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## Introduction

As a typical  $\sigma$ -lone pair donor, carbon monoxide (:C $\equiv$ O) is one of the most important ligands in chemistry.<sup>1,2</sup> The first metal carbonyl compound Ni(CO)<sub>4</sub> was synthesized in 1890,<sup>3</sup> followed by a large number of transition metal (TM) carbonyl complexes observed in experiments.<sup>4–8</sup> The  $\sigma$ -lone pair on C in the highest occupied molecular orbital (HOMO) of a CO ligand overlaps with the partially occupied (*n*-1)d orbitals of the TM center to form an effective  $\sigma$ -donation coordination bond, while the lowest unoccupied  $\pi^*$ -molecular orbital (LUMO) of CO accepts partial (*n*-1)d electrons from the TM to form a weak  $\pi$ -backdonation interaction. Main group metal octacarbonyls M(CO)<sub>8</sub> (M = Ca, Sr, Ba) in a perfect O<sub>h</sub> symmetry have also been

# Observation of boron carbonyl complexes $B_{11}(CO)_n^+$ (n = 1-6) and $B_{15}(CO)_n^+$ (n = 1-5) with conflicting aromaticity<sup>†</sup>

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Boron carbonyl complexes have received considerable attention in recent years due to their unique structures and bonding. With inspiration from the newly observed first boron carbonyl aromatics (BCAs)  $B_{13}(CO)_n^+$  (n = 1-7) and based on joint chemisorption experiments and first-principles theory investigations, we report herein observation of the first boron carbonyl complexes  $B_{11}(CO)_n^+$  (n = 1-6) and B<sub>15</sub>(CO)<sub>n</sub><sup>+</sup> (n = 1-5) with  $\pi$  and  $\sigma$  conflicting aromaticity analogous to benzene C<sub>6</sub>H<sub>6</sub> and cyclooctatetraene  $C_8H_8$  in  $\pi$ -bonding, respectively, with  $B_{15}(CO)_n^+$  being the largest boron carbonyl complexes observed to date, enriching the structures and bonding of boron carbonyls effectively.  $B_{11}^+$  and  $B_{15}^+$ which can chemisorb up to six and five CO molecules under ambient conditions, respectively, are found to be much more reactive towards the first CO than the magic-number aromatic B<sub>13</sub><sup>+</sup>. Extensive theoretical analyses unveil both the chemisorption pathways and potential energy profiles of these interesting species. Detailed bonding pattern analyses show that quasi-planar  $B_{11}(CO)_{0}^{+}$  ( $6\pi + 8\sigma$ ) exhibit global  $6\pi$ aromaticity and  $8\sigma$  antiaromaticity, while  $B_{15}(CO)_n^+$  ( $8\pi$  + 10 $\sigma$  + 4 $\sigma$ ) possess global  $8\pi$  antiaromaticity and  $10\sigma$  aromaticity, as well as local  $4\sigma$  antiaromaticity for the B<sub>4</sub> core, inheriting the delocalized bonding patterns of their parent  $B_{11}^+$  ( $B_2 @ B_9^+$ ) and  $B_{15}^+$  ( $B_4 @ B_{11}^+$ ) monocations, respectively. Both naked  $B_{11}^+$  and  $B_{15}^+$  appear to have much higher chemisorption reaction rates toward CO than  $B_{13}^+$ , while their carbonyl complexes  $B_{11}(CO)_{n}^{+}$  and  $B_{15}(CO)_{n}^{+}$  with conflicting aromaticity are found to possess obviously larger average coordination energies per CO than the previously observed BCAs  $B_{13}(CO)_n^+$ .

> discovered in recent years in a low-temperature neon matrix in which the alkaline-earth metals serve as "honorary transition metals".<sup>9</sup>

> Boron ( $[He]2s^22p^1$ ) as a prototypical electron-deficient element in the periodic table with partially occupied 2p orbitals exhibits unique structures and bonding in both its polyhedral molecules and crystal allotropes. Carbonylation of boron has generated various kinds of boron carbonyl complexes. Burg and Schlesinger reported the first carbonyl borane compound H<sub>3</sub>BCO in 1937.<sup>10</sup> The first icosahedral carborane dicarbonyl compound 1,12-B<sub>12</sub>H<sub>10</sub>(CO)<sub>2</sub> was synthesized in 1964<sup>11</sup> and crystally characterized in 1998.12 The simplest boron caybonyl complex BCO was realized in solid neon and argon matrices at 4 K in 1991.<sup>13</sup> In recent years, Zhou's group have characterized a series of boron carbonyl complexes in experiments using infrared photodissociation (IR-PD) spectroscopy, including neutral OCBBCO,14 BBCO,15  $B(CO)_2$ ,<sup>16</sup>  $B_4(CO)_2$ ,<sup>17</sup> and  $B_4(CO)_3^{18}$  and monocationic  $B(CO)_3^+$ ,  $B(CO)_4^+$ ,  $B_2(CO)_4^+$ , and  $B_3(CO)_n^+$  (n = 3-6).<sup>19-22</sup> In these  $B_m(CO)_n^{+/0}$ species ( $m \le 4, n \le 6$ ), the molecularly adsorbed CO ligands serve as  $\sigma$ -lone-pair donors, while boron atoms in the B<sub>m</sub> cores function as  $\sigma$ -lone-pair acceptors. Tian et al. recently characterized an

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umbrella-like boron-cluster boronyl complex  $C_{6v}$  [( $\eta^7$ -B<sub>7</sub>)-B-BO]<sup>-</sup> in gas phase using photoelectron spectroscopy in which the central B atom exhibits transition metal behaviors.<sup>23</sup> Based on joint gasphase mass spectroscopy, collision-induced dissociations (CID), and first-principles theory investigations, our group observed in 2024 the first gas-phase boron carbonyl aromatics (BCAs)  $B_{13}(CO)_n^+$ (n = 1-7) analogous to benzene C<sub>6</sub>H<sub>6</sub> in  $\pi$ -bonding by the chemisorption reactions of  $B_{13}^{+} + nCO \rightarrow B_{13}(CO)_n^{+}$  under ambient conditions.<sup>24</sup> In these stable BCAs, the periphery B atoms as  $\sigma$ lone-pair acceptors in the slightly wrinkled  $B_{13}^+$  ( $B_3 \otimes B_{10}^+$ ) moiety exhibit transition-metal-like behaviors, while the CO ligands as σlone-pair donors are adsorbed around the B<sub>13</sub><sup>+</sup> core. CID experiments clearly indicate that, the C $\equiv$ O ligands in B<sub>m</sub>(CO)<sub>n</sub><sup>+/0</sup> boron carbonyl complexes are molecularly coordinated to the  $B_m^{+/0}$  cores, without being activated or integrated into the B<sub>m</sub> moiety due to the existence of a strong  $C \equiv O$  triple bond in each CO unit. However, whether other aromatic boron carbonyl complexes analogous to benzene  $C_6H_6$  in  $\pi$ -bonding exist in experiments and more critically and significantly, if other boron carbonyl complexes analogous to antiaromatic hydrocarbons in  $\pi$ -bonding can be synthesized still remains unknown to date, leaving an interesting and important question to be addressed in the area.

The previously reported quasi-planar  $C_{\rm s} B_{11}^{+} (B_2 (B_9^{+})^{25,26})$  and  $C_{\rm s} \, {\rm B_{15}}^+ \, ({\rm B_4} \otimes {\rm B_{10}}^+)$  with conflicting aromaticity in ion mobility experiments<sup>27</sup> and first-principles theory calculations<sup>28</sup> intrigue us to probe the structures and bonding of their carbonyl complexes. The reactivity of  $B_{15}^+$  with  $D_2$  and  $N_2O^{29,30}$  and  $B_{11}^+$  with  $D_2$ , HF, N<sub>2</sub>O, CO<sub>2</sub>, D<sub>2</sub>O, and O<sub>2</sub> were experimentally studied between 1980s-1990s, but neither detailed structures nor the bonding patterns of the concerned reactants and products were reported during that period.<sup>29-34</sup> Joint gas-phase mass spectroscopy and first-principles theory investigations performed in this work evidence the existence of the first boron carbonyl complexes  $B_{11}(CO)_n^+$  (n = 1-6) and  $B_{15}(CO)_n^+$  (n = 1-5) with  $\sigma$  and  $\pi$  conflicting aromaticity by the chemisorption reactions of  $B_{11}^{+} + nCO \rightarrow$  $B_{11}(CO)_n^+$  and  $B_{15}^+ + nCO \rightarrow B_{15}(CO)_n^+$  under ambient conditions, with the former and latter being the boron carbonyl analogs of benzene  $C_6H_6$  and cyclooctatetraene  $C_8H_8$  in  $\pi$ -bonding, respectively.  $B_{11}(CO)_n^+$  and  $B_{15}(CO)_n^+$  are found to well inherit the delocalized bonding patterns of their parent monocations B<sub>11</sub><sup>+</sup>  $(B_2 \otimes B_9^+)$  ( $6\pi + 8\sigma$ ) and  $B_{15}^+$  ( $B_4 \otimes B_{11}^+$ ) ( $8\pi + 10\sigma + 4\sigma$ ), respectively, rendering  $\pi$  and  $\sigma$  conflicting aromaticity to the systems in (4*n* + 2)/4n Hückel rule.

## Methods

#### **Experiment methods**

We employed in this work a homemade reflection time-of-flight mass spectrometer (TOF-MS)<sup>35,36</sup> equipped with a laser ablation cluster source, a quadrupole mass filter (QMF),<sup>37</sup> and a linear ion trap (LIT)<sup>38</sup> reactor. Naked boron cluster monocations ( $B_m^+$ ) were generated by laser ablation of a rotating and translating <sup>11</sup>B disk in the presence of a 6 atm He carrier gas. A 532 nm laser with an energy of 3–5 mJ per pulse and a repetition rate of 10 Hz was used in the experiments. The monocluster cations of  $B_{11}^+$ 

and  $B_{15}^{+}$  were mass-selected by the QMF and entered into the LIT, where they were confined and thermalized by collisions with a pulse of He gas and then interacted with a pulse of CO reactant gas. The cluster ions ejected from the LIT reactor were detected by the TOF-MS. The pseudo-first-order rate constants  $(k_1)$  of the reactions between  $B_{11}^{+}/B_{15}^{+}$  clusters and CO were determined by using the following equation:

$$\ln \frac{I_{\rm R}}{I_{\rm T}} = -k_1 \frac{P_{\rm effective}}{k_{\rm B}T} t_{\rm R} \tag{1}$$

in which  $I_{\rm R}$  is the signal intensity of the reactant cluster ions after the reaction,  $I_{\rm T}$  is the total ion intensity including product ion contribution,  $P_{\rm effective}$  is the effective pressure of the reactant gas in the ion trap reactor,  $k_{\rm B}$  is the Boltzmann constant, *T* is the temperature (~300 K), and  $t_{\rm R}$  is the reaction time. More details about the method to derive  $k_1$  can be found in ref. 39.

#### Theoretical methods

Various possible initial structures were manually constructed and explored to form the  $B_{11}(CO)_n^+$  (n = 1-6) and  $B_{15}(CO)_n^+$ (n = 1-5) boron carbonyl complexes based on the fact that CO ligands in  $B_m(CO)_n^{+/0}$  are molecularly coordinated to the  $B_m^{+/0}$ cores along the periphery without being activated or integrated into the B<sub>m</sub> moiety.<sup>24</sup> Density functional theory (DFT) calculations were performed at PBE0 level to optimize the structures of the reactants  $B_{11}^+$  and  $B_{15}^+$ , products  $B_{11}(CO)_n^+$  (n = 1-6) and  $B_{15}(CO)_n^+$  (n = 1-5), and the corresponding intermediates (IMs) and transition states (TSs) on the chemisorption pathways using Gaussian 16 program.<sup>40</sup> The potential energy surfaces for the approach of CO toward  $B_m(CO)_{n-1}^+$  were obtained by relaxed scans along the B<sub>m</sub>-CO distances. The hybrid PBE0 DFT functional has proven to be reliable in boron cluster calculations.<sup>41</sup> The 6-311+G(d,p) basis sets for the B, C and O atoms were used.<sup>42</sup> More accurate single-point energies were calculated at the CCSD(T)/6-311+G(d,p) level of theory<sup>43-45</sup> with PBE0 zero-point corrections included. Vibrational frequency analyses were performed to ensure that the optimized IMs and TSs are true minima and transition states of the systems, respectively. Intrinsic reaction coordinate (IRC) calculations were performed to confirm that each TS connects two appropriate minima.<sup>46,47</sup> Born–Oppenheimer molecular dynamics (BOMD) simulations were executed on the concerned complexes in 100 ps in the time step of 1 fs using the CP2K software package48 with the GTH-PBE0 pseudopotentials and TZVP-MOLOPT-PBE-GTH basis sets.49,50 Temperature was maintained at 300 K using a Nosé-Hoover thermostat for thermal regulation. The simulations were considered converged when the energy change fell below 0.005 eV. Detailed adaptive natural density partitioning (AdNDP) bonding pattern analyses<sup>51</sup> were performed on the concerned species. Energy decomposition analyses with natural orbitals for chemical valence (EDA-NOCV)<sup>52-54</sup> were carried out on  $B_{11}(CO)^+$  (11-1A) and  $B_{15}(CO)^+$ (15-1A) at the PBE0/TZ2P level with the ADF program package<sup>55</sup> using the zeroth-order regular approximation.56

## **Results and discussion**

#### Cluster reactivity measurements

The TOF mass spectra of the laser ablation-generated, massselected, and thermalized  $B_{11}^+$  and  $B_{15}^+$  cluster cations interacting with CO at room temperatures are collectively shown in Fig. 1A and B, respectively.

Upon the reaction of  $B_{11}^{+}$  with 13 mPa CO for 2 ms, the first adduct  $B_{11}(CO)^+$  was generated (Fig. 1(a2)). Increasing the CO pressure to 172 mPa (Fig. 1(a3)), the mass signal of  $B_{11}^{+}$ disappeared, the intensity of  $B_{11}(CO)^+$  was weakened, while the signal of  $B_{11}(CO)_2^+$  was effectively enhanced and a weak signal of  $B_{11}(CO)_2^+$  appeared. Further increasing the CO pressure to 540 mPa (Fig. 1(a4)), the signal of  $B_{11}(CO)_4^+$  started to dominate. When the reaction time was extended to 10 ms (Fig. 1(a5)), a strong  $B_{11}(CO)_5^+$  peak appeared. When the reaction time was further extended to 30 ms (Fig. 1(a6)), the intensity of  $B_{11}(CO)_5^+$  remained basically unchanged, while a very weak  $B_{11}(CO)_6^+$  signal was observed, suggesting that  $B_{11}(CO)_6^+$  was difficult to be generated from  $B_{11}(CO)_5^+$ .

Fig. 1(b2–b4) shows that with a reaction time of 2 ms and a CO pressure changing from 6.4 mPa to 185 mPa, the mass signals of product ions  $B_{15}(CO)^+$ ,  $B_{15}(CO)_2^+$ , and  $B_{15}(CO)_3^+$  could be clearly identified. Increasing the CO pressure to 410 mPa and extending the reaction time to 10 ms (Fig. 1(b5)), the  $B_{15}^+$ ,  $B_{15}(CO)_4^+$ , and  $B_{15}(CO)_3^+$  started to dominate and a weak  $B_{15}(CO)_4^+$  signal emerged. Prolonging the reaction time to 30 ms (Fig. 1(b6)), the



Fig. 1 Measured TOF mass spectra for the reactions of mass-selected  $B_{11}^{+}$  with He and CO (A) and mass-selected  $B_{15}^{+}$  with He and CO (B), with the CO reactant gas pressures (mPa) and reaction times (ms) indicated. The weak mass signals marked with asterisks are due to existence of water impurities in the reaction system.

 $B_{15}(CO)_4^+$  signal was obviously strengthened and a comparable signal emerged for the  $B_{15}(CO)_5^+$ , but no signal beyond was observed for  $B_{15}(CO)_6^+$ . The above experimental results indicate that  $B_{11}^+$  and  $B_{15}^+$  can consecutively adsorb up to six and five CO molecules, respectively, in the chemisorption reactions of (R1) and (R2):

$$B_{11}^{+} + nCO \rightarrow B_{11}(CO)_{n}^{+} (n = 1-6)$$
 (R1)

$$B_{15}^{+} + nCO \rightarrow B_{15}(CO)_{n}^{+} (n = 1-5)$$
 (R2)

On the bases of the least-squares fitting procedures in Fig. 2A-C, the pseudo-first-order rate constants  $(k_1)$  for the interactions of  $B_{11}(CO)_n^+$  (n = 0-4) with CO can be the estimated to be 2.43  $\times$ 10^{-10}, 7.76  $\times$  10^{-11}, 2.34  $\times$  10^{-11}, 2.96  $\times$  10^{-12}, and 2.83  $\times$  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for n = 0, 1, 2, 3, and 4, corresponding to the reaction efficiencies of  $\Phi$  = 35.08%, 11.41%, 3.48%, 0.44% and 0.43%, respectively. For the reactions of  $B_{15}(CO)_n^+$  (n = 0-4)with CO (Fig. 2D-F), the reaction rate constants were estimated to be  $k_1 = 1.30 \times 10^{-10}$ , 7.58 × 10<sup>-12</sup>, 1.39 × 10<sup>-11</sup>, 7.80 × 10<sup>-14</sup>, and  $3.64 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for n = 0, 1, 2, 3 and 4, corresponding to the reaction efficiencies of  $\Phi$  = 19.26%, 1.13%, 2.10%, 0.01% and 0.06%, respectively. The reaction rate constants obtained here for the generations of  $B_{11}(CO)^+$  and  $B_{15}(CO)^+$ are found to be about 100 times higher than the corresponding value of  $k_1 = 4.26 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  reported for  $B_{13}(CO)^+$ ,<sup>24</sup> indicating that both naked  $B_{11}^+$  and  $B_{15}^+$  are chemically much more reactive toward CO under ambient conditions than  $B_{13}^{+}$  cluster which is well-known to be typically  $\pi$ -aromatic in nature analogous to benzene. The reactivity difference between  $B_{11}^{+}$ ,  $B_{15}^{+}$ , and  $B_{13}^{+}$  toward CO is also well supported by the observation that, with the same reaction time of 2 ms, the mass signals of B<sub>11</sub><sup>+</sup> and B<sub>15</sub><sup>+</sup> disappeared completely with the CO pressures of 172 mPa and 70 mPa, respectively (Fig. 1(a3) and (b3)), while the intensity of  $B_{13}^{+}$  was still well maintained even at the CO pressure of 184 mPa, as shown in Fig. 1(c) in ref. 24.

#### Chemisorption pathway analyses

The optimized low-lying isomers of boron carbonyl products  $B_{11}(CO)_n^+$  (n = 1-6) and  $B_{15}(CO)_n^+$  (n = 1-5) at PBE0 level are collectively shown in Fig. S1, S2 and S3, S4 (ESI<sup>†</sup>), respectively, denoted as **11-nA**, **11-nB**, **11-nC**, and **15-nA**, **15-nB**, **15-nC** etc. based on their relative energy orders. Fig. 3A and B show their lowest-lying isomers and the corresponding most favorable chemisorption pathways, with the relative energies refined at CCSD(T) with zero-point corrections included. The previously reported  $C_s B_{15}^+$  has the true symmetry of  $C_{2v}$ , as shown in Fig. 3A.<sup>27,28</sup> The fluxional mechanisms of the lowest-lying  $C_s B_{11}^+$  and  $C_{2v} B_{15}^+$  and their optimized adsorption pathways with n CO are illustrated in Fig. S5–S16 (ESI<sup>†</sup>). Fig. S5 (ESI<sup>†</sup>) indicates that  $C_s B_{11}^+$  and  $C_{2v} B_{15}^+$  exhibit typical fluxional behaviors<sup>28,57</sup> with the small energy barriers of 0.05 eV and 0.08 eV at CCSD(T), respectively.

Fig. 3A and Fig. S6a (ESI<sup>†</sup>) indicate that the first CO coordinates  $B_{11}^+$  at a tricoordinate boron atom, forming the most stable adduct product  $C_s B_{11}(CO)^+$  (**11-1A**) with the chemisorption energy of 1.47 eV at CCSD(T) in a barrier-free process.



**Fig. 2** Variation of the measured relative signal intensities of reactant and product ions with respect to CO gas pressures in  $B_{11}^+ + nCO \rightarrow B_{11}(CO)_n^+$  (n = 1-5) ((A), (B), and (C)) and  $B_{15}^+ + nCO \rightarrow B_{15}(CO)_n^+$  (n = 1-5) ((D), (E), and (F)), with the corresponding reaction times  $t_R$  indicated in ms. The solid lines are fitted to experimental data points with the approximation of pseudo-first-order reaction mechanisms.

The second-lowest lying isomer 11-1B which lies 0.05 eV higher than 11-1A (Fig. S1a, ESI<sup>+</sup>) can also be generated without a positive energy barrier (Fig. S6a, ESI<sup>+</sup>), but it can be converted to 11-1A with a small energy barrier of only 0.02 eV at the transition state 11-TS9 (Fig. S6b, ESI<sup> $\dagger$ </sup>). Thus, the observed B<sub>11</sub>(CO)<sup> $\dagger$ </sup> mass signal corresponds to 11-1A. Similarly, the experimentally observed  $B_{11}(CO)_2^+$ ,  $B_{11}(CO)_3^+$ , and  $B_{11}(CO)_4^+$  can be attributed to 11-2A, 11-3A, and 11-4A in barrierless adsorption processes (Fig. S7-S9, ESI†), while  $B_{11}(CO)_5^+$  can be assigned to 11-5A via the transition state of **11-TS1** with the favorable energy barrier of -0.08 eV relative to the entrance channel (Fig. 3C and Fig. S10, ESI<sup>†</sup>). However, as indicated in Fig. 3D and Fig. S11 (ESI<sup>+</sup>), the most favorable potential energy profile to generate 11-6A from 11-5A requires to overcome a small positive energy barrier of 0.09 eV at the transition state 11-TS2 (Fig. 3D and Fig. S11, ESI<sup>+</sup>), suggesting that the generation of  $B_{11}(CO)_6^+$  would be difficult under ambient conditions, in consistent with its extremely weak mass signal observed in Fig. 1(a6). Overall, reaction (R1) in the most favorable adsorption pathway of  $C_s B_{11}^+ \rightarrow C_s \mathbf{11} \mathbf{1A} \rightarrow C_s \mathbf{11} \mathbf{2A} \rightarrow C_1 \mathbf{11} \mathbf{3A} \rightarrow C_1$ 11-4A  $\rightarrow C_1$  11-5A  $\rightarrow C_1$  11-6A (Fig. 3A) releases the total energy of 5.86 eV to consecutively adsorb six CO ligands molecularly.

As indicated in Fig. 3B and Fig. S12 (ESI<sup>†</sup>), starting from both the previously observed  $C_{2v} B_{15}^{++}$  (15-I) and  $C_s B_{15}^{++}$  (15-II),<sup>27,28</sup> the mono-coordinated  $C_s B_{15}(CO)^+$  (15-1A) with the adsorption energy of 1.89 eV can be produced in barrierless mechanisms. Similarly, the experimentally observed  $B_{15}(CO)_2^+$  and  $B_{15}(CO)_3^+$ can be attributed to 15-2A and 15-3A in barrier-free adsorption processes, respectively (Fig. 3B and Fig. S13, S14, ESI<sup>†</sup>). When the fourth CO approaches 15-3A, the second-lowest lying isomer of  $B_{15}(CO)_4^+$  (15-4B) can be produced with a favorable energy barrier of -0.04 eV *via* the transition state of 15-TS1 relative to the free reactants (Fig. 3E and Fig. S15, ESI<sup>†</sup>). The lowest-lying  $C_s B_{15}(CO)_5^+$  (15-5A) can be generated from 15-4B with a favorable energy barrier of -0.11 eV at the transition state 15-TS2 (Fig. 3F and Fig. S16, ESI<sup>†</sup>). In the most favorable pathway of  $C_{2v}$ B<sub>15</sub><sup>+</sup>  $\rightarrow C_s$  **15-1A**  $\rightarrow C_1$  **15-2A**  $\rightarrow C_s$  **15-3A**  $\rightarrow C_1$  **15-4B**  $\rightarrow C_s$  **15-5A** (Fig. 3B), reaction (R2) releases the total energy of 5.63 eV to adsorb five CO ligands.

#### Molecular dynamics simulations

Extensive BOMD simulations are performed in Fig. S17 and S18 (ESI<sup>†</sup>) on the concerned species in the most favorable chemisorption pathways to check their dynamic stability. Two closelying isomers **11-1A** and **11-1B** of  $B_{11}(CO)^+$  were found to coexist at 300 K (Fig. S17(a), ESI<sup>+</sup>), with the latter being spontaneously converted into the former by overcoming only a small energy barrier of +0.02 eV at the transition state 11-TS9 (Fig. S6(b), ESI<sup>†</sup>). Similar structural conversion happens between the two close-lying isomers 11-2A and 11-2B of B<sub>11</sub>(CO)<sub>2</sub><sup>+</sup> (Fig. S17b, ESI<sup> $\dagger$ </sup>), further evidencing the structural fluxionality of the B<sub>11</sub><sup>+</sup> moiety at the center. In comparison, with the small calculated root mean square deviations between RMSDs = 0.05–0.10 Å and maximum bond length deviations between MAXDs = 0.13- $0.40 \text{ Å}, B_{11}(CO)_3^+, B_{11}(CO)_4^+, B_{11}(CO)_5^+, \text{ and } B_{11}(CO)_6^+ \text{ all appear}$ to be dynamically stable within 100 ps at 300 K (Fig. S17(c)-(f), ESI<sup>†</sup>). As shown in Fig. S18 (ESI<sup>†</sup>), the most favorable adsorption products of  $B_{15}(CO)_n^+$  (*n* = 1–5) (**15-1A–15-5A**) in Fig. 3B are all highly dynamically stable within 100 ps at 300 K.

#### Bonding pattern analyses

Detailed AdNDP bonding analyses are performed on  $B_{11}(CO)_n^+$ (n = 0-6) and  $B_{15}(CO)_n^+$  (n = 0-5) in Fig. S19–S26 (ESI†). As displayed in Fig. 4A and Fig. S19(a) (ESI†), the elongated global minimum  $C_s B_{11}^+$  ( $B_2 \circledast B_9^+$ ) possesses nine 2c-2e  $\sigma$  bonds on the  $B_9$  outer ring, four partially delocalized  $\sigma$  bonds (2 4c-2e, 1 5c-2e, and 1 6c-2e) on the  $B_{11}$  moiety, and three totally delocalized 11c-2e  $\pi$  bonds over the  $B_{11}$  plane. Such a  $6\pi + 8\sigma$ delocalized bonding pattern renders global  $6\pi$  aromaticity



Fig. 3 Optimized structures and most favorable chemisorption pathways of  $B_{11}(CO)_n^+$  (n = 1-6) (A) and  $B_{15}(CO)_n^+$  (n = 1-5) (B) at PBE0/6-311+G(d,p), with the chemisorption energies indicated for each adsorption step at CCSD(T) level. The energy barriers of the transition states (TSs) are indicated in eV above the arrows for the last two adsorption steps, with all the previous steps confirmed to be barrier-free as shown in Fig. S6–S9 and S12–S14 (ESI†). The calculated potential energy profiles to form 11-5A, 11-5B, and 11-5C, 11-6A, 11-6B, and 11-6C, 15-4A, 15-4B, and 15-4C, and 15-5A and 15-5B are depicted in (C), (D), (E), and (F) are depicted in (C), (D), (E), and (F) at CCSD(T), respectively. The bond lengths are given in pm.

and 8 $\sigma$  antiaromaticity to the system in (4n + 2)/4n Hückel rule, making the elongated  $C_{\rm s} {\rm B_{11}}^+ 6\pi$ -aromatic analogous to benzene but 8 $\sigma$ -antiaromatic in nature. It is the 8 $\sigma$  antiaromaticity that elongates  $C_{\rm s} {\rm B_{11}}^+$  in horizontal direction. More interestingly, as shown in Fig. 4A and Fig. S20–S22 (ESI†), the slightly wrinkled quasi-planar  ${\rm B_{11}(CO)}^+$ ,  ${\rm B_{11}(CO)_2^+ B_{11}(CO)_3^+}$ ,  ${\rm B_{11}(CO)_4^+}$ ,  ${\rm B_{11}(CO)_5^+}$ , and  ${\rm B_{11}(CO)_6^+}$  all well inherit the four partially delocalized  $\sigma$  bonds on the B<sub>11</sub> moiety and three totally delocalized 11c-2e  $\pi$  bonds over the molecular plane from their parent B<sub>11</sub><sup>+</sup>, rendering  $\pi$  and  $\sigma$  conflicting aromaticity to the whole B<sub>11</sub>(CO)<sub>n</sub><sup>+</sup> series (n = 0-6), making them all  $6\pi$ -aromatic analogous to benzene but  $8\sigma$ -antiaromatic in nature. The adsorption of a :C $\equiv$ O ligand as a  $\sigma$ -lone pair to the B<sub>11</sub><sup>+</sup> core forms one 2c-2e B–C  $\sigma$ -donation bond between the B<sub>11</sub><sup>+</sup> core



**Fig. 4** AdNDP delocalized bonding patterns of B<sub>11</sub>(CO)<sub>n</sub><sup>+</sup> (n = 0-2) (A) and B<sub>15</sub>(CO)<sub>n</sub><sup>+</sup> (n = 0-2) (B), in comparison with the π-bonding patterns of benzene  $D_{6h} C_6 H_6$  and cyclooctatetraene  $D_{2d} C_8 H_8$ , respectively, with the occupation numbers (ONs) indicated.

and CO ligand, but without changing the basic  $\pi$  and  $\sigma$  bonding patterns of the  $B_{11}^{+}$  moiety.

Fig. 4B and Fig. S23 (ESI<sup>†</sup>) indicate that the experimentally observed  $C_{2v} B_{15}^+ (B_4 \textcircled{(B}_{11}^+))$  possesses eleven localized 2c-2e  $\sigma$  bonds on the  $B_{11}$  outer ring, two partially delocalized 3c-2e  $\sigma$  bonds on the rhombus  $B_4$  core, five partially delocalized  $\sigma$  bonds (2 3c-2e, 1 4c-2e, 1 5c-2e, and 1 12c-2e) between the  $B_4$  core and  $B_{11}$  outer ring, and four partially delocalized  $\pi$ -bonds (2 3c-2e, 1 4c-2e, and 1 5c-2e) over the molecular plane. Such a

 $8\pi + 10\sigma + 4\sigma$  delocalized bonding pattern renders global  $8\pi$ antiaromaticity and 10o-aromaticity to the system, as well as local  $4\sigma$ -antiaromaticity to the B<sub>4</sub> core. It is the first boron carbonyl analog of cyclooctatetraene  $D_{2d}$  C<sub>8</sub>H<sub>8</sub> in  $\pi$ -bonding (Fig. 4B). More intriguingly, as shown in Fig. 4B and Fig. S24-S26 (ESI<sup>+</sup>), the observed  $B_{15}(CO)^+$ ,  $B_{15}(CO)_2^+$ ,  $B_{15}(CO)_3^+$ ,  $B_{15}(CO)_4^+$ , and  $B_{15}(CO)_5^+$ all possess eleven localized 2c-2e  $\sigma$  bonds on the B<sub>11</sub> outer ring, two partially delocalized 3c-2e  $\sigma$  bonds on the B<sub>4</sub> rhombus, five partially delocalized  $\sigma$ -bonds between the B<sub>4</sub> core and B<sub>11</sub> outer ring, and four partially delocalized  $\pi$ -bonds over the slightly wrinkled B<sub>15</sub> plane, similar to their parent  $B_{15}^+$  monocation. Such a  $8\pi + 10\sigma + 4\sigma$ delocalized bonding pattern renders global 8π-antiaromaticity and 10 $\sigma$ -aromaticity to the whole  $B_{15}(CO)_n^+$  series and local  $4\sigma$ antiaromaticity to be  $B_4$  core, making them all  $8\pi$ -antiaromatic analogous to cyclooctatetraene  $C_8H_8$ . The combined  $8\pi$  global antiaromaticity and local  $4\sigma$ -antiaromaticity make both the  $B_{15}^{++}$ bare cluster and its boron carbonyl complexes  $B_{15}(CO)_n^+$  elongated in vertical direction.

#### Effective $\sigma$ -donations and weak $\pi$ -back-donations

Detailed EDA-NOCV analyses in Fig. 5, Fig. S27, S28 and Table S1, S2 (ESI<sup>†</sup>) unveil the coordination bonding patterns of  $C_{\rm s}$  B<sub>11</sub>(CO)<sup>+</sup> (**11-1A**) and  $C_{2v}$  B<sub>15</sub>(CO)<sup>+</sup> (**15-1A**) more specifically, with the corresponding deformation densities  $\Delta\rho$  and shapes of the most important interacting orbitals of the pairwise orbital interactions extracted in Fig. 5. Fig. 5A shows that one effective  $\sigma$ -donation (HOMO–13) in the molecular plane which contributes 67.7% to the overall orbital interaction ( $\Delta E_{\rm orb}$ ) and two weak  $\pi$ -backdonations (HOMO and HOMO–5) in horizontal and vertical directions which contribute 13.3% and 10.1%, respectively, coexist in the coordination interactions between B<sub>11</sub><sup>+</sup> and CO in B<sub>11</sub>(CO)<sup>+</sup> (**11-1A**), with the  $\sigma$ -donation bond well reflected in the



Fig. 5 Plots of the deformation densities  $\Delta \rho$  and shapes of the most important interacting orbitals of the pairwise orbital interactions between  $B_{11}^{+}$  and CO in  $C_s B_{11}(CO)^+$  (A) and  $B_{15}^{+}$  and CO in  $C_s B_{15}(CO)^+$  (B), with the orbital interaction energies  $\Delta E_{orb}$  in kcal mol<sup>-1</sup> and their percentage contributions to the overall orbital interactions indicated. The color code of the charge flow is red  $\rightarrow$  blue.

AdNDP 2c-2e B-C σ-bond in Fig. S20a (ESI<sup>†</sup>). As clearly indicated in the red  $\rightarrow$  blue charge flow color code, the doubly occupied  $\sigma$ -HOMO of CO serves as lone-pair donor in the effective  $\sigma$ -donation interaction, while the two degenerate unoccupied  $\pi^*$ -LUMOs of CO in perpendicular and horizontal directions function as electron acceptors in the two weak  $\pi$ -back-donations. Similarly, one effective  $\sigma$ -donation (HOMO-17) which contributes 64.2% to overall orbital interactions and two weak  $\pi$ -backdonations (HOMO-2 and HOMO) which contribute 13.3% and 12.4%, respectively, coexist in  $B_{15}(CO)^+$  (15-1A), as clearly shown in Fig. 5B. The effective  $\sigma$ -donation and two weak  $\pi$ -back-donations in these boron carbonyl complexes appear to be similar to the TM-CO interactions in classic TM carbonyl complexes, indicating that the periphery B atoms in the observed boron carbonyl complexes exhibit transition-metal-like behaviors. The difference is that B atoms in these boron carbonyl complexes provide partially occupied 2p orbitals to form B-CO coordination interactions, while TM atoms in their carbonyl compounds provide partially occupied (n-1)d orbitals to form TM-CO coordination interactions.

#### Prediction of neutral $B_{10}(CO)_n$ (n = 1-6) and $B_{14}(CO)_n$ (n = 1-6)

It is known that the most stable neutral  $C_{2h}$  B<sub>10</sub> (B<sub>2</sub>@B<sub>8</sub>) is a boron analog of benzene in  $\pi$ -bonding.<sup>58</sup> As clearly shown in Fig. S19d (ESI<sup> $\dagger$ </sup>), B<sub>10</sub> possesses eight 2c-2e B-B  $\sigma$  bonds on the B<sub>8</sub> outer ring, two 4c-2e  $\sigma$  bonds and two 5c-2e  $\sigma$  bonds on the B<sub>10</sub> moiety, and three totally delocalized 10c-2e  $\pi$  bonds over the molecular plane. It exhibits therefore global  $6\pi$ -aromaticity and  $8\sigma$ -antiaromaticity. Based on  $C_{2h}$  B<sub>10</sub>, we obtained a series of optimized neutral  $B_{10}(CO)_n$  (n = 1-6) with  $\sigma$  and  $\pi$  conflicting aromaticity collectively shown in Fig. 6A and Fig. S29, S30 (ESI<sup>+</sup>), in which the CO ligands are molecularly adsorbed to the B10 core in a terminal coordination manner, similar to the situation in  $B_{11}(CO)_n^+$ . Similarly, based on the most stable neutral  $C_{2v}$   $B_{14}$  $(B_4 (a) B_{10})^{58}$  which also exhibits conflicting aromaticity with four partially delocalized  $\pi$  bonds over the molecular plane, five partially delocalized  $\sigma$  bonds between the B<sub>4</sub> core and B<sub>10</sub> outer ring, and two partially delocalized  $\sigma$  bonds on the B<sub>4</sub> core (Fig. S23b, ESI<sup>+</sup>), we obtained a series of  $B_{14}(CO)_n$  complexes (n = 1-6)with  $\sigma$  and  $\pi$  conflicting aromaticity in Fig. 6B and Fig. S31, S32 (ESI<sup>†</sup>). The chemisorption energies of  $E_c = (E_{B10} + nE_{CO})$  –  $E_{B10(CO)n}$  of  $B_{10}(CO)_n$  and  $E_c = (E_{B14} + nE_{CO}) - E_{B14(CO)n}$  of  $B_{14}(CO)_n$  are calculated at CCSD(T) level at the optimized PBE0 geometries with respect to reactions (R3) and (R4), respectively.

$$B_{10} + nCO \rightarrow B_{10}(CO)_n \quad (n = 1-6)$$
 (R3)

$$B_{14} + nCO \rightarrow B_{14}(CO)_n \quad (n = 1-6)$$
 (R4)

Interestingly, as shown in Fig. 6, the calculated  $E_c$  values increase almost linearly with the number (*n*) of CO ligands in the systems, with the approximate average coordination energies of 0.73 eV and 0.67 eV per CO ligand in B<sub>10</sub>(CO)<sub>n</sub> and B<sub>14</sub>(CO)<sub>n</sub>, respectively. The calculated chemisorption energies of the observed B<sub>11</sub>(CO)<sub>n</sub><sup>+</sup> (n = 1-6) and B<sub>15</sub>(CO)<sub>n</sub><sup>+</sup> (n = 1-5) monocations are also comparatively shown in Fig. 6A and B at the same theoretical level, where they have the approximate



**Fig. 6** Calculated chemisorption energies of  $E_c = (E_{B11+} + nE_{CO}) - E_{B11(CO)n+}$ (black) and  $E_c = (E_{B10} + nE_{CO}) - E_{B10(CO)n}$  (red) (A) and  $E_c = (E_{B15+} + nE_{CO}) - E_{B15(CO)n+}$  (black) and  $E_c = (E_{B14} + nE_{CO}) - E_{B14(CO)n}$  (red) (B) with respect to the number of CO ligands (*n*) in the systems at CCSD(T) level. The slopes of the fitted linear relationships represent the approximate average cohesive energy per CO ligand of the corresponding adsorption processes.

average coordination energies of 0.98 eV and 1.05 eV per CO, respectively, which appear to be about 21–23% of the dissociation energy of a typical B–C covalent bond (4.63 eV). Interestingly, both  $B_{11}(CO)_n^+$  and  $B_{15}(CO)_n^+$  with conflicting aromaicity appear to have obviously higher average coordination energies per CO than the corresponding value of 0.84 eV calculated at CCSD(T) (Fig. S33, ESI†) for the previously observed BCAs  $B_{13}(CO)_n^+$ . It is also noticed that the more electron-deficient  $B_{11}^+$ ,  $B_{13}^+$ , and  $B_{15}^+$  monocations possess higher coordination energies towards CO than their  $\pi$ -isovalent neutral counterparts  $B_{10}$ ,  $B_{12}$ , and  $B_{14}$ , respectively.

## Conclusions

Joint gas-phase chemisorption experiments and first-principles theory investigations performed in this work evidence the existence of the first boron carbonyl complexes  $B_{11}(CO)_n^+$  (n = 1-6) and  $B_{15}(CO)_n^+$  (n = 1-5) with  $\pi$  and  $\sigma$  conflicting aromaticity analogous to benzene  $C_6H_6$  and cyclooctatetraene  $C_8H_8$  in  $\pi$ -bonding, respectively, with their specific chemisorption pathways, potential energy profiles, and bonding patterns analyzed in details. Similar to the situation in the newly observed  $B_{13}(CO)_n^+$  (*n* = 1–7), the periphery boron atoms in the  $B_m^+$  cores in both  $B_{11}(CO)_n^+$  and  $B_{15}(CO)_n^+$ exhibit transition-metal-like behaviors, indicating that boron as a prototypical electron-deficient element can also be viewed as an "honorary transition metal". Both bare  $B_{11}^{+}$  and  $B_{15}^{+}$  monocations with conflicting aormaticity appear to have much higher chemisorption reaction rates toward CO than the experimentally known aromatic  $B_{13}^{+}$ , while their carbonyl complexes  $B_{11}(CO)_n^{+}$  and  $B_{15}(CO)_n^+$  possess obviously larger average coordination energy per CO than the corresponding  $B_{13}(CO)_n^+$ . The coherent  $OC \rightarrow B_m$  $\sigma$ -donation and OC  $\leftarrow B_m \pi$ -back-donation in  $B_{11}(CO)_n^+, B_{13}(CO)_n^+, B_{13}(CO)_n^$ and  $B_{15}(CO)_n^+$  which occupy about 20% of a typical C–B covalent bond in dissociation energies evidence the existence of the newly proposed boron bonds (BBs) in chemistry.<sup>59</sup> Larger  $B_m(CO)_n^{+/-/0}$ boron carbonyl complexes  $(m \ge 16)$  may also be possible to be synthesized and characterized in future joint experimental and theoretical investigations. Macroscopic productions and isolations of boron carbonyl complexes with  $\pi$  and  $\sigma$  conflicting aromaticity would help facilitate their applications in chemistry and further enrich the structures and bonding of boron as an amphoteric element between metals and non-metals.

## Data availability

All the data are available online on the website of PCCP.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 J. B. Peng, H. Q. Geng and X. F. Wu, Chem, 2019, 5, 526.
- 2 W. A. Herrmann, J. Organomet. Chem., 1990, 383, 21.
- 3 L. Mond, C. Langer and F. Quincke, J. Chem. Soc. Trans., 1890, 57, 749.
- 4 J. H. Jang, J. G. Lee, H. Lee, Y. Xie and H. F. Schaefer III, *J. Phys. Chem. A*, 1998, **102**, 5298.
- 5 Q. Xu, Coord. Chem. Rev., 2002, 231, 83.
- 6 A. Diefenbach, F. M. Bickelhaupt and G. Frenking, J. Am. Chem. Soc., 2000, **122**, 6449.
- 7 C. Wang, C. Y. Tian, Y. Zhao, S. Jiang, T. Wang, H. Zheng, W. Yan, G. Li, H. Xie, J. Li, H. S. Hu, X. Yang and L. Jiang, *Angew. Chem. Int. Ed.*, 2023, **62**, e202305490.
- 8 J. Jin, T. Yang, K. Xin, G. Wang, X. Jin, M. Zhou and G. Frenking, *Angew. Chem. Int. Ed.*, 2018, 57, 6236.
- 9 X. Wu, L. Zhao, J. Jin, S. Pan, W. Li, X. Jin, G. Wang, M. Zhou and G. Frenking, *Science*, 2018, **361**, 912.
- 10 A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc., 1937, 59, 780.
- 11 W. H. Knoth, J. C. Sauer, H. C. Miller and E. L. Muetterties, J. Am. Chem. Soc., 1964, 86, 115.
- 12 M. A. Fox, J. A. K. Howard, J. M. Moloney and K. Wade, *Chem. Commun.*, 1998, 2487.
- 13 Y. M. Hamrick, R. J. Vanzee, J. T. Godbout, W. Weltner, W. J. Lauderdale, J. F. Stanton and R. J. Bartlett, *J. Phys. Chem.*, 1991, **95**, 2840.
- 14 M. Zhou, N. Tsumori, Z. Li, K. Fan, L. Andrews and Q. Xu, *J. Am. Chem. Soc.*, 2002, **124**, 12936.
- 15 M. Zhou, Z. X. Wang, P. V. R. Schleyer and Q. Xu, *Chem-PhysChem*, 2003, 4, 763.
- 16 T. R. Burkholder and L. Andrews, J. Phys. Chem., 1992, 96, 10195.
- 17 M. Zhou, Q. Xu, Z. X. Wang and P. V. R. Schleyer, J. Am. Chem. Soc., 2002, 124, 14854.
- 18 Y. Zhao, T. Wang, C. Wang, Z. Zhang, H. Zheng, S. Jiang, W. Yan, H. Xie, G. Li, J. Yang, G. Wu, W. Zhang, D. Dai, X. Zheng, H. Fan, L. Jiang, X. Yang and M. Zhou, *Chem-PhysChem*, 2022, 23, e202200060.
- 19 J. Y. Jin, G. J. Wang and M. F. Zhou, *Chin. J. Chem. Phys.*, 2016, **29**, 47.
- 20 J. Jin, G. Wang and M. Zhou, J. Phys. Chem. A, 2018, 122, 2688.
- 21 J. Jin, G. Wang, M. Zhou, D. M. Andrada, M. Hermann and G. Frenking, *Angew. Chem. Int. Ed.*, 2016, 55, 2078.
- 22 J. Jin and M. Zhou, Dalton Trans., 2018, 47, 17192.
- 23 W. J. Tian, W. J. Chen, M. Yan, R. Li, Z. H. Wei, T. T. Chen, Q. Chen, H. J. Zhai, S. D. Li and L. S. Wang, *Chem. Sci.*, 2021, 12, 8157.
- 24 R. N. Yuan, J. J. Chen, Q. Chen, Q. W. Zhang, H. Niu, R. Wei,
  Z. H. Wei, X. N. Li and S. D. Li, *J. Am. Chem. Soc.*, 2024,
  146, 31464.
- 25 C. Romanescu, D. J. Harding, A. Fielicke and L. S. Wang, J. Chem. Phys., 2012, 137, 014317.
- 26 I. Boustani, Int. J. Quantum Chem., 1994, 52, 1081.
- 27 E. Oger, N. R. M. Crawford, R. Kelting, P. Weis, M. M. Kappes and R. Ahlrichs, *Angew. Chem. Int. Ed.*, 2007, 46, 8503.

- 28 Y. J. Wang, X. R. You, Q. Chen, L. Y. Feng, K. Wang, T. Ou, X. Y. Zhao, H. J. Zhai, S. D. Li and L. S. Wang, *Phys. Chem. Chem. Phys.*, 2016, 18, 15774.
- 29 S. A. Ruatta, L. Hanley and S. L. Anderson, *J. Chem. Phys.*, 1989, **91**, 226.
- 30 P. A. Hintz, M. B. Sowa, S. A. Ruatta and S. L. Anderson, J. Chem. Phys., 1991, 94, 6446.
- 31 M. B. Sowa-Resat, J. Smolanoff, A. Lapicki and S. L. Anderson, J. Chem. Phys., 1997, 106, 9511.
- 32 S. A. Ruatta, P. A. Hintz and S. L. Anderson, *J. Chem. Phys.*, 1991, **94**, 2833.
- 33 P. A. Hintz, S. A. Ruatta and S. L. Anderson, J. Chem. Phys., 1990, 92, 292.
- 34 L. Hanley and S. L. Anderson, J. Chem. Phys., 1988, 89, 2848.
- 35 X. N. Wu, B. Xu, J. H. Meng and S. G. He, Int. J. Mass Spectrom., 2012, 310, 57.
- 36 Z. Yuan, Y. X. Zhao, X. N. Li and S. G. He, *Int. J. Mass Spectrom.*, 2013, **354**, 105.
- 37 R. A. J. O'Hair, Chem. Commun., 2006, 1469.
- 38 L. D. Socaciu, J. Hagen, U. Heiz, T. M. Bernhardt, T. Leisner and L. Wöste, *Chem. Phys. Lett.*, 2001, **340**, 282.
- 39 Z. Yuan, Z. Y. Li, Z. X. Zhou, Q. Y. Liu, Y. X. Zhao and S. G. He, *J. Phys. Chem. C*, 2014, **118**, 14967.
- 40 M. J. Frisch, G. W. Trucks and H. B. Schlegel, *et al.*, *Gaussian 16*, Gaussian Inc., Wallingford CT, 2016.
- 41 C. Adamo and V. Barone, J. Chem. Phys., 1999, 110, 6158.
- 42 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.
- 43 G. D. Purvis and R. J. Bartlett, J. Chem. Phys., 1982, 76, 1910.

- 44 G. E. Scuseria and H. F. SchaeferIII, *J. Chem. Phys.*, 1989, **90**, 3700.
- 45 G. E. Scuseria, C. L. Janssen and H. F. Schaefer III, *J. Chem. Phys.*, 1988, **89**, 7382.
- 46 C. Gonzalez and H. B. Schlegel, J. Chem. Phys., 1989, 90, 2154.
- 47 C. Gonzalez and H. B. Schlegel, J. Phys. Chem., 1990, 94, 5523.
- 48 J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, *Comput. Phys. Commun.*, 2005, 167, 103.
- 49 S. Goedecker, M. Teter and J. Hutter, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, 54, 1703.
- 50 W. L. Li, K. Chen, E. Rossomme, M. Head-Gordon and T. Head-Gordon, J. Phys. Chem. Lett., 2021, 12, 10304.
- 51 N. V. Tkachenko and A. I. Boldyrev, *Phys. Chem. Chem. Phys.*, 2019, **21**, 9590.
- 52 T. Ziegler and A. Rauk, Theor. Chim. Acta, 1977, 46, 1.
- 53 M. P. Mitoraj, A. Michalak and T. Ziegler, J. Chem. Theory Comput., 2009, 5, 962.
- 54 M. Mitoraj and A. Michalak, Organometallics, 2007, 26, 6576.
- 55 G. T. E. Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S. J. A. Van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, 22, 931.
- 56 E. VanLenthe, E. J. Baerends and J. G. Snijders, J. Chem. Phys., 1993, 99, 4597.
- 57 S. Jalife, L. Liu, S. Pan, J. L. Cabellos, E. Osorio, C. Lu, T. Heine,K. L. Donald and G. Merino, *Nanoscale*, 2016, 8, 17639.
- 58 H. J. Zhai, B. Kiran, J. Li and L. S. Wang, Nat. Mater., 2003, 2, 827.
- 59 T. Zhang, C. Y. Gao, X. N. Zhao, G. Y. Han and S. D. Li, J. Mol. Model., 2025, 31, 54.