
C(52)	−2335(6)	4678(4)	8331(4)
O(52)	−2575(6)	4429(3)	8978(3)
O(53)	−4931(5)	5402(4)	6537(4)
C(53)	−3819(7)	5322(4)	6809(4)

prior to use. Dicyclopentadiene was cracked directly before use, otherwise no further purification procedures were used.

Reaction of $[Ru_6C(CO)_{17}]$ *with* C_5H_6 *and* Me_3NO.—The cluster $[Ru_6C(CO)_{17}]$ (100 mg) was dissolved in a mixture of CH_2Cl_2 (25 cm^3) and C_5H_6 (1 cm^3) and cooled to −78 °C. A solution of Me_3NO (15 mg, 2.1 mol equivalent) in CH_2Cl_2 (5 cm^3) was added dropwise and the reaction mixture allowed to warm to room temperature. After stirring for 30 min IR spectroscopy indicated complete consumption of starting material. The resultant dark brown solution was filtered and the solvent removed from the filtrate *in vacuo*. The residue was dissolved in the minimum of CH_2Cl_2 and separated by thin-layer chromatography using CH_2Cl_2–hexane (30 : 70) as eluent. The green band and bottom brown band were removed and characterised as $[Ru_5C(CO)_{10}(\eta^5\text{-}C_5H_5)_2]$ **2** (3 mg) and $[Ru_6C(CO)_{12}(\eta^5\text{-}C_5H_5)_2]$ **1** (17 mg) [IR(CH_2Cl_2): ν(CO) 2059s, 2020vs, 1976m and 1835w (br) cm^{-1}. ^1H NMR: δ 4.99], respectively.

The reaction of $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ with C_5H_6 and Me_3NO has already been reported, the green band eluted in this reaction has been identified by spectroscopy as $[Ru_5C(CO)_{10}(\eta^5\text{-}C_5H_5)_2]$ **2**.

Reaction of $[Ru_5C(CO)_{15}]$ *with* C_5H_6 *and* Me_3NO.—To a solution of the compound $[Ru_5C(CO)_{15}]$ (100 mg) in CH_2Cl_2 (25 cm^3) containing excess of C_5H_6 (1 cm^3) at −78 °C, a solution of Me_3NO (17 mg, 2.1 mol equivalent) in CH_2Cl_2 (5 cm^3) was added dropwise. The reaction mixture was allowed to warm to room temperature, during which time the colour of the solution darkened substantially. After stirring for a total period of 30 min IR spectroscopy indicated complete consumption of starting material. The solution was filtered and the solvent removed from the filtrate *in vacuo*. The residue was redissolved in the minimum of CH_2Cl_2 and separated by thin-layer chromatography using CH_2Cl_2–hexane (30 : 70) as eluent. The major green band was removed and characterised as $[Ru_5C(CO)_{10}(\eta^5\text{-}C_5H_5)_2]$ **2** (14 mg). IR(CH_2Cl_2): ν(CO) 2066w, 2033vs, 2003s, 1981m and 1820w (br) cm^{-1}. ^1H NMR: δ 5.12. Mass spectra of both **1** and **2** did not afford the correct parent ions expected and different values were obtained each time their spectra were recorded.

Crystal Structure Determination.—X-Ray measurements were made on a Stoë Stadi-4 four-circle diffractometer. Data were collected at 150 K for compound **1**, and at room temperature for compound **2**. An Oxford Cryosystems low-temperature device was used for the low-temperature determination.[12] Details of crystal data, data collection and structure refinement are summarised in Table 3, and the fractional atomic coordinates of compounds **1** and **2** are listed in Tables 4 and 5 respectively. The metal atoms were located using automatic direct methods,[13] and SHELXL 93[14] used thereafter. The H atoms in **1** and **2** were included at fixed, calculated positions. In compound **1**, the C(carbide) and ring carbons were not treated anisotropically. In compound **2**, the rings were idealised as pentagons, both rings are disordered over two sites with site-occupation factors in the ratio 6 : 4.

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

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