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Noncovalent Trapping and Stabilization of Dinuclear Ruthenium Complexes within a Coordination Cage

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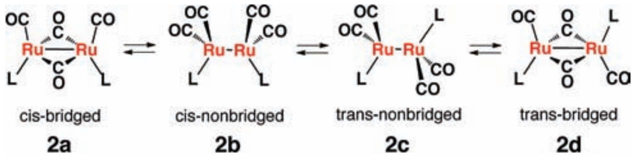
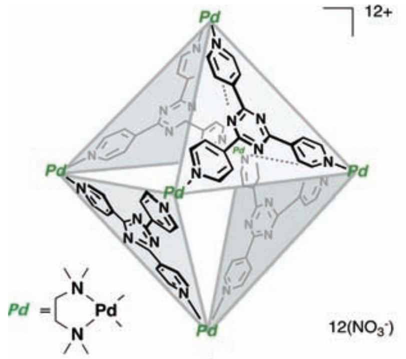
Supporting Information

ABSTRACT: A dinuclear ruthenium complex, $[(\eta^5\text{-indenyl})Ru(CO)_2]_2$, was noncovalently enclathrated within a self-assembled coordination cage. In the cavity, rapid cis–trans isomerization and ligand exchange between the terminal and bridging carbonyls were suppressed, and only the carbonyl-bridged cis configuration was observed by X-ray crystallographic analysis.

Scheme 1. Equilibrium among the Four Isomers 2a–d (L = η^5-indenyl)



Encapsulation of metal complexes by self-assembled cage hosts is a challenging but potentially efficient method for modulating the local steric and electronic environment of the enclathrated metal centers via noncovalent interactions.[1] The host cages protect the metal complexes within their cavities and can even stabilize highly reactive metal centers generated in situ.[2] Recent studies by Bergman and Raymond have shown that host complexes can also accommodate substrates and accelerate the subsequent reactions with the entrapped metal while endowing high regio- and stereocontrol due to encapsulation effects by the hosts.[3] Here we examined the encapsulation of dinuclear metal complexes with labile metal–metal bonds by coordination cage **1**. The dinuclear ruthenium complex $[(\eta^5\text{-indenyl})Ru(CO)_2]_2$ (**2**) exists as a mixture of four isomers (**2a**–**d** in Scheme 1)[4] in rapid equilibrium, and the isomer distribution is strongly dependent on the local environment.[5] Furthermore, the complex is photosensitive and undergoes facile photoinduced Ru–Ru bond cleavage and CO dissociation.[5,6] We show that self-assembled coordination cage **1** accommodates complex **2**, freezes it into the CO-bridged cis configuration (**2a**), and significantly enhances its photostability.



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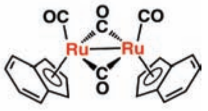

2a

When ruthenium complex **2** (8.2 mg, 0.015 mmol) was suspended in an aqueous solution of cage **1** (5.0 mM, 1.0 mL) at 100 °C for 2 h, the clear solution turned purple.[7] After excess ruthenium complex **2** was removed by filtration, the quantitative formation of the inclusion complex **1**·**2** was confirmed by ^{1}H NMR spectroscopy (Figure 1). Integration of the ^{1}H NMR spectrum of **1**·**2** indicated a 1:1 host–guest complex,[8] and this conclusion was supported by elemental analysis. The guest signals were considerably shifted upfield as a result of shielding by the panel ligands of cage **1** (Figure 1a,b). The broadened signals of the cage at lower temperature indicated slow tumbling of the closely packed ruthenium complex **2** inside cage **1** (Figure 1c).

X-ray crystallographic analysis revealed that the Ru–Ru complex was fixed in the carbonyl-bridged cis configuration **2a**, even though **2** and related $[LRu(CO)_2]_2$ complexes have previously been crystallized only as the trans-bridged isomers (**2d** and analogues). A needle-shaped single crystal of **1**·**2a** was obtained by slow evaporation of the aqueous purple solution at room temperature for 1 week. Diffraction data were collected at 90 K. The crystal structure illustrates the snug fit of ruthenium complex **2a** inside cage **1** (Figure 2). Complex **2a** was disordered over two positions, but these two positions possessed nearly identical Ru–Ru bond lengths (2.66 and 2.83 Å) and the same head-to-head orientation for the two indenyl ligands. The head-to-head orientation of the two indenyl groups in **1**·**2a** is favored because of efficient π–π interactions (~3.3 Å) between the indenyl ligands of **2a** and the panel ligands of cage **1**. Thus, the X-ray analysis of **1**·**2a** has provided the first direct structural data for the cis-bridged isomer, concerning which previous studies have only speculated.[5]

IR spectroscopy revealed that the cis configuration of **2a** in the crystal of **1**·**2a** was maintained at room temperature (Figure 3). The CO stretching bands at 1994 and 1819 cm^{-1}, which are characteristic for the cis isomer, remained unchanged,[9] and no bands for the trans isomer **2d** (1955, 1774 cm^{-1}) were observed.[10]

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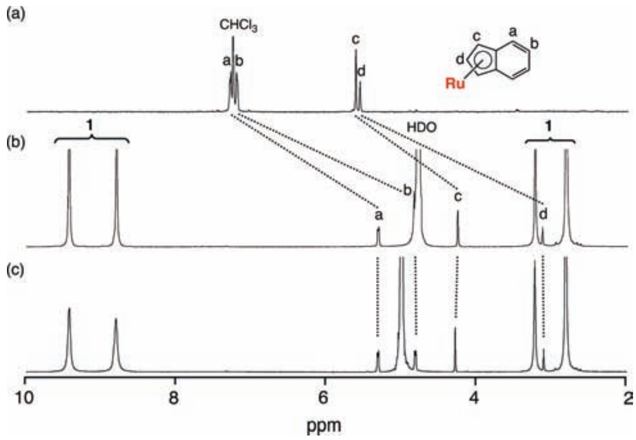


Figure 1. ^{1}H NMR spectra (500 MHz) of (a) ruthenium complex **2** in CDCl$_3$ at 300 K and (b, c) the inclusion complex **1**·**2** in D$_2$O at (b) 300 and (c) 278 K.

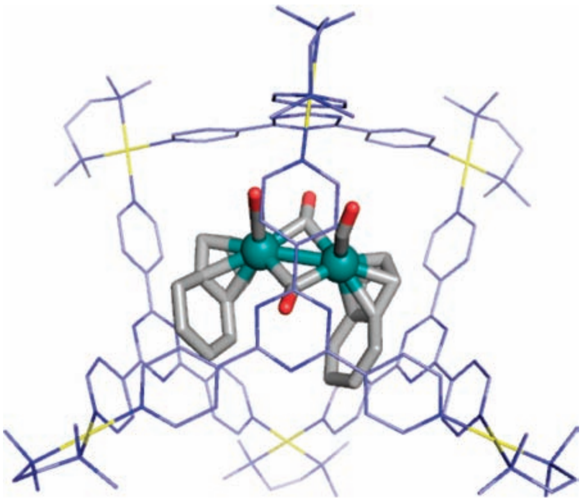


Figure 2. X-ray crystal structure of **1**·**2a**. For clarity, only one disordered position of **2a** is shown (Ru···Ru = 2.83 Å). See the SI for details.

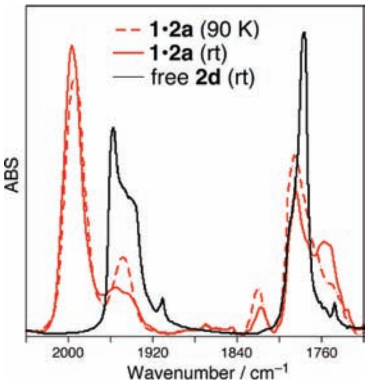


Figure 3. IR spectra of single crystals of the inclusion complex **1**·**2a** at 90 K and room temperature (rt) and free trans-bridged **2d** at rt.

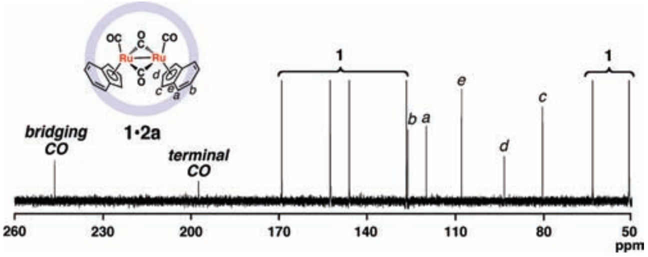
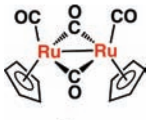


Figure 4. ^{13}C NMR spectrum (125 MHz, D$_2$O, 300 K) of inclusion complex **1**·**2a**.

Surprisingly, the intramolecular CO exchange process is suppressed in **1**·**2a**. Exchange between the terminal and bridging CO ligands can take place during equilibration between the cis isomers **2a** and **2b**. In the ^{13}C NMR spectrum, however, sharp and distinct terminal and bridging carbonyl signals were observed, indicating that ligand exchange did not occur on the NMR time scale (Figure 4). In contrast, carbonyl signals of free **2** could not be observed at room temperature because of the severe broadening from rapid ligand exchange [Figure S5 in the Supporting Information (SI)].[11]

The conversion between **2a** and **2b** requires very small changes in the volume and the structure, but the tight packing of **2a** in cage **1** precludes even such minor structural changes. When sterically less demanding [CpRu(CO)$_2$]$_2$ (**3**) was employed, we again observed that the complex was trapped in the cis-bridged configuration (**3a**).[12] However, complex **3a** is smaller than **2a**, and thus, the CO signals were broadened (and thus could not be observed) in the ^{13}C NMR spectrum as a result of rapid bridging−terminal CO exchange (Figure S7).



3a

In general, ruthenium complex **2** is photosensitive and decomposes within a few days under room light. However, encapsulated **2a** in the cage demonstrated enhanced photostability: no decomposition was observed over several months under room light. Homolytic cleavage of the Ru−Ru bond and CO dissociation (to give a mono-CO-bridged dimer) are the two main photochemical pathways for the decomposition of ruthenium dicarbonyl dimers,[5,6] but both were suppressed. Presumably, the tight encapsulation hampers an increase in the reaction volume and/or facilitates recombination processes.

In summary, we have trapped and stabilized cis-bridged dinuclear ruthenium complex **2a** noncovalently within coordination cage **1**. The snug fit of **2a** within the cavity of cage **1** geometrically fixes complex **2a** into the previously unobserved cis configuration and endows it with enhanced photostability. We believe that the encapsulation of dinuclear metal complexes will provide new or enhanced photochemical and photophysical properties that have previously been unobtainable or otherwise hidden because of rapid photodecomposition.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental procedures, physical properties, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) It should be noted that **2b** and **2c** are conformational isomers on the NMR timescale but can be distinguished by IR. See: Cotton, F. A.; Yagupsky, G. *Inorg. Chem.* **1967**, *6*, 15.

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(7) Host–guest charge-transfer absorption was observed at ∼530 nm (Figure S3).

(8) In the DOSY NMR analysis, the host and the guest signals in **1·2a** were observed at the same diffusion coefficient, $D = (1.6 \pm 0.3) \times 10^{-10}\ \mathrm{m}^2\ \mathrm{s}^{-1}$, indicating that **2a** was fully encapsulated and that free **2** did not exist in the solution (Figure S4).

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(10) Trans-bridged **2d** was characterized by X-ray diffraction analysis.

(11) For a ^{13}C NMR study of $[\mathrm{LRu(CO)_2}]_2$ complexes, see: Gansow, O. A.; Burke, A. R.; Vernon, W. D. *J. Am. Chem. Soc.* **1976**, *98*, 5817.

(12) The cis configuration was confirmed by IR spectroscopy (Figure S8).