Site Selectivity in the Reactions of Nucleophiles with $[Ru_5C(CO)_{15}]$: *X*-Ray Analysis of $[Ru_5C(CO)_{14}(\mu\text{-}\eta^2\text{-MeCO})(AuPPh_3)]$ and $[Ru_5C(CO)_{13}(\eta^5\text{-}C_5H_5)(AuPPh_3)]$, the First High Nuclearity Cyclopentadienylruthenium Cluster

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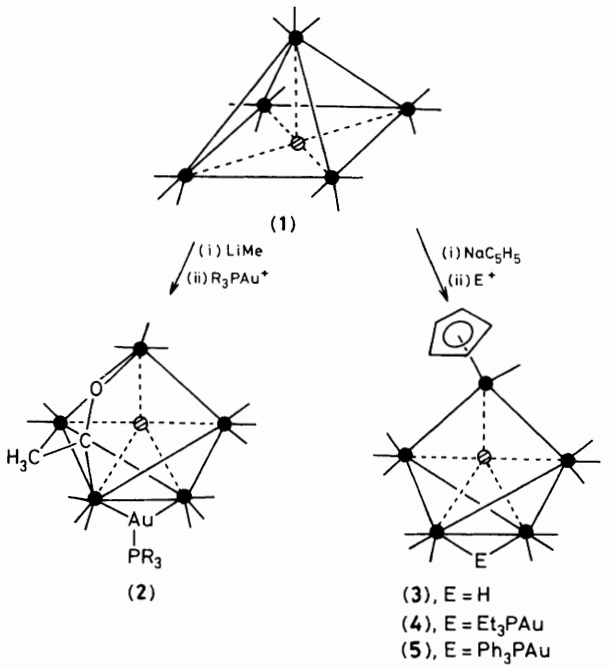
The cluster $[Ru_5C(CO)_{15}]$ reacts with LiMe, followed by $[Ph_3PAu][Cl]$, to give $[Ru_5C(CO)_{14}(\mu\text{-}\eta^2\text{-MeCO})(AuPPh_3)]$ while reaction with NaC_5H_5, followed by $[Ph_3PAu][ClO_4]$, gives $[Ru_5C(CO)_{13}(\eta^5\text{-}C_5H_5)(AuPPh_3)]$; *X*-ray analysis has confirmed that the nucleophile has attacked a carbonyl ligand in the former case but a metal centre in the latter.

We have previously reported reactions involving the addition of nucleophiles to $[Ru_5C(CO)_{15}]$ (**1**),[1] and have shown that this reaction proceeds *via* attack at a metal centre with formation of an adduct $[Ru_5C(CO)_{15}(nuc)]$, nuc = nucleophile. When the nucleophile is CO or MeCN this addition may be reversed to regenerate (**1**). In the case of phosphine addition, subsequent loss of CO occurs to give $[Ru_5C(CO)_{14}PR_3]$. Addition of EX [E = H or $Au(PR_3)$; X = Cl, Br, I, or SEt] to give $[\mu\text{-}ERu_5C(CO)_{15}X]$ may also be reversed, *via* elimination of EX (E = H; X = Cl), or alternatively CO may be lost to give the bridged species $[(\mu\text{-}E)Ru_5C(CO)_{14}(\mu\text{-}X)]$.[2,3] In an extension of this work to include carbanionic nucleophiles we now report two new types of reactivity at (**1**). In the first case attack of Me^- occurs at a carbonyl ligand, rendering its oxygen atom sufficiently nucleophilic to donate two electrons to a neighbouring ruthenium atom, thus forming a bridging acyl species. Such attack at a carbonyl ligand has only rarely been observed in ruthenium cluster chemistry.[4] In contrast $C_5H_5^-$ reacts at a metal centre in (**1**) with displacement of two carbonyls to form an η^5-C_5H_5 complex. This is the first report of a high nuclearity cyclopentadienylruthenium cluster.

Addition of a slight excess of LiMe to a solution of (**1**) in diethyl ether gave an orange solution [i.r. ν(CO): 2070w, 2043s, 2029s, 2007s, and 1984m cm^{-1}] together with a red precipitate, identified on the basis of its i.r. spectrum as $Li_2[Ru_5C(CO)_{14}]$. $[Ph_3PAu]Cl$ (1 equiv.) was added to the orange solution and after 1 h the reaction mixture was purified by chromatography. Orange crystals of the product (**2**) were obtained from CH_2Cl_2 solution. The product (**2**) was formulated on the basis of ^1H n.m.r.† and microanalysis as $[Ru_5C(CO)_{14}(MeCO)(AuPPh_3)]$. This compound may also be prepared by the direct reaction of $[Ph_3PAuMe]$ and (**1**).[3] There is evidence for removal of the acyl ligand as MeCHO by reduction of (**2**) using $[BH_4]^-$, a process which will be described in detail elsewhere.[5]

The molecular structure‡ of (**2**) is shown in Figure 1 and is closely related to that of the previously characterised compound $[HOs_5C(CO)_{14}(\mu\text{-}\eta^2\text{-}CO_2Et)]$[6] except that in the ruthenium cluster the 'hinge' of the bridged butterfly is bridged by a $(\mu\text{-}AuPPh_3)$ group instead of the similarly bonded (μ-H). Complex (**2**) also contains a bridging acyl rather than an acetoxy group, corresponding to attack of Me^- rather than EtO^-. The bridged butterfly of metal atoms is slightly distorted towards a square pyramidal structure owing to the effect of the bridging acyl group. This effect may be seen by comparing the non-bonded distances Ru(1)–Ru(5) and Ru(2)–Ru(5): Ru(1)–Ru(5) is *ca.* 0.5 Å shorter than Ru(2)–Ru(5).



Scheme 1

Addition of excess of NaC_5H_5 to a solution of (**1**) in tetrahydrofuran (THF) gave an immediate colour change from red to orange. The resulting species (A) [i.r. ν(CO) (THF): 2055w, 2071s, 1997vs, and 1969m cm^{-1}] was protonated with ethereal HBF_4. The single cluster product (**3**) in the hexane-soluble fraction was chromatographed to remove organic impurities and was obtained in good yield from hexane as a yellow–green crystalline solid [i.r. ν(CO)(hexane) 2095m, 2065s, 2054vs, 2043m, 2025m, 2007m, 1998w, 1983m, and 1949w cm^{-1}]. Mass spectrometry§ indicated the formulation $[Ru_5C(CO)_{13}(C_5H_5)H]$ and ^1H n.m.r.¶ in the range 300—

† δ (CD_2Cl_2; 298 K) 7.49 (m, 15H) and 2.16 (s, 3H).

‡ *Crystal data:* (**2**), $C_{35}H_{18}AuO_{15}PRu_5$, M = 1411.79, monoclinic, space group Pn, a = 9.613(1), b = 14.094(1), c = 15.145(2) Å, β = 90.70(1)°, U = 2051.8 Å^3, D_c = 2.28 g cm^{-3}, $F(000)$ = 1324, μ(Mo-K_α) = 53.84 cm^{-1}, $F \geq 4\sigma(F)$, 2θ range 5—50°, R value 0.052 from 3804 absorption-corrected data. (**5**), $C_{37}H_{20}AuO_{13}PRu_5$, M = 1406.01, monoclinic, space group $P2_1/n$, a = 8.863(1), b = 16.512(1), c = 27.807(2) Å, β = 94.02 (1)°, U = 4059.4 Å^3, D_c = 2.30 g cm^{-3}, $F(000)$ = 2640, μ(Mo-K_α) = 54.39 cm^{-1}, $F \geq 4\sigma(F)$, 2θ range 5—50°, present R value 0.036 from 6323 absorption-corrected data. Data were collected on a Stoe 4-circle diffractometer using Mo-K_α radiation.

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.

§ Highest mass multiplet m/z 947; mass of $[H^{101}Ru_5C(CO)_{13}(C_5H_5)]$ 947.

¶ δ ($CDCl_3$; 298 K) 5.19 (s, 5H), −22.28 (s, 1H); ($[^2H_8]$toluene–CS_2; 151 K) 4.30 (s, 5H), and −22.7 (s, 1H).

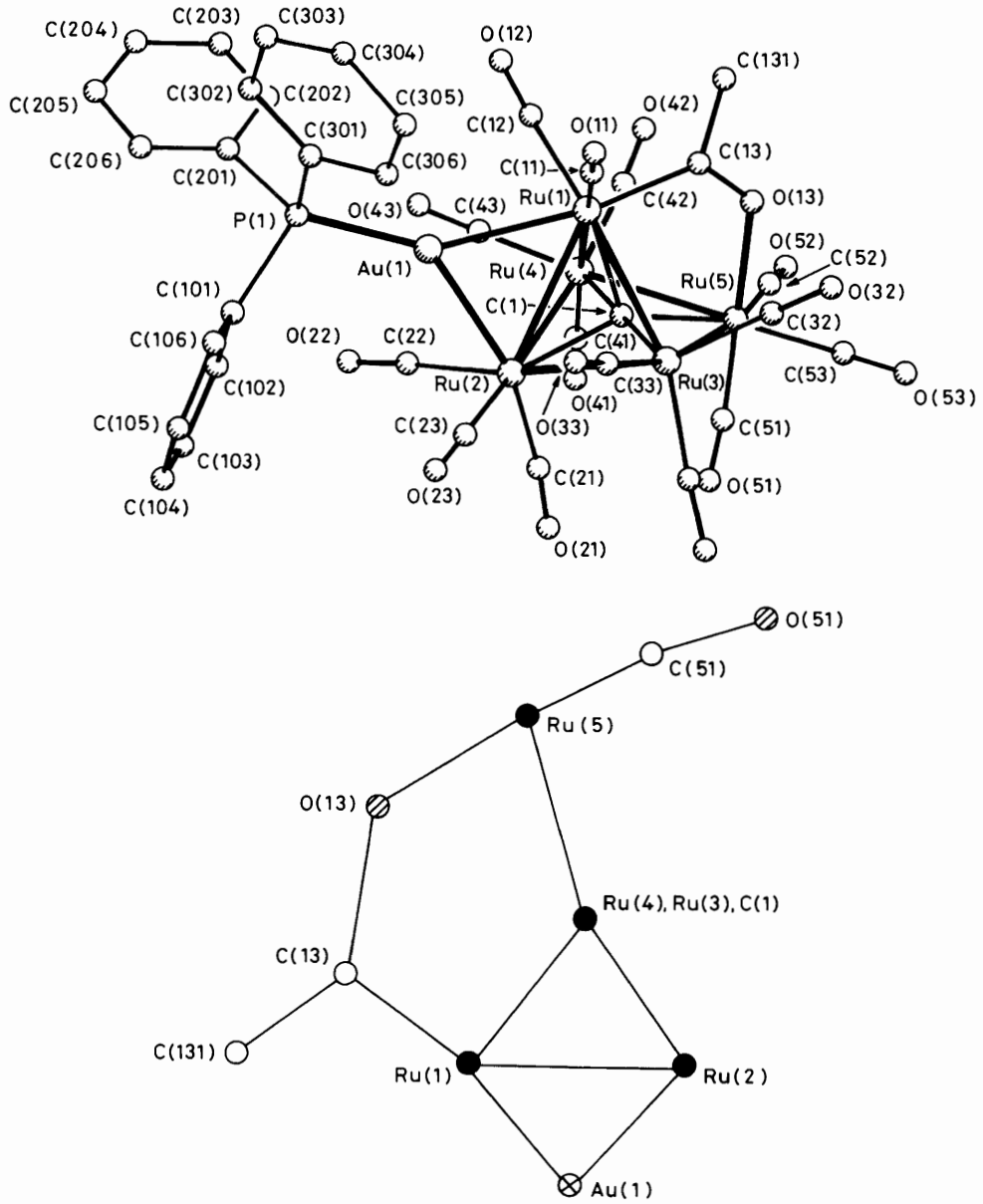


Figure 1. Molecular structure of $[Ru_5C(CO)_{14}(\mu\text{-}\eta^2\text{-MeCO})(AuPPh_3)]$. Important bond distances and angles: Ru(1)–Ru(2) 2.989(3), Ru(1)–Ru(3) 2.817(3), Ru(1)–Ru(4) 2.822(3), Ru(2)–Ru(3) 2.867(3), Ru(2)–Ru(4) 2.879(3), Ru(4)–Ru(5) 2.880(3), Ru(1)–Au(1) 2.721(3), Ru(2)–Au(1) 2.764(3), Ru(1)–C(1) 2.035(19), Ru(2)–C(1) 2.080(18), Ru(3)–C(1) 1.906(24), Ru(4)–C(1) 1.977(18), Ru(5)–C(1) 1.087(18), Ru(1)–C(13) 1.006(22), Ru(5)–O(13) 2.115(15), Ru–CO(av.) 1.91 Å. Ru(1)···Ru(5) 3.537(5), Ru(2)···Ru(5) 4.012(5) Å. Ru(1)–C(1)–Ru(5) 118, Ru(2)–C(1)–Ru(5) 148, Ru(1)–C(1)–Ru(2) 93, Ru(1)–C(13)–O(13) 123, C(13)–O(13)–Ru(5) 123, and C(1)–Ru(5)–C(51) 95°, hinge angle 71°.

151 K showed only a singlet for the cyclopentadienyl hydrogens, suggesting η^5 co-ordination, and one metal hydride resonance. In a similar way reaction of anion (A) in THF with $[R_3PAu][ClO_4]$ (R = Et and Ph) gave orange solutions from which crystalline solids (**4**) and (**5**)‖ were obtained in very high yields. Mass spectrometry‖ suggested the formulation $[Ru_5C(CO)_{12}(C_5H_5)(R_3PAu)]$; however this does not rule out the presence of thirteen carbonyls in the products since many clusters readily lose CO in the mass spectrometer with the result that no molecular ion is observed. Microanalysis,‖ too, did not permit distinction between the formulations $[Ru_5C(CO)_n(C_5H_5)(R_3PAu)]$ (n = 12 or 13). Crystals of (**5**), suitable for *X*-ray diffraction were given by slow evaporation of a CH_2Cl_2–hexane solution.

The structure of (**5**) is as shown in Figure 2.‡ The structure is closely related to that of $[Ru_5C(CO)_{15}(\mu\text{-}AuPPh_3)Cl]$;[2] the main difference being that the cyclopentadienyl ring replaces the chlorine and two carbonyl ligands on the bridging Ru atom. The bond to the remaining carbonyl on Ru(5) is significantly shorter than the other Ru–CO distances. The

‖ (**4**): i.r. ν(CO)(hexane): 2071w, 2043vs, 2032s, 2021m, 2001m, 1979m, 1966w, 1958w, and 1942w cm^{-1}; Found: C, 23.8; H, 1.8; P, 2.3. Calc. for $C_{25}H_{20}AuO_{13}PRu_5$: C, 23.8; H, 1.6; P, 2.5. Calc. for $C_{24}H_{20}AuO_{12}PRu_5$: C, 23.4; H, 1.6; P, 2.5%; highest mass multiplet *m/z* 1233; mass of $[^{101}Ru_5C(CO)_{12}(C_5H_5)(Et_3PAu)]$ 1233. (**5**) i.r. ν(CO)(hexane): 2071w, 2042vs, 2030s, 2021m, 1998m, 1949w, and 1931w cm^{-1}; Found: C, 32.0; H, 1.7. Calc. for $C_{37}H_{20}AuO_{13}PRu_5$: C, 31.6; H, 1.4. Calc. for $C_{36}H_{20}AuO_{12}PRu_5$: C, 31.4; H, 1.5%; highest mass multiplet *m/z* 1377; mass of $[^{101}Ru_5C(CO)_{12}(C_5H_5)(Ph_3PAu)]$ 1377.

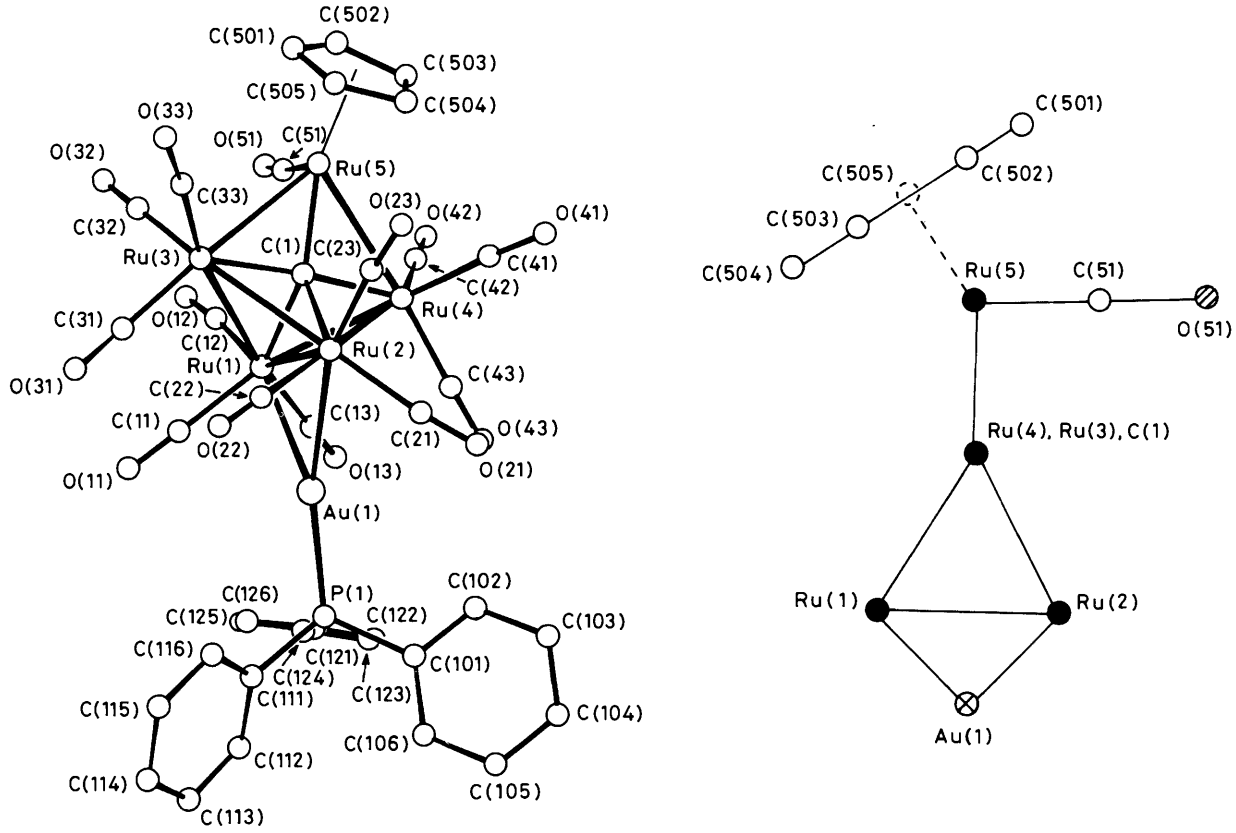


Figure 2. Molecular structure of $[Ru_5C(CO)_{13}(\eta^5\text{-}C_5H_5)(AuPPh_3)]$. Important bond distances and angles: Ru(1)–Ru(2) 2.894(1), Ru(1)–Ru(3) 2.839(1), Ru(1)–Ru(4) 2.867(1), Ru(2)–Ru(3) 2.880(1), Ru(2)–Ru(4) 2.844(1), Ru(3)–Ru(5) 2.905(1), Ru(4)–Ru(5) 2.890(1), Ru(1)–Au(1) 2.780(1), Ru(2)–Au(1) 2.750(1), Ru(1)–C(1) 2.115(6), Ru(2)–C(1) 2.111(6), Ru(3)–C(1) 1.980(5), Ru(4)–C(1) 2.001(5), Ru(5)–C(1) 2.023(6), Ru(5)–C(501—505) (av.) 2.23, Ru(5)–C(51) 1.838(25), Ru(1—4)–CO (av.) 1.912 Å. Ru(1) · · · Ru(5) 3.877(3) and Ru(2) · · · Ru(5) 3.812(3) Å. Ru(1)–C(1)–Ru(5) 139, Ru(2)–C(1)–Ru(5) 134, Ru(1)–C(1)–Ru(2) 87, C(1)–Ru(5)–C(51) 95, and C(1)–Ru(5)–centre of C_5H_5 ring 139°, 'hinge' angle 72°.

carbonyl lies directly over the C(1)–Ru(2) vector and makes an angle of 126° to the perpendicular from the C_5H_5 ring to Ru(5). The C_5H_5 ring lies approximately parallel to the Ru(1)Ru(3)Ru(4) plane.

The combined spectroscopic data for compounds (**3**), (**4**), and (**5**) lead us to propose that these compounds have a common formula $[ERu_5C(CO)_{13}(C_5H_5)]$ (E = H, Ph_3PAu, or Et_3PAu) and a common structure, shown in Scheme 1.

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