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## Preliminary communication

# The isolation and crystal structure of azulenetriruthenium heptacarbonyl, a probable intermediate in the formation of tetrahedral azulene–ruthenium–carbonyl clusters

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We have reported previously[1,2] that the reaction of 4,6,8-trimethylazulene and $Ru_3(CO)_{12}$ yields $(Me_3C_{10}H_5)Ru_4(CO)_9$, in which the substituted azulene ligand is bonded to one face of a tetrahedral $Ru_4$ cluster. More recently, analogous products have been prepared from unsubstituted azulene and guaiazulene[3].

The mechanism by which these tetranuclear complexes were formed has, however, been a matter of some concern. The reaction of azulene and $Ru_3(CO)_{12}$ (in refluxing ligroin, b.p. 110°, for 5 days) has now led to the isolation of azulenetriruthenium heptacarbonyl, $(C_{10}H_8)Ru_3(CO)_7$, as a red crystalline product. The IR spectrum ($CHCl_3$) shows bands at 2050 s, 2005 s, 1967 w, 1958 w and 1764 m $cm^{-1}$, indicative of both terminal and bridging carbonyl ligands. The mass spectrum shows fragmentation patterns (successive loss of $^{12}C^{16}O$) based on the parent peak $[C_{10}H_8Ru_3(CO)_7]^+$ (*m/e* 627) and on the species $[C_{10}H_8Ru_4(CO)_9]^+$ and $[C_{10}H_8Ru_2(CO)_4]^+$. {N.B. a strong feature of the mass spectrum of $(Me_3C_{10}H_5)Ru_4(CO)_9$ is the fragmentation pattern for $[Me_3C_{10}H_5Ru_2(CO)_4]^+$.}[2]

The presence of a bridging carbonyl ligand and the ambiguous results of the mass-spectral study have prompted a single-crystal X-ray diffraction study of the complex, in the expectation of showing its relationship to the previously-prepared tetrahedral species.

The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ ($C_{2h}^5$; No. 14) with $a = 17.18$ Å, $b = 13.36$ Å, $c = 16.41$ Å, $\beta = 108.7°$. The measured density ($\rho_{obsd.} = 2.2 \pm 0.1$ g·$cm^{-3}$) is consistent with eight molecules per unit cell ($\rho_{calcd.} = 2.336$ g·$cm^{-3}$ for $M = 627.46$ and $Z = 8$).

Three-dimensional diffraction data complete to $\sin\theta = 0.38$ (Mo-$K_\alpha$ radiation, $\bar{\lambda}$ 0.7107) were collected with a Supper-Pace "Buerger Automated Diffractometer" using a "stationary-background/$\omega$-scan/stationary-background" counting sequence and equi-inclination Weissenberg geometry. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. Using anisotropic thermal parameters for the ruthenium atoms and isotropic thermal parameters for all other atoms, the discrepancy index has been reduced to $R_F = 8.9\%$ for the 2285 independent non-zero reflections.

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The asymmetric unit consists of two $(C_{10}H_8)Ru_3(CO)_7$ molecules (each having approximate $C_s$ symmetry) centered at 0.1280, 0.2702, 0.3764 and 0.6285, 0.2482, 0.3734. Dimensions within these two crystallographically independent molecules are sufficiently similar that only mean values need be discussed. As shown in Fig.1, the molecule consists of an azulene ligand bonded to a triangular $Ru_3(CO)_7$ cluster. Atom Ru(1) is associated with the five-membered carbocyclic system while Ru(2) and Ru(3) lie below the seven-membered ring. Each ruthenium atom bears two terminal carbonyl ligands, with a bridging carbonyl group between Ru(2) and Ru(3). Individual metal–metal bond distances are Ru(1)–Ru(2)≡Ru(1)–Ru(3) = 2.944(5) and Ru(2)–Ru(3) = 2.740(4) Å.

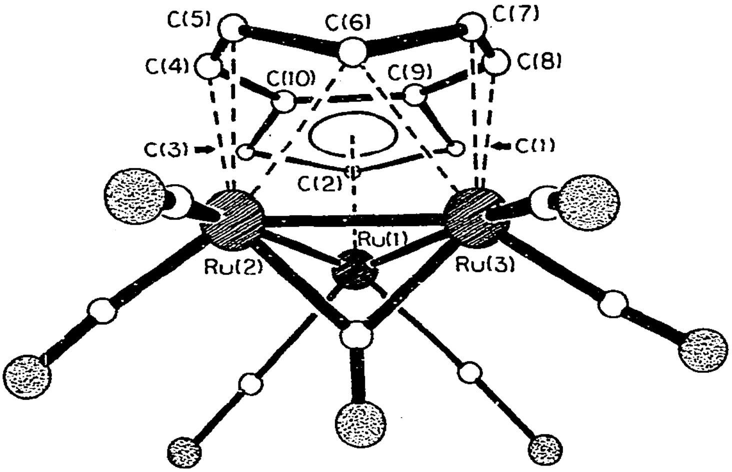

Fig.1. Stereochemistry of $(azulene)Ru_3(CO)_7$.

Average ruthenium–azulene distances are Ru(1)–C(2) = 2.307(22), Ru(1)–C(1)≡Ru(1)–C(3) = 2.231(51), Ru(1)–C(9)≡Ru(1)–C(10) = 2.243(63), Ru(2)–C(4)≡Ru(3)–C(8) = 2.398(40), Ru(2)–C(5)≡Ru(3)–C(7) = 2.279(5), and Ru(2)–C(6)≡Ru(3)–C(6) = 2.472(15) Å. Unlike the case of $(Me_3C_{10}H_5)Ru_4(CO)_9$[2], Ru(2) and Ru(3) are appreciably removed from the five-membered ring, with Ru(2) · · ·C(10)≡Ru(3) · · ·C(9) = 2.925(25) Å. The azulene ligand in $(C_{10}H_8)Ru_3(CO)_7$ [relative to that in $(Me_3C_{10}H_5)Ru_4(CO)_9$] has thus "slipped" along the triangular $Ru_3$ bonding face towards the atom Ru(1).

Within the seven-membered ring, C(6) lies 0.406(21) Å below the C(4)–C(5)–C(7)–C(8) plane, being displaced towards the plane of the ruthenium atoms. The five atoms C(4) to C(8) thus do not define a simple $\pi$-dienyl system as in $(azulene)Mo_2(CO)_6$[4] or $(azulene)Mn_2(CO)_6$[5]. Rather, their behavior is similar to that found in dipentadienyldinickel, which Krüger[6] has explained in terms of two individual metal–olefin bonds and a three center molecular orbital over the M–C–M fragment (M = metal). [Mean carbon–carbon distances within this system in the $(C_{10}H_8)Ru_3(CO)_7$ molecule are C(4)–C(5)≡C(8)–C(7) = 1.371(25), and C(5)–C(6)≡C(7)–C(6) = 1.459(46) Å.]

It should be emphasized, however, that the above description of (azulene)$Ru_3(CO)_7$ results in Ru(1) being assigned a different formal oxidation state to Ru(2) and Ru(3); clearly, as in the case of tetrahedral[2,7,8] and octahedral[9,10] metal clusters, a more sophisticated molecular orbital treatment of the ligand to metal-cluster bonding is required.

The structure of the molecule suggests it as an intermediate in the formation of $(C_{10}H_8)Ru_4(CO)_9$, the reaction proceeding by displacement of the bridging carbonyl in $(C_{10}H_8)Ru_3(CO)_7$ by a $Ru(CO)_3$ (or related) fragment, along with a concomitant rearrangement of metal–metal bonds. Further synthetic work in this area is in progress.

The successive aggregation of metal carbonyl fragments is reminiscent of the cyclododecatriene/$Ru_3(CO)_{12}$ system from which both trinuclear $[C_{12}H_{15}Ru_3(CO)_9H]$[10] and tetranuclear $[C_{12}H_{16}Ru_4(CO)_{10}]$[11] species have been isolated.

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