NiB₁₀, NiB₁₁⁻, NiB₁₂, and NiB₁₃⁺: Half-Sandwich Complexes with the Universal Coordination Bonding Pattern of σ Plus π Double Delocalization

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Abstract
Transition-metal-doped boron clusters have received considerable attention in recent years. The experimentally observed planar or quasi-planar C₂ᵥB₁₀(I), C₂ᵥB₁₁⁻(II), C₃ᵥB₁₂(III), and C₂ᵥB₁₃⁺(IV) are known to be boron analogs of benzene. Extensive global minimum searches and first-principles theory investigations performed herein indicate that doping these aromatic boron clusters with a nickel atom generates the closed-shell half-sandwich complexes C₂ᵥNiB₁₀(1, 1A₁), CsNiB₁₁⁻(2, 1A₀), C₃ᵥNiB₁₂(3, 1A₁), and CsNiB₁₃⁺(4, 1A₀) which are all well-defined global minima of the systems with the coordination numbers of CN = 10, 11, 12, and 13, respectively. Detailed bonding analyses indicate that these Ni-doped boron complexes are effectively stabilized by coordination interactions between the Ni center and aromatic Bₙ⁻/₀⁺ ligands (n = 10–13) and follow the universal coordination bonding pattern of σ plus π double delocalization. Molecular dynamics simulations show that, among these complex clusters, NiB₁₁⁻(2) behaves like a Wankel motor at room temperature with the B₃ inner wheel rotating almost freely inside the quasi-rotating B₈ outer bearing in a concerted mechanism, revealing typical bonding fluctuations/fluxionalities in a molecular motor due to thermal vibrations. The IR, Raman and electronic spectra of the concerned species are computationally simulated to facilitate their experimental characterizations.

Keywords Half-sandwich complexes • Wankel motor • First-principles theory • Structures • Bonding fluctuations

Introduction
As prototypical electron deficient element in the periodic table, boron has a vast variety of geometrical and electronic structures in both bulk allotropes and polyhedron molecules due to its strong propensity to form multicenter-two-electron (mc-2e) bonds. Persistent joint photoelectron spectroscopy (PES) and first-principles theory (FPT) investigations in the past decade have shown that Bₙ⁻ monoanions possess planar or quasi-planar (2D) structures in an unexpectedly wide range of cluster sizes (n = 3–30, 33–38, and 40), [1–19] while Bₙ neutrals favor 2D geometries with n up to at least 20 [20] and Bₙ⁺ monocations remain planar with n ≤ 15, [21] unveiling a flat world of boron in close analogy with polycyclic aromatic hydrocarbons. Flat boron clusters are governed by localized two-center-two-electron (2c-2e) σ-bonds on the periphery and delocalized multicenter mc-2e σ and π bonds over the molecular moieties involving both the inner and peripheral atoms. 2D aromatic boron clusters prototyped with B₁₂ (n = 1) and B₁₆²⁻ (n = 2) conform to the 4n + 2 Hückel rule and are expected to be effective inorganic ligands to various transition metal centers. Furthermore, 2D C₂ᵥB₁₁⁻, C₂ᵥB₁₃⁺, C₅ B₁₅⁺, C₆ B₁₈²⁻, and C₂ᵥB₁₉⁻ have been proposed to be molecular Wankel motors with the inner wheels rotating almost barrierlessly inside the pseudo-rotating outer bearings [5, 22–27].

Inspired by the observation of the boron-centered 2D aromatic B(BO₂)²⁻ and B(BO₂)⁻ clusters, a series of
transition-metal-centered 2D boron wheels M\(\text{B}_n^-(\text{M} = \text{Co}, \text{Rh}, \text{Ir}, \text{Ru}, \text{Ta}, \text{and} \text{Nb}, n = 8–10)\) [28–30] have been characterized in PES experiments in combination with extensive FPT calculations. It has been concluded that the wheel-like NbB\(_{10}^-\) and TaB\(_{10}^-\) possess the highest possible coordination number of CN = 10 in planar environments in chemistry. Two larger metal-doped boron clusters, CoB\(_{12}^-\) and RhB\(_{12}^-\) [31] were later found to adapt half-sandwich structures. Interestingly, half-sandwich IrB\(_{12}^-\) was found to be a molecular Wankel motor [32] with the energy barrier effectively decreased by doping an Ir atom into B\(_{12}^-\). A tubular molecular rotor B\(_2^-\)Ta@B\(_{18}^-\) was observed via a joint PES and FPT investigation with an energy barrier of 1.13 kcal mol\(^{-1}\). [33] Very recently, Chen and co-workers found that TaB\(_n^-\) (n = 11–15) clusters adapted half-sandwich geometries. [34] Small half-sandwich MnB\(_{10}\) (n = 10–13) [35] in high spin states and MoB\(_{10}\) and MoB\(_{12}\) [36] in singlet states are also found to be the most stable isomers of the systems. Different and even controversial bonding analyses have been presented to be the most stable isomers of the systems. Computational methods [37] and TGmin [40, 41] algorithms, in combination with extensive GM searches were performed on NiB\(_{10}\), NiB\(_{11}\), NiB\(_{12}\), and NiB\(_{13}\)\(^+\) using both the Coalescence Kick (CK) [39] and TGmin [40, 41] algorithms, in combination with manual structural constructions based on low-lying isomers of the previously reported B\(_{10}\), B\(_{11}\), B\(_{12}\), and B\(_{13}\)\(^+\) [22, 23, 25]. Approximately 5000 trial structures were generated for each species in both singlet and triplet spin states. The low-lying isomers were then fully re-optimized at both PBE0/6-311 + G* [42, 43] and TPSSH/6-311 + G* [44] levels [45] using Gaussian 09 package [46] with vibrational frequencies checked. Single-point energies of the first twenty low-lying structures were further refined using the more accurate CCSD(T)/def2-TZVP//PBE0/6-311 + G* method [47–49] at PBE0 geometries. TS and QST2 calculations was performed to search the transition state (TS) of NiB\(_{11}\) which turned out to have a C\(_s\) symmetry. Intrinsic reaction coordinate (IRC) [50] calculation was carried out to confirm that the obtained structure is a true TS. Born–Oppenheimer molecular dynamics (BOMD) simulations were performed on NiB\(_{11}\) (2) for 30 ps at PBE level using the CP2 K software package [51] with the time step of 10 fs. Bonding analyses were performed using the adaptive natural density partitioning (AdNDP) method [52] at PBE0/6-31G* level. The visualization of the AdNDP results was realized using the Molekel 5.4.0.8 program. [53].

## Results and Discussion

### Structures and Stabilities

Extensive GM searches and FPT calculations indicate that, with a nickel dopant, NiB\(_{10}\), NiB\(_{11}\), NiB\(_{12}\), and NiB\(_{13}\)\(^+\) possess closed-shell half-sandwich GM structures of C\(_{2v}\) NiB\(_{10}\)(I), C\(_{3v}\) NiB\(_{11}\)(II), C\(_{2v}\) B\(_{12}\)(III), and C\(_{2v}\) B\(_{13}\)\(^+\) (IV) as effective ligands and a Ni atom (Ni[Ar]4\(\text{S}^{2}\text{D}^{8}\)) as dopant, extensive global minimum (GM) searches and FPT calculations performed in this work indicate that the closed-shell half-sandwich C\(_{2v}\) NiB\(_{10}\)(I, 1\(\text{A}\)), C\(_{3v}\) NiB\(_{11}\)(2, 1\(\text{A}\)), C\(_{2v}\) NiB\(_{12}\)(3, 1\(\text{A}\)), and C\(_{2v}\) NiB\(_{13}\)\(^+\)(4, 1\(\text{A}\)) are well-defined GMs of the systems with the coordination numbers of CN = 10, 11, 12, and 13, respectively. Detailed bonding analyses show that these Ni-doped boron complexes conform to the universal coordination bonding pattern of \(\sigma + \pi\) double delocalization between the Ni center and B\(_{n}^-/0^+\) ligands. Molecular dynamics simulations show that the half-sandwich NiB\(_{11}\)(2) behaves like a Wankel motor at room temperature in a concerted mechanism, revealing the bonding fluctuation nature of structural flexuonality in a molecular motor.

### Computational Methods

Extensive GM searches were performed on NiB\(_{10}\), NiB\(_{11}\), NiB\(_{12}\), and NiB\(_{13}\)\(^+\) using both the Coalescence Kick (CK) [39] and TGmin [40, 41] algorithms, in combination with
respectively. More alternative low-lying isomers are collectively depicted in Fig. S1-Fig. S4. The bare B_{10}(I), B_{11}^- (II), B_{12}(III), and B_{13}^+ (IV) with a B_2, B_3, or B_3 unit inside a B_8, B_9, or B_{10} outer bearing possess the structural patterns of (2 + 8) (2 + 9), (3 + 9), and (3 + 10), respectively. Addition of a Ni dopant into the system induces remarkable intramolecular rearrangements in both NiB_{11}^- (2) and NiB_{13}^+ (4) in which the B_{11}^- and B_{13}^+ ligands have been rearranged from B_{11}^- (II) (2 + 9) and B_{13}^+ (IV) (3 + 10) to NiB_{11}^- (2) (3 + 8) and NiB_{13}^+ (4) (4 + 9), respectively. The B_2 bar in B_{11}^- (II) has been changed into a B_3 triangle in NiB_{11}^- (2) and the B_3 triangle in B_{13}^+ (IV) transferred to a B_4 rhombus in NiB_{13}^+ (4) (Fig. 1). Such structural rearrangements effectively improve the metal–ligand coordination interactions in both 2 and 4, as evidenced by the increase of the total Ni Wiberg bond order from WBI_{Ni} = 1.46 in the fourth isomer of C, NiB_{11}^- (2) (9) (Fig. S2) to WBI_{Ni} = 1.76 in C, NiB_{11}^- (2) (3 + 8) and from WBI_{Ni} = 1.51 in the seventh isomer C, NiB_{13}^+ (3 + 10) (Fig. S4) to WBI_{Ni} = 1.85 in C, NiB_{13}^+ (4) (4 + 9). The structural patterns of C_{2v} B_{10}(I) (2 + 8) and C_{3v} B_{12}(III) (3 + 9) are basically maintained in both C_{2v}, NiB_{10}(I) (2 + 8) and C_{3v}, NiB_{12}(3) (3 + 9), with more severe buckling in the complexes than in bare ligands. We notice that C_{2v}, NiB_{10}(I) possesses an imaginary vibrational frequency of 142i cm^{-1} at PBE0 which leads to the second lowest-lying isomer of C, NiB_{10}(I) (Fig. S1) when fully relaxed. However, the two isomers are practically iso-energetic, with the former being 0.01 eV more stable than the latter at CCSD(T). C_{2v}, NiB_{10}(I) is therefore the vibrationally averaged GM of the system possible to exist in experiments. The open-shell triplet C_{2v}, NiB_{10} (A_2) (Fig. S1) as the third isomer of the system appears to be 0.18 eV less stable than the C_{2v} GM at CCSD(T) (Fig. S1). As shown in Fig. S2-S4, similar to NiB_{10}(I), half-sandwich NiB_{11}^- (2), NiB_{13}^+ (3), and C, NiB_{13}^+ (4) are all well-defined GMs of the systems lying at least 0.17 eV lower than their alternative low-lying counterparts at CCSD(T). Triplet C, NiB_{11}^- (A_2) and C, NiB_{13}^+ (A') are found to lie much higher in energy (by + 1.25 eV and + 1.17 eV) than their singlet GMs at CCSD(T).

### Bonding Analyses

To interpret the high thermodynamic stabilities of 1–4, we performed detailed structural and natural bonding orbital (NBO) [54] analyses on them. As shown in Table 1, the Ni–B distances between r_{Ni–B} = 2.01–2.51 Å and averaged Ni–B distances between r_{Ni–B(av)} = 2.17–2.34 Å in 1–4 belong to typical transition-metal-boron coordination bond lengths [38]. NBO analyses indicate that 1–4 possess the average Ni–B Wiberg bond orders of WBI_{Ni–B(av)} = 0.14–0.16, showing that all the Ni–B coordination interactions in these complexes contribute almost equally to the overall Ni–B coordination interaction and all the boron atoms in the complexes should be treated as effective ligands to the Ni center. The calculated total Wiberg bond orders of Ni lie between WBI_{Ni} = 1.62–1.85 in 1–4, suggesting that the Ni centers in these half-sandwich complexes possess approximately an overall covalent valence of two. Molecular orbital analyses further show that the Ni ([Ar]3d^8 4s^2) atoms in 1–4 possess the electronic configurations of [Ar]3d^8 2p_1 1/2 4p_0 0.12^2 1/2 4p_0 0.02, [Ar]3d^8 2p_1 1/2 4p_0 0.14^2 1/2 4p_0 0.02, [Ar]3d^8 2p_1 1/2 4p_0 0.03^2 1/2 4p_0 0.07 and [Ar]3d^8 4s^2 1/2 4p_0 0.14^2 1/2 4p_0 0.03 and carry the positive net atomic charges of + 0.63, + 0.65, + 0.64, and + 0.71 lel, respectively. These results show that a Ni atom in 1–4 donates its 4s^2 electrons almost completely to the bowl-shaped B_n ligands, while, in return, accepts approximately 1.0 ~ 1.3 electrons in its partially occupied 3d^8 orbitals from the half-sandwich B_n^{4+} ligands via effective p → d back donations. Ni 4p orbitals with the low occupation numbers of 0.02–0.03 make negligible contribution to Ni–B_n^{4+/0} coordination interactions.

Detailed AdNDP analyses recover both the localized and delocalized bonding elements in these complexes. As depicted in Fig. 2, the chemical bonding elements in 1–4 can be divided into four categories: the localized and delocalized σ-bonds on the B_{10}^{4+/0} ligands in the first row, lone pairs on Ni in the second row, partially delocalized multiconfigurational σ- or σ-coordination bonds between Ni and B_n ligands in the third row, and the totally delocalized π-coordination bonds over the whole complexes in the fourth row. In specific, C_{2v}, NiB_{10} (I) possesses 8 localized 2c-2e

### Table 1 Calculated Ni–B distances (r_{Ni–B}), average Ni–B distances (r_{Ni–B(av)}), average Ni–B Wiberg bond orders (WBI_{Ni–B(ave)}), and total Wiberg bond orders (WBI_{Ni}); natural atomic charges (q_{Ni}); and electronic configurations of the Ni centers in NiB_{10}(I), NiB_{11}^- (2), NiB_{12}(3), and NiB_{13}^+ (4) at PBE0/6-311+G(d) level

<table>
<thead>
<tr>
<th>System</th>
<th>r_{Ni–B} Å</th>
<th>r_{Ni–B(ave)} Å</th>
<th>WBI_{Ni–B(ave)}</th>
<th>WBI_{Ni}</th>
<th>q_{Ni}/lel</th>
<th>Electronic-configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiB_{10}(I)</td>
<td>2.04–2.41</td>
<td>2.22</td>
<td>0.16</td>
<td>1.62</td>
<td>+ 0.63</td>
<td>Ni[Ar] 3d^{8} 4s^2 4p_{1/2} 0.12^2 1/2 4p_{0/2}</td>
</tr>
<tr>
<td>NiB_{11}^- (2)</td>
<td>2.01–2.30</td>
<td>2.17</td>
<td>0.16</td>
<td>1.76</td>
<td>+ 0.65</td>
<td>Ni[Ar] 3d^{8} 4p_{1/2} 0.14^2 1/2 4p_{0/2}</td>
</tr>
<tr>
<td>NiB_{12}(3)</td>
<td>2.03–2.51</td>
<td>2.34</td>
<td>0.14</td>
<td>1.64</td>
<td>+ 0.64</td>
<td>Ni[Ar] 3d^{8} 4p_{1/2} 0.11^2 1/2 4p_{0.03}</td>
</tr>
<tr>
<td>NiB_{13}^+ (4)</td>
<td>2.01–2.39</td>
<td>2.27</td>
<td>0.14</td>
<td>1.85</td>
<td>+ 0.71</td>
<td>Ni[Ar] 3d^{8} 4p_{1/2} 0.14^2 1/2 4p_{0.03}</td>
</tr>
</tbody>
</table>
peripheral $\sigma$-bonds, 2 delocalized 3c-2e and 2 delocalized 4c-2e $\sigma$-bonds on the $C_{2v}$ $B_{10}$ ligand, 2 1c-2e long pairs ($3d_{xz}$ and $3d_{yz}$) on the Ni center, 1 3c-2e $\pi$ coordination bond between Ni ($3d_{z^2}$) and the $B_3$ unit directly under it at the center of the $C_{2v}$ $B_{10}$ ligand and 2 4c-2e $\sigma$-bonds between Ni ($3d_{x^2-y^2}$ and $3d_{xy}$) and the two long edges of the $B_{10}$ ligand, and three totally delocalized 11c-2e $\pi$-coordination bonds over the whole half-sandwich complex, in an overall symmetry of $C_{2v}$ (Fig. 2a). As shown in Fig. 2b–d, similar $\sigma + \pi$ double delocalization coordination covalent bonding interactions exist in NiB$_{11}^{-}$(2), NiB$_{12}$(3), and NiB$_{13}^{-}$(4). In particular, NiB$_{11}^{-}$(2) possesses 1 delocalized 3c-2e $\sigma$ bond on the central $B_3$ triangle, 5 delocalized 3c-2e $\sigma$ bonds between the $B_3$ inner ring and $B_8$ outer bearing, and 3 totally delocalized 12c-2e $\pi$ bonds over the whole molecule (Fig. 2b). NiB$_{11}^{-}$(2) is therefore triply aromatic according to the $4n + 2$ Hückel rule, including one $\sigma$-aromatic system with 2 electrons (n = 0) on the central $B_3$ triangle, one $\sigma$-aromatic system with 10 electrons (n = 2) between the inner $B_3$ ring and the $B_8$ outer bearing, and one $\pi$-aromatic system with 6 electrons (n = 1) over the whole half-sandwich complex. For $C_{3}$, B$_{12}$(3), we define 3 equivalent 4c-2e $\sigma$ bonds between Ni and the three edges of the $C_{3v}$ B$_{12}$ ligand in Fig. 2c, based on the fact that the three B atoms on each edge have almost the same Ni–B bond orders with WBI$_{Ni-B}$ = 0.14, 0.16 and 0.14, respectively. Our $\sigma$ bonding pattern is different from that of $C_{3v}$ RhB$_{12}^{-}$ which was reported to contain 3 localized 2c-2e $\sigma$ bonds between Rh center and three B atoms at the center of each edge of the $C_{3v}$ B$_{12}$ ligand [31]. Thus, 1–4 complexes follow the universal coordination bonding pattern of $\sigma + \pi$ double delocalization which renders high stability to their half-sandwich structures.

**Intramolecular Pseudorotations and Bonding Fluctuations**

Extensive molecular dynamics (MD) simulations show that, among these half-sandwich complexes, $C_s$ NiB$_{11}^{-}$(2) behaves like a molecular Wankel motor at room temperature, with the $B_3$ inner triangle rotating almost freely inside the quasi-rotating $B_8$ outer bearing. Both the GM and transition state (TS) of NiB$_{11}^{-}$ possess $C_s$ symmetry (Fig. 3). The GM possesses the smallest vibrational frequency of 71.3 cm$^{-1}$ at PBE0 which corresponds to a soft mode of intramolecular rotation of the peripheral $B_8$ ring with respect to the inner $B_3$ triangle. Following this mode, the TS structure is reached straightforward with an imaginary frequency of 55.1i cm$^{-1}$ which, interestingly, corresponds to a pseudorotation of the peripheral ring against the $B_3$ inner ring leading to a neighboring GM. The energy barrier between the GM and TS of NiB$_{11}^{-}$ turns out to be 0.08, 0.13, and 0.06 kcal mol$^{-1}$ at PBE0, TPSSH, and CCSD(T) levels, respectively. Such an energy barrier is much lower than the corresponding value of 0.35 kcal/mol.

**Fig. 2** AdNDP bonding patterns of NiB$_{10}$(1) (a), NiB$_{11}^{-}$(2) (b), NiB$_{12}$(3) (c), and NiB$_{13}^{-}$(4) (d), with the occupation numbers ON indicated.

**Fig. 3** Two views of the half-sandwich global minimum $C_s$ NiB$_{11}^{-}$(2) and the corresponding transition state (TS) $C_s$ NiB$_{13}^{-}$ at PBE0/6-311 + G(d) level. Arrows indicate the lowest-frequency (for GM) and the imaginary-frequency (for TS) normal vibrational modes.
in the experimentally observed bare Wankel motor $\text{B}_{11}^{-}$ (II) [25] due to the existence of the Ni dopant in the complex.

Lipscomb proposed a general mechanism for the framework rearrangement in boranes and carboranes in 1966 [55]. Such a process involves the cooperative stretching of a diamond-shaped group of atoms into a square and back into a diamond shape. This diamond-square-diamond mechanism requires relatively little atomic motion. Merino et al. [56] found that the dynamical behavior of boron clusters also follows this mechanism. Both the soft mode of 71.3 cm$^{-1}$ of boron clusters also follows this mechanism. Merino et al. [56] found that the dynamical behavior of boron clusters also follows this mechanism.

Fig. 4 σ bonding fluctuations in NiB$_{11}^-$(2) (3c-2e σ-bonds shaded in gray) during intramolecular rotation in 45° (with 15° in each step) the σ cloud is islanded on this triangle. It leans to the B7B1B10 triangle in TS$_{1-2}$, where a σ cloud migrates spontaneously from B1B8B10 to B8B2B10 in GM$_2$ in a concerted mechanism. From GM$_2$ to TS$_{2-3}$, the σ cloud migrates from B2B11B5 to B5B11B6, initiating the second rotational step. Upon rotation of the peripheral ring in a full circle, the σ clouds accomplish a full period of electron density migration via continuous and synergetic breakages and formations of a series of closely related 3c-2e σ bonds, revealing typical bonding fluctuations due to thermal vibrations in a molecular Wankel motor with a low energy barrier. An extracted short movie illustrating the intramolecular rearrangements of NiB$_{11}^-$(2) during the MD simulation at 300 K for 20 ps is provided in the ESI.

**Simulated IR, Raman and PES Spectra of NiB$_{11}^-$**

Infrared photodissociation (IR-PD) spectroscopy in combination with first-principles calculations has proven to be a powerful approach in the characterizations of novel cluster monocations [57, 58]. We calculate the vibrational frequencies and simulate the IR and Raman spectra of NiB$_{11}^-$(2) in Fig. 5 and that of NiB$_{10}$(I), NiB$_{12}$(3), and NiB$_{13}^-$(4) in Fig S6 to facilitate their spectroscopic characterizations. The major IR bands NiB$_{11}^-$(2) appear at 550 cm$^{-1}$ (a$^0$), 637 cm$^{-1}$ (a$''$), 693 cm$^{-1}$ (a$''$), 922 cm$^{-1}$ (a$''$), 1089 cm$^{-1}$ (a$''$), 1144 cm$^{-1}$ (a$''$), and 1209 cm$^{-1}$ (a$''$). Its major Raman features occur at 550 cm$^{-1}$ (a$''$), 785 cm$^{-1}$ (a$''$), 1085 cm$^{-1}$ (a$''$), and 1240 cm$^{-1}$ (a$''$). As mentioned above, the energy barrier between the GM and TS is extremely low for NiB$_{11}^-$(2) (0.06 kcal/mol at CCSD(T)). It is expected that the TS may coexist with the GM in IR and Raman measurements, similar to the situation in B$_{13}^+$ which has the GM-TS energy barrier of about 0.4 kcal/mol [58].

Finally, we simulate the PES spectrum of C$_6$ NiB$_{11}^-$(2) using the TD-DFT approach [59] at PBE0 (Fig. 5c). It features six sharp peaks at X (3.69 eV), A (3.94 eV), B...
that of the neutral, while the other PES features originate from vertical detachment transitions to the excited states of $C_\text{s}$ NiB$_{11}$. PES spectroscopy has served as the major experimental approach to characterize boron-based monoanions in gas phase in the past decade [1–19].

Conclusions

We have presented herein a systematic FPT investigation on half-sandwich NiB$_{10}$($^1$), NiB$_{11}$($^2$), NiB$_{12}$($^3$), and NiB$_{13}$($^4$, $^1$A) which all turn out to be well-defined global minima of the systems with a universal coordination bonding pattern of $\sigma$ plus $\pi$ double delocalization. Perfectly planar Ni@B$_{18}$ and cage-like heteroborospherenes Ni$_n$B$_{40}$ ($n = 1–4$) have been predicted for bigger Ni-doped boron clusters in theory. [60] MD simulations show that NiB$_{11}$($^2$) behaves like a Wankel motor at room temperature in a concerted mechanism, reflecting the bonding fluctuation nature of structural fluxionality in molecular motors. Fluxional bonds may play an important role in molecular dynamics and catalysis processes with low energy barriers and deserves further theoretical and experimental investigations. The metal-doped half-sandwich complexes predicted in this work invite experimental syntheses and characterizations to form novel transition-metal borides and boron nanomaterials.

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References


Fig. 5 Simulated IR, Raman and PES spectra of NiB$_{11}$($^2$) at the PBE0/6-311 + G*level (4.29–4.38 eV), C (4.98 eV), D (5.32–5.39 eV), and E (6.17 eV), respectively. The vertical detachment energies (VDEs) of the corresponding excitations are summarized in Table S1 (ESI†). The first peak X represents the vertical detachment transition from the ground state of the anion to...