

Sandwich-type transition metal complexes $[(\text{CBO})_n]_2\text{M}$ with carbon boronyl ligands $(\text{CBO})_n$ ($n=4-6$)

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Abstract

A density functional theory investigation on a series of sandwich-type transition metal complexes $[(\text{CBO})_n]_2\text{M}$ ($n=4-6$; M =transition metals) with carbon boronyls $(\text{CBO})_n$ as effective aromatic ligands has been presented in this work at B3LYP level. The ground-states of these complexes possess staggered D_{nd} symmetries, while the corresponding eclipsed D_{nh} structures exist as transition states with slightly higher energies (within 5.8 kJ/mol). Carbon boronyl complexes $[(\text{CBO})_n]_2\text{M}$ are confirmed to be much more stable than their boron carbonyl isomers $[(\text{BCO})_n]_2\text{M}$, which, on the other hand, take eclipsed ground-states with D_{nh} symmetries. The carbon boronyl complexes $[(\text{CBO})_n]_2\text{M}$ proposed in this work parallelize the well-known sandwich-type hydrocarbon complexes $[\text{C}_n\text{H}_n]_2\text{M}$ in coordination chemistry with boronyl groups $-\text{B}=\text{O}$ isolobal to $-\text{H}$ atoms in corresponding ligands.

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1. Introduction

In a recent paper [1], Wu and co-workers presented a series of monocyclic boron carbonyls $(\text{BCO})_n$ ($n=3-7$) at density functional theory (DFT) level, providing intriguing examples to derive new aromatic compounds from $(\text{CH})_n$ hydrocarbons using the isolobal relationship of a BCO fragment to a CH group. These planar monocyclic structures have been extended to $(\text{BCO})_n$ cages ($n=4-24$) in the latest development in the series [2]. In a comparative study [3], our group investigated the geometric and electronic properties of monocyclic carbon boronyls $(\text{CBO})_n$ ($n=3-7$). We found that monocyclic carbon boronyls $(\text{CBO})_n$ possess aromaticities and are systematically much more stable than their boron carbonyl isomers $(\text{BCO})_n$. The extra stability of $(\text{CBO})_n$ over $(\text{BCO})_n$ mainly originate from their first three occupied π orbitals delocalized over the central C_n polygons which are absent in boron carbonyls, while the three widely delocalized inner π orbitals (which are mainly composed of the contributions from the n $-\text{B}=\text{O}$ tails) help to keep the n $-\text{B}=\text{O}$ groups stay within the same plane as the central C_n rings. The calculated nucleus independent chemical

shift (NICS) indexes [4] indicate that $(\text{CBO})_n$ ($n=4-6$) carbon boronyls possess comparable aromaticities with cyclopentadienyl anion C_5H_5^- and benzene C_6H_6 . As C_6H_6 and C_5H_5^- are well-known planar organic ligands to transition metal atoms in sandwich-type complexes, this finding reminds us that, carbon boronyls $(\text{CBO})_n$, $(\text{CBO})_4^{2-}$, $(\text{CBO})_5^-$, and $(\text{CBO})_6$, which are all planar aromatic systems with 6π electrons, may serve as effective ligands to coordinate transition metal centers to form similar sandwich-type complexes. In this work, we present a DFT investigation on these possible novel structures. DFT evidences obtained indicate that planar carbon boronyls $(\text{CBO})_n$ ($n=4-6$) can serve as effective aromatic ligands to coordinate a wide range of transition metals in groups VB–VIII B of the periodic table to form stable sandwich-type complexes $[(\text{CBO})_n]_2\text{M}$. The $(\text{CBO})_n$ carbon boronyls proposed previously by this group [3] and their sandwich-type transition metal complexes $[(\text{CBO})_n]_2\text{M}$ investigated in this work are expected to be confirmed in future experiments to open a new branch of chemistry on carbon boronyls which may find important applications in both fundamental research and materials sciences.

2. Computational procedure

Initial structural optimizations, frequency analyses, and natural bonding orbital (NBO) analyses were performed with the hybrid DFT-B3LYP method [5] with the basis of

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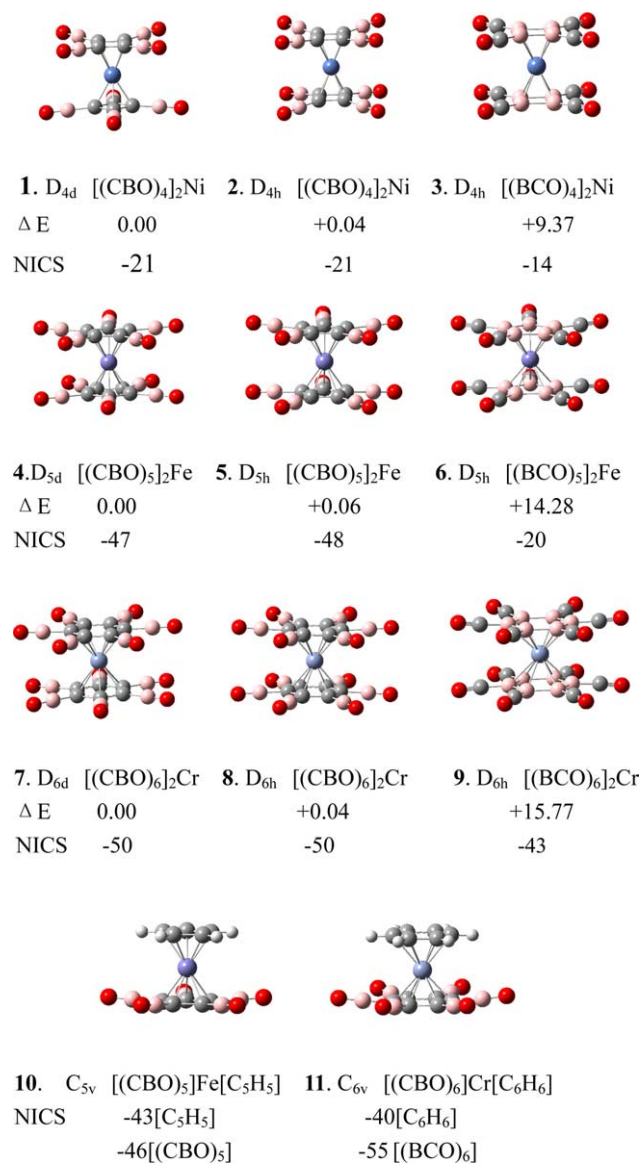


Fig. 1. Staggered structures of D_{nd} $[(CBO)_n]_2M$ neutral complexes ($n=4,5,6$; $M=Ni, Fe, Cr$) compared with their eclipsed isomers D_{nh} $[(CBO)_n]_2M$ and the corresponding boron carbonyl isomers D_{nh} $[(BCO)_n]_2M$ at BLYP/6-311+G(d) level, with the relative energies $\Delta E/eV$ and NICS values (ppm) indicated. Mixed sandwich-type complexes C_{5v} $[(CBO)_5]Fe[C_5H_5]$ (**10**) and $[(CBO)_6]Cr[C_6H_6]$ (**11**) are also shown for comparison.

6-31+G(d) for C, B, and O and the first-row transition metals and Lan12dz for the second- and third-row transition metal centers (Lan12dz contains a Los Alamos effective core potential for transition metals [6] and the combined basis will be denoted as 6-31+G(d)/Lan12dz hereafter). The optimized structures were finally refined at DFT-B3LYP with a bigger basis of 6-311+G(d) for the first row transition metal complexes and the obtained results proved to be quite insensitive to the bases employed. Based upon this observation, the B3LYP/6-31+G(d)/Lan12dz results obtained for complexes with the second- or third-row transition metals are directly used in this work without further optimizations. NICS values were calculated for ghost atoms located at the center of the planar $(CBO)_n$ ligands (about 1.7 Å from the transition metal centers)

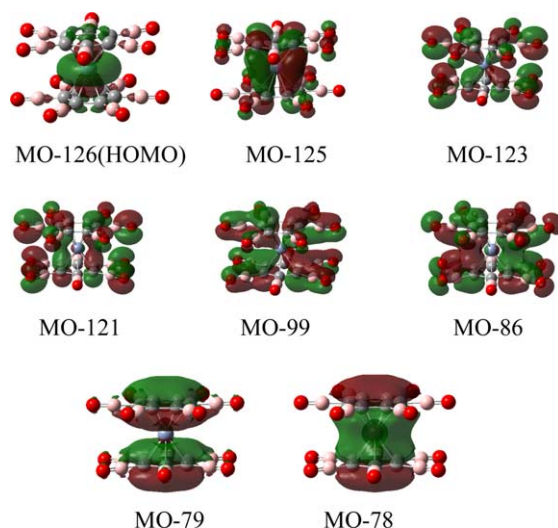


Fig. 2. MO pictures of D_{6d} $[(CBO)_2]Cr$ at DFT-B3LYP/6-311+G(d) level mainly involving the Cr 3d orbitals and the delocalised π orbitals of the ligands. For doubly degenerate orbitals, only one of them is depicted.

to assess the ring current effects of the systems. The optimized staggered structures of $[(CBO)_n]_2M$ neutrals ($n=4,5,6$; $M=Ni, Fe, Cr$) are depicted in Fig. 1, compared with their eclipsed isomeric structures and the corresponding boron carbonyl isomers with the relative energies and NICS values indicated. Fig. 2 shows the molecular orbital (MO) pictures of $[(CBO)_6]_2Cr$ involving the partially filled 3d orbitals of Cr center and typical π orbitals of the $(CBO)_6$ ligands. As examples, the calculated infrared (IR) spectra of D_{4d} $[(CBO)_4]_2Ni$, D_{5d} $[(CBO)_5]_2Fe$, and D_{6d} $[(CBO)_6]_2Cr$ are shown in Fig. 3 to facilitate future spectroscopic measurements. The bond lengths, lowest vibrational frequencies, HOMO energies, HOMO–LUMO energy gaps, and natural atomic charges of D_{nd} $[(CBO)_n]_2M$ complexes are summarized in Table 1. Results obtained for $[(CBO)_4]_2Ni$, D_{5d} $[(CBO)_5]_2Fe$, and D_{6d} $[(CBO)_6]_2Cr$ neutrals at PBE1PBE/6-311+G(d) [7] level have also been provided in Table 1 for comparison. It is obvious that B3LYP and PBE1PBE density functional methods produce essentially the same structures for these complexes. All the calculations in this work were performed employing the GAUSSIAN 03 program [8].

3. Results and discussion

As can be seen from Fig. 1, first-row transition metal complex $[(CBO)_n]_2M$ ($n=4, 5, 6$; $M=Ni, Fe, Cr$) containing two carbon boronyl $(CBO)_n$ ligands all turned out to favor the staggered sandwich-type D_{nd} structures slightly over their eclipsed D_{nh} isomers, while the corresponding boron carbonyl complexes $[(BCO)_n]_2M$, on the other hand, prefer the eclipsed D_{nh} structures to the staggered D_{nd} ones. The staggered \rightarrow eclipsed structural transitions of $[(CBO)_n]_2M$ complexes are practically free rotations of the ligands about the molecular axes of the systems with very low energy barriers (<0.06 eV or 5.8 kJ/mol), similar to the lowest-energy vibrational modes of $[C_5H_5]_2Fe$ and $[C_6H_6]_2Cr$. In fact, $[(CBO)_5]_2Fe$ (**4**) and

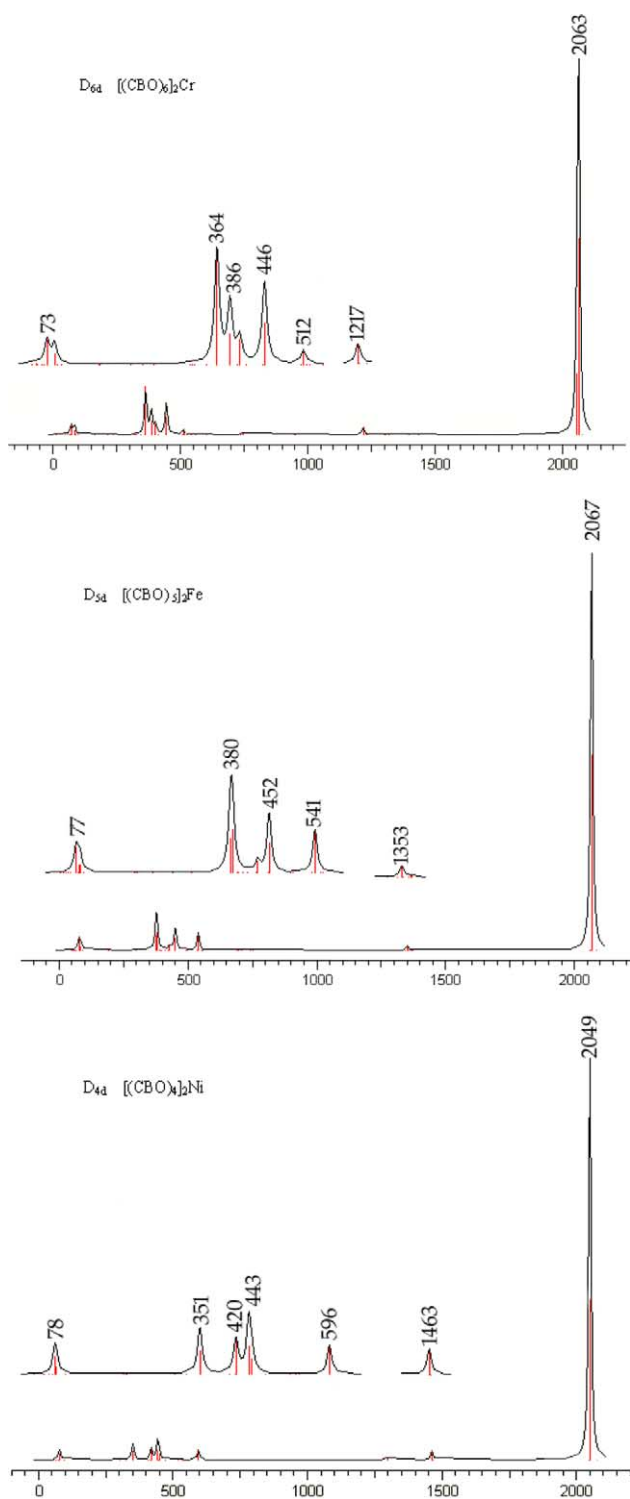


Fig. 3. Calculated IR spectrum of D_{4d} $[(CBO)_4]_2Ni$, D_{5d} $[(CBO)_5]_2Fe$, and D_{6d} $[(CBO)_6]_2Cr$ at FT-B3LYP/6-311+G(d) level.

$[(CBO)_6]_2Cr$ (**7**) are isolobal to $[C_5H_5]_2Fe$ and $[C_6H_6]_2Cr$, respectively. As pointed out in our previous report [3], monocyclic carbon boronyls $(CBO)_n$ at D_{nh} symmetries are much more stable than their boron carbonyl isomers $(BCO)_n$ in thermodynamics. Their transition metal complexes $[(CBO)_n]_2M$ studied in this work follow the same trend: carbon boronyl complexes $[(CBO)_n]_2M$ lie much lower in

energies than their boron carbonyl isomers $[(CBO)_n]_2M$, as clearly indicated in Fig. 1 by the huge DFT energy differences of 9.37, 14.28, and 15.77 eV between $[(CBO)_4]_2Ni$ (**1**), $[(CBO)_5]_2Fe$ (**4**), and $[(CBO)_6]_2Cr$ (**7**) and their corresponding $[(BCO)_n]_2M$ isomers, respectively. This further strengthens our statement that carbon boronyls possess higher viable possibility to be synthesized in experiments than their boron carbonyl isomers [3]. Second- and third-row transition metal neutral complexes $[(CBO)_4]_2Pd$, $[(CBO)_5]_2M$ ($M=Ru, Os$), and $[(CBO)_6]_2M$ ($M=Mo, W$) follow the same structural patterns and energy orders as first-row transition metal complexes. The only exception observed occurs to $[(CBO)_6]V^-$ monoanion, which slightly favors an eclipsed D_{6h} structure over its D_{6d} isomer within the accuracy of the DFT method employed in this work. Concerning the bond lengths and bond orders of these complexes, the prototypic D_{5d} $[(CBO)_5]_2Fe$ (**4**) possesses the normal bond lengths of $r_{Fe-C}=2.104$, $r_{C-C}=1.440$ Å, $r_{C-B}=1.525$ Å, and $r_{B-O}=1.199$ Å, with the corresponding Wiberg bond indices (WBIs) of $WBI_{Fe-C}=0.28$, $WBI_{C-C}=1.23$, $WBI_{C-B}=0.88$, and $WBI_{B-O}=2.00$, respectively. The total atomic Wiberg bond indices are $WBI_{Fe}=3.03$, $WBI_C=3.86$, $WBI_B=2.94$, and $WBI_O=2.07$, again, satisfying the bonding requirements of the component atoms. However, the mixed sandwich-type complexes C_{5v} $[(CBO)_5]Fe[C_5H_5]$ (**10**) and C_{6v} $[(CBO)_6]Cr[C_6H_6]$ (**11**) follow the symmetries of their parent complexes of D_{5h} $(C_5H_5)_2Fe$ and D_{6h} $(C_6H_6)_2Cr$ by taking eclipsed ground-state structures with the Fe–C bond lengths of $r_{Fe-C}(C_5H_5)=2.082$ Å and $r_{Fe-C}(C_5B_5O_5)=2.078$ Å in (**10**) and $r_{Cr-C}(C_6H_6)=2.238$ Å and $r_{Cr-C}(C_6B_6O_6)=2.148$ Å in (**11**), while their staggered isomers serve as transition states lying 3.18 and 2.91 kJ/mol higher in energies, respectively. These closely comparable M–C bond lengths indicate that $(CBO)_n$ and C_nH_n units serve as similar ligands in these mixed complexes, with the metal centers M lying slightly closer to the $(CBO)_n$ sides. As indicated in Table 1, all the optimized structures possess negative HOMO energies greater than -3.77 eV and HOMO–LUMO energy gaps bigger than 1.71 eV, providing further evidences to support the stability of these complexes. Detailed parameters obtained for other $[(CBO)_n]_2M$ complexes can be found in Table 1.

It is well known that both D_{5h} $[C_5H_5]_2Fe$ and D_{6h} $[C_6H_6]_2Cr$ complexes favor eclipsed structures over staggered geometries in gaseous phases. Why their carbon boronyl isolobals $[(CBO)_n]_2M$ prefer staggered structures? D_{4d} $[(CBO)_4]_2Ni$, D_{5d} $[(CBO)_5]_2Fe$, and D_{6d} $[(CBO)_6]_2Cr$ possess the transition-metal–carbon (M–C) distances of $r_{Ni-C}=2.025$, $r_{Fe-C}=2.104$, and $r_{Cr-C}=2.219$ Å, well in agreement in corresponding bond lengths of $r_{Ni-C}=2.008$ Å in D_{4h} $[C_4H_4]_2Ni$, $r_{Fe-C}=2.078$ Å in D_{5h} $[C_5H_5]_2Fe$, and $r_{Cr-C}=2.173$ Å in D_{6h} $[C_6H_6]_2Cr$ at the same DFT level, respectively. These calculated DFT values also agree well with the measured Fe–C distance of 2.06 Å in D_{5h} $[C_5H_5]_2Fe$ and Cr–C distance of 2.15 Å in $[C_6H_6]_2Cr$. The major differences between $[(CBO)_n]_2M$ and $[C_nH_n]_2M$ exit in their atomic charge distributions. It is the strong Coulomb repulsion between the two parallel $(CBO)_n$ ligands around the coordination center M that

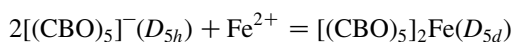
Table 1
 Calculated bond lengths ($r/\text{\AA}$), the lowest vibrational frequencies ($\nu_{\min}/\text{cm}^{-1}$), HOMO energies ($E_{\text{HOMO}}/\text{eV}$), HOMO–LUMO energy gaps (ΔE_{gap}), and the natural atomic charges ($q_X/|e|$) ($X = \text{C}, \text{B}, \text{and O}$) of $[(\text{CBO})_n]_2\text{M}$ complexes with D_{nd} or D_{nh} symmetries at B3LYP/6-311 + G(d) level

$[(\text{CBO})_n]_2\text{M}$	$r_{\text{M-C}}$	$r_{\text{C-C}}$	$r_{\text{C-B}}$	$r_{\text{B=O}}$	ν_{\min}	E_{HOMO}	ΔE_{gap}	q_{C}	q_{B}	q_{O}
$D_{4d} [(\text{CBO})_4]_2\text{Ni}$	2.025 (1.994)	1.468 (1.463)	1.515 (1.515)	1.201 (1.200)	+13	-9.10 (-9.40)	3.55 (4.07)	-0.45 (-0.45)	+1.03 (+1.03)	-0.69 (-0.69)
$D_{4d} [(\text{CBO})_4]_2\text{Co}^-$	2.009	1.471	1.503	1.208	+19	-5.07	4.46	-0.49	+1.05	-0.76
$D_{4d} [(\text{CBO})_4]_2\text{Pd}$	2.220	1.470	1.516	1.207	+12	-8.77	3.21	-0.46	+1.09	-0.73
$D_{5d} [(\text{CBO})_5]_2\text{Fe}$	2.104 (2.068)	1.440 (1.435)	1.525 (1.525)	1.199 (1.197)	+18	-9.67 (-10.11)	4.73 (5.54)	-0.39 (-0.39)	+1.04 (+1.04)	-0.68 (-0.68)
$D_{5d} [(\text{CBO})_5]_2\text{Mn}^-$	2.121	1.444	1.513	1.205	+7	-4.66	4.22	-0.43	+1.07	-0.74
$D_{5d} [(\text{CBO})_5]_2\text{Co}^+$	2.105	1.441	1.543	1.195	+23	-14.00	3.95	-0.36	+1.02	-0.62
$D_{5d} [(\text{CBO})_5]_2\text{Ru}$	2.250	1.446	1.526	1.205	+17	-9.73	4.91	-0.41	+1.10	-0.72
$D_{5d} [(\text{CBO})_5]_2\text{Os}$	2.239	1.451	1.527	1.205	+13	-9.58	5.23	-0.43	+1.11	-0.72
$D_{6d} [(\text{CBO})_6]_2\text{Cr}$	2.219 (2.172)	1.433 (1.428)	1.533 (1.533)	1.199 (1.197)	+15	-8.85 (-9.20)	3.37 (3.88)	-0.37 (-0.37)	+1.04 (+1.04)	-0.67 (-0.67)
$D_{6h} [(\text{CBO})_6]_2\text{V}^-$	2.263	1.438	1.525	1.204	+31	-3.77	1.71	-0.43	+1.06	-0.73
$D_{6d} [(\text{CBO})_6]_2\text{Mn}^+$	2.208	1.430	1.542	1.195	+19	-13.53	4.51	-0.33	+1.02	-0.62
$D_{6d} [(\text{CBO})_6]_2\text{Mo}$	2.353	1.439	1.536	1.204	+4	-8.32	2.64	-0.26	+1.06	-0.71
$D_{6d} [(\text{CBO})_6]_2\text{W}$	2.340	1.441	1.536	1.204	+5	-8.05	2.27	-0.28	+1.06	-0.71

The values obtained for $\text{M} = \text{Ni}, \text{Fe}, \text{and Cr}$ at PBE1PBE/6-311 + G(d) level are also provided in parentheses for comparison.

causes the $D_{nh} \rightarrow D_{nd}$ structural transitions in $[(\text{CBO})_n]_2\text{M}$ complexes. For example, $D_{5d} [(\text{CBO})_5]_2\text{Fe}$ carries the natural atomic charges of C $-0.39|e|$, B $+1.04|e|$, and O $-0.68|e|$, while its isolobal $D_{5h} [\text{C}_5\text{H}_5]_2\text{Fe}$ possesses much lower atomic charges of C $-0.25|e|$ and H $+0.22|e|$. These atomic charges, especially the high positive charges on B atoms and negative charges on O atoms, exert strong enough static repulsions to force the two $(\text{CBO})_5^-$ ligands to rotate to D_{5d} positions. As shown in Table 1, very similar charge distributions exist in the whole $[(\text{CBO})_n]_2\text{M}$ complex series. It is also interesting to notice that $-\text{B}=\text{O}$ groups in $[(\text{CBO})_n]_2\text{M}$ possess the approximate net charge values of $+0.30|e|$, comparable with the positive charges of H atoms which have the averaged values of $+0.22|e|$ in $[\text{C}_n\text{H}_n]_2\text{M}$ series. Obviously, the $-\text{B}=\text{O}$ groups in $[(\text{CBO})_n]_2\text{M}$, which are isolobal to $-\text{H}$ atoms in $[\text{C}_n\text{H}_n]_2\text{M}$, donate partial electrons to the C_n central rings which coordinate the transition metal centers M in $D_{nd} [(\text{CBO})_n]_2\text{M}$ complexes.

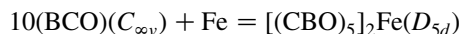
As all the component atoms of C, B, and O in $(\text{CBO})_n$ are fully satisfied in their bonding requirements, $(\text{CBO})_n$ possess the highest stabilities in their isomers with the stability order of $(\text{CBO})_n > (\text{BCO})_n > (\text{COB})_n$ ($n = 4-6$). For instances, $(\text{CBO})_5^-$ is 10.36 and 16.92 eV more stable than its isomer $(\text{BCO})_5^-$ and $(\text{COB})_5^-$ at DFT, respectively. With such huge energy differences between these isomers, ligand isomerizations of $[(\text{CBO})_n]_2\text{M}$ complexes are almost impossible. Concerning the stabilities of these sandwich-type complexes towards various dissociation channels, the DFT energy changes of the following sample processes are calculated:



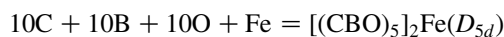
$$\Delta E = -1745.1 \text{ kJ/mol};$$



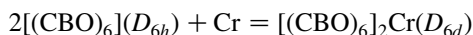
$$\Delta E = -682.9 \text{ kJ/mol};$$



$$\Delta E = -5916.6 \text{ kJ/mol};$$



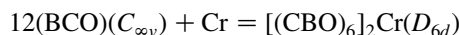
$$\Delta E = -17664.7 \text{ kJ/mol};$$



$$\Delta E = -153.1 \text{ kJ/mol};$$



$$\Delta E = -123.6 \text{ kJ/mol};$$



$$\Delta E = -6952.7 \text{ kJ/mol};$$



$$\Delta E = -21050.7 \text{ kJ/mol}.$$

in which, the ground-state of linear BCO is quadruplet [9,10]. These negative formation energies indicate that $[(\text{CBO})_n]_2\text{M}$ complexes are stable in thermodynamics towards the dissociation processes discussed above. However, it should be pointed out that, carbon boronyls $(\text{CBO})_n$ are weaker ligands to transition metals than typical hydrocarbons C_nH_n , as demonstrated in the following $(\text{CBO})_n/\text{C}_n\text{H}_n$ ligand exchange reactions:



$$\Delta E = -509.5 \text{ kJ/mol}$$



$$\Delta E = -144.8 \text{ kJ/mol.}$$

This implies that mixed sandwich-type complexes $[(\text{CBO})_n]\text{-M}[\text{C}_n\text{H}_n]$ are possible species to be targeted in experiments. Detailed kinetic studies of the fragmentation processes and ligand-exchange reactions of these carbon boronyl complexes are beyond the reach of available computing resources.

The stability of $[(\text{CBO})_n]_2\text{M}$ complexes originate from their bonding patterns involving effective interactions between the partially filled d orbitals of the transition metal centers M and the delocalized π orbitals of the $(\text{CBO})_n$ ligands, similar to the bonding situations in the corresponding $[\text{C}_n\text{H}_n]_2\text{M}$ complexes. In the case of D_{6d} $[(\text{CBO})_6]_2\text{Cr}$ (see Fig. 2), the HOMO (MO-126) mainly consists of the contribution of Cr $3d_{z^2}$, the degenerate MO-125 and MO-124 involve Cr $3d_{xy}$ and $3d_{x^2-y^2}$, while the degenerate MO-123 and MO-122 are mainly composed of the Cr $3d_{xz}$ and $3d_{yz}$. The degenerate MO-121 and MO-120, degenerate MO-99 and -98, degenerate MO-86 and -85, and MO-79 and -78 represent typical in-phase and out-of-phase overlaps of the delocalized π orbitals of the two D_{6h} $(\text{CBO})_6$ ligands perpendicular to the ligand planes [3]. The delocalized σ orbitals along the peripheries of C_n rings are found to be well maintained in $[(\text{CBO})_n]_2\text{M}$ complexes with more or less distortions. The negative NICS values calculated for $[(\text{CBO})_n]_2\text{M}$ complexes depicted in Fig. 1 are comparable with the corresponding values of NICS = -46 ppm for $[\text{C}_5\text{H}_5]_2\text{Fe}$ and -48 ppm for $[\text{C}_6\text{H}_6]_2\text{Cr}$, indicating that the ring current effects at the centers of the $[(\text{CBO})_n]$ ligands in $[(\text{CBO})_n]_2\text{M}$ complexes are similar to that of C_nH_n ligands in the well-known $[\text{C}_5\text{H}_5]_2\text{Fe}$ and $[\text{C}_6\text{H}_6]_2\text{Cr}$. The comparable NICS values obtained for ghost atoms at the two ends of the mixed sandwich complexes of $[(\text{CBO})_5]\text{Fe}[\text{C}_5\text{H}_5]$ (**10**) and $[(\text{CBO})_6]\text{Cr}[\text{C}_6\text{H}_6]$ (**11**) (see Fig. 1) further support the similarities between carbon boronyl ligands $[(\text{CBO})_n]$ and hydrocarbon ligands $[\text{C}_n\text{H}_n]$ in these sandwich-type complexes.

The calculated IR spectra of D_{4d} $[(\text{CBO})_4]_2\text{Ni}$, D_{5d} $[(\text{CBO})_5]_2\text{Fe}$, and D_{6d} $[(\text{CBO})_6]_2\text{Cr}$ turned out to be similar in general shapes (see Fig. 3), with the strongest absorptions peaking at 2049, 2067, and 2063 cm^{-1} , respectively, and two weaker absorption bands located at lower frequencies with much lower intensities. The strongest IR peaks of these complexes all originate from the stretching vibrational modes of the $2n$ B=O bonds in slightly different environments. The symmetrical breathing vibrations of C_4 , C_5 , and C_6 rings at the centers of the corresponding $(\text{CBO})_n$ ligands possess the vibrational frequencies of 1463, 1353, and 1217 cm^{-1} , respectively, in decreasing energies with increasing ring sizes. The three weaker absorption peaks at 351, 380, and 364 cm^{-1} mainly involve vertical or horizontal movements of the central metal atoms M in D_{4d} $[(\text{CBO})_4]_2\text{Ni}$, D_{5d} $[(\text{CBO})_5]_2\text{Fe}$, and D_{6d} $[(\text{CBO})_6]_2\text{Cr}$, respectively.

4. Summary

The monocyclic carbon boronyl molecules $(\text{CBO})_n$ proposed previously by this group [3] have been employed to design new sandwich-type complexes $[(\text{CBO})_n]_2\text{M}$ ($n=4-6$) at DFT level in this work. The results obtained provide a parallelizing complex series to the well-known $[\text{C}_5\text{H}_5]_2\text{Fe}$ and $[\text{C}_6\text{H}_6]_2\text{Cr}$ systems in coordination chemistry. Derivatives with various substituting groups and multiple metal centers are possible systems to be studied. Kinetic studies on the formation processes of these systems form interesting future research topics. It is anticipated that experimental characterizations of -B=O-containing systems may open a new area of boronyl chemistry.

Acknowledgements

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