Electronic Supplementary Information

Synthesis and Characterization of Bis-triruthenium Cluster Derivatives of an all Equatorial [60]Fullerene Tetramalonate

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Experimental section

General methods

All reactions were conducted under an atmosphere of purified dinitrogen using standard Schlenk techniques. All chemicals were obtained from commercial sources and used without further purification. Infrared spectra were recorded on a Bruker Tensor27 IR spectrometer. The NMR spectra were recorded using a JEOL 600 NMR spectrometer. The UV−vis spectrum was recorded using a Cary 5000 UV−vis−NIR spectrophotometer. Matrix-assisted laser desorption ionization (MALDI) mass spectra were recorded on a Bruker Microflex LRF mass spectrometer. Tetrakis-[di(ethoxycarbonyl)methao]-C_{60} was prepared as described in the literature.¹

Reaction of 1 and Ru_{3}(CO)_{12}.

Compound 1 (20 mg, 0.015 mmol) and Ru_{3}(CO)_{12} (21 mg, 0.033 mmol) were placed in an oven-dried 25 mL Schlenk flask, equipped with a condenser, under a dinitrogen atmosphere. Chlorobenzene (10 mL) was introduced into the flask via a syringe, and the solution was heated to reflux for 20 min. The solution was cooled to room temperature, dried under vacuum, and the residue was subjected to TLC, with dichloromethane as eluent. Compound 1 was recovered in 18% (3.5 mg). Isolation of the material forming the first red band afforded two isomers parallel-[Ru_{3}(CO)_{9}]_2{μ_3-η^2, η^2, η^2}-C_{60}[C(COOC_2H_5)_2]_4, tilted-[Ru_{3}(CO)_{9}]_2{μ_3-η^2, η^2, η^2}-C_{60}[C(COOC_2H_5)_2]_4 (parallel-3, tilted-3; 11.7 mg, 21%), the second red band afforded Ru_{3}(CO)_{9}{μ_3-η^2, η^2, η^2}-C_{60}[C(COOC_2H_5)_2]_4 (2; 8.7 mg, 12%).

Characterization of 2. MS (MALDI) m/z 1894.94 (M+ − O, ^{102}Ru); ATR-IR ν(CO) 2073 s, 2045sh, 2032 vs, 1980 br cm⁻¹; ^1H NMR (CDCl_3, 20 °C) δ 4.49–4.42 (m, 8H, OCH_2), 4.33 (m, 4H, ABX_3, δ A = 4.36, δ B = 4.29, J_{AX} = J_{BX} = 7.1 Hz, J_{AB} = 10.7 Hz), 4.21 (m, 4H, ABX_3, δ A = 4.24, δ B = 4.19, J_{AX} = J_{BX} = 7 Hz, J_{AB} = 10.9 Hz), 1.42 (t, 6H, J_{H-H} = 6 Hz, CH_3), 1.39 (t, 6H, J_{H-H} = 6 Hz, CH_2), 1.32 (t, 6H, J_{H-H} = 6 Hz, CH_2), 1.24 (t, 6H, J_{H-H} = 6 Hz, CH_3); ^13C{^1H} NMR (CDCl_3, 25 °C) δ 196.51 (C=O), 163.73, 163.60, 163.06, 162.96 (C=O), 151.62, 150.72, 147.14, 146.66, 146.47, 146.38, 145.80, 145.68, 145.38, 145.28, 145.18, 145.01, 144.58, 143.81, 143.70, 143.47, 143.41, 142.67, 142.19, 140.05, 140.00, 139.92, 135.66 (C_{60}), 77.92, 75.30, 70.97 (Ru-C_{60}), 72.51, 69.92, 69.81, 69.45, 66.24 (Malonate-C_{60}), 63.22, 63.18, 63.09, 62.96 (OCH_2), 46.69, 44.44, 42.93 (OC-C-CO), 14.12, 13.92, 13.90 (CH_3); UV-vis (CH_2Cl_2): λ_{max}/nm (ε, 10^3 M⁻¹ cm⁻¹) = 570 (6), 466 (18), 314 (76), 283 (102), 242 (166).
Characterization of parallel-3 and tilted-3. Two isomers were present in the $^1$H NMR spectrum in a ratio of 1:1. MS (MALDI) m/z 2439.46 (M$^+$ – CO, $^{102}$Ru); ATR-IR ν(ν) 2070 s, 2045 sh, 2034 vs, 2004 sh, 1996 br 1982 br cm$^{-1}$; $^1$H NMR (CDCl$_3$, 20 °C) δ 4.42 (q, 4H, OCH$_2$-tilted-3), δ 4.31 (m, 8H, ABX$_3$, δ A = 4.33, δ B = 4.28, δH$_{ABX} = 7.1$ Hz, $J_{AB} = 10.9$ Hz, parallel-3), 4.27–4.17 (m, 16H, OCH$_2$-parallel-3/tilted-3), 4.15 (q, 4H, OCH$_2$, tilted -3), 1.39 (t, 6H, CH$_3$, $J_{CH-H} = 7.1$ Hz, tilted -3), 1.31 (t, 12H, CH$_3$, $J_{CH-H} = 7.1$ Hz, parallel-3), 1.25 (t, 24H, CH$_3$, $J_{CH-H} = 7.1$ Hz, parallel-3/tilted-3), 1.20 ppm (t, 6H, CH$_3$, $J_{CH-H} = 7.1$ Hz, tilted-3); $^{13}$C ($^1$H) NMR (CDCl$_3$, 25 °C) δ 196.56 (C = O), 163.36, 163.05, 162.99, 162.70, 161.70 (C = O), 151.60, 149.64, 147.30, 147.05, 146.81, 146.45, 146.38, 145.91, 145.72, 145.50, 145.41, 144.34, 141.01, 140.89 (C$_{60}$), 79.70, 75.98, 75.86, 75.63, 74.93, 73.21, 72.33, 71.69, 70.91, 70.78, 70.69, 67.85, 67.49 (Ru-C$_{60}$, Malonate-C$_{60}$), 63.28, 63.19, 63.09 (OCH$_2$), 48.61, 46.34, 45.59, 42.70, 42.37 (OC-C-CO), 14.10, 13.91, 13.67 (CH$_3$)

X-ray Crystallography and Data Collection of 2.

Compound 2 was crystallized by slow diffusion of methanol into a dichloromethane solution of the complex. Crystal data for 2, Ru$_3$(CO)$_3$[μ$_3$-η$_2$-η$_2$-C$_{60}$][C(COOC$_2$H$_3$)$_2$]$_4$ (2) (CCDC 1039743). C$_{47}$H$_{40}$O$_{25}$Ru$_3$, $M = 1908.50$, red plate, 0.066×0.042×0.009 mm, $λ = 0.8266$ Å (synchrotron radiation at Beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley Laboratory), monoclinic, space group $P2_1/c$ (no. 14), $a = 22.5380$(11), $b = 34.0435$(15), $c = 18.4298$(8) Å, $β = 92.787(2)$°, $T = 100(2)$ K, $V = 14124.0$(11) Å$^3$, $Z = 8$, 443665 reflections measured, 33679 unique ($R_{int} = 0.0692$), Bruker ApexII; $2θ_{max} = 65.89$°; min/max transmission = 0.691/ 0.747 (multi-scan absorption correction applied); direct and Patterson methods solution; full-matrix least squares based on $F^2$ (SHELXT and SHELXL-2014); Final $wR(F_2) = 0.0839$ (all data), conventional $R_1 = 0.0322$ computed for 28087 reflections with I > 4σ (F$_0$) and 0.0433 for all 33679 data, with 2267 parameters and 0 restraints.

X-ray Crystallography and Data Collection of parallel-3.

Crystals of parallel-3 were obtained by slow diffusion of methanol into a dichloromethane solution of the complex. Crystal data for parallel-3, [Ru$_3$(CO)$_3$_2[μ$_3$-η$_2$-η$_2$-C$_{60}$][C(COOC$_2$H$_3$)$_2$]$_4$] (CCDC 1039742). C$_{107}$H$_{12}$Cl$_2$O$_{34}$Ru$_6$, $M = 2548.78$, red plate, 0.207×0.078×0.062mm, $λ = 0.71073$ Å, triclinic, space group $P$-1 (no. 2), $a = 16.3234$(10), $b = 16.3914$(10), $c = 18.3063$(11) Å, $α = 64.2930$(8)°, $β$
= 83.7400(9)°, γ = 83.3010(9)°, T = 90(2) K, V = 4373.8(5) Å³, Z = 2, 52962 reflections measured, 17896 unique (R_{int} = 0.0514), Bruker ApexII; 2θ_{max} = 52.74°; min/max transmission = 0.6855/ 0.7456 (multi-scan absorption correction applied); direct and Patterson methods solution; full-matrix least squares based on F^2 (SHELXT and SHELXL-2014); Final wR(F^2) = 0.0903 (all data), conventional R_1 = 0.0379 for 13187 reflections with I > 2σ(I) with 1369 parameters and 16 restraints. Formula given corresponds to full occupancy of the Ru_3(CO)_9. However, the group Ru1/Ru2/Ru3/O9-O17/C45-C53 refined to an occupancy of 0.9530(14) and the group Ru4/Ru5/Ru6/O26-O34/C98-C106 refined to an occupancy of 0.9400(14).

Reference

Fig. S1 (a) Front and (b) side views of the 2 configuration. The ethyl formate groups (COOC_2H_5) are denoted by green balls and the Ru(CO)_3 groups are denoted by blue balls. The four different chemical environments for the methyl groups are CH_3^a = CH_3^c / CH_3^b = CH_3^d / CH_3^e = CH_3^f / CH_3^g = CH_3^h.
Fig. S2 HPLC profile shows the first and second cycles in 2 recycling chromatogram. (Cosmosil Buckyprep column (20 mm x 250 mm), toluene as eluent and flow rate is 1mL/min)

Fig. S3 Expanded region of the $^1$H NMR spectrum of the mixture of parallel-3/tilted-3 (600 MHz, CDCl$_3$) at -20°C.
Fig. S4 van’t Hoff plot for the tilted-3 ⇄ parallel-3 interconversion.

Fig. S5 $^{13}$C NMR spectrum of compound 2 (150 MHz, CDCl$_3$)
Fig. S6 $^{13}$C NMR spectrum of mixture parallel-3/tilted-3 (150 MHz, CDCl$_3$)

Fig. S7 $^1$H-$^1$H-COSY NMR of mixture of parallel-3/tilted-3 (the region of the CH$_3$ proton signals is shown)
Fig. S8 A drawing showing the complete two molecules in crystalline 2.
Fig. S9 A drawing showing the complete two molecules in crystalline parallel-3.