Computational Study of Multiple-Decker Sandwich and Rice-Ball Structures of Neutral Titanium−Benzene Clusters

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Density functional theory calculations were applied to systematically and directly compare the relative energetic stability of multiple-decker sandwich and rice-ball structures for a variety of neutral Ti_mBz_n clusters ($m = 1-4$, $n = 1-5$). Almost all structures favored the multiple-decker sandwich structure, as observed experimentally for early transition metals. The strength of each metal−benzene interaction averages 37 kcal/mol and remains relatively constant for sandwiches with three or more Ti atoms. The most stable smaller rice-ball structures did not have η^6-Bz bound to a single metal atom. Instead, the preferred coordination was having the plane of the benzene molecule parallel to a Ti_2 bond or a Ti_3 face, leading to some distortion of the benzene ring. The larger rice-ball structures, on the other hand, preferred to weaken the metal−metal bonds and retain η^6-Bz bound to a single metal atom, a structural motif shared with sandwiches.

Introduction

The discovery of ferrocene[1] was responsible for extending research in the field of organometallic chemistry to sandwich complexes where a metal atom or ion is sandwiched between two aromatic molecules. Following this there were several reports of sandwich complexes involving two or three metals.[2−4] Further application of laser vaporization/ionization techniques allowed for the synthesis of symmetric one-dimensional multiple-decker sandwich complexes of vanadium and benzene.[5−7] The properties of these clusters including ferromagnetism, electronic structure, infrared bands, and magnetic properties continue to be actively studied both experimentally and theoretically.[8−13] Vanadium and group I metal cations have also been doped into ferrocene to form multiple-decker sandwich polyferrocene complexes.[14,15]

When Co was used in place of V, instead of forming multiple-decker sandwiches, the cobalt atoms clustered together and these clusters were decorated on the outside with benzene molecules.[16] These structures have been dubbed “rice-ball” structures. In fact, it was found that early transition metals (Sc, Ti, V) formed the sandwich structure with benzene, whereas late transition metals (Fe, Co, Ni) form the rice-ball structure.[7,17] A schematic comparing the multiple-decker sandwich and rice-ball structures is shown in Figure 1.

Measurements of the electric dipole of gas-phase MBz_2 clusters found that early transition metals (M = Sc, Ti, V, Nb, Ta, Zr) are indeed symmetric sandwiches with a net zero dipole; the late transition metals M = Co, Ni had net dipoles of 0.7 and 1.3 D, respectively, suggesting that late transition metal sandwiches with benzene adopt an asymmetric structure.[18] The binding energies of several of MBz_2 and M_2Bz_3 sandwich clusters (M = Ti, V, Cr) have also been calculated using several different electronic structure methods.[19] Calculations on late transition metals found that [Cp*ZnZnCp*] (Cp* = C_5Me_5) adopts a coaxial structure where the plane of the Cp* rings is perpendicular to the Zn−Zn bond axis giving the structure 5-fold rotational symmetry,[20,21] whereas for Cu_2 and Ni_2 the predicted stable structure has the plane of the Cp* rings parallel to the metal−metal bond axis such that each ring is bound to both metals.[22] Similar computational results were found for Ni_2Bz_2.[23] A computational study of coaxial BzMMBz (M = Co, Ni, Cu) found that although Co can indeed adopt a highly symmetrical coaxial structure with η^6-Bz, in the Ni and Cu clusters the lower symmetry η^2-Bz was preferred.[24]

Because the laser vaporization/ionization method for producing these clusters results in the formation of charged transition-metal ion−benzene clusters, most of the experimental and theoretical work in this area has focused on cationic or anionic rather than neutral clusters. Recent computational work and vibrational spectroscopy to probe details of the structure, bonding and energetics of these clusters has focused mainly on a single metal atom with one, two or three benzenes,[25−28] providing good benchmarks for further study of the larger clusters. In this study, we have chosen to focus on neutral clusters first. This will serve as a basis for later studies of the charged clusters.

The focus of our present study is to calculate the most stable structures and other low-lying structures corresponding to the multiple-decker sandwich or rice-ball structures of neutral Ti_mBz_n clusters ($m = 1-4$, $n = 1-5$). To our knowledge, this is the first study that systematically and directly compares the energetic stability of multiple-decker sandwich versus rice-ball structures, and that also includes a significant number of clusters. On the basis of these results, we can begin to elucidate the energetic factors controlling why the sandwich structure is favored over the rice-ball structure for titanium and early transition metals. We have not gone into a detailed analysis of the electronic structure of these clusters. Several theoretical studies have covered this, at least for sandwich complexes.[11,13,19]

We find that the rice-ball structure was marginally favored over the sandwich structure for two clusters, Ti_2Bz_2 and Ti_4Bz_4. All other clusters favored the sandwich structure when a direct comparison was made. In the sandwiches, the strength of each Ti−Bz interaction averages 37 kcal/mol; this value remains relatively constant for the larger sandwiches.

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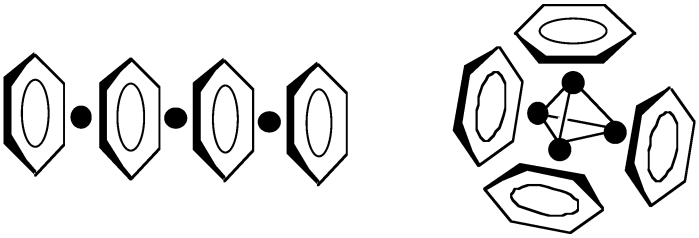

Figure 1. Schematic of multiple-decker sandwich and rice-ball structures of metal−benzene clusters.

The most stable smaller rice-ball structures did not have η^6-Bz bound to a single metal atom. Instead, the preferred coordination was having the plane of the benzene molecule parallel to a Ti_2 bond or a Ti_3 face, leading to some distortion of the benzene ring. In contrast, benzene in multiple-decker sandwiches remained relatively planar and undistorted. On the other hand, the larger rice-ball structures retained relatively planar η^6-Bz bound to a single metal atom and instead preferred weakening the metal−metal bonds; i.e., they preferred to have TiBz units that loosely interacted via the metals. Clusters containing this structural motif (Ti_4Bz_2, Ti_4Bz_3 and Ti_4Bz_4), interestingly, have average binding energies per Bz in the 34−38 kcal/mol range, similar to those for the sandwiches.

We also found that the lowest energy rice-ball structures either were closed shell or were in the triplet state. In contrast, the quintet state was consistently the lowest energy structure for the multiple-decker sandwiches with one exception; the ground state of $TiBz_2$ is a singlet.

The article is organized as follows. After describing the computational methods, we will discuss the results of the bare titanium clusters. This will be followed by the results of each Ti_mBz_n cluster ($m = 1-4$, $n = 1-5$), grouped by molecular formula, with increasing values of m and n. Optimized geometric information, spin state and energetics will be presented for each cluster. The final part of the discussion will cover larger trends comparing the rice-ball structures and the multiple-decker sandwiches.

Computational Methods

All calculations were carried out using Jaguar 5.5[29] at the B3LYP[30−33] flavor of density functional theory. Ti was treated with the Hay and Wadt relativistic effective core potential (ECP),[34] denoted as LACVP in the Jaguar suite. This ECP is a core-valence potential; i.e., the 3s and 3p electrons of Ti are treated explicitly on equal footing with the 3d and 4s valence electrons. C and H atoms were treated at the 6-31G** level. To ensure that we found the ground state structures, optimizations were carried out for several different spin multiplicities. In addition, in some cases where the possibility that other low-lying configurations are easily accessible within a given spin multiplicity, we varied the orbital occupations to find the ground state. This often arises when metal−metal bonds are present in the cluster, corresponding to rice-ball structures. Symmetry constraints, if present, were also removed in the final optimization to ensure that optimized structures were not artificially trapped in higher energy local minima. Zero-point energies and enthalpic corrections were not included because our calculated electronic energies and geometries are in reasonable agreement with the few existing experimental and theoretical values. A more extensive discussion comparing DFT with other methods (and various basis sets, including bases larger than ours) can be found in Pandey et al.,[11] who chose to use GGA for the exchange-correlation functional.[35] We chose B3LYP because we found it more robust for converging the wave function of metal clusters with bound organic molecules.[36]

TABLE 1: Raw Energies, Spin Multiplicities and Average Ti−Bz Interaction Energies of All Clusters Calculated

cluster	$2S + 1$	electronic energy (hartree)	av Ti−Bz interaction energy[a] (kcal/mol)	description
Ti	3	−57.96916		
Ti_2	3	−115.98930		
Ti_3	5	−173.98686		
Ti_4	5	−232.04092		
Bz	1	−232.25318		
TiBz	5	−290.26137	24.5	
$TiBz_2$	1	−522.60405	40.4	sandwich
Ti_2Bz	5	−348.29105	31.3	sandwich
	3	−348.28668	27.7	bridge
	3	−348.25825	9.9	linear
Ti_2Bz_2	5	−580.60328	33.2	sandwich
	3	−580.61489	37.7	2-bridge
	3	−580.52754	10.0	linear
Ti_2Bz_3	5	−812.94455	38.7	sandwich
	1	−812.90636	30.3	rice-ball
Ti_3Bz	3	−406.31821	25.9	bridge
	3	−406.31834	25.9	face
Ti_3Bz_2	5	−638.62782	33.6	sandwich
	1	−638.60784	41.7	rice-ball
Ti_3Bz_3	5	−870.96795	37.8	sandwich
	1	−870.96214	45.1	rice-ball (2-bridge, 1-face)
	1	−870.90920	30.1	rice-ball (3-bridge)
Ti_3Bz_4	5	−1103.27519	37.1	sandwich
	3	−1103.20859	33.1	rice-ball
Ti_4Bz	1	−464.34175	28.8	bridge
	1	−464.34005	27.7	face
Ti_4Bz_2	1	−696.68671	41.8	rice-ball (1-side, 1-face)
	3	−696.66348	34.5	rice-ball (2-bridge)
Ti_4Bz_3	5	−928.98060	36.0	sandwich
	3	−928.96677	34.8	rice-ball
Ti_4Bz_4	3	−1161.29421	37.8	rice-ball
	5	−1161.29187	36.1	sandwich
Ti_4Bz_5	5	−1393.62516	37.9	sandwich

[a] For nonsandwich structures, this is the average binding energy per Bz to the Ti_m cluster.

Results and Discussion

The electronic energies and spin states of all the lowest energy structures for multiple-decker sandwich and rice-ball structures is compiled in Table 1. The average Ti−Bz interaction energies listed have two different reference states. In sandwiches, the total binding energy is referenced to separated Ti atoms; i.e., we assume there is no interaction between the Ti atoms in sandwiches. The average interaction energy is the total binding energy divided by the number of Ti−Bz interactions, e.g., six in the Ti_3Bz_4 sandwich shown in Figure 1. In nonsandwich structures, which include the rice-balls, the total binding energy is referenced to the Ti_m cluster. The average interaction energy is the total binding energy divided by the number of Bz molecules, e.g., four in the Ti_4Bz_4 rice-ball shown in Figure 1. In the text, this is also referred to as the average binding energy to distinguish it from the different reference in the sandwich structures. In the larger rice-ball clusters, we will see an energetic correlation between the interaction energy of Ti atoms decorated with Bz in the rice-ball and in the naked Ti_m cluster.

Titanium Clusters. The ground-state calculated Ti_2 dimer (triplet state) has a bond distance of 1.91 Å and a binding energy of 32.0 kcal/mol in close agreement with experimental results (1.94−1.95 Å, 35.5 kcal/mol).[37,38] Yanagisawa and co-workers calculated a series of transition metal dimers using a series of different DFT functionals and ab initio MO methods using a different basis set.[39] With B3LYP, they calculated a bond distance of 1.88 Å and a binding energy of 40.8 kcal/mol.

The ground-state Ti_3 trimer (quintet state) is an isoceles triangle with one short Ti−Ti bond (2.04 Å) and two longer ones (both 2.61 Å). The Ti−Ti−Ti acute bond angle is 46°. The binding energy is 49.8 kcal/mol with respect to its atoms (i.e., the average Ti−Ti bond is worth 13.6 kcal/mol); however, another way of describing this structure is a Ti_2 dimer loosely interacting with a single Ti atom.

The ground-state Ti_4 tetramer (quintet state) is a distorted tetrahedron with two short Ti−Ti bond distances at 2.12 Å and four long Ti−Ti bond distances averaging 2.67 Å. The binding energy with respect to four Ti atoms is 103.1 kcal/mol. If the tetrahedron is considered to have six Ti−Ti bonds, the average bond is worth 17.2 kcal/mol; perhaps, a better description is to consider Ti_4 as two Ti_2 units that interact less strongly with each other as extrapolated from bond distances.

TiBz. The ground-state TiBz cluster is the quintet state with η^6-Bz bound. The distance of Ti to the center of the Bz ring is 1.95 Å. The binding energy is 24.5 kcal/mol. This is in reasonable agreement with previous computational studies by Chaquin et al.[27] (1.94 Å, 27.7 kcal/mol) and Pandey et al.[11] (21 kcal/mol), and experimental results from Kurikawa et al.[7] (22 kcal/mol). Note that the latter two numbers were back-calculated by subtracting the triplet to quintet state excitation energy of Ti atom worth 0.8 eV (approximately 18 kcal/mol).

$TiBz_2$. The ground state of the $TiBz_2$ sandwich is the singlet state with the benzenes eclipsed. The staggered conformation is less than 1 kcal/mol higher in energy. The distance of Ti to the center of the Bz rings is 1.97 Å. The binding energy is 80.7 or 40.4 kcal/mol per Ti−Bz interaction. There are no direct experimental binding energies. A previous computational study by Yasuike et al.[19] gave 83.7 kcal/mol with UB3LYP and 89.7 kcal/mol with ROMP2. Pandey et al.[11] calculate the binding energy to be 76.6 kcal/mol with GGA. The larger binding energy in $TiBz_2$ compared to TiBz suggests a cooperative binding effect. Once the first Bz binds, the second binds even more readily.

$TiBz_3$. Attempts to find an optimized structure with all three benzenes bound to a single Ti atom were unsuccessful. One of the benzenes would move away during the optimization and the other benzenes would open up the Bz−Ti−Bz angle to form the linear sandwich $TiBz_2$.

Ti_2Bz. Three structures were considered: a sandwich structure (Ti−Bz−Ti), a linear structure maintaining the titanium dimer (Ti−Ti−Bz), and a bridged structure with Bz bridging both Ti atoms in the dimer. These structures are schematically shown in Figure 2. The sandwich structure (quintet state) has the lowest energy. The distance between Ti to the center of the Bz ring is quite short, averaging 1.74 Å. For the sandwich structure,

$$\mathrm{Ti_2Bz\ (sandwich)} \rightarrow \mathrm{2Ti + Bz} \qquad \Delta E = 62.5\ \mathrm{kcal/mol}$$

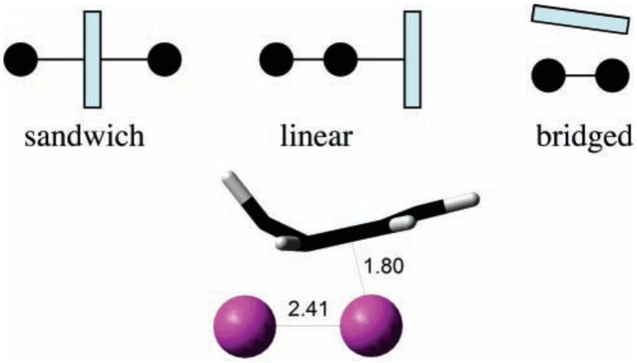

Figure 2. Schematic of Ti_2Bz structures and optimized structure of bridged Ti_2Bz.

The average Ti−Bz interaction energy is 31.3 kcal/mol, stronger than in TiBz, but weaker than in $TiBz_2$.

The bridged and linear structures (both triplet state) are 2.8 and 20.6 kcal/mol, respectively, higher in energy than the sandwich structure. For these other two structures, the binding energies can be calculated with reference to Ti_2 (as a unit) and Bz, assuming that the Ti−Ti bond does not change significantly in Ti_2Bz compared to Ti_2.

$$\mathrm{Ti_2Bz\ (bridged)} \rightarrow \mathrm{Ti_2 + Bz} \qquad \Delta E = 27.7\ \mathrm{kcal/mol}$$

$$\mathrm{Ti_2Bz\ (linear)} \rightarrow \mathrm{Ti_2 + Bz} \qquad \Delta E = 9.9\ \mathrm{kcal/mol}$$

In the linear structure, the Ti−Ti distance remains short at 1.95 Å. The distance of the Ti closer to the center of the ring is longer at 2.25 Å. Hence, our assumption in calculating a binding energy with respect to Ti_2 of 9.9 kcal/mol for the linear structure is quite reasonable.

In the bridged structure, the Bz is distorted and asymmetrically bound, as shown in Figure 2 on the right. The Ti−Ti distance opens to 2.41 Å. One of the Ti atoms interacts with the center of the ring with a distance of 1.80 Å to the center of the planar part of the ring. (The average Ti−C distance to the five C atoms in the plane is 2.29 Å.) The other Ti atom is responsible for the distortion of Bz. The shortest Ti−C distance is 2.01 Å. Because the Ti−Ti bond is essentially broken in the bridged structure (the Ti−Ti bond energy is worth only 3.2 kcal/mol at this longer distance), we can also express the interaction energy with reference to two separate Ti atoms.

$$\mathrm{Ti_2Bz\ (bridged)} \rightarrow \mathrm{2Ti + Bz} \qquad \Delta E = 59.7\ \mathrm{kcal/mol}$$

The "average" interaction energy between each Ti atom and Bz would then be 29.7 kcal/mol, which is slightly weaker than that in the sandwich structure (31.3 kcal/mol); however, note that the interaction of Bz to each Ti is quite different in this bridged structure. For consistency, we will reference the nonsandwich structures to the Ti_m cluster and separated Bz molecules. Thus, the binding energy listed in Table 1 for this cluster is 27.7 kcal/mol when referenced to Ti_2 and Bz.

Ti_2Bz_2. Three structures were considered: a sandwich structure (Ti−Bz−Ti−Bz), a linear structure with Bz bound to each Ti in the dimer, and having both Bz molecules bridge the dimer. These structures are shown in Figure 3. The doubly bridged structure (triplet state) has the lowest energy.

The bridged structure is quite interesting. There is still a relatively strong Ti−Ti bond (2.11 Å), about 75% the strength of fully optimized Ti_2. The two benzenes are distorted in such a way that the Bz rings adopt a V-shape so that each metal atom can bind to "half" the benzene ring. The binding energy

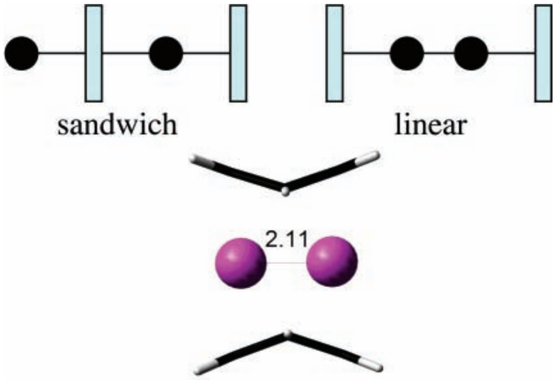

Figure 3. Schematic of sandwich and linear Ti_2Bz_2 structures and optimized structure of bridged Ti_2Bz_2.

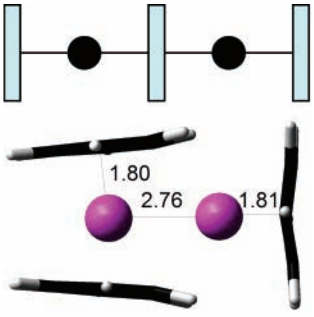

Figure 4. Schematic of the Ti_2Bz_3 sandwich and optimized structure of the Ti_2Bz_3 rice-ball.

can be calculated according to

$$Ti_2Bz_2\ (\text{bridged}) \rightarrow Ti_2 + 2Bz \qquad \Delta E = 74.8\ \text{kcal/mol}$$

Hence, the binding energy per Bz to the Ti_2 dimer is 37.4 kcal/mol, which is stronger than the 27.7 kcal/mol calculated for bridged Ti_2Bz.

The sandwich structure (quintet state) is 7.3 kcal/mol higher in energy than the bridged structure. For the sandwich structure,

$$Ti_2Bz_2\ (\text{sandwich}) \rightarrow 2Ti + 2Bz \qquad \Delta E = 99.5\ \text{kcal/mol}$$

With three Ti−Bz interactions, the average Ti−Bz interaction energy is 33.2 kcal/mol. The distance between Ti and the ring centers from left to right (according to Figure 3) are 1.71, 1.77 and 1.89 Å respectively.

The linear structure (triplet state) is much less stable, 54.8 kcal/mol higher in energy compared to the bridged structure. The Ti−Ti bond distance is 1.83 Å and the distance between Ti and the ring centers is 2.22 Å; the rings prefer to be eclipsed. The binding energy of the Bz rings with respect to the dimer is rather weak.

$$Ti_2Bz_2\ (\text{linear}) \rightarrow Ti_2 + 2Bz \qquad \Delta E = 20.0\ \text{kcal/mol}$$

Hence, the average binding energy is 10.0 kcal/mol.

Ti_2Bz_3. Two structures were considered: the sandwich structure and a rice-ball structure (see Figure 4). The sandwich (quintet state) has the lower energy. The rice-ball structure (triplet state) is 24.0 kcal/mol higher in energy.

For the sandwich structure,

$$Ti_2Bz_3\ (\text{sandwich}) \rightarrow 2Ti + 3Bz \qquad \Delta E = 154.8\ \text{kcal/mol}$$

With four Ti−Bz interactions, the average Ti−Bz interaction energy is 38.7 kcal/mol. The three Bz rings are eclipsed in the optimum structure. The distance of Ti to the center of the inner and outer Bz rings are 1.80 and 1.87 Å, respectively.

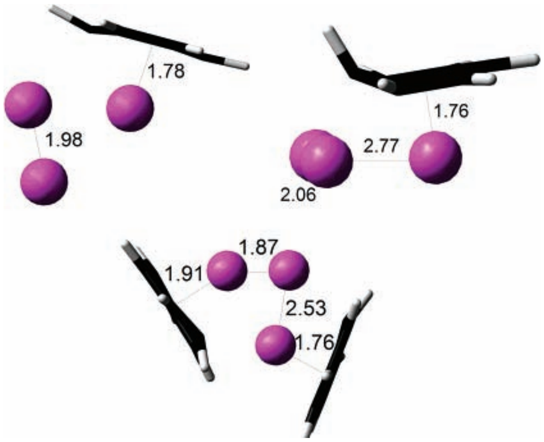

Figure 5. Optimal rice-ball structures of Ti_3Bz and Ti_3Bz_2.

For the rice-ball structure, the Ti−Ti bond is practically broken (2.76 Å). One Ti atom is sandwiched between two slightly distorted Bz molecules. The distance of Ti to the center of the Bz rings is 1.80 Å. The other Ti atom interacts with a single Bz molecule; the distance of Ti to the center of the Bz ring is 1.81 Å. If we assume that there is no Ti−Ti bond,

$$Ti_2Bz_3\ (\text{rice-ball}) \rightarrow 2Ti + 3Bz \qquad \Delta E = 122.8\ \text{kcal/mol}$$

With three interactions, the average Ti−Bz interaction energy is 40.9 kcal/mol. Although this structure at first glance looks like a rice-ball, it is perhaps more accurate to describe it as two loosely interacting sandwich structures: one $TiBz_2$ unit interacting with one TiBz unit. We have not quantified the interaction energy between these two units.

However, to be consistent, if we choose Ti_2 as the reference state,

$$Ti_2Bz_3\ (\text{rice-ball}) \rightarrow Ti_2 + 3Bz \qquad \Delta E = 90.8\ \text{kcal/mol}$$

With three interactions, the average Ti−Bz interaction energy is 30.3 kcal/mol.

Ti_2Bz_4. Attempts to find an optimized structure of Ti_2Bz_4 were unsuccessful. Ti_2Bz_4 separated into two $TiBz_2$ sandwich molecules from several reasonable starting structures that contained a Ti−Ti bond.

Ti_3Bz. Two rice-ball structures were considered, one corresponding to a face-bound Bz (which interacts with all three Ti atoms in Ti_3) and one corresponding to a bridged structure. Both structures (shown in Figure 5, top) have a triplet ground state and coincidentally have the same energy. Both structures can also best be described by a TiBz unit interacting with a Ti_2 dimer. In the bridged structure, the Ti−Bz distance to the center of the ring is 1.78 Å, the Ti−Ti bond in the Ti_2 unit is 1.98 Å, and the average distance of the Ti_2 unit to the other Ti atom is 2.68 Å. In the face-bound structure, one of the CH units in the Bz ring is severely distorted by the Ti_2 unit. The Ti−Bz distance to the center of the ring (discounting the distortion) is 1.76 Å, the Ti−Ti bond in the Ti_2 unit is 2.06 Å, and the average distance of the Ti_2 unit to the other Ti atom is 2.77 Å. The binding energy of Bz to Ti_3 is

$$Ti_3Bz \rightarrow Ti_3 + Bz \qquad \Delta E = 25.9\ \text{kcal/mol}$$

Ti_3Bz_2. Two structures were considered: the sandwich structure and a rice-ball structure (see Figure 5, bottom). The

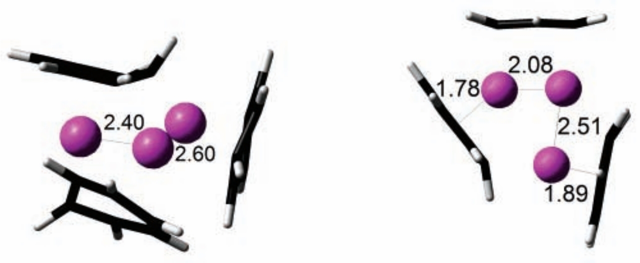

Figure 6. Rice-ball structures of Ti_3Bz_3.

sandwich (quintet state) has the lower energy. For the sandwich structure,

$$Ti_3Bz_2\ (\text{sandwich}) \rightarrow 3Ti + 2Bz \qquad \Delta E = 134.3\ \text{kcal/mol}$$

With four Ti−Bz interactions, the average Ti−Bz interaction energy is 33.6 kcal/mol. The distance between the internal Ti atom and the center of the Bz ring is 1.80 Å. For the external Ti atoms, this distance is 1.66 Å. The Bz rings are eclipsed.

The rice-ball structure with both benzenes bridge-bound (singlet state) is only 1.1 kcal/mol higher in energy than the sandwich structure. For the rice-ball structure,

$$Ti_3Bz_2\ (\text{rice-ball}) \rightarrow Ti_3 + 2Bz \qquad \Delta E = 83.5\ \text{kcal/mol}$$

The average binding energy for each Bz to the Ti_3 unit is 41.7 kcal/mol. The Ti_3 unit is significantly distorted with one short Ti−Ti bond (1.87 Å) and two longer ones (2.53, 2.69 Å). The Bz rings are mildly distorted. One way of describing this structure may be a BzTiTi unit interacting with a TiBz unit.

Ti_3Bz_3. Besides the sandwich structure (quintet state), which has the lowest energy, we found two energetically low-lying rice-ball structures. For the sandwich structure,

$$Ti_3Bz_3\ (\text{sandwich}) \rightarrow 3Ti + 3Bz \qquad \Delta E = 188.8\ \text{kcal/mol}$$

With five Ti−Bz interactions, the average Ti−Bz interaction energy is 37.8 kcal/mol. The average distance between Ti and the center of the Bz ring is 1.79 Å and the rings are eclipsed.

The lowest energy rice-ball structure has one Bz face-bound and two bridged-bound Bz. The next low-lying rice-ball structure has all three bridge-bound Bz. Both rice-ball structures (see Figure 6) prefer the singlet state, and they are 3.6 and 36.8 kcal/mol, respectively, higher in energy than the sandwich structure. The lowest energy rice-ball structure has a rather distorted structure. The Ti_3 unit is V-shaped with Ti−Ti bond distances of 2.40, 2.60 and 3.22 Å respectively. The binding energy with reference to Ti_3 and separated benzenes is

$$Ti_3Bz_3\ (\text{rice-ball}) \rightarrow Ti_3 + 3Bz \qquad \Delta E = 135.5\ \text{kcal/mol}$$

Hence, the average binding energy per benzene is 45.1 kcal/mol.

The second lowest energy structure also has a distorted L-shaped Ti_3 unit (Ti−Ti bond distances are 2.08, 2.51, 2.96 Å). All three Bz are roughly bridge-bound and there is minor distortion in all three rings. The binding energy calculated in a similar way is

$$Ti_3Bz_3\ (\text{rice-ball}) \rightarrow Ti_3 + 3Bz \qquad \Delta E = 102.3\ \text{kcal/mol}$$

Hence, the average binding energy per benzene is 30.1 kcal/mol.

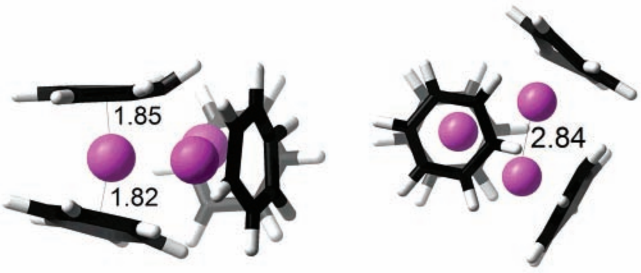

Figure 7. Two views of the Ti_3Bz_4 rice-ball structure.

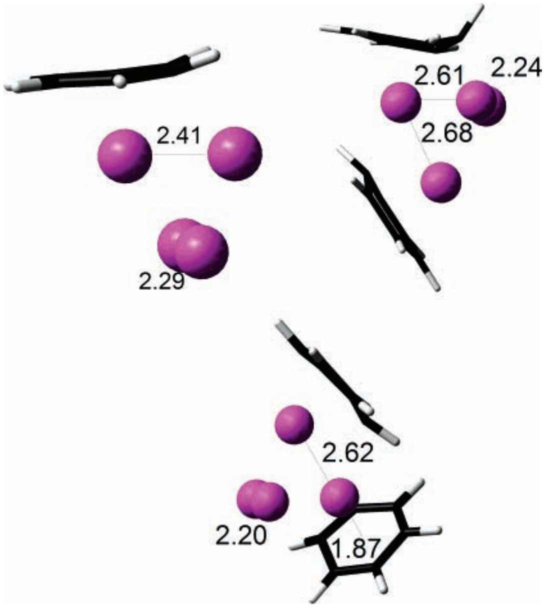

Figure 8. Optimum rice-ball structures of Ti_4Bz and Ti_4Bz_2.

Ti_3Bz_4. The sandwich structure (quintet state) was more stable than the optimal rice-ball structure (singlet state), the latter being 41.8 kcal/mol higher in energy. For the sandwich structure,

$$Ti_3Bz_4\ (\text{sandwich}) \rightarrow 3Ti + 4Bz \qquad \Delta E = 222.8\ \text{kcal/mol}$$

With six Ti−Bz interactions, the average Ti−Bz interaction energy is 37.1 kcal/mol. The distance between Ti and the center of the Bz ring averages 1.81 Å and the Bz rings are eclipsed.

Two views of the rice-ball structure are shown in Figure 7. The Ti_3 triangle has Ti−Ti bond distances of 2.61, 2.84 and 3.06 Å. One of the Ti atoms has two η^6-Bz bound resembling a $TiBz_2$ sandwich. The other two Ti atoms each have one η^6-Bz bound. The structure can be described as a $TiBz_2$ unit interacting with two TiBz units.

$$Ti_3Bz_4\ (\text{rice-ball}) \rightarrow Ti_3 + 4Bz \qquad \Delta E = 132.3\ \text{kcal/mol}$$

Hence, the average binding energy per Bz is 33.1 kcal/mol. We will see this binding motif (and similar binding energies) again in the larger Ti_4Bz_n clusters. We did not calculate Ti_3 clusters with more than four Bz.

Ti_4Bz. Two rice-ball structures were considered: Bz bridged to two Ti or face-bound to three Ti. The bridged structure (see Figure 8, top left) was marginally lower in energy than the face-bound structure by 1.1 kcal/mol. Both structures prefer the singlet state. In the optimum bridged structure,

$$Ti_4Bz\ (\text{bridge}) \rightarrow Ti_4 + Bz \qquad \Delta E = 28.8\ \text{kcal/mol}$$

The Ti_2 unit bridged by Bz has a Ti−Ti bond distance of 2.41 Å. The other Ti_2 unit has a shorter Ti−Ti bond of 2.29 Å. The

Ti−Ti bond distances between the two Ti_2 units average 2.63 Å, close to those found in the optimized Ti_4 cluster.

Ti_4Bz_2. The optimal rice-ball structure (singlet state) shown in the top right of Figure 8 has one Bz face-bound and the other bridge-bound. For this optimal rice-ball structure,

$$\mathrm{Ti_4Bz_2\ (rice\text{-}ball) \rightarrow Ti_4 + 2Bz} \qquad \Delta E = 83.5\ \mathrm{kcal/mol}$$

Hence, the average binding energy for each Bz is 41.8 kcal/mol. The face-bound Bz is heavily distorted whereas the bridge-bound Bz is just mildly distorted. The Ti atom closest to the face-bound Bz is at least 2.60 Å away from the other three Ti atoms. The Ti_2 unit furthest away from either Bz has a Ti−Ti bond distance of 2.24 Å. This Ti_2 unit is separated from the Ti atom closest to the bridge-bound Bz by 2.81 Å.

There is a structure (triplet state) 14.6 kcal/mol higher in energy having each Bz bound to just one Ti atom, as shown on the bottom in Figure 8. These two Ti atoms are separated by 2.62 Å. These two loosely interacting TiBz units also further interact with a Ti_2 unit (Ti−Ti bond distance of 2.20 Å). The average distance between Ti in the TiBz units and Ti in the Ti_2 unit is 2.67 Å. For this structure,

$$\mathrm{Ti_4Bz_2\ (rice\text{-}ball) \rightarrow Ti_4 + 2Bz} \qquad \Delta E = 68.9\ \mathrm{kcal/mol}$$

Hence, the average binding energy for each Bz is 34.5 kcal/mol.

Ti_4Bz_3. Two structures were considered: the optimal sandwich and rice-ball structures. The sandwich structure (quintet state) is lower in energy by 6.7 kcal/mol.

$$\mathrm{Ti_4Bz_3\ (sandwich) \rightarrow 4Ti + 3Bz} \qquad \Delta E = 216.1\ \mathrm{kcal/mol}$$

With six Ti−Bz interactions, the average Ti−Bz interaction energy is 36.0 kcal/mol. The distance between Ti and the center of the Bz ring averages 1.75 Å, and the Bz rings are eclipsed.

The optimum rice-ball structure (see Figure 9, left) has weak Ti−Ti bonds. All six Ti−Ti bond distances range from 2.62 to 2.95 Å; the Ti atoms adopt a tetrahedral arrangement. Two of the Bz molecules look asymmetrically bridge-bound and the last Bz looks like it interacts with just one Ti. However, even the two bridge-bound benzenes look like they are more closely associated with one Ti, and there is only marginal distortion to the Bz rings. Hence, this structure approaches having three TiBz units interacting with each other and with another Ti atom that does not have a bound Bz. If we consider the binding energy of benzenes to a Ti_4 cluster analogous to how we have been analyzing the rice-ball structures thus far,

$$\mathrm{Ti_4Bz_3\ (rice\text{-}ball) \rightarrow Ti_4 + 3Bz} \qquad \Delta E = 104.3\ \mathrm{kcal/mol}$$

Hence, the average binding energy for each Bz is 34.8 kcal/mol, which is quite close to the second Ti_4Bz_2 structure (34.5 kcal/mol) that is closely related in geometry by possessing the TiBz unit motif. (Recall that the Ti_3Bz_4 structure, also exhibiting this motif, has an average binding energy of 35.1 kcal/mol.) Notice that this is starting to approach the average Ti−Bz interaction energy in sandwiches. We think this is correlated with the rice-ball structure preferring to have separate TiBz units interacting with each other, rather than a metal core with strong metal−metal bonds and decorating benzenes.

Ti_4Bz_4. As in Ti_4Bz_3, only the optimal sandwich and rice-ball structures were considered. In this case the rice-ball structure (triplet state) is surprisingly lower in energy than the sandwich structure (quintet state) by just 1.5 kcal/mol. This rice-ball structure is interesting because it has four TiBz units that loosely interact via the metals (see Figure 9, right). The Ti atoms adopt a tetrahedral arrangement and all six Ti−Ti bond distances are in the narrow range 2.64−2.69 Å. Using the same analysis for the binding energy,

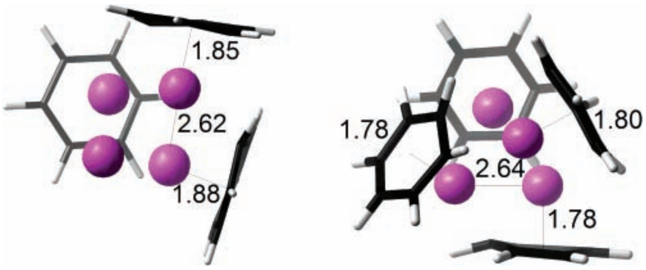

Figure 9. Optimum rice-ball structures of Ti_4Bz_3 and Ti_4Bz_4.

$$\mathrm{Ti_4Bz_4\ (rice\text{-}ball) \rightarrow Ti_4 + 4Bz} \qquad \Delta E = 151.0\ \mathrm{kcal/mol}$$

Hence, the average binding energy for each Bz is 37.8 kcal/mol. This is now right in the range of the average Ti−Bz interaction energy in sandwiches.

In the sandwich structure, the average distance between Ti and the center of the Bz rings is 1.76 Å. The Bz rings are eclipsed. The total interaction energy is

$$\mathrm{Ti_4Bz_4\ (sandwich) \rightarrow 4Ti + 4Bz} \qquad \Delta E = 252.6\ \mathrm{kcal/mol}$$

With seven Ti−Bz interactions, the average Ti−Bz interaction energy is 36.1 kcal/mol.

Ti_4Bz_5. Only the sandwich structure was considered. The quintet state is preferred.

$$\mathrm{Ti_4Bz_5\ (sandwich) \rightarrow 4Ti + 5Bz} \qquad \Delta E = 302.9\ \mathrm{kcal/mol}$$

With eight Ti−Bz interactions, the average Ti−Bz interaction energy is 37.9 kcal/mol. The average distance between Ti and the center of the Bz rings is 1.79 Å and the Bz rings are eclipsed.

Overall Trends. Except for Ti_2Bz_2 and Ti_4Bz_4, we find that the multiple-decker sandwich structure is energetically favored over the rice-ball structure. Though in TiBz, the Ti−Bz interaction energy was small (24.5 kcal/mol), we saw a cooperative effect of having a second Bz to form the sandwich; the average Ti−Bz interaction in $TiBz_2$ was 40.4 kcal/mol. As the sandwiches became larger, we found that the average Ti−Bz interaction energy converges to approximately 37 kcal/mol. All the optimal sandwich structures preferred the quintet state (except $TiBz_2$). The optimal conformation has all Bz rings eclipsing each other. In the TiBz and $TiBz_2$ sandwiches, the distances between Ti and the center of the Bz ring were longer (1.95 and 1.97 Å respectively). In all larger sandwiches this distance shortens to 1.75−1.80 Å. Several initial cluster geometries could not retain the rice-ball structure and either dissociated (e.g., $TiBz_3$ and Ti_2Bz_4) into sandwich structures or altered their geometry (e.g., Ti_4Bz_3 and Ti_4Bz_4) so as to retain TiBz units at the cost of weakening the metal−metal bonds.

The most stable small rice-ball structures did not have η^6-Bz bound to a single metal atom. Instead, the preferred coordination was having the plane of the benzene molecule parallel to a Ti_2 bond or a Ti_3 face, leading to some distortion of the benzene ring. These clusters generally preferred the singlet state. The larger rice-ball structures, on the other hand, retained relatively planar η^6-Bz bound to a single metal atom, preferring to have TiBz units that interacted via the metals. In this case, the triplet state was optimal rather than the singlet state. We found four clusters containing this structural motif (Ti_3Bz_4, second-lowest rice-ball $\mathrm{Ti_4Bz_2}$, rice-ball $\mathrm{Ti_4Bz_3}$ and rice-ball $\mathrm{Ti_4Bz_4}$) that have Ti−Bz interaction energies averaging 35 kcal/mol (from 33.1, 34.5, 34.8 and 37.8 kcal/mol respectively), close to the converged 37 kcal/mol found for the sandwiches that also have the same structural motif of planar η^6-Bz bound to Ti.

Note that the reference states for calculating the Ti−Bz interaction energies are different. For sandwiches, the reference state is the separated metal atoms; for rice-balls, the reference state is the metal cluster containing metal−metal bonds. The energies can be compared directly if the weakening of the metal−metal bonds is equally compensated by the interaction energy between TiBz units. It is not straightforward to parse out the different contributions. For example, if we chose TiBz as a reference state,

$$\mathrm{Ti_4Bz_4}\ \text{(rice-ball)} \rightarrow 4\mathrm{TiBz} \qquad \Delta E = 156.1\ \text{kcal/mol}$$

Because the four Ti atoms are roughly located at the vertices of a tetrahedron, there are six "two-body" interactions between TiBz units for an average of 26.0 kcal/mol per interaction between TiBz units. Compare this to Ti−Ti bond energies of 17.2 kcal/mol in the bare $\mathrm{Ti_4}$ cluster. However, this assumes that the Ti−Bz interaction in $\mathrm{Ti_4Bz_4}$ is the same as in TiBz (where the Ti−Bz bond energy is only 24.5 kcal/mol), which is unlikely to be the case. It is more likely that the Ti−Bz interaction is stronger and the corresponding interaction among TiBz units weaker. For example, if we take 37 kcal/mol to be the Ti−Bz interaction energy, then the two-body interaction among TiBz units drops to 17.6 kcal/mol. In this case, the weakening of the metal−metal bonds is almost equally compensated by the interaction energy between TiBz units, although this may not be the case for much larger rice-ball structures where metal cores will retain metal−metal bonds.

Considering our choice of reference states, our results suggest that η^6-Bz bound to Ti is the dominant interaction in both sandwich and rice-ball structures, and that even in clusters as small as three to four metal atoms, the interaction energy between Ti and η^6-Bz is consistently in the 33−38 kcal/mol range. Metal−metal interactions and even the interaction among TiBz units are weaker in strength. Therefore, a possible explanation for why multiple-decker sandwiches are energetically favored over rice-ball structures is that, for clusters with the same molecular formula, there are simply more Ti−Bz interactions in the sandwich geometry, and so this geometry should be favored under conditions of excess benzene. Our preliminary work suggests that this is also true of scandium. Copper and nickel, on the other hand, have rather weak metal−benzene interaction energies, comparable in magnitude to or weaker than their metal−metal bond energies; this might explain why later transition metals favor the rice-ball structures that maximize metal−metal interactions over metal−benzene interactions.

Conclusions

We have applied density functional theory calculations to systematically and directly compare the relative energetic stability of multiple-decker sandwich and rice-ball structures for a variety of $\mathrm{Ti}_m\mathrm{Bz}_n$ clusters ($m = 1-4$, $n = 1-5$). The multiple-decker sandwich structure was favored in most cases, as observed experimentally for early transition metals. The strength of each Ti−Bz interaction averages 37 kcal/mol. Larger rice-ball structures preferred to weaken the metal−metal bonds and retain η^6-Bz bound to a single metal atom, a structural motif shared with sandwiches. Strong Ti−Bz interaction energies lead to the sandwich being favored over the rice-ball because metal−benzene interactions are maximized.

Current and future work includes comparing the neutral clusters with their corresponding cationic and anionic clusters, and extending this work to include several early and late transition metals.

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