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Metal-centered monocyclic carbon wheel clusters with record coordination numbers in planar species†

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The highest coordination number identified to date in planar species is CN = 10 in metal-centered monocyclic boron wheel clusters D_{10h} $M@B_{10}^-$ ($M = Ta$ and Nb) (Galeev *et al.*, *Angew. Chem. Int. Ed.*, 2012, 51, 2101). Extensive global minimum searches and first-principles theory calculations performed herein indicate that the experimentally observed LaC_{13}^+ and LaC_{14}^+ possess the well-defined global minima of perfect metal-centered monocyclic carbon wheel D_{13h} $La@C_{13}^+$ (1) ($1A_1'$) and slightly off-centered C_{2v} $La@C_{14}^+$ (4) ($1A_1$) with record coordination numbers of CN = 13 and 11 in planar structures, respectively, further pushing the boundary of our understanding of chemical structures and bonding. Detailed molecular orbital, nucleus-independent chemical shift, and ring current analyses indicate that D_{13h} $La@C_{13}^+$ (1) is $\sigma + \pi$ dually aromatic in nature, with 14 totally delocalized in-plane σ electrons and 14 totally delocalized out-of-plane π electrons each matching the $4N + 2$ aromatic rule ($N_\sigma = N_\pi = 3$). Similar $\sigma + \pi$ dually aromatic metal-centered monocyclic wheel clusters D_{13h} $Ca@C_{13}$ (2), C_{13v} $Ac@C_{13}^+$ (3), C_{2v} $Y@B_6C_6^+$ (5), and C_{2v} $Sc@B_5C_6$ (6) have also been obtained with CN = 13, 13, 12, and 11, respectively. The results obtained in this work effectively enrich the chemical structures and bonding patterns of planar hypercoordinated complexes.

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1. Introduction

Searching for the maximum coordination number in planar species has fascinated chemists for many years and continuously pushed the boundary of our understanding of chemical structures and bonding.^{1,2} The central atom and periphery atoms around it in the ligand in stable planar hypercoordinated structures must match both geometrically and electronically, *i.e.*, they must have the right atomic sizes and electronic configurations. The experimentally observed boron-centered monocyclic boron wheel clusters D_{7h} $B@B_7^{2-}$ and D_{8h} $B@B_8^-$ are good examples in which the central B atoms have the coordination numbers of CN = 7 and 8, respectively.³ These boron cluster monoanions prove to be $\sigma + \pi$ dually aromatic in nature with six delocalized σ and six delocalized π electrons ($6\sigma + 6\pi$) each conforming to the $4N + 2$ aromatic rule ($N_\sigma = N_\pi = 1$). Based on the double aromaticity requirement in bare boron wheel clusters, a general electronic design principle $x + n + k = 12$ or 16 was developed for metal-centered monocyclic boron wheel clusters $M@B_n^{k-}$ by the groups of Wang and Boldyrev,^{1,4-6} where x stands for the formal valence of the metal center M . This design principle has been successfully applied to the

experimentally characterized octacoordinated D_{8h} $Co@B_8^-$ with CN = 8,⁵ nonacoordinated D_{9h} $Ru@B_9^-$, D_{9h} $Rh@B_9^-$, and D_{9h} $Ir@B_9^-$ with CN = 9,^{7,8} and, finally, to the decacoordinated D_{10h} $Ta@B_{10}^-$ and D_{10h} $Nb@B_{10}^-$ with CN = 10 which has proven to be the highest coordination number in planar species observed to date.^{1,2}

However, planar hypercoordination chemistry may go well beyond metal-centered monocyclic boron wheel clusters. The recent experimental characterization of perfect planar D_{9h} C_{18} by atom manipulations and high-resolution atomic force microscopy⁹ inspires us to coordinate transition metal centers with bare cyclo[n]carbon ring-like clusters (C_n , $n \geq 11$) to form metal-centered monocyclic carbon wheel complexes $M@C_n^{k+}$. Very recently, the electronic properties of metal-carbon ring complexes such as $Li@C_{18}$ and MC_{16} have been reported.^{10,11} Carbon ($[He]2s^22p^2$) is known to be effective ligand to various transition metals with a smaller covalent radius than boron ($[He]2s^22p^1$), while group IIIB metals La, Y, and Sc with the valence electronic configurations of $(n-1)d^1ns^2$ possess the largest covalent radii in the periodic table.¹² Metal-centered monocyclic carbon wheel clusters $M@C_n^{k+}$ ($M = La, Y, Sc$) are thus possible to have even higher coordination numbers than their boron counterparts $M@B_n^{k-}$. In fact, two families of LaC_n^+ monocations ($n = 12-40$) were observed in mobility measurements as early as in 1994, with a La atom inserted into the carbon ring for even-numbered clusters or attached to the inside or outside of the carbon ring for odd-numbered

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clusters.¹³ More detailed mass spectra were reported late on LaC_n^+ in which LaC_{13}^+ appeared to be a prominent species with the La center most likely attached inside a C_{13} ring (ring Ib), while LaC_{14}^+ was the only LaC_{2n}^+ cluster with even number of C atoms for which ring Ib structure had a higher mass intensity than its competing isomer with a La atom inserted into a C_{14} ring (ring Ia).¹⁴ Similar prominent mass peaks were also observed for YC_{13}^+ , CeC_{13}^+ , and ScC_{13}^+ .¹⁵ Early density functional theory (DFT) calculations indicated that the most stable isomer of LaC_{13}^+ possessed a nearly-cumulenenic structure with the La atom located at the center of the carbon ring.^{16,17} However, the unique role these experimentally observed LaC_n^+ species ($n = 13, 14$) play in planar hypercoordination chemistry has largely omitted in previous investigations and their accurate geometrical and electronic structures and detailed La-C coordination bonding patterns remain to be fully evaluated using the state-of-the-art theoretical approaches to interpret their behaviors observed in experiments.

Detailed first-principles theory calculations performed in this work indicate that the experimentally observed LaC_{13}^+ (1) with a perfect D_{13h} symmetry and slightly off-centered LaC_{14}^+ (4) with a C_{2v} geometry achieve the record coordination numbers of CN = 13 and 11 in planar species reported to date. The enhanced stability of LaC_{13}^+ (1) originates from its $\sigma + \pi$ dual aromaticity with 14 delocalized σ electrons and 14 delocalized π electrons (14 $\sigma + 14 \pi$) each matching the $4N + 2$ aromatic rule ($N_\sigma = N_\pi = 3$). $\sigma + \pi$ dually aromatic D_{13h} CaC_{13} (2), C_{13v} AcC_{13}^+ (3), C_{2v} YB_6C_6^+ (5), and C_{2v} ScB_5C_6 (6) have also been obtained at first-principles theory level with CN = 13, 13, 12, and 11, respectively. The highly stable LaC_{13}^+ (1) is found to behave like a super-hydrogen monocation (H^+) in its substituted complex compounds.

2. Theoretical procedure

Extensive global-minimum (GM) searches were performed on LaC_{13}^+ , LaC_{14}^+ , CaC_{13} , AcC_{13}^+ , YB_6C_6^+ , ScB_5C_6 , and $\text{CeC}_{13}^{+/2+}$ using the TGmin2 code¹⁸ at DFT level based on the constraint basin-hopping algorithm.¹⁹ In total, more than 1000 stationary points with different spin multiplicities were probed for each species at PBE/DZVP level using the CP2K program.^{20,21} Low-lying isomers were then fully optimized at the M06-2X and PBE0 level,^{22,23} with the 6-311+G(d,p) basis sets for C, B, N, Ca, and Sc²⁴ and Stuttgart relativistic small-core pseudopotentials for La, Y, Ce, and Ac,^{25,26} using the Gaussian-16 program suite.²⁷ Frequency analyses were performed to make sure all the optimized structures are true minima of the systems. Relative energies for the five lowest-lying isomers were further refined using the more accurate coupled cluster method with triple excitations CCSD(T)^{28–30} implemented in Molpro³¹ with the basis set of cc-pVTZ for C, B, N, Ca, and Sc and the Stuttgart small-core pseudopotential for La, Y, and Ac. The optimized GM structures are summarized in Fig. 1 and more alternative isomers tabulated in Fig. S1–S6.† Natural bonding orbital (NBO) analyses were performed using the NBO 6.0 program.³² Born–Oppenheimer molecular dynamics (BOMD) simulations were performed on LaC_{13}^+ (1) for 30 ps using the CP2K software suite

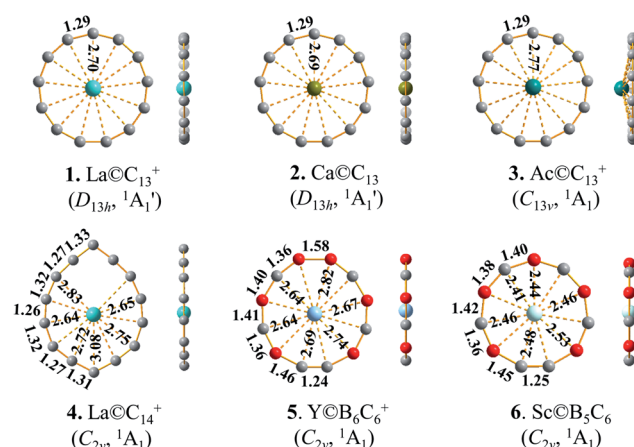


Fig. 1 Top and side views of the optimized LaC_{13}^+ (1), CaC_{13} (2), AcC_{13}^+ (3), LaC_{14}^+ (4), YB_6C_6^+ (5), and ScB_5C_6 (6) at M06-2X level, with bond lengths indicated in Å.

at 300, 800, and 1000 K.²¹ The anisotropy of the current-induced density (ACID)³³ analyses were performed using the ACID code, with the ring-current maps generated using POV-Ray 3.7.³⁴ The iso-chemical shielding surfaces (ICSSs)^{35,36} were generated with the Multiwfn 3.8 code.³⁷ The UV-vis spectra were simulated using the time-dependent TD-DFT-M06-2X approach.³⁸

3. Results and discussion

We start from LaC_{13}^+ , the most concerned species observed in LaC_n^+ series ($n = 12\text{--}40$).¹³ Encouragingly and interestingly, as shown in Fig. 1 and S1,† extensive GM searches indicate that LaC_{13}^+ possesses the well-defined perfect planar GM of D_{13h} LaC_{13}^+ (1) which contains a La atom located exactly at the center of the C_{13} wheel ligand, with the optimized La–C coordination bond lengths of $r_{\text{La-C}} = 2.70$ Å which are slightly longer than the sum of the self-consistent single-bond covalent radii of La and C (2.55 Å)¹² and C–C bond lengths of $r_{\text{C-C}} = 1.29$ Å which lie between C=C double-bond (1.34 Å) and C≡C triple bond (1.20 Å), setting up the highest coordination number of CN = 13 in planar species reported to date. LaC_{13}^+ (1) possesses the huge HOMO–LUMO gap of $\Delta E_{\text{gap}} = 5.33$ eV at M06-2X level, well underlying its high chemical stability. The slightly distorted triplet C_s LaC_{13}^+ ($^3A'$) appears to be the second lowest-lying isomer lying 2.41 eV above the GM at CCSD(T). The seventh C_{2v} isomer with a La inserted into the C_{13} ring and the fifth C_{2v} isomer with a La attached to the outside of the C_{13} ring are found to lie 3.36 eV and 3.09 eV higher in energy than the GM at M06-2X, respectively. Extensive BOMD simulations indicate that LaC_{13}^+ (1) is highly dynamically stable at both 800 K and 1000 K, with the small average root-mean-square-deviations of RMSD = 0.11 and 0.13 Å and maximum bond length deviations of MAXD = 0.31 and 0.36 Å, respectively (Fig. S7†). No high-lying isomers were observed during the dynamical simulations.

Replacing the La center in LaC_{13}^+ (1) with a Ca atom generates the charge-transfer neutral complex D_{13h} CaC_{13} (2). The Ca center in CaC_{13} (2) matches the C_{13} wheel ligand



perfectly both electronically and geometrically though it has a much lower Wiberg bond index of $\text{WBI}_{\text{Ca}} = 0.26$ than La in $\text{La}@\text{C}_{13}^+$ (1) where $\text{WBI}_{\text{La}} = 1.76$ (Table 1). The Ca–C coordination interaction with the low bond order of $\text{WBI}_{\text{Ca-C}} = 0.02$ in $\text{Ca}^{2+}@\text{C}_{13}^{2-}$ (2) is thus almost purely ionic. Using an Ac atom which has a larger atomic radius than La to replace La in $\text{La}@\text{C}_{13}^+$ (1), the slightly buckled $\text{C}_{13\text{v}} \text{Ac}@\text{C}_{13}^+$ (3) is generated in which the Ac atom lies 0.59 Å above the C_{13} ring, with the periphery C–C distances of $r_{\text{C-C}} = 1.29$ Å remaining basically unchanged. The experimentally observed prominent ScC_{13}^+ and YC_{13}^+ monocations¹⁵ have severely off-centered $\text{C}_{2\text{v}} \text{Sc}@\text{C}_{13}^+$ ($^1\text{A}_1$) (with CN = 8) and $\text{C}_{2\text{v}} \text{Y}@\text{C}_{13}^+$ ($^1\text{A}_1$) (with CN = 9) GM structures due to strong ring strains, respectively, while the open-shell CeC_{13}^+ possesses a slightly distorted GM $\text{C}_{2\text{v}} \text{Ce}@\text{C}_{13}^+$ ($^2\text{B}_2$) which has practically a $D_{13\text{h}}$ symmetry (Fig. S8†). With one more valence electron detached, the $\text{Ce}@\text{C}_{13}^{2+}$ dication iso-valent with $\text{La}@\text{C}_{13}^+$ (1) has indeed a perfect $D_{13\text{h}}$ GM (Fig. S8†).

It is natural to ask at current stage whether it is possible to form metal-centered monocyclic carbon wheel clusters with coordination numbers greater than thirteen (*i.e.*, CN > 13). We carefully checked the hypercoordination chemistry of the experimentally observed $\text{La}@\text{C}_{14}^+$ in this work. Although a bare C_{14} has a perfect $\text{C}_{7\text{h}}$ acetylenic structure,³⁹ with a La atom added in, the La-doped LaC_{14}^+ possesses the off-centered planar GM of $\text{C}_{2\text{v}} \text{La}@\text{C}_{14}^+$ (4) which has the actual coordination number of CN = 11 (Fig. 1 and S4†). The three C atoms on the top part of $\text{La}@\text{C}_{14}^+$ (4) with La–C distances great than 3.1 Å have the practically negligible La–C coordination bond orders (with $\text{WBI}_{\text{La-C}} \approx 0.00$). Using Ac, the largest actinide metal in the periodical table, to replace La,¹² an elongated planar $D_{2\text{h}} \text{Ac}@\text{C}_{14}^+$ (Fig. S8†) with CN = 12 is generated. A C_{14} ring is obviously too big in size to host a transition-metal atom at its geometrical center comfortably to form a perfect wheel complex $D_{nh} \text{M}@\text{C}_n$ with the same M–C coordination bonding distances. We conclude that CN = 13 is the highest coordination number in metal-centered monocyclic carbon wheel clusters $\text{M}@\text{C}_n^+$ with effective M–C coordination interactions.

Introducing certain numbers of B atoms into the carbon rings generates more structural diversities in B–C binary wheel ligands B_mC_n with CN ≤ 13. As examples, the metal-centered

monocyclic C–B binary wheel complexes $\text{Y}@\text{B}_6\text{C}_6^+$ (5) and $\text{Sc}@\text{B}_5\text{C}_6$ (6) in Fig. 1 and $\text{C}_{2\text{v}} \text{La}@\text{BC}_{12}$ in Fig. S8† as the GMs of the systems possess the coordination numbers of CN = 12, 11, and 13, respectively. These planar C–B binary wheel complexes have larger C–B and B–B periphery distances than the corresponding C–C distances in $\text{La}@\text{C}_{13}^+$ (1) because B has a larger covalent radius than C.

To interpret the high stabilities of these hypercoordinated planar species, we performed detailed NBO and molecular orbital analyses on $\text{La}@\text{C}_{13}^+$ (1), $\text{Y}@\text{B}_6\text{C}_6^+$ (5), and $\text{Sc}@\text{B}_5\text{C}_6$ (6). As tabulated in Table 1, the La center in $\text{La}@\text{C}_{13}^+$ (1) possesses the natural atomic charge of $q_{\text{La}} = +2.08$ |e|, electronic configuration of $\text{La}[\text{Xe}]4\text{f}^{0.43}5\text{d}^{0.41}6\text{s}^{0.02}$, and total Wiberg bond order of $\text{WBI}_{\text{La}} = 1.76$. The C atoms on the C_{13} wheel ligand have the total Wiberg bond orders of $\text{WBI}_{\text{C}} = 3.99$ and C–C bond orders of $\text{WBI}_{\text{C-C}} = 1.73$, revealing the cumulenic nature of the complex. Obviously, the La center donates its 6s electron almost completely to the C_{13} ligand. The La– C_{13} coordination

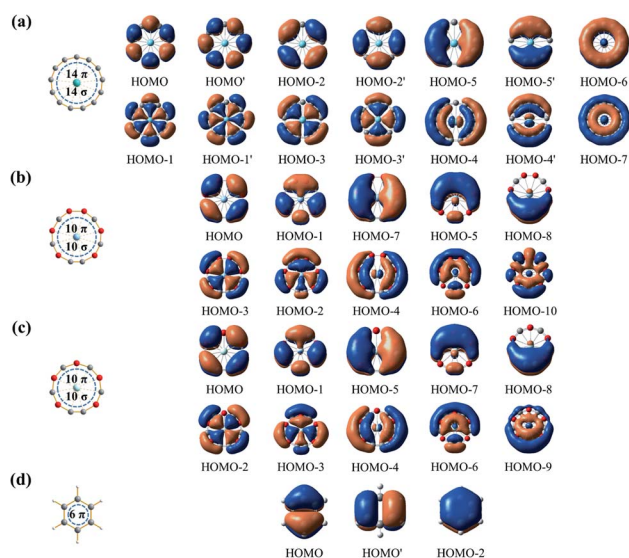


Fig. 2 Delocalized π - and σ -CMOs of (a) $\text{La}@\text{C}_{13}^+$ (1), (b) $\text{Y}@\text{B}_6\text{C}_6^+$ (5), and (c) $\text{Sc}@\text{B}_5\text{C}_6$ (6), in comparison with the delocalized π -CMOs of (d) $D_{6\text{h}} \text{C}_6\text{H}_6$.

Table 1 Calculated HOMO–LUMO gaps ΔE_{gap} /eV, natural atomic charges q_{M} , electronic configurations, and Wiberg bond indexes WBI_{M} of the metal centers M and Wiberg bond indexes of the M–C ($\text{WBI}_{\text{M-C}}$) and M–B ($\text{WBI}_{\text{M-B}}$) coordination interactions and NICS values 1.0 Å above the metal centers (NICS (1)) of the $\text{M}^{(x)}@\text{B}_m\text{C}_n^{k\pm}$ complex series (1–6) at M06-2X level

$\text{M}^{(x)}@\text{B}_m\text{C}_n^{k\pm}$	CN	ΔE_{gap} /eV	q_{M}	Electronic configurations of central metal M	WBI_{M}	$\text{WBI}_{\text{M-C}}$	$\text{WBI}_{\text{M-B}}$	NICS (1)
$D_{13\text{h}} \text{La}@\text{C}_{13}^+$ (1)	13	5.33	2.08	$[\text{Xe}] 4\text{f}^{0.43}5\text{d}^{0.41}6\text{s}^{0.02}$	1.76	0.14	—	−58.54
$D_{13\text{h}} \text{Ca}@\text{C}_{13}$ (2)	13	5.63	1.87	$[\text{Ar}] 3\text{d}^{0.09}4\text{s}^{0.03}4\text{p}^{0.01}$	0.26	0.02	—	−44.68
$\text{C}_{13\text{v}} \text{Ac}@\text{C}_{13}^+$ (3)	13	5.26	2.38	$[\text{Rn}] 5\text{f}^{0.19}6\text{d}^{0.35}7\text{s}^{0.03}$	1.22	0.10	—	−55.16
$\text{C}_{2\text{v}} \text{La}@\text{C}_{14}^+$ (4)	11	3.72	2.15	$[\text{Xe}] 4\text{f}^{0.28}5\text{d}^{0.50}6\text{s}^{0.03}$	1.64	0.07–0.16	—	−29.21
$\text{C}_{2\text{v}} \text{Y}@\text{B}_6\text{C}_6^+$ (5)	12	5.70	2.12	$[\text{Kr}] 5\text{s}^{0.06}4\text{d}^{0.70}5\text{p}^{0.01}$	1.67	0.10–0.22	0.09–0.12	−24.08
$\text{C}_{2\text{v}} \text{Sc}@\text{B}_5\text{C}_6$ (6)	11	5.32	1.94	$[\text{Ar}] 3\text{d}^{0.87}4\text{s}^{0.07}4\text{p}^{0.02}$	1.94	0.13–0.29	0.13–0.14	−29.62



interactions mainly originate from contributions involving the 5d and 4f atomic orbitals of the La center, as indicated in the degenerated π -HOMO/HOMO', π -HOMO-2/HOMO-2', σ -HOMO-1/HOMO-1', and σ -HOMO-3/HOMO-3 in Fig. 2(a). Although each La–C coordination interaction in La@C_{13}^+ (**1**) has a relatively low bond order ($\text{WBI}_{\text{La-C}} = 0.14$), the thirteen equivalent La–C coordination bonds function together to effectively stabilize the hypercoordinated cluster, making it the well-defined GM of the system observed solely in gas-phase experiments.^{13,14} Similar situations happen in Ac@C_{13}^+ (**3**), $\text{Y@B}_6\text{C}_6^+$ (**5**), and $\text{Sc@B}_5\text{C}_6$ (**6**).

The 14 totally delocalized canonical molecular orbitals (CMOs) of La@C_{13}^+ (**1**) are collectively shown in Fig. 2(a), including 7 delocalized π -CMOs and 7 delocalized σ -CMOs. Its remaining 13 σ -CMOs correspond to 13 two-center-two-electron (2c-2e) C–C σ bonds along the periphery of the C_{13} ligand (Fig. S9†). The degenerate f-type HOMO/HOMO', d-type HOMO-2/HOMO-2' and p-type HOMO-5/HOMO-5' and non-degenerate s-type HOMO-6 possess three, two, one, and zero nodal surfaces, respectively, forming an out-of-plane 14 π electron system matching the $4N_\pi + 2$ aromatic rule with $N_\pi = 3$. Similarly, the degenerate HOMO-1/HOMO-1', HOMO-3/HOMO-3', and HOMO-4/HOMO-4' and non-degenerate HOMO-7 form an in-plane 14 σ electron system matching the $4N_\sigma + 2$ aromatic rule with $N_\sigma = 3$. Such a unique 14 $\sigma + 14 \pi$ electronic configuration renders $\sigma + \pi$ dual aromaticity to La@C_{13}^+ (**1**), effectively stabilizing the monocation observed in experiments, similar to the situation in the $\sigma + \pi$ dually aromatic D_{10h} Ta@B_{10}^- which possesses a 10 $\sigma + 6 \pi$ electronic configuration.¹ It is noticed that metal-centered wheel D_{13h} La@C_{13}^+ (**1**) has the same numbers of delocalized σ and π electrons (14 $\sigma + 14 \pi$) as the highly stable ring-like acetylenic C_{7h} C_{14} .³⁹

As shown in Fig. 2(b) and (c), both the metal-centered monocyclic C–B binary wheel clusters $\text{Y@B}_6\text{C}_6^+$ (**5**) and $\text{Sc@B}_5\text{C}_6$ (**6**) have 5 delocalized π -CMOs and 5 delocalized σ -CMOs, forming an out-of-plane 10 π electron system conforming to the $4N_\pi + 2$ π -aromatic rule ($N_\pi = 2$) and an in-plane 10 σ electron system conforming to $4N_\sigma + 2$ σ aromatic rule ($N_\sigma = 2$). Such 10 $\sigma + 10 \pi$ electronic configurations make both $\text{Y@B}_6\text{C}_6^+$ (**5**) and $\text{Sc@B}_5\text{C}_6$ (**6**) $\sigma + \pi$ dually aromatic in nature, similar to but with more delocalized electrons than the previously reported Co@B_8^- and Ru@B_9^- with 6 $\sigma + 6 \pi$ delocalized electrons and Ta@B_{10}^- and Nb@B_{10}^- with 10 $\sigma + 6 \pi$ delocalized electrons.^{1,5–8}

The La– C_{13} coordination interactions in La@C_{13}^+ (**1**) mainly originate from d–p and f–p σ -coordination interactions involving the in-plane La $5d_{x^2-y^2}/5d_{xy}$ and $4f_{x(x^2-3y^2)}/4f_{y(y^2-3x^2)}$ atomic orbitals and C $2p_x/2p_y$ hybridized atomic orbitals, as demonstrated in the degenerated HOMO-3/HOMO-3' (5d–2p σ -coordination) and HOMO-1/HOMO-1' (4f–2p σ -coordination) in Fig. 2(a), respectively. Quantitatively, the La center contributes more to the delocalized in-plane σ -CMOs (2.81–7.63%) than to the delocalized out-of-plane π -CMOs (0.08–3.66%). The delocalized in-plane σ -CMOs thus dominate the La–C coordination bonding interactions. Similarly, the in-plane 4d–2p σ -coordination interactions (HOMO-2 and HOMO-3) in $\text{Y@B}_6\text{C}_6^+$ (**5**) and 3d–2p σ -coordination interactions (HOMO-2 and HOMO-3) in

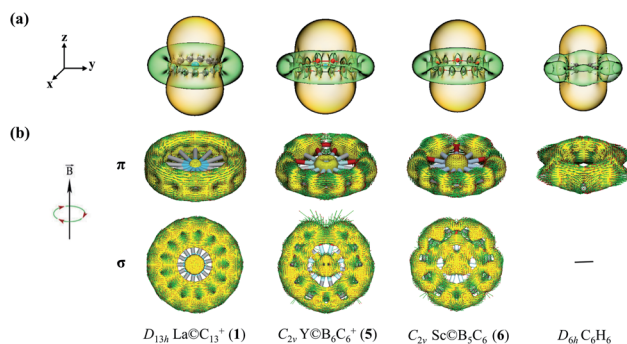


Fig. 3 (a) Calculated iso-chemical shielding surfaces (ICSSs) of La@C_{13}^+ (**1**), $\text{Y@B}_6\text{C}_6^+$ (**5**), and $\text{Sc@B}_5\text{C}_6$ (**6**), compared with that of aromatic benzene C_6H_6 . Yellow and green regions stand for chemical shielding and de-shielding areas, respectively. (b) Calculated π - and σ -ring current maps of La@C_{13}^+ (**1**), $\text{Y@B}_6\text{C}_6^+$ (**5**), and $\text{Sc@B}_5\text{C}_6$ (**6**), respectively, in comparison with the π -ring current map of D_{6h} C_6H_6 . The external magnetic field is perpendicular to the wheel plane. The red arrows represent directions and magnitudes of the ring currents at various positions on the ACID iso-surfaces.

$\text{Sc@B}_5\text{C}_6$ (**6**) dominate the metal–ligand interactions in the two 10 $\sigma + 10 \pi$ systems.

The aromatic nature of La@C_{13}^+ (**1**), $\text{Y@B}_6\text{C}_6^+$ (**5**), and $\text{Sc@B}_5\text{C}_6$ (**6**) is further evidenced by their calculated nucleus-independent chemical shift (NICS) values. Based on the calculated NICS-ZZ components, Fig. 3(a) depicts the ICSS surfaces of **1**, **5**, and **6** with the Z-axis perpendicular to the molecular planes to illuminate the chemical shielding around the metal centers, in comparison with that of the prototypical aromatic benzene (C_6H_6). Obviously, the space inside the C_{13} , B_6C_6 , or B_5C_6 rings in horizontal direction or within about 1.0 Å above the metal centers in vertical direction belong to chemical shielding regions with negative NICS-ZZ values (highlighted in yellow), while the chemical de-shielding areas with positive NICS values (highlighted in green) are located outside the wheel ligands in horizontal direction. Fig. 3(a) clearly shows the ICSS surfaces of these metal-centered planar complexes are exactly similar to that of the aromatic benzene.

Calculating the anisotropy of current-induced density (ACID)³⁴ is an effective approach to graphically display the ring currents induced by an external magnetic field in vertical directions perpendicular to the molecular planes. ACID can be decomposed into σ and π components separately. Fig. 3(b) clearly indicates the π -ring current maps of La@C_{13}^+ (**1**), $\text{Y@B}_6\text{C}_6^+$ (**5**), and $\text{Sc@B}_5\text{C}_6$ (**6**) are extremely similar to the corresponding π -ring current map of π -aromatic benzene C_6H_6 . Besides, in contrast to benzene which possesses no delocalized σ -electrons, La@C_{13}^+ (**1**), $\text{Y@B}_6\text{C}_6^+$ (**5**), and $\text{Sc@B}_5\text{C}_6$ (**6**) also exhibit strong σ -ring currents, rendering additional σ -aromaticity to stabilize the systems, as shown in Fig. 3(b) (see Fig. S10† for high-resolution π - and σ -ring current maps of **1**, **5**, and **6**). The observation of both σ - and π -diatropic ring currents in **1**, **5**, and **6** well supports the $\sigma + \pi$ dually aromatic nature of these planar hypercoordinated complexes.

Based on the planar hypercoordinated species discussed above, we develop a universal electronic design principle for $\sigma + \pi$



π dually aromatic metal-centered monocyclic boron, carbon, or boron-carbon binary wheel clusters $M^{(x)}@B_mC_n^{k\pm}$. There exist $m + n$ $2c-2e$ σ bonds along the periphery of the monocyclic B_mC_n wheel ligand. With each C atom providing two delocalized electrons and each B atom contributing one delocalized electron, the total number of the delocalized electrons in $M^{(x)}@B_mC_n^{k\pm}$ matches the requirement of $\sigma + \pi$ dual aromaticity of the system:

$$m + 2n + x \pm k = L \quad (L = 12, 16, 20, \text{ or } 28) \quad (1)$$

where L is the total number of delocalized σ and π electrons each matching the $4N + 2$ rule and x stands for the formal valence of the central atom M . Such an electronic design principle covers the previously observed D_{7h} $B@B_7^{2-}$, D_{8h} $B@B_8^-$, D_{9h} $Co@B_8^-$, and D_{9h} $Ru@B_9^-$ where $L = 12$ and $x = 3, 3, 3$, and 2 and D_{10h} $Ta@B_{10}^-$ and D_{10h} $Nb@B_{10}^-$ where $L = 16$ and $x = 5$ and 5 , respectively. For the currently discussed $La@C_{13}^+$ (1), $Ca@C_{13}$ (2), and $Ac@C_{13}^+$ (3), $L = 28$ and $x = 3, 2$, and 3 , while for $Y@B_6C_6^+$ (5) and $Sc@B_5C_6$ (6), $L = 20$ and $x = 3$ and 3 , respectively. The slightly buckled C_{13v} $Ac@C_{13}^+$ (3) follows the same electronic design principle though the Ac center in it slightly mismatches the C_{13} wheel ligand in geometry. Eqn (1) can be easily extended to $\sigma + \pi$ dually aromatic B–C–N ternary wheel complexes $M^{(x)}@B_mC_nN_l^{k\pm}$ where it reads: $m + 2n + 3l + x \pm k = 28$, as demonstrated in the cases of C_s $La@BNC_{11}^+$ and C_s $La@B_4N_4C_5^+$ (Fig. S8†) in which each N atom contributes three valence electrons to the delocalized systems. However, extensive test calculations indicate that inclusion B or N atoms in the wheel ligands does not help to improve the maximum coordination numbers of the systems.

The highly stable $La@C_{13}^+$ (1) with a wide HOMO–LUMO gap and fully occupied bonding inner-shell CMOs can be used as a super-hydrogen monocation (H^+) to form various substituted multi-nuclei complexes. Typical examples include C_{13v} $[La@C_{13}]X$ ($X = F, Cl, Br$) (7), D_{13h} $[La@C_{13}]^+L_2$ ($L = Ar, Kr$) (8), C_{2v} $[La@C_{13}]_2O$ (9), and C_{3v} $N[La@C_{13}]_3$ (10) (Fig. 4) which can be derived from the parent species $C_{\infty v}$ HX , $D_{\infty h}$ H^+L_2 , C_{2v} H_2O , and C_{3v} NH_3 by substituting H^+ monocation(s) with $La@C_{13}^+$ (1) unit(s), respectively, presenting the viable possibility to form complex compounds with multiple hypercoordinated metal centers.

Finally, as examples, the simulated IR, Raman, and UV-vis spectra of D_{13h} $La@C_{13}^+$ (1) and C_{2v} $Y@B_6C_6^+$ (5) are presented in Fig. S11† to facilitate their spectroscopic characterizations. $La@C_{13}^+$ (1) possesses highly simplified spectra due to its perfect D_{13h} symmetry. It has two main IR peaks at 39 (a_2'') and

866 (e_1') cm^{-1} , three Raman peaks at 272 (e_2'), 664 (a_1'), and 1280 (e_2') cm^{-1} , and three UV absorption peaks at 156 (A_1'), 174 (E_2'), and 200 (E_2') nm, respectively. C_{2v} $Y@B_6C_6^+$ (5) has more complicated spectra, with two main IR absorption peaks at 499 (b_1) and 588 (b_2) cm^{-1} , two major Raman scattering bands at 211 (b_2) and 623 (a_1) cm^{-1} , and five UV absorption bands around 134 (1B_2), 161 (1A_1), 191 (1B_2), 207 (1A_1), and 219 (1B_2) nm, respectively.

4. Conclusions

Extensive first-principles theory calculations performed in this work unveil the highest coordination numbers of $CN = 13$ in $La@C_{13}^+$ (1), $Ca@C_{13}$ (2), and $Ac@C_{13}^+$ (3), $CN = 12$ in $Y@B_6C_6^+$ (5), and $CN = 11$ in $La@C_{14}^+$ (4) and $Sc@B_5C_6$ (6) reported to date in planar species, effectively enriching the structural and bonding patterns in planar hypercoordination chemistry. $\sigma + \pi$ dually aromatic metal-centered monocyclic B–C binary wheel complexes $M^{(x)}@B_mC_n^{k\pm}$ follow the electronic design principle of $m + 2n + x \pm k = L$ ($L = 12, 16, 20$, or 28) which can be readily extended to more complicated systems containing other periphery atoms rather than B and C. The recent experimental identification of the sp -hybridized molecular carbon allotrope, π -aromatic C_{18} , induced by atom manipulations,⁹ presents the possibility to synthesize and characterize the $\sigma + \pi$ dually aromatic $La@C_{13}^+$ (1) and its complex compounds to open a new area in planar hypercoordination chemistry, catalysis, and materials science.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 T. R. Galeev, C. Romanescu, W. L. Li, L. S. Wang and A. I. Boldyrev, *Angew. Chem., Int. Ed.*, 2012, **51**, 2101–2105.
- 2 T. Heine and G. Merino, *Angew. Chem., Int. Ed.*, 2012, **51**, 4275–4276.
- 3 H. J. Zhai, A. N. Alexandrova, K. A. Birch, A. I. Boldyrev and L. S. Wang, *Angew. Chem., Int. Ed.*, 2003, **42**, 6004–6008.
- 4 C. Romanescu, T. R. Galeev, W. L. Li, A. I. Boldyrev and L. S. Wang, *Angew. Chem., Int. Ed.*, 2011, **123**, 9506–9509.
- 5 C. Romanescu, T. R. Galeev, W. L. Li, A. I. Boldyrev and L. S. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 9334–9337.
- 6 C. Romanescu, T. R. Galeev, W. L. Li, A. I. Boldyrev and L. S. Wang, *Acc. Chem. Res.*, 2013, **46**, 350–358.
- 7 C. Romanescu, T. R. Galeev, W. L. Li, A. I. Boldyrev and L. S. Wang, *J. Chem. Phys.*, 2013, **138**, 134315.
- 8 W. L. Li, C. Romanescu, T. R. Galeev, Z. A. Piazza, A. I. Boldyrev and L. S. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 165–168.

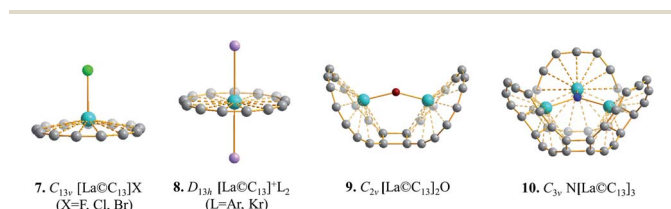


Fig. 4 Optimized structures of $[La@C_{13}]X$ (7) ($X = F, Cl, Br$), $[La@C_{13}]^+L_2$ (8) ($L = Ar, Kr$), $[La@C_{13}]_2O$ (9), and $N[La@C_{13}]_3$ (10) at M06-2X level.



- 9 K. Kaiser, L. M. Scriven, F. Schulz, P. Gawel, L. Gross and H. L. Anderson, *Science*, 2019, **365**, 1299–1301.
- 10 Z. Liu, X. Wang, T. Lu, A. Yuan and X. Yan, *ChemRxiv*, 2021, DOI: 10.26434/chemrxiv.14601168.v1.
- 11 Y. Jiang, Y. Wu, J. Deng and Z. Wang, *Phys. Chem. Chem. Phys.*, 2021, **23**, 8817–8824.
- 12 P. Pykkö and M. Atsumi, *Chem.–Eur. J.*, 2009, **15**, 12770–12779.
- 13 D. E. Clemmer, K. B. Shelimov and M. F. Jarrold, *J. Am. Chem. Soc.*, 1994, **116**, 5971–5972.
- 14 K. B. Shelimov, D. E. Clemmer and M. F. Jarrold, *J. Phys. Chem.*, 1995, **99**, 11376–11386.
- 15 R. Klingeler, P. S. Bechthold, M. Neeb and W. Eberhardt, *J. Chem. Phys.*, 2000, **113**, 4.
- 16 S. Roszak and K. Balasubramanian, *Chem. Phys. Lett.*, 1997, **264**, 80–84.
- 17 D. L. Strout and M. B. Hall, *J. Phys. Chem. A*, 1998, **102**, 641–645.
- 18 X. Chen, Y. F. Zhao, Y. Y. Zhang and J. Li, *J. Comput. Chem.*, 2019, **40**, 1105–1112.
- 19 D. J. Wales and H. A. Scheraga, *Science*, 1999, **285**, 1368–1372.
- 20 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 21 J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, *Comput. Phys. Commun.*, 2005, **167**, 103–128.
- 22 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.
- 23 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.
- 24 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650–654.
- 25 D. Feller, *J. Comput. Chem.*, 1996, **17**, 1571–1586.
- 26 L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li and T. L. Windus, *J. Chem. Inf. Model.*, 2007, **47**, 1045–1052.
- 27 M. J. Frisch, *et al.*, *Gaussian 16, Revision A.03*, Gaussian Inc., Wallingford, CT, 2016.
- 28 J. Čížek, *Adv. Chem. Phys.*, 1969, **14**, 35.
- 29 G. D. Purvis III and R. J. Bartlett, *J. Chem. Phys.*, 1982, **76**, 1910.
- 30 K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479–483.
- 31 H. J. Werner, *et al.*, *Molpro, version.1.*, 2012, (www.molpro.net).
- 32 P. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, *NBO 6.0*, 2013.
- 33 D. Geuenich, K. Hess, F. Köhler and R. Herges, *Chem. Rev.*, 2005, **105**, 3758–3772.
- 34 Povray, Persistence of vision raytracer, *POV-Ray 3.7*, <http://www.povray.org>.
- 35 S. Klod and E. Kleinpeter, *J. Chem. Soc., Perkin Trans. 2*, 2001, **2**, 1893–1898.
- 36 E. Kleinpeter, S. Klod and A. Koch, *J. Mol. Struct.*, 2007, **811**, 45–60.
- 37 T. Lu and F. W. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.
- 38 R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.*, 1996, **256**, 454–464.
- 39 S. Arulmozhiraja and T. Ohno, *J. Chem. Phys.*, 2008, **128**, 114301.

