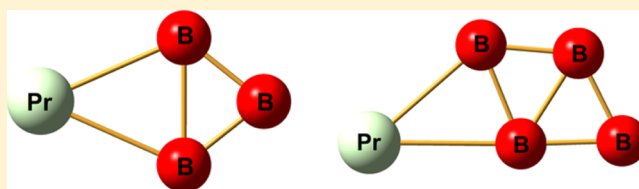


Lanthanides with Unusually Low Oxidation States in the  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$  Boride ClustersXin Chen,<sup>†,||</sup> Teng-Teng Chen,<sup>‡,||</sup> Wan-Lu Li,<sup>†</sup> Jun-Bo Lu,<sup>†</sup> Li-Juan Zhao,<sup>†</sup> Tian Jian,<sup>‡</sup> Han-Shi Hu,<sup>†</sup> Lai-Sheng Wang,<sup>\*,‡,§</sup> and Jun Li<sup>\*,†,§</sup><sup>†</sup>Department of Chemistry and Key Laboratory of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China<sup>‡</sup>Department of Chemistry, Brown University, Providence, Rhode Island 02912, United States<sup>§</sup>Department of Chemistry, Southern University of Science and Technology, Shenzhen, Guangdong 518055, China

## S Supporting Information

**ABSTRACT:** Lanthanide elements typically exhibit a +III oxidation state (OS) in chemical compounds with a few in +IV or even +V OS. Although lanthanides with +II OS have been observed recently in organometallic compounds, +I OS is extremely rare. Using a joint photoelectron spectroscopy and quantum theoretical study, we have found two low OS lanthanides in doped boron clusters,  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$ . These two clusters are shown to have planar structures, in which the Pr atom is bonded to the aromatic boron clusters via two Pr–B  $\sigma$  bonds. Chemical bonding and electronic structure analyses reveal that the Pr atom is in a very low OS in the two boride clusters: +II in  $\text{PrB}_3^-$  and +I in  $\text{PrB}_4^-$ . The current finding suggests that there should exist a whole class of boride complexes featuring rather low-valent lanthanides and expands the frontier of lanthanide chemistry.



## 1. INTRODUCTION

Oxidation state (OS) is a highly useful concept in chemical science as well as in the teaching of chemistry. The discovery of new and unusual OS for chemical elements has been of great interest in chemistry and materials science. The highest OS in neutral compounds is +VIII, only occurring in a few  $\text{MO}_4$  ( $M = \text{Ru, Os, Ir, Xe}$ ) oxides.<sup>1–7</sup> The only known compound with +IX OS is the gaseous  $\text{IrO}_4^+$  cation, as recently verified both theoretically and experimentally.<sup>8,9</sup> Subsequently, Yu and Truhlar suggested a rare  $\text{Pt(X)}$  species in  $\text{PtO}_4^{2+}$  using single-reference calculations with density functional theory (DFT).<sup>10</sup> However, more extensive calculations with open-shell singlet DFT and multireference ab initio wavefunction theory have proved very recently that the  $\text{Pt(X)}$  species is extremely high in energy and the  $\text{PtO}_4^{2+}$  cation is unlikely to be stable in ambient conditions.<sup>11</sup>

The 4f orbitals in lanthanides (Ln) are rather contracted radially<sup>12</sup> and usually do not participate in chemical bonding unless in molecules with extremely short multiple-bond distances.<sup>13</sup> The more favorable and common OS for the lanthanides is +III, though high-valent +IV OS is also known for Ce, Pr, Nd, Tb, and Dy.<sup>14</sup> Recent experimental and theoretical studies have shown that pentavalent lanthanides can exist in, for instance,  $\text{PrO}_4$ ,  $\text{PrO}_2^+$ ,  $\text{NPrO}$ , and  $\text{NPrO}^-$ ,<sup>13,15</sup> and OS of +II can be found in all lanthanides.<sup>16–21</sup> Therefore, lanthanide compounds with OS = +II, +III, +IV, and +V have all been identified thus far. However, monovalent Ln(I) species are still quite rare except in diatomic halide molecules.<sup>22</sup>

Recently, we have studied a lanthanide-doped boron cluster,  $\text{PrB}_7^-$ , and found the rare Pr(II) OS in a half-sandwich  $\text{Pr(II)}[\eta^7\text{-B}_7^{3-}]$  complex,<sup>23</sup> in which the Pr(II) center is coordinated by an aromatic quasipolar  $\text{B}_7^{3-}$  ligand. The low electronegativity of boron and the aromatic stabilization of boron clusters provide unique opportunities to tune the lanthanide OS via rational design. Here, we report a joint photoelectron spectroscopy (PES) and quantum chemistry study on two small Pr boride clusters,  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$ , to search for even lower Ln OS. We find that the  $\text{B}_3^{3-}$  and  $\text{B}_4^{3-}$  clusters formally accept two and one electron, respectively, upon bonding with the Pr atom, forming  $[\text{Pr}^{\text{II}}][\text{B}_3^{3-}]$  and  $[\text{Pr}^{\text{I}}][\text{B}_4^{2-}]$  species. The optimal structures of  $\text{PrB}_3^-$ ,  $\text{PrB}_4^-$ , and their corresponding neutrals are shown in Figure 1. The latter is the first monovalent Ln(I) boride compound observed experimentally.

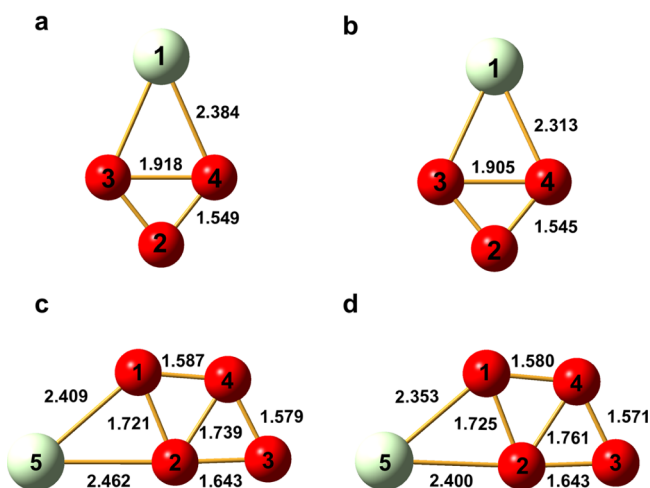
## 2. METHODS

**2.1. Experimental Details.** Figure 2 shows the PE spectra of  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$ . The experiment was done with a magnetic-bottle-type PES apparatus equipped with a laser vaporization supersonic cluster source and a time-of-flight mass spectrometer, details of which have been published elsewhere.<sup>24,25</sup> Briefly, both the  $\text{PrB}_3^-$  and the  $\text{PrB}_4^-$  clusters were produced by laser ablation of a Pr/<sup>11</sup>B composite target followed by supersonic expansion with a He carrier gas containing 5% argon. Various  $\text{PrB}_n^-$  clusters were produced and the  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$  clusters of current interest were mass-selected and

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**Figure 1.** Global minimum structures for (a)  $\text{PrB}_3^-$  ( $C_{2v}$ ,  $4A_2$ ), (b)  $\text{PrB}_3$  ( $C_{2v}$ ,  $3A_2$ ), (c)  $\text{PrB}_4^-$  ( $C_s$ ,  $3A'$ ), and (d)  $\text{PrB}_4$  ( $C_s$ ,  $4A'$ ) at the PBE0/TZP level. The bond lengths are given in Å.

decelerated before photodetachment by the 193 nm (6.424 eV) radiation from an ArF excimer laser. The photoelectron spectra were calibrated using the known spectrum of  $\text{Bi}^-$ . The energy resolution of the apparatus was about 2.5%, that is, around 25 meV for 1 eV electrons.

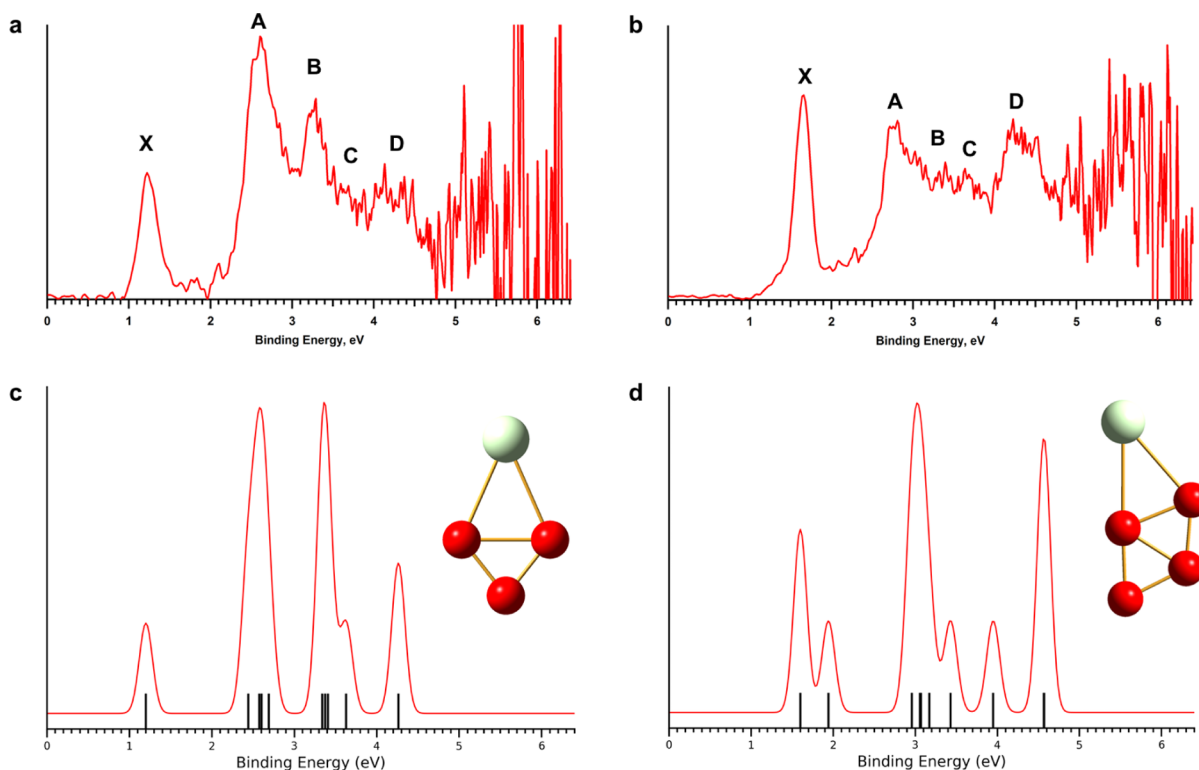
**2.2. Computational Details.** The constraint Basin-Hopping algorithm-based Tsinghua Global Minimum 2 (TGMIn-2) program<sup>26–28</sup> was used to search for the global minima of  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$ . The Amsterdam Density Functional program (ADF 2016.101)<sup>29</sup> with the Perdew-Burke-Ernzerhof (PBE) functional<sup>30</sup> and the polarized triple-zeta (TZP) basis set<sup>31</sup> was used for structural optimization. Vibrational frequencies were calculated at the same

level. For both clusters, the frozen-core approximation was used for the inner shells, that is,  $[1s^2]$  for B and  $[1s^2-4d^{10}]$  for Pr. The scalar relativistic effects were taken into account by the zero-order-regular approximation.<sup>32</sup>

Figure S1 shows the stable isomers found for  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$  by using the TGMIn code. The isomers were further optimized using DFT at the hybrid PBE0/TZP level.<sup>33</sup> Ab initio RHF-ROCCSD(T)<sup>34</sup> single-point calculations using MOLPRO 2012<sup>35</sup> were performed to evaluate the electron configurations of the global minimum  $\text{PrB}_3^-$  [ $\text{Pr}(s^1f^2, f^3, f^2)$ ] and  $\text{PrB}_4^-$  [ $\text{Pr}(s^2f^2, s^1d^1f^2, s^1f^2)$ ]. In the RHF-ROCCSD(T) calculations, the valence triple-zeta basis set (cc-pVTZ) was applied for B<sup>36</sup> and the Stuttgart energy-consistent relativistic pseudopotential ECP28MWB with the corresponding ECP28MWB-ANO basis set was used for Pr.<sup>37–39</sup> Vertical detachment energies (VDEs) were calculated using the  $\Delta\text{SCF-TDDFT}$  approach, as described before.<sup>40</sup> The first VDEs ( $\text{VDE}_1$ ) for  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$  were calculated as the difference in energy between the anionic ground state and the corresponding neutral ground state at the optimized anion geometry. Vertical excitation energies of the neutral species calculated using the time-dependent DFT method<sup>41–43</sup> and the SAOP functional (TDDFT-SAOP)<sup>44</sup> were added to  $\text{VDE}_1$  to yield the higher VDEs. The first adiabatic detachment energy ( $\text{ADE}_1$ ), calculated only for the global minimum anion isomers, was obtained as the energy difference between the anionic and neutral species at their respectively optimized geometries (Table 1). Adaptive natural density partitioning (AdNDP)<sup>45</sup> results were obtained with Multiwfn-3.4.1<sup>46</sup> using the PBE0/cc-pVTZ/ECP28MWB results from Gaussian 09, revision D.01.<sup>47</sup>

### 3. RESULTS AND DISCUSSION

**3.1. Global Minimum Structures.** The optimized geometries for the global minima of  $\text{PrB}_3^-$ ,  $\text{PrB}_4^-$  and their corresponding neutrals at the PBE0/TZP level are shown in Figure 1. The detailed coordinates of these structures are given



**Figure 2.** Photoelectron spectrum of  $\text{PrB}_3^-$  (a) and  $\text{PrB}_4^-$  (b) at 193 nm. (c,d) are the simulated spectra from the global minima structures of  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$  by fitting the calculated VDEs (vertical bars) with a unit area Gaussian function of 0.08 eV half-width. The  $\text{VDE}_1$  of  $\text{PrB}_4^-$  is shifted to align with the X band (see Table 2).

**Table 1.** Experimental and Theoretical VDE<sub>1</sub> and ADE (eV) of PrB<sub>3</sub><sup>−</sup> and PrB<sub>4</sub><sup>−a</sup>

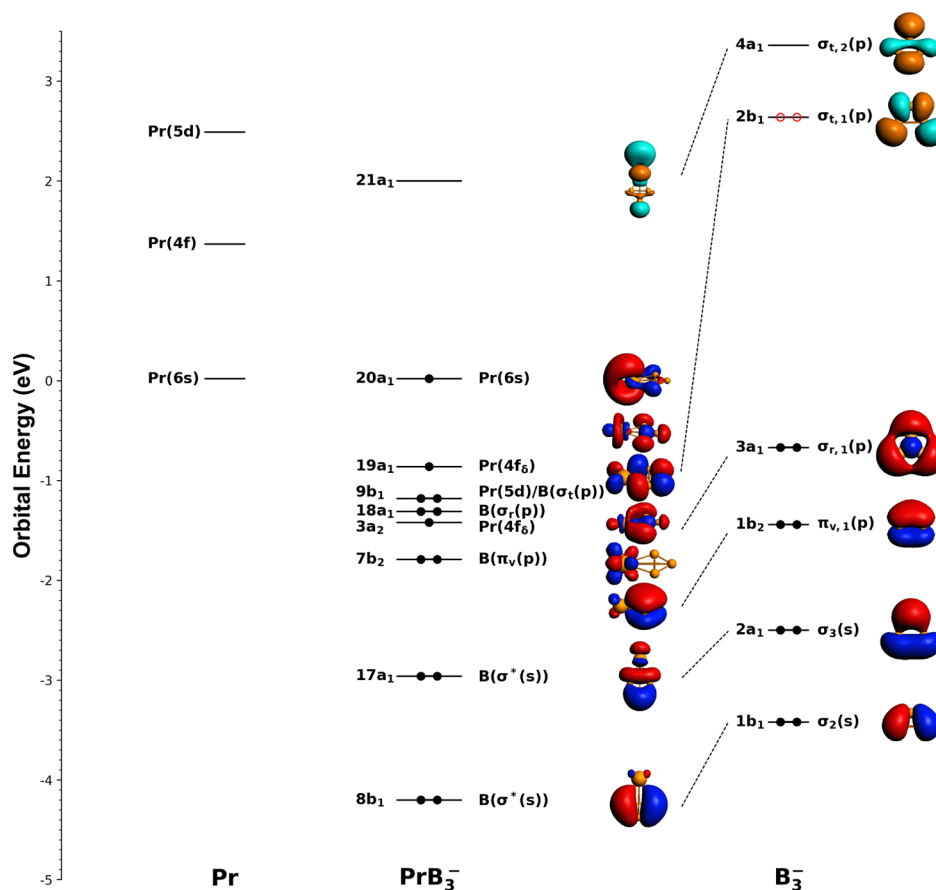
		exp	PBE0	CCSD(T)
PrB <sub>3</sub> <sup>−</sup>	ADE <sub>1</sub> (eV)	1.15	1.14	0.86
	VDE <sub>1</sub> (eV)	1.22	1.20	0.90
PrB <sub>4</sub> <sup>−</sup>	ADE <sub>1</sub> (eV)	1.56	1.43	1.43
	VDE <sub>1</sub> (eV)	1.66	1.50	1.44

<sup>a</sup>The calculated CCSD T1 diagnostics are: 0.043 (PrB<sub>3</sub><sup>−</sup>), 0.034 (PrB<sub>3</sub>), 0.045 (PrB<sub>4</sub><sup>−</sup>), and 0.047 (PrB<sub>4</sub>), indicating that accurate calculations of the energies of these systems require multireference ab initio methods.

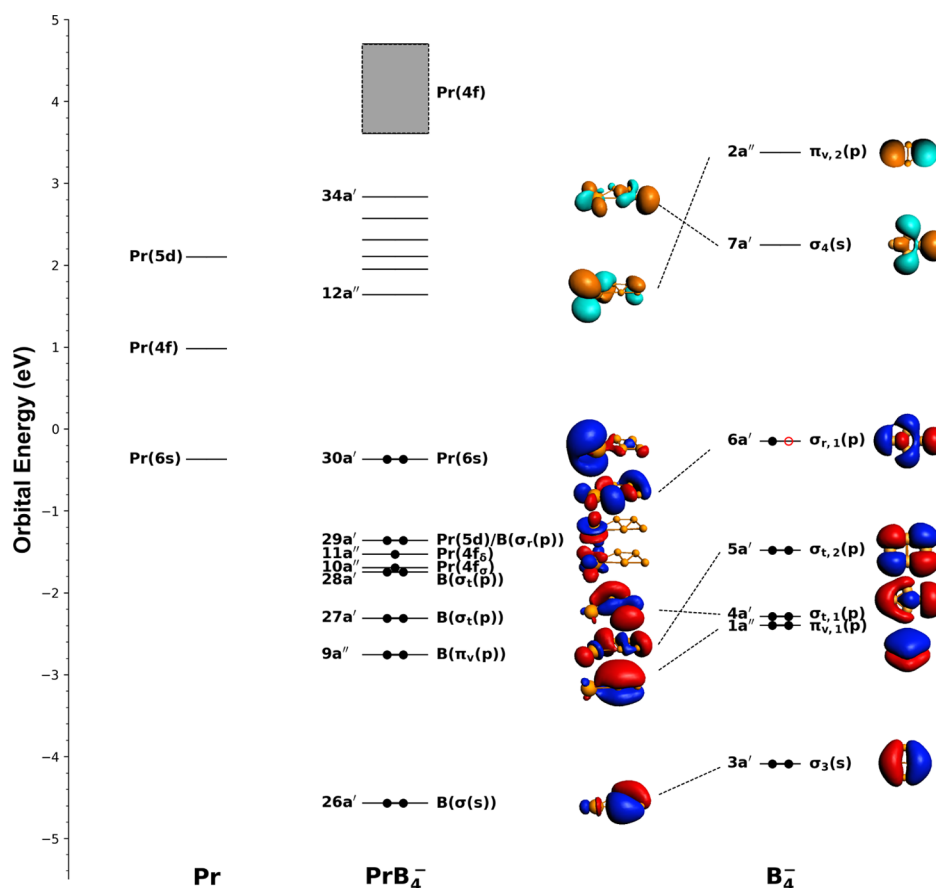
in Table S1 (PrB<sub>3</sub><sup>−</sup> and PrB<sub>3</sub>) and Table S2 (PrB<sub>4</sub><sup>−</sup> and PrB<sub>4</sub>). Both PrB<sub>3</sub><sup>−</sup> and PrB<sub>4</sub><sup>−</sup> can be seen as substituting one terminal B atom from the planar B<sub>4</sub><sup>−</sup> and B<sub>5</sub><sup>−</sup> clusters.<sup>48,49</sup> The global minimum of PrB<sub>3</sub><sup>−</sup> has a C<sub>2v</sub> symmetry and a quartet (<sup>4</sup>A<sub>2</sub>) ground electronic state with a pseudoatomic Pr(s<sup>1</sup>f<sup>2</sup>) configuration. The electronic states with other Pr configurations are higher in energy: f<sup>2</sup> (~20 kcal/mol), f<sup>3</sup> (~27 kcal/mol) at the RHF-ROCCSD(T) level. The global minimum of PrB<sub>4</sub><sup>−</sup> is found to have a C<sub>s</sub> symmetry and a triplet ground electronic state (<sup>3</sup>A') with a Pr(s<sup>2</sup>f<sup>2</sup>) configuration. A high-spin quintet state (<sup>5</sup>A') with a Pr(s<sup>1</sup>d<sup>1</sup>f<sup>2</sup>) configuration is ~9 kcal/mol higher in energy at the RHF-ROCCSD(T) level. The Pr(s<sup>2</sup>f<sup>2</sup>) configuration means a Pr(I) OS, which is quite unusual in lanthanide chemistry. Hence, we also tested Pr<sup>II</sup>(s<sup>1</sup>f<sup>2</sup>), which is ~18 kcal/mol higher at the RHF-

ROCCSD(T) level, and Pr<sup>III</sup>(f<sup>2</sup>), which is ~40 kcal/mol higher at the PBE0/TZP level. These results show that the Pr atom favors the unprecedentedly low +I OS in the PrB<sub>4</sub><sup>−</sup> cluster. The Kohn–Sham canonical molecular orbitals (MOs) for the global minima of PrB<sub>3</sub><sup>−</sup> and PrB<sub>4</sub><sup>−</sup> are shown in Figures 3 and 4, respectively, as well as the MOs of the B<sub>3</sub><sup>−</sup> and B<sub>4</sub><sup>−</sup> moieties in the local coordinate system (LCS, Figure 5).

**3.2. Comparison of Experimental and Theoretical Photoelectron Spectra.** Figure 2 shows the PE spectra of PrB<sub>3</sub><sup>−</sup> and PrB<sub>4</sub><sup>−</sup>, compared with the simulated spectra from the respective global minima. Each of the two spectra displays a sharp low binding energy band (X) followed by a sizable energy gap. Band X corresponds to the detachment transition from the ground electronic state of the anion (PrB<sub>3</sub><sup>−</sup> and PrB<sub>4</sub><sup>−</sup>) to the corresponding neutral ground electronic state (PrB<sub>3</sub> and PrB<sub>4</sub>), whereas the higher binding energy bands denote detachment transitions to excited electronic states of the neutrals. For PrB<sub>3</sub><sup>−</sup> (Figure 2a), band X yields a VDE<sub>1</sub> of 1.22 eV. The first ADE is estimated from the onset of band X to be 1.15 eV, which also represents the electron affinity (EA) of neutral PrB<sub>3</sub>. Band A at 2.61 eV is quite strong and broad, followed by a well-defined band B at 3.29 eV. Beyond band B, the spectrum is not well resolved, and bands C and D are labeled for the sake of discussion. For PrB<sub>4</sub><sup>−</sup> (Figure 2b), band X gives rise to a VDE<sub>1</sub> of 1.66 eV, and an estimated ADE<sub>1</sub> of 1.56 eV from the band onset, that is the EA of PrB<sub>4</sub>. Band A of PrB<sub>4</sub><sup>−</sup> with a VDE of 2.81 eV is quite broad. The spectrum of



**Figure 3.** Kohn–Sham molecular orbital energy levels of PrB<sub>3</sub><sup>−</sup> and the LCS orbitals of the B<sub>3</sub><sup>−</sup> moiety at the PBE0/TZP level. The valence MOs of the B<sub>3</sub><sup>−</sup> are divided into four types:  $\sigma(s)$ ,  $\sigma_t(p)$ ,  $\sigma_r(p)$ , and  $\pi_v(p)$ . Here “t”, “r” and “v” denote tangential, radial, and vertical, respectively. The atomic orbitals of Pr are shifted for clarity.



**Figure 4.** Kohn–Sham molecular orbital energy levels of  $\text{PrB}_4^-$  and the LCS orbitals of the  $\text{B}_4^-$  moiety at the PBE0/TZP level. The atomic orbitals of Pr are shifted for clarity.

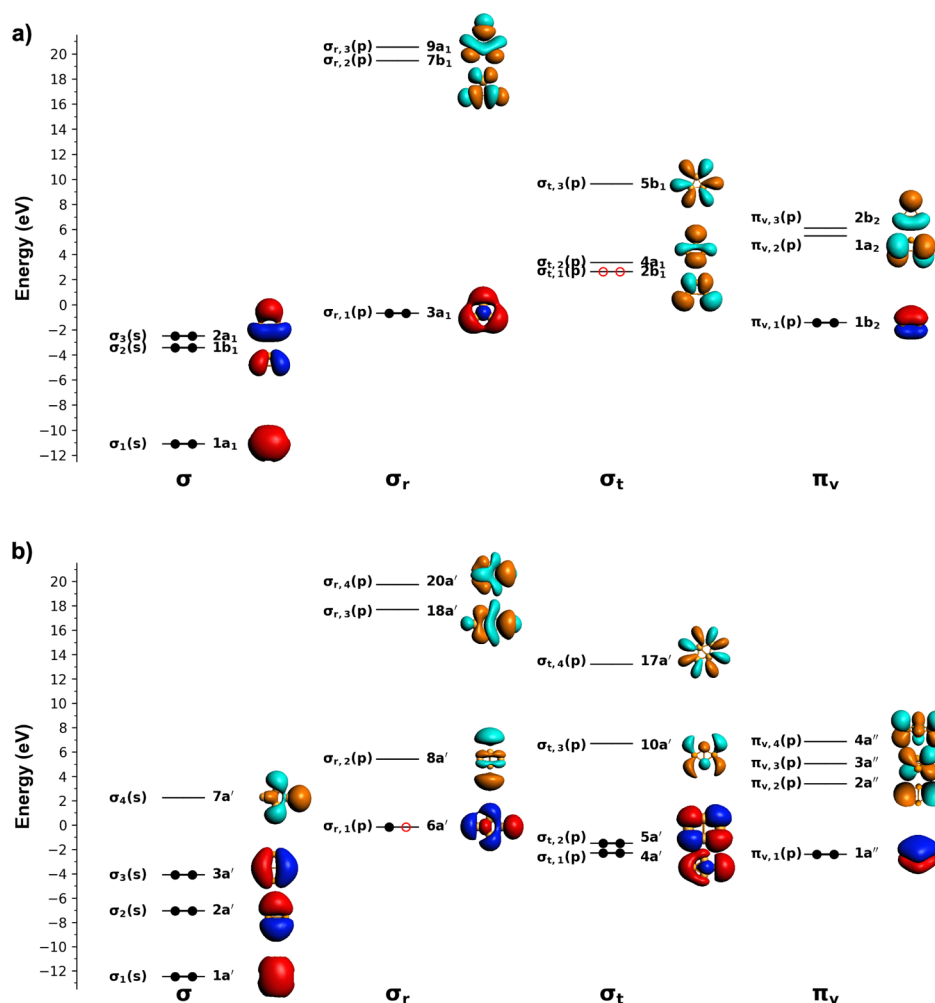
$\text{PrB}_4^-$  at high binding energies is also very complicated and three bands (B, C, D) are tentatively identified. For both spectra, the relatively sharp peak X suggests detachment of a nonbonding electron and very little geometry change between the ground states of the anion and the corresponding neutral. The experimental VDEs of all the observed bands for  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$  are given in Table 2, where they are compared with the theoretical data (vide infra).

The calculated  $\text{VDE}_1$  and  $\text{ADE}_1$  for both  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$  at the PBE0/TZP and RHF-ROCCSD(T) levels are given in Table 1. For  $\text{PrB}_3^-$ , the first electron detachment corresponds to the removal of the single Pr(6s) electron from the relatively diffuse singly occupied MO (SOMO)  $20a_1$  (Table 2 and Figure 3). The calculated  $\text{VDE}_1$  at the PBE0/TZP level is 1.20 eV, which agrees well with the experimental result (1.22 eV). The resulting neutral state is triplet  $^3A_2$ , corresponding to an  $f^2$  configuration with Pr in its favorite +III OS, which explains the energy gap following band X and the low EA of  $\text{PrB}_3$ . The broad band A corresponds to four detachment channels from the Pr–B bonding orbital  $9b_1$  and the B–B bonding orbital  $18a_1$  (Figure 3):  $^5B_2$  at 2.44 eV,  $^5A_2$  at 2.58 eV,  $^3A_2$  at 2.60 eV, and  $^3B_2$  at 2.69 eV (Table 2). Band B comes from electron detachment from the mainly  $\pi$  bonding orbital  $7b_2$  of the  $\text{B}_3^-$  moiety:  $^5B_1$  at 3.44 eV and  $^3B_1$  at 3.41 eV. Detachment from the primarily Pr(4f)  $19a_1$  orbital also contributes to band B:  $^3A_2$  at 3.37 eV, though the detachment cross sections for 4f orbitals are usually low. Higher binding energy detachment channels are all from primarily B–B bonding orbitals on the  $\text{B}_3^-$  moiety.

For  $\text{PrB}_4^-$ , the first electron detachment also corresponds to the removal of a 6s electron from the closed-shell highest occupied molecular orbital (HOMO)  $30a'$  (Figure 4), leading to the  $4A'$  final neutral state with a  $\text{Pr}(f^2s^1)$  configuration and +II OS. The calculated  $\text{VDE}_1$  at the PBE0 level (1.50 eV) is in good agreement with the experiment value of 1.66 eV (Table 1). The corresponding low-spin detachment channel ( $^2A'$  at 1.84 eV) from the HOMO  $30a'$  should also contribute to the X band or the weak signals between bands X and A. The broad band A at about 2.81 eV corresponds to four detachment channels: the Pr–B bonding MO ( $29a'$ ) ( $^4A'$  at 2.86 eV and  $^2A'$  at 2.96 eV) and the two 4f-based SOMO ( $11a''$  and  $10a''$ ) giving rise to two  $^2A''$  final states at calculated VDEs of 2.97 and 3.07 eV (Table 2 and Figure 4). The B and C bands are assigned to the low spin states from detachment of  $28a'$  and  $27a'$  (two B–B bonding MOs). The high-spin final states from detachment of these two MOs result in similar VDEs, but their weights were low in the TD-DFT calculations, suggesting difficulties of using the single-referenced DFT to describe these states. Band D is mainly from detachment from the  $\pi$  MO ( $9a''$ ) on the  $\text{B}_4^-$  moiety (Figure 4); the computed VDE of 4.47 eV is in good agreement with the experimental value of 4.25 eV. Overall, the theoretical results agree well with the experimental data for both clusters, confirming the global minima for  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$ , as well as the adequacy of the theoretical methods.

**3.3. Oxidation States and Chemical Bonding.** The geometry changes from the anion to neutral are similar in the two cluster systems (Figure 1). The Pr–B bonds are noticeably





**Figure 5.** MOs in the LCS of (a)  $B_3^-$  moiety and (b)  $B_4^-$  at the PBE0/TZP level. The valence MOs of the  $B_3^-$  and  $B_4^-$  moieties are divided into four types:  $\sigma$ ,  $\sigma_v$ ,  $\sigma_r$ , and  $\pi_v$ . Here “t” denotes tangential, “r” means radial with regards to the  $B_x^-$  ring, and “v” represents vertical. Black dots denote electrons from the  $B_x^-$  moiety, whereas additional electrons required are displayed as red dots.

shorter in the two neutrals than those in the anions, mainly because of the increased electrostatic interactions between the Pr center and the boron clusters. The  $B_3$  and  $B_4$  moieties are almost the same from the anions to the neutrals, consistent with the fact that the first detachment channels in both systems come from the diffuse and nonbonding 6s orbitals. Thus, the  $PrB_3^-$  anion can be viewed as  $Pr^I(B_3^{3-})$  and the  $PrB_4^-$  anion can be viewed as  $Pr^I(B_4^{2-})$ , whereas the corresponding neutrals can be viewed as  $Pr^{III}(B_3^{3-})$  and  $Pr^{II}(B_4^{2-})$ , respectively. The calculated Mulliken charges and spin distributions of the Pr and B atoms are consistent with the OS assignments, as given in Table S3 ( $PrB_3^-$  and  $PrB_3$ ) and Table S4 ( $PrB_4^-$  and  $PrB_4$ ). Hence, the rare Pr(I) OS exists in the  $PrB_4^-$  anion with an electron configuration of  $f^2s^2$ , and the Pr in  $PrB_3^-$  exists in the low +II OS with a configuration of  $f^2s^1$ , as can be seen in the MO diagrams of Figures 3 and 4.

Boron is electron-deficient, and it is therefore surprising that such low OSs exist in the boride clusters. Analyzing the MOs of the  $B_3^-$  and  $B_4^-$  moieties in the LCS (Figure 5) can help better understand why Pr prefers low OSs in these small boride clusters. Because of the lower electronegativity of Pr compared to B, Pr is expected to lose electrons to the B clusters. The ground state of the  $B_3^-$  moiety is a singlet and the HOMO is a  $\sigma_{t,1}(p)$  orbital ( $2b_1$ ),<sup>48</sup> where t means the tangential direction

along the  $B_3^-$  framework. The  $\sigma_{t,1}(p)$  and  $\sigma_{r,1}(p)$  orbitals, where r denotes the radial direction pointing to the center of the plane, interact with the d orbitals on Pr to form two Pr–B  $\sigma$  bonds (Figure 3). Hence, in  $PrB_3^-$ , Pr essentially loses two electrons to the  $B_3^-$  moiety, resulting in the  $Pr^{II}$  OS. The ground state of  $B_4^-$  is doublet and the HOMO ( $6a'$ ) is singly occupied (Figure 5b).<sup>48</sup> In  $PrB_4^-$ , the 5d orbitals on Pr interact with the HOMO and HOMO – 1 to form two Pr–B  $\sigma$  bonds, effectively resulting in the transfer of one electron to  $B_4^-$  and the rare  $Pr^I$  OS. Our RHF-ROCCSD(T) calculations suggest that transferring three electrons from Pr to the  $B_4^-$  moiety is not favorable as the  $Pr^{III}(f^2)$  configuration is some 20 kcal/mol higher in energy than the  $Pr^I(f^2f^2)$  configuration.

We further analyzed the chemical bonding in  $PrB_3^-$  and  $PrB_4^-$  using the AdNDP method (Figure 6).<sup>45</sup> In  $PrB_3^-$  the occupation number of Pr is 3.00 lel (Figure 6a), consisting of one 6s and two 4f electrons in agreement with the +II OS for Pr. The  $B_3^-$  moiety consists of two delocalized 3c–2e bonds ( $\sigma$  and  $\pi$ ), two peripheral 2c–2e B–B  $\sigma$  bonds, and two 2c–2e Pr–B  $\sigma$  bonds. The AdNDP results for  $PrB_4^-$  (Figure 6b) show a 6s long pair and two 4f electrons, consistent with the +I OS for Pr. The  $B_4^-$  moiety consists of two 4c–4e delocalized bonds ( $\sigma$  and  $\pi$ ), three peripheral 2c–2e B–B  $\sigma$  bonds, and two 2c–2e Pr–B  $\sigma$  bonds. The delocalized  $\sigma$  and  $\pi$  bonds

Table 2. Experimental VDEs of  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$  Compared with the Theoretical Data at the TDDFT–SAOP/TZP Level<sup>a</sup>

observed band	VDE (exp)	final state	final-state electron configurations	VDE (theo)
<b><math>\text{PrB}_3^-</math></b>				
X	1.22(3)	$^3\text{A}_2$	... $(17a_1)^2(7b_2)^2(3a_2)^1(18a_1)^2(9b_1)^2(19a_1)^1(20a_1)^0$	1.20
A	2.61(1)	$^5\text{B}_2$	... $(17a_1)^2(7b_2)^2(3a_2)^1(18a_1)^2(9b_1)^1(19a_1)^1(20a_1)^1$	2.44
		$^5\text{A}_2$	... $(17a_1)^2(7b_2)^2(3a_2)^1(18a_1)^1(9b_1)^2(19a_1)^1(20a_1)^1$	2.58
		$^3\text{A}_2$	... $(17a_1)^2(7b_2)^2(3a_2)^1(18a_1)^1(9b_1)^2(19a_1)^1(20a_1)^1$	2.60
		$^3\text{B}_2$	... $(17a_1)^2(7b_2)^2(3a_2)^1(18a_1)^2(9b_1)^1(19a_1)^1(20a_1)^1$	2.69
B	3.29(2)	$^5\text{B}_1$	... $(17a_1)^2(7b_2)^1(3a_2)^1(18a_1)^2(9b_1)^2(19a_1)^1(20a_1)^1$	3.34
		$^3\text{A}_2$	... $(17a_1)^2(7b_2)^2(3a_2)^1(18a_1)^2(9b_1)^2(19a_1)^0(20a_1)^1$	3.37
		$^3\text{B}_1$	... $(17a_1)^2(7b_2)^1(3a_2)^1(18a_1)^2(9b_1)^2(19a_1)^1(20a_1)^1$	3.41
C	~3.69	$^3\text{A}_1$	... $(17a_1)^2(7b_2)^2(3a_2)^0(18a_1)^2(9b_1)^2(19a_1)^1(20a_1)^1$	3.63
D	~4.13	$^5\text{A}_2$	... $(17a_1)^1(7b_2)^2(3a_2)^1(18a_1)^2(9b_1)^2(19a_1)^1(20a_1)^1$	4.26
<b><math>\text{PrB}_4^-</math></b>				
X	1.66(1)	$^4\text{A}'$	... $(9a'')^2(27a')^2(28a')^2(29a')^2(10a'')^1(11a'')^1(30a')^1$	1.50
A	2.81(3)	$^2\text{A}'$	... $(9a'')^2(27a')^2(28a')^2(29a')^2(10a'')^1(11a'')^1(30a')^1$	1.84
		$^4\text{A}'$	... $(9a'')^2(27a')^2(28a')^2(29a')^1(10a'')^1(11a'')^1(30a')^2$	2.86
		$^2\text{A}'$	... $(9a'')^2(27a')^2(28a')^2(29a')^1(10a'')^1(11a'')^1(30a')^2$	2.96
		$^2\text{A}''$	... $(9a'')^2(27a')^2(28a')^2(29a')^2(10a'')^1(11a'')^0(30a')^2$	2.97
		$^2\text{A}''$	... $(9a'')^2(27a')^2(28a')^2(29a')^2(10a'')^0(11a'')^1(30a')^2$	3.07
B	3.39(6)	$^2\text{A}'$	... $(9a'')^2(27a')^2(28a')^1(29a')^2(10a'')^1(11a'')^1(30a')^2$	3.30 <sup>a</sup>
C	3.63(5)	$^2\text{A}'$	... $(9a'')^2(27a')^1(28a')^2(29a')^2(10a'')^1(11a'')^1(30a')^2$	3.85 <sup>a</sup>
D	~4.25	$^4\text{A}''$	... $(9a'')^1(27a')^2(28a')^2(29a')^2(10a'')^1(11a'')^1(30a')^2$	4.47

<sup>a</sup>The VDE<sub>1</sub> is calculated at the PBE0/TZP level. All energies are in eV.

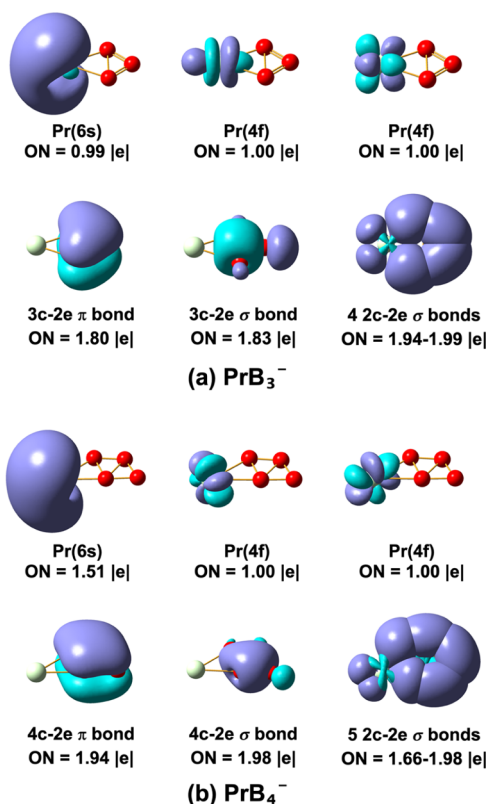


Figure 6. AdNDP bonding analyses for  $\text{PrB}_3^-$  (a) and  $\text{PrB}_4^-$  (b) at the PBE0/cc-pVTZ/ECP28MWB level.

render the boron moieties doubly aromatic in both clusters. Hence,  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$  each can be viewed as a Pr atom bonded to doubly aromatic boron clusters via two Pr–B covalent bonds, underlying their stabilities relative to other isomers (Figure S1). The stability of the two clusters can also

be glimpsed from the large binding energies between Pr and the boron clusters. The calculated binding energy of  $\text{PrB}_3^-$  ( $^4\text{A}_2$ )  $\rightarrow$   $\text{Pr}(s^2f^3) + \text{B}_3^-$  ( $^1\text{A}_1$ ) is 108.98 kcal/mol and that of  $\text{PrB}_4^-$  ( $^3\text{A}'$ )  $\rightarrow$   $\text{Pr}(s^2f^3) + \text{B}_4^-$  ( $^2\text{A}'$ ) is 120.83 kcal/mol.

Previous studies on larger lanthanide–boron clusters show that they prefer half-sandwich or inverse-sandwich structures.<sup>23,50,51</sup> In order to explore the geometry preferences of  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$ , we computed their relative energy changes as a function of  $\angle\text{Pr}-\text{B}_x$  angle  $\theta$ , as shown in Figure 7. The

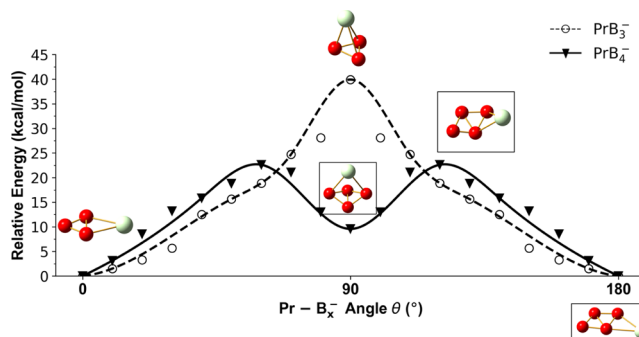


Figure 7. Relative PBE0/TZP energies for  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$  as a function of  $\text{Pr}-\text{B}_x$  angle  $\theta$ . For each cluster, the energy for  $\theta = 0^\circ$  is chosen to be zero.

$\text{PrB}_3^-$  cluster becomes more and more unstable as  $\theta$  increases from  $0^\circ$  (planar) to  $90^\circ$  (half-sandwich), which represents an energy maximum, ~40 kcal/mol higher than the planar structure. The  $\text{PrB}_4^-$  cluster shows a different trend, for which the half-sandwich structure represents a local minimum, ~10 kcal/mol higher than the planar structure. These observations as well as previous results of  $\text{SmB}_6^-$  and  $\text{PrB}_7^-$  suggest that the half-sandwich structures become more energetically favorable when the  $\text{B}_x^-$  moiety becomes larger.<sup>22,49</sup> Thus, the  $\text{PrB}_5^-$  and  $\text{PrB}_6^-$  clusters are likely to

have the planar and half-sandwich structures co-exist, as was the case for  $\text{SmB}_6^{-50}$ .

#### 4. CONCLUSIONS

In conclusion, we have studied Pr-doped  $\text{B}_3^-$  and  $\text{B}_4^-$  clusters using PES and density-functional and ab initio quantum chemical calculations. The global minimum of the  $\text{PrB}_3^-$  cluster is found to be a planar  $\text{C}_{2v}$  structure with a  $\text{Pr}^{\text{II}}$  center interacting with a  $\text{B}_3^{3-}$  moiety. The  $\text{PrB}_4^-$  cluster is found to have a  $\text{C}_s$  symmetry with a rare  $\text{Pr}^{\text{I}}$  center interacting with a  $\text{B}_4^{2-}$  moiety. Both boron moieties exhibit  $\sigma$  and  $\pi$  double aromaticity. The unusually low OS Pr in the boride clusters are interesting, largely owing to the relatively low electronegativity of boron and the stability of the aromatic boron moieties. The current results reveal the possibility of forming unusually low OS for lanthanide elements with boron clusters. The monovalent OS suggests that lanthanide elements can behave like alkali or alkali earth elements in suitable coordination environments, expanding the chemistry of the lanthanides.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b02572.

Coordinates of the  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$  isomers at the PBE0/TZP level; calculated Mulliken charges and spin density distributions of  $\text{PrB}_3^-/\text{PrB}_3/\text{PrB}_4^-/\text{PrB}_4$ ; and relative energies of the stable isomers of  $\text{PrB}_3^-$  and  $\text{PrB}_4^-$  at the PBE/TZP, PBE0/TZP levels (PDF)

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##### Notes

The authors declare no competing financial interest.

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