

Carbon–carbon bond cleavage and rearrangement of benzene by a trinuclear titanium hydride

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The cleavage of carbon–carbon (C–C) bonds by transition metals is of great interest, especially as this transformation can be used to produce fuels and other industrially important chemicals from natural resources such as petroleum and biomass. Carbon–carbon bonds are quite stable and are consequently unreactive under many reaction conditions. In the industrial naphtha hydrocracking process, the aromatic carbon skeleton of benzene can be transformed to methylcyclopentane and acyclic saturated hydrocarbons through C–C bond cleavage and rearrangement on the surfaces of solid catalysts^{1–6}. However, these chemical transformations usually require high temperatures and are fairly non-selective. Microorganisms can degrade aromatic compounds under ambient conditions, but the mechanistic details are not known and are difficult to mimic⁷. Several transition metal complexes have been reported to cleave C–C bonds in a selective fashion in special circumstances, such as relief of ring strain, formation of an aromatic system, chelation-assisted cyclometallation and β -carbon elimination^{8–15}. However, the cleavage of benzene by a transition metal complex has not been reported^{16–19}. Here we report the C–C bond cleavage and rearrangement of benzene by a trinuclear titanium polyhydride complex. The benzene ring is transformed sequentially to a methylcyclopentenyl and a 2-methylpentenyl species through the cleavage of the aromatic carbon skeleton at the multi-titanium sites. Our results suggest that multinuclear titanium hydrides could serve as a unique platform for the activation of aromatic molecules, and may facilitate the design of new catalysts for the transformation of inactive aromatics.

The investigation of the reactivity of multimetallic complexes with benzene is of great interest and importance, in view of the fact that the activation of aromatic compounds on industrial solid catalysts might rely on the cooperation of multiple metal sites^{1–6,20,21}. In our recent studies on multinuclear rare-earth and transition metal hydride complexes, we found that the multiple metal–hydride sites could have unique synergistic effects on the activation of small molecules such as CO, CO₂, H₂ and N₂ (refs 22–26). In particular, the unusually high reactivity of the trinuclear titanium heptahydride complex [(C₅Me₄SiMe₃)Ti]₃(μ -H)₆ (**1**)²⁶ motivated us to examine carefully whether the hydride cluster could activate other chemically inactive molecules such as benzene.

When a benzene solution of **1** was left to stand at room temperature (22 °C) under an argon atmosphere for a few days, a methylcyclopentenyl complex [(C₅Me₄SiMe₃)Ti]₃(C₅H₄Me)(μ -H)₄ (**2**) was formed as dark green crystals. Complex **2** could be obtained almost quantitatively, when a benzene solution of **1** was kept at 40 °C for 36 h (Fig. 1a). An X-ray diffraction study revealed that **2** contains one methylcyclopentenyl (MeC₅H₄) moiety, three (C₅Me₄SiMe₃)Ti units and four hydride ligands (Fig. 1a). The methylcyclopentenyl moiety formally bears three negative charges, one being distributed among C39, C40 and C41 to form an allylic moiety and two being placed on C37 and C38. Four (C37, C38, C39, C41) of the five ring carbon atoms in the [MeC₅H₄]³⁻ unit are μ - η^4 -bonded to the Ti₃ triangle.

Remarkably, here a benzene molecule was partly hydrogenated and ring-contracted to a five-membered ring species, [MeC₅H₄]. This reaction

required breaking a robust aromatic C–C bond of benzene and making a new C–C bond. In this transformation, three of the seven hydride ligands in **1** were consumed, one being transferred to benzene and two released as H₂ by donating two electrons, thus affording the trianionic [MeC₅H₄]³⁻ species. The formal oxidation state of the Ti atoms in **1** and **2** remained unchanged; both complexes formally contain one Ti(IV) and two Ti(III) atoms²⁶.

When ¹³C-enriched benzene ¹³C₆H₆ was used to react with **1** under similar conditions, the corresponding ¹³C-enriched methylcyclopentenyl complex, [(C₅Me₄SiMe₃)Ti]₃(¹³C₅H₄¹³CH₃)(μ -H)₄ (**2**-¹³C), was obtained (Supplementary Information), confirming that the methylcyclopentenyl unit in **2** was indeed derived from benzene. The reaction of **1** with benzene-*d*₆ (C₆D₆) afforded [(C₅Me₄SiMe₃)Ti]₃[C₅Z₄CZ₃](μ -Z)₄ (Z = H_{0.7-0.5}D_{0.3-0.5}) (**2**-HD), in which H and D atoms are randomly distributed between the methylcyclopentenyl unit and the titanium framework as shown by ¹H and ²H NMR spectroscopy.

To isolate a possible reaction intermediate, we kept a benzene solution of **1** at a lower temperature (10 °C) for about two days. Evaporation of the solvent under vacuum yielded dark-green solids, which appeared to be a mixture of **2** (25%) and a new compound, [(C₅Me₄SiMe₃)Ti]₃(μ - η^6 -C₆H₆)(μ -H)₃ (**4**) (75%), as shown by ¹H NMR spectroscopy. Although complete separation of **2** and **4** was difficult, a single crystal of **4** suitable for X-ray diffraction studies was obtained by recrystallization in tetrahydrofuran (THF). We found that **4** is formally composed of a tetra-anionic [C₆H₆]⁴⁻ moiety and a tetra-cationic titanium trihydride unit, [Cp'₃Ti₃H₃]⁴⁺ (Fig. 1a). The [C₆H₆] unit is μ - η^6 -bonded to the Ti₃ framework. The ¹H NMR spectrum of **4** exhibited a singlet at a chemical shift of δ = 4.88 p.p.m. (tetramethylsilane reference) for the six protons of the [C₆H₆] unit in a temperature range of 22 °C to -80 °C, showing that the structure is highly fluxional.

Complex **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 in THF-*d*₈, the immediate formation of another new compound assignable to [(C₅Me₄SiMe₃)Ti]₃(C₆H₇)(μ -H)₄ (**3**) was observed (Supplementary Information; see also **6** in Fig. 2, and below). In this reaction, the [C₆H₆]⁴⁻ unit in **4** was formally hydrogenated (or protonated) to [C₆H₇]³⁻.

When kept at 40 °C for about 3 h, **3** was transformed quantitatively to the methylcyclopentenyl [MeC₅H₄]³⁻ complex **2** through ring contraction of the [C₆H₇]³⁻ unit (Fig. 1a). This transformation occurred even at room temperature, albeit slower. Kinetic studies on the transformation of **3** to **2** revealed the activation parameters of $\Delta H^\ddagger = 21.7(6)$ kcal mol⁻¹ and $\Delta S^\ddagger = -4.7(19)$ entropy units (Supplementary Information). The entropy of activation is in agreement with a unimolecular process. In the absence of H₂, **3** rapidly changed to **4** by release of H₂, demonstrating that **3** and **4** are easily interconvertible through hydrogenation/dehydrogenation.

To gain more information on the reaction process, we monitored the reaction of **1** with benzene-*d*₆ (C₆D₆) at 22 °C by ¹H NMR spectroscopy. With the decrease of **1**, gradual formation of **2**-HD was observed (Fig. 1b). In this process, simultaneous formation of two species assignable

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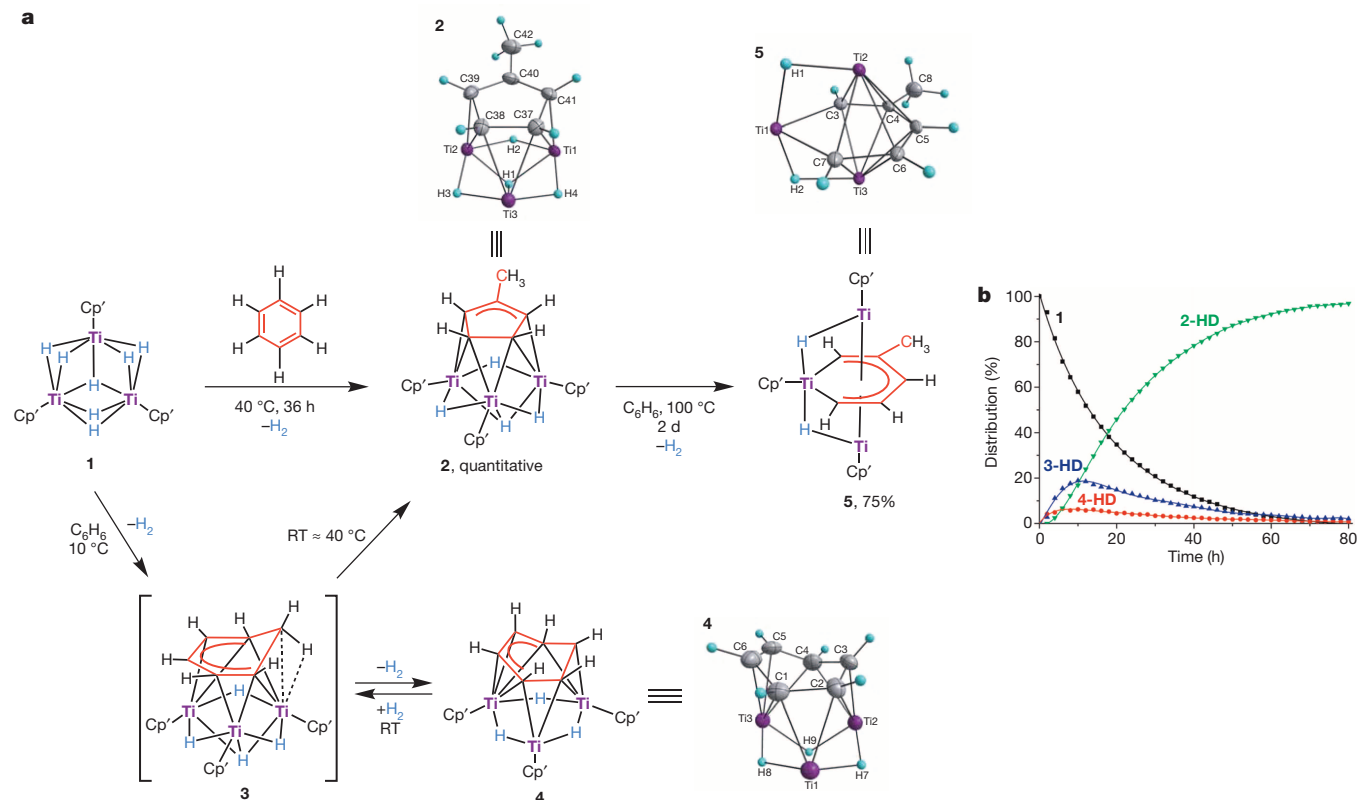


Figure 1 | Reactions of a trinuclear titanium heptahydride complex (**1**) with benzene and benzene- d_6 . **a**, Reaction of **1** with benzene ($\text{Cp}' = \text{C}_5\text{Me}_4\text{SiMe}_3$). The X-ray core structures of **2**, **4** and **5** are shown as ball and stick diagrams

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.

The above experimental results suggest that **3** may be first formed by the reductive hydrogenation of benzene by the heptahydride complex **1** through hydride transfer and H_2 elimination (Fig. 1a). There is an equilibrium between **3** and **4** through dehydrogenation and rehydrogenation. The isomerization (ring contraction) of the $[\text{C}_6\text{H}_7]$ unit in **3** would finally yield the methylcyclopentenyl complex **2**.

When **2** was heated at 100°C for two days in a sealed Schlenk tube, insertion of a Ti atom into a C–C bond of the methylcyclopentenyl ring took place, yielding a titanacycle product, $[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Ti}]_3[\mu\text{-}\eta^2, \eta^5, \eta^5\text{-CHC(Me)(CH}_3\text{)}](\mu\text{-H})_2$ (**5**), as a major product (about 75%) (Fig. 1a). This transformation was accompanied by liberation of H_2 . Heating $2\text{-}^{13}\text{C}$ under the same conditions (in benzene) afforded the corresponding

(Cp' ligands omitted for clarity). Me, methyl. **b**, Conversion versus time for the reaction of **1** with benzene- d_6 at 22°C . The solid lines are interpolations.

^{13}C -enriched complex, $5\text{-}^{13}\text{C}$, suggesting that this rearrangement should be a unimolecular process. Complex **5** could formally be viewed as a combination of a penta-anionic 2-methylpentenyl group, $[\text{CHC(Me)(CH}_3\text{)}]^{5-}$, and a penta-cationic titanium dihydride unit, $[(\text{C}_5\text{Me}_4\text{SiMe}_3)_3\text{Ti}_3\text{H}_2]^{5+}$. An X-ray diffraction study established that one $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Ti}$ unit is incorporated into the 2-methylpentenyl framework to form a planar, six-membered titanacycle. Each side of the metallacycle plane is η^5 -bonded to a $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Ti}$ unit, leading to formation of a double stacker structure. There are two hydride ligands in **5**, each bridging the Ti atom in the metallacycle and one Ti atom outside of the metallacycle.

For comparison, we also examined the reaction of **1** with toluene. When a toluene solution of **1** was kept at 20°C for 42 h, the partial hydrogenation of toluene took place to give $[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Ti}]_3(\text{C}_6\text{H}_6\text{Me})(\mu\text{-H})_4$ (**6**), which contains a $[\text{C}_6\text{H}_6\text{Me}]^{3-}$ unit and could be viewed as an analogue

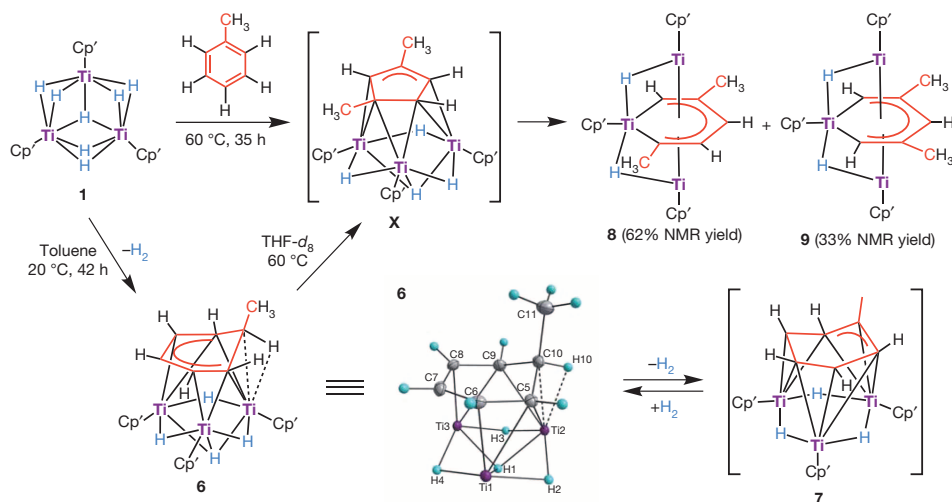


Figure 2 | Reaction of complex **1** with toluene. The X-ray core structure of **6** is shown as a ball and stick diagram (Cp' ligands omitted for clarity).

of **3** formed in the reaction of **1** with benzene (Fig. 2; see also Fig. 1a). A single crystal of **6** suitable for X-ray diffraction studies was obtained by recrystallization under an atmosphere of H₂ in hexane. It was revealed that there is an agostic interaction between a C–H bond in the C₆H₆Me unit, which is formed by hydrogenation of toluene at the *ipso*-position, and a Ti atom (Ti2) (Ti2–C10: 2.326(3) Å; Ti2–H10: 2.11(3) Å). There are four hydride ligands in **6**, one capping the Ti₃ triangle in a μ₃-fashion and three bridging the Ti··Ti sides in a μ₂-mode, analogously to complex **2** (Figs 2 and 1a). In agreement with the solid structure, the *ipso*-proton in the [C₆H₆Me] unit in **6** exhibited a singlet at a high field δ = –2.23 p.p.m. in the ¹H NMR spectrum, showing that an agostic Ti··H interaction remained in solution. The ¹³C-enriched analogue **6**-¹³C, prepared by the reaction of **1** with ¹³C-enriched toluene (¹³C₆H₅¹³CH₃), showed a doublet at δ = –2.23 p.p.m. with a relatively small ¹³C–¹H coupling constant (J_{C–H} = 108 Hz) in the ¹H NMR spectrum, thus providing further proof for the presence of an agostic Ti··H interaction (for comparison, normally J_{C–H} = 120–130 Hz; ref. 27).

In the absence of H₂, the dehydrogenation of **6** took place rapidly to give [(C₅Me₄SiMe₃)Ti]₃(C₆H₅Me)(μ-H)₃ (**7**) (Fig. 2), an analogue of **4** formed in the case of benzene. When **6** (or **1** plus toluene) was heated in a THF-*d*₈ solution at 60 °C for 36 h, the six-membered ring metallocycle products [(C₅Me₄SiMe₃)Ti]₃[μ-η²,η⁵,η⁵-CHC(Me)(CH)₂C(Me)](μ-H)₂ (**8**) (62% NMR yield) and [(C₅Me₄SiMe₃)Ti]₃[μ-η²,η⁵,η⁵-CHC(Me)(CH)C(Me)CH](μ-H)₂ (**9**) (33% NMR yield), which are analogues of **5** formed in the case of benzene, were obtained. The formation of the two regioisomers **8** and **9** suggests that a dimethylcyclopentenyl species such as **X** (an analogue of **2**; Fig. 2) should be an intermediate in this reaction. But in contrast to the reaction of benzene, such a five-membered ring intermediate was not observed in the case of toluene (at either 60 °C or lower temperatures), possibly because of its instability caused by the steric hindrance of the methyl groups on the cyclopentenyl ring.

Obviously, the reactions of the hydride cluster **1** with benzene and toluene involved various events, including C = C double-bond hydro-metallation, H₂ release, and C–H and C–C bond cleavage and formation. It is certainly due to the cooperation of the multiple Ti–H sites that all of these different events could be accomplished at once, although the mechanistic details are subject to further studies. It is also worth noting that the C–C bond cleavage of cyclic alkenes such as cyclopentadiene and cyclohexene has been successfully achieved by using multimetallic ruthenium hydride and carbonyl complexes^{28,29}, but the breaking of a benzene ring did not take place under similar conditions³⁰. The present sequential transformation of benzene to **2** and **5** by the hydride cluster **1** also stands in contrast with the hydrocracking reaction of a benzene ring on solid catalysts, which gave a mixture of methylcyclopentane and acyclic saturated hydrocarbons^{1–6}. This work thus demonstrates that multimetallic titanium hydrides such as **1** can serve as a unique platform for the activation of aromatic molecules, offering new opportunities for the transformation and functionalization of inactive aromatics.

METHODS SUMMARY

All reactions were performed under an argon atmosphere. Complex **1** was prepared according to literature procedures²⁶ and stored in a glovebox.

Reaction of **1 with benzene.** A benzene solution (5.0 ml) of **1** (151 mg, 0.21 mmol) in a 30 ml Schlenk tube was stirred at 40 °C for 36 h. Removal of the solvent under vacuum gave [(C₅Me₄SiMe₃)Ti]₃(C₆H₄Me)(μ-H)₄ (**2**) (163 mg, 98%) as a dark-green solid. Recrystallization from hexane at –33 °C afforded dark-green crystals (121 mg, 0.15 mmol, 71%) suitable for X-ray diffraction.

Received 1 February; accepted 27 June 2014.

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Supplementary Information is available in the online version of the paper.

Acknowledgements This work was supported by a Grant-in-Aid for Young Scientists (B) (no. 26810041), a Grant-in-Aid for Scientific Research (C) (no. 26410082) and a Grant-in-Aid for Scientific Research (S) (no. 26220802) from JSPS, and an Incentive Research Grant from RIKEN. We thank J. Cheng for help with X-ray structure analyses, and A. Karube for conducting elemental analyses.

Author Contributions Z.H., S.H. and T.S. had the idea for and designed the experiments. S.H. and T.S. conducted the experiments. Z.H. and S.H. wrote the manuscript. All authors participated in data analyses and discussions. Z.H. directed the project.

Author Information X-ray crystallographic coordinates of **2**, **4**, **5** and **6** have been deposited at the Cambridge Crystallographic Database under accession numbers 981670–981673. Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to Z.H. (houz@riken.jp).