

Ru₃(CO)₉(μ₃-η²,η²,η²-C₆₀): A Cluster Face-Capping, Arene-Like Complex of C₆₀

Hsiu-Fu Hsu and John R. Shapley*

Department of Chemistry and the Frederick Seitz
Materials Research Laboratory
University of Illinois, Urbana, Illinois 61801

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The macroscopic synthesis of C₆₀¹ made it possible to envision developing the organometallic chemistry of C₆₀ as a ligand. Initial approaches to forming metal complexes were based on the view dating to the initial report² on C₆₀ that the molecule was highly aromatic. However, well-known arene-coordinating reagents failed to form the expected hexahapto derivatives, and these notions were swept aside by the synthesis and structure determination of Pt(PPh₃)₂(η²-C₆₀), in which the C₆₀ ligand is coordinated as a dihaptoalkene.³ Subsequent metal π-complex chemistry⁴ as well as related developments in derivative chemistry involving both metal-containing⁵ and purely organic⁶ reagents have reinforced the idea that C₆₀ reacts primarily as a moderately electronegative alkene. Nevertheless, diene-like behavior has been observed occasionally for C₆₀, as in examples of 1,4- instead of 1,2-placement of σ-bonded addends⁷ and in reports of tetrahapto coordination of adjacent π-bonds to two connected metal centers.⁸ The failure to form stable M(η⁶-C₆₀) compounds has been attributed to the curvature of C₆₀,³ which orients each exohedral p-π-orbital at an angle (ca. 10°)⁹ away from the perpendicular to the face of the six-membered ring; both calculations¹⁰ and experiment¹¹ indicate

that C₆₀ is a weaker ligand than benzene toward a single metal. However, benzene and related arenes can also bond to triangular faces of metal clusters,^{12,13} and geometric considerations suggest that a metal triangle should provide for effective overlap with the C₆₀ p-π-orbitals. We report the synthesis and first structural characterization of a hexahapto C₆₀ complex,¹⁴ in which C₆₀ displays arene-like coordination to the open face of a triruthenium cluster.

A mixture of C₆₀ (1 equiv) and Ru₃(CO)₁₂ (2 equiv) was heated in *n*-hexane under reflux for 2 days. The black precipitate present during this time changed little in appearance, but after separation of the orange Ru₃(CO)₁₂-containing supernatant, the remaining black residue was only partially soluble when extracted with carbon disulfide. The components of the extract were separated by thin layer chromatography (SiO₂/CS₂), which provided a large purple band of C₆₀ (44% recovered) and a small red band of a new compound (4% yield based on unrecovered C₆₀). The latter compound was formulated as Ru₃(CO)₉(C₆₀) (**1**) on the basis of a molecular ion multiplet at *m/z* 1278 in a FAB mass spectrum together with its IR (ν_{CO}) spectrum (2078 (s), 2045 (vs), 2012 (m), 1985 (w, sh) cm⁻¹ in CS₂), which is similar in pattern to that reported for Ru₃(CO)₉(μ₃-η²,η²,η²-C₆H₆) (**2**) (2071 (m), 2027 (vs), 1996 (s), 1976 (sh) cm⁻¹ in CH₂Cl₂).^{15a} Red crystals were obtained by diffusion of methanol at room temperature into a solution of **1** in carbon disulfide, and the structure of **1** has been established by a single-crystal X-ray diffraction study at 195 K.¹⁶

Figure 1 shows a perspective view of the molecular structure, and the caption summarizes important internuclear distances in the molecule. The Ru₃ triangle is positioned centrally over a ring of six carbons in the fullerene framework; the two planes are essentially parallel (angle 0.9°). One Ru–Ru bond is slightly longer (0.02 Å) than the other two Ru–Ru bonds; the average distance for the Ru₃ triangle (2.88(1) Å) is longer than that for Ru₃(CO)₁₂ (2.855(1) Å).¹⁷ The carbon–carbon bonds in the six-membered ring appear to alternate in length, but the difference between the average “short” distance of 1.427(19) Å and the average “long” distance of 1.466(15) Å is on the margin of statistical significance.¹⁸ The Ru atoms are positioned over the short C–C bonds, and the Ru–C distances also show a short–long pattern at each metal center; the average short

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(16) (a) Crystallographic data for **1**·CS₂: monoclinic, space group C2/c, *a* = 17.0389(3) Å, *b* = 9.98870(10) Å, *c* = 51.1596(7) Å, β = 91.352(1)°, *V* = 8704.8(2) Å³, *Z* = 8; crystal size 0.01 × 0.52 × 0.60 mm³. (b) Diffraction data were collected at 198 K on a Siemens Platform/CCD automated diffractometer. A total of 22 896 reflections were corrected for absorption (μ (Mo Kα) = 1.202 mm⁻¹; max/min transmission factor = 0.0742/0.0370) and used for structure solution and refinement (SHELXTL, Siemens). Full-matrix least-squares refinement on *F*² of 767 parameters against 7608 independent reflections gave final agreement factors of *R*₁ = 0.076 and *wR*₂ = 0.145 (for 5784 data with *I* > 2σ(*I*)).

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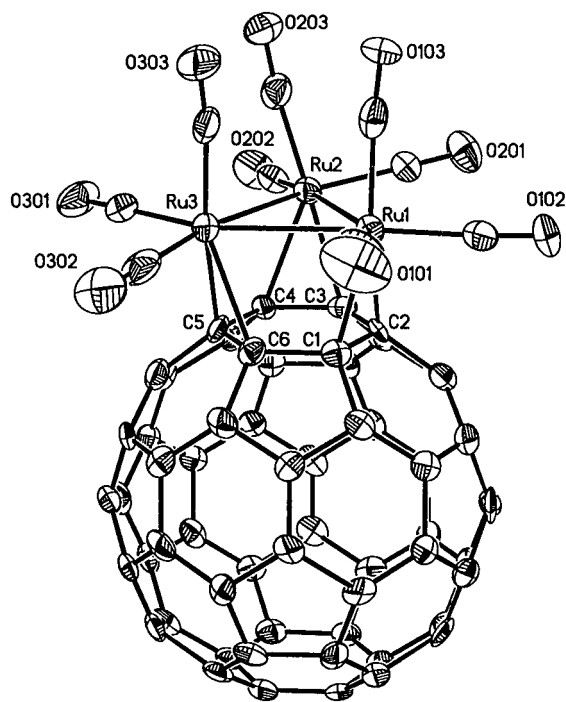


Figure 1. An ORTEP diagram of the molecular structure of compound **1**. Selected bond distances (Å): Ru(1)–Ru(2) = 2.8737(13), Ru(2)–Ru(3) = 2.8988(12), Ru(3)–Ru(1) = 2.8790(12); Ru(1)–C(1) = 2.245(9), Ru(1)–C(2) = 2.324(9), Ru(2)–C(3) = 2.228(9), Ru(2)–C(4) = 2.301(9), Ru(3)–C(5) = 2.213(9), Ru(3)–C(6) = 2.296(9), C(1)–C(2) = 1.417(13), C(2)–C(3) = 1.456(13), C(3)–C(4) = 1.447(13), C(4)–C(5) = 1.469(13), C(5)–C(6) = 1.416(13), C(6)–C(1) = 1.473(14).

distance is 2.229(16) Å, and the average long distance is 2.307(15) Å. This pattern of Ru–C distances reflects a slight twist (ca. 4°) about the idealized 3-fold axis linking the Ru₃ triangle and the C₆ ring. At the same time, the Ru(CO)₃ groups at each Ru center are slightly twisted, each in the same sense, such that each axial carbonyl is bent away from the 3-fold axis and each pair of equatorial carbonyls is positioned one above and one below their common plane.

The structural features seen for **1** are closely comparable to those reported for the benzene complex **2**, especially the metrics of the low-temperature study at 193 K.^{15b} The C–C distances alternate in **2**, reported as averaging 1.41(1) and 1.45(1) Å for the short and long bonds, respectively. Thus, Δ(C–C) is essentially the same (0.04 Å) for both complexes. The Ru–C distances in **2** also alternate, with the averages listed as 2.303(5) and 2.361(5) Å. Again, the values of Δ(Ru–C) = 0.08 Å for **1** and 0.06 Å for **2** are very similar, but the average for the entire set of Ru–C distances is ca. 0.06 Å shorter for **1** than for **2**. For compound **2**, the alternating pattern of Ru–C

distances is also related to a twist (by ca. 4.5°) of the C₆ ring relative to the Ru₃ triangle. The origin of this twist in **2**, which is not observed for the Os₃ analog **3**,¹⁹ has been attributed primarily to intermolecular packing interactions dominating an inherently low intramolecular barrier (<5 kcal/mol).^{15b} The remarkable congruence of the twist deformations in the structures of **1** and **2** raises a question about the balance between the responsible intermolecular and intramolecular forces (potential energy calculations on **2** showed ring carbon–equatorial carbonyl repulsions^{15b}) and also suggests a relatively low barrier for rotation of C₆₀ against the Ru₃ framework.

The bonding of C₆₀ to a single transition metal center has been analyzed in terms of the familiar Dewar–Chatt–Duncanson donation/back-donation model, with a “double bond” donor orbital largely generated from the HOMO (h_u) and the corresponding acceptor orbital formed from the LUMO (t_{1u}).²⁰ Because of the relatively low energies of the C₆₀ orbitals (high electron affinity), there is strong charge transfer (back-donation) from the metal center to coordinated C₆₀, consistent with experimental data on stable compounds.^{3,4} A qualitatively similar bonding model, in terms of donor/acceptor interactions of C₆₀ with the Ru₃(CO)₉ fragment, is likely for **1**; theoretical studies of the bonding in the benzene complexes **2** and **3** provide analogies.^{15b,19,21} However, the relative contribution of back-donation to bonding with the metal triangle should be higher for C₆₀ than for benzene, which is consistent with both the higher ν_{CO} values and the shorter Ru–C distances seen for **1** compared with those of **2**.

Further investigation of properties related to the unique structure of **1** is underway.

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Supporting Information Available: Tables of the details of crystallographic data collection and atomic coordinates for **1** (3 pages). See any current masthead page for ordering and Internet access instructions.

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