Observation of Four-Fold Boron–Metal Bonds in RhB(BO−) and RhB

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ABSTRACT: The maximum bond order between two main-group atoms was known to be three. However, it has been suggested recently that there is quadruple bonding in C2 and analogous eight-valence electron species. While the quadruple bond in C2 has aroused some debates, an interesting question is: are main-group elements capable of forming quadruple bonds? Here we use photoelectron spectroscopy and computational chemistry to probe the electronic structure and chemical bonding in RhB,O− and RhB− and show that the boron atom engages in quadruple bonding with rhodium in RhB(BO)− and neutral RhB. The quadruple bonds consist of two π-bonds formed between the Rh 4dσ/4dxz and B 2pσ/2pπ orbitals and two σ-bonds between the Rh 4dπ and B 2s/2pσ orbitals. To confirm the quadruple bond in RhB, we also investigate the linear Rh=≡B−H+ species and find a triple bond between Rh and B, which has a longer bond length, lower stretching frequency, and smaller bond dissociation energy in comparison with that of the Rh=≡B quadruple bond in RhB.

Ever since Lewis’s epochal work on chemical bonds,1 the maximum bond order between two main-group atoms has been known to be three. A quadruple bond between two Re atoms was first discovered in [Re2X8]2− type compounds,2 while five-fold bonding was realized between two Cr(I) centers.3 The maximum bond order between two atoms is now known to be six between two group-VIB atoms (Cr2, Mo2, W2) based on theoretical analyses.4 Recently, the idea of quadruple bonding between two main-group atoms has been suggested in C2 and analogous eight-valence electron species on the basis of high-level theoretical analyses.5 Further theoretical studies also indicated that carbon is involved in quadruple bonding with uranium in the linear triatomic CUO molecule,6 as well as in terminal transition metal carbides.7 However, the quadruple bond in C2 has aroused some debates,8−13 primarily due to the fact that the putative CC quadruple bond strength in C2 is weaker than that in the classical HC≡CH triple bond in terms of bond lengths and force constants. Boron is electron-deficient and favors delocalized bonding in boranes and finite-sized clusters.14−18 Localized boron–boron triple bonds are possible if electron-donor ligands are used. Boron–boron triple bonds were first observed in isolated molecules with CO and BO− ligands19,20 and synthesized with bulky carbene ligands.21,22 Although many compounds containing metal–boron double bonds (borylenes) were known,23 a metal–boron triple bond was found only recently in the Bi≡B−BO− molecule both experimentally and theoretically.24 In searching for similar triple-bonded M≡B−BO− molecules with transition metal elements, we have examined RhB,BO−. Surprisingly, we found that it does not have the expected linear Rh≡B−BO− structure. Rather, its most stable structure is found to be bent with the BO− ligand coordinated to the Rh atom and a very short terminal Rh−B bond. Subsequently, we have investigated the diatomic RhB− molecule and found that it has an even shorter Rh−B bond. Both experimental and theoretical analyses reveal that the B atom engages in quadruple bonding with Rh in RhB and RhB(BO−).

We did the experiments using two separate photoelectron spectroscopy (PES) apparatuses (see the SI for more experimental details). Briefly, the RhB− and RhB,BO− species were produced by laser vaporization of a Rh/11B/Bi mixed target. The RhB,BO− cluster was formed from the trace amount of oxide impurity on the target surface. The anionic clusters were extracted and analyzed using a time-of-flight mass spectrometer. The cluster of interest was mass-selected before being photodetached by a second laser. The photoelectron kinetic energies were measured with either a magnetic bottle time-of-flight analyzer18,25 or a photoelectron imaging (PEI) system.26 Figure 1 shows the photoelectron images and spectra of RhB− at three photon energies using the PEI apparatus. Peak X represents the transition from the ground state of RhB− to that of RhB, yielding the electron affinity (EA) of neutral RhB to be 0.961 eV. Short vibrational progression was observed for the ground-state transition with a vibrational frequency of 994 cm−1. Peaks A at 1.339 eV and B at 1.428 eV are intense transitions, followed by a weak peak C at 1.525 eV. Although the separations between peaks A, B, and C are

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The lowest binding energy band X corresponds to the ground state of RhB₂O⁻ to that of neutral RhB₂O, whereas the higher binding energy bands (A–F) indicate detachment transitions to excited states of neutral RhB₂O. Band X yielded the first vertical detachment energy (VDE) of 1.452 eV, which was taken on the magnetic bottle PES apparatus at 193 nm. The vertical lines represent vibrational structures, and the double arrow below the images indicates the laser polarization.

The photoelectron spectrum of RhB₂O⁻ displayed in Figure 2 was taken on the magnetic bottle PES apparatus at 193 nm. The lowest binding energy band X corresponds to the ground state of RhB₂O⁻ to that of neutral RhB₂O, whereas the higher binding energy bands (A–F) indicate detachment transitions to excited states of neutral RhB₂O. Band X yielded the first vertical detachment energy (VDE) of 1.452 eV, which was taken on the magnetic bottle PES apparatus at 193 nm. The vertical lines represent vibrational structures, and the double arrow below the images indicates the laser polarization.

Band E at ∼6.0 eV and band F at ∼6.2 eV were tentatively identified. The photoelectron spectra of RhB⁻ and RhB₂O⁻ serve as electronic fingerprints to allow analyses of their structures and bonding by comparison with theoretical calculations. The observed PES features and their binding energies are compared with the theoretical results in Tables S1 and S2 for RhB⁻ and RhB₂O⁻, respectively.

The calculated structures for RhB⁻ and RhB₂O⁻ and their corresponding neutrals are shown in Figure 3 (see the SI for the theoretical details). The bond lengths of RhB and RhB⁻ were calculated at various levels of theory, which all predicted similar values between Rh and B. 1.703–1.712 Å for RhB⁻ and 1.685–1.689 Å for RhB (Table S3). The neutral Rh–B bond length agrees well with a previous experimental value (1.692 Å) obtained from optical spectroscopy, and as well as a previous theoretical calculation (1.698 Å). Different structures were computed for RhB₂O⁻. Surprisingly, the global minimum of RhB₂O⁻ was found to be bent (Cₛ, 4A'), consisting of a BO⁻ unit coordinated to the Rh atom (Figure 3b). The expected linear structure was found to be higher in energy by 0.60 eV (Figure S1a). The calculated Rh–B bond length between Rh and the BO unit was 1.996 Å, while that between Rh and the terminal B was 1.747 Å in the bent global minimum. There was a huge bond angle change between the BO unit and the RhB unit upon electron detachment, reducing from 99.8° in the anion to 80.4° in the neutral (Figure 3b). The Rh–BO bond length was also slightly shortened, and that between Rh and the terminal B was slightly lengthened in the neutral.

The Kohn–Sham molecular orbitals (MOs) for RhB and the global minimum RhB(BO⁻) bent structure are given in Figure S2. There is similarity between the MOs related to the terminal RhB unit in RhB(BO⁻) and the bare RhB, as shown in Figure 4. A MO diagram for RhB, along with the atomic orbital compositions, is shown in Figure S5. The LUMO (3σ) of RhB, where the extra electron in the RhB⁻ anion resides, is a weakly antibonding orbital between the Rh 5s5p and the B 2s2p orbitals. The increased bond length and reduced vibrational frequency in the anion compared to those of the neutral are consistent with the weak antibonding character of the LUMO (Figure 3 and Table S1). The calculated VDE of 1.445 eV for the 3σ state into three closely spaced states, 3Δ, 3Σ, 3Σ, consistent with the observed peaks A, B, C (Table S1). The computed VDE of 1.445 eV for the 3σ state is in excellent agreement with the average of the three spin—
orbit components (Table S1). Furthermore, no vibrational progression is observed, consistent with the nonbonding nature of the $1\delta$ MO. The computed VDE for the corresponding $1\Delta$ final state is 2.140 eV, which is somewhat higher than the observed value. In addition, a short vibrational progression is observed for the $1\Delta$ state, suggesting possible vibronic coupling of the $1\Delta$ state with other nearby electronic states. The remaining four valence MOs are bonding orbitals between the Rh $4d_{z^2}/4d_{xz}/4d_{yz}$ and B $2s/2p_x/2p_y/2p_z$ orbitals.

The structure of RhB(BO$^-$) is basically a BO$^-$ ligand coordinated to the RhB unit, as revealed in the MOs (Figure S2b). The HOMO, HOMO−1 to HOMO−4, and HOMO−9 correspond to the RhB unit, as compared with those of the bare RhB in Figure 4. The remaining five valence MOs (HOMO−5 to HOMO−8 and HOMO−10) belong to the BO$^-$ ligand. The HOMO of RhB(BO$^-$), corresponding to one of the $1\delta$ MOs in RhB, is involved in bonding interactions with the BO$^-$ ligand. The calculated VDEs are in good agreement with the experimental data, as shown in Table S2 and Figure S3a. The calculated VDEs for the linear RhB–BO$^-$ structure completely disagree with the observed spectrum (Figure S3b). A high-resolution PEI experiment was done for the X band, but a very congested spectrum was obtained (Figure S4a). This confirms the large geometry change between the RhB(BO$^-$) anion and its corresponding neutral, as borne out in the Franck–Condon simulation (Figure S4b).

The unusual bent structure of RhB(BO$^-$) with a short Rh–B bond prompted us to investigate the bonding in RhB. The computed Rh–B bond length of 1.685 Å is much shorter than the Rh≡B triple bond length using Pyykko’s self-consistent Rh and B atomic covalent radii, which give a triple bond length of 1.79 Å. Our computed Rh–B bond length agrees well with the previous experimental value of 1.692 Å and the previous theoretical value of 1.698 Å. The MOs of Rh−B reveal four bonding orbitals (1σ, 1π, and 2σ) and two nonbonding orbitals (Figure 5). The extremely short Rh–B bond length is consistent with a quadruple bond between Rh and B (Rh≡B). The RhB bonding was considered to be a triple...
bond previously because the 1σ MO was classified essentially as a 2σ lone pair. However, the bonding nature of the 1σ MO can be glimpsed by the fact that the bent Rh≡B(BO\textsuperscript{−}) structure is more stable than the linear Rh≡B=BO\textsuperscript{−} isomer, in which the B atom can form only a triple bond with Rh. The bonding of the two structures is compared in Figure S5 using the Adaptive Natural Density Partitioning (AdNDP) analyses. It can be seen readily that four Rh−B bonds exist in the bent Rh≡B(BO\textsuperscript{−}) global minimum with two 4d lone pairs, whereas there are three Rh−B bonds and three 4d lone pairs in the linear Rh≡B−BO\textsuperscript{−} higher-energy isomer. The 1σ MOs comprise the two π bonds. The 2σ MO consists of significant bonding interactions between the 4d\textsuperscript{z} orbital of Rh and the sp\textsubscript{z} hybridized orbital of B, as shown more clearly in Figure 6 at a smaller isovalue. This bonding orbital was called a “doughnut” σ bond previously.

![HOMO-1, 2σ](image)

Figure 6. HOMO−1 (2σ) of RhB at isovalue = 0.020 e/Å\textsuperscript{3}.

While this manuscript was being prepared, a similar quadruple bonding pattern between boron and iron was suggested in the BFe(CO)\textsubscript{3}− complex. On the other hand, it is noteworthy that the diatomic FeB was reported to have a bent Rh\textsuperscript{1.61 Å}. The carbonyl groups coordinating to the Fe atom can have only a Rh\textsuperscript{1.73 Å} quartet ground state and its bond length was calculated to be 1.685−1.747 Å, whereas there are three Rh−B bonds in comparison with theoretical data; calculated Rh−B bond lengths at different levels of theory; energy decomposition analysis for RhB; structure and bonding of the linear RhB−BO\textsuperscript{−} isomer; MO analyses for RhB and RhB(BO\textsuperscript{−}); comparison between experimental and theoretical data for the two isomers of RhB\textsubscript{2}O\textsubscript{2}−; Franck–Condon simulation for RhB(BO\textsuperscript{−}); AdNDP bonding analyses for the two isomers of RhB\textsubscript{2}O\textsubscript{2}−; and structure and bonding of Rh−B\textsuperscript{−} (PDF)

### Table 1. Comparison of the Quadruple Bond Energy in Rh≡B and the Triple Rh≡B Bond Energy in RhBH\textsuperscript{+}

<table>
<thead>
<tr>
<th>species</th>
<th>reference states</th>
<th>ΔE (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh≡B (‘Σ’\textsuperscript{−})</td>
<td>→ Rh (5s\textsuperscript{2}4d\textsuperscript{3}4f\textsuperscript{3}) + B (2s\textsuperscript{2}2p\textsuperscript{3}, 3p\textsuperscript{0})</td>
<td>508</td>
</tr>
<tr>
<td>Rh≡B (‘Σ’\textsuperscript{−})</td>
<td>→ Rh (5s\textsuperscript{2}4d\textsuperscript{3}4f\textsuperscript{3}) + B (2s\textsuperscript{2}2p\textsuperscript{3}, 3p\textsuperscript{0})</td>
<td>543</td>
</tr>
<tr>
<td>Rh≡BH\textsuperscript{+} (‘Σ’\textsuperscript{−})</td>
<td>→ Rh\textsuperscript{+} (5s\textsuperscript{2}4d\textsuperscript{3}, 4f\textsuperscript{3}) + BH (‘Σ’\textsuperscript{+})</td>
<td>402</td>
</tr>
<tr>
<td>Rh≡BH\textsuperscript{+} (‘Σ’\textsuperscript{−})</td>
<td>→ Rh\textsuperscript{+} (5s\textsuperscript{2}4d\textsuperscript{3}, 4f\textsuperscript{3}) + BH (‘Π’)</td>
<td>529</td>
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“The calculations were done at the CCSD(T)/B/aug-cc-pVQZ/Rh/aug-cc-pVQZ-pp level of theory.
Author Contributions

L.F.C. and T.-T.C. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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