

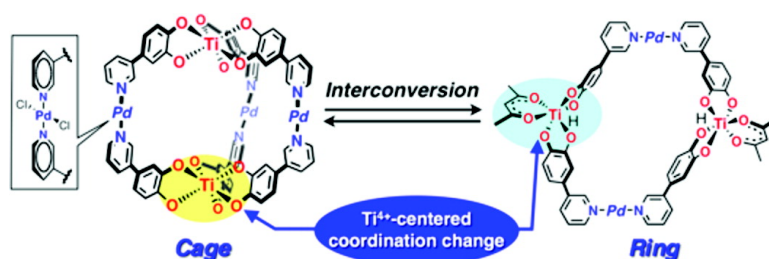
Communication

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Ti(IV)-Centered Dynamic Interconversion between Pd(II), Ti(IV)-Containing Ring and Cage Molecules

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Supramolecular coordination compounds with dynamic functions¹ have provided a series of mechanical devices^{1a} and containers with an inclusion/release control function.^{1h} Such unique functions are based on their structural changes between multistable states arising from the intrinsic, dynamic natures of metals, which are strongly influenced by the structures of metal ligands,^{1d,e} the component fractions,^{1b,c,g-i} photoexcitation,^{1f} and the oxidation state of metals.^{1a} So far, most of dynamic supramolecules have been achieved using soft metal ions with a normal coordination geometry. To construct multifunctional molecular devices, heterometal systems containing both hard and soft metal ions would have the potential to exhibit high site-selectivity and cooperativity in their structural changes and thereby novel molecular functions that are not seen in homonuclear metal complexes. Although a number of supermolecules with hard metal ions and their unique functions² have been reported so far, examples of dynamic supramolecular systems that allow an interconversion of their multistable states by a hard metal ion-centered coordination change are scarce.^{3,4} Herein, we report a novel Ti⁴⁺-catecholato complex, TiH₂(acac) (acac = acetylacetonato), formed from H₂I and TiO(acac)₂ in the presence of a weak base. This Ti⁴⁺ complex was successfully converted into [TiI₃]²⁻ with a stronger base. In addition, this conversion was found to take place reversibly by changing the basicity condition and the component fraction in solution. On the basis of this finding and the HSAB theory, we established an interconvertible system with multinuclear Pd(II), Ti(IV)-containing ring- and cage-shaped complexes (Figure 1).

In order to investigate dynamic natures of Ti⁴⁺ centers in detail, a ¹H NMR titration study of H₂I and TiO(acac)₂ in the presence of *n*-Bu₄NOH was conducted (Figure 1). Upon addition of TiO(acac)₂ to a mixture of H₂I and *n*-Bu₄NOH in DMF-*d*₇, a reaction mixture turned dark red immediately, and its ¹H NMR spectrum showed the formation of two distinct species (Figure 2b). The color of the mixture gradually changed to orange in 20 h, and finally, the signals for one species completely disappeared and only one set of signals for the other species remained (Figure 2d). In either case, the proton signals of the catechol moiety in **1**, H^{*e-g*}, were shifted significantly upfield ($\Delta\delta = -0.26$ to -0.79 ppm), but those of the pyridyl moiety did not. This result indicates that both of the two species include Ti⁴⁺-catecholato complexes. In ESI-TOF mass measurements of the mixture at specified time intervals, two prominent signals were observed at *m/z* = 845.4 and 516.8 for [TiI₃·*n*-Bu₄N]⁻ and [TiH₂(acac)]⁺, respectively, immediately after mixing all components, whereas only a signal for [TiI₃·*n*-Bu₄N]⁻ was observed after 20 h (Figure S3). These results exhibited that a novel Ti⁴⁺ species bound by one acac and two

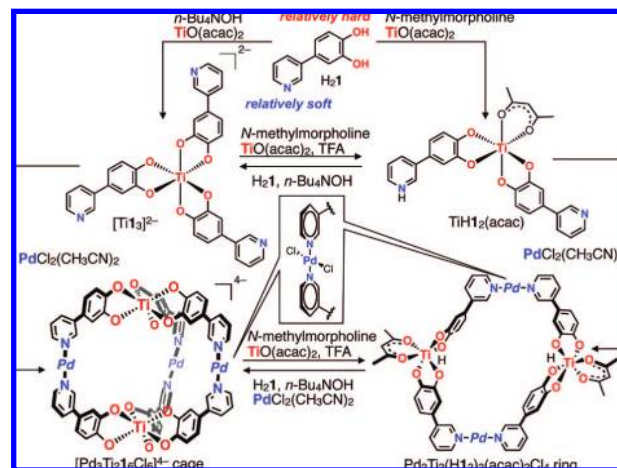


Figure 1. Formation of Ti⁴⁺ and heteronuclear Pd²⁺-Ti⁴⁺ complexes.

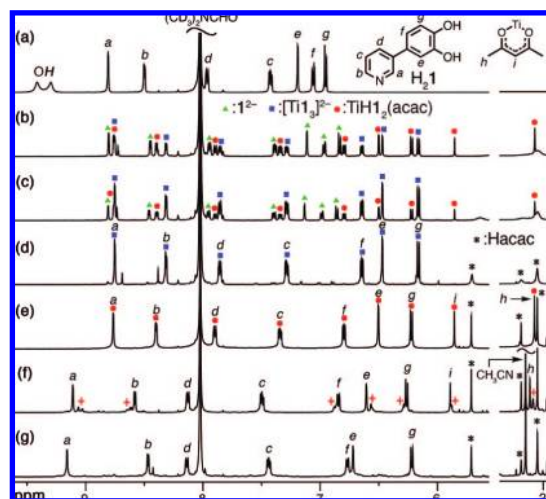


Figure 2. ¹H NMR spectra (500 MHz, DMF-*d*₇, 293 K, [H₂I] = 15 mM): (a) H₂I; (b–d) a 1:0.43:0.67 mixture of H₂I, TiO(acac)₂, and *n*-Bu₄NOH: (b) 5 min; (c) 1 h; (d) 20 h ([TiI₃]²⁻); (e) a 4:4:3 mixture of H₂I, TiO(acac)₂, and *N*-methylmorpholine (TiH₂(acac)); (f) Pd–Ti ring ([Pd₂Ti₂(HI₂)₂(acac)₂Cl₄]²⁺); (g) Pd–Ti cage ([Pd₃Ti₂(HI₂)₂(acac)₂Cl₆]⁴⁺). Signals with a + mark in (f) are assigned to those of a cyclic 3:3 complex [Pd₃Ti₃(HI₂)₃(acac)₃Cl₆]³⁺ (see Figures S13 and S14).

catecholato ligands was thus generated in a kinetically controlled way prior to the formation of a [TiI₃]²⁻ species.

The Ti⁴⁺ complex as a kinetic intermediate was also detected in its ESI-TOF mass measurement as [TiH₂(acac)]⁺ at *m/z* = 519.1 (Figure S4). On the basis of this observation, we deduced that the intermediate species would be a neutral TiH₂(acac) with

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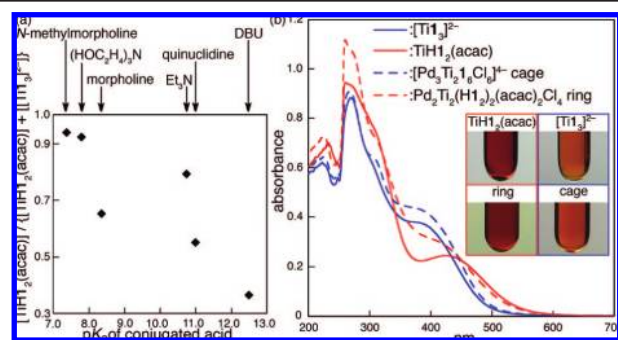


Figure 3. (a) Plot of the molar fractions of $\text{TiH}_2(\text{acac})$ in the mixture against the $\text{p}K_a$ values of the conjugated acids; (b) UV-vis spectra of Ti^{4+} and Pd^{2+} - Ti^{4+} complexes of **1** ($l = 1$ mm, $[\text{H}_2\text{I}] = 0.5$ mM, 293 K). Inset: photographs of DMF solutions of the complexes.

a protonated pyridine ring. To confirm this, we performed complexation using a weaker base, *N*-methylmorpholine, instead of *n*- Bu_4NOH (Figure 1). The ^1H NMR spectrum was identical to that of the intermediate (Figure 2e). A series of amine bases was examined to clarify the relationship between the degree of basicity and the molar fractions of the two species. As shown in Figure 3a, the molar fraction of the generated kinetic intermediate is potentially correlated with the $\text{p}K_a$ values of the conjugated acids.⁵ It should be noted that the ^1H NMR signals of the intermediate species remained nearly unaffected by these bases, whereas those of anionic $[\text{Ti}_3]^{2-}$ complex were actually affected by the protonated amine bases as counteranions (Figure S10), suggesting that the kinetic intermediate has a neutral $\text{TiH}_2(\text{acac})$ structure. Such $\text{TiH}_2(\text{acac})$ species were also formed from various catechol derivatives (H_2L), such as catechol and 4-*tert*-butylcatechol (**3**), using *N*-methylmorpholine as a base (Figures S1, S2, S5, and S6).^{6,7}

Furthermore, the coordinating acac in the $\text{TiH}_2(\text{acac})$ was also characterized by IR spectroscopy of a solid sample prepared by removal of volatile portions: 1525 ($\text{C}=\text{C}$) and 1558 cm^{-1} ($\text{C}=\text{O}$) (Figure S9). Its UV-vis spectrum in DMF showed a characteristic LMCT band at 424 nm ($\epsilon = 23\,000\ \text{M}^{-1}\ \text{cm}^{-1}$) that is red-shifted compared with a DMF solution of $[\text{Ti}_3]^{2-}$ ($\lambda_{\text{max}} = 380$ nm, $\epsilon = 9700\ \text{M}^{-1}\ \text{cm}^{-1}$).

Since the formation of the two distinct Ti^{4+} complexes depends on the component fraction and the basicity condition of the media, these complexes are interconvertible by changing these factors. When $\text{TiO}(\text{acac})_2$ and TFA were added to a solution of $[\text{Ti}_3]^{2-}$, $\text{TiH}_2(\text{acac})$ was produced after 12 h (Figure S15). Subsequently, when **1** and *n*- Bu_4NOH were added to the solution of $\text{TiH}_2(\text{acac})$, $[\text{Ti}_3]^{2-}$ was quantitatively regenerated.

In the next step, the heteronuclear metal complexation of the coordinatively free pyridyl groups of the Ti^{4+} complexes was examined with softer, square-planar-coordinating Pd^{2+} ions. In the ^1H NMR spectrum of a 1:1 mixture of $\text{TiH}_2(\text{acac})$ with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$, the pyridyl proton signals, H^{a-d} , were shifted downfield ($\Delta\delta = 0.15$ – 0.35 ppm), whereas those of catecholato protons, H^{e-f} , were shifted only slightly (Figure 2f). This indicates that site-selective complexation with Pd^{2+} took place at pyridyl nitrogens. The ESI-TOF mass spectrum of the mixture showed a signal for $[\text{Pd}_2\text{Ti}_2(\text{H}_2\text{O})_2(\text{acac})_2\text{Cl}_6]^+$ at $m/z = 1357.4$, indicating the formation of a cyclic 2:2 complex (Figure S8). The complexation of $[\text{Ti}_3]^{2-}$ with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ also showed a highly symmetric ^1H NMR spectrum, in which pyridyl proton signals were shifted downfield ($\Delta\delta = 0.15$ – 0.41 ppm; Figure 2g). The ESI-TOF mass spectrum of its potassium salt showed a signal at $m/z = 1934.5$ for $[\text{Pd}_3\text{Ti}_2(\text{H}_2\text{O})_2\text{Cl}_6\text{K}_5]^+$ consisting of two $[\text{Ti}_3]^{2-}$ and three PdCl_2 units to form a cage-shaped complex (Figure S7). The LMCT

bands for these Pd^{2+} - Ti^{4+} complexes were found in the same region as those of the original Ti^{4+} complexes (Figure 3b), indicating that the coordination geometries around the Ti^{4+} centers in the resulting complexes remained unchanged after Pd^{2+} complexation.

A *trans* configuration of the square-planar Pd^{2+} center in the complexes was suggested by the selection rule for an IR-active vibration. In the far-IR region of the ring-shaped complex, only a peak characteristic for asymmetric stretching vibration was observed for $\text{Pd}-\text{Cl}$ and $\text{Pd}-\text{N}(\text{py})$ at 351 and 313 cm^{-1} , respectively (Figure S18). A similar result was obtained for the cage-shaped complex: 353 ($\text{Pd}-\text{Cl}$) and 325 cm^{-1} ($\text{Pd}-\text{N}(\text{py})$).

The molecular modeling study was performed for the ring and cage complexes. A $\Delta\Delta$ (or $\Delta\Lambda$) isomer arising from the two $\text{Ti}(\text{IV})$ centers was found to be more stable for both complexes. As for the ring complex, among several possible isomers, a structure shown in Figure 1 was found the most likely structure (Figure S21).

Finally, the interconversion between the ring and cage was achieved by Ti^{4+} -centered coordination changes similarly to the interconversion between $[\text{Ti}_3]^{2-}$ and $\text{TiH}_2(\text{acac})$ (Figure S16). The interconversion was complete within 12 h in either direction.

In conclusion, an interconvertible molecular system was achieved between heteronuclear $\text{Pd}(\text{II})$, $\text{Ti}(\text{IV})$ -containing ring- and cage-shaped complexes. This quantitative interconversion is triggered by Ti^{4+} -centered coordination changes between a $\text{Ti}(\text{catecholato})_3$ and a newly established $\text{TiH}(\text{catecholato})_2(\text{acac})$ structures. Studies on their functions of structure-dependent molecular recognition and inclusion/release control are currently underway.

Acknowledgment. We thank JASCO Co., Ltd., for measuring the far-IR spectra of the $\text{Pd}(\text{II})$, $\text{Ti}(\text{IV})$ -containing complexes. This work was supported by Grants-in-Aid from MEXT of Japan and the Global COE Program for Chemistry Innovation.

Supporting Information Available: Synthetic procedures, ^1H NMR, ESI-TOF mass, and IR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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