Preparation and Crystallographic Characterization of C$_{60}$\{η^1-Ru(CO)$_2$(η^5-C$_5$H$_5$)\}$_2$: A Locally Crowded Organometallic Fullerene Without the Usual η^2-Bonding

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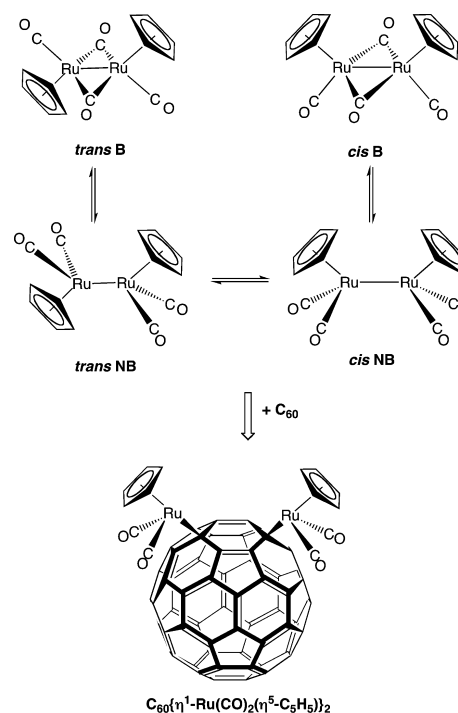
S *Supporting Information*

ABSTRACT: The reaction of \{(η^5-C$_5$H$_5$)Ru(CO)$_2$\}$_2$ with C$_{60}$ in toluene solution under thermal or photolytic conditions produces C$_{60}$\{η^1-Ru(CO)$_2$(η^5-C$_5$H$_5$)\}$_2$, whose structure has been determined by single crystal X-ray diffraction. The two Ru(CO)$_2$(η^5-C$_5$H$_5$) units are bound at the opposite ends of a hexagon on the fullerene surface and are closely intertwined.

Ever since the initial preparation and structural characterization of (η^2-C$_{60}$)Pt(PPh$_3$)$_2$ and (η^2-C$_{70}$)Ir(CO)Cl-(PPh$_3$)$_2$,[1,2] the vast majority of organometallic complexes of fullerenes have involved η^2 attachment of the metal to a 6:6 ring junction on the carbon cage.[3,4] Notable exceptions include: η^5-coordination in cases where five additional addends have been placed to isolate a unique pentagonal face,[5] and η^1-coordination in cases where metal clusters are attached to fullerenes through multiple sites that utilize η^1 and η^2 bonding.[6] A few cases of η^1-coordination of silver ions to fullerene cases are also known.[7,8] Here, we report the synthesis and structural characterization of a C$_{60}$ adduct with two ruthenium atoms coordinated in η^1 fashion.

We were interested in the interaction of the dimer, \{(η^5-C$_5$H$_5$)Ru(CO)$_2$\}$_2$, with C$_{60}$ for two reasons. \{(η^5-C$_5$H$_5$)Ru-(CO)$_2$\}$_2$,[9−12] like Co$_2$(CO)$_8$,[13,14] exists in several different tautomeric forms as shown in Scheme 1. Both Co$_2$(CO)$_8$ and \{(η^5-C$_5$H$_5$)Ru(CO)$_2$\}$_2$ have been shown to crystallize in a bridged structure,[15,16] specifically the *trans* B form for the ruthenium dimer.[17] This laboratory recently demonstrated that Co$_2$(CO)$_8$ can also be crystallized as the nonbridged D_{3h} tautomer through cocrystallization with C$_{60}$.[18] Thus, we wanted to explore the possibility that \{(η^5-C$_5$H$_5$)Ru(CO)$_2$\}$_2$ might also be crystallized in one of the other three tautomeric forms shown in Scheme 1 and attempted to cocrystallize it with C$_{60}$. However, we were cognizant that C$_{60}$ could chemically react with the ruthenium dimer through either cleavage of the Ru−Ru bond and addition of the resulting radicals to C$_{60}$ or substitution of the fullerene for one or more of the carbonyl ligands. Here we show that cleavage and addition occurs to form an adduct with two (η^5-C$_5$H$_5$)Ru(CO)$_2$ units bound to the fullerene cage in η^1 fashion.

Treatment of C$_{60}$ with the dimer, \{(η^5-C$_5$H$_5$)Ru(CO)$_2$\}$_2$, in benzene, dichloromethane, or a mixture of hexane and dichloromethane results in the gradual precipitation of the adduct, C$_{60}$\{η^1-Ru(CO)$_2$(η^5-C$_5$H$_5$)\}$_2$, as shown in Scheme 1. Black crystals of C$_{60}$\{η^1-Ru(CO)$_2$(η^5-C$_5$H$_5$)\}$_2$ suitable for X-ray

Scheme 1. Tautomeric Forms of \{(η^5-C$_5$H$_5$)Ru(CO)$_2$\}$_2$ and the Formation of C$_{60}$\{η^1-Ru(CO)$_2$(η^5-C$_5$H$_5$)\}$_2$

trans B   *cis* B

trans NB   *cis* NB

+ C$_{60}$

C$_{60}$\{η^1-Ru(CO)$_2$(η^5-C$_5$H$_5$)\}$_2$

diffraction were obtained under inert atmosphere conditions by allowing a saturated solution of \{(η^5-C$_5$H$_5$)\}Ru(CO)$_2$\}$_2$ dissolved in hexane to diffuse into a saturated solution of C$_{60}$ in dichloromethane.[19,20] The process occurred over a period of 4 months and produced a yield of 10−18%. Despite the long time involved, the reaction is reproducible.

Figures 1 and 2 show the structure of the compound. Selected bond distances and angles are given in Table 1. In forming C$_{60}$\{η^1-Ru(CO)$_2$(η^5-C$_5$H$_5$)\}$_2$, two Ru(CO)$_2$(η^5-C$_5$H$_5$) units have been added to the opposite ends of a hexagon of the fullerene surface. The resulting adduct has no symmetry. Simply adding two atoms to C$_{60}$ in the *para* positions of a hexagon reduces the symmetry of the fullerene cage from I_h itself to C_s for the adduct. The two Ru(CO)$_2$(η^5-C$_5$H$_5$) units are oriented in such a fashion that the mirror plane is also destroyed, which produces an adduct of C_1 symmetry. Thus,

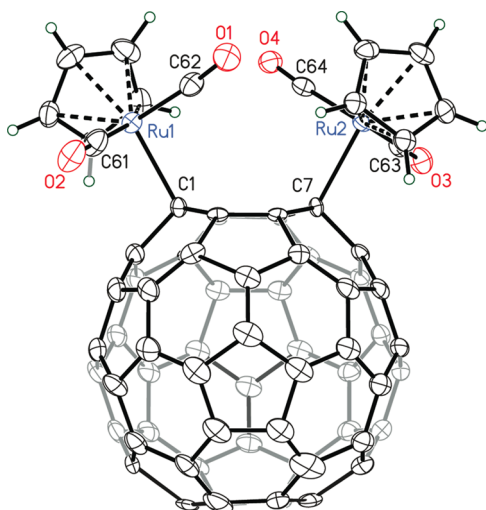**Figure 1.** Crystallographic structure of $C_{60}\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$ with thermal ellipsoids shown at 50%. Only the major orientation of the cage is shown with fractional occupancy of 0.68.

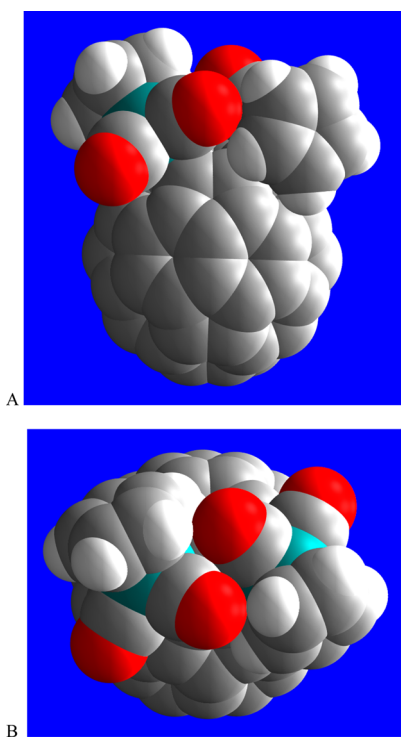**Figure 2.** Space filling drawings of $C_{60}\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$. (A) Fullerene cage with the two $\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}$ groups at the top. (B) Interlocking of the two $\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}$ groups.

Table 1. Comparison of Selected Experimental and Computed Bond Distances and Angles for $C_{60}\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$

	crystal structure	computed
Distances (Å)		
Ru1−C1	2.206(18)	2.250
Ru2−C7	2.201(13)	2.255
Ru1−C61	1.879(4)	1.873
Ru1−C62	1.877(3)	1.887
Ru2−C63	1.898(3)	1.886
Ru2−C64	1.875(3)	1.871
range of Ru1−Cp	2.246(3) to 2.266(3)	2.374 to 2.385
range of Ru2−Cp	2.253(3) to 2.263(3)	2.371 to 2.391
Ru1···Ru2	5.2666 (13)	5.337
Angles (°)		
C61−Ru1−C62	90.07(17)	91.13
C63−Ru2−C64	88.31(13)	90.97

which has the *trans* B structure shown in Scheme 1, the Ru−Ru distance is much shorter, 2.7377(5) Å.[17]

The placement of the two $Ru(CO)_2(\eta^5\text{-}C_5H_5)$ groups distorts the adjacent hexagonal ring into a shallow boat conformation as can been seen in Figure 1. Thus, carbon atoms C1 and C7 are 0.1644(3) and 0.2091(3) Å out of the plane of the other four carbon atoms of the hexagon. A similar distortion of the fullerene is seen in $C_{60}\{CH_2(C_6H_5)\}_2$, which also has the addends attached to *para* positions in a hexagon.[23] As seen in Figure 2, the two $Ru(CO)_2(\eta^5\text{-}C_5H_5)$ groups are tightly intertwined. The bulk of these two groups effectively precludes attachment to two *ortho* carbon atoms of a hexagon.

There is disorder in the position of the fullerene cage, a situation that is common with adducts that place groups at opposite ends of a hexagon.[24] The form shown in Figure 1 has 0.68 fractional occupancy. The minor form, with 0.32 occupancy, has the fullerene cage atoms rotated by 180° about a vertical axis that passes through the center of the top hexagon, which contains C1 and C7.

While $C_{60}\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$ forms slowly by allowing a solution of the reactants to stand for several weeks, the process can be accelerated by photolysis. Photo irradiation is known to cleave organometallic metal−metal bonded dimers to produce the corresponding metal-centered radicals.[25,26] The photolysis of a solution containing $\{(\eta^5\text{-}C_5H_5)Ru(CO)_2\}_2$ and C_{60} has been monitored by infrared spectroscopy. For reference, the infrared spectrum of crystalline $C_{60}\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$ shows terminal carbonyl absorptions at 2016 and 1960 cm^{-1}. In toluene solution these carbonyl stretches occur at 2020 and 1960 cm^{-1}. Figure 3 shows infrared spectra taken during the photolysis of a solution of $\{(\eta^5\text{-}C_5H_5)Ru(CO)_2\}_2$ and C_{60} in toluene. The spectrum in Trace (A) is that of $\{(\eta^5\text{-}C_5H_5)Ru(CO)_2\}_2$ itself. Note the prominent bands at 1760 and 1765 cm^{-1} due to the bridging carbonyl ligands. As photolysis proceeds, two new bands in the terminal carbonyl region appear, while the bands due to the starting ruthenium complex lose intensity and vanish. Finally, the spectrum shows only the bands at 2020 and 1960 cm^{-1} due to the product, $C_{60}\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$. For comparison, the related compounds, $Ru(\eta^5\text{-}C_{60}Me_5)CH_3(CO)_2$ and $\{(\eta^5\text{-}C_5H_4)Ru(CO)_2\}_2$ show carbonyl stretching frequencies at 2014 and 1955 and at 2000 and 1960 cm^{-1}, respectively.[20,21] While the photolytic cleavage of the Ru−Ru bond in $\{(\eta^5\text{-}C_5H_5)Ru(CO)_2\}_2$ is the most likely process to lead to adduct

individual adduct molecules are chiral, but the centrosymmetric crystal contains a racemate.

Each ruthenium atom is bonded to a single carbon atom of the fullerene. The Ru−C distances (2.206(18), 2.201(13) Å) are similar but somewhat longer than other Ru−C single bonds in compounds such as $Ru(\eta^5\text{-}C_{60}Me_5)CH_3(CO)_2$ (2.168(5) Å)[20] and $\{(\eta^5\text{-}C_5H_4)\}Ru(CO)_2\}_2$ (2.077(5)).[22] The elongation of the Ru−C bonds is likely to be a consequence of the steric bulk of the addends. In $C_{60}\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$, the distance between the two ruthenium atoms is long, 5.2666 (13) Å. For comparison, in crystalline $\{(\eta^5\text{-}C_5H_5)\}Ru(CO)_2\}_2$,
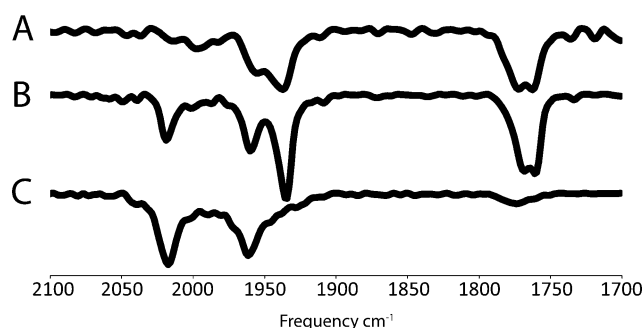
Figure 3. IR spectra from the reaction of $\{Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$ with C_{60} fullerene in toluene solution. The spectrum of the initial solution (A) before irradiation, (B) after 20 min of irradiation, and (C) after 70 min of irradiation.

formation, it is also possible that the strongly absorbing fullerene is activated by photolysis. It seems less likely that the photolytic process involves carbon monoxide loss from the ruthenium dimer as an activating step, since the two intact halves of $\{(\eta^5\text{-}C_5H_5)Ru(CO)_2\}_2$ are added to the fullerene.

Related photolytic studies of the reaction of $Re_2(CO)_{10}$ with C_{60} produced spectroscopic evidence for the formation of the related adduct, $C_{60}\{\eta^1\text{-}Re(CO)_5\}_2$.[26] However, this adduct could not be isolated, since it reverted into the starting materials, $Re_2(CO)_{10}$ and C_{60}, once photolysis ceased. We have examined the reaction of C_{60} with $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2$, both thermally and photochemically, without finding any evidence for the formation of an analogous adduct.

Computational studies at the B3LYP level of theory with a Lanl2dz basis set confirm the stability of the adduct, $C_{60}\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$ (more details in Supporting Information).The computed bond distances and angles shown in Table 1 agree well with the experimentally measured distances and angles. The computations also show that a corresponding adduct with the two addends placed in *ortho* positions on a hexagon is unstable and refines into the experimentally observed structure. While 1,2 addition is the preferred mode of reaction for C_{60}, particularly with less bulky addends, many cases of 1,4 addition are known.[23,28−30] With 1,4 addition, one of the fullerene double bonds is forced to be within a pentagon (i.e., at a 5:6 ring junction), which is energetically less favorable than the situation with 1,2 addition, where all the double bonds radiate from the pentagons and occur at 6:6 ring junctions. However, the decrease in steric interactions between bulky addends allows the 1,4 addition to become energetically favorable.

Our results add a new dimension to the chemistry of organometallic fullerene compounds. A stable compound with two η^1-coordinated organometallic groups $(\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\})$ attached to C_{60} has been prepared and isolated in crystalline form. Due to the bulk of the $-\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}$ addends, these two moieties are situated in *para* positions on one hexagon of the fullerene. As Figure 2 shows, there is considerable crowding of the two addends even with their *para* orientation. Our results indicate that confining the steric bulk of potential organometallic addends may facilitate the formation of other η^1-bound compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic and spectroscopic details and X-ray crystallographic files in CIF format for $C_{60}\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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(19) Crystal data for $C_{60}\{\eta^1\text{-}Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2$. $C_{74}H_{10}O_4Ru_2$: M_w = 1164.96, black parallelepiped 0.024 × 0.009 × 0.004 mm, λ = 0.74490 Å, Advanced Light Source, beamline 11.3.1, monoclinic, space group $P2_1/c$ (no. 14), a = 15.408(3), b = 13.224(3), c = 20.014(4) Å, β = 104.28(3), T = 100(2) K, V = 3952.0(15) Å^3, Z = 4, 64292 reflections measured, 17211 unique (R_{int} = 0.033) which were used in all calculations, Bruker SMART Apex II; $2\theta_{max}$ = 77.55°; min/max transmission = 0.976/0.996 (multiscan absorption correction applied); direct and Patterson methods solution; full-matrix least-squares based on F^2 (SIR2004 and SHELXL-2013).[20] The final $wR(F_2)$ was 0.158 (all data), conventional $R1$ = 0.051 computed for 15519 reflections

with $I > 2\sigma(I)$ using 1142 parameters with 12 restraints. Infrared spectrum in paratone oil: 2016 s, 1960 s, 1955 sh, 1426 m, 1181 m, 1125w, 1033 w, 996 w, 816 m, 745 m, 643 m, 575 s, 548 s, 524 s. UV−vis spectrum in toluene solution: 425, 475, 565, 670, 810 nm.

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