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Multidecker Organometallic Complexes for Hydrogen Storage

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Calculations based on density functional theory show that $\text{TiC}_3\text{B}_2\text{H}_5$ multidecker complexes can not only store up to 5.1 wt % hydrogen reversibly in nearly molecular form, but, with an average binding energy of 0.58 eV/ H_2 molecule, they also possess the thermodynamics and kinetics of an ideal hydrogen storage material. In addition, these complexes can be synthesized by capping the metal atoms with the organic molecules so that clustering of Ti is prevented during repeated hydrogen cycling. Unlike NaAlH_4 , which is a leading candidate for reversible hydrogen storage with a gravimetric density of 5.6 wt %, $\text{TiC}_3\text{B}_2\text{H}_5$ multidecker complexes have the added advantage that they can operate without any catalysts. Practical applications of the predicted complexes in hydrogen storage are feasible as transition metal decorated $\text{C}_3\text{B}_2\text{H}_5$ complexes have already been synthesized in the laboratory.

I. Introduction

The success of a new hydrogen economy depends critically on our ability to find storage materials that meet some very stringent requirements for vehicular applications. These requirements are (1) large hydrogen gravimetric and volumetric density, (2) fast hydrogen uptake and release kinetics, (3) structural stability of the storage material during repeated hydrogen cycling, and (4) cost effectiveness. Although considerable amounts of effort are being expended to find such materials, none exist at this time. To meet the Department of Energy system target of 9 wt % for the hydrogen gravimetric density by the year 2015, the storage materials have to consist of only light elements such as Li, B, C, Na, Mg, and Al. Three main classes of materials are currently being pursued, namely, (1) complex light metal hydrides and chemical hydrides, (2) pure and metal-coated C- and BN-based nanostructures, and (3) clathrates and metal–organic frameworks (MOFs). In the first group of materials, hydrogen is bound strongly to the host atoms, and thus, thermodynamics, kinetics, and reversibility are rather poor. Catalysts can improve these properties, but finding an ideal catalyst is a challenge. The second group of materials, namely, C and BN fullerenes and nanotubes, bind to hydrogen weakly, and hydrogen desorbs at very low temperatures. Although this can be improved by decorating these complexes with metal atoms, their tendency to cluster under repeated hydrogen cycling does not make them ideal materials either. The third group of materials also suffers from poor thermodynamics as the hydrogen molecules are physisorbed and thus weakly bound.

In this article we show that multidecker complexes consisting of $\text{Ti}(\text{C}_3\text{B}_2\text{H}_5)$ complexes as building blocks have many of the positive but none of the negative attributes discussed above and may be suitable candidates for hydrogen storage. The empty 3d orbitals of Ti along with the electron-deficient nature of the $\text{C}_3\text{B}_2\text{H}_5$ molecule allow multiple hydrogen atoms to attach to the Ti atoms in both dissociative and associative form. Unlike

the $\text{Ti}_n(\text{C}_5\text{H}_5)_n$ multidecker complexes where Ti atoms prefer to cluster, the Ti atoms in a $\text{Ti}_n(\text{C}_3\text{B}_2\text{H}_5)_{n+1}$ complex remain isolated and the resulting multidecker complex can bind hydrogen reversibly with gravimetric density as high as that in sodium alanate.

We begin with a brief review of the earlier work on the interaction of hydrogen with transition metal atoms. It was demonstrated by Kubas et al.^{1,2} a long time ago that hydrogen can bind to transition metal atoms in molecular form. This interaction involves the forward charge donation of the bonding electron in H_2 to the partially filled d orbital of the transition metal atom and back-donation from the metal atom to the σ^* antibonding orbital of H_2 . Recent calculations³ show that as many as six hydrogen molecules can be bound to a Cr atom. This binding energy lies in the ideal range (0.3–1.0 eV/ H_2 molecule) necessary for the hydrogen storage material to operate at near ambient thermodynamic conditions. Similarly, Niu et al.⁴ had demonstrated that a metal cation can also bind at least six H_2 molecules in molecular form through a charge polarization mechanism.

It is only recently that these concepts of dihydrogen bonding have been exploited in the design and synthesis of novel hydrogen storage materials. In a pioneering work, Zhao et al.⁵ showed that transition metal atoms supported on a C_5H_5 (cyclopentadiene, Cp) molecule can bind up to five H_2 molecules associatively with an average binding energy of 0.68 eV/ H_2 molecule, and the maximum number of hydrogen molecules bound to a given transition metal–Cp complex can be predicted using the 18-electron rule. These concepts have been extended by Kiran et al.⁶ to different molecular complexes such as TiC_4H_4 and TiC_8H_8 , and the 18-electron rule has been found to correctly predict the maximum hydrogen uptake. In another study, Weck et al.⁷ further extended the concept of the applicability of 18-electron rule to organometallic systems consisting of early transition metal atoms bound to different organic templates, C_nH_n ($n = 4–6$). However, it is not clear if these building blocks will retain their structural and electronic identity when assembled into a bulk material. In particular, will the metal atoms that

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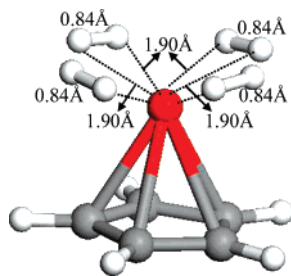


Figure 1. Ground-state geometry of the $\text{Ti}(\text{C}_5\text{H}_5)(\text{H}_2)_4$ complex.

bind to hydrogen remain isolated or cluster? In the latter case, will the hydrogen storage capability be affected?

The problem of clustering of metal atoms supported on a substrate was first brought into focus by Sun et al.⁸ It was shown^{5,9,10} earlier that isolated transition metal atoms such as Sc and Ti supported on a C_{60} fullerene or C nanotube can bind up to four hydrogen molecules yielding a gravimetric density of about 8 wt %. In addition, these complexes can store hydrogen reversibly and operate at near ambient thermodynamic conditions. However, these materials are not stable as the transition metal atoms prefer to cluster. More importantly, this clustering severely lowers the amount of hydrogen uptake. The central question then is this: how can the transition metal atoms be prevented from clustering in a macroscopic sample so that they can retain their ability to adsorb hydrogen? We have investigated this problem theoretically by first concentrating on TiC_5H_5 complexes and then by finding ways in which clustering, if it exists, can be prevented. In the following, we outline our theoretical approach followed by results on the structure and stability of multidecker complexes with TiCp and $\text{TiC}_3\text{B}_2\text{H}_5$ as building blocks. Finally, we discuss the ability of these materials to store hydrogen.

II. Computational Method

All calculations were carried out using spin-polarized density functional theory (DFT) level and DMol3 software.¹¹ Perdew–Wang (PW91)¹² GGA functional along with double-numeric basis sets with polarization functions (DNP) were used. The reliability and accuracy of this functional form and the basis set were established in our earlier work on hydrogen storage in Ti decorated organic templates.⁶ A more detailed discussion on the reliability of the PW91 in the present software (DMol) has been addressed in our earlier work⁶ by comparing the binding energies with the previous studies. In the SCF calculations, a convergence criterion for energy was set to 10^{-6} hartree, while density tolerance was set to 10^{-6} e/bohr³. In the geometry optimization, all the structural parameters were fully optimized without any symmetry constraints, with an energy convergence of 10^{-5} hartree and a maximum gradient of 10^{-4} hartree/bohr.

III. Results and Discussion

We first start by reviewing the hydrogen storage in a single TiCp complex. The bare TiCp complex prefers to be in a quartet spin state, with the Ti atom occupying the on-top position of the Cp ring. In Figure 1, we provide the equilibrium geometry of a single TiCp complex with the maximum number of hydrogen molecules that can be bound. Note that with four H_2 molecules bound with an average binding energy of 0.72 eV/ H_2 , the gravimetric density of hydrogen reaches 6.61 wt %. However, from a materials perspective, it is important to demonstrate that, in a bulk material composed of TiCp complex as a building block, the Ti atoms would remain isolated. Thus,

one must understand how these complexes interact with each other. It is known that transition metal–benzene (C_6H_6) complexes form¹³ two distinct types of structures: a multidecker sandwich complex containing Sc, Ti, V where metal atoms remain isolated from each other. On the other hand, metal–benzene complexes containing Fe, Co, and Ni form rice-ball structures where metal atoms cluster and are capped by the benzene molecules.

To understand how TiCp complexes interact with each other we started with a dimer of TiCp, namely, $(\text{TiCp})_2$. The three likely geometries of this dimer are given in Figure 2a–c where the two Ti atoms cluster and are capped by two Cp rings ($\text{I}\cdots\text{I}$), the metal atoms are separated by Cp rings ($\text{I}\cdots\text{I}$) forming a sandwich structure, or the Ti atoms cluster but the two Cp rings are not parallel to each other. The optimized geometries corresponding to these three configurations are given in Figure 2a–c. Note that the ground-state structure is the one where the Ti atoms cluster with the two Cp rings remaining almost parallel to each other. The structure where they remain isolated and form a sandwich complex (Figure 2b) is 0.50 eV higher in energy than the structure in Figure 2a. The structure in Figure 2c is 1.02 eV above the ground state.

A possible way to avoid Ti clustering in these systems is to make sure every Ti atom is sandwiched between the Cp rings. That can be achieved by increasing the number of ligands from Ti_nCp_n to $\text{Ti}_n\text{Cp}_{n+1}$. In order to verify this, we have considered three different structures for a Ti_2Cp_3 complex, where Ti atoms are arranged in various configurations between the Cp rings. The corresponding optimized geometries are given in Figure 3. Interestingly, in the ground-state structure (Figure 3a), the Ti atoms remain isolated although the structure where they cluster (Figure 3b) is only 0.06 eV higher in energy.

The interaction of hydrogen with the multidecker structure given in Figure 3a was studied by initially placing a H_2 molecule near each Ti atom. The initial interaction of the first hydrogen molecule with the Ti atom leads to the dissociation of the H_2 molecule and adds to the Ti atom with a binding energy of 0.42 eV/ H_2 molecule. We recall that in the TiCp complex, the first H_2 molecule also splits and the hydrogen atoms binds dissociatively, but their binding energy is much higher, namely, 1.36 eV/ H_2 . However, it was not possible to attach additional H_2 molecules to the Ti_2Cp_3 sandwich structure in Figure 3a. This is in contrast to the TiCp complex where four H_2 molecules could be bound to the Ti atom. The reason why four H_2 molecules could be bound to a single TiCp complex, whereas only two H_2 molecules can be bound to the Ti_2Cp_3 complex, is simple: The empty d orbitals of the Ti atom are preoccupied by the back-donation from the two Cp ligands in the sandwich complex. Therefore, they are not available for bonding with subsequent H_2 molecules. On the other hand, for the TiCp complex the d orbitals are not only free, but also the coordination sites are available. In other words, even though the clustering of Ti atoms can be prevented by capping the Ti atoms, namely, in a $\text{Ti}_n\text{Cp}_{n+1}$ complex, its hydrogen uptake is severely reduced due to the back-donation of Cp rings to Ti atoms.

One way to decrease the back-donation from the Cp rings is to reduce the number of electrons available in the system. This can be achieved by replacing two or three carbon atoms by boron atoms. The resulting ligands, $\text{C}_3\text{B}_2\text{H}_5$ and $\text{C}_2\text{B}_3\text{H}_5$, are well-known, and several multidecker complexes with different metal atoms have been synthesized in large quantities.^{14,15} It was also observed that these complexes are stable at room temperature. Therefore, we considered the potential of a $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3$ complex for hydrogen storage. In Figure 3, parts a'

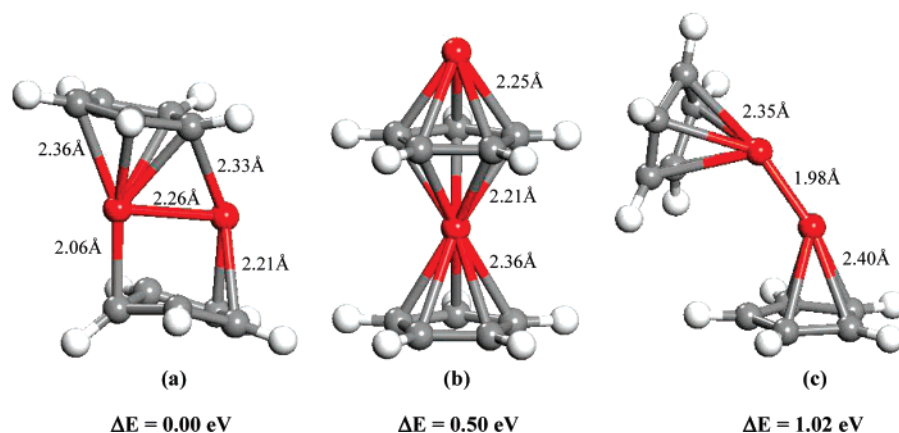


Figure 2. Lowest energy and other higher energy isomers of the $\text{Ti}_2(\text{C}_5\text{H}_5)_2$ complex. The relative energies of the isomers are also shown.

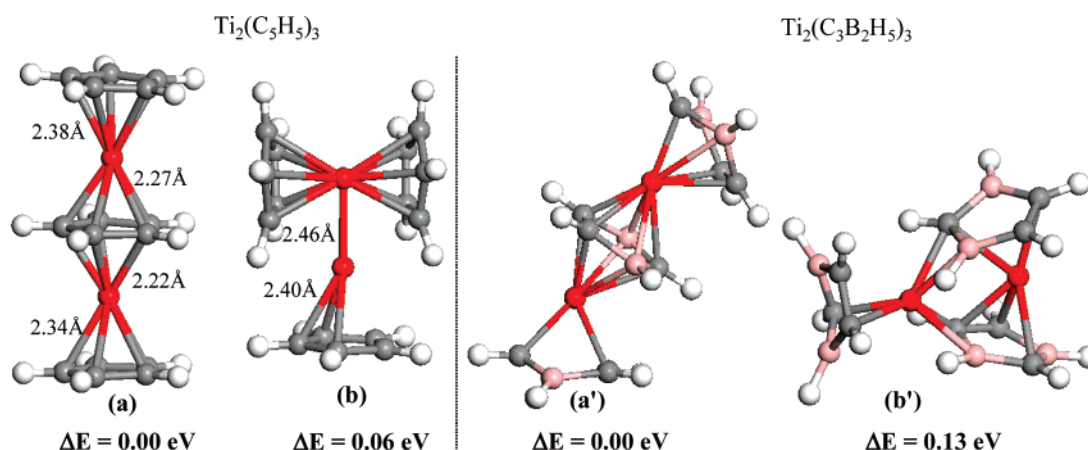


Figure 3. Multidecker sandwich (a and a') and rice-ball (b and b') structures of the $\text{Ti}_2(\text{C}_5\text{H}_5)_3$ and $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3$ complexes. The corresponding relative energies are also shown.

and b', we show the optimized structures of two isomers of $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3$ complexes. In the ground-state configuration, the Ti atoms are sandwiched between the $\text{C}_3\text{B}_2\text{H}_5$ rings forming a triple-decker complex. The ground-state configuration prefers doublet spin state ($2S + 1 = 2$). There exists a higher energy nonsandwich isomer which is more compact than the ground state. In this isomer, the Ti atoms do not cluster in the sense that there is no Ti–Ti bond.

We next studied the sequential hydrogenation of the $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3$ complex. The resulting optimized geometries are shown in Figure 4a–f where up to six H_2 molecules have been added. The ground-state geometries of all these complexes are in doublet spin state. Quartet spin states are found to be higher in energy and thus have not been discussed. The first H_2 molecule dissociates with one H atom binding to the C atom while the other H atom bridges between the B atom and the nearest Ti atom (see Figure 4a). The binding energy of the H_2 molecule to the $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3$ complex is 1.15 eV. Binding of hydrogen to the higher energy isomer of the $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3$ complex (Figure 3b') has very different characteristics. Here, hydrogen binds molecularly to one of the Ti atoms and the resulting structure is 0.72 eV higher in energy than the ground-state structure. It is for this reason that we have concentrated on adding successive H_2 molecules to the ground-state sandwich structure of $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3$ (Figure 3a').

As mentioned above, the first hydrogen interacts dissociatively with each Ti atom in the $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3$ complex. Therefore, the second hydrogen molecule adds to the second Ti atom. The optimized structure of $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3(\text{H}_2)_2$ is shown in Figure 4b. Here again the binding energy of hydrogen is 1.15

eV/ H_2 with one of the H atoms binding to a C atom while the other binds to B and the nearest Ti atom. It is only when the third H_2 molecule is added that the binding becomes molecular (Figure 4c), with a binding energy of 0.40 eV. The fourth, fifth, and sixth H_2 molecules also bind to the Ti atoms in nearly molecular form where the H–H bond length is stretched to 0.81 Å. Note that the bond length of an isolated H_2 molecule is 0.74 Å. The binding energies of each successive H_2 molecule are 0.40, 0.32, 0.23, and 0.22 eV as one proceeds from $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3(\text{H}_2)_3$ to $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3(\text{H}_2)_6$. Thus, the average binding energy per H_2 molecule of $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3(\text{H}_2)_6$ is 0.58 eV. This energy is ideal for reversible hydrogen storage at near ambient conditions. In the $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3(\text{H}_2)_6$ complex the gravimetric density of stored hydrogen is 5.1 wt %.

In order to validate the stability and hydrogen storage capability of larger $\text{Ti}_n(\text{C}_3\text{B}_2\text{H}_5)_{n+1}$ systems, we have extended our study to the tetradeccker sandwich complex, $\text{Ti}_3(\text{C}_3\text{B}_2\text{H}_5)_4$. The optimized $\text{Ti}_3(\text{C}_3\text{B}_2\text{H}_5)_4$ complex (see Figure 5a) exhibits similar bonding and structural features as that of the triple-decker complex, namely, the middle rings are nearly planar and the terminal ligands are puckered. Similar to the triple-decker complex, the tetradeccker complex also prefers to be in its lowest spin state, which in this case is a singlet ($2S + 1 = 1$).

The $\text{Ti}_3(\text{C}_3\text{B}_2\text{H}_5)_4$ system can bind a maximum of nine H_2 molecules, with three H_2 's bound atomically, while the rest of the six H_2 's are bound in molecular form. As anticipated, the coordination of the middle Ti atom changed from η^5 - to η^2 -type bonding to accommodate the molecular form of H_2 (see Figure 5b). It is also observed that the addition of H_2 molecules did not alter the spin state of the $\text{Ti}_3(\text{C}_3\text{B}_2\text{H}_5)_4$ complex. The

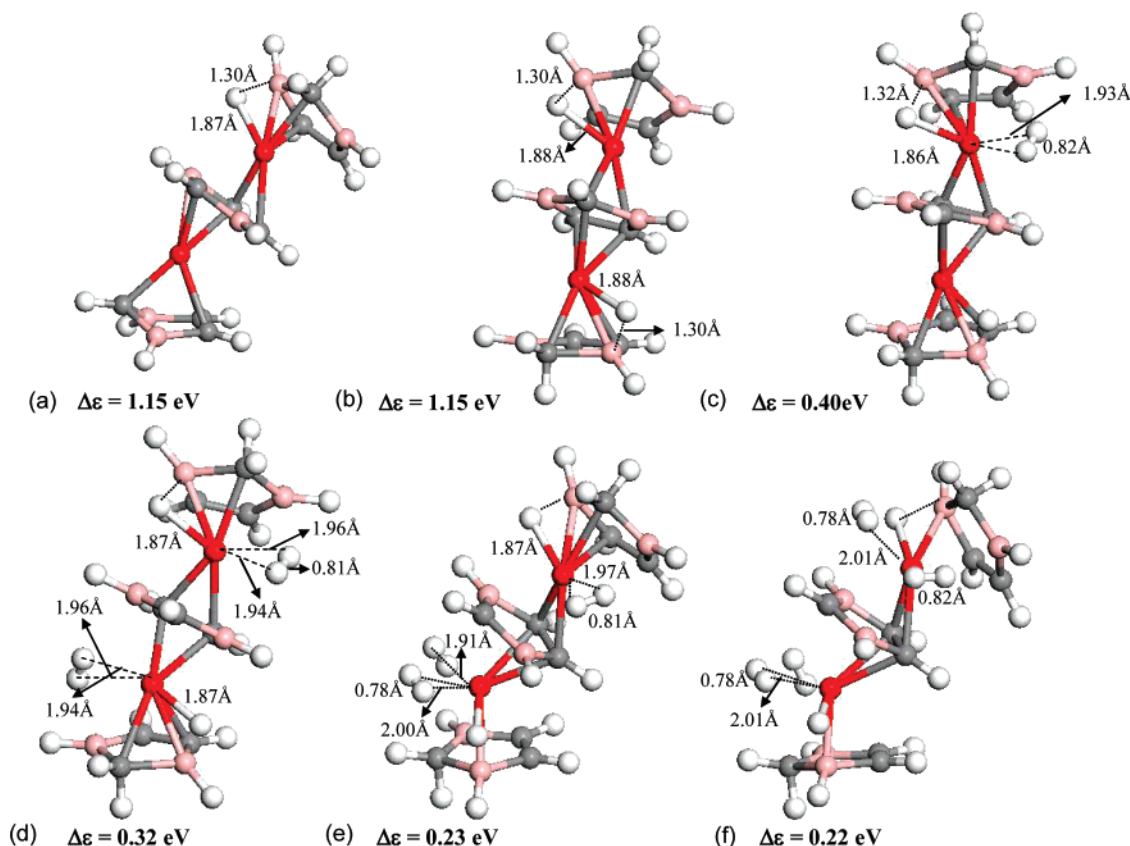


Figure 4. Optimized geometries of $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3(\text{H}_2)_n$ ($n = 1-6$) along with important bond lengths (angstroms). The energy gain, $\Delta\epsilon$, by the successive addition of H_2 molecules is also shown.

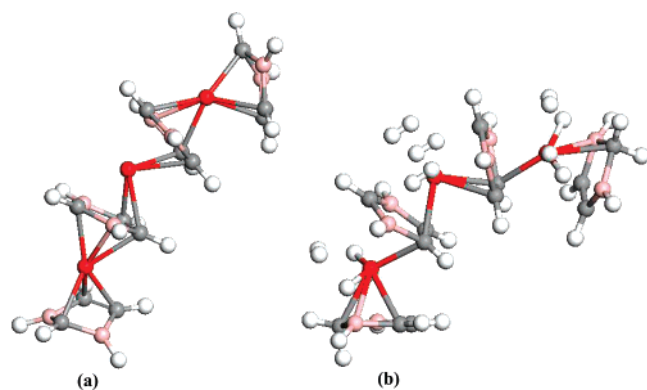


Figure 5. Equilibrium geometries of $\text{Ti}_3(\text{C}_3\text{B}_2\text{H}_5)_4$ and $\text{Ti}_3(\text{C}_3\text{B}_2\text{H}_5)_5$ complexes.

average binding energy per H_2 molecule in the $\text{Ti}_3(\text{C}_3\text{B}_2\text{H}_5)_4$ system is calculated to be 0.48 eV, which is again ideal for reversible hydrogen storage. Thus, the larger systems indeed reveal similar bonding interaction with the hydrogen molecule and the number of hydrogen molecules that each Ti atom can accommodate remains same.

It is mentioned earlier in this article that the hydrogen uptake by Ti can be increased by decreasing the total number of electrons in the system. Therefore, does a further substitution of more carbon atoms by boron increase the hydrogen storage capacity? As the next logical step, we have examined the hydrogen storage capacity of metal-carborane, $\text{Ti}_2(\text{C}_2\text{B}_3\text{H}_5)_3$, multidecker sandwich complex. Our preliminary studies on this system reveal that the maximum number of H_2 molecules that can be bound to a Ti atom remains the same as that in the case of $\text{Ti}_n(\text{C}_3\text{B}_2\text{H}_5)_{n+1}$.

IV. Summary and Conclusions

In summary, we carried out a systematic calculation of the structure and stability of multidecker TiCp complexes and determined their ability to store hydrogen. We found that in Ti_nCp_n complexes, the Ti atoms would prefer to cluster. Although this clustering can be partially avoided by capping the Ti atom in a $\text{Ti}_n\text{Cp}_{n+1}$ complex, the ability of such a complex to store hydrogen is severely undermined as the Ti atoms, sandwiched between two Cp rings, are unable to bind additional H_2 molecules through back charge donation. We have found that this problem can be remedied by reducing the number of electrons available for bonding in the Cp ring. By replacing two of the C atoms in the C_5H_5 ring with B, the rings can be made electron-deficient. Thus, Ti atoms sandwiched between the $\text{C}_3\text{B}_2\text{H}_5$ rings can bind to more hydrogen molecules. We have shown that in a $\text{Ti}_2(\text{C}_3\text{B}_2\text{H}_5)_3$ complex the Ti atoms can remain isolated and be able to bind up to six H_2 molecules with an average binding energy of 0.58 eV/ H_2 molecule. Thus, one can achieve a gravimetric density of 5.1 wt % with a material that can not only store hydrogen reversibly at near ambient conditions but also can be synthesized in bulk quantities. This material meets the Department of Energy target set for 2008. We hope that this prediction will stimulate experimental study.

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