Mechanistic Insights into Ring Cleavage and Contraction of Benzene over a Titanium Hydride Cluster

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S *Supporting Information*

ABSTRACT: Carbon−carbon bond cleavage of benzene by transition metals is of great fundamental interest and practical importance, as this transformation is involved in the production of fuels and other important chemicals in the industrial hydrocracking of naphtha on solid catalysts. Although this transformation is thought to rely on cooperation of multiple metal sites, molecular-level information on the reaction mechanism has remained scarce to date. Here, we report the DFT studies of the ring cleavage and contraction of benzene by a molecular trinuclear titanium hydride cluster. Our studies suggest that the reaction is initiated by benzene coordination, followed by H_2 release, C_6H_6 hydrometalation, repeated C−C and C−H bond cleavage and formation to give a MeC_5H_4 unit, and insertion of a Ti atom into the MeC_5H_4 unit with release of H_2 to give a metallacycle product. The C−C bond cleavage and ring contraction of toluene can also occur in a similar fashion, though some details are different due to the presence of the methyl substituent. Obviously, the facile release of H_2 from the metal hydride cluster to provide electrons and to alter the charge population at the metal centers, in combination with the flexible metal−hydride connections and dynamic redox behavior of the trimetallic framework, has enabled this unusual transformation to occur. This work has not only provided unprecedented insights into the activation and transformation of benzene over a multimetallic framework but it may also offer help in the design of new molecular catalysts for the activation and transformation of inactive aromatics.
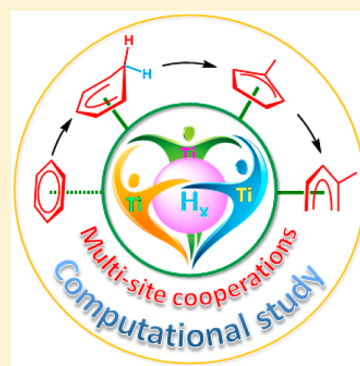
INTRODUCTION

Benzene is the most fundamental aromatic hydrocarbon compound and one of the most elementary petrochemicals. The hexagonal aromatic benzene ring is a ubiquitous structure motif, widely existing in natural resources such as petroleum and biomass. Cleavage of a benzene ring by transition metals is therefore of great interest and importance. However, the carbon skeleton of benzene is among the most robust chemical bonds because of its high aromaticity and nonpolarity. In contrast to a great number of examples of C−H bond cleavage and functionalization, studies on the C−C bond cleavage of a benzene skeleton are scarce. In the industrial naphtha hydrocracking process, the cleavage of a benzene ring is performed on solid catalysts at high temperatures, which usually yields a mixture of several products, including the ring-contraction product methylcyclopentane and ring-opening acyclic saturated hydrocarbons (Figure 1a).[1−3] Because of the complexity of the catalyst system and difficulty in identifying the true active species in solid catalysts, little molecular-level information is available concerning the C−C bond cleavage and rearrangement. Microorganisms are known to degrade aromatic compounds under ambient conditions, but the mechanistic details are not clear and are difficult to mimic.[4]

The cleavage of benzene by well-defined molecular systems has been hardly explored. In 2002, Kira and co-workers reported the photochemical insertion of a silylene species into benzene initiated by a radical process.[5] Recently, Sekiguchi and co-workers reported the formal fragmentation of benzene into C_2H_2 and C_4H_4 units via a Diels−Alder/retro-Diels−Alder reaction with a cyclobutadiene compound.[6] With respect to the activation of benzene by a transition-metal complex, Suzuki and co-workers found that a binuclear ruthenium tetrahydride complex could partially hydrogenate benzene to a 1,3-cyclohexadiene species in a reversible fashion without causing C−C bond cleavage.[7]

We recently found that a trinuclear titanium polyhydride complex $[(C_5Me_4SiMe_3)Ti]_3(\mu_3\text{-}H)(\mu_2\text{-}H)_6$ (**1**) could act as a unique platform for the activation of benzene, which sequentially transformed benzene to a monohydrogenated species $[C_6H_7]^{3−}$ (**2**), a ring-contraction product $[MeC_5H_4]^{3−}$ (**3**), and a ring-opening species $[CHC(Me)(CH)_3]^{5−}$ (a titanium insertion product) (**4**) under mild conditions (Figure 1b).[8] This is the first example of C−C bond cleavage and rearrangement of benzene by a metal complex at room
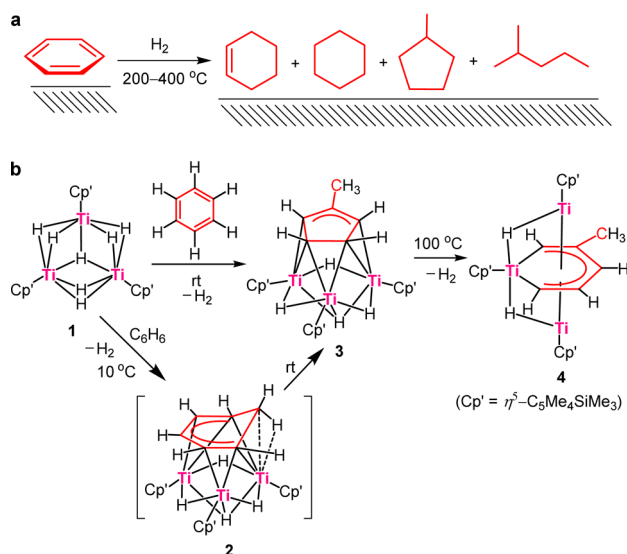
Figure 1. Hydrogenation and ring cleavage and contraction of benzene (a) on solid catalyst surface and (b) by a molecular titanium hydride cluster.

temperature. However, the mechanistic details of this transformation are still unclear. Several fundamental questions arose from this intriguing discovery, such as, (1) how is the reaction of benzene with the metal hydride initiated, (2) how is a six-membered ring contracted (broken and rearranged) to a methyl-substituted five-membered ring, (3) how is a titanium atom inserted into the five-membered ring in **3** to give **4**, and (4) what possible roles can the multiple metal hydrides play? To answer these questions, theoretical calculations are obviously required.

Previously, a number of theoretical and experimental studies on the C–C bond cleavage by transition-metal complexes have been reported, most of which concerned the reactions taking place in quite special circumstances, such as relief of ring strain, formation of an aromatic system, chelation-assisted cyclo-metalation, and β-carbon elimination.[9−20] Regarding ring breaking, Morokuma and co-workers reported the theoretical studies on the Csp^2–Csp^3 bond cleavage of cyclopentadiene at a triruthenium hydride cluster.[16] Ellis et al. reported an accessible pathway for the dirutheniumcarborane-mediated C–C bond cleavage of an arene ligand.[17] The groups of Zhang, Bottoni, and Yoshizawa reported the computational studies on the insertion of tungsten into an aromatic C–C bond of quinoxaline.[18−20] A theoretical study on the ring cleavage and contraction of benzene by a metal complex has not been reported previously. Obviously, cleavage of a benzene skeleton could be much more difficult than that of other C–C bonds, and its reaction mechanism could also be distinctly different from those reported previously in other cases, because benzene possesses high aromaticity with no ring-strain, no heteroatom, and no polarity that could facilitate an interaction with a metal atom.

As part of our research project on understanding of the synergistic effects of multimetallics, we previously reported computational studies of the structure and reactivity of a series of multinuclear rare-earth and transition-metal complexes,[21−28] including the activation of dinitrogen (N_2) by the titanium hydride cluster **1**.[26] In this paper, we wish to report the DFT studies of the reaction of benzene with the trinuclear titanium hydride cluster **1** (Figure 1b).[8] We found that dynamic

rearrangement of the hydride ligands in the trimetallic framework could easily take place, thereby facilitating the activation of benzene through coordination of benzene to a titanium atom and the subsequent H_2 release, C=C double bond hydrometalation, and C–C (as well as C–H) bond cleavage and formation. These findings have provided unprecedented insights into the mechanistic details of the C–C bond activation and transformation of a benzene ring over a multimetallic framework and may also help the design of new catalysts for the activation and transformation of inactivated aromatics.

■ COMPUTATIONAL DETAILS

Due to large molecular size, each methyl group of the $C_5Me_4SiMe_3$ ligands in the complexes was replaced by an H atom for the mechanism calculations. For example, $[(C_5H_4SiH_3)Ti]_3(\mu_3\text{-H})(\mu_2\text{-H})_6$ (**1m**) was used for modeling $[(C_5Me_4SiMe_3)Ti]_3(\mu_3\text{-H})(\mu_2\text{-H})_6$ (**1**). The stationary points were optimized by the (U)TPSSTPSS functional,[29] which has been previously reported to show better performance in geometrical optimization of trinuclear organometallic complexes compared to B3LYP and BP86.[28b] In the geometrical optimizations, the 6-31G(d) basis set was considered for the C and H atoms. The Stuttgart/Dresden effective potentials as well as the associated basis sets[30,31] (4s4p)/[2s2p] and (8s7p6d1f)/[6s5p3d1f] were used for the Si and Ti atoms, respectively. The basis set of the Si atom was also augmented by one d polarization function (exponent of 0.284).[32] This basis set is denoted as "BSI". The combination of the spin-unrestricted strategy and "scf = nosymm" keyword was used in the optimizations. Each optimized structure was subsequently analyzed by harmonic vibration frequencies for characterization of a minimum ($N_{imag} = 0$) or a transition state ($N_{imag} = 1$). The transition state structures are shown to connect the reactant and product on either side via following the intrinsic reaction coordinate (IRC). To obtain more reliable relative energies, the single-point calculations of optimized structures were carried out at the level of (U)M06[33,34]/BSII, taking into account the solvation effect of benzene. In the BSII, the 6-311G(d,p) basis set was used for C, H, and Si atoms, while the basis set together with associated pseudopotentials for Ti atoms is the same as that in the geometry optimization. The "stable = opt" keyword was used to obtain a stable wave function solution, and the solvation effect was considered with the CPCM model.[35,36] To reduce the overestimation of the entropy contribution derived from the gas-phase model, corrections for free energies were made by −2.6 (or +2.6) kcal/mol for two-to-one (or one-to-two) transformations.[37] The relative enthalpies and uncorrected relative free energies of all stationary points are also provided in the Supporting Information (SI) for reference (Table S11). To test whether the diffusion function has significant effects on the computed relative energies, the 6-31+G(d,p) basis set was considered for C, H, and Si atoms in the single-point calculations on some key stationary points, and no significant effects were found (see Table S1, SI). All of the model complexes were optimized without any geometrical symmetry restriction. The energy profile reported is the lowest pathway, and the free energies were used for discussion. Single-point calculations at the level of (U)M06/BSII indicate that the singlet states of the X-ray structures of **1**, **3**, and **4** are lower in energy than their triplet states, respectively (see Table S2, SI), being in line with the NMR analyses.[8] Under the broken symmetry strategy, calculations on the model compounds (**1m**,
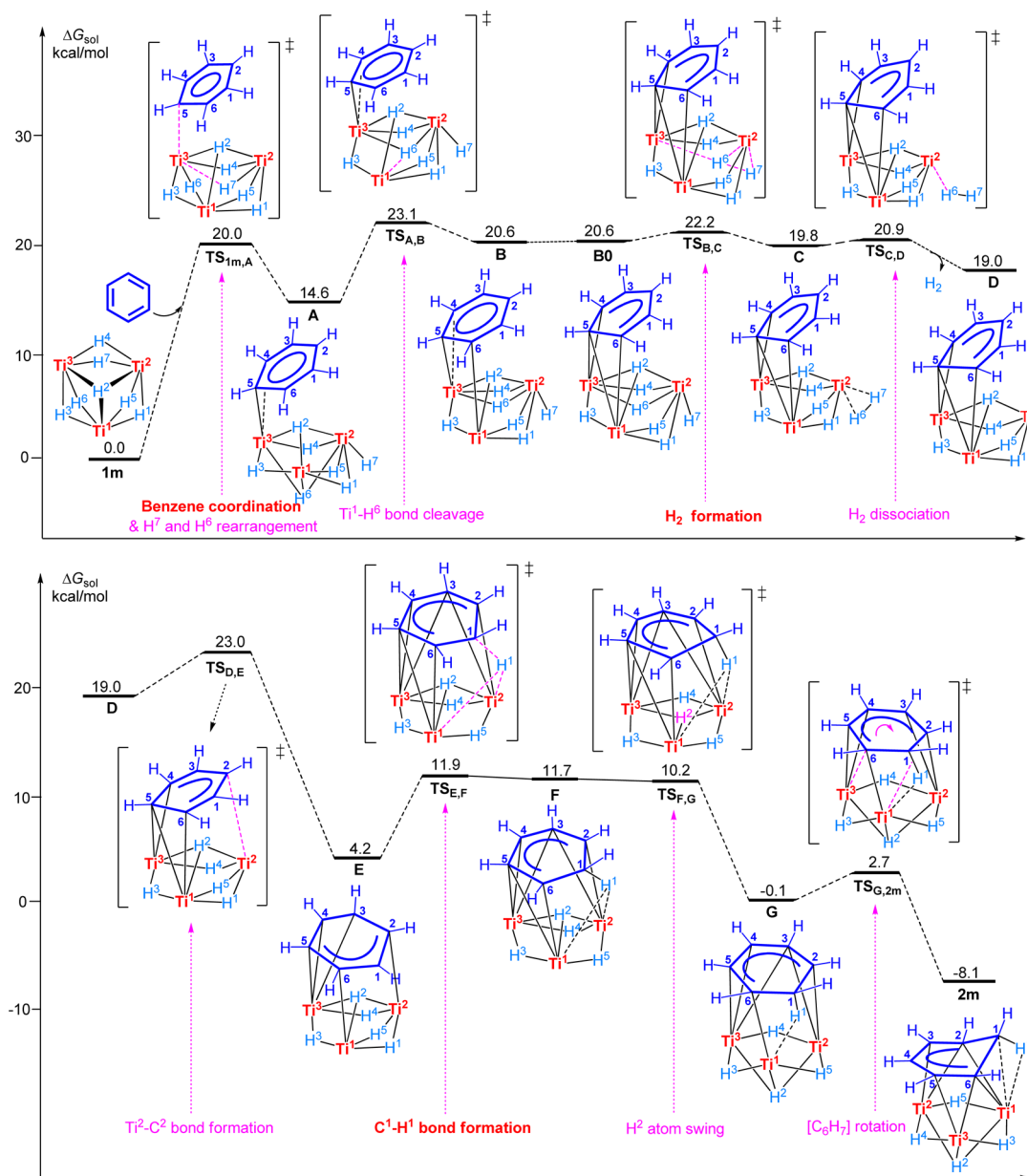
Figure 2. Energy profile for the sequential release of H_2 and hydrometalation of benzene to give **2m**. The Gibbs free energies in solution are relative to **1m** and benzene. The solid lines connected to Ti denote ionic covalent bonding interaction, and the dashed lines denote neutral coordinative or agostic interaction. The $C_5H_4SiH_3$ ligands have been omitted for clarity.

2m, **3m**, and **4m**) indicate that these complexes also have singlet ground states (see Table S3, SI) at the theoretical level of (U)M06/BSII//(U)TPSSTPSS/BSI. The selected important interatomic distances in these optimized model structures are also in reasonable agreement with the corresponding crystallographic data (see Table S4, SI). Actually, the calculated activation energy is also in line with the experimental value (vide infra). These results suggest that the theoretical method including the combination of (U)TPSSTPSS and (U)M06 functionals adopted here is reliable for such a system. The calculations of reaction mechanism were carried out by utilizing Gaussian 09 program.[38]

■ RESULTS AND DISCUSSION

Formation of 2 (C_6H_7) through Hydrometalation of Benzene by Titanium Hydride Cluster 1. Prior to calculations of the reaction mechanism, the electronic structure of **1** was computationally investigated (see the electronic structure calculations of **1** in SI). The DFT studies suggest that **1** possesses a BS(1,1) antiferromagnetic singlet ground state. This was also confirmed by CASSCF calculations (see Table S5 and Figure S3, SI). There are two major chemical events in the reaction of **1** with benzene to give the partially hydrogenated species C_6H_7 (**2**) (Figure 1b), viz., the transfer of a hydride (H^-) from **1** to benzene and the elimination of one molecule of H_2 from the hydride cluster. Computationally, we were able to find a route leading to **2m** initiated by the 1,4-hydrometalation of benzene. But this route required overcoming an energy barrier as high as 43.0 kcal/mol (Figure S4, SI), which does not seem realistic for a reaction taking place at 10 °C. We then decided to search for an alternative route by examining if H_2 elimination could be possible prior to the hydrometalation of
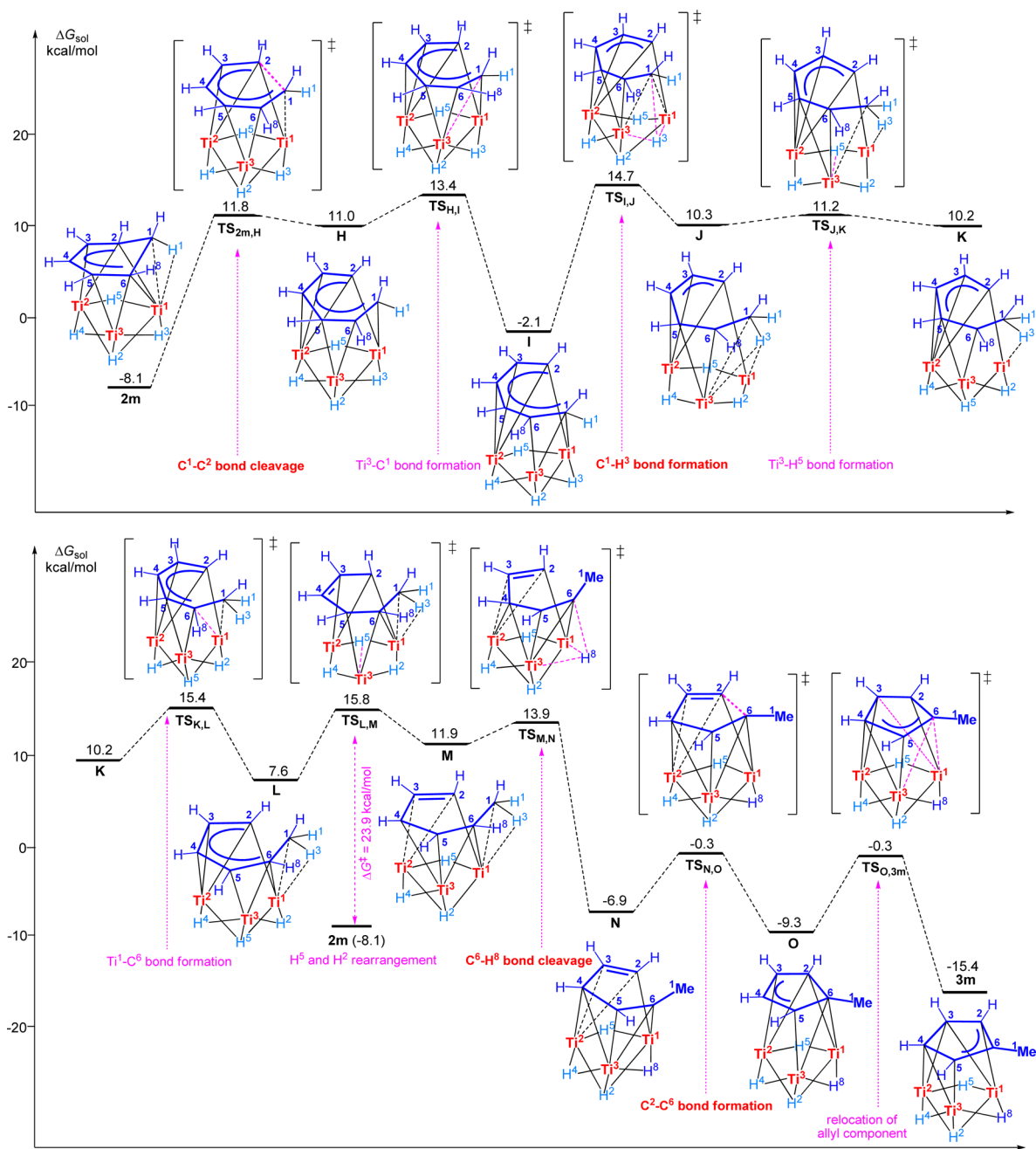
Figure 3. Energy profile for the ring contraction of C_6H_7 to MeC_5H_4. The Gibbs free energies in solution are relative to those of **1m** and benzene. The solid lines connected to Ti denote an ionic covalent bonding interaction, and the dashed lines denote a neutral coordinative or agostic interaction. The $C_5H_4SiH_3$ ligands have been omitted for clarity.

benzene. To our delight, the coordination of benzene to the Ti3 atom in **1m** gave an intermediate **A** by overcoming an energy barrier of 20.0 kcal/mol (Figure 2). In this transformation, the μ_2-H7 ligand bridging Ti3 and Ti2 in **1m** changed to a terminal ligand bonding only to Ti2, while the μ_2-H6 ligand in **1m** became a μ_3-H ligand in **A**. Further interaction between the benzene moiety and the Ti atoms sequentially broke the H6−Ti1 and H6−Ti3 bonds with simultaneous formation of the H6−H7 bond and then gave a H_2-coordinated species **C** via intermediate **B**. During this transformation, the average C−C bond distance of the benzene ring was lengthened gradually (**A**, 1.41 Å; **B**, 1.42 Å; **C**, 1.44 Å; Figure S5, SI). The dissociation of one molecule of H_2 (H6−H7) from Ti2 in **C** gave the pentahydride complex **D**. The release of H_2

resulted in the reduction of the benzene moiety and yielded a relatively electron deficient Ti2 center, as suggested by the NBO charge on atom Ti2 (**C**, −0.53; **D**, 0.48). Accompanying such a reduction event, the C_6H_6 moiety in **D** lost aromaticity (NICS(1)_ZZ = 7.0). The interaction between Ti2 and C2 driven by the electron-deficiency of Ti2 easily yielded a more stable intermediate, **E**. The shift of a hydride ligand (H1) to C1 in **E** afforded the tetrahydride complex **F** with formation of a C_6H_7 moiety. The NBO charge of the original C_6H_6 unit decreased from −0.20 in **E** to −0.41 in **F**, suggesting that the six-membered ring was further reduced. **F** easily isomerized to **G**, in which an easy rotation of the C_6H_7 unit over the Ti1−Ti2−Ti3 framework afforded the more stable species **2m** (rotated counterclockwise and horizontally about 120° relative
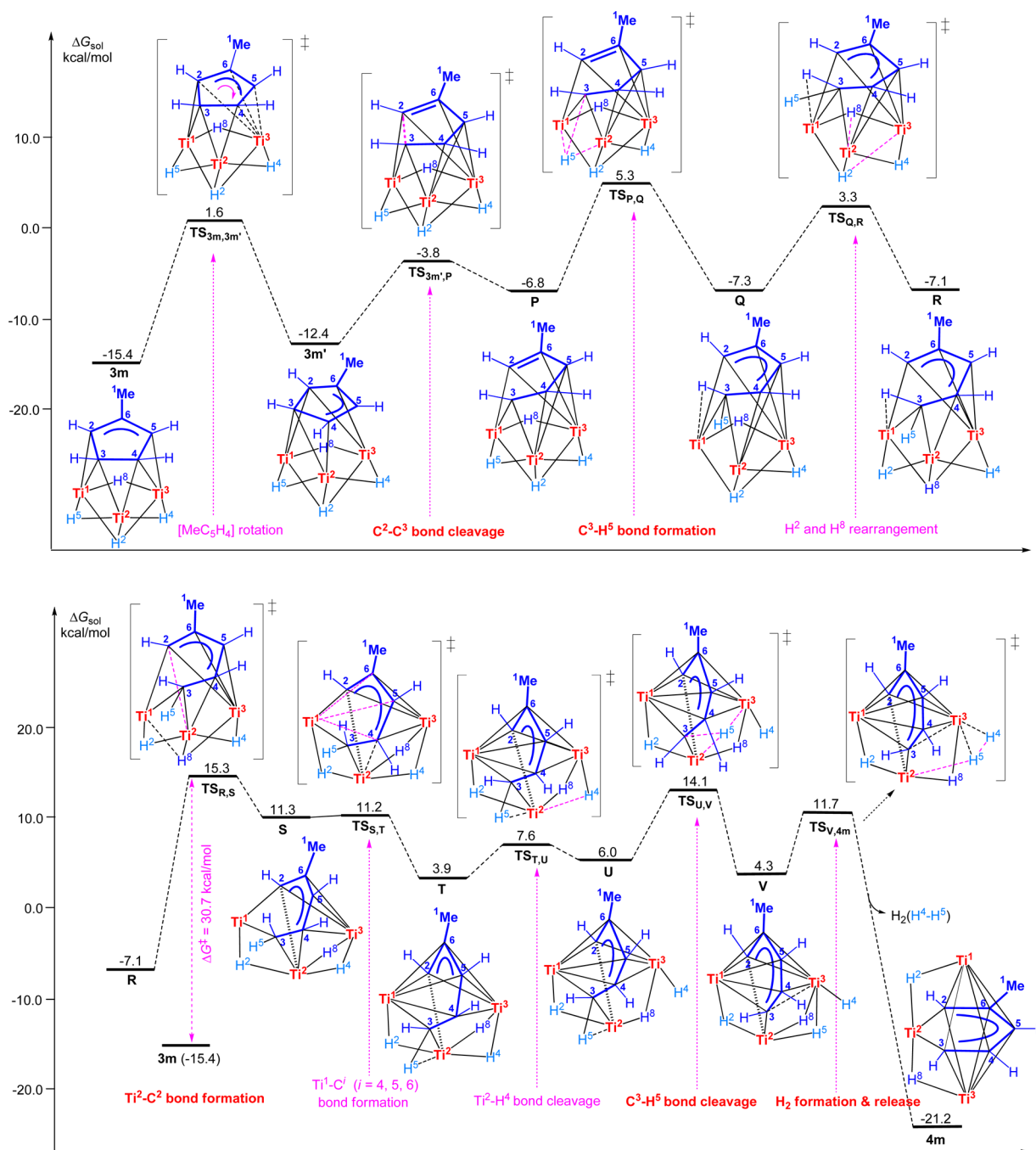
Figure 4. Energy profile for the insertion of titanium into the ring skeleton of MeC₅H₄. The Gibbs free energies in solution are relative to those of **1m** and benzene. The solid lines connected to Ti denote an ionic covalent bonding interaction, and the dashed lines denote a neutral coordinative or agostic interaction. The C₅H₄SiH₃ ligands have been omitted for clarity. The structure **3m** shown in this figure was rotated counterclockwise and horizontally about 120° relative to that in Figure 3 for a better view of the structure.

to **G** for a better view of the structure), which is equivalent to **2** (in Figure 1b) observed experimentally. Overall, the transformation of **1m** to **2m** is accompanied by three-electron reduction of the C_6 ring through H_2 elimination and hydrometalation.

As a result of three-electron reduction of the C_6 ring, the C1−C2 and C1−C6 bonds of the C_6H_7 unit in **2m** showed a standard single-bond character manifested by their bond length (1.54 Å), while the other four C−C bonds showed partial double-bond character (bond length 1.44−1.46 Å). The sp^3-hybridized C1 methylene unit in **2m** is out of the C2−C3−

C4−C5−C6 plane, tilting away from the titanium framework. It is worth noting that the NBO charges on the titanium metal atoms and the hydride ligands changed with an opposite trend during the transformation from **1m** and benzene to **2m** (Figure S6, SI), suggesting an interactive electron transfer. The whole process of the transformation from **1m** and benzene to **2m** is exergonic by 8.1 kcal/mol with an overall energy barrier of 23.1 kcal/mol. Such an energy barrier is understandable in view of the experimental observation that this transformation occurred in neat benzene, which could greatly promote the reaction kinetically even at 10 °C.[8]

Alternatively, a possible pathway of H_2 elimination prior to benzene coordination was also computed (Figure S7, SI). It was found that although the free energy barrier of direct dehydrogenation of **1** is not so significantly different (only slightly higher) from that observed in the benzene-associated mechanism described above ($\Delta G^{\ddagger}$ = 23.8 vs 23.1 kcal/mol) due to the entropy effect, the enthalpy barrier of the direct dehydrogenation process is significantly higher than that of the benzene-associated one ($\Delta H^{\ddagger}$ = 22.2 vs 16.8 kcal/mol). Experimentally, it was found that **1** was stable both in the solid state and in hexane solution at room and higher temperatures (60 °C) under reduced pressure. This suggests that perturbation of the benzene substrate is essential for H_2 elimination. In view of the calculation result and the experimental observation, the benzene associative mechanism shown in Figure 2 is more likely to be operative.

It is worth noting that, during the transformation of "**1m** + benzene" to "**2m** + H_2", the open-shell triplet and closed-shell singlet states of the stationary points were also considered for comparison. A spin crossover between the triplet and closed-shell singlet states was observed prior to formation of **E** (Figure S8, SI), while the triplet path and the open-shell singlet path are quite close to each other in energy. Interestingly, the antiferromagnetic coupling exists in the stationary points involved in H_2 elimination (**1m** + C_6H_6 → **D** + H_2), as suggested by the spin density population (Table S9, SI), thereby reducing the energy barrier (Figure S8, SI). These results again suggest that the broken-symmetry strategy is necessary for the calculations of the present system.

During the transformation of **E** to **2m** (Figure S8, SI), the antiferromagnetic coupling singlet states were computationally found to converge to closed-shell singlet states (RKS) due to the degeneration of α- and β-orbitals of HOMOs (Figure S9, SI). To corroborate this point, CASSCF calculations on **E** and **2m** were performed, and the results suggest that their electronic states are the closed-shell singlet states (Tables S6 and S7 and Figure S10, SI).

Transformation of 2 to 3 through Ring Contraction of C_6H_7 to MeC$_5$H$_4$. Experimentally, complex **2** could be quantitatively transformed to **3** at room temperature or 40 °C by ring contraction of the C_6H_7 unit to a MeC$_5$H$_4$ species (Figure 1b). This transformation involves several fundamental events, viz., C−C bond cleavage (ring opening), C−H bond formation and cleavage, and C−C bond formation (ring closing). It was computationally found that the reaction could be initiated by breaking the C1−C2 bond of the C_6H_7 unit, which is accompanied by formation of stronger Ti1−C1 and Ti1−C2 bonds to afford **H** via **TS$_{2m,H}$** (Figure 3). This step needs to overcome a free energy barrier of 19.9 kcal/mol and could be viewed as oxidative addition of the C1−C2 bond to the Ti1 atom in **2m**. Conversion of **H** to a more stable species **I** easily took place through breaking the Ti3−C5 bond and forming a new Ti3−C1 bond. In **I**, transfer of H3 to C1 (reductive elimination of H3 and C1 from Ti1) produced a CH_3 group and afforded **J**. Sequential isomerization of **J** to **M** could take place through multiple rearrangement of the Ti−H and Ti−C connections via intermediates **K** and **L**. Subsequently, oxidative addition of C6−H8 (C6−H8 bond cleavage) to Ti1 in **M** could occur to give a more stable species **N**. In **N**, reductive elimination of C2 and C6 (C2−C6 bond formation) from Ti1 could take place to yield **O**, a methyl-substituted five-membered ring species MeC$_5$H$_4$. Relocation of the allyl component in the MeC$_5$H$_4$ ring of **O**

via the transition state **TS$_{O,3m}$** finally gave the more stable complex **3m**, which is equivalent to **3** obtained experimentally (Figure 1b). The transformation of **2m** to **3m** has an overall free energy barrier of 23.9 kcal/mol, in good agreement with the experimental observation (23.1 kcal/mol).[8] Thermodynamically, the conversion of **2m** to **3m** is exergonic by 7.3 kcal/mol. It is also worth noting that although the major events in the transformation of **2m** to **3m**, such as ring opening, C−H bond formation and cleavage, and ring closure, seemed to occur mainly at the Ti1 center, the cooperative participation of the whole trimetallic framework is obviously essential in all steps.

Transformation of 3 to 4 through Insertion of a Titanium Atom into MeC$_5$H$_4$. When heated at 100 °C for 2 days, complex **3** was transformed to **4** by insertion of a titanium atom into the ring skeleton of the MeC$_5$H$_4$ unit with release of one molecule of H_2 (Figure 1b).[8] This transformation consists of several chemical changes: C−C bond cleavage, Ti frame rearrangement, and H_2 elimination. We computationally found that the reaction could start with rotation of the MeC$_5$H$_4$ unit over the titanium framework of **3m** to give **3m'** by overcoming a free energy barrier of 17.0 kcal/mol (Figure 4). Then, cleavage of the C2−C3 bond in **3m'** through oxidative addition to Ti1 could give **P**. The migration of H5 to C3 (reductive elimination of H5 and C3 from Ti1) in **P** would afford **Q**, which contains a newly formed CH_2 group. Isomerization of **Q** could easily take place to give the isoenergetic **R** by rearrangement of the hydride ligands. An interaction between C2 and Ti2 in **R**, accompanied by Ti1−H8 bond cleavage, could afford **S**, which contains a μ_3-C2 unit. This process needs to overcome an overall energy barrier of 30.7 kcal/mol. Further interactions between the Ti1 atom and the carbon skeleton of the MeC$_5$H$_5$ moiety in **S** could take place to give a more stable complex **T** through formation of the Ti1−C6 (2.23 Å), Ti1−C5 (2.18 Å), and Ti1−C4 (2.30 Å) bonds. In **T**, the C4, C5, and C6 atoms all have bonding interactions with Ti1 and Ti3 in a μ_2-bonding fashion, and the C3 atom shows bonding interactions with the Ti1 and Ti2 in a similar μ_2-fashion, while the C2 atom is connected to all three Ti atoms in a μ_3-bonding mode. The dissociation of μ_2-H4 from Ti2 in **T** could generate **U**, which bears a terminal hydride ligand H4 at the Ti3 atom. The subsequent oxidation addition of the C3−H5 bond across to the Ti2 and Ti3 atoms would produce **V**, which processes a newly formed μ_2-H5 ligand. The reductive elimination of the H4 and H5 ligands via **TS$_{v,4m}$** could yield the final product **4m**, which is equivalent to **4** obtained experimentally (Figure 1b). The whole transformation of **3m** to **4m** is exergonic by 5.8 kcal/mol relative to **3m**. The rate-determining step in this transformation would be the Ti2−C2 bond formation process via **TS$_{R,S}$**, with an overall energy barrier of 30.7 kcal/mol. Such transformation should be accessible both kinetically and thermodynamically at 100 °C, as observed experimentally.[8]

Previously, a μ-CH_2 flipping mechanism was proposed for the isomerization of a metallocycle in a triruthenium complex system.[39] However, such a mechanism seemed not operative in the present titanium system, as the formation of a μ-CH_2 species by cleavage of the C3−C4 bond in **Q** is computationally found to have an energy barrier of 39.5 kcal/mol (see Figure S11, SI), which is unlikely to occur at the experimental temperature of 100 °C.

An Overview of Transformation of Benzene by Titanium Hydride Cluster 1. On the basis of the computational results described above, a possible overall scheme
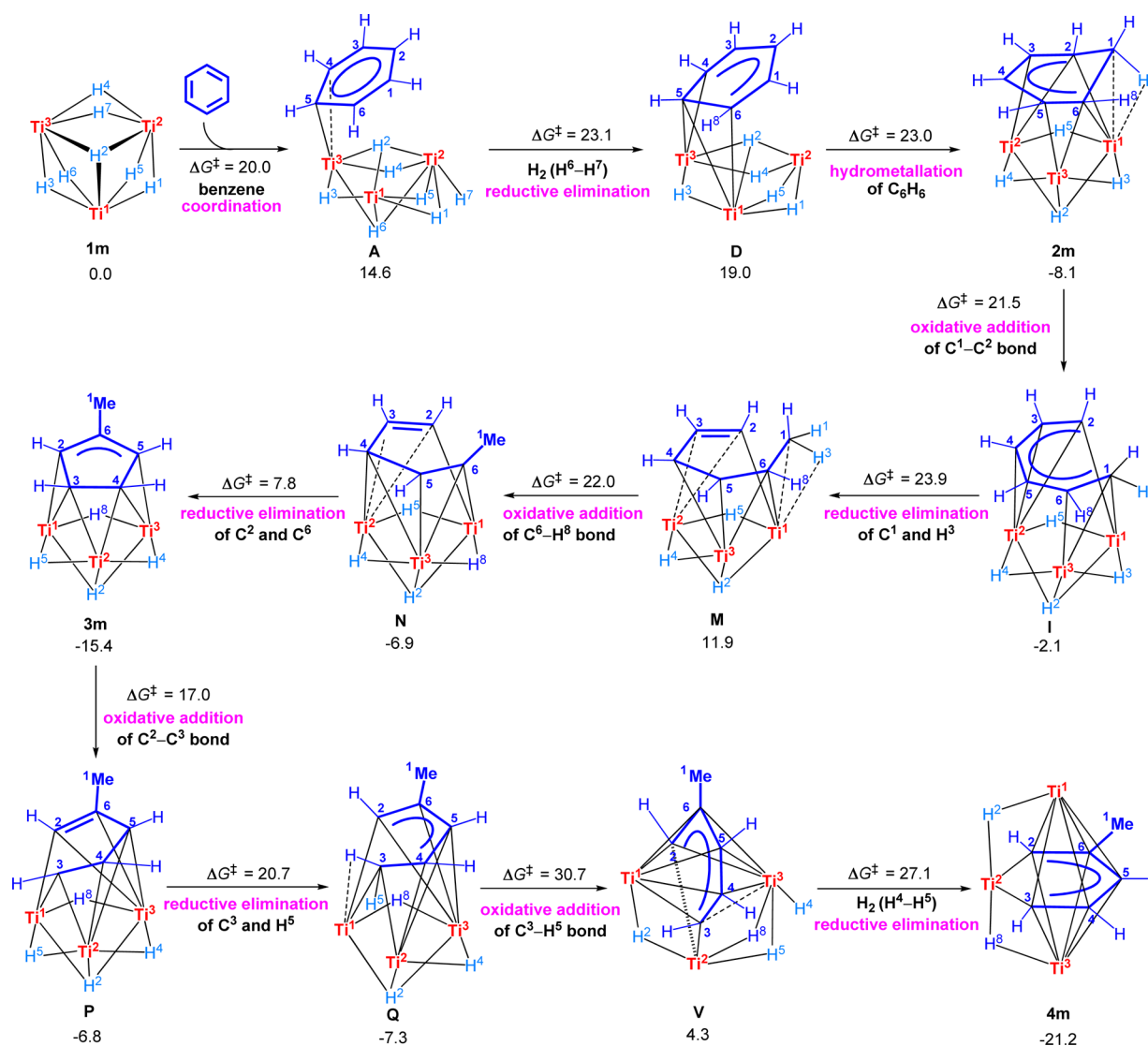
Figure 5. A computationally suggested overall scenario for the ring cleavage and contraction of benzene by **1m**. The C₅H₄SiH₃ ligands have been omitted for clarity. The relative free energies and overall energy barrier of each stage are given in kilocalories per mole.

showing some of the key steps in the transformation of **1m** and benzene to **4m** is summarized in Figure 5.

In the conversion of **1m** + C₆H₆ to **2m** + H₂, the initial coordination of benzene to the Ti3 atom in **1m** could induce the release of one molecule of H₂ through reductive elimination of two hydride ligands from the metal hydride cluster. The electrons generated in this process could be used for the reduction of benzene to give **D**. Hydrometalation of the C₆H₆ unit in **D** would then yield the C₆H₇ species **2m**. This transformation overcomes an overall free energy barrier of 23.1 kcal/mol and is exergonic by 8.1 kcal/mol.

In the transformation of **2m** to **3m**, the oxidative addition of the C1−C2 bond of the C₆H₇ unit to the Ti1 atom in **2m** (i.e., C1−C2 bond cleavage) could occur to yield the ring-opening species **I**. The subsequent reductive elimination of the C1 atom and the hydride ligand H3 (i.e., C1−H3 bond formation) would lead to the formation of a CH₃ group, as shown in **M**. Then, the oxidative addition of the C6−H8 bond (i.e., C6−H8 bond cleavage) in **M** could take place to give **N**. Reductive elimination of C2 and C6 from Ti1 (i.e., C2−C6 bond formation) would give the product **3m**, which contains a MeC₅H₄ unit. The whole process of ring cleavage and

contraction of C₆H₇ to MeC₅H₄ is exergonic by 7.3 kcal/mol and needs to overcome an overall energy barrier of 23.9 kcal/mol.

In the conversion of **3m** to **4m** + H₂, the oxidative addition of the C2−C3 bond to Ti1 atom in **3m** (i.e., C2−H3 bond cleavage) could take place to give the ring-opening species **P**. The reductive elimination of C3 and H5 (i.e., C3−H5 bond formation) would afford **Q**, which possesses a CHC(Me)-CHCHCH₂ moiety. Oxidative addition of the newly formed C3−H5 bond accompanied by the metal framework rearrangement could then afford **V**, which after reductive elimination of H4 and H5 (H4−H5 formation) from the metal framework could yield the titanacycle product **4m**. This process overcomes an overall energy barrier of 30.7 kcal/mol and is exergonic by 5.8 kcal/mol relative to **3m**.

Obviously, the dynamic rearrangements of the hydrides and the redox-active metals and the cooperation of the multiple metal sites in the trimetallic hydride framework have played a critically important role in this transformation, as manifested by the dynamic changes in metal−hydride connection, charge population, and multisite Ti−C bindings.

Ring Cleavage and Contraction of Toluene. To examine whether the reaction mechanism of ring cleavage and contraction of benzene could work for other aromatic compounds, such as toluene, we then computed the reaction of **1** with toluene, which was experimentally described.[8] In this reaction, a 1,3-dimethylcyclopentenyl species **t-3** was proposed as a possible reaction intermediate formed via **t-2** (see Figure 6).[8] Because **t-2** was isolated and structurally characterized as
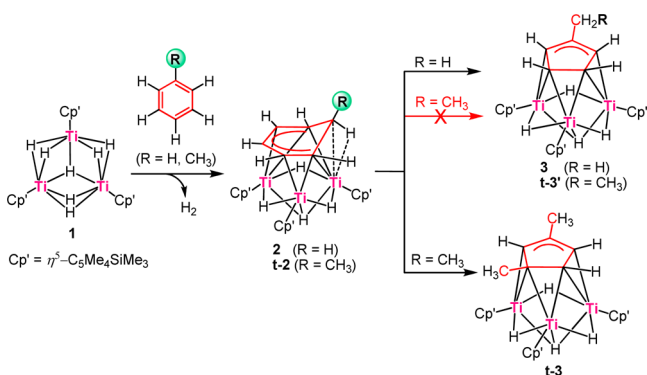

Figure 6. Comparison of reactions of **1** with benzene and toluene.

an intermediate, the formation of **t-2** by the reaction of **1** with toluene was first calculated. It has been found that three-electron reduction of toluene via H_2 elimination and hydrometalation to give **t-2** takes place similarly as in the case of benzene (Figures 6 and S16, SI). However, attempts to locate a transition state for the subsequent cleavage of a HC−CH(CH$_3$) in **t-2m** (a model of **t-2**) were unsuccessful. Actually, a relaxed scan of the HC−CH(CH$_3$) distance in **t-2m** indicates that the energy increases monotonously as the C−C distance increases from 1.5 to 3.5 Å (see the scan curve of C1−C2 distance in Figure S17, SI). These results suggest that cleavage of the HC−CH(CH$_3$) bond in **t-2m** is unlikely to occur. This is reasonable

because the cleavage of the HC−CH(CH$_3$) bond in **t-2** would finally result in an ethyl-substituted five-membered ring product like **t-3′**, which is obviously inconsistent with the experimental observation of formation of the 1,3-dimethyl-substituted cyclopentenyl species **t-3** in the reaction of toluene (Figure 6).[8]

Alternatively, isomerization of **t-2m**, which has a tilted CH(CH$_3$) unit, to **t-2m′** that possesses a tilted CH$_2$ group was found to feasibly occur, as shown in Figure 7. This transformation involves ring rotation and C−H bond cleavage and formation at the C$_6$H$_6$Me moiety, resulting in stronger interactions between the C$_6$H$_6$Me unit and the metal framework (see Table S10 and the related discussion, SI). The whole transformation of **t-2m** to **t-2m′** has an energy barrier of 14.7 kcal/mol, which could be easily achieved under the experimental conditions. The ring cleavage and contraction of **t-2m′** to the 1,3-dimethylcyclopentenyl species **t-3m** can then take place through the initial cleavage of a HC−CH$_2$ bond, as in the case of benzene (see Figure S18, SI).

Overall, the transformation of benzene and toluene by **1m** to the methyl-substituted cyclopentenyl species follows almost the same mechanism, viz., sequential H$_2$ elimination, hydrometalation, ring opening through cleavage of a HC−CH$_2$ bond, and ring closing through formation of a new CH−CMe bond (Figure 8). The only difference between toluene and benzene is that isomerization of **t-2m** to **t-2m′** is required in the case of toluene to induce the ring contraction through energetically favorable cleavage of a HC−CH$_2$ bond rather than a HC−CH(CH$_3$) bond (Figure 8).

■ CONCLUDING REMARKS

By computationally modeling the reaction of benzene with the trinuclear titanium heptahydride complex **1**, we have elucidated the mechanistic details of the carbon−carbon bond cleavage and skeleton rearrangement of an aromatic compound over a multimetallic polyhydride framework. Coordination of benzene to **1**, which has an antiferromagnetic singlet ground state, could
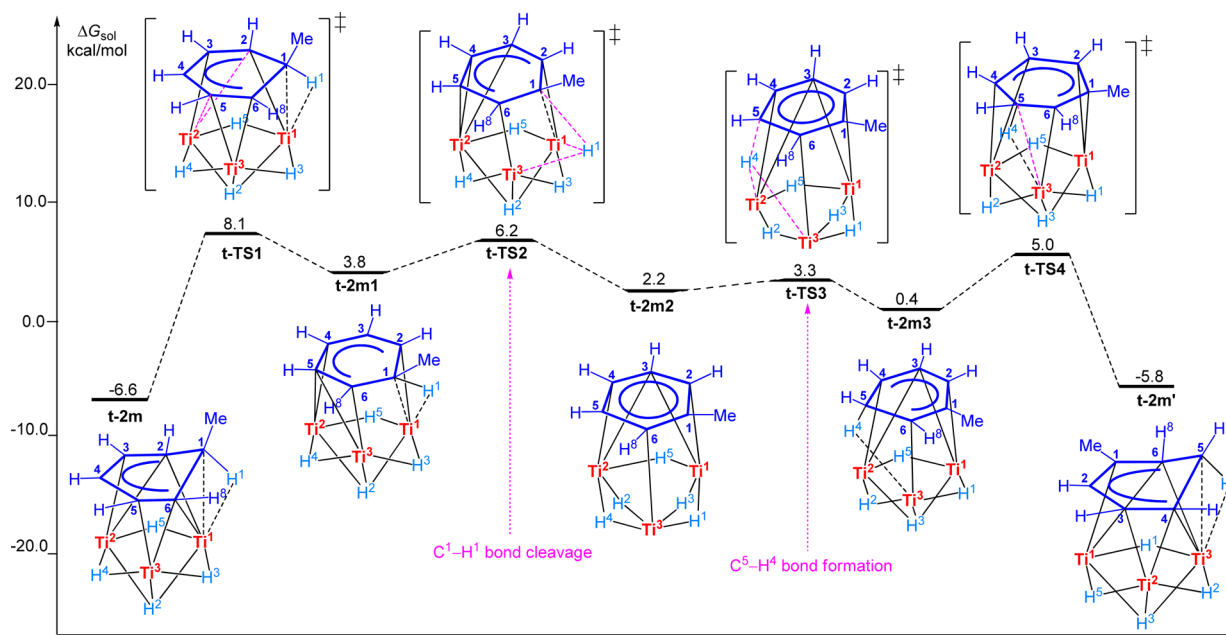

Figure 7. Computed energy profile (kcal/mol) for isomerization of **t-2m** to **t-2m′**. The Gibbs free energy is relative to those of **1m** and toluene. The solid lines connected to Ti denote an ionic covalent bonding interaction, and the dashed lines denote a neutral coordinative or agostic interaction. The C$_5$H$_4$SiH$_3$ ligands have been omitted for clarity.
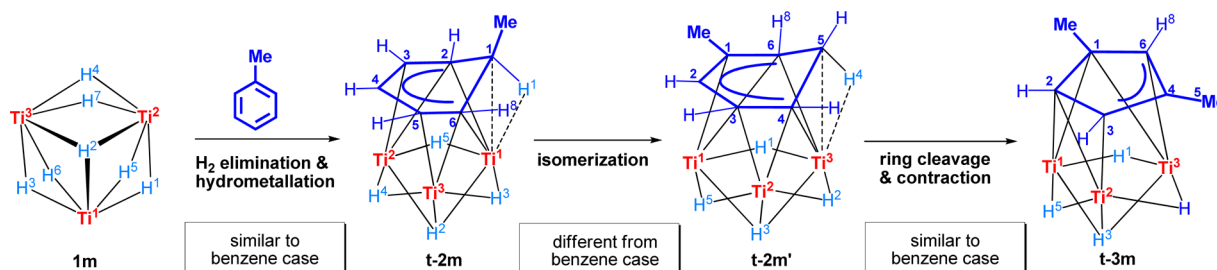
Figure 8. A computationally suggested overall scenario for the ring cleavage and contraction of toluene. The $C_5H_4SiH_3$ ligands have been omitted for clarity.

induce release of one molecule of H_2. Subsequently, hydrometalation of the coordinated C_6H_6 unit can take place to afford a C_6H_7 species (**2**). Repeated C−C and C−H bond cleavage and formation in the C_6H_7 moiety, accompanied by rearrangement of the hydride ligands in **2**, would yield the ring contraction product MeC_5H_4 (**3**). The analogous C−C bond cleavage and C−H bond formation in the MeC_5H_4 unit in **3**, followed by metal framework rearrangement and H_2 release, could afford the metallacycle product **4**. The mechanism elucidated for the ring cleavage and contraction of benzene can also be generally applied to the transformation of toluene, though structural isomerization of some reaction intermediates is needed to induce a C−C bond cleavage (ring-opening) because of the presence of a methyl substituent.

Obviously, the dynamic rearrangements of the multiple hydride ligands and redox-active metal centers and the cooperation of the multiple metal sites in the trimetallic hydride framework of **1** have played a critically important role throughout the whole transformation. The dearomatization (or three electron reduction) of a benzene ring via H_2 release and hydrometalation seems essential to induce the C−C bond cleavage (ring-opening). Oxidative addition and reductive elimination at the multimetallic framework are key elemental steps for the C−C (as well as C−H) bond cleavage and formation involved in the benzene ring cleavage and rearrangement. These findings should be of help for the design of molecular metal catalysts for the activation and transformation of inactive aromatics. In particular, a multimetallic polyhydride framework that possesses redox-active metal centers and that can facilely release H_2 to provide electrons and alter charge population on the metal centers should be among the most desirable features or requisites for an active catalyst, as demonstrated by the complex **1**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03545.

> Tables/figures providing comparison of the electronic energies of compounds in their singlet and triplet states; electronic structure calculations of **1**, **1m**, **E**, and **2m**; spin densities; energy profiles for H_2 elimination prior to benzene coordination in **1m** and toluene activation; and the optimized Cartesian coordinates and energies for all of the stationary points and the imaginary frequencies of TSs (PDF)

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Notes
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