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研究課題名(和文) Selective Isomerization and Transformation of Aromatic Hydrocarbons by Using Polynuclear Transition Metal Hydride Complexes

研究課題名(英文) Selective Isomerization and Transformation of Aromatic Hydrocarbons by Using Polynuclear Transition Metal Hydride Complexes

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研究成果の概要(和文)：遷移金属による炭素-炭素(C-C)結合の切断反応は、石油やバイオマスなどの天然資源からガソリンや基礎化学品などを作る際に極めて重要な反応である。しかし、C-C結合は非常に安定で、様々な反応条件下で反応性に乏しい。今回我々は、常温下で三核チタンポリヒドリド錯体がベンゼンのC-C結合の切断と骨格変換反応を起こすことを見出した。反応機構に関する理論計算の結果、3つのチタン金属が互いに協力し合って炭素-炭素結合の切断に働いていることを明らかにした。我々の結果は、多核チタンヒドリド錯体が安定な芳香環活性化のためのユニークなプラットフォームとして機能しうることを示唆している。

研究成果の概要(英文)：The cleavage of carbon-carbon (C-C) bonds by transition metals is of fundamental interest. Here we found that the reaction of a trinuclear titanium polyhydride complex with benzene, in which benzene molecule was transformed to a methylcyclopentenyl unit through the cleavage and rearrangement of the benzene skeleton at ambient temperature. The DFT calculation was carried out to clarify the reaction mechanism, which indicated that this transformation was accomplished through the cooperation of the multiple Ti-H sites in a trinuclear titanium framework. Besides, we found the titanium hydride complex could show special reactivities toward other aromatics. This work demonstrated that multimetallic titanium hydrides can serve as a unique platform for the activation of aromatic molecules, offering new opportunities for the transformation and functionalization of inactive aromatics.

研究分野：化学

キーワード：C-C bond cleavage titanium polyhydride aromatic hydrocarbons

1. 研究開始当初の背景

The cleavage of carbon-carbon (C-C) bonds by transition metals is of great fundamental interest and plays an important role in the production of fuels and chemicals from natural resources such as petroleum and biomass. Generally, C-C bonds are stable and difficult to break under ordinary conditions. Among the most robust C-C bonds is the aromatic carbon skeleton of benzene. Some micro-organisms are known to degrade aromatic compounds at ambient conditions by using enzymes. In the industrial naphtha hydrocracking process, a benzene ring could be transformed to methylcyclopentane and acyclic saturated hydrocarbons through C-C bond cleavage and rearrangement on the surface of solid catalysts at high temperatures. However, these heterogeneous reactions generally lack selectivity, and the mechanistic details are not clear. For this reason, much effort has been devoted to developing transition-metal complexes that can be inserted into C-C bonds in homogeneous media, which might be used as catalysts with high selectivity and reactivity.

Some molecular transition metal complexes have been reported to cleave C-C bonds in a selective fashion under special circumstances, such as relief of ring strain, formation of an aromatic system, chelation-assisted cyclometallation, and β -carbon elimination. However, neither C-C bond cleavage nor further transformation with skeletal rearrangement of benzene molecule by a transition metal complex has been explored to date. At the same time, current studies have mainly focused on the reactions of mononuclear transition metal complexes with aromatic compounds, the information on the reaction of multimetallic complexes with benzene remained scarce. In view of the fact that the activation of aromatic compounds on industrial solid catalysts might rely on the cooperation of multiple metal sites, the investigation of the reactivity of multimetallic complexes with benzene is of great interest and importance.

2. 研究の目的

This research aims to investigate the reactions of benzene with multimetallic hydride complexes, expecting C-C bond cleavage and further transformation. The reaction mechanisms will be clarified through experimental and computational analysis. Based on the obtained results, selective isomerization and transformation of aromatic hydrocarbons by multimetallic hydride complexes will be explored.

3. 研究の方法

The research starts with the investigation of reaction of benzene and trinuclear Ti hydride complex, which was proved to be extremely active and could cleave and hydrogenated inert dinitrogen molecule. The reaction mechanisms will be clarified by isolation of intermediates and DFT calculation. Then the reaction will be extended to other substrates to check the universality of reactivity. Effect of ligands and metals will be investigated. Further exploration of the reactions to liberate the isomerized carbon units in complexes will be conducted through hydrogenolysis and addition of simple hydride reagents respectively.

4. 研究成果

Here we report the reaction of a trinuclear titanium polyhydride complex (**1**) with benzene, which led to formation complex **2** with a methylcyclopentenyl unit [CH₃C₅H₄] through the cleavage and rearrangement of the aromatic carbon skeleton at ambient temperature (Fig. 1). The ¹H, ¹³C nuclear magnetic resonance (NMR), and X-ray crystallographic confirmed the product and transformation. When ¹³C-enriched benzene (¹³C₆H₆) was used to react with **1** under the similar conditions, the corresponding ¹³C-enriched methylcyclopentenyl complex was obtained, confirming that the methylcyclopentenyl unit in **2** was indeed derived from benzene. When **2** was heated at 100 °C for two days in a sealed Schlenk tube, the insertion of a Ti atom into a C-C bond of the methylcyclopentenyl ring took place to give a titanacycle product **5** as a major product, accompanied by liberation of H₂.

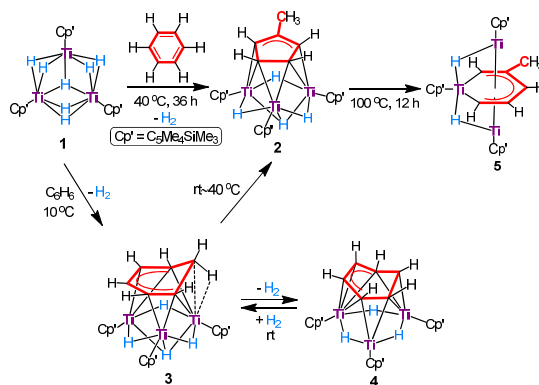


Figure 1

In order to isolate a possible reaction intermediate, we kept a benzene solution of **1** at a lower temperature (10 °C) for two days. A new compound **4** was isolated and characterized by NMR spectroscopy and X-ray diffraction. **4** decomposed slowly to unidentified products at room temperature. The direct transformation of **4** to **2** was not observed. When **4** was exposed to an atmosphere

of H₂, the immediate formation of complex **3** was observed, in which the [C₆H₆]⁴⁻ unit in **4** was formally hydrogenated (or protonated) to [C₆H₇]³⁻. When kept at room temperature or 40 °C, **3** transformed quantitatively to the methylcyclopentenyl [MeC₅H₄]³⁻ complex **2** through ring contraction of the [C₆H₇]³⁻ unit. Monitoring the reaction of **1** with benzene-*d*₆ (C₆D₆) at 22 °C by ¹H NMR spectroscopy, we found that with the decrease of **1**, gradual formation of **2-HD** was observed (Fig. 2). In this process, simultaneous formation of two species assignable to **3-HD** and **4-HD** was also observed. After 78 h, **3-HD**, **4-HD** and **1** all disappeared to yield **2-HD** almost quantitatively. These suggest that **3** may be first formed by the reductive hydrogenation of benzene by the heptahydride complex **1** through H₂ elimination and hydride transfer. There exists an equilibrium between **3** and **4** through dehydrogenation and rehydrogenation. The isomerization (ring contraction) of the [C₆H₇] unit in **3** would finally yield the methylcyclopentenyl complex **2**.

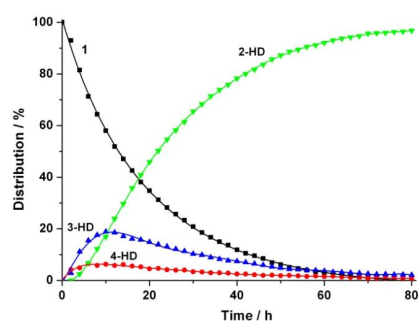


Figure 2

The mechanistic details of the carbon-carbon bond cleavage and skeleton rearrangement of benzene over a multinuclear framework was analysed by DFT calculation. The LUMO of **1** matches well with the HOMO of benzene, thus enabling the coordination of benzene to the Ti(IV) atom of the metal hydride cluster to initiate the reaction. The subsequent release of one molecule of H₂ and the hydrometallation of the coordinated C₆H₆ unit affords **3**. Repeated C-C and C-H bond cleavage and formation in the C₆H₇ moiety, accompanied by redox of the titanium atoms and the rearrangements of the hydride ligands, yield the ring-contraction product **2**. The analogous C-C bond cleavage, C-H bond formation and metal framework rearrangement afford the metallacycle product **5**. The facile redox of the titanium atoms and the cooperation of the multiple metal hydrides have played an essential role in these transformations.

Besides, we also examined the reaction of **1** with other substrates, such as toluene. We

observed similar transformation and successfully isolated and characterized the intermediate which could be viewed as an analogue of **3** formed in the reaction of **1** with benzene. Other trial of complex **1** with fused ring aromatics, such as naphthalene and anthracene, was not successful.

To liberate the carbon unit from the complexes, hydrogenolysis reactions of **2** with hydrogen gas and hydride reagents have been conducted. However, these trials encountered unsuccessful and the reactions of complex **2** with hydrogen or hydride reagents were proved to be difficult. Further efforts should be directed to the transformation of aromatics with other multinuclear hydride complexes to enable a catalytic cycle. On the other hand, when complex **2** was treated with hydrochloric acid, methylcyclopentene was obtained selectively.

Our findings demonstrate that multinuclear titanium hydrides can serve as a unique platform for the activation of aromatic molecules, and may help design and construct new catalysts for the transformation of inactive aromatics.

Some of these results have been published in *Nature* and presented in conferences. Manuscripts concerning reactions with aromatic substrates are in preparation.

5. 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

[雑誌論文](計 1 件)

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〔図書〕(計 件)

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〔その他〕
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