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Coordination of C₆₀ to Penta- and Hexaruthenium Cluster Frames

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Summary: In refluxing chlorobenzene C₆₀ reacts with Ru₅C(CO)₁₅ or with Ru₆C(CO)₁₇ to form new complexes, which are isolated following treatment with tertiary phosphines to give the structurally characterized, face-bonded derivatives Ru₅C(CO)₁₁(PPh₃)(μ₃-η²:η²:η²-C₆₀) (**1**) and Ru₆C(CO)₁₂(dppm)(μ₃-η²:η²:η²-C₆₀) (**2**).

Benzene binds to the face of the Ru₃ triangle in Ru₃(CO)₉(μ₃-η²:η²:η²-C₆H₆),¹ but both terminal and face-bonded isomers are known for benzene coordination to Ru₅C² and Ru₆C³ frameworks. Recently, we demonstrated the first example of C₆₀ binding to a cluster face in Ru₃(CO)₉(μ₃-η²:η²:η²-C₆₀),⁴ and the structural features of this C₆₀ complex are remarkably similar to those in the corresponding benzene complex.¹ In view of this comparison we were attracted to examine the prospects of C₆₀ as a ligand toward the larger ruthenium cluster frameworks. We now report the synthesis and characterization of new, robust fullerene cluster complexes prepared by the direct interaction of C₆₀ with either Ru₅C(CO)₁₅ or Ru₆C(CO)₁₇ followed by carbonyl ligand substitution with a tertiary phosphine or diphosphine to give the stable derivatives Ru₅C(CO)₁₁(PPh₃)(μ₃-η²:η²:η²-C₆₀) (**1**) and Ru₆C(CO)₁₂(dppm)(μ₃-η²:η²:η²-C₆₀) (**2**).

When a mixture of Ru₅C(CO)₁₅ and C₆₀ in chlorobenzene was heated to reflux, the color changed over 1 h from red-purple to dark brown, and a new set of peaks developed in the IR (ν_{CO}) spectrum. Subsequent separation by TLC (silica gel, CS₂) gave a purple band of unreacted C₆₀ and a major brown band that exhibited IR peaks at 2087 (s), 2060 (m), 2038 (m), and 2024 (vs) cm⁻¹. This pattern is consistent with the presence of Ru₅C(CO)₁₂(C₆₀),² but the brown material was extremely insoluble after solvent removal, despite its mobility on the TLC plate. To overcome this solubility problem, substitution of the brown intermediate by PPh₃ was effected in situ by treating the Ru₅C(CO)₁₅/C₆₀ reaction mixture with PPh₃ (1 equiv) at reflux for 5 min. TLC separation and crystallization from CS₂ afforded compound **1** (26%), which was formulated as Ru₅C(CO)₁₁(PPh₃)(C₆₀) on the basis of microanalytical, mass spectrometric, and NMR spectroscopic data.⁵

A single-crystal X-ray study has defined the structure of **1**,⁶ and a diagram is shown in Figure 1. The metal framework is a square pyramid, and the C₆₀ ligand is bound on one triangular face as a μ₃-η²:η²:η² ligand. All carbonyl ligands are terminal, and the phosphine ligand is positioned in an axial position on one of the basal ruthenium atoms not bonded to the C₆₀ ligand. The Ru–Ru bonds in **1** associated with the C₆ ring of the C₆₀ ligand are slightly elongated (ca. 0.02 Å) from those of the benzene adduct Ru₅C(CO)₁₂(μ₃-η²:η²:η²-C₆H₆).² The Ru–C_{carbide} distances are all similar to those of both Ru₅C(CO)₁₂(μ₃-η²:η²:η²-C₆H₆)² and Ru₅C(CO)₁₄(PPh₃).⁷ The carbon–carbon distances in the C₆ ring of C₆₀ bound to the metal framework in **1** alternate in length (average 1.44 and 1.48 Å, respectively). The Ru–C interactions in **1** also alternate in length (average 2.23 and 2.27 Å, respectively), resulting in a slight twist of the Ru₃ triangle with respect to the C₆ ring. Analogous bond length alternations in the benzene ring (average 1.36 and 1.44 Å, respectively) and in the Ru–C distances (average 2.23 and 2.29 Å, respectively) were determined for the face-capped benzene complex Ru₅C(CO)₁₂(μ₃-η²:η²:η²-C₆H₆).²

Compound **1** can also be prepared from the direct interaction of C₆₀ and Ru₅C(CO)₁₄(PPh₃) in refluxing chlorobenzene.⁷ The ³¹P NMR spectrum of **1** in solution is a singlet, indicating a high structural specificity for the C₆₀–Ru₅C cluster interaction. The phosphine ligand Ru₅C(CO)₁₄(PPh₃) adopts an axial position on one of the basal ruthenium atoms⁸ (as in **1**), so that at least two reaction sites, the apical ruthenium and the basal ruthenium positioned trans to the PPh₃-substituted ruthenium, are available for possible η⁶-C₆₀ coordination. However, no Ru₅C compound with a terminally bound C₆₀ was observed.

(5) From the reaction of Ru₅C(CO)₁₅ (40.0 mg, 0.0427 mmol) and C₆₀ (33.8 mg, 0.0469 mmol) in 30 mL of chlorobenzene followed by addition of PPh₃ (12.3 mg, 0.0469 mmol) were obtained unreacted C₆₀ (10.1 mg, 0.0140 mmol, 33% recovery) and **1** (14.7 mg, 0.0081 mmol, 26% based on C₆₀ reacted) after TLC separation. No other significant product was observed. Anal. Calcd for C₆₀H₁₅O₁₁PRu₅: C, 59.78; H, 0.84. Found: C, 59.93; H, 0.63. Negative-ion FAB mass spectrum (¹⁰²Ru): *m/z* 1812 (Ru₅C(CO)₁₁(PPh₃)(C₆₀)), 1784 (Ru₅C(CO)₁₁(PPh₃)(C₆₀)-CO). IR (CS₂): ν_{CO} 2068 (s), 2031 (s), 2021 (s), 2013 (s) cm⁻¹. ¹H NMR (400 MHz, 1:2 CS₂/CD₂Cl₂, 20 °C): δ 7.70–7.55 (m, 15H). ³¹P NMR (162 MHz, 1:2 CS₂/CD₂Cl₂, 20 °C): δ 47.3 (s).

(6) (a) Crystallographic data for **1**·1.5CS₂: triclinic, space group *P* $\bar{1}$, *a* = 10.0091(1) Å, *b* = 13.3885(2) Å, *c* = 26.9508(3) Å, α = 77.552(1)°, β = 80.590(1)°, γ = 70.210(1)°, *V* = 3302.26(7) Å³, *Z* = 2; crystal size 0.06 × 0.30 × 0.82 mm³. (b) Diffraction data were collected at 198(2) K on a Siemens SMART/CCD diffractometer. A total of 12 621 reflections were corrected for absorption (*μ*(Mo Kα) = 1.310 mm⁻¹; max/min transmission factor 0.9953/0.7000) and used for structure solution and refinement (SHELXTL, Siemens). Full-matrix least-squares refinement on *F*² of 1006 parameters against 8406 independent reflections gave final agreement factors of *R*1 = 6.95% and *wR*2 = 17.06% (*I* > 2σ(*I*)).

(7) Separation by TLC (silica gel, CS₂) gave C₆₀ (18% recovery), **1** (21%), and Ru₅C(CO)₁₄(PPh₃) (17% recovery) in order of elution.

(8) Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Puga, J.; Raithby, P. R.; Rosales, M. J.; McMartin, M.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 277.

[®] Abstract published in *Advance ACS Abstracts*, August 15, 1997.

(1) (a) Johnson, B. F. G.; Lewis, J.; Martinelli, M.; Wright, A. H.; Braga, D.; Grepioni, F. *J. Chem. Soc., Chem. Commun.* **1990**, 364. (b) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Lewis, J.; Housecroft, C. E.; Martinelli, M. *Organometallics* **1991**, 10, 1260.

(2) (a) Bailey, P. J.; Braga, D.; Dyson, P. J.; Grepioni, F.; Johnson, B. F. G.; Lewis, J.; Sabatino, P. *J. Chem. Soc., Chem. Commun.* **1992**, 177. (b) Braga, D.; Grepioni, F.; Sabatino, P.; Dyson, P. J.; Johnson, B. F. G.; Lewis, J.; Bailey, P. J.; Raithby, P. R.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1993**, 985.

(3) (a) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2606. (b) Gomez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wright, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1682. (c) Adams, R. D.; Wu, W. *Polyhedron* **1992**, 2123. (d) Dyson, P. J.; Johnson, B. F. G.; Lewis, J.; Martinelli, M.; Braga, D.; Grepioni, F. *J. Am. Chem. Soc.* **1993**, 115, 9062.

(4) Hsu, H.-F.; Shapley, J. R. *J. Am. Chem. Soc.* **1996**, 118, 9192.

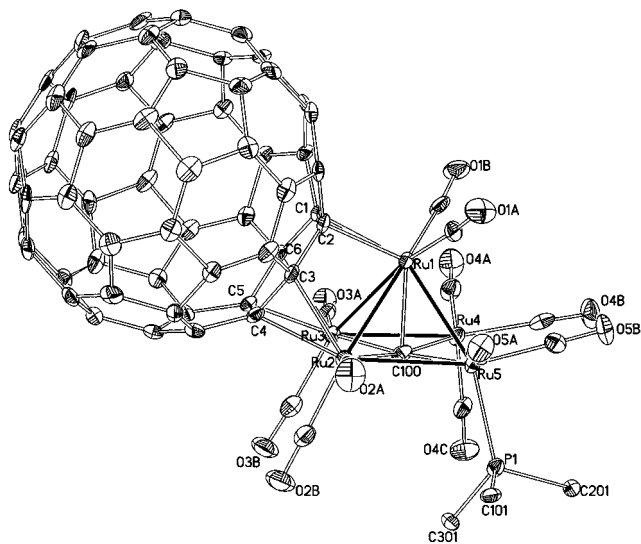


Figure 1. ORTEP diagram of **1** (35% thermal ellipsoids). Only ipso carbons (C101, C201, and C301) of the phenyl groups are shown. The darker lines denote the Ru–Ru bonds. Selected bond distances (Å): Ru1–Ru2 = 2.855(1); Ru1–Ru3 = 2.851(1); Ru1–Ru4 = 2.828(1); Ru1–Ru5 = 2.876(1); Ru2–Ru3 = 2.865(1); Ru2–Ru5 = 2.885(1); Ru3–Ru4 = 2.837(1); Ru4–Ru5 = 2.882(1); Ru1–C100 = 2.13(1); Ru2–C100 = 2.04(1); Ru3–C100 = 2.04(1); Ru4–C100 = 2.03(1); Ru5–C100 = 2.02(1); Ru1–C1 = 2.29(1); Ru1–C2 = 2.26(1); Ru2–C3 = 2.26(1); Ru2–C4 = 2.22(1); Ru3–C5 = 2.25(1); Ru3–C6 = 2.21(1); C1–C2 = 1.42(2); C2–C3 = 1.47(2); C3–C4 = 1.44(2); C4–C5 = 1.48(2); C5–C6 = 1.46(2); C6–C1 = 1.48(2).

Compound **2** was formed by heating a mixture of C₆₀ and Ru₆C(CO)₁₇ in chlorobenzene under reflux for 5 h followed by treatment with dpmm for 10 min.⁹ The compound was isolated following TLC separation and formulated as Ru₆C(CO)₁₂(dpmm)(C₆₀) on the basis of a molecular ion in the positive-ion FAB mass spectrum. Crystals of **2** suitable for an X-ray diffraction study¹⁰ were prepared by diffusion of benzene into a carbon disulfide solution.

Figure 2 shows a perspective view of the molecular structure of **2**. The metal framework remains a carbon-centered octahedron, and one of the triangular faces (Ru1, Ru2, Ru3) is bonded to a ring of six carbon atoms of C₆₀. The dpmm ligand bridges two of the remaining three ruthenium atoms (Ru4, Ru5), and carbonyl ligands bridge two Ru–Ru edges (Ru1–Ru4 and Ru4–Ru6). In

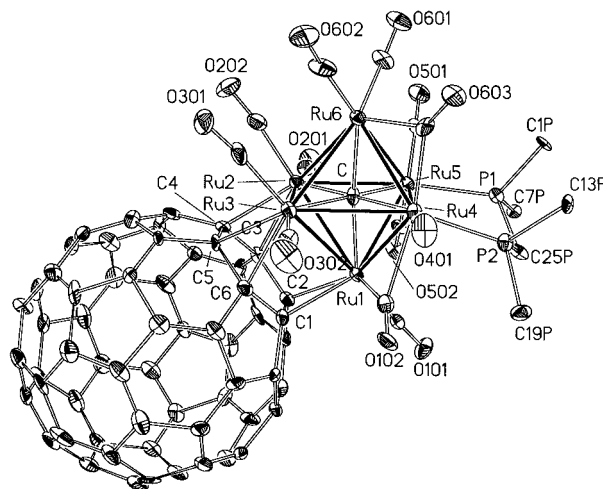


Figure 2. ORTEP diagram of **2** (35% thermal ellipsoids). Only ipso carbons (C1P, C7P, C13P, and C19P) of the phenyl groups are shown. The darker lines denote the Ru–Ru bonds. Selected bond distances (Å): Ru1–Ru2 = 2.976(2); Ru1–Ru3 = 2.877(2); Ru1–Ru4 = 2.808(2); Ru1–Ru5 = 2.872(2); Ru2–Ru3 = 2.816(2); Ru2–Ru5 = 2.828(2); Ru2–Ru6 = 3.001(2); Ru3–Ru4 = 2.996(2); Ru3–Ru6 = 2.900(2); Ru4–Ru5 = 3.040(2); Ru4–Ru6 = 2.803(2); Ru5–Ru6 = 2.940(2); Ru1–C = 2.04(2); Ru2–C = 2.05(1); Ru3–C = 2.05(2); Ru4–C = 2.09(1); Ru5–C = 2.07(2); Ru6–C = 2.02(2); Ru1–C1 = 2.16(1); Ru1–C2 = 2.20(1); Ru2–C3 = 2.25(1); Ru2–C4 = 2.22(1); Ru3–C5 = 2.25(1); Ru3–C6 = 2.27(1); C1–C2 = 1.48(2); C2–C3 = 1.47(2); C3–C4 = 1.44(2); C4–C5 = 1.46(2); C5–C6 = 1.44(2); C6–C1 = 1.49(2).

2, no systematic alternation in either the Ru–C distances or the C–C distances of the ligated C₆ ring is observed, although both of these features may be affected by the unsymmetrical distribution of ligands on the remainder of the cluster framework. The former result contrasts with the structures of similar Ru₆C–arene complexes, including Ru₆C(CO)₁₄(μ₃-η²: η²-C₁₆H₁₆),¹¹ for which distinct alternation in Ru–C distances is common.³

In summary, we have demonstrated that compounds **1** and **2** with coordination of C₆₀ to a triangular face of the square-pyramidal Ru₅C and octahedral Ru₆C frameworks can be prepared by the interaction of C₆₀ with Ru₅C(CO)₁₅ or Ru₆C(CO)₁₇ followed by a substituting ligand. The fact that the proposed intermediates Ru_nC(CO)_x(C₆₀) can undergo substitution reactions by PPh₃ or CH₂(PPh₂)₂ under severe conditions reveals the robust nature of the C₆₀–Ru_nC cluster interaction. Structural specificity for this interaction is indicated also by the observation that compound **1** can be prepared directly from C₆₀ and Ru₅C(CO)₁₄(PPh₃).

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Supporting Information Available: Tables of positional parameters and isotropic thermal parameters for the crystal structure analyses of **1** and **2** (8 pages). Ordering information is given on any current masthead page.

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(9) A chlorobenzene solution (20 mL) of C₆₀ (25.0 mg, 0.0347 mmol) and Ru₆C(CO)₁₇ (50.0 mg, 0.0457 mmol) was heated under reflux for 5.5 h. The solution was cooled, 1,2-bis(diphenylphosphino)methane (dpmm; 18.0 mg, 0.0468 mmol) was added, and the solution was again heated under reflux for 10 min. The reaction solvent was removed under vacuum, and the dark CS₂-soluble residue separated by TLC (silica gel, CS₂) to give unreacted C₆₀ (2.0 mg, 0.0028 mmol, 8% recovery), **2** (7.0 mg, 0.0034 mmol, 11% based on C₆₀), and Ru₆C(CO)₁₅-(dpmm) (25.0 mg, 0.0176 mmol, 39%). Data for **2** are as follows: FAB⁺ mass spectrum (¹⁰²Ru): *m/z* 2064 ([Ru₆C(CO)₁₂(dpmm)(C₆₀)⁺]). IR (CS₂): ν_{CO} 2045 (m), 2023 (s), 2010 (m), 1998 (m), 1987 (m), 1966 (w), 1951 (sh, w), 1804 (w, br) cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂, 20 °C): δ 7.42 (24H, m, Ph), 5.15 (1H, q, J_{HH} = 12 Hz, J_{HP} = 12 Hz, CH₂), 4.59 (1H, q, J_{HH} = 12 Hz, J_{HP} = 12 Hz, CH₂). ³¹P{¹H} NMR (162 MHz, CDCl₃, 20 °C): δ 30.92.

(10) (a) Crystallographic data for **2**·3CS₂: triclinic, space group *P* $\bar{1}$, *a* = 14.626(3) Å, *b* = 14.747(3) Å, *c* = 19.227(4) Å, α = 95.99(3)°, β = 92.09(3)°, γ = 113.18(3)°, *V* = 3777.9(13) Å³, *Z* = 2; crystal size 0.6 × 0.04 × 0.02 mm³. (b) Diffraction data were collected at 293(2) K on a Siemens SMART/CCD diffractometer. A total of 18 483 reflections were corrected for absorption (μ(Mo Kα) = 1.451 mm⁻¹; max/min transmission factor 0.9573/0.7651) and used for structure solution and refinement (SHELXTL, Siemens). Full-matrix least-squares refinement on *F*² of 1124 parameters against 11 314 independent reflections gave final agreement factors of *R*₁ = 8.51% and *wR*₂ = 15.09% (*I* > 2σ(*I*)).

(11) Braga, D.; Grepioni, F.; Parisini, E.; Dyson, P. J.; Blake, A. J.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1993**, 2951.