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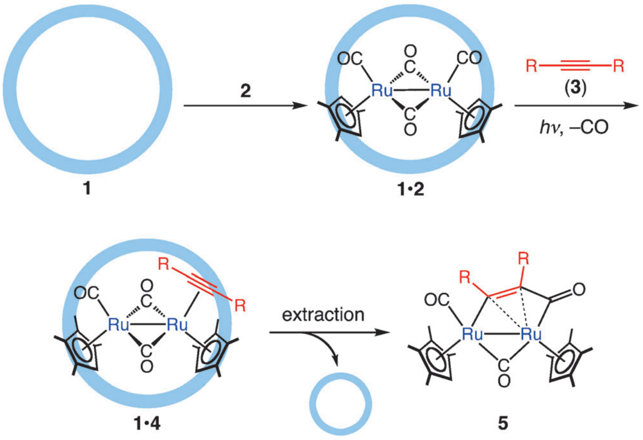
Host–Guest Systems

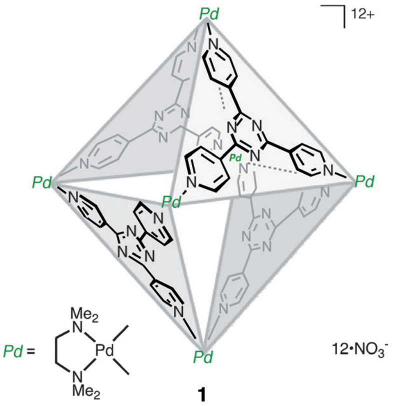
A Remarkable Organometallic Transformation on a Cage-Incarcerated Dinuclear Ruthenium Complex**

*Shinnosuke Horiuchi, Takashi Murase, and Makoto Fujita**

Multinuclear metal complexes promote organometallic transformations in a manner different from that of mononuclear complexes.[1] Although a variety of transformations on multinuclear metal centers have been reported, they are mostly thermal reactions and surprisingly, in contrast to the rich photochemistry of mononuclear complexes,[2] photochemical transformations on multinuclear metal complexes have been largely unexplored. This is because metal–metal bonds are in general photolabile and quite apt to undergo photocleavage prior to desired transformations across the multimetal centers.[3] Recently, we have shown that a photolabile Ru_2 dinuclear complex $[(indenyl)Ru(CO)_2]_2$ gains photostability toward ambient light through encapsulation in coordination cage **1**[4,5] because the Ru−Ru bond cleavage is suppressed by the cage effect.[6] We thus expect that cage **1** enables the photochemical transformation on the dinuclear center without Ru−Ru bond photocleavage. Herein we report that $[(Me_4Cp)Ru(CO)_2]_2$ (**2**; Cp = cyclopentadienyl) encapsulated in cage **1** undergoes photosubstitution of a CO ligand with alkyne **3**, without Ru−Ru bond cleavage, to form Ru–alkyne π complex **4** (Scheme 1). We show that this π complex is a cage-trapped metastable species and, when ejected from the cage, it is further converted to diruthenacyclopentenone framework **5** by intramolecular CO insertion.[7] The overall reaction provides the first example of a photochemical organometallic transformation of a Ru_2 dinuclear complex that occurs across the two metal centers.



Scheme 1. The overall reaction involves the inclusion of guest **2** by cage **1**, photosubstitution of a CO ligand with alkyne **3** on a Ru center, and the rearrangement of **4** into diruthenacyclopentenone **5** upon extraction from the cage.



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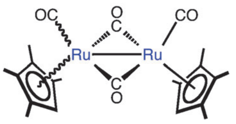

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3a: R = Et
3b: R = *n*Pr

Inclusion complex **1·2** was obtained by suspending ruthenium complex **2** in an aqueous solution of cage **1** in a similar manner to that described in our previous report.[6] After encapsulation, the ^1H NMR spectrum of **1·2** showed that the guest signals were significantly shifted upfield ($\Delta\delta$ up to −2.15 ppm) and, unlike the previous case, the host signals were split into six pairs of PyH_α and PyH_β signals (Py = 4-pyridyl), as confirmed by ^1H–^1H COSY NMR spectroscopy (Figure S2 in the Supporting Information). This splitting indicates the reduction of the cage symmetry from T_d to C_{2v}, which is in good agreement with the inclusion of the C_{2v}-symmetric cis isomer of **2**.[8] The symmetry reduction of the cage stems from the restricted motion of **2**, which is more tightly packed in the cavity than the previously used guest $[(indenyl)Ru(CO)_2]_2$. The terminal and bridging CO ligands of **2** were independently observed by ^{13}C NMR spectroscopy, thus indicating that their interconversion was suppressed in the cage (Figure S3 in the Supporting Information).[9]

The tight encapsulation and the cis configuration of **2** were clearly shown by X-ray crystallographic analysis (Figure 1). The Me_4Cp ligand of **2** and the triazine panel of **1** are within the distance necessary for π–π interaction (ca. 3.3 Å).[10] The oxygen atom of the bridging CO ligand is also close to the ligand of **1** (ca. 2.8 Å).[11] The steric demand of the Me_4Cp ligand is ideal for the snug fit of complex **2** in the cavity. With

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[*] S. Horiuchi, Dr. T. Murase, Prof. Dr. M. Fujita
Department of Applied Chemistry, School of Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
E-mail: mfujita@appchem.t.u-tokyo.ac.jp

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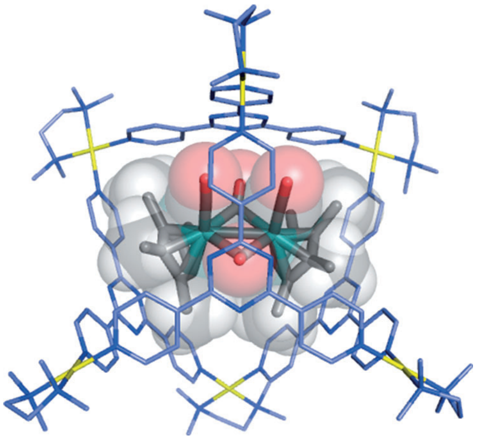


Figure 1. Crystal structure of **1·2**. H atoms, nitrate anions, and solvent molecules have been omitted for clarity. Cage **1** is shown with thin sticks, ruthenium complex **2** with thick sticks. A space-filling depiction of **2** is shown in the background. **1**: C light blue; N dark blue; Pd yellow; **2**: C gray; O red; Ru turquoise.

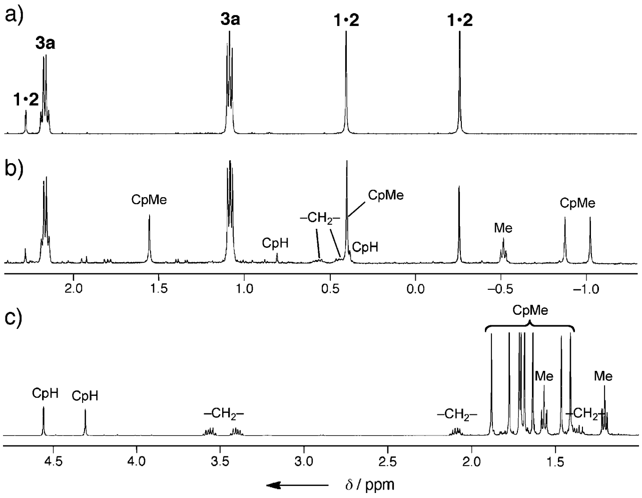


Figure 2. ^{1}H NMR spectra (500 MHz, 300 K) of a) a mixture of **1·2** and alkyne **3a** before irradiation (in D_2O), b) a reaction mixture after irradiation (in D_2O, signals of intermediate **4a** within cage **1** are assigned), and c) final product **5a** after extraction (in C_6D_6).

the Me_5Cp (Cp*) ligand, the Ru_2 complex was too bulky to be encapsulated. With the sterically less demanding Cp ligand, the Ru_2 complex was loosely bound by the cage, as revealed by the averaged host signals in the ^{1}H NMR spectrum.

The suppression of Ru–Ru bond cleavage by the tight encapsulation of **2** resulted in a remarkably enhanced photostability. No decomposition was observed over six months under ambient light, in sharp contrast to free **2**, which decomposed to oligomeric products within only two days. The sterically less bulky $[CpRu(CO)_2]_2$ did not gain sufficient photostability because of its loose encapsulation.

Within the cage, the Ru–Ru bond of **2** was even tolerant toward UV irradiation. Instead, the CO ligand was photodissociated to generate an unsaturated Ru center, which was trapped by an alkyne to form Ru–alkyne complex **4**. Thus, when complex **1·2** was irradiated with a high-pressure mercury lamp (< 400 nm) at 0 °C for 2 h in the presence of alkyne **3a** (3 equiv), Ru–alkyne complex **4a** was formed as a single product in 42 % yield (calculated from the NMR spectrum; Figure 2 a, b).[12] The ^{1}H NMR spectrum showed the signals of **3a** to be shifted upfield: CH_3CH$_2$- at −0.52 ppm ($\Delta\delta = -1.60$ ppm) and CH$_3$$CH_2$- at 0.45 and 0.57 ppm ($\Delta\delta = -1.71$ and −1.59 ppm; Figure 2 b). Alkyne **3a** is presumably η^2-coordinated to one of the two ruthenium centers and differentiates the two Me_4Cp ligands.

To our surprise, alkyne complex **4a** was not the final product in this reaction, but a reaction intermediate trapped by cage **1**. When extracted from the cage with CH_2Cl_2, **4a** immediately rearranged into diruthenacyclopentenone **5a** by intramolecular CO insertion.[13] The rearranged product **5a** was isolated by column chromatography on alumina and fully characterized by NMR and IR spectroscopy. In the ^{1}H NMR spectrum, the two ethyl substituents of alkyne **3a** are inequivalent (Figure 2 c), and two diastereotopic protons were observed for each methylene group. The C_1 symmetry of **5a** makes all the methyl groups on the two Me_4Cp ligands inequivalent, and eight singlet signals were observed around 1.4–1.9 ppm. The terminal, bridging, and ketonic carbonyl groups were clearly assigned both in the ^{13}C NMR and IR spectra (Figure S8 in the Supporting Information).

The rearranged structure of **5a** was confirmed by X-ray crystallographic analysis (Figure 3 a). The Ru1 atom was intramolecularly η^2-coordinated by the olefin moiety while the Ru2 atom was σ-coordinated by the olefinic carbon atom (C5).[13] The C4–C5 bond was considerably longer (1.4240(19) Å) than the average C=C bond (1.33 Å) because

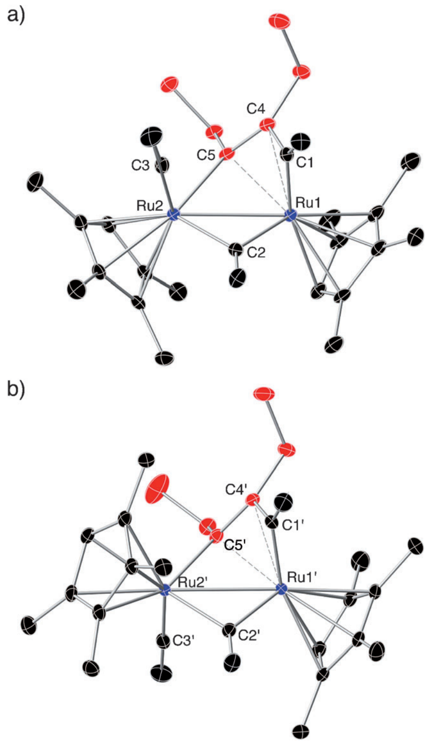
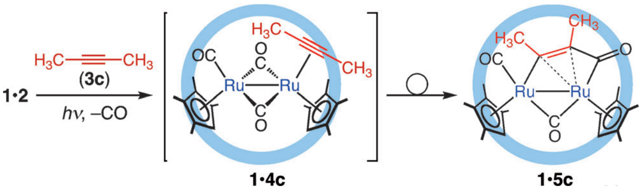


Figure 3. ORTEP drawings of a) cis isomer **5a** and b) trans isomer **5a'** (50 % probability). Hydrogen atoms and solvent molecules are omitted for clarity.

of the backdonation from the two metal centers through η^2 and σ coordination.

From the solution of **5a**, we unexpectedly obtained a single crystal of its trans isomer **5a′**, the molecular structure of which was also confirmed by X-ray crystallography (Figure 3b). The geometries around the diruthenacyclopentenone framework of **5a** and **5a′** are almost identical. In solution, only one set of signals was observed for the two isomers. Thus, **5a** and **5a′** are in rapid equilibrium in solution by intramolecular exchange between the bridging and terminal CO ligands as in free **2**.[8]

The steric bulk of alkyne **3** was crucial for trapping the reaction intermediate **4**. With 4-octyne (**3b**), alkyne complex **4b** was again trapped in the cavity. With sterically less demanding 2-butyne (**3c**), however, intermediate **4c** was not trapped and the rearranged product **5c** was directly formed in the cage (Scheme 2), presumably because of the loose packing of intermediate **4c**. Thus the efficient trapping of intermediates **4a** and **4b** is ascribed not to the electronic effect of the substrate but to the steric effect of the cage. In fact, force-field calculations indicate that the cage cavity reasonably encapsulated **5c**, but not **5a** or **5b** (Figure S13 in the Supporting Information).



Scheme 2. Direct formation of **5c** from **3c** within cage **1**.

In summary, we have revealed two remarkable cage effects in an organometallic transformation on a Ru_2 dinuclear metal complex. Firstly, a cage-incarcerated Ru_2 dinuclear complex gains remarkable photostability and undergoes CO/alkyne photosubstitution without Ru–Ru photocleavage to give a Ru–alkyne π complex. Secondly, the Ru–alkyne π complex is a cage-trapped reaction intermediate that is further converted by intramolecular CO insertion from the other Ru center to give a diruthenacyclopentenone framework. These transformations are usually unobservable because of the predominant fragmentation of the Ru–Ru bond by photocleavage. Thus the hydrophobic cavity of cage **1** is an effective tool to promote new reactions on dinuclear metal centers, and this is reminiscent of reactions in the pockets of metalloenzymes.

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