Reaction of Cycloheptatriene with Ruthenium Carbonyl: *X*-Ray Crystallographic Determination of the Molecular Structure of $Ru_3(CO)_6(C_7H_7)(C_7H_9)$

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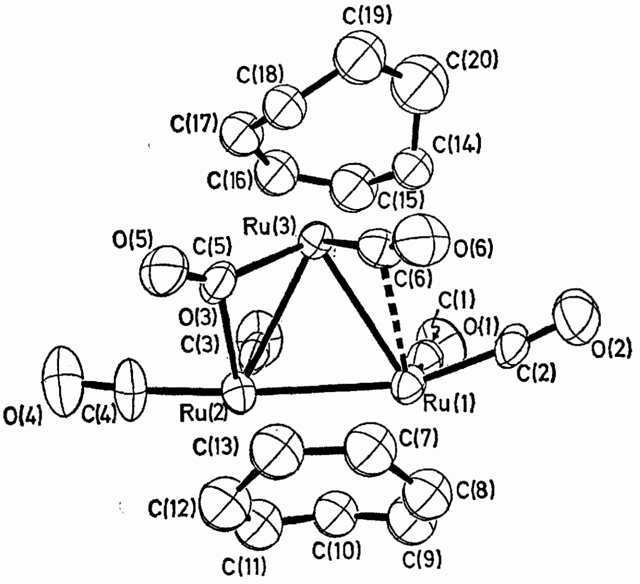
Summary Cycloheptatriene reacts with dodecacarbonyltriruthenium to give *inter alia* a fluxional complex $Ru_3(CO)_6(C_7H_7)(C_7H_9)$ (I), an *X*-ray diffraction study of which reveals that the C_7H_7 ring bridges two of the ruthenium atoms whereas the C_7H_9 ring is attached to the remaining metal atom as a cycloheptadienyl ligand.

DESPITE extensive studies[1] of reactions between cyclic polyolefins and carbonyls of metals of the iron triad there has been only one report[2] of a cycloheptatriene derivative of ruthenium carbonyl, *viz.*, $Ru(CO)_3(C_7H_8)$ prepared by ligand displacement of cyclo-octa-1,5-diene from $Ru(CO)_3(C_8H_{12})$ with cycloheptatriene (CHT). We describe here the reaction of CHT with $Ru_3(CO)_{12}$, and the unique molecular structure of the major product, $Ru_3(CO)_6(C_7H_7)(C_7H_9)$ (I), a fluxional complex.



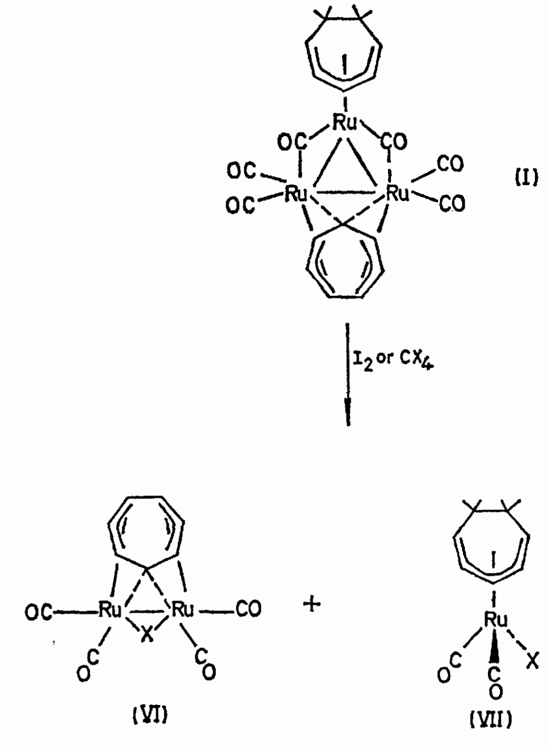
FIGURE

In heptane at reflux, excess of CHT reacts with $Ru_3(CO)_{12}$ to give low yields of $Ru(CO)_3(C_7H_{10})$ (II) (a derivative of cycloheptadiene), $Ru(CO)_3(C_7H_8)$ (III), $Ru(CO)_2(C_7H_8)$ (IV), and $Ru_2(CO)_6(C_7H_8)$ (V), and a high yield (62%) of complex (I). The inter-relations of (I)—(V), both thermally and upon reaction with CHT, suggest that the $Ru_3(CO)_{12}$ cluster is initially broken down in this reaction to form (III), which then further reacts to yield other products.

Complex (I) was characterised by elemental analyses, and by i.r. (ν_{CO} 2012w, 1989s, 1957s, 1936w, and 1836w cm^{-1}), mass [$(M - n\mathrm{CO})^+$, n = 0—6], and ^{1}H n.m.r. [τ 4·80 (1H, t), 5·15 (2H, m), 5·95 (2H, m), 6·86 (7H, s), 7·90 (2H, m), and 8·30 (2H, m)] spectroscopy. The indications of a bridging carbonyl group [ν_{CO} 1836 cm^{-1}], a fluxional C_7H_7 ring [τ 6·86 (7H, s)], and a co-ordinated cycloheptadienyl ring (remaining resonance signals) have been confirmed by a single-crystal *X*-ray diffraction study.

Crystals of (I) are monoclinic, space group $P2_1/c$, a = 8·90, b = 26·82, c = 8·83 Å, β = 110·7°, Z = 4. Data were collected using Mo-K_α radiation on a fully-automated Nonius CAD-3 diffractometer. The structure was solved by heavy-atom methods; R factor of 7·2% (Figure).

The Ru atoms form a near-equilateral triangle [Ru(1)–Ru(2) = 2·840, Ru(1)–Ru(3) = 2·836, Ru(2)–Ru(3) = 2·864 Å], with two terminal carbonyl groups attached to Ru(1) and Ru(2) each. The two bridging carbonyl groups are asymmetric, with C(6)O(6) more so than C(5)O(5) [Ru(3)–C(5) = 1·97, Ru(2)–C(5) = 2·25, Ru(3)–C(6) = 1·85, Ru(1)··C(6) = 2·77 Å, Ru(3)–C(6)–O(6) = 169°], yet another indication that this phenomenon is more prevalent[3] than had been originally supposed. While the C_7H_9 ring is attached only to Ru(3), the C_7H_7 ring is equally shared between Ru(1) and Ru(2). The co-ordinated atoms of the non-fluxional ring are equidistant from the metal atom [the five carbons C(14) to C(18) are all 2·24—2·29 Å from



SCHEME

Ru(3)], while those from the fluxional ring are not [the Ru–C distances associated with the C_7H_7 ring vary between 2·14 and 2·62 Å]. The atoms C(7)C(8)C(9) and C(11)C(12)-C(13) form π-allylic linkages to Ru(1) and Ru(2), respectively, but C(10) is more or less equidistant from the two metal atoms [Ru(1)–C(10) = 2·57, Ru(2)–C(10) = 2·62 Å], and resembles other "bridging carbons" found in several cyclo-octatetraene complexes.[4]

Although there are sufficient electrons in (I) to satisfy the so-called Effective Atomic Number Rule overall, electron delocalisation is obviously extensive, and in the solid state the bonding is perhaps best represented as shown in the Scheme summarising the degradation reactions of (I). On warming (I) with iodine in hexane for 1 h, $Ru_2(CO)_4(C_7H_7)(X)$ (VI; X = I) and $Ru(CO)_2(C_7H_9)(X)$ (VII; X = I) are formed, while CX_4 (X = Cl, Br) similarly affords (VI; X = Cl, Br) and (VII; X = Br). Like (I), the complexes (VI; X = Cl, Br, I) are fluxional molecules, exhibiting only singlet n.m.r. signals at room temperature, and are assigned a similar metal–ring co-ordination system. Neither (I) nor (VI; X = Cl; τ5·89) shows any change in their n.m.r. spectra on cooling to −100°.

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[1] F. A. Cotton, *Accounts Chem. Res.*, 1968, **1**, 257 and refs. therein.

[2] A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1973, **49**, C33.

[3] F. A. Cotton, B. A. Frenz, and L. Kruczynski, *J. Amer. Chem. Soc.*, 1973, **95**, 951; D. B. Yawney and R. J. Doedens, *Inorg. Chem.*, 1972, **11**, 838 and refs. therein.

[4] E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Amer. Chem. Soc.*, 1966, **88**, 3158; F. A. Cotton and M. D. LaPrade, *ibid.*, 1968, **90**, 2026; M. J. Bennett, F. A. Cotton and P. Legzdins, *ibid.*, p. 6335.