The route to highly stable MeB\(_{x}\)N\(_{y}\)C\(_{z}\) molecular wheels. I. The features of preliminary results

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**A B S T R A C T**

By means of *ab initio* quantum chemical methods we have determined the energies and electronic structures of molecular wheels TiB\(_{n}\), TiB\(_{n}\)N\(_{x}\), TiC\(_{n}\)N\(_{x}\), and TiC\(_{n}\)B\(_{n}\) (for \(n = 0\)–10). The ground state energies and the corresponding spin states of each atom, cluster and molecular wheel were calculated first in the framework of Hartree-Fock self-consistent-field (HF-SCF) using minimal and more accurate basis sets STO-3G and 6-31G. Computations at higher level and accuracy are processing in a follow-up study. The most stable wheel system is TiC\(_{6}\)B\(_{10}\) (for \(n = 5\)–10). Thereof particularly highly stable is the TiC\(_{6}\)B\(_{5}\) molecular wheel followed by the TiC\(_{6}\)B\(_{4}\). At the HF-SCF/6-31G level, however, we have calculated the wheel system MeC\(_{5}\)B\(_{5}\) considering for Me, the first row transition metal atoms Me = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn. The molecular wheel MeC\(_{5}\)B\(_{5}\) favours Sc atom at the centre, but also Ti and Fe are the next favoured atoms.

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1. Introduction

Interest in synthesis and exploration of structure and energetics of boron clusters and boron-compounds has both academic and practical aspects. Such structures should have a wide variety of applications. The reason lies simply by the atomic boron which is the only element except carbon that can build molecules of any size by covalently bonding to itself. Due to sp\(^2\) hybridization of the valence electrons, large coordination number and short covalent radius, boron prefers to form strong directional bonds with various elements. Due to its electron deficiency boron makes multi-centre bonds where pair of electrons is shared between two atoms and more [1].

At the molecular level, elemental boron clusters B\(_{n}\) (for \(n = 2\)–8) were investigated in 1990 by I. Boustani et al. (unpublished results) using a double-\(\zeta\) basis set with polarization function (D\(2\)P) in the framework of the Hartree-Fock (HF) self-consistent-field (SCF) theory and configuration interaction (CI), published in part 1991 [2]. The most interesting structure is the so-called molecular wheel B\(_{8}\), which is composed of a central boron atom surrounded by a regular boron heptagon. The ground state of B\(_{8}\) molecular wheel is \(D\_7h\) (\(\bar{A}\_2\)). The bondlength of the heptagon is 1.516 Å, and the distance to the central atom is about 1.747 Å. Further pure boron clusters have been extensively explored namely both theoretically [3] and experimentally [4]. Thus boron clusters B\(_{n}\) were found to exhibit planar configurations for \(n \leq 14\) and consequently are aromatic. The aromatic (planar) boron clusters possess more circular shapes whereas anti-aromatic ones are elongated. Recent experimental [5] and theoretical [6] studies on boron clusters show that the anionic and neutral B\(_{19}\) clusters are the largest two-dimensional aggregates of boron.

On the other hand, small clusters of the neighbouring element carbon C\(_{n}\) determined for \(n \leq 10\), are linear chains for odd \(n\) and closed rings for even \(n\) [7]. Carbon clusters C\(_{n}\) for \(6 \leq n \leq 13\) were also investigated Slanina et al. [8]. They found that the carbon clusters C\(_{n}\) for \(\leq 10\) have also linear chains for odd \(n\) and cyclic structures for even \(n\). But however, the carbon clusters C\(_{14}\), C\(_{15}\) and C\(_{16}\) have cyclic structures. Larger carbon clusters C\(_{n}\) for \(14 \leq n \leq 24\), \(n\) even were investigated by Jones and Seifert [9]. They found that the carbon clusters have chains, rings, graphitic plate, bowl and cage-like structures. They also found that the most stable isomers for the carbon clusters C\(_{14}\), C\(_{16}\) and C\(_{18}\) have monocyclic ring structures.

Binary compounds of boron and carbon atoms, known as boron carbides, are the most widely investigated compounds. The rhombohedral elemental cell of a single-crystal boron carbide is composed of boron icosahedra residing at each vertex containing three atomic linear chains, like C–B–C or C–C–C, located at the main cell diagonal of the rhombohedron [10]. However, small neutral and charged boron carbide B\(_{8}\)\(_{m}\)C\(_{m}\) clusters for \(m = 1\) to 3
are recently studied by S. S. Park [11] using density functional theory. He investigated eight B$_2$C$_{y}$, twelve B$_2$C$_{2z}$, and twelve B$_2$C$_{5z}$ isomers and found that the most stable structures are molecular wheels with a central boron atom. Molecular-dynamics simulation of structural and thermodynamic properties of cubic boron nitride c-BN were studied by Sekkal et al. [12] using well-tested Tersoff potential. They predicted the corresponding various physical quantities including the thermal expansion coefficient and heat capacity. They extended these simulations to study liquid boron nitride at various densities.

Titanium carbide clusters were also studied by Wang et al. [13]. They reported the vibrationally resolved photoelectron spectra of a series of TiC$_{n}$ clusters for $n = 2$–$5$ and observed that ground state vibrational frequencies and electron affinities are tentatively interpreted to support ring-type structures for these clusters. Furthermore, small clusters of metal boride MeB$_n$ (n $\leq$ 7) particularly those of transition metals (Cr to Ni) were investigated by X. Liu et al. [14]. They used first-principles DFT-GGA methods and studied their electronic and magnetic properties. They found that MeB$_n$ clusters with $n \leq 5$ have planar triangular geometries, those with $n = 6$–$8$ have wheel forms, while MeB$_n$ clusters with $n = 7$ are three-dimensional. Metal-boron molecular wheels were studied by Pu et al. [15] using also density functional theory. They found that B$_9$ and B$_{10}$ rings accommodate the first row of transition metals. Microstructure and properties of superhard Ti–B–C–N films deposited on stainless steel substrates by dc unbalanced magnetron sputtering were studied by I.-W. Park et al. [16]. They found that the hardness of the Ti–B–C–N films increases with the increase of N content up to a maximum value of approximately 45 GPa at 10 at. % N, with a subsequent decrease in hardness at higher N.

The purpose of this study is to show first that the formation of TiB$_n$ systems, composed of a single transition metal atom like Ti and of boron atoms embedded one by one, favours aromatic two-dimensional (2D) over three-dimensional (3D) structures, as it is the case of planar boron clusters, and leads to molecular wheels. Furthermore it is to show the route of stability of the molecular wheels when boron atoms are replaced by nitrogen then by carbon atoms. Since the metal atom Ti can link and accommodate in a plane maximum 10 boron atoms so that the surrounding binding boron atoms around the central metal atom just building reasonable bonds to each other and also to the centre Ti. Therefore the size of the molecular wheels beside Ti atom is limited by 10 atoms and thus the stability of the MeB$_n$N$_x$C$_{10-n-x}$ wheels does not depend more on the size but only on the combination of boron, nitrogen and carbon atoms around the central transition metal atoms. Thereupon, we will study the geometry, electronic structures and cluster stability of the molecular wheels of the TiB$_n$, TiB$_n$N$_{10-n}$, TiC$_n$N$_{10-n}$ and TiC$_n$B$_{10-n}$ (for $n = 1$–$10$) systems as well as MeC$_n$B$_{10-n}$ (Me = Sc, V, Cr, Mn, Fe, Co, Ni, Cu and Zn). This paper is organized as follows: the computational details, 2. Results and discussion

3. Results and discussion

Earlier ab initio calculations of boron clusters have shown that small clusters favour 2D quasiplanar formations [20,21]. But how do behave these structures as soon as we dope a single transition metal atom into the cluster? The best way to approach the answer is to take a metal atom like Ti adding boron atoms solong until acheiving stable structures. The first route is the planar system TiB$_n$ (for $n = 1$–$10$) starting by the TiB$_2$ dimer adding boron atom by building a cyclic ring around Ti. In order to show that the TiB$_n$ clusters favour 2D structures we have determined also some isomers of arbitrary 3D structures mostly pyramids with an apex or central Ti atom. These calculations were carried out at the HF-SCF/STO-3G level of theory considering doublet- and triplet-states for clusters with odd and even $n$, respectively.

3.1. The 2D TiB$_n$ systems

The linear TiB$_2$ and the equilateral triangle TiB$_3$ with Ti as an apex atom have been determined having binding energies of 1.83 and 2.32 eV/atom. The linear TiB$_2$ molecule of C$_{2}$- symmetry and state has a bondlength of 1.84 Å. Concerning TiB$_2$, the atomic distance between the apex atom Ti and both boron atoms in the triangular trimer is about 2.18 Å, while the bondlength between both boron atoms is about 1.64 Å. The 2D structure TiB$_2$ cluster is a rectangle in which the Ti atom is connected to three bonding boron atoms forming an angle as shown in Fig. 1. The calculated $E_b$ of the planar TiB$_2$ cluster of C$_{2v}$-symmetry and state is about 2.47 eV/atom. The bondlength between the Ti atom and the middle boron atom is 2.14 Å, while the it is about 2.08 Å to the outer atoms. The atomic distance between the boron atoms is 1.54 Å. The 2D...
structure of the TiB4 cluster is developed from the planar TiB3 cluster, as shown in Fig. 1. The $E_b$ of TiB4 determined in $C_{2v}(^2A_1)$ symmetry and state is about 2.88 eV/atom. The distances in planar TiB4 between Ti atom and the arc of four boron atoms are 2.25 Å to the middle atoms, while 2.07 Å to the outer atoms. The atomic distance between the middle boron atoms is 1.50 Å, while the distance to the outer atoms is 1.53 Å. The planar structure of TiB5 of $C_{2v}(^2B_2)$ symmetry and state is determined to 3.23 eV/atom is a further development of TiB4. The average bond distance from Ti atom to the central arc of boron atoms is about 2.15 Å, while the average bondlength between the boron atoms is about 1.53 Å.

The stability of the planar TiB7 and TiB9 clusters of odd boron atoms, both of $C_{2v}$ symmetry, obtained from planar TiB5 and TiB8 clusters by adding further boron atom to each one, is 3.27 and 3.42 eV/atom, respectively. The average atomic distance between Ti atom and the arc of boron atoms for TiB7 of $C_{2v}(^2A_1)$ is about 2.20 Å and the average bondlength between boron atoms is about 1.58 Å. The TiB9 cluster optimized in $C_{2v}(^2B_2)$ symmetry and state approaches a wheel structure with an average radial distance of 2.22 Å, while the average distance between the peripheral boron atoms is about 1.52 Å. The final 2D structure TiB10 is a wheel with a $D_{10h}$ symmetry calculated in $D_{2h}(^3B_2g)$ symmetry and state as shown in Fig. 1. The calculated $E_b$ of the 2D TiB10 structure is about 3.69 eV/atom. The atomic distance between the Ti atom and the cyclic boron atoms is about 2.39 Å, while the bondlength of the decagon is about 1.48 Å.

3.2. The 3D TiBₙ systems

The 3D structure of the TiB3 cluster is a trigonal pyramid of $C_{3v}(^4A_1)$ symmetry and state in which Ti is the apex atom, is shown in Fig. 2. The calculated $E_b$ of the trigonal pyramid TiB3 cluster is about 2.05 eV/atom. The distance between the triangle boron atoms and the apex Ti atom is about 1.85 Å, while the bondlength of the triangle boron atoms is 1.56 Å. The binding energy of the
tetragonal pyramid TiB₄ of C₄ᵥ(3A₁) symmetry and state, as presented in Fig. 2, is about 2.42 eV/atom. The apex Ti atom departs to the boron square about 2.46 Å, while the bondlength of the square is about 1.56 Å. The E_b of the pentagonal pyramid TiB₅ of C₅ᵥ(2A₁) symmetry and state is about 3.11 eV/atom. The atomic distance between the apex Ti and the five fold boron atoms is 2.23 Å, while the bondlength of the pentagon is about 1.52 Å.

The 3D structures, the hexagonal pyramid TiB₆ of C₆ᵥ(3A₁) symmetry and state and the octagonal pyramid TiB₈ with C₈ᵥ(3B₁) symmetry and state, as presented in Fig. 2, are less stable than the 2D structures, where their binding energies are assigned to 3.07 and 3.30 eV/atom, respectively. For the TiB₆ cluster, the atomic distance between the apex Ti and the hexagon is 2.29 Å, while the bondlength of the hexagon is about 1.53 Å. For the TiB₈ cluster, the atomic distance between the apex Ti and the octagon is 1.94 Å, while the bondlength of the octagon is about 1.49 Å. The heptagonal pyramid TiB₇ with an E_b of 3.25 eV/atom is slightly less stable than the planar one. The atomic distance of the apex Ti atom to the heptagon is about 2.19 Å and the bondlength of the heptagon is about 1.51 Å.

The 3D TiB₉ cluster of C₈ᵥ symmetry, calculated in C₂ᵥ(2B₂) symmetry and state, is an octagonal umbrella or satellite dish in form of an octagon in which Ti atom is located at the centre and bonded to boron atom localized at the focus. The corresponding E_b is about 3.32 eV and thus less stable than the planar one. The atomic distance from the Ti atom to the octagon is 2.34 Å and to the boron atom at the focus is 2.01 Å, while the bondlength of the octagon is about 1.49 Å. Finally we determined the 3D structure of TiB₁₀ cluster of C₉ᵥ symmetry, calculated in Cs(3A₀) symmetry and state. It is a nonagonal umbrella or satellite dish with Ti at the centre of the nonagon bonded to boron atom at the focus, as can be seen in Fig. 2. The calculated E_b is about 3.56 eV and thus is less stable than the planar one. The atomic distance between the Ti atom and the cyclic boron atoms is about 2.36 Å, and the distance to
the boron atom lying at the focus is 2.03 Å, while the bondlength of the nonagon is about 1.48 Å.

Due to the fact that the all 2D structures of TiBₙ are energetically favoured over the 3D pyramids, we have considered the planar clusters and presented their stability in Fig. 3, as a function of cluster size or the number of boron atoms. It can be asserted that the function $E_b$ of the system TiBₙ for ($n = 1–10$) increases with increasing the number of boron atoms, represented by the stars. In addition, we have selected some 2D and 3D structures of TiBₙ for ($n = 3, 4, 6, 8$ and $10$) and presented in Figs. 1 and 2, respectively. In addition, we have listed the stability of the 2D and 3D structures and the corresponding point group symmetry and spin states in Table 1.

### 3.3. The TiBₙN₁₀₋ₙ system

After obtaining the titanium boron molecular wheel, we have started to dope this wheel with nitrogen atoms by replacing boron by nitrogen atoms one by one calculating the $E_b$ at each step of doping and keeping the original geometry of TiB₂. The binding energies $E_b$ are listed in Table 2. As can be seen in Fig. 3, we have recorded the $E_b$ of this TiB₂N₁₀₋ₙ system as a function of the number of nitrogen atoms $n$ for ($n = 10$ to 0). For $n = 10$ we still have the system TiB₁₀. For $n = 9$ means the first doping occurs by replacing the first nitrogen with boron atom to get TiB₁₀N with an $E_b$ of 4.19 eV/atom. The next value $n = 8$ means TiB₈N₂ and the corresponding binding energy is about 4.42 eV/atom. The $E_b$ values increase with increasing the number of nitrogen atoms until arriving the maximum of this function labelled by $n = 5$ achieving an $E_b$ of 5.80 eV/atom. Afterwards the $E_b$ function of TiBₙN₁₀₋ₙ decreases down to 2.70 eV/atom with increasing the number of nitrogen atoms until TiB₅N₅. The substitution of nitrogen atoms occurs first alternately, like $b−n−b−n$, until $n = 5$ obtaining symmetrical wheel TiB₅N₅. Afterwards the residual boron atoms will be replaced by nitrogen one by one. The $E_b$ function of the TiBₙN₁₀₋ₙ system is assigned by red squares.

### 3.4. The TiCₙN₁₀₋ₙ system

We proceed in the same manner doping now the TiN₁₀ system with carbon atoms. Starting by $n = 1$ and replacing one nitrogen by a carbon atom we receive the molecular wheel TiC₂N₈ with an $E_b$ of 2.91 eV/atom. The next step is assigned by substituting the next nitrogen atom by carbon getting for $n = 2$ the wheel TiC₂N₆. The corresponding $E_b$ is about 3.31 eV/atom. However, The calculated $E_b$ values of this system are also listed in Table 2. Further steps are continued by replacing nitrogen by carbon atoms one by one in clockwise direction obtaining for $n = 10$ the cluster TiC₁₀ with an $E_b$ of 5.80 eV/atom. The substitution of nitrogen by carbon atoms occurs first alternately, like $c−n−c−n$, until $n = 5$ obtaining the symmetrical wheel TiC₅N₅. Afterwards for $n ≥ 6$ the residual nitrogen atoms are replaced by carbon one by one. It is to observe that the $E_b$ function of the TiC₅N₅₀₋ₙ system, as shown in Fig. 3 and assigned by a green triangle down, increases upwards with increasing the number of carbon atoms $n$.

### 3.5. The TiCₓB₁₀₋ₓ system

The substitution of carbon with boron atoms up to $n = 5$ occurs first alternately receiving the wheel system TiCₓB₁₀, with the corresponding $E_b$ listed in Table 2. Afterwards the residual carbon atoms will be replaced by boron atoms approaching the TiB₁₀ system once again. As can be seen in Fig. 3, the $E_b$ function increases with increasing the number of boron atoms up to $n = 5$. Thereafter it drops towards the $E_b$ value of 3.69 eV/atom of the wheel TiB₁₀. A distinguishable maximum in Fig. 3 can be observed by $n = 5$ corresponding to the largest $E_b$ value of 6.25 eV/atom for the symmetrical molecular wheel TiC₅B₅. The next stable wheel is the TiCₓB₄ with an $E_b$ of 6.10 eV/atom, calculated at the HF-SCF/STO-3G level.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Structure</th>
<th>Symmetry(State)</th>
<th>$E_b$ (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D Clusters</td>
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<td>C₁₀($A_{1g}$)</td>
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<tr>
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<tr>
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<td>C₉₀($B_{1g}$)</td>
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<tr>
<td>TiB₁₀-Wheel</td>
<td>D₂₀(B₁₀)</td>
<td>3.69</td>
<td></td>
</tr>
</tbody>
</table>

| 3D Clusters | TiB₂-Trigonal Pyramid | C₃₀($A_{1g}$) | 2.05 |
| TiB₄-Tetragonal Pyramid | C₄₀($A_{1g}$) | 2.42 |
| TiB₅-Pentagonal Pyramid | C₅₀($A_{1g}$) | 3.07 |
| TiB₆-Hexagonal Pyramid | C₆₀($A_{1g}$) | 3.11 |
| TiB₇-Heptagonal Pyramid | C₇₀($A_{1g}$) | 3.25 |
| TiB₈-Octagonal Pyramid | C₈₀($A_{1g}$) | 3.30 |
| TiB₉-Nonagonal Umbrella | C₉₀($A_{1g}$) | 3.37 |

### Table 2

The $E_b$ values of TiBₙN₁₀₋ₙ and TiCₓB₁₀₋ₓ systems are calculated at the HF-SCF/STO-3G level.

<table>
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<tr>
<th>TiBₙN₁₀₋ₙ</th>
<th>$E_b$</th>
<th>TiCₓN₁₀₋ₓ</th>
<th>$E_b$</th>
<th>TiCₓB₁₀₋ₓ</th>
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<td>5.80</td>
<td>TiC₁₀B₁₀</td>
<td>3.69</td>
</tr>
</tbody>
</table>

Footnotes:

- TiB₁₀N₀ and TiC₁₀B₁₀ means TiB₁₀.
- TiB₁₀N₀ and TiC₁₀N₁₀ means Ti₁₀N₁₀.
- TiC₁₀N₀ and TiC₁₀B₁₀ means TiC₁₀.
level of theory, as the case of whole substitutions in the TiC$_n$B$_{10-n}$ system. Both molecular wheels TiC$_5$B$_5$ and TiC$_6$B$_4$ are represented in Fig. 4. The distribution of the $E_b$ function of the TiC$_n$B$_{10-n}$ system is assigned in Fig. 3 by a blue triangle up. However, further computations beyond the HF-SCF level show that the sequence of the stability of both wheels TiC$_5$B$_5$ and TiC$_6$B$_4$ is reversed when considering the functionals B3LYP and 6-31G basis set[17].

3.6. The MeC$_5$B$_5$ system

In order to understand the nature of chemical bonds of metal atoms with boron and carbon wheels we have computed the wheel system MeC$_5$B$_5$ considering for Me the first row of transition metal atoms Me = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn. Of course higher spin multiplicity could mean lower ground state energy of individual metal atoms. However, we have optimized each structure at the HF-SCF/6-31G level of theory, and calculated the ground state energies at different spin states for each metal atom. We selected the lowest energy and determined the corresponding binding energy, symmetry, spin state and bondlengths between the central and peripheral atoms as well as between carbon and boron atoms, all are listed in Table 3. The calculated $E_b$, as defined in eq (1), is plotted in Fig. 5 as a function of the metal atoms. As shown in Fig. 5, the molecular wheel MeC$_5$B$_5$ favours Sc atom at the centre, but also Ti or Fe are the next favoured transition metal atoms. The spin multiplicity considered in the MeC$_5$B$_5$ wheels for the Sc, Ti and Fe atoms was triplet, quadruplet and octuplet, respectively. In Fig. 5, the $E_b$ function of the system MeC$_5$B$_5$, determined at the HF-SCF/6-31G level, is represented by blue squares. However, further computations of MeC$_5$B$_5$ and MeC$_6$B$_4$ in a follow-up study[17] are running at higher level of theory to verify the final stability of these structures.

4. Summary and conclusions

Based on the fact that small boron clusters B$_n$ ($n \leq 19$) have planar or quasiplanar structures, we have doped boron clusters with transition metal atoms and enquired whether the planarity would keep consistent. Therefore we have investigated 2D and 3D structures of TiB$_n$ for ($n \leq 10$) using simple STO-3G basis set at the HF-SCF level of theory. The 2D TiB$_n$ structures where chosen to be flat where Ti is at the focus and the boron atoms located at one side forming arcs and growing up to cycles or precisely to molecular wheels. The 3D structures of TiB$_n$ where choose to be pyramids.
where Ti is always an apex atom. The obtained structure of the wheel of TiB10 was fixed, then boron atoms where replaced by nitrogen then by carbon one by one. The metal atom in the most stable molecular wheel of TiB8S8 was then replaced by all atoms of the first row of transition metals.

We have developed 2D TiBn system staying by two atomic molecule TiB adding boron atoms as long as the cycle closes gaining a wheel. Because of similarity, we present in Fig. 1 selected 2D TiBn clusters for n = 3, 4, 6, 8 and 10. We have also determined 3D clusters of TiBn in form of pyramids to show that the 3D pyramidal structures are energetically less favoured. Due to similarity, we present in Fig. 2 selected 3D TiBn clusters for n = 3, 4, 6, 8 and 10. The E0 of 2D and 3D structures are listed in Table 1. The E0 of the 2D TiB10 system is presented in Fig. 3 as a function of cluster size. As can be seen, it increases with increasing the number of boron atoms n arriving the maximal value 3.69 eV/atom for n = 10. Furthermore, we have doped the TiBn system with nitrogen atoms by substituting boron first alternately then completely with nitrogen atoms receiving the TiBnN0-n system. For n = 10 we have the original system TiB10, but for n = 9 we dope the first nitrogen atom obtaining TiB5N5, and improving its stability. Further doping with nitrogen atoms improves the stability upwards until fivefold substitutions of boron with nitrogen atoms are reached with 5.0 eV/atom, the maximum of the E0 for the TiB5N5 wheel. Replacing the residual boron atoms by nitrogen up to TiN10 the stability diminishes down to a value of 2.7 eV/atom.

We follow the same procedure in the TiBnN0-n system by keeping the nitrogen atoms and substituting boron by carbon atoms to produce the TiCnN0-n system. We embrace the issue whether carbon can re-establish the lost stability. The substitution of nitrogen by carbon atoms follows first alternately then completely causing progression in stability up to an E0 value of 5.8 eV/atom for the TiC10 wheel. However, further substitution of carbon with boron into the system TiC10B-n leads to increase the stability achieving by n = 5 another maximum of stability of 6.26 eV/atom, obtaining the wheel TiC6B4. Afterwards the stability decreases so far until the carbon atoms are completely replaced by boron returning back to the wheel TiB10, obtained by the first route, with the original E0 value 3.69 eV/atom. After structural optimization of TiC6B4, we found that the distance between Ti and carbon atoms is shorter as to boron atoms. Thus, the atomic distance between the centre Ti and peripheral atoms B and C is respectively 2.27 and 2.21 Å, while the bondlength of B–C is about 1.38 Å. As above mentioned, we will see in the follow-up paper [17] that at the B3LYP functionals and 6–31G basis set the TiC6B4 wheel is with 0.04 eV/atom slightly more stable than the TiC5B5.

All systems studied above where carried out considering the transition metal atom Ti. Now arises the question: could another atom of the first row of transition metals induce better stability! Therefore we have established further computations at the HF-SCF/6–31G level to determine the MeCnB system for Me = Sc to Zn. These calculations are presented in Fig. 5 showing that Sc atom at the centres exhibits the highest binding energy, followed by Ti then by Fe atoms. In the second part of this work [17] we will ascertain that the wheel TiC4B4 at the B3LYP/6–31G level is energetically favoured over the ScC4B4 one.

We conclude that we have developed a new path of molecular wheels and determined how to increase the stability of molecular structures by substituting boron by nitrogen and carbon. However, the behaviour of the binding energy in increasing and dropping seems to depend on the ratio and sequence of the involved boron, nitrogen and carbon atoms around the central titanium atom. Consequently, a further study at a higher quality basis sets and functionals is in progress [17] to verify these points mentioned above. We have established that metal boride clusters favour 2D structures forming molecular wheels similar to those cyclic rings of the boron wheel B3 [1], to carbon rings [9] or to boron carbide wheels [11]. In addition, the α- and β-spin HOMO-LUMO gaps of TiB10 are 0.330 and 0.253 Hartree, respectively. Slightly larger HOMO-LUMO gaps values 0.90 and 0.27 eV of α- and β-spin of TiC6B4 versus those of TiB10 are a clear evidence for the stabilization character of carbon atoms involved into the wheel.

According to the Mulliken analysis, the electron charge transfer in the most stable molecular wheel TiC6B4 at the HF-SCF/STO–3G level of theory occurs slightly from titanium and boron to carbon atoms. The extent of electron charge of titanium and the average of five boron atoms is respectively 0.854 and 0.136 e, while the average of the charge transfer to the five carbon atoms is likely −0.306 e. In contrast, the electron transfer in TiB10 occurs with 0.450 e from the Ti atom to the each of the ten boron atoms to achieve a charge of −0.045 e, approving the true electron deficient character of boron. The variation of the stability of molecular wheels over the transition metal as central atoms, as presented in Fig. 5, gives no insight about the reason. However, in our follow-up study we will try to verify the role and number of d-electrons and their contributions in bonding and character as well as the correlation between the p- and d-electrons. Calculations on molecular wheel systems MeBnCn, for different combinations of nonzero x, y and z are still missing. Also some electronic properties like vibrational frequencies, bond order analysis, and aromaticity in connection with the π-orbitals are desirable.

References