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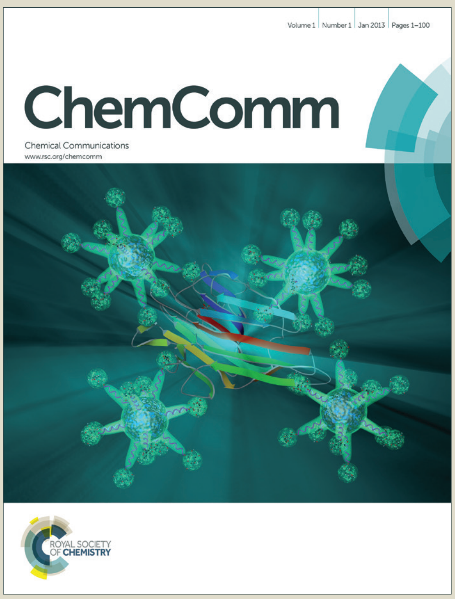

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Synthesis and Characterization of *Bis*-triruthenium Cluster Derivatives of an all Equatorial [60]Fullerene Tetramalonate

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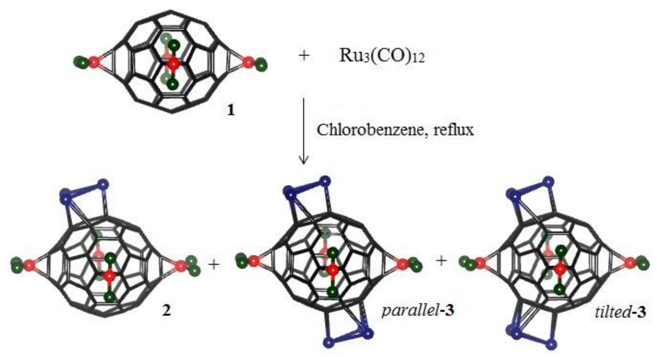
The reaction of the tetrakis[di(ethoxycarbonyl)methano]-C_{60} (1) with $Ru_3(CO)_{12}$ afforded the first *bis-parallel* C_{60}-metal cluster complex : *parallel*-$[Ru_3(CO)_9]_2\{\mu_3$-η^2,η^2,η^2-$C_{60}[C(COOC_2H_5)_2]_4\}$. The two triruthenium groups are found in either a *parallel* or a *tilted* orientation relative to each other, as determined by NMR. Only the *parallel* form was characterized by X-ray crystallography.

Many C_{60}-based derivatives have been reported and their potential applications as electronic, magnetic, catalytic, biological and optical materials have been explored.[1] Exohedral metal-C_{60} complexes exhibit unique physicochemical properties which can be tuned by the selection of the metal cluster centers.[2] This is important in the study of the reactivity and electrochemical properties of exohedral metal-C_{60} complexes, as it might result in the development of new nanomaterials.[3]

[60]Fullerene is a three-dimensional polyene that offers a variety of possible binding modes for metal centers. For example, several organometallic clusters use the μ_3-η^2, η^2, η^2-C_{60} binding motif.[4] Park *et al.* reported three *tilted* isomers of $[Os_3(CO)_6(PMe_3)_3](\mu_3$-$\eta^2$, η^2, η^2-$C_{60})$ $[Re_3(\mu$-$H)_3(CO)_9]$ as the 1:2 adducts of C_{60} and metal cluster moieties, but the *parallel* isomer was not observed.[5] Functionalized C_{60} derivatives possess different reactivities from pristine C_{60}, and some of them may be suitable to form *parallel* complexes. Kräutler *et al.* developed an orthogonal transposition method to synthesize C_{60} tetrakis-adducts with all addends located on the equatorial belt, compound **1**, leaving the two *trans*-1 positions available for further functionalizations.[6] The presence of the tetrakis[di(ethoxycarbonyl)methano] groups limits the number of possible *bis*-adduct regioisomers that can form. Here, we report that compound **1** reacts with triruthenium clusters to form the first *parallel*-form of the C_{60}-metal cluster complex.

C_{60} reacts with $Ru_3(CO)_{12}$ in refluxing chlorobenzene to afford the face-capping complex $Ru_3(CO)_9(\mu_3$-η^2,η^2,η^2-$C_{60})$ in very low yield.[4] In contrast, when compound **1** reacts with $Ru_3(CO)_{12}$ in refluxing chlorobenzene, the monoadduct complex $Ru_3(CO)_9\{\mu_3$-η^2,η^2,η^2-$C_{60}[C(COOC_2H_5)_2]_4\}$ (**2**; 21 %), and two *bis*-adduct complexes, arbitrarily assigned to an *parallel*-$[Ru_3(CO)_9]_2\{\mu_3$-η^2,η^2,η^2-$C_{60}[C(COOC_2H_5)_2]_4\}$, and to a *tilted*-$[Ru_3(CO)_9]_2\{\mu_3$-$\eta^2,\eta^2,\eta^2$-$C_{60}[C(COOC_2H_5)_2]_4\}$ (*parallel*-**3**, *tilted*-**3**; 12%) were formed in 27 minutes. The results are summarized in Scheme 1. This reaction also proceeded in refluxing toluene and *o*-dichlorobenzene, but the yields of compound **2**, *parallel*-**3**, and *tilted*-**3** were lower.

Compound **2** is an air-stable red solid. The IR spectrum displays several absorption peaks in the range 2073–1980 cm^{-1} for the terminal carbonyl stretches. The ^1H NMR spectrum (Fig. 1) displays multiplets at δ 4.49–4.42 ppm for the methylene protons of the equatorial ethyl malonate groups. Two sets of ABX_3 multiplets centered at δ 4.33 (δ A = 4.36, δ B = 4.29) and 4.21 ppm (δ A = 4.24, δ B = 4.19) for the diastereotopic methylene protons are observed. The ^{13}C resonances for the methylene carbons appear at δ 63.23, 63.20, 63.10 and 62.97 ppm.



Scheme 1 Reaction of **1** with $Ru_3(CO)_{12}$. The ethyl formate groups ($COOC_2H_5$) are denoted by green balls and the $Ru(CO)_3$ groups are denoted by blue balls.

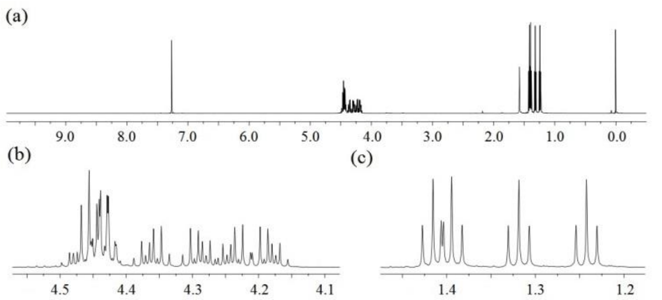


Fig. 1 (a) ^{1}H NMR spectrum of **2** (600 MHz, $CDCl_3$) and expanded parts: (b) 4.60 - 4.05 ppm, (c) 1.50 - 1.15 ppm.

Four triplets at δ 1.42, 1.39, 1.32 and 1.24 ppm are observed for the methyl protons (Fig. 1). These features (the equivalency of the protons and carbons of the malonates) clearly indicate a C_s symmetry for **2**, possessing only one plane of symmetry passing through Ru2, C61 and C75 (Fig. S1, ESI†). There are four different chemical environments for the methyl groups and these are clearly resolved. The integral ratio of the four signals is 1 / 1 / 1 / 1. (Fig. S1, ESI†) The UV-visible absorption peaks of **2** in CH_2Cl_2 are located at λ_{max}: 242, 283, 314, 466 and 570 nm. The absorptions between 240 and 410 nm are mainly due to $\pi \rightarrow \pi^*$ transitions of the fullerene cage.[7] The bands at ca. 466 and 570 nm could be attributed to the MLCT (metal to ligand charge transfer) transition of the Ru_3 cluster.[8]

The recycling HPLC profile for the $[Ru_3(CO)_9]_2\{\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60}[C(COOC_2H_5)_2]_4\}$ mixture clearly shows two peaks in the first cycle, but they are less resolved in the second cycle (Fig. S2, ESI†). This suggests that we have two isomeric forms, probably the *parallel*-**3** and *tilted*-**3**, that interconvert at room temperature in toluene by changing the coordination sites of the triruthenium clusters on C_{60}. We were unsuccessful in separating *parallel*-**3** and *tilted*-**3**, using either preparative thin-layer chromatography or HPLC (high-performance liquid chromatography). This behavior is similar to the fluxional behavior reported for *cis*-**1** / *cis*-**2** $[Os_3(CO)_6(PMe_3)_3](\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})[Re_3(\mu\text{-}H)_3(CO)_9]$.[5]

The isotope distribution for the molecular ion peaks at m/z 2434 matches a Ru_6 pattern, but its composition is [**1** + $Ru_6(CO)_{17}$]. This indicates that a carbonyl group is lost from the compound in the gas-phase before its detection in the mass spectrometer.

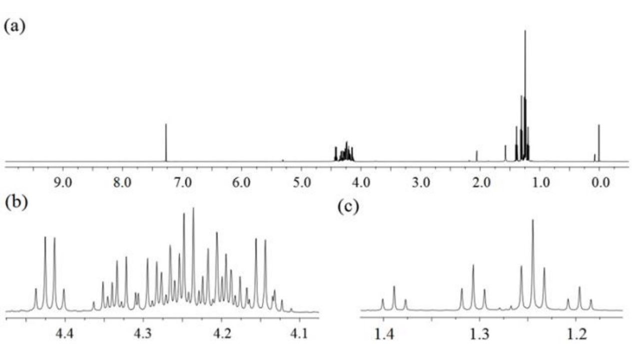


Fig. 2 (a) ^{1}H NMR spectrum of mixture *parallel*-**3**/*tilted*-**3** (600 MHz, $CDCl_3$) and expanded parts: (b) 4.45 - 4.10 ppm, (c) 1.45 - 1.15 ppm.

Assuming that compounds *parallel*-**3** and *tilted*-**3** slowly interconvert on the NMR timescale, as suggested by the HPLC results, a total of five different methyl resonances would be anticipated in the ^{1}H NMR spectrum: two for the *parallel*-arrangement and three for the *tilted*-arrangement, if there are no accidental overlaps. Fig. 2c clearly shows four different methyl resonances at δ 1.39 (relative intensity = 1), 1.31 (relative intensity = 2), 1.25 (relative intensity = 4) and 1.20 ppm (relative intensity = 1). Considering that the energy difference between these isomeric species is likely to be very small, see below, a 50:50 statistical distribution of isomers would be anticipated. Lowering the temperature to -20 °C (Fig. S3, ESI†) resulted in the separation of two methyl resonances at 1.24 and 1.23 ppm, derived from the intense room temperature resonance observed at 1.25 ppm. This leads to the predicted observation of five different methyl resonances and provides additional evidence for the presence of the two slowly interconverting regioisomers in the sample. Upon lowering the temperature it was observed that the resonances at 1.39 and 1.20 ppm retained the same intensities relative to each other as observed at room temperature (1:1) but the one at 1.31 ppm was proportionally smaller (1.39 ppm to 1.31 ppm intensities of 1:1.5 versus 1:2 observed at 25 °C). Given that the environment for methyls 5 and 6 is expected to be very different from that for 7 and 8 (see Fig. 3 for *tilted*-**3**), we tentatively assign the resonances at 1.39 and 1.20 ppm to isomer *tilted*-**3**. Correspondingly, the methyl resonance at 1.31 ppm is assigned exclusively to *parallel*-**3** (e, f, g and h in Fig. 4), and that at 1.25 ppm (at 25 °C) contains contributions from both *tilted*-**3** and *parallel*-**3**. Based on these assignments, we measured the equilibrium constants (K_{eq}= *tilted*-**3**/ *parallel*-**3**, by direct integration of the corresponding signals) as a function of temperature for the interconversion and obtained a value of the thermodynamic ΔH = -0.74 Kcal/mol from a van't Hoff plot (Fig. S4, ESI†). This indicates that there is a very small enthalpy difference between these isomers, with a slight preference for the *tilted* form. The observed resonances for the methylene hydrogens of the malonates are perfectly consistent with a 50:50 *parallel*-**3** to *tilted*-**3** ratio at room temperature. The ^{1}H NMR (Fig. 2), ^{13}C NMR (Fig. S6, ESI†) and COSY spectra (Fig. S7, ESI†) provide evidence for the C_{2v} symmetry of *tilted*-**3** and C_{2h} symmetry of *parallel*-**3**.

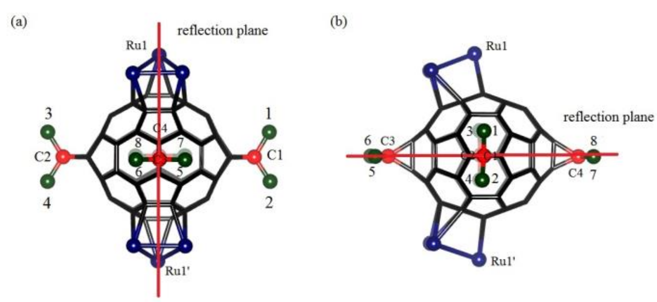


Fig. 3 (a) Front and (b) side views of the *tilted*-**3** isomer. The ethyl formate groups ($COOC_2H_5$) are denoted by green balls and the $Ru(CO)_3$ groups are denoted by blue balls.

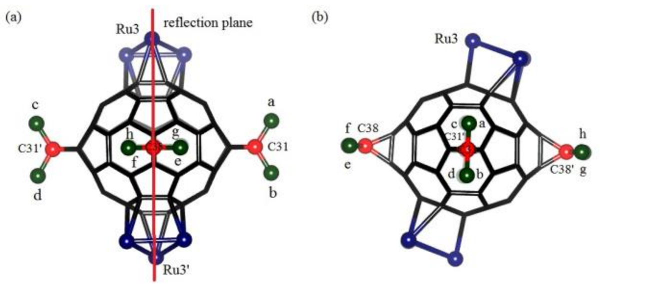


Fig. 4 (a) Front and (b) side views of the *parallel*-**3** isomer. The ethyl formate groups ($COOC_2H_5$) are denoted by green balls and the $Ru(CO)_3$ groups are denoted by blue balls.

Density functional theory (DFT) was used to optimize and compute the energies of compounds *parallel*-**3** and *tilted*-**3**. The structures were optimized with the M06 functional and the 6-31G** basis set (def2-TZVP for Ru) using the Gaussian 09 code.[9] The calculated energies for compounds *parallel*-**3** and *tilted*-**3** (-11.3817 Kcal/mol and -11.3818 Kcal/mol, respectively) are essentially identical, consistent with all observations. However, the fact that the interconverting isomeric forms exhibit time resolved resonances on the NMR timescale indicates that a reasonably high activation energy must exist, consistent with the multiply bonded metallic clusters on the surface of C_{60} [the Ru-(η^2-C_{60}) bonding energy for $Ru_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2(CO)_5(\eta^2\text{-}C_{60})$ has been estimated to be 46.6 kcal/mol][10].

Compound **2** was crystallized by slow diffusion of methanol into a dichloromethane solution of the complex. The single-crystal X-ray diffraction study of **2** revealed two independent molecules in the asymmetric unit with no crystallographically imposed symmetry on either molecule. The structure of one of the two very similar molecules of **2** is shown in Figure 5. The $Ru_3((CO)_9$ unit is placed above a hexagon on the fullerene surface with the ruthenium atoms situated over the three 6:6 ring junctions. The structure is similar to that of $Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ and $Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_6H_6)$.[4b,11]

Crystals of *parallel*-**3** were obtained by slow diffusion of methanol into a dichloromethane solution of a mixture of *parallel*-**3**/*tilted*-**3**. The X-ray diffraction study shows that there are two half-molecules in the asymmetric unit with the other half obtained by inversion through a center of symmetry. The two molecules are virtually identical in structure. A drawing of one of these is shown in Figure 6. In both **2** and *parallel*-**3,** the average Ru-Ru distances (2.877(3) and 2.876(3) in **2**, 2.860(12) Å, and 2.869(7) Å in *parallel*-**3**), are similar and similar to that in $Ru_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$ (2.883(1) Å) and slightly longer than that in $Ru_3(CO)_{12}$ (2.787(1) Å).[4b,11] In both **2** and *parallel*-**3**, the Ru_3 triangles are almost parallel to the adjacent 6-membered ring (dihedral angle: **2**, 1.29° and *parallel*-**3**, 1.30°). The occupancy of the $Ru_3(CO)_9$ groups is 0.95 and 0.94 in the two independent molecules; some of compound **2** appears to be substituted for *parallel*-**3** in some sites.

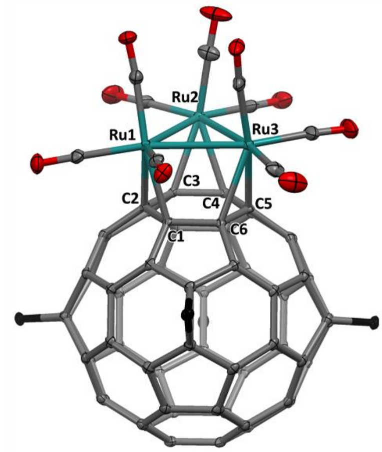


Fig. 5 A drawing of **2** with 30 % thermal ellipsoids and only the methano carbon atoms of the di(ethoxycarbonyl)methano addends shown as black ellipsoids.

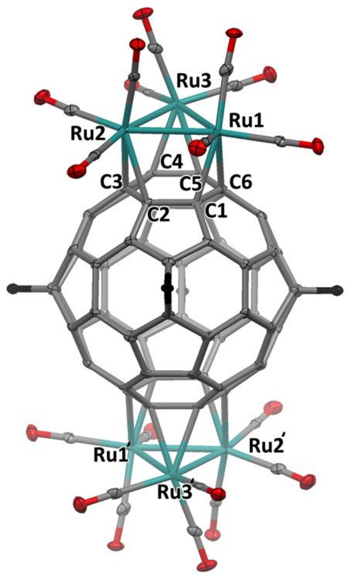


Fig. 6 A drawing of one centrosymmetric molecule of *parallel*-**3** with 30 % thermal ellipsoids and only the methano carbon atoms of the di(ethoxycarbonyl)methano addends shown in black.

In summary, *parallel*-**3** and *tilted*-**3** were synthesized from compound **1** and $Ru_3(CO)_{12}$ by refluxing in chlorobenzene, and these isomers interconvert slowly at room temperature. NMR measurements as a function of temperature allowed the determination of ΔH for the *parallel*-**3** → *tilted*-**3** isomerization. The experimental value obtained for the thermodynamic enthalpy difference (-0.74 Kcal/mol) is in agreement with the nearly degenerate energies calculated using DFT. Compound *parallel*-**3** is the first complex where the two face-capping trinuclear metallic clusters coordinate to C_{60} on opposite sites, in a *parallel* orientation.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Experimental details, Fig. S1-S9. CCDC 1039742, 1039743. See DOI: 10.1039/c000000x/

‡ Crystal data for **2**, $Ru_3(CO)_9\{\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60}[C(COOC_2H_5)_2]_4$ (CCDC 1039743). $C_{97}H_{40}O_{25}Ru_3$, 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; $2\theta_{max}$ = 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_O) and 0.0433 for all 33679 data, with 2267 parameters and 0 restraints.

Crystal data for *parallel*-**3**, $[Ru_3(CO)_9]_2\{\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60}[C(COOC_2H_5)_2]_4\}$ (CCDC 1039742). $C_{107}H_{42}Cl_2O_{34}Ru_6$, 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) Å^3, Z = 2, 52962 reflections measured, 17896 unique (R_{int} = 0.0514), Bruker ApexII; $2\theta_{max}$ = 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).

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