

In-situ Synchrotron Crystallographic Observation of a Labile Unsaturated CpMn(CO)₂ Complex Photo-induced within a Self-Assembled Cage

Masaki Kawano,^{1*} Yasuhiro Kobayashi,¹ Michito Yoshizawa,¹ Tomoji Ozeki,² and Makoto Fujita^{1*}

¹ Department of Applied Chemistry, The University of Tokyo, CREST, Japan Science and Technology Corporation (JST), Bunkyo-ku, Tokyo 113-8656, Japan

² Department of Chemistry and Materials Science, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan

Introduction

Coordinationally unsaturated transition metals exist as important intermediates of a variety of organometallic reactions that are frequently involved in the catalytic cycles of organic transformations. The direct observation of these species is particularly important for understanding the mechanistic insights of the organometallic/organic reactions. Such reactive intermediates have been investigated with spectroscopic methods such as inert matrix isolation techniques. Nevertheless, they are seldom observed by crystallography because of their labile nature. An efficient method for observing such species is to isolate them by encapsulation within molecular cages or capsules. Here we report in-situ crystallographic observation of a coordinationally unsaturated manganese complex within a self-assembled coordination cage (1), which we have shown to be an efficient host for a variety of neutral organic molecules.

Results

Treatment of an aqueous solution of 1 with excess amount (10 mol equiv) of liquid 2 at 25 °C for 1 h gave a yellow solution of clathrate compound 1·(2)₄. A single crystal of 1·(2)₄ was obtained by slow evaporation of the yellow solution at 25 °C. The crystallographic analysis confirmed the 1:4 complexation of 1·(2)₄ (Figure 1). Diffraction data of 1·(2)₄ were collected at low temperatures (15 to 100 K) by using synchrotron

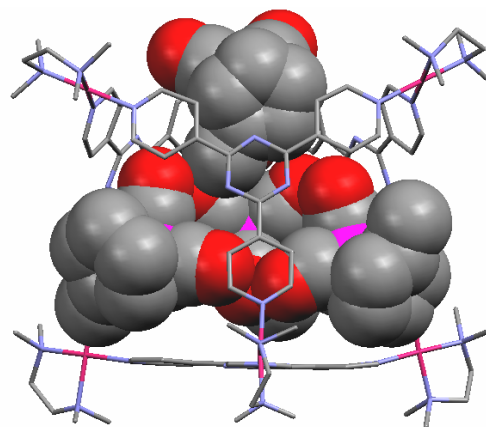


Figure 1. Molecular structure of 1·(2)₄.

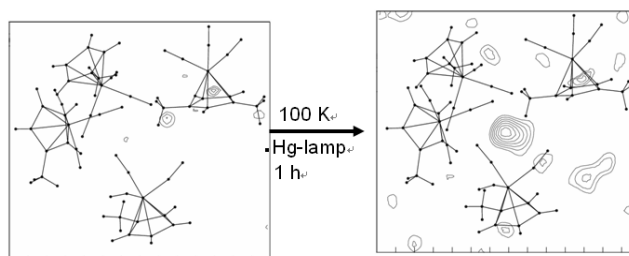
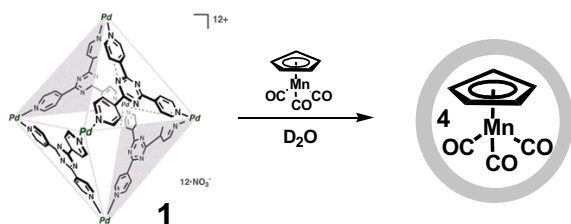


Figure 2. Difference electron density map before and after irradiation at 100 K. Contour: 0.2 e/Å³

radiation at KEK (PF-AR NW2 beamline). void of 1 (Figure 2). Because the position of the trapped CO is away from that of the initial Mn complexes by ca. 3 to 4 Å, the recombination of CO with Mn may be suppressed. On a basis of the D map, the molecular structure was modeled and refined. At 100 K, we successfully observed coordinationally unsaturated complexes among four manganese complexes in the cage.

Whether the geometry of the unsaturated Mn complex was pyramidal or planar remained unclear from investigation by conventional matrix isolation IR spectroscopy and from indirect chemical approach using either CpMn(CO)₂(solvent) or 16-electron analogue compound. For the first time, our experimental results support that a coordinationally unsaturated 16 electron Mn complex is pyramidal rather than planar in the range of 15 to 100 K and no hybridization of d⁶-orbitals occurred.

*mkawano@appchem.t.u-tokyo.ac.jp



radiation at KEK (PF-AR NW2 beamline).

Photolysis of a single crystal of 1·(2)₄ with a 365 nm light at low temperatures for ca 1 h on a diffractometer showed a color change from pale yellow to green-yellow. A difference electron density map (D map) of 1·(2)₄ before and after 365 nm-irradiation at 15 to 100 K provided similar features in that new peaks corresponding to a dissociated CO clearly appeared in the center of a