

Supporting Information for:

Introduction of a $(\text{Ph}_3\text{P})_2\text{Pt}$ Group into the Rim of an Open-cage Fullerene by Breaking a Carbon-Carbon Bond.

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Preparation of $(\text{Ph}_3\text{P})_2\text{Pt}$ -MMK-9 (1). MMK-9 and $\text{Pt}(\text{PPh}_3)_4$ were prepared in accordance with literature methods.^{1,2} The cage-opening reagent 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine was purchased from Sigma-Aldrich and used without further purification, whereas the solvents toluene, hexanes (mixture of isomers), ethyl acetate and 1-chloronaphthalene were purchased from Sigma-Aldrich and degassed over molecular sieves prior to use, as needed. C_{60} was purchased from SES Research Inc. and used without further purification.

A purged and nitrogen-backfilled round bottom flask was charged with 19 mg of $(\text{Ph}_3\text{P})_4\text{Pt}$ (0.015 mmol), which was dissolved in 15 mL of degassed toluene. To this solution, a separate solution of 11.5 mg of MMK-9 (0.011 mmol) in 20 mL toluene was added. A color change from yellow to brown to black was observed within seconds. The reaction mixture was stirred at room temperature for 90 minutes. Subsequently the reaction mixture was evaporated to ~1 mL under reduced pressure. The residue was subjected to column chromatography (eluent, 20:1 toluene:EtOAc; support, silica gel) giving first an orange band that contained MMK-9 followed by a broad black band that contained $(\text{Ph}_3\text{P})_2\text{Pt}$ -MMK-9 (1) (12.2 mg, 0.007 mmol, 46%). Single crystals for X-ray diffraction were prepared by slow diffusion of hexanes (mixture of isomers) into a solution of $(\text{Ph}_3\text{P})_2\text{Pt}$ -MMK-9 in 3:1 CS_2 :hexanes to produce the solvate $(\text{Ph}_3\text{P})_2\text{Pt}$ -MMK-9•*n*-hexane•methylcyclopentane. Diffusion of pentane into a benzene solution of $(\text{Ph}_3\text{P})_2\text{Pt}$ -MMK-9 (1) yielded another solvate, $(\text{Ph}_3\text{P})_2\text{Pt}$ -MMK-9•3benzene.

Characterization. Cyclic voltammetry was carried out on a CHE 610E Electrochemical Analyzer using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/0.01M AgCl reference electrode. The potentials were calibrated against ferrocene added as an internal standard after each measurement. Infrared (IR) spectra were recorded on a Bruker Alpha FT-IR spectrometer using attenuated total reflectance (ATR). Ultraviolet-visible (UV-vis) spectra of benzene solutions of MMK-9 and $(\text{Ph}_3\text{P})_2\text{Pt}$ -MMK-9 in quartz cuvettes were recorded on a Shimadzu UV-3600 UV-vis NIR spectrophotometer.

Spectral Data.

MMK-9: M.p. >210 °C; IR (solid): $\nu = 1700 \text{ cm}^{-1}$, 1744 cm^{-1} (C=O); UV/Vis (C_6H_6): λ_{max} (log ϵ) = 331 nm (4.29), 425 nm (3.75).

$(\text{Ph}_3\text{P})_2\text{Pt}$ -MMK-9 (1): M.p. >210 °C; IR (solid): $\nu = 1685 \text{ cm}^{-1}$, 1731 cm^{-1} (C=O); UV/Vis (C_6H_6): λ_{max} (log ϵ) = 295 nm (4.62), 438 nm (3.84), 570 nm (3.43).

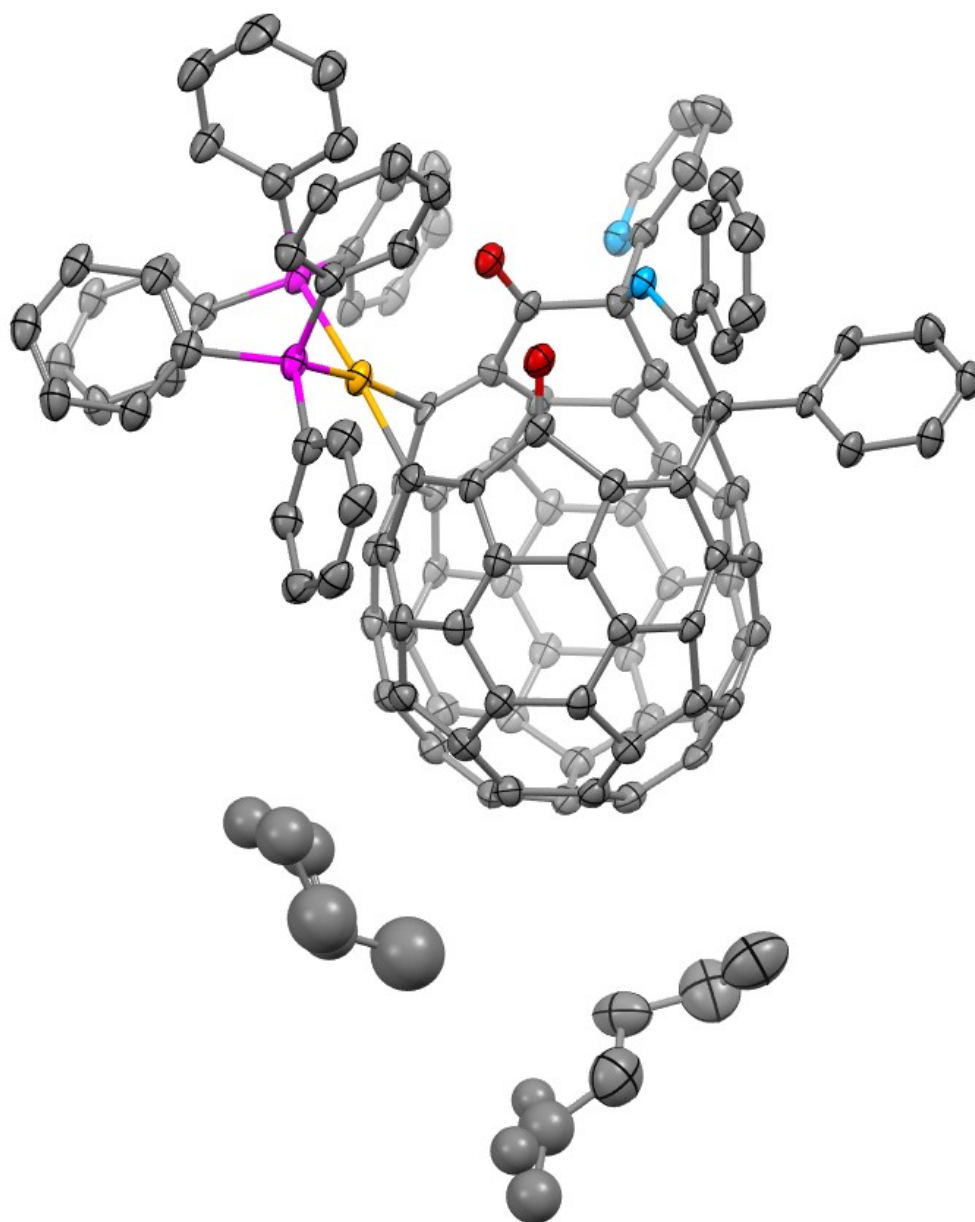


Figure SI-1. A drawing of $(\text{Ph}_3\text{P})_2\text{Pt-MMK-9}\cdot n\text{-hexane}\cdot\text{methylcyclopentane}$ showing the molecular structure and the location of the disordered solvate molecules.

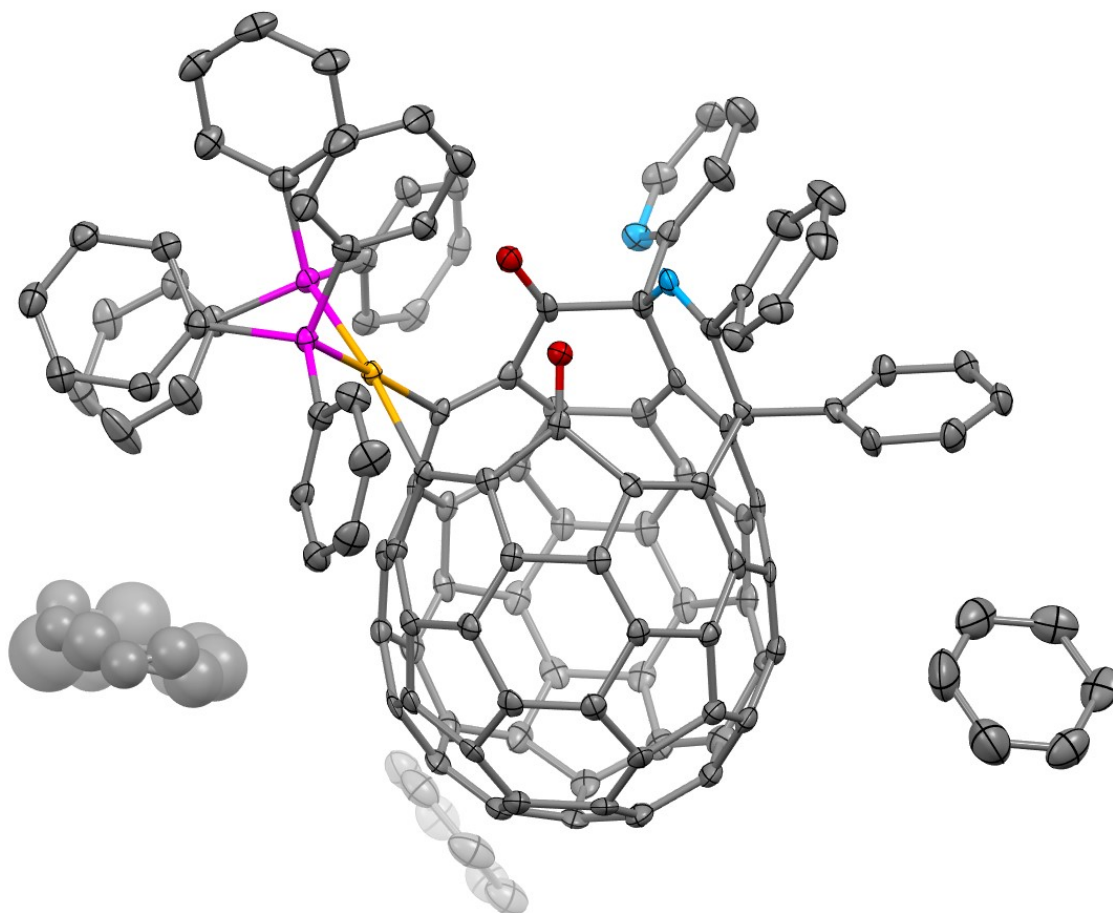


Figure SI-2. A drawing of $(\text{Ph}_3\text{P})_2\text{Pt-MMK-9}\cdot 3\text{benzene}$ showing the molecular structure and the location of the disordered solvate molecules.

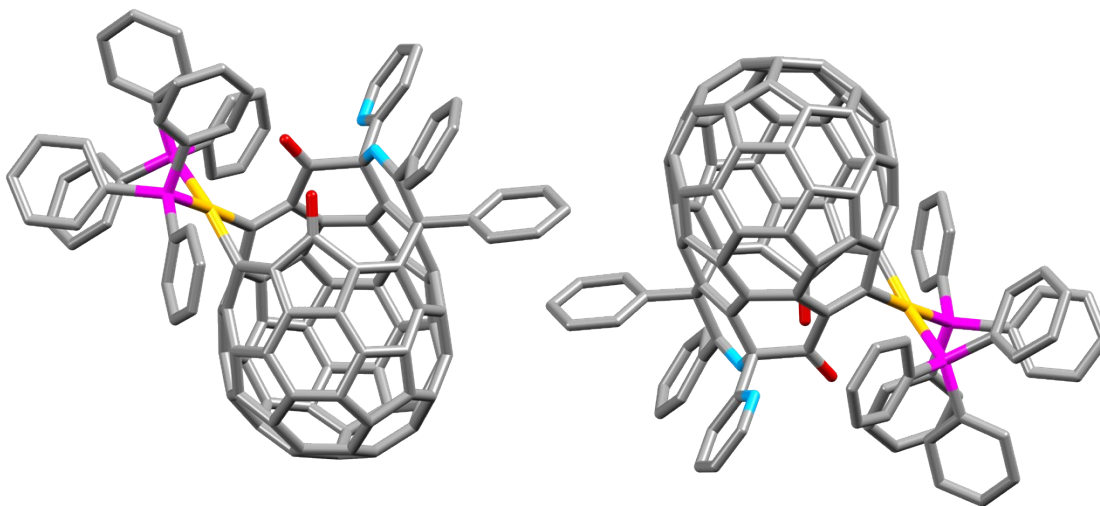


Figure SI-3. A drawing of the two enantiomers of $(\text{Ph}_3\text{P})_2\text{Pt-MMK-9}$ (**1**) packed about a center of symmetry in crystals of the benzene solvate $(\text{Ph}_3\text{P})_2\text{Pt-MMK-9}\cdot 3\text{benzene}$.

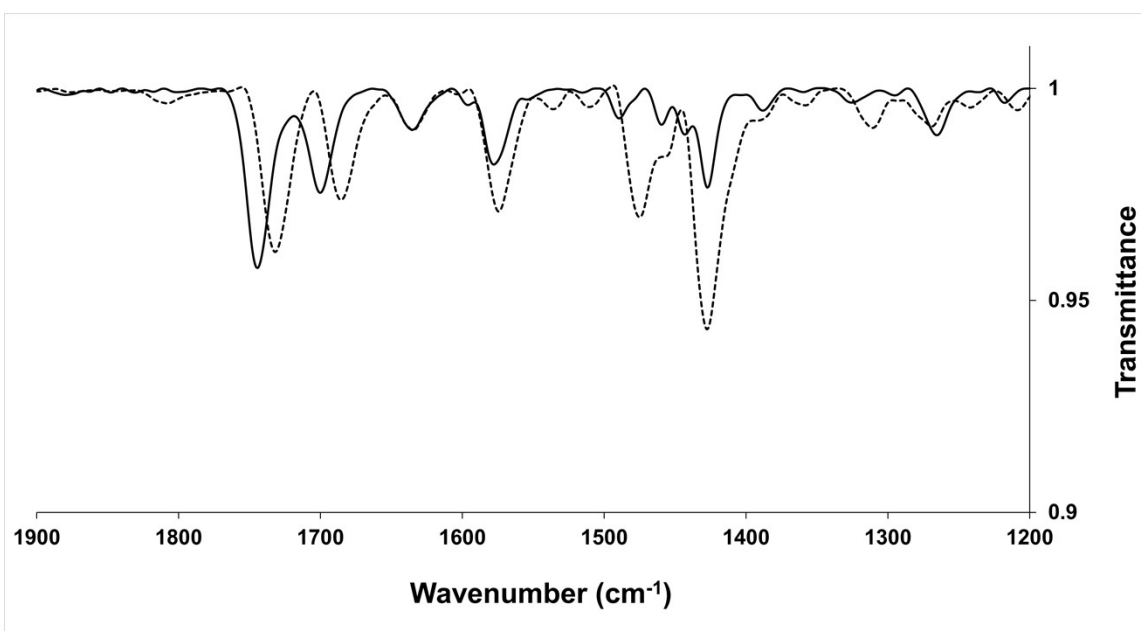


Figure SI-4. A portion of the infrared spectra of crushed crystals of $(\text{Ph}_3\text{P})_2\text{Pt-MMK-9}$ (**1**) (dashed line) at the top and MMK-9 (solid line). IR spectra were recorded on a Bruker Alpha FT-IR spectrometer using attenuated total reflectance (ATR).

Crystal Structure Procedures:

Hexanes (mixed) solvate: A crystal of compound **1** was mounted on in the 90 K nitrogen cold stream provided by a Cryo Industries cryostat low temperature apparatus on a Bruker Apex II diffractometer employing a fine-focus Mo sealed tube ($\lambda = 0.71043 \text{ \AA}$). Dataset was reduced with the use of Bruker SAINT³, and a multi-scan absorption correction was applied with the use of SADABS. Structure solutions and refinements were conducted with SHELXT-2018.⁴

Benzene solvate: A crystal of compound **1** was mounted in the 100 K nitrogen cold stream provided by an Oxford Cryostream low temperature apparatus on a Bruker Venture Kappa DUO diffractometer. Data were collected with the use of a molybdenum microsource ($\lambda = 0.71073 \text{ \AA}$). Dataset was reduced with the use of Bruker SAINT,³ and a multiscan absorption correction was applied with the use of SADABS. Structure solutions and refinements were conducted with SHELXT-2018.⁴

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² Malatesta, M.; Cariello, C. Platinum(0) Compounds with Triarylphosphines and Analogous Ligands. *J. Chem. Soc.*, **1958**, 2323-2328

³ SAINT and SADABS, Bruker AXS Inc., Madison, WI, 2018

⁴ Sheldrick, G. M. *Acta Crystallogr., Sect. C: Struct. Chem.*, **2015**, 71, 3-8