

Supporting Information for

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

By Faye L. Bowles, Marilyn M. Olmstead,* Alan L. Balch*

Preparation of $C_{60}\{\eta^1\text{-Ru(CO)}_2(\eta^5\text{-C}_5\text{H}_5)\}_2$. Under air-free conditions in a dinitrogen filled glove box, a filtered solution of 15 mg (0.067 mmol) of $\{(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\}_2$ in 14 mL of hexane was layered over a solution of 100 mg (0.139 mmol) of C_{60} in 3.5 mL of 1,2-dichlorobenzene. The sample was sealed and allowed to stand. Very small black crystals of $C_{60}\{\eta^1\text{-Ru(CO)}_2(\eta^5\text{-C}_5\text{H}_5)\}_2$ formed after four to six months. Yield, 4 to 8 mg, (10 to 18 %). Identical crystals could also be obtained by conducting the synthesis in dichloromethane or in benzene solution. 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.

Photochemical reaction of $\{(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\}_2$ and C_{60} . A 100 mL flask, an air-free solution of $\{(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\}_2$ (55mg, 0.056 mmol), and C_{60} (25 mg, 0.035 mmol) in 50 mL of dry toluene was stirred under a nitrogen atmosphere at room temperature. The flask was irradiated with a xenon lamp with aluminum foil was placed on the opposite side of the flask to reflect any light back onto the flask. The solution was initially yellow, and after 20 minutes the solution turned to a purple-brown color. The solution stayed this color for the rest of the photolysis. Every ten minutes an aliquot was removed and was used to obtain an infrared spectrum using an ATR-FTIR.

Instrumentation. Photolysis was conducted using a compact xenon light source LAX-102 by Asahi. Infrared spectra were obtained through the use of a Bruker ALPHA FT-IR spectrometer.

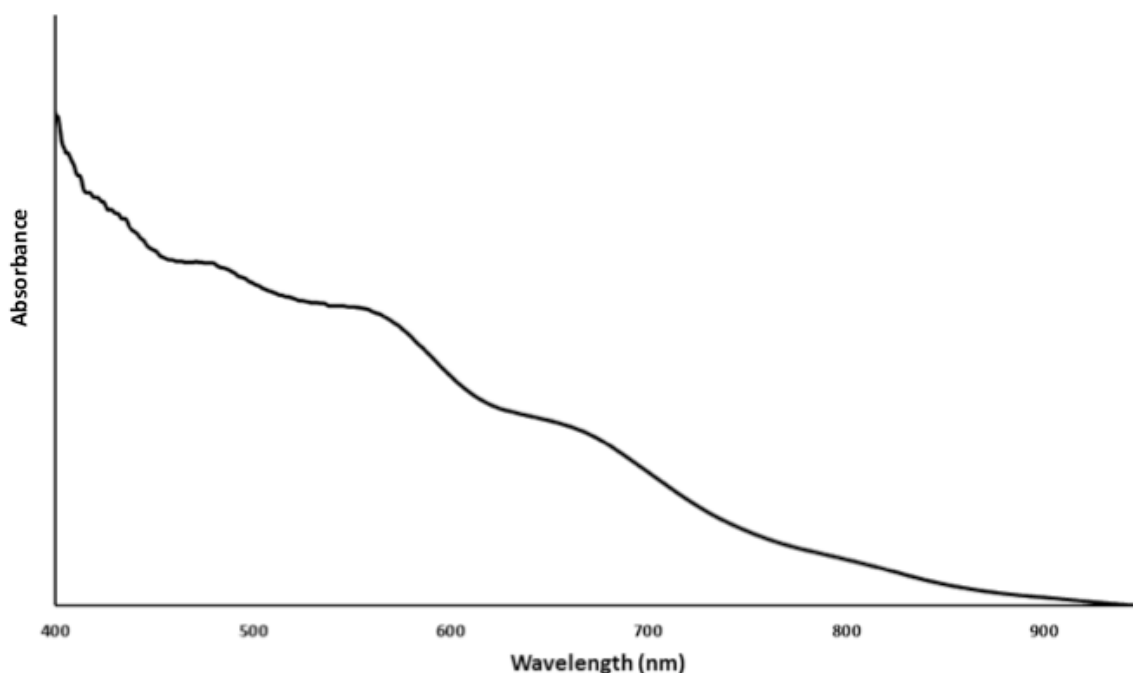


Figure SI 1. The UV/vis absorption spectrum of a toluene solution of $C_{60}\{\eta^1\text{-Ru(CO)}_2(\eta^5\text{-C}_5\text{H}_5)\}_2$.

Computational details. Density functional calculations were carried out using the GAUSSIAN94 package.¹ The hybrid B3LYP-DFT method was applied, in which the Becke three parameters exchange functional² and the Lee-Yang-Parr correlation functional³ were used. The double- ζ basis set for the valence and outermost core orbitals combined with pseudo-potentials known as LANL2DZ were used for all the atoms.⁴ The geometries were fully optimized.

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