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 $M \odot B_7 O_7^+$ (M = Ni, Pd, Pt): aromatic molecular stars with a planar heptacoordinate transition metal[†]

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The dynamically stable global minima $M \odot B_7 O_7^+$ (M = Ni, Pd, Pt) are interesting in that they possess σ -aromaticity alone within the $B_7 M$ core moiety, which can be attributed to the strong peripheral localized O $\rightarrow B \pi$ back-bonding that leads to the less favourable delocalized M $\rightarrow B \pi$ back-bonding over the $B_7 M$ core moiety.

As one of the central concepts in chemistry, aromaticity is usually employed to explain the additional stabilization effect related to π electron delocalization in comparison with the conjugation effect alone, for example: benzene over the hypothetical cyclohexatriene.¹ Aromatic stabilization effects (ASE) commonly exist in clusters where the number of delocalized π electrons meets Hückel's 4n + 2 rule.² Remarkably, the concept of aromaticity has been extended to the exotic σ and δ electron delocalization during the study of some non-classical systems, corresponding to the exotic σ -³ and δ -aromaticity,⁴ respectively and also obeying Hückel's rule. The numbers of delocalized σ -, π - and δ -electrons should be counted individually when Hückel's rule is applied.

In general, one would agree that the π electron delocalization is crucial in achieving the planar arrangement for the ligand atoms of the exotic planar hypercoordinate atom(s). However, since the ligand atom(s) are frequently electron deficient to meet the requirement of σ -donating and π -accepting properties,⁵ the π electron delocalization is commonly accompanied by the exotic σ electron delocalization, *i.e.*, their core moieties featuring planar hypercoordination are usually σ and π doubly aromatic.^{3d,6} Nevertheless, exceptions can be found in some binary transition metal clusters that

possess a planar hypercoordinate Sc/Y and feature σ aromaticity alone, as exemplified by YAu₆⁻, ScCu₇, YCu₇, YAg₇, and YAu₇, etc.⁷ The absence of global π -aromaticity in these clusters can be attributed to the insufficient valence electrons in the central Sc or Y atom and the absence of π accepting properties for peripheral group 11 metals. Herein, one would wonder: can the exotic planar hypercoordination be involved in the exotic σ -aromaticity if the key ligand atom(s) are σ -donating and π -accepting? The answer is positive! In this work, we report a case in $M \odot B_7 O_7^+$ (M = Ni, Pd, Pt, see Fig. 1), whose planar heptacoordinate transition metal (phM) atom is only involved in five delocalized σ -orbitals, *i.e.* their B₇M core moieties only possess σ -aromaticity. It is worth noting that combined experimental and theoretical studies have extensively characterized the eight- to ten-membered boron rings enclosing a hypercoordinate planar transition metal.⁸ Neverthe less, the corresponding transition metal atoms possess σ and π double aromaticity rather than σ -aromaticity alone.

The present study was inspired by our recently reported $CAl_5O_5^+$ cluster⁹ with a novel planar pentacoordinate carbon. In



Fig. 1 PBE0–BS1-optimized structures of $M_{\odot}^{O}B_7O_7^{-}$ and $M_{\odot}^{O}B_7O_7^{+}$ (M = Ni, Pd, Pt). The interatomic distances are given in Å.

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 $[\]dagger$ Electronic supplementary information (ESI) available: AdNDP bonding patterns of 1', 1, 2' and 2, the distribution of NICS values for 1', 1, 2' and 2, optimized structures and the relative energies of 1'-3', 1-3 and their four lowest isomers, BOMD plots of 1-3, and Cartesian coordinates for the species reported in this work. See DOI: 10.1039/d1cc05844d

comparison with its parent cluster CAl_5^+ , it showed relatively high oxygen resistance due to the protecting effect provided by the peripheral O atoms. On the top $CAl_5O_5^+$, we wanted to design the clusters with the phM using the similar structural pattern. Simultaneously, we also wanted to achieve the monoanions to facilitate the experimental studies in negative ion photoelectron spectroscopy. Initially, we tried an Al_7O_7 ring, but found that it was too big for any transition metal element to stay inside. Therefore, the smaller B_7O_7 ring was chosen to achieve the oxygen-protected species with a phM atom.

By complying with the 18-valence electron (18ve) rule, the B₇O₇ ring fits a group 10 metal to give the mono-anionic cluster $M \odot B_7 O_7^-$ [M = Ni (1'), Pd (2'), Pt (3')]. They are the energy minima adopting the high symmetry of D_{7h} at the PBE0/BS1 level using the Gaussian 16 package,¹⁰ where BS1 denotes a mixed basis set with cc-pVTZ for B, O, and Ni, and cc-pVTZ-PP¹¹ for Pd and Pt. As shown in Fig. 1, the B-O distances are relatively rigid (elongating from 1.390 to 1.407 Å when M atom goes from Ni to Pt), while the B-B distances show obvious flexibility (elongating from 1.750 to 1.844 Å when an M atom goes from Ni to Pt). The B-M distances are directly related to the size of M atoms, being 2.017, 2.093, and 2.125 Å for M = Ni, Pd, and Pt, respectively. These distances are very close to the standard B-M single bond lengths (sum of covalent radii of B and corresponding M atoms, being 1.95, 2.05, and 2.08 Å).¹² Therefore, 1'-3' are the qualified cluster having a phM atom.

However, the analysis of the energy levels of their molecular orbitals (MOs) indicates their instability, as reflected by the rather high energy levels of their highest occupied MOs (HOMOs, being -0.27, -0.16, and -0.32 eV at the PBE0/BS1 level), suggesting that it is very easy for 1'-3' to lose the electrons in their HOMOs. This feature can be verified by the low vertical detachment energies (VDEs) of 2.29, 1.68, and 1.93 eV for 1'-3', respectively, at the OVGF/BS1 level (OVGF denotes outer valence Green's function).¹³ Interestingly, the gaps between their HOMOs and HOMO-1s are very large, being 3.46, 3.83, and 3.80 eV, which are comparable to their HOMO-LUMO gaps of 3.76, 3.53, and 3.83 eV, respectively. The above results indicate that cations $M \odot B_7 O_7^+$ (M = Ni, Pd, Pt) may be more stable than corresponding anions. Delightfully, the M \bigcirc B₇O₇⁺ [M = Ni (1), Pd (2), Pt (3)] are also the energy minima adopting the high symmetry of D_{7h}. The HOMO-LUMO gaps of these cations, 5.36, 5.14, and 5.09 eV, are obviously wider than that of 1'-3' by 1.60, 1.61, and 1.26 eV, respectively, suggesting that it is harder to excite an electron in 1-3 than in 1'-3'. As shown in Fig. 1, despite the elimination of the Coulombic explosion effect in anions, the B7M moieties in 1-3 are still slightly larger than those in 1'-3', as mirrored by the slightly longer B-M distances of 2.090, 2.159, and 2.169 Å for M = Ni, Pd, Pt, respectively. Nevertheless, these distances are also close to the B-M single bond lengths, so 1-3 are eligible clusters with a phM as well.

Mono-cationic 1–3 possess 16ve rather than 18ve found for mono-anionic 1'-3'. What is the difference in their electronic structures? Adaptive natural density partitioning (AdNDP) analysis¹⁴ can give some clues by representing the bonding



Fig. 2 AdNDP bonding patterns of $Pt@B_7O_7^-(\mathbf{3}')$ and $Pt@B_7O_7^+(\mathbf{3})$. Only one orbital is shown when multiple orbitals in a pattern are identical due to the molecular symmetry.

with *n*-center two electron (nc-2e) electron pairs. The AdNDP results for 3' and 3 are shown representatively in Fig. 2, while those for 1', 2', 1, and 2 are given in Fig. S1 and S2 in the ESI.† As exemplified in Fig. 2, 3' has thirty-seven pairs of valence electrons, in which seven pairs are the 1c-2e lone pairs of O atoms (element A) with occupation number (ON) of 1.94 |e|, fourteen pairs are B-O 2c-2e σ bonds (element **B**, ON = 1.97 [e]), and another seven pairs are B–O–B 3c–2e π bonds (element C, ON = 2.00 |e|). The remaining nine pairs are related to the central Pt atom, including three 1c-2e d lone pairs (d_{z^2}, d_{z^2}) d_{xz} , d_{yz}) of Pt (elements D-F, ON = 1.90–1.99 |e|), five B₇M 8c–2e delocalized σ bonds (element G-K, average ON = 1.98 |e|), and one delocalized π bond, which can be partitioned into two schemes. In one scheme, it is partitioned as a B_7M 8c-2e π bond (element L1) with ON of only 1.33 |e|, while in the other scheme, it can be partitioned as a 15c–2e π bond (element L2) with ON as high as 2.00 |e|. Note that this 15c–2e π bond is almost identical in orbital shape to the HOMO of 3' (element **M**) and the LUMO of 3 (element \mathbf{M}'), together with its high ON, suggesting that the 15c-2e scheme is more appropriate.

If the orbital shape and ON are compared between elements L1 and L2, we can conclude that the electron cloud concerning their difference of 0.67 |e| in ON values is mainly distributed on the peripheral oxygen atoms and has the opposite phase in the

two sides of the nodal plane to the central part concerning the B_7M moiety. Such a result suggests that this π orbital has significant anti-bonding characters, which may be the reason why the energy level of this orbital is so high. We rationalize that the peripheral oxygen atoms play the crucial role in determine the anti-bonding characters and high energy level of this orbital: through forming the B–O–B 3c–2e π bonds (element C) showing obvious $O \rightarrow B \pi$ back-bonding characters, the electron deficiency of boron is significantly lowered so that its π -accepting capability is substantially reduced. Therefore, 3' tends to lose the electrons in this orbital to give the cationic counterpart 3. As shown in Fig. 2, the delocalized π bond is absent in 3, which should be responsible for the relatively larger B7M moiety in 3. Except for the occupation status of this delocalized π bond, other AdNDP bonding patterns of 3 are almost identical in both orbital shape and ON to that of 3' (see elements A'-K').

To independently demonstrate the aromaticity, the nucleusindependent chemical shift (NICS) calculations¹⁵ were performed and the results were presented in the form of colorfilled cross-section (CS) of NICS values¹⁶ in the molecular planes [CS-NICS(0)] or the planes parallel to but located 1 Å above the molecular plane [CS-NICS(1)], which were employed to access the σ and π aromaticity, respectively. Shown in Fig. 3 are the CS-NICS(0) and CS-NICS(1) for 3' and 3. Panels A and C revealed that the color-fill in the B₇Pt regions of 3' and 3 were very similar to each other and suggested the aromatic electron circulations, which was consistent with the existence of five delocalized σ orbitals revealed by AdNDP analysis. Nevertheless, though the color-fill in panels **B** and **D** both indicate the aromatic electron circulations, the color-fill in **B** shows an



Fig. 3 The distribution of NICS values for **3**' and **3**. Panels A and C correspond to the molecular planes, while panels B and D correspond to the planes parallel to and located 1 Å above the molecular planes. The NICS values that are negative, positive, and close to zero indicate aromaticity, anti-aromaticity, and non-aromaticity, respectively.

obvious blue-shift in comparison with that in D, suggesting that the region located 1 Å above the B₇Pt in 3' possesses more obvious aromatic electron circulations than that in 3, which may be attributed to the absence of the delocalized π bond in 3, as revealed by the AdNDP analysis. Nonetheless, as shown in panels D, the regions above the B-O-B triangles of 3 possess the color-fill of light green, which cannot be observed in the corresponding area of 3' in panel B. This suggests that 3 possesses more obvious peripheral local π aromaticity¹⁷ than 3' and may contribute to the better stability of 3. The differences in NICS results between 1'/2' and 1/2 are similar to that between 3' and 3, so the corresponding figures are given in the ESI[†] as Fig. S3 and S4. The above results demonstrated that even in the presence of σ -donating and π -accepting ligand atoms, the planar hypercoordinate arrangement can be achieved in the cluster(s), where the planar hypercoordinate atoms themselves are involved not in the π electron delocalization, but in the σ electron delocalization alone.

Next, we studied the thermodynamic stability of 1-3 and 1'-3' by extensively exploring their potential energy surfaces (PESs) using a basin hopping algorithm.¹⁸ The relative energies of the isomers were compared using CCSD(T)/BS1 single point energies plus the Gibbs free energy corrections of PBE0/BS1 (abbreviated as CCSD(T)//PBE0). At this level of theory, 1-3 are the global minima (GMs), which are 27.1, 10.2, and 23.7 kcal mol^{-1} lower in energy than their corresponding second lowest isomers (see Fig. S5 in the ESI[†]), respectively. Therefore, they are less likely to be experimentally realized. As a comparison, 1'-3' are the local energy minima, which are 9.7, 36.4, and 22.3 kcal mol^{-1} higher in energy than their corresponding GMs (see Fig. S5 in the ESI⁺), respectively. The exploration on the PESs revealed that the thermodynamic stability of these phM clusters were significantly influenced by the status of that delocalized π orbital (occupied or not).

To evaluate the dynamic stability of GMs 1–3, the 50 picosecond (ps) Born–Oppenheimer molecular dynamic (BOMD)¹⁹ simulations were performed at the PBE/DZVP level and concerned temperatures (including 298, 1000, and 1500 K). The results of the simulations were represented using root-meansquare deviation (RMSD, relative to PBE/DZVP-optimized structures). As shown in Fig. 4, the RMSD plots for the simulations at 1500 K have no meaningful upward jumps, the average RMSD values are small (being 0.113, 0.118, and 0.107 Å for 1, 2, and 3, respectively), and the fluctuation is very gentle. The BOMD simulations indicate their high dynamic stability. The RMSD plots for the simulations at lower temperatures are given in the ESI† as Fig. S6 and S7.

In conclusion, we have demonstrated, through comparison between $M \odot B_7 O_7^{-}$ and $M \odot B_7 O_7^{+}$ (M = Ni, Pd, Pt), that even in the presence of σ -donating and π -accepting ligand atoms, the planar hypercoordinate arrangement can be achieved in the cluster(s), where the planar hypercoordinate atom itself is involved not in the π electron delocalization, but in the σ electron delocalization alone. The O \rightarrow B π back-bonding played the crucial role destabilizing anionic clusters $M \odot B_7 O_7^{-}$ by determining the high energy levels and anti-bonding



Fig. 4 RMSD (in Å) versus simulation time (in ps) for the BOMD simulations of $M @B_7O_7^+$ (M = Ni, Pd, Pt, **1–3**) at the PBE/DZVP level and 1500 K.

characters of delocalized π orbitals. Consequently, the M \odot B₇O₇⁺ (M = Ni, Pd, Pt) clusters without a delocalized π orbital over the B₇M core phM moieties are not only electronically robust, but also thermodynamically and dynamically stable for possible experimental generation and characterization.

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Conflicts of interest

There are no conflicts to declare.

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