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

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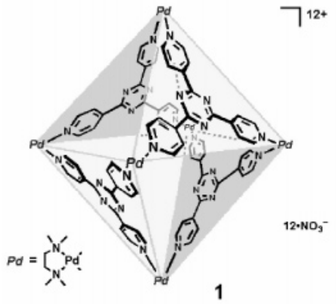
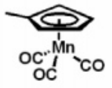
Coordinatively unsaturated transition metals exist as key intermediates of a variety of organometallic reactions that are frequently involved in the catalytic cycles of organic transformations.[1−4] The direct observation of these reactive intermediates is particularly important for understanding the mechanistic insights of organometallic/organic reactions. To date, they have been investigated only by spectroscopic methods, such as inert matrix isolation techniques[5−7] and time-resolved IR spectroscopy,[8] 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.[9−15] Here we report the in situ crystallographic observation[16−20] 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.[21,22] We show that, within the cavity of cage **1**, stable $Cp'Mn(CO)_3$ (**2**, Cp′ = methylcyclopentadienyl) liberates CO via photodissociation in the crystalline state, and in situ generated $Cp'Mn(CO)_2$ (**3**)[23] 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 an unsaturated transition-metal center is pyramidal or planar.[24−26,28−33] The crystallographic analysis clearly concludes that the 16-electron unsaturated manganese complex adopts a pyramidal geometry.



1



2

Treatment of an aqueous solution of **1** (15 μmol, 1 mL) with an excess amount (10 molar equiv) of liquid **2** at 25 °C for 1 h gave a yellow solution of clathrate compound **1**·(**2**)$_4$ in 85% yield (by NMR). The yellow solution was separated from a trace amount of solid byproducts and a surplus of **2** by filtration and decantation. A single crystal of **1**·(**2**)$_4$ was obtained by slow evaporation of the yellow solution at 20 °C. The crystallographic analysis confirmed the 1:4 complexation, where guests **2** in **1**·(**2**)$_4$ were loosely packed (Figure 1a).

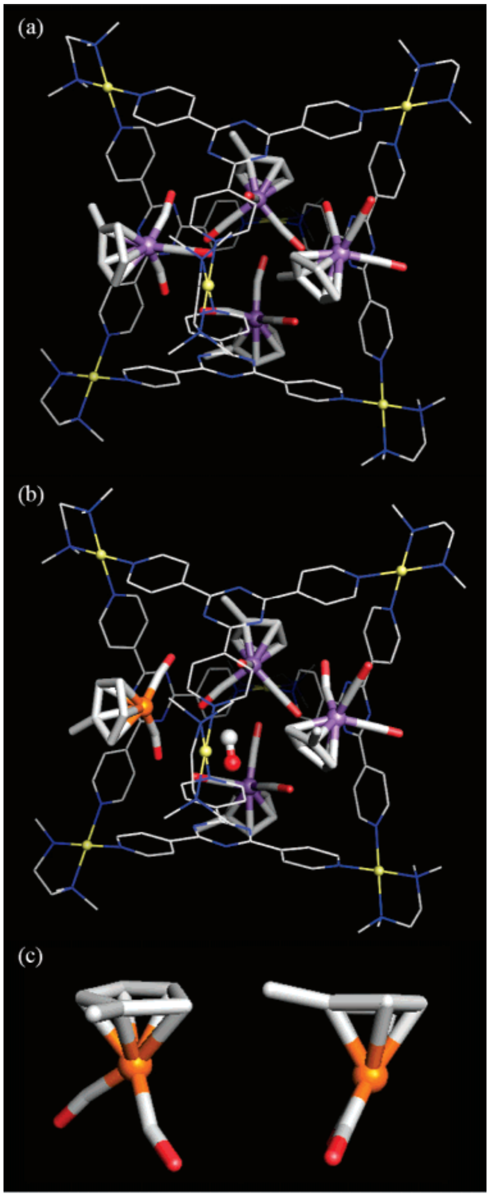


Figure 1. In situ X-ray observation of the photodissociation reaction of the **1**·(**2**)$_4$ complex: (a) before irradiation; (b) after irradiation. Note the generation of coordinatively unsaturated **3** (Mn center, orange) and free CO. (c) Views of **3** generated within **1**. The side view (right) shows pyramidal geometry at the Mn center. See Supporting Information for the details.

Upon photoirradiation, 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, 60, 80, and 100 K. At 100 K, we achieved 100% conversion of the CO dissociation photoreaction. The photolysis of the single crystal of **1**·(**2**)$_4$ on a diffractometer at

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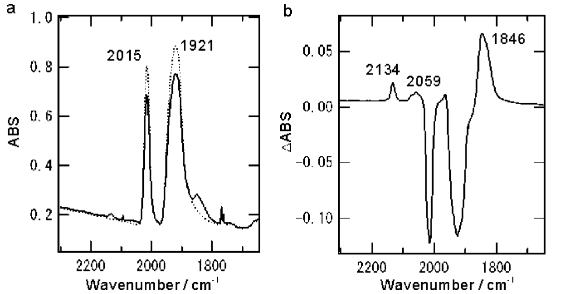

Figure 2. FTIR spectra of **1**·(**2**)$_4$ before and after irradiation. (a) FTIR spectral changes before (broken line) and after 2 min irradiation ($\lambda = 365$ nm, solid line) at 80 K in a KBr matrix. (b) FTIR difference spectrum between before and after 2 min irradiation.

100 K with UV light for ca. 30 min resulted in crystal color change from pale yellow to green−yellow and a slight change of lattice parameters. The difference electron density maps (D maps) of **1**·(**2**)$_4$ before and after 365 nm irradiation at 100 K showed the clear appearance of new distinct peaks assignable to dissociated CO at the center of the void of **1**. On the basis of the D map, we successfully refined the molecular structure and observed the formation of coordinatively unsaturated $Cp'Mn(CO)_2$ (**3**) from one of four manganese complexes in the cage (Figure 1b).[27] Dissociated free CO was clearly trapped in the void of the cage. In addition, we observed no electron density peaks corresponding to the initial Mn complex.

Most interestingly, unsaturated 16-electron complex **3**, in situ generated from **2**, showed a pyramidal geometry at the manganese center, indicating no rehybridization of d^6-orbitals (Figure 1c). Whether the geometry of the unsaturated Mn complex is pyramidal or planar has remained unclear from conventional matrix isolation IR spectroscopy[28−32] or from comparison with 16-electron analogous compounds, such as CpMnNO(C(O)Ph).[33] In this study, we provided the direct experimental evidence for the pyramidal geometry of unsaturated 16-electron complex **3**. This result agrees with theoretical prediction by Hofmann and co-workers[25,26] that the pyramidal ground state geometry is more stable than the planar one for an unsaturated 16-electron manganese cyclopentadienyl carbonyl complex.

In this experiment, a large free volume of cage **1** allowed the loose packing of **2**, facilitating the dissociation and migration of CO in the cavity. Because free CO entrapped around the center of the void was away from the unsaturated Mn atom by more than 3.5 Å, the recombination of CO with the Mn center was suppressed. Since the void can accommodate only one free CO, other CO ligands are not allowed to dissociate or immediately recombined to the Mn center. Thus, only one CO ligand selectively dissociated.

The methyl group of the Cp′ ring was also essential to the loose packing. $CpMn(CO)_3$ (**4**) that has no methyl group on the ring was more tightly packed in the cavity of **1′** (an analogue of **1** with 2,2′-bipyridine auxiliary on Pd).[22] Photolysis on the crystal of **1′**·(**4**)$_4$ caused color change, but only a small amount of photoproduct was generated, indicating that CO dissociation was suppressed or once dissociated CO was immediately recombined. A crystal of **4** itself was also irradiated, but no reaction was observed. Presumably, this is also because of very tight packing of **4** in the crystal as revealed by its crystallographic analysis.[34]

IR spectroscopy supported the crystallographic results. The clathrate compound of **1**·(**2**)$_4$ showed a drastic IR spectral change in intensity on 365 nm irradiation at 80 K. As shown in Figure 2, intensity of CO stretching bands of **2** decreased at 2015 and 1921 cm^{-1} on irradiation. Instead, new bands appeared at 2134 cm^{-1} for free CO and at 1846 cm^{-1} for coordinatively unsaturated 16-electron complex **3**. These IR spectral changes correspond to those reported in references.[28−32] Further irradiation produced another band at 2059 cm^{-1}, which is attributed to decomposed products.

In summary, we succeeded in the crystallographic observation of an extremely labile, coordinatively unsaturated manganese complex by enclathrating the precursor in a self-assembled cage followed by in situ generation of the target species in a crystal. Thanks to the highly crystalline nature and the high binding ability of the cage, our approach demonstrated here is expected to be a general and powerful method for determining the structure of highly reactive, short-lived species which can be hardly observed by conventional methods.

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Supporting Information Available: Experimental details and additional supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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