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Ti-Substituted Boranes as Hydrogen Storage Materials: A Computational Quest for the Ideal Combination of Stable Electronic Structure and Optimal Hydrogen Uptake

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Abstract: Based on the Wade–Mingos $n+1$ rule for the *closo*-boranes ($B_nH_n^{2-}$), a family of Ti-substituted *closo*-boranes has been designed computationally. Due to the isolobal relation of Ti to a BH^{2-} group, these Ti-substituted boranes have $n+1$ pairs of skeletal electrons to fulfill the bonding requirement for such stable cages. The reported representatives, $B_4H_4Ti_2H_2$ in particular, not only have stable electronic structures but also superior capability to adsorb hydrogen. The optimal binding energies and high gravimetric densities of hydrogen storage indicate their potential to store hydrogen for practical applications. Simultaneously achieving electronic stability and optimal hydrogen uptake may provide a way of overcoming the issue of aggregation in designing transition-metal-decorated hydrogen storage materials. This study invites experimental realization of novel boranes and provides new ideas for searching for hydrogen storage materials.

Keywords: ab initio calculations · boranes · hydrogen · hydrogen storage · titanium

Introduction

The dream of driving hydrogen-powered vehicles hinges on overcoming the challenge to find safe and efficient materials for onboard hydrogen storage.[1,2] For practical applications, hydrogen storage materials should firstly have certain gravimetric and volumetric densities of hydrogen storage under ambient conditions. The U.S. Department of Energy (DOE) has set targets of a gravimetric density of 6.0% in 2010 and 9.0% in 2015, and volumetric capacity of 45 $g L^{-1}$ in 2010 and 81 $g L^{-1}$ in 2015 for usable specific energy from H_2 (net useful energy/max. system mass or volume).[3] Another important requirement is reversibility of hydrogen uptake and release in the temperature range of −20 to 50 °C and moderate pressure (max. 100 atm). High-pressure and cryogenic hydrogen storage systems are not ideal for civilian applications due to safety concerns and the energy consumed in pressurizing and cooling the systems. Storing hydrogen in complex hydrides,[2a,b,4] metal–organic frameworks (MOF),[2c,5] and molecular clathrates[2d,6] are actively pursued areas. Ammonia–borane complex ($NH_3{\cdot}BH_3$) also shows promise for hydrogen storage.[7]

Hydrogen sorbents in which hydrogen weakly binds to the host materials are viable candidates for onboard hydrogen storage because of their possible low binding energy, fast kinetics, and structural stability in operation, which meet DOE requirements for low thermal management, high efficiency, and fast charging/discharging rate. Unfortunately, none of the available sorbents has met the volumetric and gravimetric requirements at room temperature. The binding energy of molecular hydrogen is crucial in designing hydrogen storage materials. To achieve the DOE target under ambient conditions, the ideal H_2 binding energy should be in the range of 20–40 $kJ mol^{-1}$ per hydrogen molecule,[8] which is intermediate between those of physisorbed and chemisorbed states.

Dihydrogen coordination, discovered by Kubas and co-workers,[2g,9] laid the foundation for searching for hydrogen storage materials in the realm between physisorption and chemisorption. The reversible binding of H_2 molecules to metal complexes and the low energies for hydrogen uptake and release under near-ambient conditions are ideal properties for hydrogen storage. However, the synthesized metal complexes often have "heavy ligands" to ensure thermal and electronic stability, which result in low gravimetric density of hydrogen storage and limit their practical applications. The issue of reducing the number of heavy ligands to improve the gravimetric density needs to be solved for practical applications.[2g] The metal-free "frustrated Lewis pairs", recently reported by Stephan and co-workers,[10] also face the same issue if applied for hydrogen storage.

Computational chemists and physicists have also played active roles in searching for such new materials. They provided ideas and designed candidates for experimental realization.[11–13] For example, the titanium–ethylene-based materials designed by Yildirim and co-workers[11a] were recently realized experimentally by Phillips and Shivaram;[14] encouraged by theoretical studies that showed boron doping can enhance hydrogen adsorption in fullerenes[15] and carbon nanotubes,[15b] Wu and co-workers[16] synthesized microporous boron-substituted carbon materials which exhibit a significantly higher hydrogen binding energy (−11 $kJ mol^{-1}$)

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than the corresponding carbonaceous materials; guided by the predictions that hypothetical Ti-decorated fullerenes[11a] and carbon nanotubes[12a] can have high hydrogen storage capabilities and ideal H_2 binding energies (20–30 kJ mol^{-1}) for room-temperature hydrogen storage, Antonelli et al.[17] synthesized Ti-grafted mesoporous silica with H_2 binding enthalpies up to 22 kJ mol^{-1}.

On the other hand, there is a large gap between experiment and theory in terms of what can be achieved in the laboratory and what holds the best promises for room-temperature reversible storage. Extensive first-principles computations have been performed to search for promising hydrogen storage materials, among which a major class consists of transition metal (TM) decorated nanostructures such as fullerenes,[11a,18] carbon nanotubes,[12a,b] boron nitride nanotubes,[19] and boron-based nanosystems.[20] However, these predicted TM-decorated nanostructures remain hypothetical structures because of clustering of the TM atoms.[11b,21] To tame the aggregation issue, one possible approach is to have the TM guests optimally match the host (or base) electronically. It has also been proposed that the lithium-coated fullerene $C_{60}Li_{12}$ can overcome the clustering problem,[11c] and this species has been detected as a stable entity by mass spectrometry,[22] but energetic estimations suggest that in the bulk $C_{60}Li_{12}$ should be unstable with respect to decomposition into C_{60} and lithium metal,[23] so preparation of $C_{60}Li_{12}$ is expected to be rather difficult and has not been achieved so far.

To search for promising hydrogen adsorbents, a good approach is to simultaneously optimize the H_2 binding strength, structural stability, and chemical stability. Here we propose to incorporate transition metals into *closo*-boranes to achieve both stable electronic structures and hydrogen uptake with ideal gravimetric densities greater than the 2010 DOE target.[3]

Computational Details

Nonbonding interactions are not treated well by classical density functional theory (DFT).[8] Typically, the local density approximation (LDA) overestimates and the generalized gradient approximation (GGA) underestimates dihydrogen binding energies.[15a,24] Therefore, we employed the wave-function-based second-order Møller–Plesset (MP2) and fourth-order Møller–Plesset (MP4) methods, which include both (weakly) overlapping densities and dispersion interactions, to evaluate the dihydrogen binding energies.

All structures were optimized and ascertained to be energy minima by frequency analyses at the MP2/6-311++G(d,p) level. The binding (i.e., H_2-adsorption) energies used in the following discussion are estimated by $\Delta E = E_{complex} - E_{sorbent} - nE_{H2} + \Delta E_{BSSE} + \Delta E_{ZPE}$, where $E_{complex}$, $E_{sorbent}$, and E_{H2} are the MP4/6-311++G(3df,2p)//MP2/6-311++G(d,p) single-point energies of the H_2-loaded complex, the sorbent (substituted *closo*-boranes), and free H_2 molecule, respectively, and n is the number of adsorbed H_2 molecules. The basis set superposition error ΔE_{BSSE} is estimated at the same level by using the standard counterpoise method[25] implemented in Gaussian 03.[26] ΔE_{ZPE} is the zero-point energy correction at the MP2/6-311++G(d,p) level. Note that including ZPE correction is critical to get accurate H_2 static binding energies,[27] and BSSE may also be important for nonbonding interactions,[28] though such corrections have not been well implemented in searching for hydrogen storage materials.

For comparison, the dihydrogen binding energies were evaluated with PBEPBE[29] and M05-2X[30] density functionals with 6-311++G** basis set and are provided in the Supporting Information (SI1). PBEPBE is a widely used density functional in theoretical investigations on hydrogen storage, while M05-2X typically performs very well in treating noncovalent interactions. However, both density functionals can overestimate or underestimate the molecular hydrogen binding energies for the systems considered here when the MP4 data are used as reference; the largest deviations are about 17 kJ mol^{-1} for M05-2X and about 9 kJ mol^{-1} for PBEPBE. This calls for further attention when density functional methods are used to study molecular-hydrogen binding energies. Nevertheless, due to their large sizes, the PBEPBE density functional was used in this work to study the dimerization of TM-substituted *closo*-boranes and the Gibbs free energies at different temperatures and pressures of our designed hydrogen storage materials. All the above calculations were carried out with the Gaussian 03 program suite.[26]

Periodic boundary conditions (PBC) DFT computations were performed to optimize the three-dimensional (3D) solids of TM-substituted *closo*-boranes linked with C≡C bonds. The plane-wave basis set with the ultrasoft pseudopotential proposed by Vanderbilt[31] was used to model the ion–electron interaction, as implemented in the CASTEP code.[32] The generalized gradient approximation (GGA) with the PBE functional[29] and a 340 eV cutoff for the plane-wave basis set were adopted in all the computations. $3\times3\times2$ Monkhorst–Pack special k points were used for sampling the Brillouin zone, and the convergence threshold was set as: energy changes per atom less than 2×10^{-5} eV, root mean square (RMS) of the forces less than 0.05 e Å^{-1}, and the RMS displacement of atoms less than 2×10^{-3} Å. The positions of all the atoms in the cell were not constrained and were fully relaxed as well as the lattice parameters of the cell.

Results and Discussion

Geometries of Ti-substituted *closo*-boranes (B_nH_nTi, $n=5$–11): Boranes are intriguing compounds due to their aesthetically pleasing polyhedral structures, nonclassical bonding, and potential in materials and medical applications. The Wade–Mingos electron counting rule[33] states that $n+1$ pairs of skeletal electrons are required for the stable *closo*-boranes ($B_nH_n^{2-}$). To design TM-containing boranes for hydrogen storage, the transition metal atoms should be exposed to have space available for adsorbing hydrogen, and the substituted boranes should have stable electronic structures. Conventional metallaboranes, clusters that contain boron and metal atoms,[34] can not adsorb hydrogen because of the ligands around the TM atoms, and simply removing the ligands from the metallaboranes will result in unstable electronic structure. To introduce a TM into a *closo*-borane and maintain its neutrality (to avoid unfavorable Coulomb repulsion), the TM must have four valence electrons to fulfill the Wade–Mingos rule[33] and therefore give a stable electronic structure. Titanium is a good candidate, and its heavier congeners are inferior for reasons of gravimetric density. Titanium has also been used in designing organometallic molecules for hydrogen storage.[11a–f] The qualitative reasoning is supported by ab initio calculations. The Ti-substituted *closo*-boranes (B_nH_nTi, $n=5$–11) are all minima, and their lowest (smallest) vibrational frequencies (SVFs) are given in Figure 1. The large Hartree–Fock HOMO–

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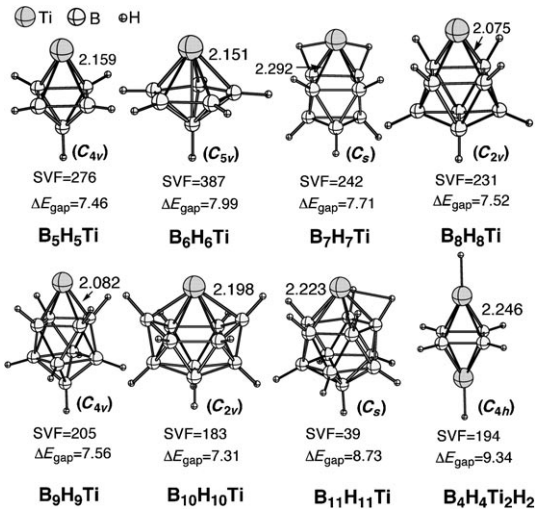

Figure 1. MP2/6-311++G** optimized structures of Ti-substituted boranes and $B_4H_4Ti_2H_2$, including the key bond lengths in ångstrom and the Hartree–Fock HOMO–LUMO gaps (ΔE_{gap} [eV]) obtained in the geometric optimizations.

LUMO gaps, which range from 7.31 to 8.73 eV at the MP2/6-311++G(d,p) level, imply optimal electronic structures. However, optimal electronic structures do not ensure they are global minima. Whether they are global minima was not confirmed. In metallaboranes, ligands are required to achieve stable electronic structures, while the four valence electrons in Ti are used up as skeletal electrons to sustain the cage structure and achieve stable electronic structure. While textbooks[35] often treat metallaboranes with late TMs (e.g., Fe, Co, Ni, and Cu), metallaboranes containing early TMs (e.g., Cr, Mo, W, Ta, and Zr)[36] and Ti^{III}-containing hydroborates have also been synthesized.[37]

Electronic structures and dihydrogen binding energies: Among the Ti-substituted boranes (B_nH_nTi, $n=5$–11), B_5H_5Ti was found to have potential for hydrogen storage with gravimetric density suitable for practical applications. Its isoelectronic analogue $B_4H_4Ti_2H_2$ (Figure 1) is superior according to the dihydrogen binding energies (Table 1). We also investigated the isoelectronic analogue $B_4H_4(CH)Sc$ and found that it has inferior dihydrogen binding energies (for details, see SI2, Supporting Information). In the following, we focus on the electronic structures and hydrogen uptake capabilities of B_5H_5Ti and its analogue $B_4H_4Ti_2H_2$. To our knowledge, various organometallic molecules for hydrogen storage have been designed previously,[2c,5e–l] but using such TM-substituted boranes to store hydrogen has not been explored.

B_5H_5Ti: The optimum electronic structure of B_5H_5Ti is illustrated by the frontier molecular orbitals. Figure 2 A and B display the three highest occupied orbitals, corresponding to the triply degenerate T_{2g} orbitals of the $B_6H_6^{2-}$ prototype. Note that Figure 2 B represents the two degenerate E orbitals in the C_{4v} point group. The Ti d_{xy} orbital in the HOMO−1 orbital (Figure 2 A) lies on the top of the B_4H_4 peripheral orbital with the right atomic orbital phase overlapped. The Ti d_{xz} and d_{yz} orbitals (Figure 2 B) appropriately bridge the fragment orbitals of the B_5H_5 moiety. Unlike the antibonding LUMO in $B_6H_6^{2-}$, the B_5H_5Ti LUMO (Fig-

Table 1. MP4 (ΔE_{MP4}) and MP2 (ΔE_{MP2}) binding energies [kJmol^{-1}], corrected for ZPE (ΔE_{ZPE}) and BSSE (ΔE_{BSSE}), per adsorbed H_2, along with those at the PBEPBE/6-311++G** level. For comparison, the uncorrected values are given in parentheses.

		H_2	$2H_2$	$3H_2$	$4H_2$	$5H_2$
B_5H_5Ti	ΔE_{ZPE}[a]	11.6	14.4	13.8	14.7	14.5
	ΔE_{BSSE}[b]	2.9	2.4	2.6	2.9	3.1
	ΔE_{MP4}[b]	−28.0	−30.4	−28.6	−22.9	−23.5
		(−42.5)	(−47.3)	(−45.0)	(−40.5)	(−41.1)
	ΔE_{BSSE}[c]	2.9	2.9	2.9	3.1	3.3
	ΔE_{MP2}[c]	−22.2	−26.1	−26.1	−21.5	−22.2
		(−36.7)	(−43.4)	(−42.8)	(−39.6)	(−39.9)
	ΔE_{PBE}[d]	−34.7	−36.7	−32.2	−29.7	−27.8
		(−48.2)	(−52.1)	(−46.3)	(−46.1)	(−45.2)
		$2H_2$	$4H_2$	$6H_2$	$8H_2$	
$B_4H_4Ti_2H_2$	ΔE_{ZPE}[a]	4.8	9.7	13.8	15.9	
	ΔE_{BSSE}[b]	2.0	2.2	2.6	2.8	
	ΔE_{MP4}[b]	−40.1	−37.6	−33.8	−35.0	
		(−47.3)	(−49.5)	(−50.2)	(−53.7)	
	ΔE_{BSSE}[c]	2.4	2.7	2.9	3.0	
	ΔE_{MP2}[c]	−34.8	−28.5	−25.3	−24.3	
		(−42.0)	(−40.7)	(−42.0)	(−43.2)	
	ΔE_{PBE}[d]	−34.3	−29.0	−27.0	−26.7	
		(−51.7)	(−47.1)	(−45.0)	(−44.3)	

[a] At the MP2/6-311++G(d,p) level. [b] At the MP4/6-311++G-(3df,2p)//MP2/6-311++G(d,p) level. [c] At the MP2/6-311++G-(3df,2p)//MP2/6-311++G(d,p) level. [d] The ZPEs and BSSEs are corrected at the PBEPBE/6-311++G** level and the values are given in SI1 (Supporting Information).

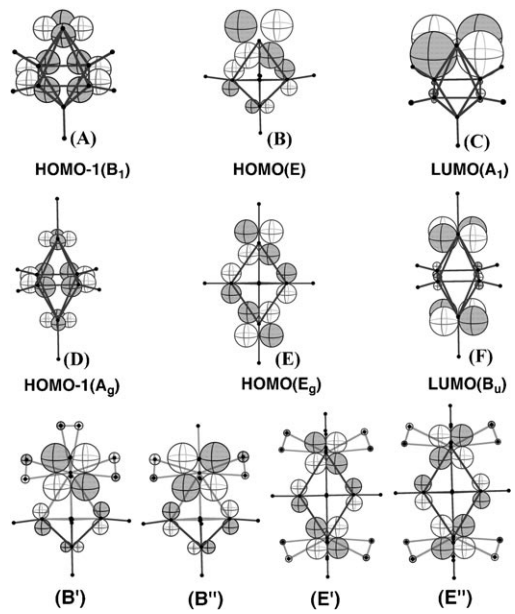

Figure 2. Occupied and unoccupied frontier orbitals of B_5H_5Ti (A–C) and $B_4H_4Ti_2H_2$ (D–F). Orbital interactions between the σ* antibonding orbitals of H_2 and the orbitals in B) in $B_5H_5Ti(H_2)_5$ (B′ and B″) and with the orbitals in E) of $B_4H_4Ti_2H_2(H_2)_8$ (E′ and E″).

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ure 2C) is a nonbonding orbital dominated by the Ti $d_{x^2-y^2}$ orbital. The right occupation of the electrons results in the large HOMO–LUMO gap of 7.46 eV, larger than that of 4.64 eV in $B_6H_6^{2-}$.

B_5H_5Ti not only has the optimum electronic structure but also can adsorb H_2 molecules. The geometrical optimizations show B_5H_5Ti can adsorb up to five H_2 molecules (Figure 3).

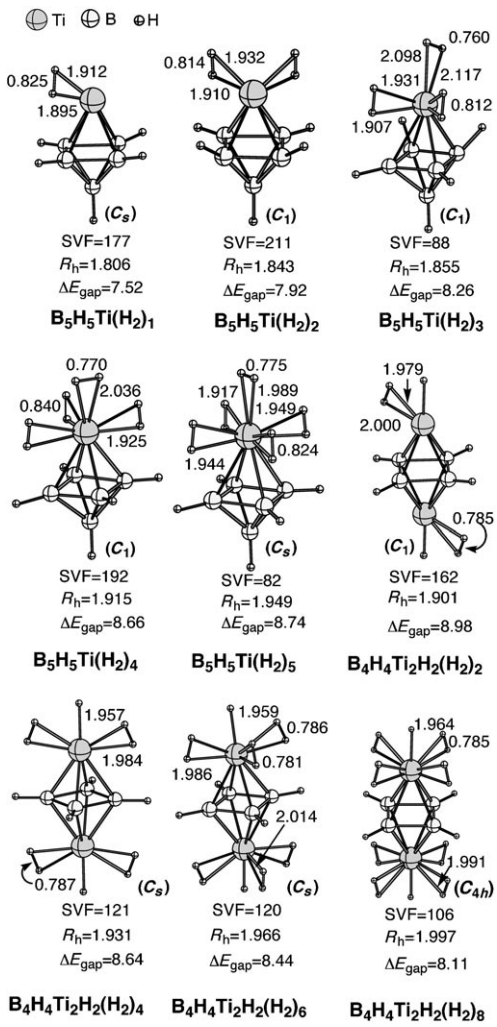

Figure 3. MP2/6-311++G(d,p) optimized structures of the H_2 complexes, including key bond lengths [Å], the lowest (smallest) vibrational frequencies (SVFs), the distances R_h between Ti and the center of the equatorial B_4H_4 ring, and the HOMO–LUMO gaps (ΔE_{gap} [eV]).

The distance between Ti and the center of the equatorial B_4H_4 ring (R_h) in B_5H_5Ti is 1.771 Å. As H_2 molecules are consecutively adsorbed, the B_5H_5Ti moiety expands progressively; the distances R_h in $B_5H_5Ti(H_2)_n$ ($n=1$–5) are 1.806, 1.843, 1.855, 1.915, and 1.949 Å, respectively. In $B_5H_5Ti(H_2)_3$, the hydrogen atoms in the equatorial B_4H_4 ring are bent up toward the Ti atom due to electrostatic attraction (see below), but they return to the equator after the fourth and fifth H_2 molecules are adsorbed to give $B_5H_5Ti(H_2)_4$ and $B_5H_5Ti(H_2)_5$. The dihydride isomer of $B_5H_5TiH_2$ (the product of homolytic dihydrogen splitting) is 52.6 kJ mol^{-1} higher in energy than $B_5H_5Ti(H_2)$ at the MP4/6-311++G(3df,2p)//MP2/6-311++G**+ZPE level. Thus, it is unlike that hydrogen molecules can be chemically adsorbed at the low temperature required for hydrogen storage.

The orientation of the Ti d orbitals along the Ti–B edges (Figure 2B), results in a preferred orientation of hydrogen adsorption. The H_2 molecules prefer to attach to the Ti atom in a propeller-like pattern in which they eclipse the Ti–B edges. Initial structures constrained to have H_2 molecules parallel to the equatorial B–B edges, went back to the propeller-like pattern during geometrical optimization. H_2 adsorption on the top is less favorable than that on the side. As a consequence, the H–H distances (less than 0.78 Å) of the top H_2 molecules are consistently shorter than the 0.81–0.84 Å of the side H_2 molecules. The on-top adsorption isomer of $B_5H_5Ti(H_2)$ is 14.1 kJ mol^{-1} less stable than that shown in Figure 3 at the MP2/6-311++G(d,p) level. On-top adsorption in $B_5H_5Ti(H_2)_n$ ($n=3$ and 4) can be attributed to minimizing the steric effect.

The longer H–H distances (ca. 0.76–0.78 Å for the top and 0.81–0.84 Å for the side H_2 molecules) relative to free H_2 (0.738 Å), as well as the average Ti–H distances (1.883–2.108 Å), indicate favorable interactions of the H_2 molecules with Ti atoms. Figure 2 includes the molecular orbitals involved in the bonding between H_2 and Ti, which are similar to dihydrogen bonding with transition metals [d_π(TM)–$\sigma^*(H_2)$] uncovered by Kubas et al.[9] The orbitals of $B_5H_5Ti(H_2)_5$, shown in Figure 2B′ and B″, originate from interactions between H_2 antibonding σ^* orbital and the degenerate occupied orbitals shown in Figure 2B. The interaction pattern explains the aforementioned hydrogen-adsorption preference.

The molecular orbitals (Figure 2B) indicate that the B_5H_5 moiety in B_5H_5Ti can be considered as a 4π-electron donor ligand to Ti. Therefore, the total formal electron count on the Ti center in $B_5H_5Ti(H_2)_5$ is 18, which implies that B_5H_5Ti can not adsorb more than five H_2 molecules. The restriction exerted by the 18-electron rule has been applied to interpret the maximum number of hydrogen molecules adsorbed by organometallic systems.[11c,12d] Because of the participation of more Ti d electrons in the bonding with dihydrogen, the Ti–B bonding becomes weaker and weaker when more hydrogen molecules are adsorbed. This explains the expansion of the borane cages as H_2 molecules are adsorbed.

Table 2 lists the natural bond orbital (NBO) charges on the TM centers of the two parent TM-substituted boranes

Table 2. Natural charges [a.u.] on Ti and molecular hydrogen in TM-substituted *closo*-borane hydrogen complexes at the MP2/6-311++G(d, p) level.

B_5H_5Ti	Ti	$(H_2)_1$	$(H_2)_2$	$(H_2)_3$	$(H_2)_4$	$(H_2)_5$
	+1.24	+0.91	+0.38	−0.10	−0.28	−0.82

$B_4H_4Ti_2H_2$	Ti	$(H_2)_2$	$(H_2)_4$	$(H_2)_6$	$(H_2)_8$
	+1.26	+0.88	+0.47	−0.02	−0.60
	+1.26	+0.88	+0.47	−0.02	−0.60

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and their H_2 absorption complexes. The adsorbed hydrogen molecules in all complexes have positive charges. The Ti center in B_5H_5Ti bears positive charge (1.24 e). As more and more hydrogen molecules are adsorbed, the Ti center becomes less and less positively charged, and even has negative a charge when more than three hydrogen molecules are adsorbed. The change in charge on the Ti center is due to the electron donation from the dihydrogen σ bond to Ti. Consequently, the H–H bonds are elongated.

Relative to B_5H_5Ti, the binding energies per H_2 adsorption in $B_5H_5Ti(H_2)_n$ (n=1–5) are −28.0, −30.4, −28.6, −22.9, and −23.5 kJ mol^{-1} (Table 1), respectively. According to the above analyses, the molecular hydrogen binding energies include contributions from orbital interactions and electrostatic interactions. The former are always favorable to the binding, whereas the latter may change their role, depending on the number of adsorbed hydrogen molecules. The electrostatic interaction in $B_5H_5Ti(H_2)_n$ (n=1 and 2) is unfavorable because of the like positive charges on Ti and the adsorbed hydrogen molecules, but it becomes attractive in $B_5H_5Ti(H_2)_n$ (n=3, 4, and 5). Glancing at their structures, one might expect that the binding energy in $B_5H_5Ti(H_2)_5$ would be much smaller than that in $B_5H_5Ti(H_2)$ because of van der Waals repulsion among the adsorbed hydrogen molecules. However, they have very similar binding energies, partially due to the compensation from the attractive electrostatic interactions in $B_5H_5Ti(H_2)_5$. We attribute the above-mentioned upward bending of the equatorial hydrogen atoms toward Ti in $B_5H_5Ti(H_2)_3$ to the electrostatic attraction between them (Ti bears a negative charge and the hydrogen atoms are positively charged). However, as more H_2 molecules are adsorbed, the steric effects push them back.

The substantial binding energies indicate its potential for hydrogen storage. The significant ZPE corrections (ca. 20–50% of the uncorrected binding energies) suggest that cautions be taken when estimate the adsorption energies without ZPE corrections in the computational design. B_5H_5Ti can adsorb five H_2 molecules with average hydrogen binding energy of −23.5 kJ mol^{-1}, and the theoretical gravimetric density (i.e., not including the density decrease due to packaging etc.) is 8.6%, greater than the 2010 target (6.0%), but less than the 2015 target (9.0%) set by DOE.[3]

$B_4H_4Ti_2H_2$: $B_4H_4Ti_2H_2$ has the same number of skeletal electron pairs as B_5H_5Ti. The HOMO–LUMO gap of 9.34 eV is larger than those of 7.46 eV in B_5H_5Ti and 8.99 eV in carborane $C_2B_4H_6$. The optimum electronic structure can be appreciated by examining the frontier orbitals. Figure 2D and E display the three highest occupied orbitals, and Figure 2F the LUMO. Note that Figure 2E represents the two degenerate E_g orbitals in the C_{4h} point group. The optimized structures (Figure 3) of the $B_4H_4Ti_2H_2(H_2)_n$ (n=2, 4, 6, 8), as well as the exemplified orbital interactions (Figure 2E′ and E″), indicate that they have adsorption and bonding patterns similar to those of the B_5H_5Ti-based complexes, which confirm the robust adsorption preference. Relative to $B_4H_4Ti_2H_2$, the binding energies per H_2 molecule are −40.1 (n=2), −37.6 (n=4), −33.8 (n=6), and −35.0 kJ mol^{-1} (n=8), respectively. In comparison with B_5H_5Ti, $B_4H_4Ti_2H_2$ has better hydrogen uptake capability if the same numbers of H_2 molecules are adsorbed per Ti center; the average molecular hydrogen binding energies of $B_4H_4Ti_2H_2(H_2)_n$ (n=2, 4, 6, and 8) are about 20–50% larger than those of $B_5H_5Ti(H_2)_n$ (n=1, 2, 3, and 4; −28.0, −30.4, −28.6, and −22.9 kJ mol^{-1}, respectively). It seems that there is a discrepancy between the hydrogen binding energies and the elongations of the adsorbed H_2 molecules; the H_2 molecules in $B_4H_4Ti_2H_2(H_2)_n$ are less lengthened than those in $B_5H_5Ti(H_2)_n$ (see Figure 3). The discrepancy can be reconciled by considering the expansion as H_2 molecules are adsorbed. Because the Ti atom in $B_4H_4Ti_2H_2$ (R_h=1.881 Å) is further from the equatorial B_4H_4 ring than that in B_5H_5Ti (R_h=1.771 Å), the $B_4H_4Ti_2H_2$ moiety expands less than the B_5H_5Ti moiety on H_2 adsorption. Consequently, the strains due to H_2 adsorption in the former are smaller than those in the latter, which benefits the binding energies. The theoretical hydrogen uptake of $B_4H_4Ti_2H_2(H_2)_8$ is 10.0 wt%, larger than the DOE targets of 6.0% in 2010 and 9.0% in 2015.

While the PBEPBE binding energies of $B_4H_4Ti_2H_2(H_2)_n$ are close to the MP2 values, within about 2 kJ mol^{-1}, relatively large differences, ranging from 5.6 to 12.7 kJ mol^{-1}, are observed in the case of $B_5H_5Ti(H_2)_n$ (Table 1). Relative to the MP4 values, the PBEPBE method overestimates the binding energies in $B_4H_4Ti_2H_2(H_2)_n$, but underestimates the binding energies in $B_5H_5Ti(H_2)_n$.

The HOMO–LUMO gaps of the two types of H_2-loaded complexes as a function of the number of adsorbed H_2 molecules are shown in Figure 4. For B_5H_5Ti-containing complexes, the HOMO–LUMO gaps increase as more H_2 molecules are adsorbed. The increase in the HOMO–LUMO gaps implies that the adsorption of H_2 molecules benefits the electronic stability. The gap of 8.74 eV in $B_5H_5Ti(H_2)_5$ is larger than that of 7.46 eV in isolated B_5H_5Ti. In contrast,

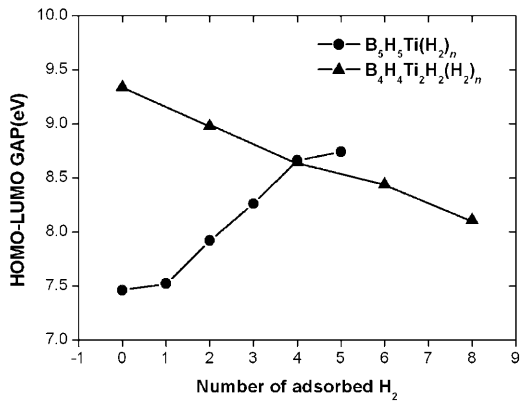

Figure 4. HOMO–LUMO gaps versus the number of the adsorbed hydrogen molecules.

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the adsorption of H_2 molecules to $B_4H_4Ti_2H_2$ narrows the HOMO–LUMO gap, but the smallest gap in $B_4H_4Ti_2H_2(H_2)_8$ is still large (8.11 eV).

Gibbs free energy at different temperatures and pressures: As discussed above, the TM-substituted boranes have desirable binding energies for hydrogen molecules. However, the unfavorable entropic contributions due to the loss of transitional and rotational freedom are not taken into account in the binding energies. Using the ideal gas model as implemented in Gaussian 03, we computed free energies at different temperatures and pressures (50–300 K, 1–200 atm, Figure 5), which allow us to estimate the conditions for

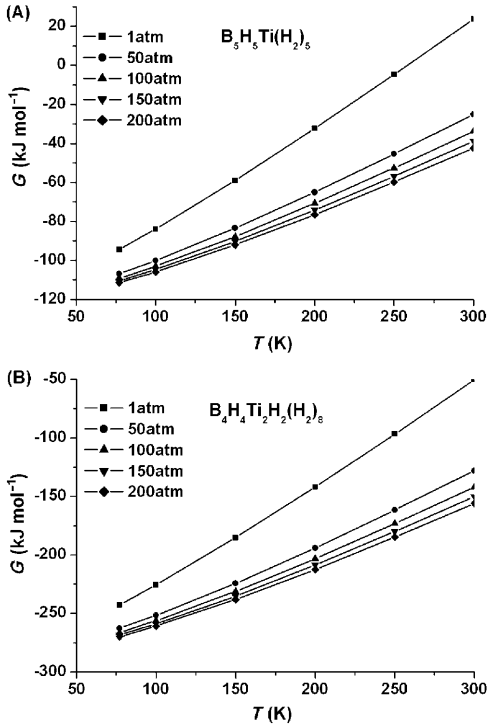

Figure 5. Gibbs free energies of $B_5H_5Ti(H_2)_5$ (A) and $B_4H_4Ti_2H_2(H_2)_8$ (B) at different temperatures and pressures.

"loading" and "unloading" hydrogen molecules from these materials. The binding free energies of $B_5H_5Ti(H_2)_5$ and $B_4H_4Ti_2H_2(H_2)_8$ have similar variation with temperature and pressure; they decrease with increasing temperature and decreasing pressure. However, in light of binding free energy, $B_4H_4Ti_2H_2(H_2)_8$ has better performance than other two, having negative binding free energies in the whole range of the given temperatures and pressures. The ideal gas model only gives an estimation of the thermal contribution to the free energy, and the entropic penalty due to H_2 adsorption is overestimated, because translation and rotation of H_2 molecules are suppressed at high pressure, which is not taken into account in the ideal gas model. Therefore, the predicted binding free energies are underestimated. Nevertheless, Figure 5 can guide us in picking an appropriate temperature and pressure to minimize the cost for pressurizing and cooling the systems.

Dimerization of TM-substituted *closo*-boranes and hydrogen storage capability of the dimers: Due to the large sizes of the dimers, PBEPBE/6-311++G** calculations were used to investigate the dimers of B_5H_5Ti and $B_4H_4Ti_2H_2$ and their hydrogen storage capability and the energetics at this level are used in the following discussions. Though the TM-substituted *closo*-boranes follow the Wade–Mingos electron counting rule and have optimum electronic structures, they may dimerize when approaching each other if the barriers separating the respective monomers are not high. To address this question, we studied the interaction between two Ti-substituted *closo*-boranes. Figure 6 shows the optimized

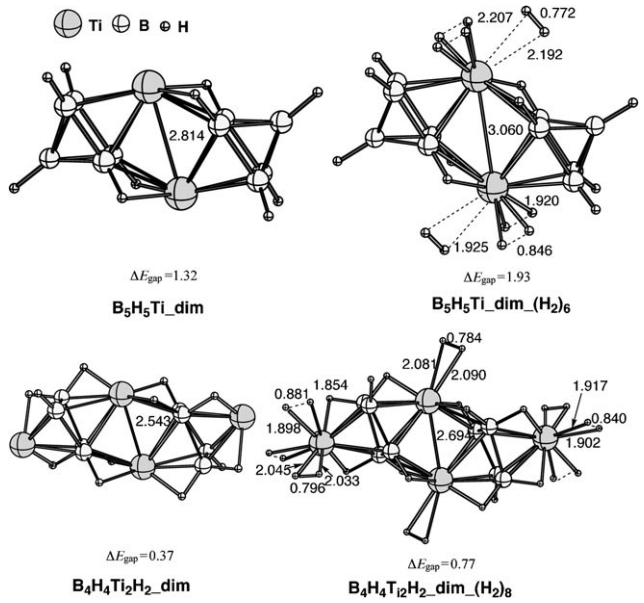

Figure 6. PBEPBE/6-311++G(d,p) optimized structures of the dimers, together with key bond lengths [Å] and the HOMO–LUMO gaps (ΔE_{gap} [eV]).

dimers of B_5H_5Ti and $B_4H_4Ti_2H_2$, $B_5H_5Ti_dim$ and $B_4H_4Ti_2H_2_dim$, respectively. The Ti–Ti bond lengths are 2.814 and 2.843 Å in $B_5H_5Ti_dim$ and $B_4H_4Ti_2H_2_dim$, respectively, and the dimerization energies are −494.1 and −616.3 kJ mol^{-1}, respectively.

This would lower the hydrogen storing capacity of each Ti-substituted *closo*-borane. However, we examined whether the dimers can bind hydrogen. The optimized structures with H_2 molecules attached to the dimers are shown in Figure 6. $B_5H_5Ti_dim$ and $B_4H_4Ti_2H_2_dim$ can adsorb six and eight H_2 molecules, respectively.

As listed in Table 3, relative to the monomers with the same number of adsorbed hydrogen molecules, $B_5H_5Ti_dim(H_2)_n$ ($n=2$, 4) have smaller molecular hydrogen binding energies (−18.9 and −20.9 kJ mol^{-1} per H_2, respectively; the corresponding binding energies for the monomer

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Table 3. PBEPBE/6-311++G** binding energies ΔE_{PBE} [kJ mol^{-1}], corrected for ZPE (ΔE_{ZPE}) and BSSE (ΔE_{BSSE}), per adsorbed H_2. For comparison, the uncorrected values are given in parentheses.

B_5H_5Ti_dim		$2H_2$	$4H_2$	$6H_2$	
	ΔE_{ZPE}	16.2	16.7	14.6	
	ΔE_{BSSE}	0.7	0.9	0.8	
	ΔE_{PBE}	−18.9	−20.9	−12.8	
		(−35.8)	(−38.4)	(−28.2)	
$B_4H_4Ti_2H_2$_dim		$2H_2$	$4H_2$	$6H_2$	$8H_2$
	ΔE_{ZPE}	13.3	15.9	14.7	13.9
	ΔE_{BSSE}	0.6	0.9	0.8	0.8
	ΔE_{PBE}	−43.2	−64.5	−37.5	−32.1
		(−57.1)	(−81.4)	(−53.0)	(−46.7)

are −36.7 and −29.7 kJ mol^{-1} per H_2 at the same theoretical level), while $B_4H_4Ti_2H_2$_dim$(H_2)_n$ ($n=2$, 4, 6, and 8) have larger binding energies (−43.2, −64.5, −37.5 and −32.1 kJ mol^{-1} per H_2; in comparison, the binding energies for the monomer are −34.3, −29.0, −27.0 and −26.7 kJ mol^{-1} per H_2, respectively). These indicate that, though the Ti-substituted *closo*-boranes may dimerize, the binding energies of H_2 to Ti atoms are not or only slightly weakened. The maximum gravimetric densities of hydrogen storage in B_5H_5Ti_dim$(H_2)_6$ and $B_4H_4Ti_2H_2$_dim$(H_2)_8$ are 5.2 and 5.0%, and the molecular hydrogen binding energies −12.8 and −32.1 kJ mol^{-1} per H_2, respectively. The ideal H_2 binding energies suggest that $B_4H_4Ti_2H_2$ is a good hydrogen storage material even in dimeric form, while lower temperatures must be employed when B_5H_5Ti dimer is used to store hydrogen.

Possibility of constructing 2D and 3D networks: To avoid unfavorable dimerization and to further stabilize these building blocks under real conditions, we considered the possibility of constructing 2D and 3D solids.

The B_5H_5Ti molecules are linked with C≡C triple bonds and form a layered solid with interlayer interaction of Ti–H bonding, as shown in Figure 7a. After hydrogen adsorption, the interlayer distance is enlarged to 3.337 Å and the layers are stabilized by van der Waals interaction (Figure 7b). In this configuration the nearest distance between H_2 molecules adsorbed on neighboring Ti atoms is larger than 3 Å; therefore, C≡C is long enough as linker. When $B_4H_4Ti_2H_2$ units are linked with C≡C bonds to build a 3D solid (Figure 7c), there is much larger repulsion between layers, and the interlayer distance is 4.133 Å. Accordingly, in the crystal built from $B_4H_4Ti_2H_2(H_2)_8$ units linked with C≡C bonds (Figure 7d), the layer distance is as large as 5.659 Å to eliminate interlayer repulsion.

The $B_5H_5Ti(H_2)_5$-based solid (Figure 7b) has a molecular hydrogen binding energy of −9.0 kJ mol^{-1} per H_2, and its maximum gravimetric and volumetric densities are 6.26 wt% and 38.2 kg m^{-3}, respectively. The $B_4H_4Ti_2(H_2)_8$-based solid has even better dihydrogen binding energy and gravimetric and volumetric densities: −33.1 kJ mol^{-1} per H_2, 7.86 wt%, and 45.1 kg m^{-3}, respectively, which reach the U.S. DOE 2010 targets. Moreover, carba-*closo*-dodecaborates with one or two alkynyl substituents bonded to boron have been synthesized experimentally,[38] which strongly suggests the viability of our designed solids. Therefore, well-designed 3D solids based on Ti-substituted *closo*-boranes are promising for hydrogen storage, and we strongly invite experimental explorations in this direction.

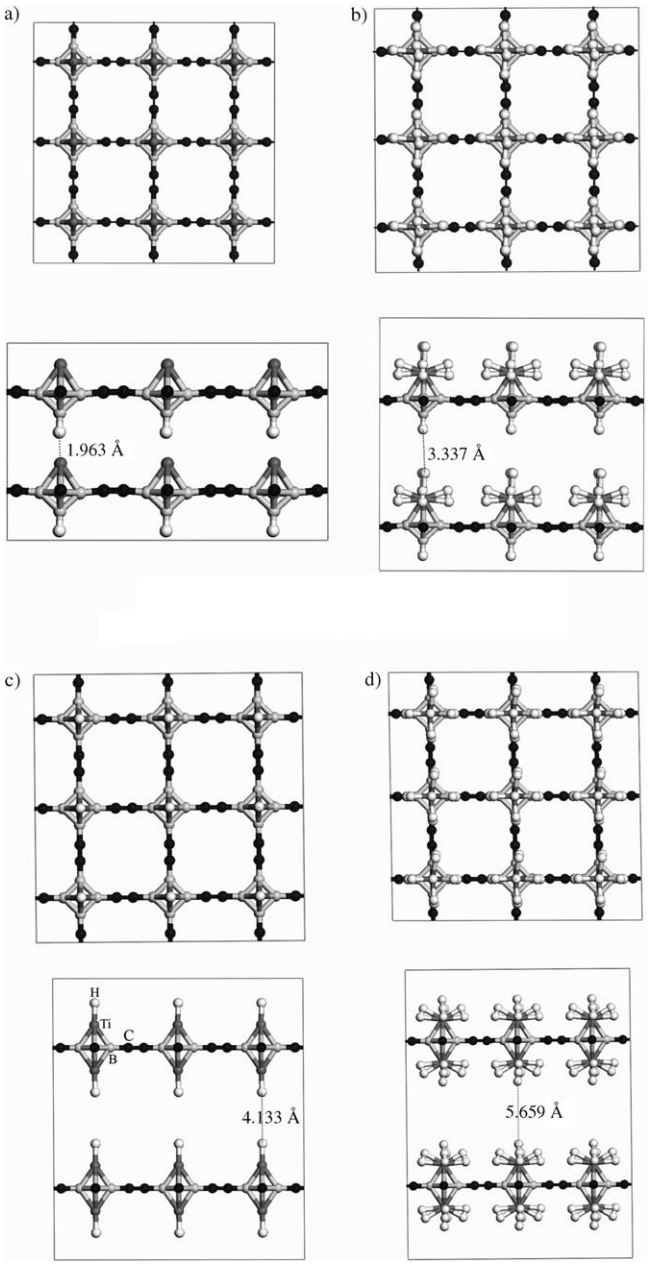

Figure 7. 3D solids constructed by using B_5H_5Ti (a), $B_5H_5Ti(H_2)_5$ (b), $B_4H_4Ti_2H_2$ (c), and $B_4H_4Ti_2H_2(H_2)_8$ (d) as building blocks linked with C≡C bonds. The upper and lower panels are top and side view, respectively.

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Conclusions

In summary, we have computationally designed a family of Ti-substituted *closo*-boranes with stable electronic structures based on the Wade–Mingos electron counting rule, and investigated their ability to store hydrogen. Computations were done at the MP2 and MP4 levels of theory, ZPE and BSSE corrections included, and free-energy profiles studied.

B_5H_5Ti and its TiH-substituted analogue $B_4H_4Ti_2H_2$ have maximum hydrogen uptakes of 8.6 and 10.0 wt%, and desirable ideal molecular hydrogen binding energies (−23.5 and −35.0 kJ mol^{-1} per H_2, respectively), making them promising hydrogen storage materials for practical applications. Such favorable molecular binding energies come from a combination of orbital interactions (Kubas type) and electrostatic interactions. Achieving both stable electronic structure and optimal hydrogen uptake is a big advantage for reversibility, because they can remain electronically stable in the process of hydrogen uptake and release. Free energies at different temperatures and pressures (50–300 K, 1–200 atm) were computed to estimate the conditions for "loading" and "unloading" molecular hydrogen. $B_4H_4Ti_2H_2(H_2)_8$ has the best performance, with negative binding free energies in the whole range of the given temperatures and pressures. Using B_5H_5Ti and $B_4H_4Ti_2H_2$ as building blocks, we designed three-dimensional solids which have optimal dihydrogen binding energies and gravimetric and volumetric densities that reach the U.S. DOE 2010 targets.

The computed Ti-substituted boranes and their solids have not been prepared so far; however, they are similar to available materials and may be obtainable by chemical modification. We warmly invite our experimental peers to realize them experimentally. Materials with stable electronic structure, optimal hydrogen uptake and chemical viability, such as the Ti-substituted *closo*-boranes investigated in this work, may offer new ideas for searching materials as hydrogen storage media.

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