Coordination of C_{60} to Penta- and Hexaruthenium Cluster Frames

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*Summary: In refluxing chlorobenzene C_{60} reacts with $Ru_5C(CO)_{15}$ or with $Ru_6C(CO)_{17}$ to form new complexes, which are isolated following treatment with tertiary phosphines to give the structurally characterized, face-bonded derivatives $Ru_5C(CO)_{11}(PPh_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**1**) and $Ru_6C(CO)_{12}(dppm)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**2**).*

Benzene binds to the face of the Ru_3 triangle in $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$,[1] but both terminal and face-bonded isomers are known for benzene coordination to Ru_5C[2] and Ru_6C[3] frameworks. Recently, we demonstrated the first example of C_{60} binding to a cluster face in $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$,[4] and the structural features of this C_{60} 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 C_{60} 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 C_{60} with either $Ru_5C(CO)_{15}$ or $Ru_6C(CO)_{17}$ followed by carbonyl ligand substitution with a tertiary phosphine or diphosphine to give the stable derivatives $Ru_5C(CO)_{11}(PPh_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**1**) and $Ru_6C(CO)_{12}(dppm)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**2**).

When a mixture of $Ru_5C(CO)_{15}$ and C_{60} 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, CS_2) gave a purple band of unreacted C_{60} 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 $Ru_5C(CO)_{12}(C_{60})$,[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 PPh_3 was effected in situ by treating the $Ru_5C(CO)_{15}/C_{60}$ reaction mixture with PPh_3 (1 equiv) at reflux for 5 min. TLC separation and crystallization from CS_2 afforded compound **1** (26%), which was formulated as $Ru_5C(CO)_{11}(PPh_3)(C_{60})$ 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 C_{60} ligand is bound on one triangular face as a $\mu_3\text{-}\eta^2{:}\ \eta^2{:}\ \eta^2$ 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 C_{60} ligand. The Ru−Ru bonds in **1** associated with the C_6 ring of the C_{60} ligand are slightly elongated (ca. 0.02 Å) from those of the benzene adduct $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\ \eta^2{:}\ \eta^2\text{-}C_6H_6)$.[2] The $Ru-C_{carbide}$ distances are all similar to those of both $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\ \eta^2{:}\ \eta^2\text{-}C_6H_6)$[2] and $Ru_5C(CO)_{14}(PPh_3)$.[7] The carbon−carbon distances in the C_6 ring of C_{60} 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 Ru_3 triangle with respect to the C_6 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 $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\ \eta^2{:}\ \eta^{2-}C_6H_6)$.[2]

Compound **1** can also be prepared from the direct interaction of C_{60} and $Ru_5C(CO)_{14}(PPh_3)$ in refluxing chlorobenzene.[7] The ^{31}P NMR spectrum of **1** in solution is a singlet, indicating a high structural specificity for the $C_{60}-Ru_5C$ cluster interaction. The phosphine ligand $Ru_5C(CO)_{14}(PPh_3)$ adopts an axial position on one of the basal ruthenium atoms[8] (as in **1**), so that at least two reaction sites, the apical ruthenium and the basal ruthenium positioned trans to the PPh_3-substituted ruthenium, are available for possible $\eta^6\text{-}C_{60}$ coordination. However, no Ru_5C compound with a terminally bound C_{60} was observed.

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(5) From the reaction of $Ru_5C(CO)_{15}$ (40.0 mg, 0.0427 mmol) and C_{60} (33.8 mg, 0.0469 mmol) in 30 mL of chlorobenzene followed by addition of PPh_3 (12.3 mg, 0.0469 mmol) were obtained unreacted C_{60} (10.1 mg, 0.0140 mmol, 33% recovery) and **1** (14.7 mg, 0.0081 mmol, 26% based on C_{60} reacted) after TLC separation. No other significant product was observed. Anal. Calcd for $C_{90}H_{15}O_{11}PRu_5$: C, 59.78; H, 0.84. Found: C, 59.93; H, 0.63. Negative-ion FAB mass spectrum (^{102}Ru): *m/z* 1812 ($Ru_5C(CO)_{11}(PPh_3)(C_{60})$), 1784 ($Ru_5C(CO)_{11}(PPh_3)(C_{60})-CO$). IR ($CS_2$): ν_{CO} 2068 (s), 2031 (s), 2021 (s), 2013 (s) cm^{-1}. ^1H NMR (400 MHz, 1:2 CS_2/CD_2Cl_2, 20 °C): δ 7.70−7.55 (m, 15H). ^{31}P NMR (162 MHz, 1:2 CS_2/CD_2Cl_2, 20 °C): δ 47.3 (s).

(6) (a) Crystallographic data for $\mathbf{1}\cdot 1.5CS_2$: triclinic, space group $P\bar{1}$, $a = 10.0091(1)$ Å, $b = 13.3885(2)$ Å , $c = 26.9508(3)$ Å, $\alpha = 77.552(1)°$, $\beta = 80.590(1)°$, $\gamma = 70.210(1)°$, $V = 3302.26(7)$ Å^3, $Z = 2$; crystal size $0.06 \times 0.30 \times 0.82$ mm^3. (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 R1 = 6.95% and wR2 = 17.06% ($I > 2\sigma(I)$).

(7) Separation by TLC (silica gel, CS_2) gave C_{60} (18% recovery), **1** (21%), and $Ru_5C(CO)_{14}(PPh_3)$ (17% recovery) in order of elution.

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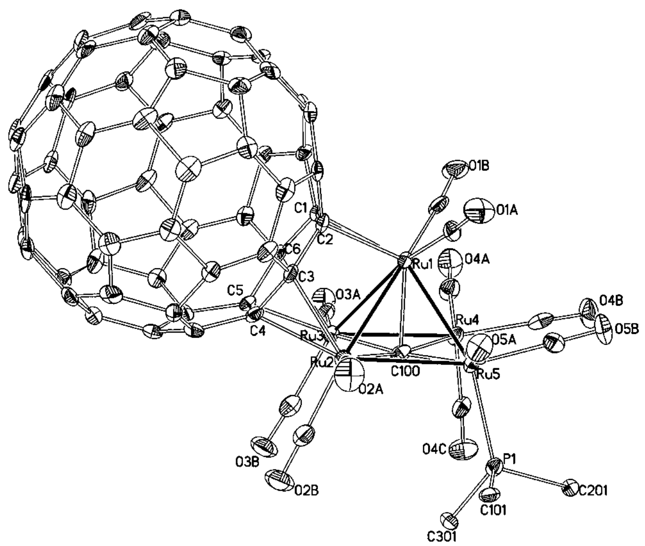

Figure 1. ORTEP diagram of **1** (35% thermal ellipsoids). Only ipso carbons (C101, C201, and C301) of the phenyl groups are shown. The darker lines denote the Ru−Ru bonds. Selected bond distances (Å): Ru1−Ru2 = 2.855(1); Ru1−Ru3 = 2.851(1); Ru1−Ru4 = 2.828(1); Ru1−Ru5 = 2.876(1); Ru2−Ru3 = 2.865(1); 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 C_{60} and $Ru_6C(CO)_{17}$ in chlorobenzene under reflux for 5 h followed by treatment with dppm for 10 min.[9] The compound was isolated following TLC separation and formulated as $Ru_6C(CO)_{12}(dppm)(C_{60})$ on the basis of a molecular ion in the positive-ion FAB mass spectrum. Crystals of **2** suitable for an X-ray diffraction study[10] 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 C_{60}. The dppm 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 **2**, no systematic alternation in either the Ru−C distances or the C−C distances of the ligated C_6 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 Ru_6C−arene complexes, including $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2{:}\ \eta^2{:}\ \eta^2\text{-}C_{16}H_{16})$,[11] for which distinct alternation in Ru−C distances is common.[3]

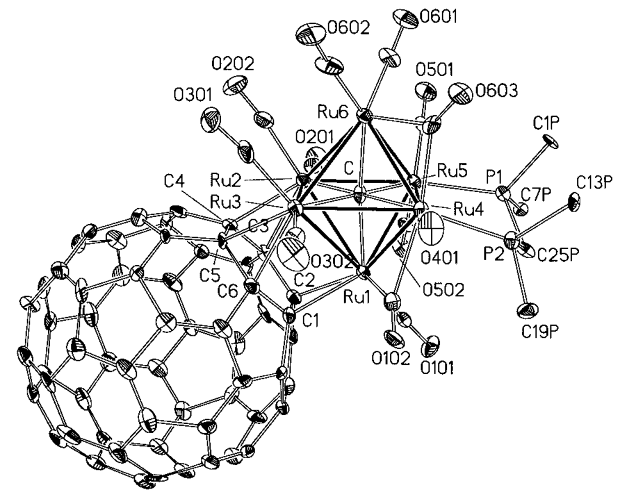

Figure 2. ORTEP diagram of **2** (35% thermal ellipsoids). Only ipso carbons (C1P, C7P, C13P, and C19P) of the phenyl groups are shown. The darker lines denote the Ru−Ru bonds. Selected bond distances (Å): Ru1−Ru2 = 2.976(2); Ru1−Ru3 = 2.877(2); Ru1−Ru4 = 2.808(2); Ru1−Ru5 = 2.872(2); Ru2−Ru3 = 2.816(2); 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).

In summary, we have demonstrated that compounds **1** and **2** with coordination of C_{60} to a triangular face of the square-pyramidal Ru_5C and octahedral Ru_6C frameworks can be prepared by the interaction of C_{60} with $Ru_5C(CO)_{15}$ or $Ru_6C(CO)_{17}$ followed by a substituting ligand. The fact that the proposed intermediates $Ru_nC(CO)_x(C_{60})$ can undergo substitution reactions by PPh_3 or $CH_2(PPh_2)_2$ under severe conditions reveals the robust nature of the C_{60}−Ru_nC cluster interaction. Structural specificity for this interaction is indicated also by the observation that compound **1** can be prepared directly from C_{60} and $Ru_5C(CO)_{14}(PPh_3)$.

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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 C_{60} (25.0 mg, 0.0347 mmol) and $Ru_6C(CO)_{17}$ (50.0 mg, 0.0457 mmol) was heated under reflux for 5.5 h. The solution was cooled, 1,2-bis(diphenylphosphino)methane (dppm; 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 CS_2-soluble residue separated by TLC (silica gel, CS_2) to give unreacted C_{60} (2.0 mg, 0.0028 mmol, 8% recovery), **2** (7.0 mg, 0.0034 mmol, 11% based on C_{60}), and $Ru_6C(CO)_{15}$(dppm) (25.0 mg, 0.0176 mmol, 39%). Data for **2** are as follows: FAB^+ mass spectrum (^{102}Ru): *m/z* 2064 ($[Ru_6C(CO)_{12}(dppm)(C_{60})]^+$). IR ($CS_2$): 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, CD_2Cl_2, 20 °C): δ 7.42 (24H, m, Ph), 5.15 (1H, q, $J_{HH} = 12$ Hz, $J_{HP} = 12$ Hz, CH_2), 4.59 (1H, q, $J_{HH} = 12$ Hz, $J_{HP} = 12$ Hz, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 20 °C): δ 30.92.

[10] (a) Crystallographic data for $\mathbf{2}\cdot 3CS_2$: triclinic, space group $P\bar{1}$, $a = 14.626(3)$ Å, $b = 14.747(3)$ Å, $c = 19.227(4)$ Å, $\alpha = 95.99(3)°$, $\beta = 92.09(3)°$, $\gamma = 113.18(3)°$, $V = 3777.9(13)$ Å^3, $Z = 2$; crystal size 0.6 × 0.04 × 0.02 mm^3. (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 R1 = 8.51% and wR2 = 15.09% ($I > 2\sigma(I)$).

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