#### **ORIGINAL PAPER**



# $(C_6H_6Cr)_n\&B_{40}$ (n = 1–6): Exohedral Borospherene Complexes with Cage-like $B_{40}$ as an Effective Ligand with Multiple Coordination Sites

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#### Abstract

The newly discovered cage-like borospherene  $D_{2d}$  B<sub>40</sub> with two  $\eta^6$ -B<sub>6</sub> hexagons and four  $\eta^7$ -B<sub>7</sub> heptagons on the surface may serve as an effective multi-dentate ligand to coordinate transition metals. Based upon extensive density functional theory calculations, we present herein the possibility of the exohedral complex series (C<sub>6</sub>H<sub>6</sub>Cr)<sub>n</sub>&B<sub>40</sub> (n = 1–6) with n Cr centres sandwiched between the central  $\eta^{6/7}$ -B<sub>40</sub> unit and n planar  $\eta^6$ -C<sub>6</sub>H<sub>6</sub> ligands. C<sub>6</sub>H<sub>6</sub>Cr fragments in (C<sub>6</sub>H<sub>6</sub>Cr)<sub>n</sub>&B<sub>40</sub> occupy the  $\eta^6$ -B<sub>6</sub> hexagonal coordination site atop the B<sub>40</sub> cage first, the four neighboring  $\eta^7$ -B<sub>7</sub> heptagons on the waist next, and finally the  $\eta^6$ -B<sub>6</sub> hexagon at the bottom, forming a multinuclear complex series effectively stabilized by n C<sub>6</sub>H<sub>6</sub>Cr fragments. The two  $\eta^6$ -B<sub>6</sub> hexagons and four  $\eta^7$ -B<sub>7</sub> heptagons on the spherical surface of B<sub>40</sub> can be practically viewed as six independent coordination sites to coordinate Cr centers with almost the same coordination energies. Detailed bonding analyses indicate that the eclipsed  $C_{2\nu}$  C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> (**1**-**1**) possesses a coordination bonding pattern similar to that of dibenzenechromium, with the B<sub>40</sub> ligand inheriting the  $\sigma + \pi$  double delocalization bonding pattern of the parent borospherene. The IR, Raman, and UV-vis absorption spectra of  $C_{2\nu}$  C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> (**1**-**1**) are theoretically simulated to facilitate its future experimental characterization.

**Keywords** First-principles theory  $\cdot$  Borospherene complexes  $\cdot$  Geometrical structures  $\cdot$  Bonding patterns  $\cdot$  Spectral simulations

# Introduction

Since the discovery of  $C_{60}$ , fullerene complexes comprised of a cage-like  $C_{60}$ , a transition metal (TM) center, and an organic molecular ligand have formed an active area of research in both experiments and theory [1–10]. ( $C_6H_6$ )-TMC<sub>60</sub> and ( $C_5H_5$ )TMC<sub>60</sub> (TM = Sc–Co) are two types of typical complexes among them [7, 8].  $C_{60}$  can act as an

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<sup>1</sup> Institute of Molecular Science, Shanxi University, Taiyuan 030006, China

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As the light neighbor of carbon, boron has a rich chemistry second only to carbon in the periodic table. The first cage-like all-boron fullerene  $D_{2d}$  B<sub>40</sub>, dubbed borospherene, was discovered in gas phase in 2014 which features two equivalent  $\eta^6$ -B<sub>6</sub> at the top and bottom and four equivalent  $\eta^7$ -B<sub>7</sub> heptagons on the waist [11]. The discovery of  $D_{2d}$  B<sub>40</sub> paves the way for borospherene chemistry. It has been expanded to a borospherene family B<sup>q</sup><sub>n</sub> (n = 36–42, q = n - 40) which are all composed of twelve interwoven boron double chains (BDCs) with the universal bonding pattern of  $\sigma + \pi$  double delocalization [11–16]. Various endohedral and exohedral metalloborospherenes of alkali metals (Li, Na, K) [17–21], alkaline earth metals (Be, Mg, Ca, Sr, Ba) [20, 22, 23], and transition metals (Cu, Ag, Au, Sc, Y, La, U, Fe, Mn, Ni, Co)

[24–29] have been predicted in theory since 2014. More recently, our group presented the possibility of 3D aromatic heteroborospherenes Ni<sub>n</sub> $\in$ B<sub>40</sub> (n = 1–4) [30] which contains 1–4 planar or quasi-planar heptacoordinate Ni centers in  $\eta^7$ -B<sub>7</sub> heptagons on the cage surface with the universal bonding pattern of  $\sigma + \pi$  double delocalization on the B<sub>40</sub> ligand. In comparison, the hexacoordinate Ni centers in Ni<sub>5</sub> $\in$ B<sub>40</sub> and Ni<sub>6</sub> $\in$ B<sub>40</sub> at the top and bottom of the B<sub>40</sub> cage possess obviously lower coordination energies [30].

Exohedral complexation of B<sub>40</sub> was recently predicted by Jemmis et al. [31]. Both the  $\eta^6$ -B<sub>6</sub> hexagonal and  $\eta^7$ -B<sub>7</sub> heptagonal faces of B<sub>40</sub> can be used as ligands to sandwich Cr, with  $C_6H_6Cr$  fragment preferring  $\eta^6$ -coordination. As an extension along this line, we present herein the possibility of the exohedral complex series (C<sub>6</sub>H<sub>6</sub>Cr)<sub>n</sub>&B<sub>40</sub> (n = 1-6) with n Cr centers sandwiched between the central  $\eta^{6/7}$ -B<sub>40</sub> cage-like unit and n planar  $\eta^6$ -C<sub>6</sub>H<sub>6</sub> ligands. Cr centers in  $(C_6H_6Cr)_n\&B_{40}$  (n = 1-6) are coordinated to the  $\eta^{6}$ -B<sub>6</sub> hexagonal coordination site atop the B<sub>40</sub> cage first, the four neighboring  $\eta^7$ -B<sub>7</sub> heptagonal sites on the waist next, and finally the  $\eta^6$ -B<sub>6</sub> hexagonal site at the bottom, in the highest possible geometrical symmetries of the systems. Detailed bonding analyses indicate that the  $(C_6H_6Cr)_n\&B_{40}$  complexes possess a spd- $\pi$  coordination bonding pattern similar to that of dibenzenechromium  $D_{6h}$ (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr, with cage-like B<sub>40</sub> as a multi-dentate ligand inheriting the  $\sigma + \pi$  double delocalization bonding pattern of the parent borospherene.

# **Computational Details**

Various manually constructed eclipsed and staggered (C<sub>6-</sub>  $H_6Cr_{n}\&B_{40}$  (n = 1-6) complexes with Cr centers at different  $\eta^6$ - and  $\eta^7$ -coordination sites were optimized at the PBE0/6-31G(d) level, with their vibrational frequencies checked to make sure the optimized structures were true minima of the systems. The initially optimized structures were then fully re-optimized at PBE0 level with the basis set of 6-311 + G(d) [32]. Nucleus Independent Chemical Shifts (NICS) [33, 34] were calculated at the cage center of  $B_{40}$  at the PBE0/6-311 + G(d). Natural bonding orbital (NBO) analyses were performed using the NBO 6.0 program [35]. Detailed bonding analyses on  $C_{2\nu}$  C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> (1-1) were performed using the Adaptive Natural Density Partitioning (AdNDP) method [36, 37] which has been successfully applied to various molecules and clusters [11–16]. UV–vis absorption spectrum was calculated using time-dependent DFT approach (TD-DFT) [38, 39]. All calculations were performed using the Gausssian16 program [40].

# **Results and Discussion**

## **Structures and Stabilities**

#### Structures and Relative Stabilities

Structures of the lowest-lying isomers obtained for  $(C_6 H_6Cr)_n \& B_{40}$  (n = 1–6) are depicted in Fig. 1. Alternative isomers of  $(C_6H_6Cr)_n \& B_{40}$  along with their relative energies at the PBE0/6-311 + G(d) are presented in Fig. S1. A sketch comparison of the eclipsed and staggered conformations between  $C_6$  six-membered ring in  $C_6H_6$  and  $B_6$  hexagon and  $B_7$  heptagon on the surface of  $B_{40}$  is shown in Fig. S2.

The lowest-lying isomer  $C_{2\nu}$  C<sub>6</sub>H<sub>6</sub>Cr&[ $\eta^{6}$ -B<sub>40</sub>] (1-1) obtained in this work agrees well with that previously predicted in Ref.31 in which the C<sub>6</sub>H<sub>6</sub>Cr fragment is coordinated to the  $\eta^{6}$ -B<sub>6</sub> hexagonal coordination site atop the B<sub>40</sub> cage in an eclipsed motif. The corresponding staggered conformation  $C_{2\nu}$  C<sub>6</sub>H<sub>6</sub>Cr&[ $\eta^{6}$ -B<sub>40</sub>] turned out to be a transition state with an imaginary frequency at 56i cm<sup>-1</sup> at PBE0/6-31G(d).  $C_{2\nu}$  C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> (1-1) lies 0.05 and 0.06 eV lower than the staggered  $C_s$  C<sub>6</sub>H<sub>6</sub>Cr&[ $\eta^{7}$ -B<sub>40</sub>] (1-2) and eclipsed  $C_s$  C<sub>6</sub>H<sub>6</sub>Cr&[ $\eta^{7}$ -B<sub>40</sub>] (1-3), respectively (Fig. S1), in which Cr atom occupies the  $\eta^{7}$ -B<sub>7</sub> heptagonal coordination sites of the B<sub>40</sub> cage on the waist. It can be concluded that a C<sub>6</sub>H<sub>6</sub>Cr fragment slightly favors  $\eta^{6}$ -coordination over  $\eta^{7}$ -coordination in C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> though the energy difference is small.

With the second  $C_6H_6Cr$  fragment added in, the situation becomes complicated in  $(C_6H_6Cr)_2\&B_{40}$ . The two  $C_6H_6Cr$  fragments may be coordinated to two  $\eta^6$ -B<sub>6</sub> hexagonal coordination sites on the top and bottom, two  $\eta^7$ -B<sub>7</sub> heptagonal sites on the waist, or one  $\eta^6$ -B<sub>6</sub> hexagon on the top and one  $\eta^7$ -B<sub>7</sub> heptagon on the waist, in either staggered or eclipsed motifs. The four lowest-lying isomers thus obtained for  $(C_6H_6Cr)_2\&B_{40}$  are depicted in Fig. S1. The lowest-lying isomer  $C_1$   $(C_6H_6Cr)_2\&B_{40}$  (**2-1**) can be obtained by coordinating the second  $C_6H_6Cr$  fragment in a  $\eta^7$ -B<sub>7</sub> heptagon in  $C_{2\nu}$   $C_6H_6Cr\&B_{40}$  (**1-1**). It lies 0.02 eV



Fig. 1 Lowest-lying isomers of  $(C_6H_6Cr)_n\&B_{40}$  (n = 1–6) at PBE0/6-311 + G(d) level

lower in energy than  $C_2$  (C<sub>6</sub>H<sub>6</sub>Cr)<sub>2</sub>&B<sub>40</sub> (**2-2**) which contains two Cr atoms occupying two adjacent  $\eta^7$ -B<sub>7</sub> heptagonal coordination sites. Isomers  $D_{2d}$  (C<sub>6</sub>H<sub>6</sub>Cr)<sub>2</sub>&B<sub>40</sub> (**2-3**) and  $C_{2\nu}$  (C<sub>6</sub>H<sub>6</sub>Cr)<sub>2</sub>&B<sub>40</sub> (**2-4**) with two Cr atoms occupying the two  $\eta^6$ -B<sub>6</sub> hexagons or two  $\eta^7$ -B<sub>7</sub> heptagons on the opposite sides lie + 0.21 eV and + 0.28 eV higher than (C<sub>6</sub>H<sub>6</sub>Cr)<sub>2</sub>&B<sub>40</sub> (**2-1**), respectively.

The situation becomes more complicated in  $(C_6H_6Cr)_3\&B_{40}$  which contains three  $C_6H_6Cr$  fragments coordinately bonded to the  $B_{40}$  cage. Various possible structures are considered to compare their relative stabilities. The lowest-lying isomer  $C_1$  ( $C_6H_6Cr)_3\&B_{40}$  (3-1) constructed by adding one  $C_6H_6Cr$  unit at the adjacent  $\eta^7$ -B<sub>7</sub> heptagon of  $C_1$  ( $C_6H_6Cr)_2\&B_{40}$  (2-1) turns out to be at least 0.20 eV lower in energy than the other six isomers considered.

The axially chiral  $C_2$  (C<sub>6</sub>H<sub>6</sub>Cr)<sub>4</sub>&B<sub>40</sub> (**4-1**) turns out to be the lowest-lying isomer of (C<sub>6</sub>H<sub>6</sub>Cr)<sub>4</sub>&B<sub>40</sub> which can be constructed by adding one C<sub>6</sub>H<sub>6</sub>Cr fragment at the  $\eta^6$ -B<sub>6</sub> coordination site at the bottom of  $C_1$  (C<sub>6</sub>H<sub>6</sub>Cr)<sub>3</sub>&B<sub>40</sub> (**3-1**). It lies only 0.01 eV lower in energy than the second lowestlying isomer  $C_s$  (C<sub>6</sub>H<sub>6</sub>Cr)<sub>4</sub>&B<sub>40</sub> (**4-2**) which can be obtained by coordinating one C<sub>6</sub>H<sub>6</sub>Cr unit to a  $\eta^7$ -B<sub>7</sub> heptagon in  $C_1$  (C<sub>6</sub>H<sub>6</sub>Cr)<sub>3</sub>&B<sub>40</sub> (**3-1**). The two isomers are practically degenerate in thermodynamics. The optimized (C<sub>6</sub>H<sub>6</sub>Cr)<sub>4</sub>&B<sub>40</sub> (**4-3**), (**4-4**), (**4-5**) and (**4-6**) lie 0.25, 0.33, 0.33 and 0.34 eV above (C<sub>6</sub>H<sub>6</sub>Cr)<sub>4</sub>&B<sub>40</sub> (**4-1**).

With five  $C_6H_6Cr$  fragments over six possible coordination sites on  $B_{40}$  surface, the situation in  $(C_6H_6Cr)_5\&B_{40}$  becomes simpler. Two almost degenerate low-lying isomers with the energy difference of only 0.01 eV are obtained, with  $C_{2\nu}$  ( $C_6H_6Cr)_5\&B_{40}$  (5-1) and  $C_s$  ( $C_6H_6$  Cr)<sub>5</sub>&B<sub>40</sub> (5-2) constructed by adding one  $C_6H_6Cr$  unit at a  $\eta^7$ - $B_7$  heptagonal coordination site in  $C_s$  ( $C_6H_6Cr)_4\&B_{40}$  (4-2) and  $C_2$  ( $C_6H_6Cr)_4\&B_{40}$  (4-1), respectively.

Adding one more  $C_6H_6Cr$  fragment to  $C_{2\nu}$  ( $C_6H_6$ Cr)<sub>5</sub>&B<sub>40</sub> (5-1) at the final  $\eta^6$ -B<sub>6</sub> hexagonal coordination site at the bottom produces the perfect cage-like  $D_{2d}$  ( $C_6$  $H_6Cr$ )<sub>n</sub>&B<sub>40</sub> (6-1) as the lowest-lying isomer of the system. It possesses the highest symmetry in the complex series, with the  $\eta^6$ -B<sub>6</sub> and  $\eta^7$ -B<sub>7</sub> coordination sites on the opposite sides of B<sub>40</sub> cage in staggered and eclipsed motifs, respectively. It can be concluded that the n  $C_6H_6Cr$  fragments in ( $C_6H_6Cr$ )<sub>n</sub>&B<sub>40</sub> (n = 1–6) are coordinated to the  $\eta^6$ -B<sub>6</sub> hexagonal coordination site atop the B<sub>40</sub> cage first, the four neighboring  $\eta^7$ -B<sub>7</sub> heptagonal sites on the waist next, and finally the  $\eta^6$ -B<sub>6</sub> hexagonal site at the bottom, forming a multinuclear complex series with n Cr centres sandwiched between the central  $\eta^{6/7}$ -B<sub>40</sub> unit and n planar  $\eta^6$ -C<sub>6</sub>H<sub>6</sub> ligands.

#### **Coordination Energies**

To better interpret the complexation process of  $B_{40}$ , we define the coordination energies (E<sub>c</sub>) of the  $(C_6H_6Cr)_n\&B_{40}$  (n = 1–6) complexes as following:

$$E_c \ = \ - \big\{ E\big[ (C_6 H_6 Cr)_n \& B_{40} \big] - E[B_{40}] - n E[Cr] - n E[C_6 H_6] \big\}$$

where  $E[(C_6H_6Cr)_n\&B_{40}]$ ,  $E[B_{40}]$ , E[Cr], and  $E[C_6H_6]$  are the total energies of the  $(C_6H_6Cr)_n\&B_{40}$  complex, isolated  $B_{40} (D_{2d}, {}^{1}A_{1}), Cr (O_{H}, {}^{7}A_{1g}), and C_{6}H_{6} (D_{6h}, {}^{1}A_{1g}) at the$ PBE0/6-311 + G(d) level, respectively. Intriguingly, the  $E_c$  values of the  $(C_6H_6Cr)_n\&B_{40}$  (n = 1-6) series increase almost perfectly linearly with the number of C6H6Cr fragments, with the average coordination energy per ligand of  $E_c = 70.89$  kcal/mol (3.07 eV/C<sub>6</sub>H<sub>6</sub>Cr) at PBE0 (Fig. 2). The  $E_c \sim n$  linear relationship clearly indicates that the two  $\eta^6$ -B<sub>6</sub> hexagons and four  $\eta^7$ -B<sub>7</sub> heptagons on the cage surface of  $D_{2d}$  B<sub>40</sub> can be practically viewed as six independent and almost equivalent coordination sites to transition metal centers. The small energy differences between different isomers of the same complexes discussed above well support the conclusion. Multiple isomers may therefore co-exist in experiments for  $(C_6H_6Cr)_n\&B_{40}$ complexes.

We calculated the energy changes ( $\Delta E$ ) from  $D_{6h}$ ( $C_6H_6$ )<sub>2</sub>Cr to  $C_{3\nu}$   $C_6H_6Cr(\eta^6-C_{60})$  in reaction (1), from  $D_{6h}$ ( $C_6H_6$ )<sub>2</sub>Cr to  $C_{2\nu}$   $C_6H_6Cr\&B_{40}$  (1-1) in reaction (2), and from  $C_{3\nu}$   $C_6H_6Cr(\eta^6-C_{60})$  to  $C_{2\nu}$   $C_6H_6Cr\&B_{40}$  (1-1) in reaction (3) in the following processes

$$(C_6H_6)_2Cr + C_{60} = C_6H_6Cr(\eta^6 - C_{60}) + C_6H_6 \qquad (1)$$

$$(C_6H_6)_2Cr + B_{40} = C_6H_6Cr\&B_{40} + C_6H_6$$
(2)

$$C_{6}H_{6}Cr(\eta^{6} - C_{60}) + B_{40} = C_{6}H_{6}Cr\&(\eta^{6} - B_{40}) + C_{60}$$
(3)



Fig. 2 Coordination energies (kcal/mol) of the  $(C_6H_6Cr)_n\&B_{40}$ (n = 1–6) complexes at the PBE0/6-311 + G(d) level

which turn out to have the calculated energy changes of  $\Delta E =+ 19.95$ , - 28.28, and - 48.23 kcal/mol at PBE0/6-311 + G(d) level, respectively. These values clearly indicate that the formation of  $C_{3\nu}$  C<sub>6</sub>H<sub>6</sub>Cr( $\eta^{6}$ -C<sub>60</sub>) is endothermic from  $D_{6h}$  (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr, while the formations of  $C_{2\nu}$  C<sub>6</sub>H<sub>6</sub>Cr( $\Re^{6}$ -C<sub>60</sub>). B<sub>40</sub> is therefore an effective ligand to replace C<sub>6</sub>H<sub>6</sub> in (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr and to replace C<sub>60</sub> in C<sub>6</sub>H<sub>6</sub>Cr( $\eta^{6}$ -C<sub>60</sub>). Complexation of B<sub>40</sub> with C<sub>6</sub>H<sub>6</sub>Cr fragments effectively helps to stabilize B<sub>40</sub> in its complexes.

#### Aromaticity and HOMO-LOMO Gaps

NICS values at cage centers have been widely used as an index for 3D-aromaticity, while HOMO–LUMO gaps reflect the kinetic stability of the concerned systems [41]. We calculated the NICS values at the centroid of the  $B_{40}$  cage in  $(C_6H_6Cr)_n\&B_{40}$  (n = 1–6) complexes which all turn out to possess negative NICS values ranging from – 49.29 to – 56.28 ppm at PBE0/6-311 + G(d) (Table 1). These values are even more negative than the corresponding value of – 41.59 ppm at the center of a bare  $B_{40}$ . They are therefore all 3D-aromatic in nature, similar to bare  $B_{40}$  [11].

 $(C_6H_6Cr)_n\&B_{40}$  (n = 1–6) complexes possess the sizable HOMO–LUMO gaps of 2.63, 2.50, 2.52, 2.41, 2.41, and 2.29 eV for n = 1, 2, 3, 4, 5, and 6 at PBE0, respectively. Although these values decrease gradually with increasing n, they all have wider HOMO–LUMO gaps than that (2.26 eV) of  $C_{3\nu} C_6H_6Cr(\eta^6-C_{60})$  at the same theoretic level. However, both borospherene and fullerene complexes possess obviously smaller HOMO–LUMO gaps than  $D_{6h} (C_6H_6)_2Cr$  (4.46 eV) (Table 1).

## **Bonding Analyses**

#### **NBO** Analyses

Detailed NBO analyses show that the total Wiberg bond orders of the Cr centers in  $(C_6H_6Cr)_n\&B_{40}$  (n = 1–6) fall in

a narrow range between 4.34 and 4.49 (Table 1). These values are systematically higher than the corresponding values of 4.12 in  $C_{3\nu}$  C<sub>6</sub>H<sub>6</sub>Cr( $\eta^6$ -C<sub>60</sub>) and 4.22 in  $D_{6h}$  (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr at PBE0/6-311 + G(d) level, suggesting that effective coordination interactions are formed in (C<sub>6</sub>H<sub>6</sub> Cr)<sub>n</sub>&B<sub>40</sub> complexes at both  $\eta^6$ -B<sub>6</sub> and  $\eta^7$ -B<sub>7</sub> coordination sites. As a specific example, Cr centers in (C<sub>6</sub>H<sub>6</sub>Cr)<sub>2</sub>&B<sub>40</sub> (**2-1**) have the overall Cr–B coordination bond orders of WBI<sub>Cr</sub> = 4.45 at  $\eta^6$ -B<sub>6</sub> and WBI<sub>Cr</sub> = 4.34 at  $\eta^7$ -B<sub>7</sub>, with both of them being slightly higher than the corresponding overall Cr–C coordination bond order of WBI<sub>Cr</sub> = 4.12 in  $D_{6h}$  (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr.

It is also interesting to notice that the Cr centers in  $(C_6H_6Cr)_n\&B_{40}$  (n = 1-6) have higher valence electron numbers than that in  $D_{6h}$  (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr. For example, Cr in  $C_{2\nu}$  C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> (1-1) has the electron configuration of Cr  $[Ar]4s^{0.19}3d^{6.39}$  and the natural atomic charge of  $q_{Cr} =$ - 0.67 lel, while the Cr center in  $D_{6h}$  (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr possesses the electron configuration of Cr[Ar]4s<sup>0.18</sup>3d<sup>5.77</sup> and natural atomic charge of  $q_{Cr} = -0.02$  lel. Similar results exist in other borospherene complexes (Table 1). These results have their origin from the fact that boron possesses a lower electronegativity (2.04) than carbon (2.55). B<sub>40</sub> is therefore a better electron donor than both  $C_{60}$  and  $C_6H_6$ . It is true that the Cr centers in  $(C_6H_6Cr)_n\&B_{40}$  (n = 1-6) possess the sizable negative atomic charges of  $q_{Cr} = -0.45$  to -0.69lel, while Cr centers in both  $(C_6H_6)_2$ Cr and  $C_6H_6$ Cr $(\eta^6-C_{60})$ remain practically neutral with  $q_{Cr}\,\approx\,+\,0.01\,$  to  $\,-\,0.02$ lel.

#### AdNDP Analyses on $C_{2\nu}$ C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> (1-1)

The high stabilities of  $(C_6H_6Cr)_n\&B_{40}$  (n = 1–6) originate from their unique electronic structures and bonding patterns. Detailed AdNDP analyses are performed on  $C_{2\nu}$  $C_6H_6Cr\&B_{40}$  (1-1) to compare with that of the prototypic sandwich complex dibenzenechromium  $D_{6h}$  ( $C_6H_6$ )<sub>2</sub>Cr. As shown in Fig. 3,  $D_{6h}$  ( $C_6H_6$ )<sub>2</sub>Cr possesses 12 2c–2e C–H  $\sigma$ bonds and 12 2c–2e C–C  $\sigma$  bonds on both the C<sub>6</sub>H<sub>6</sub> ligands with the occupation numbers of ON = 1.98 lel and 1.97 lel, respectively. The central Cr atom mainly participates in 9

	NICS	∆Gap	WBI <sub>Cr</sub>	$q_{Cr}$
$C_{2\nu}$ C <sub>6</sub> H <sub>6</sub> Cr&B <sub>40</sub>	- 49.29	2.63	4.46	- 0.67
$C_1 (C_6H_6Cr)_2\&B_{40}$	- 53.01	2.50	4.34 ~ 4.45	- 0.53 to - 0.67
$C_2 (C_6 H_6 Cr)_3 \& B_{40}$	- 54.10	2.52	4.34 ~ 4.45	- 0.53 to - 0.69
$C_2 (C_6 H_6 Cr)_4 \& B_{40}$	- 52.72	2.41	4.37 ~ 4.45	- 0.53 to - 0.66
$C_{2\nu}$ (C <sub>6</sub> H <sub>6</sub> Cr) <sub>5</sub> &B <sub>40</sub>	- 55.86	2.41	4.35 ~ 4.49	-0.49 to $-0.67$
D <sub>2d</sub> (C <sub>6</sub> H <sub>6</sub> Cr) <sub>6</sub> &B <sub>40</sub>	- 56.28	2.29	4.38 ~ 4.47	-0.45 to $-0.65$
$C_{3\nu} C_6 H_6 Cr(\eta^6 - C_{60})$	- 8.47	2.26	4.12	+ 0.01
$D_{6h}$ (C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub> Cr	_	4.46	4.22	- 0.02

values (NICS/ppm), HOMO– LUMO gaps ( $\Delta$ Gap/eV), overall Wiberg bond orders of the Cr centers (WBI<sub>Cr</sub>), and atomic charge (q<sub>cr</sub>/lel) of the Cr centers of (C<sub>6</sub>H<sub>6</sub>Cr)<sub>n</sub>&B<sub>40</sub> (n = 1–6) complexes compared with that of C<sub>3</sub>, C<sub>6</sub>H<sub>6</sub>Cr( $\eta^{6}$ -C<sub>60</sub>) and D<sub>6h</sub> (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr at PBE0/6-311 + G(d) level

Table 1 Calculated NICS



Fig. 3 Comparison of the AdNDP bonding patterns of C<sub>2v</sub> C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> (1-1) and D<sub>6h</sub> (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr, with the occupation numbers (ONs) indicated

multicenter spd- $\pi$  coordination bonds, including 3 7c–2e coordination  $\pi$  bonds with ON = 2.0 lel between Cr center and the C<sub>6</sub>H<sub>6</sub> ligand on the top, 3 7c–2e coordination  $\pi$ bonds with ON = 2.0 lel between Cr center and the C<sub>6</sub>H<sub>6</sub> ligand at the bottom, and 3 13c–2e  $\pi$  bonds involving both the C<sub>6</sub>H<sub>6</sub> ligands and Cr center with ON = 1.96–2.00 lel which are totally delocalized. Our AdNDP bonding pattern is different from that previously reported in [42, 43] which contains 9 totally delocalized spd- $\pi$  coordination bonds (9 13c–2e bonds) [42, 43]. We believe both patterns are reasonable based on the fact that both of them have the right bonding symmetries (*D*<sub>6h</sub>) and possess high ON values. In comparison, as shown in Fig. 3,  $C_{2\nu}$  C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> (1-1) exhibits a clearly similar coordination bonding pattern with  $D_{6h}$  (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr around the  $\eta^6$ -B<sub>6</sub> coordination site. The localized  $\sigma$  bonds on the two ligands include 6 C–H 2c–2e bonds with ON = 1.98 lel and 6 C–C 2c–2e bonds with ON = 1.97 lel on C<sub>6</sub>H<sub>6</sub> and 48 3c–2e bonds with ON = 1.74–1.96 lel on the B<sub>40</sub> cage. The B<sub>40</sub>-only  $\pi$ -bonds include 2 5c–2e  $\pi$  bonds with ON = 1.93 lel and 2 7c–2e  $\pi$ bonds with ON = 1.77 lel at the bottom of the B<sub>40</sub> cage and 4 6c–2e  $\pi$  bonds on the waist with ON = 1.93 lel. They originate from the 8  $\pi$  bonds at the same locations in isolated  $D_{2d}$  B<sub>40</sub> [11]. The remaining 10 bonds form the  $\pi$  framework involving both the ligands and Cr center which are readily categorized into three groups. The first group includes 3 7c–2e  $\pi$  bonds with ON = 1.96 lel involving the Cr center and the  $C_6H_6$  ligand at the top. They are similar to the 3 7c-2e  $\pi$  bonds between Cr and the C<sub>6</sub>H<sub>6</sub> ligand in  $D_{6h}$  (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr on the top. The second group contains 4  $17c-2e \pi$  bonds with ON = 1.84–1.96 lel involving the Cr atom and the 16 boron atoms in the boron double chain around the  $\eta^6$ -B<sub>6</sub> coordination site. They are formed between Cr spd-hybridized atomic orbitals and the 4  $\pi$ bonds (2 5c-2e  $\pi$  and 2 7c-2e  $\pi$ ) over the boron double chain around the  $\eta^6$ -B<sub>6</sub> hexagon atop the B<sub>40</sub> cage [11]. These 4 17c–2e  $\pi$  coordination interactions are similar to the 3 7c–2e  $\pi$  bonds between Cr and the C<sub>6</sub>H<sub>6</sub> ligand in the  $D_{6h}$  (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr at the bottom (though the former has one more  $\pi$  coordination bond than the latter as explained above). The third group includes 3 23c–2e delocalized  $\pi$ bonds with ON = 1.77 - 1.99 lel involving the Cr center,  $C_6H_6$  ligand, and the 16 boron atoms in the boron double chain around the  $\eta^6$ -B<sub>6</sub> coordination site. They exhibit a one-to-one correspondence relationship with the 3 13–2e  $\pi$ bonds in  $D_{6h}$  (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr. Overall, the coordination bonding pattern of  $C_{2\nu}$  C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> (1-1) is similar to that of  $D_{6h}$ (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr though the former possesses 10-coordination bonds between the Cr center and B<sub>40</sub> ligand due to the existence of four delocalized  $\pi$  bonds around the  $\eta^6$ -B<sub>6</sub> hexagon atop the  $B_{40}$  cage [11]. Other  $(C_6H_6Cr)_n\&B_{40}$ complexes follow similar coordination patterns with  $C_{2\nu}$  $C_6H_6Cr\&B_{40}$  (1-1), with the highest-symmetry  $D_{2d}$  ( $C_6$ H<sub>6</sub>Cr)<sub>6</sub>&B<sub>40</sub> possessing a coordination bonding pattern in which each of the 12 delocalized  $\pi$  molecular orbitals over the B<sub>40</sub> cage is shared by two neighbouring coordination cites.

## Spectral Simulations for $C_{2\nu}$ C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> (1-1)

The IR, Raman, and UV–vis absorption spectra of  $C_{2\nu}$ C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> (1-1) are computationally simulated in Fig. 4 to facilitate its future spectral characterizations. The simulated IR and Raman spectra display numerous active absorption peaks which encompass 50 IR (17a<sub>1</sub> + 18b<sub>1</sub> + 15b<sub>2</sub>) and 103 Raman (25a<sub>1</sub> + 35a<sub>2</sub> + 19b<sub>1</sub> + 24b<sub>2</sub>) active modes. The major IR bands lie between 400–1400 cm<sup>-1</sup>, with four strong peaks at 417 (a<sub>1</sub>), 523 (a<sub>1</sub>), 1237 (b<sub>2</sub>), and 1319 (a<sub>1</sub>) cm<sup>-1</sup> which may serve as fingerprints to characterize the complex. The major Raman active peaks occur at 428 (a<sub>1</sub>), 645 (a<sub>1</sub>), 1008 (a<sub>1</sub>), and 1319 (a<sub>1</sub>) cm<sup>-1</sup>, respectively. The four peaks at 142 (a<sub>1</sub>), 188 (a<sub>1</sub>), 230 (a<sub>1</sub>), and 428 (a<sub>1</sub>) cm<sup>-1</sup> belong to typical radial breathing modes (RBMs) of the B<sub>40</sub> unit which can be used to characterize cage-like structures.

The simulated UV-vis spectrum exhibits three major peaks at 336, 395, and 501 nm and two weak bands at 631,



**Fig. 4** Simulated **a** IR, **b** Raman and **c** UV–vis absorption spectra of  $C_{2\nu}$  C<sub>6</sub>H<sub>6</sub>Cr&B<sub>40</sub> (1-1) at PBE0/6-311 + G(d) level

and 732 nm, respectively. Detailed analyses indicate that the two weak bands in visible-light range at 631 and 732 nm correspond mainly to HOMO  $\rightarrow$  LUMO + 1 and HOMO  $\rightarrow$  LUMO electronic transitions, respectively, while the three strong UV absorption peaks at 336, 395, and 501 nm involve electronic transitions from the inner shells (Table S1).

## Summary

Based upon extensive DFT calculations, we present in this work the viable possibility of exohedral complexes ( $C_6$  $H_6Cr_{n}\&B_{40}$  (n = 1-6) which contain n Cr centres sandwiched between the central  $\eta^{6/7}$ -B<sub>40</sub> unit and n planar  $\eta^6$ -C<sub>6</sub>H<sub>6</sub> ligands. These borospherene complexes are effectively stabilized by n C<sub>6</sub>H<sub>6</sub>Cr fragments at n  $\eta^{6/7}$ -coordination sites which can be practically viewed as n independent coordination sites with almost the same coordination energies.  $(C_6H_6Cr)_n\&B_{40}$  complexes possess coordination bonding patterns similar to that of dibenzenechromium ( $D_{6h}$  ( $C_6H_6$ )<sub>2</sub>Cr). Investigations to sandwich transition metals in 1D TM&B<sub>40</sub>, 2D TM<sub>2</sub>&B<sub>40</sub>, and 3D TM<sub>3</sub>&B<sub>40</sub> crystals with unique magnetic properties are currently in progress. The structural and bonding patterns developed in this work can be utilized to design novel complexes of the borospherene family.

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### **Compliance with Ethical Standards**

**Conflict of interest** All the authors of this paper have no conflict of interest.

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