Synthesis, *X*-Ray Structure, and Reactivity of $[Ru_3H_3(CO)_3(\eta\text{-}C_5H_5)_3]$: An Entry into the Organic Chemistry of the Triruthenium Centre

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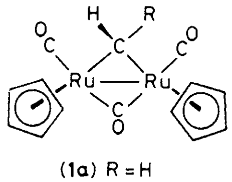
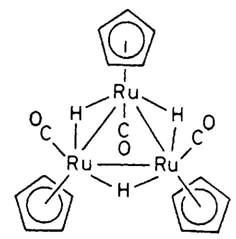
Treatment of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHR)(\eta\text{-}C_5H_5)_2]$ (R = H, Me, CO_2Et) with H_2 (1 atm) under u.v. irradiation provides fluxional $[Ru_3H_3(CO)_3(\eta\text{-}C_5H_5)_3]$, the structure of which has been established by *X*-ray diffraction; the complex reacts readily with unsaturated hydrocarbons.

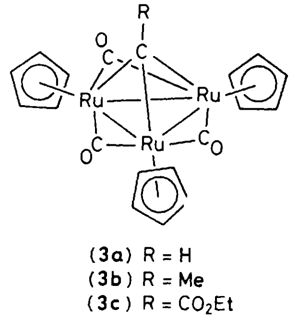
The discovery[1] of a good synthetic route to very reactive $[Os_3H_2(CO)_{10}]$ led to a rapid expansion in the important organic chemistry of the triosmium centre, exemplified by the work of Deeming, Lewis and Johnson, and Shapley. We now describe a trihydrido-triruthenium cluster complex $[Ru_3H_3(CO)_3(\eta\text{-}C_5H_5)_3]$ which appears capable of providing an equally convenient entry into organo-triruthenium chemistry. Unlike $[Ru_3(CO)_{12}]$, which fragments readily, $[Ru_3H_3(CO)_3(\eta\text{-}C_5H_5)_3]$ tends to retain the triruthenium cluster in reactions with unsaturated hydrocarbons.



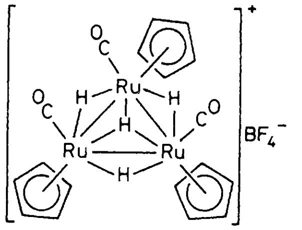
(1a) R = H
(1b) R = Me
(1c) R = CO_2Et



(2)



(3a) R = H
(3b) R = Me
(3c) R = CO_2Et



(4)

U.v. irradiation (250 W mercury lamp, silica reaction flask, 25 °C, 1—3 days) of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHR)(\eta\text{-}C_5H_5)_2]$ (**1a—c**)[2,3] in toluene solution while purging with H_2 (1 atm) gives $[Ru_3H_3(CO)_3(\eta\text{-}C_5H_5)_3]$ (**2**)† in 40—60% yield, the alkylidyne complexes $[Ru_3(\mu_3\text{-}CR)(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)_3]$ (**3a—c**)† in 10—20% yield, and $[Ru_4(\mu_3\text{-}CO)_4(\eta\text{-}C_5H_5)_4]$[4] in up to 30% yield. These products are probably derived from the intermediate mononuclear species $[RuH(CO)(\eta\text{-}C_5H_5)]$, $[Ru(CR)(CO)(\eta\text{-}C_5H_5)]$, and $[Ru(CO)(\eta\text{-}C_5H_5)]$, which combine to give the Ru_3 and Ru_4 clusters. Recently it has been shown[5]

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† (**2**): ν(CO) (in CH_2Cl_2) 1 946m and 1 917s cm^{-1}; ^1H n.m.r. {in $[^2H_5]$pyridine, 25 °C} δ 5.18 (s, 5 H), 5.15 (s, 10 H), −16.94 (s, 1 H), and −17.27 (s, 2 H); ^{13}C n.m.r. (in $CDCl_3$, 25 °C), δ 82.8 (C_5H_5) and 81.6 ($2C_5H_5$) p.p.m.
(**3b**): ν(CO) (in CH_2Cl_2) 1 804s and 1 748m cm^{-1}; ^1H n.m.r. (in $CDCl_3$) δ 5.13 (s, 15 H) and 4.96 (s, 3 H); ^{13}C n.m.r. δ 308.8 (*C*Me), 243.0 (3CO), 92.5 ($3C_5H_5$), and 54.5 (Me) p.p.m.
(**4**): ν(CO) (in CH_2Cl_2) 2 028s and 1 982w cm^{-1}; ^1H n.m.r. {in $[^2H_6]$acetone} δ 5.89 (s, 15 H), −3.14 (s, 1 H), and −12.11 (s, 3 H); ^{13}C n.m.r. (in CD_3NO_2) δ 200.1 (3CO) and 86.5 ($3C_5H_5$) p.p.m.

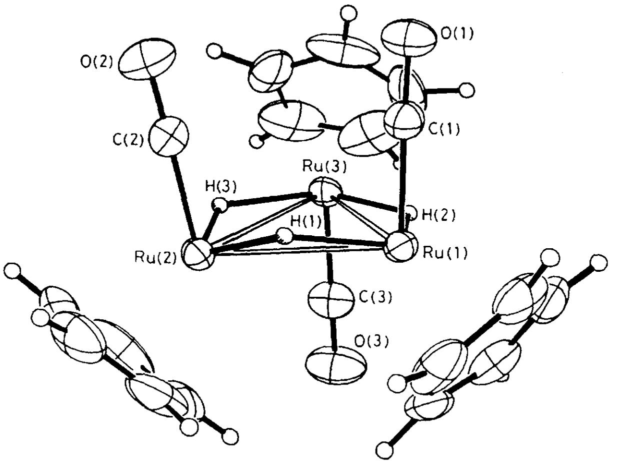

Figure 1. Molecular structure of (2). Pertinent parameters: bond lengths, Ru(1)–Ru(2) 2.949(1), Ru(1)–Ru(3) 2.947(1), Ru(2)–Ru(3) 2.954(1), mean Ru–H 1.69(4) Å; bond angles, mean Ru–H–Ru 121(2), mean Ru–Ru–C(O) 92.0(14)°.

that $[OsH(CO)_2(\eta\text{-}C_5Me_5)]$ reacts with H_2 under photochemical conditions to form $[Os_2(\mu\text{-}H)_2(CO)_2(\eta\text{-}C_5Me_5)_2]$, a dimer rather than a trimer, like (**2**), of $[MH(CO)(\eta\text{-}C_5R_5)]$. Complex (**2**) is not formed when $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ is irradiated under 1 atm of H_2, but $[Ru_2(CO)(L)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (L = C_2H_4[2] or MeCN[6]), containing a labile ligand, yields *ca.* 20% of (**2**) under these conditions.

The molecular structure of blue, air-stable, crystalline (**2**) was determined by *X*-ray diffraction‡ and is given in Figure 1. It is based on an equilateral triangle of ruthenium atoms whose edges are symmetrically bridged by hydride ligands. The ruthenium atoms carry terminal CO and η-C_5H_5 groups arranged to give the molecule approximate C_s symmetry, with the mirror plane passing through H(1), Ru(3), C(3), and O(3). The unique hydride H(1) lies significantly out of the Ru_3 plane compared to the other two [displacements of 0.50(5), −0.12(5), and 0.20(5) Å for H(1), H(2), and H(3), respectively]. Interestingly, the non-hydrogen skeleton of the molecule bears a strong resemblance to that of $[Ir_3(CO)_3(\eta\text{-}C_5H_5)_3]$.[7]

At room temperature the ^1H and ^{13}C n.m.r. spectra of (**2**) show that the molecule is present in solution with the mirror symmetry determined for the solid state. On warming, however, the pairs of η-C_5H_5 and μ-H signals broaden, coalesce at *ca.* 50 and 75 °C respectively, and at higher temperatures sharpen to a single time-averaged signal for each type of proton. Calculation of free energies of activation from the two sets of coalescing signals provides values of 62.6 and 61.2 kJ mol^{-1}, indicating that a single fluxional process is responsible for the environmental averaging. It is clear that this must involve the passage of η-C_5H_5 and CO ligands from one side of the Ru_3 plane to the other, but the mechanism of this exchange is not yet defined. The ease with which the terminal ligand arrangement may be altered is also apparent when (**2**) is protonated with HBF_4. This produces a quantitative yield of purple crystalline $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}H)(CO)_3(\eta\text{-}C_5H_5)_3][BF_4]$ (**4**),† containing a non-fluxional cation with C_{3v} symmetry (*i.e.* all three η-C_5H_5 ligands are on the same side of the Ru_3 plane).

In boiling toluene the trihydride (**2**) reacts readily with a wide variety of unsaturated hydrocarbons. For example, ethylene (1 atm) affords the ethylidyne complex (**3b**) in 56% yield and $[Ru_2(CO)(C_2H_4)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]^2$ in 9% yield. The major product (45%) from acetylene (1 atm) is a μ-vinyl species $[Ru_3(CO)_3(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_3]$, which is under investigation, but a 16% yield of (**3b**) is again obtained. The formation of (**3b**) from either ethylene or acetylene reveals a striking capacity of (**2**) to effect both dehydrogenation and hydrogenation of the C_2 unit on bringing it into co-ordination. It is noteworthy in this regard that ethylene or acetylene chemisorbed on a Pt(111) surface are transformed at 300—350 K to the same μ_3-ethylidyne surface species.[8]

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‡ 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. *Crystal data* for (**2**): $C_{18}H_{18}O_3Ru_3$, M = 585.6, triclinic, space group $P\bar{1}$, a = 9.212(5), b = 8.223(4), c = 12.308(6) Å, α = 101.12(4), β = 93.47(4), γ = 97.71(4)°, U = 903.0(8) Å^3, Z = 2, D_c = 2.15 g cm^{-3}, Mo-K_α X-radiation ($\bar{\lambda}$ = 0.71069 Å), μ(Mo-K_α) = 24.4 cm^{-1}. Current R 0.022 for 3 564 unique, observed [$I \geqslant 3\sigma(I)$] intensity data, corrected for absorption and extinction, collected on a Nicolet $R3m$ diffractometer in the range $4 \leqslant 2\theta \leqslant 55°$; blocked cascade least squares refinement. All hydrogen atoms were located directly and included in the structural model; the positional parameters of the μ-hydrogens were allowed to refine without constraint.