

Direct Crystallographic Observation of a Coordinatively Unsaturated Transition-Metal Complex in situ Generated within a Self-Assembled Cage

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Introduction

The direct observation of key intermediates of a variety of organometallic reactions is particularly important for understanding the mechanistic insights of organometallic/organic reactions. To date, they have been investigated only by spectroscopic methods, but never by crystallography because of their labile nature. An efficient method for stabilizing and observing such labile species is to isolate them by encapsulation within molecular cages or capsules. Here we report the in situ crystallographic observation of a coordinatively unsaturated manganese complex within a self-assembled coordination cage (**1**), which is an efficient host for a variety of neutral organic molecules. We show that, within the cavity of cage **1**, stable $\text{Cp}^*\text{Mn}(\text{CO})_3$ (**2**, Cp^* = methylcyclopentadienyl) liberates CO via photodissociation in crystalline state and in-situ generated $\text{Cp}^*\text{Mn}(\text{CO})_2$ (**3**) is directly observed by X-ray diffraction. There is a long discussion based on theoretical calculations, spectroscopic observation, and chemical analyses whether the geometry of unsaturated transition metal center is pyramidal or planar. The crystallographic analysis clearly concludes that the 16-electron unsaturated manganese complex adopts a pyramidal geometry.¹

Results

Upon photo-irradiation of a single crystal of $\mathbf{1} \cdot (\mathbf{2})_4$ with a 365 nm light, the dissociation of a CO ligand took place in the crystal without loss of crystallinity. We measured X-ray data at several temperatures of 15 - 100 K. At 100 K we achieved 100% conversion of CO-dissociation photoreaction. On the basis of the D map, we successfully refined the molecular structure and observed the formation of coordinatively unsaturated $\text{Cp}^*\text{Mn}(\text{CO})_2$ (**3**) from one of four manganese complexes in the cage (Figure 1b). Dissociated free CO was clearly trapped in the void of the cage. Since the void can accommodate only one free CO, other CO ligands are not allowed to dissociate or immediately recombined to the Mn center.

In summary, we succeeded in the direct crystallographic observation of an extremely labile, coordinatively unsaturated manganese complex by enclathrating the precursor in a self-assembled cage.

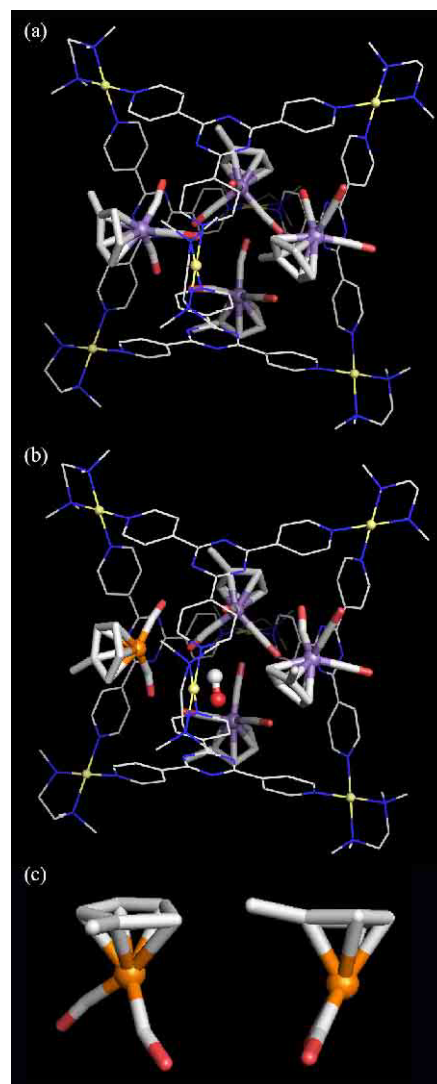


Figure 1. In situ X-ray observation of the photo-dissociation reaction of $\mathbf{1} \cdot (\mathbf{2})_4$ complex. (a) Before irradiation. (b) After irradiation. Note the generation of coordinatively unsaturated **3** (Mn center: orange) and free CO. (c) Views of **3** generated within **1**.

References

[1] M. Kawano et al, *J. Am. Chem. Chem.*, 128, 6558 (2006).

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