Triruthenium cluster complexes of C_{70}. Synthesis and structural characterization of $\{Ru_3(CO)_9\}_x(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{70})]$ (x = 1, 2)

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The interaction of C_{70} and $[Ru_3(CO)_{12}]$ provides $[Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{70})]$, in which the Ru_3 triangle is coordinated to only one of the three possible six-membered ring types; analogous double-addition products are isolated and one structurally characterized.

The prolate ellipsoidal fullerene D_{5h}-C_{70} displays a striking variety of structural features, with five types of carbon atoms, eight types of C–C bonds, two types of five-membered rings, and three types of six-membered rings (Scheme 1). Theoretical as well as structural studies of C_{70} are in agreement that bond types 2 and 4 near the poles are the shortest in the molecule, whereas the equatorial belt bonds of type 8 are the longest.[1] Within the six-membered rings, bond distance alternation is marked in type I rings, moderate in type II rings, and non-existent in type III rings; the equatorial type III rings have been characterized as 'aromatic'.[2]

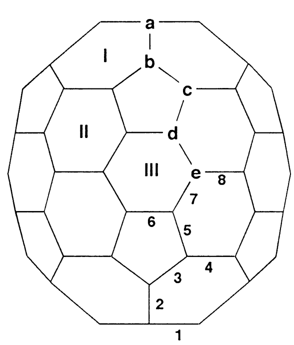
Additions to C_{70} occur primarily at the 'double' bonds of types 2 and 4, with addition at the more pyramidalized bond 2 generally favoured.[3–7] We were interested in the possible ligating characteristics of six-membered ring types I–III toward an arene-complexing fragment, in particular, $Ru_3(CO)_9$.[8] Recently, the coordination of this group to C_{60} has been described.[9] Here we report the preparation and structure of the first hexahapto complex of C_{70}, $[Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{70})]$ **1**, in which the Ru_3 triangle is bonded to a six-membered ring of type I. In addition, we have prepared and separated the expected three isomers of the double substitution product, $[\{Ru_3(CO)_9\}_2C_{70}]$ **2** and have determined the structure of one isomer.

Heating a mixture of C_{70} and $[Ru_3(CO)_{12}]$ in *n*-hexane for several days produces little visible change, since the fullerene is poorly soluble and a precipitate is present throughout. However, extraction of the precipitate with carbon disulfide followed by preparative thin-layer chromatography on silica provides a new compound in addition to recovered C_{70}. Compound **1** was crystallized from carbon disulfide by slow infusion of benzene. The results of a single-crystal X-ray diffraction study of $\mathbf{1}\cdot CS_2$ revealed two inequivalent molecules (A and B) in the unit cell; the structure of molecule A is illustrated in Fig. 1.†

The triruthenium unit is coordinated to one of the type I rings, with one Ru bonded to a type 4 C–C bond and the other two Ru atoms bonded to type 2 C–C bonds. However, each Ru–C_2 interaction shows one longer and one shorter Ru–C distance, which alternate around the ring, consistent with a slight twist of the Ru_3 triangle with respect to the C_6 ring. The Ru–C distances average 2.24, 2.27 Å in A and 2.23, 2.32 Å in B, and the twist angles are 2 and 4° in A and B, respectively. Accompanying the twist between the two attached rings is a threefold twist of each $Ru(CO)_3$ moiety that positions each axial carbonyl at an angle to the axis perpendicular to the Ru_3 plane; these angles average 10° in A and 12° in B. These structural features were also seen in $[Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})]$ **3**[9] as well as in $[Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_6H_6)]$ **4**,[8] and they were attributed to packing forces acting on a relatively flat potential for small angles of rotation around the Ru_3–C_6 axis. The two different sets of structural parameters observed for molecules A and B of **1** provide direct support for this idea. Overall, the local structures for **1** and **3** are closely comparable.

The Ru–Ru bond distances in **1** [2.894(5), 2.918(3), 2.836(3) Å in A and 2.861(4), 2.875(4), 2.869(3) Å in B] are on average slightly longer than those in $[Ru_3(CO)_{12}]$ [2.855(1) Å].[10] Although the e.s.d.s are large, the C–C bond distances of the coordinated six-membered ring seem to show short–long alternation, with averages 1.39, 1.49 Å for A and 1.40, 1.48 Å for B. The average C–C bond lengths for the different types of bond in the unsubstituted halves of the C_{70} ligands in molecules A and B of **1** show the same patterns seen in previous C_{70} structure analyses.[1,6,7]

The coordination of the Ru_3 triangle to a six-membered ring of type I is in conformity with the positions of other single-metal addends as mentioned above. This result suggests that the formation of **1** may be a kinetically controlled reaction, in which coordination of the first metal atom at a type 2 bond determines



Scheme 1

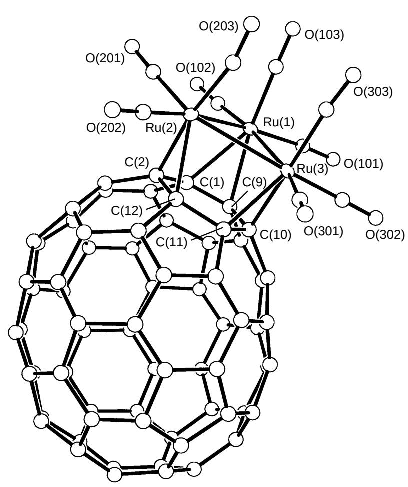
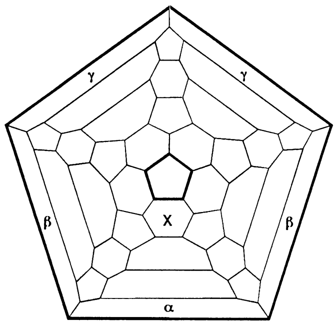


Fig. 1 A perspective view of **1** (molecule A), showing part of the atom labelling scheme. Selected bond lengths (Å): Ru(1)–Ru(2) 2.894(5), Ru(2)–Ru(3) 2.918(3), Ru(1)–Ru(3) 2.836(3), Ru(1)–C(1) 2.33(2), Ru(1)–C(9) 2.25(2), Ru(2)–C(2) 2.21(2), Ru(2)–C(12) 2.26(2), Ru(3)–C(10) 2.24(2), Ru(3)–C(11) 2.27(2), C(1)–C(2) 1.48(3), C(1)–C(9) 1.37(3), C(2)–C(12) 1.45(3), C(9)–C(10) 1.51(3), C(10)–C(11) 1.36(3), C(11)–C(12) 1.48(3).

the coordination sites of the remaining two metal atoms. On the other hand, these sites are already the most pyramidal in the molecule, and they require relatively little further distortion to coordinate favourably to the Ru_3 framework, by comparison of bond angles at coordinated *vs.* uncoordinated carbons. In contrast the type III rings, which have been characterized as aromatic on the basis of their essentially equivalent C–C distances, are actually slightly concave (carbons e,e are *ca.* 0.1 Å below the plane of the four d carbons[7]), so that coordination of one of these rings to a metal triangle would involve considerable distortion of the C_{70} framework. However, since good evidence for the addition of radical moieties in the equatorial region has been presented,[11] the possible coordination of ring types II and III with more reactive reagents or in the formation of higher addition products remains to be explored.



Scheme 2

The addition of a second Ru_3 unit to the C_{70} ligand in **1** could result in three disubstituted isomers, as shown in Scheme 2, assuming the second unit is added to the same type of six-membered ring in the opposite polar region. Indeed, increasing the ratio of $[Ru_3(CO)_{12}]$ to C_{70} under the same reaction conditions produces three new products, **2α**, **2β**, and **2γ**, which can be separated by preparative thin-layer chromatography (CS_2/SiO_2). The new compounds **2α**, **2β**, and **2γ** (isolated ratio 2 : 3 : 1) are formulated as disubstituted derivatives $C_{70}[Ru_3(CO)_9]_2$ on the basis of molecular ion multiplets seen by FABMS spectroscopy. All three isomers have two IR (ν_{CO}) bands at 2074 and 2046 cm^{-1}, and the only difference among them is the position of the third peak at 2010, 2013 and 2012 cm^{-1} for **2α**, **2β**, and **2γ**, respectively. These IR spectra are almost identical to that of **1**, which suggests the same bonding mode is adopted for both Ru_3 units as in **1**. Single crystals of isomer **2β** suitable for X-ray diffraction study were obtained from carbon disulfide by slow diffusion of methanol; a structural diagram of **2β** is shown in Fig. 2.‡ The two Ru_3 units are each bonded to type I six-membered rings in a fashion analogous to **1**, and their relative positions conform to the idealized C_2 symmetry of isomer **2β**. Attempts to characterize the structures of the other two double addition products, presumably C_{2v}-**2α** and C_2-**2γ**, are underway.

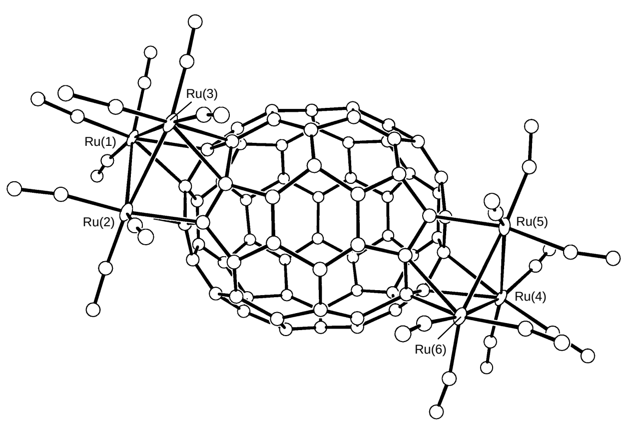


Fig. 2 A perspective view of **2β**, showing part of the atom labelling scheme. Selected bond lengths (Å): Ru(1)–Ru(2) 2.911(3), Ru(2)–Ru(3) 2.889(3), Ru(1)–Ru(3) 2.855(3), Ru(4)–Ru(5) 2.877(3), Ru(5)–Ru(6) 2.878(3), Ru(6)–Ru(4) 2.866(3).

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Footnotes

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† *Crystallographic data*: for **1**·CS_2: orthorhombic, space group $Pna2_1$, a = 18.9367(8), b = 49.491(2), c = 10.0460(4), U = 9415.1(6) Å^3, Z = 8; crystal size 0.05 × 0.09 × 0.46 mm. Diffraction data were collected at 198 K on a Siemens Platform/ CCD automated diffractometer. A total of 33 910 reflections were corrected for absorption [empirical; μ(Mo-Kα) = 1.122 mm^{-1}; max., min. transmission factor = 0.922, 0.824] and used for structure solution and refinement (SHELXTL, Siemens). The ruthenium triangles in both molecules (A and B) were disordered. Primary site occupancy for Ru(1,2,3) converged at 0.878(5) and for Ru(4,5,6) at 0.883(2). Anisotropic displacement parameters for disordered pairs of ruthenium atoms were constrained to equivalent values. Full-matrix least-squares refinement on F^2 of 892 parameters against 8383 independent reflections gave final agreement factors of R_1 = 0.0858 (against $|F|$) and wR_2 = 0.1650 [against $|F^2|$ for 6041 data with $I > 2\sigma(I)$].

For **2β**·1.5CS_2: triclinic, space group $P\bar{1}$, a = 10.2197(4), b = 17.0637(5), c = 19.3880(8) Å, α = 99.2130(10)°, β = 98.6960(10)°, γ = 105.9410(10)°, U = 3140.5(2) Å^3, Z = 2; crystal size 0.26 × 0.11 × 0.04 mm. Diffraction data were collected at 198 K on a Siemens Platform/ CCD automated diffractometer. Intensities from the major component (75%) of this twinned crystal that suffered from overlap with intensities from the minor component were omitted. A total of 6468 reflections were corrected for absorption [empirical; μ(Mo-Kα) = 1.595 mm^{-1}; max., min. transmission factor = 0.985, 0.749] and used for structure solution and refinement (SHELXTL, Siemens). Full-matrix least-squares refinement on F^2 of 511 parameters against 4374 independent reflections gave final agreement factors of R_1 = 0.0850 (against $|F|$) and wR_2 = 0.1746 [against $|F^2|$, for 2985 data with $I > 2\sigma(I)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/470.

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