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Theoretical study on [3]- and [4]radialene complexes CpM($C_{2n}H_{2n}$) (n = 3, 4; M = Sc~Ni): Special metal-aromatic interaction along with metal-alkene bonds

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ABSTRACT

The coordination and electron configuration of radialene complexes CpM($C_{2n}H_{2n}$) (n = 3, 4) are investigated. For M = Sc, Ti, Fe, Co, Ni, the ground states of CpM($C_{2n}H_{2n}$) are low-spin states (singlet or doublet), while for M = V, Cr, Mn, the ground states are high-spin states (triplet or quartet). For M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, [3]radialene in the ground states of CpM(C_6H_6) are η^6-, η^6-, η^6-, η^4-, η^4-, η^4-, η^4-, and η^2-coordinated; and [4]radialene in the ground states of CpM(C_8H_8) are η^8-, η^8-, η^6-, η^4-, η^4-, η^4-, η^4-, and η^2-coordinated, respectively. Between metal atom and radialene in CpM($C_{2n}H_{2n}$), the metal-alkene interactions, which are caused by the exocyclic C–C π-bonds that donate the lone pair electrons to the empty d-orbitals of metal atom, are dominant and fundamental. Besides, the special π-backbonding metal-aromatic interactions, which is overlapped by the lone pair on metal atom and the empty 2π-aromatic orbital on the cyclic C_3 or C_4 ring of [n]radialenes, may also exist in some ground states of CpM($C_{2n}H_{2n}$) complexes.

1. Introduction

[n]Radialenes ($C_{2n}H_{2n}$) are cyclic hydrocarbons containing n cross-conjugated exocyclic double bonds adjacent to the n member ring [1]. The synthetic approaches and chemical properties of radialenes have been focused on by various theoretical and experimental researches [2–7]. Although [3]-, [4]- and [6]radialene have been synthesized nearly forty years ago [2–4], the synthetic methods for radialenes were still continually updated [5]radialene, which was considered as the missing link for several decades, has just been finally obtained via the synthesis and decomplexation of the bis-Fe(CO)$_3$ coordinated complex of [5]radialene [8]. The unique structures of radialenes also aroused strong interests on their geometry, conjugation, as well as aromaticity [9–12]. Besides, much concerns were put on the potential utility of radialenes as building blocks for materials such as polymers, organic conductors and ferromagnets [1,5,13].

The individual characters for radialenes are the exocyclic double bonds, while their isomers containing cross-conjugated monocyclic double bonds in the carbon ring are classified as annulenes, e.g. [6]annulene (benzene, C_6H_6) and [8]annulene (cyclooctatetraene, C_8H_8). Annulenes have been well-known as a kind of important and common ligands in organometallic chemistry. As reported, [6]annulene basically acts as planar η^6-coordinated ligand in sandwiches, e.g. CpMn(η^6-C_6H_6) and Cr(η^6-C_6H_6)$_2$ [14,15], while [8]annulene could be planer or bent with variable hapticity in sandwiches due to its flexible structure, e.g. U(η^8-C_8H_8)$_2$, CpTi(η^8-C_8H_8), CpCr(η^6-C_8H_8), CpCo($\eta^{2,2}$-C_8H_8), and CpCo($\eta^{2,2}$-C_8H_8) [16–21]. In many cases, the whole molecules or some local areas of annulenes would act as aromatic ligands in their coordinated organometallic complexes. Besides, dendralenes, also with chemical formula as $C_{2n}H_{2n}$, are the isomers containing acyclic cross-conjugated double bonds, such as [3]dendralene (C_6H_6) and [4]dendralene (C_8H_8) [22,23]. Although the metal complexes of dendralenes has not been widely investigated like those of annulene. The branched dendralenes with 1,3-butadiene fragment are also ligand in the tricarbonyliron complexes of [3]dendralene, [4]dendralene, and etc. [24,25]. As [n]radialenes have the same chemical formula as $C_{2n}H_{2n}$ and different type of cross-conjugated C–C double bonds with [2n]annulenes and [2n]dendralenes, it is of interest how different the radialenes act as ligands in their coordinated

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complexes. Whether radialenes act as simple alkene ligand or aromatic ligand is intriguing.

Herein we present a theoretical study on the coordination mode of [3]- and [4] radialene complexes $CpM(C_{2n}H_{2n})$ (n = 3, 4; M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni; Cp = C_5H_5). The singlet and triplet isomers for M = Sc, V, Mn and Co, as well as the doublet and quartet isomers for M = Ti, Cr, Fe and Ni are considered.

2. Theoretical methods

The geometries of all structures were fully optimized using the density functional theory methods PBEPBE and BPW91 with TZVP basis set [26–31]. Harmonic vibrational frequencies are calculated to ensure the correct minima. To obtain more reliable energy, the single piont energies of all the structures are performed at PBEPBE/aug-cc-pvdz and BPW91/aug-cc-PVDZ levels based on the optimized geometries at PBEPBE/TZVP and BPW91/TZVP levels, respectively [32]. The natural localized molecular orbitals (NLMO) and nuclear independent chemical shift (NICS) of selected molecules are provided by NBO and NMR analyses. All the above calculations are performed using the Gaussian 09 program package [33]. Mayer bond orders, Shannon aromaticity (SA) index and Multicenter bond index are obtained using Multiwfn program [34].

3. Results and discussion

3.1. The aromaticity of free [n]radialenes (n = 3, 4)

[n]radialenes (n = 3, 4) are assessed to be non-aromatic [9,10]. Although the planar equilateral dianionic [3]radialene has aromatic C_3 ring, it is not a local minimum with three imaginary frequencies. Besides, the planar equilateral dianionic [4]radialene is reported to have no significant aromaticity [9].

At PBEPBE/TZVP level, the calculated NICS(1)_ZZ values of [3]radialene, [4]radialene, the dianionic [3]radialene and the dianionic [4]radialene are −13.44, 2.46, −17.22 and −1.35, respecively. The NICS(1)_ZZ values of −13.44 and −17.22 for [3]radialene and the dianionic [3]radialene are very close to the previously reported values of −13.8 and −17.6 [10]. The dianionic [3]radialene has the lowest NICS(1)_ZZ value, but it is also not a local minimum. [4]radialene should not be aromatic because of the positive NICS(1)_ZZ value.

Moreover, the orbital analyses suggest that free [3]radialene has no traditional aromaticity. Although there were no previous reports involving the comparision of [3]radialene and guanidinium cation $[C(NH_2)_3]^+$, infact the NLMOs and MOs of [3]radialene is somehow similar with those of $[C(NH_2)_3]^+$, which is described to be Y-aromatic [35]. Fig. 1 describes the NLMOs and MOs of the conjugated π-bonding of [3]radialene and $[C(NH_2)_3)]^+$. The Y-aromaticity of $[C(NH_2)_3]^+$ relys on the cross-conjugation through the central carbon atom, while the cross-conjugation of [3]radialene occurs through the central cycilc carbon ring. If considering the central cycilc carbon ring as a unit, the aromaticity of [3]radialene would be similar with the case of $[C(NH_2)_3)]^+$. Nevertheless, [3]radialene is still lack of the independent cyclic π-bond. Whether Y-aromatic or not, [3]radialene has no traditional aromaticity.

3.2. The coordination of $CpM(C_6H_6)$ complexes

The possible hapticity of η^2, η^4, and η^6 of [3]radialene are considered for the optimization of $CpM(C_6H_6)$ isomers, only the local minima are provided herein. Fig. 2 shows the geometries and relative energies of $CpM(C_6H_6)$ isomers. The bond distances are listed in Table S1 of the supporting information. To clearly indicate the spin states, the singlet, doublet, triplet and quartet are represented as S, D, T and Q, respectively. For M = Sc, Ti, Fe, Co, Ni, the ground states of $CpM(C_6H_6)$ are low-spin states (singlet or doublet), while for M = V, Cr, Mn, the ground states are high-spin states (triplet or quartet). Since the relative energies of $CpM(C_{2n}H_{2n})$ isomers are close to each other obtained under PBEPBE and BPW91 methods, only the values obtained at PBEPBE/aug-cc-pVDZ level are used in the following discussions.

The natural localized molecular orbitals (NLMO) [36] of the ground states of $CpM(C_6H_6)$ at PBEPBE/TZVP level are shown in Fig. 3. NLMOs are semi-localized MOs that adopt the characteristic bonding pattern of a localized Lewis structure. Compared with molecular orbital (MO) and natural bond orbital (NBO), NLMO could provide a more intuitive isovalue surface on coordinated interactions for organometallic complexes.

3.2.1. $CpSc(C_6H_6)$ and $CpTi(C_6H_6)$

$CpSc(C_6H_6)$ and $CpTi(C_6H_6)$ only have η^6-coordinated isomers. At PBEPBE/aug-cc-pVDZ level, the ground states of singlet $CpSc(C_6H_6)$-1S and doublet $CpTi(C_6H_6)$-1D are 40.1 and 37.0 kcal/mol lower in energy than the triplet $CpSc(C_6H_6)$-2T and quartet $CpTi(C_6H_6)$-2D, respectively.

As shown in Fig. 2, the NLMO-1~3 of $CpSc(C_6H_6)$-1S and $CpTi(C_6H_6)$-1D represent the three metal-alkene interactions between the metal atom and the three exocyclic double bonds of [3]radialene. NLMO-5~7 represent the metal-aromatic interaction between the metal atom and the 6π-aromatic Cp ring (Sc-C_5H_5 and Ti-C_5H_5). The NLMO-8 of $CpTi(C_6H_6)$-1D shows one single d-electron locating on Ti atom. NLMO-4 of $CpSc(C_6H_6)$-1S and $CpTi(C_6H_6)$-1D may indicate a possible metal-aromatic interaction between the metal atom and the 2π-aromatic cyclic C_3 ring of [3]radialene (Sc-C_3 and Ti-C_3). The potential aromaticity of radialene ligand will be disscussed in the following section. The NLMOs indicate that the Sc and Ti atoms adopt 14- and 15-electron configurations, respectively.

3.2.2. $CpV(C_6H_6)$, $CpCr(C_6H_6)$ and $CpMn(C_6H_6)$

$CpV(C_6H_6)$ only has two η^6-coordinated isomers. The ground state triplet $CpV(C_6H_6)$-2T is 12.2 kcal/mol lower than the singlet $CpV(C_6H_6)$-1S. NLMO-1~3 of $CpV(C_6H_6)$-2T are the three metal-alkene interactions, NLMO-4 is the metal-aromatic interaction of V-C_3, and NLMO-5~7 represent the metal-aromatic interaction of V-C_5H_5. NLMO-8~9 are two single d-electrons located on V atom. V atom adopts 16-electron configurations.

The ground states of $CpCr(C_6H_6)$ and $CpMn(C_6H_6)$ are the η^4-coordinated quartet $CpCr(C_6H_6)$-2Q and triplet $CpMn(C_6H_6)$-2T, which are 1.7 and 3.3 kcal/mol lower than the doublet $CpCr(C_6H_6)$-1D and singlet $CpMn(C_6H_6)$-1S, respectively. For $CpCr(C_6H_6)$-2Q and $CpMn(C_6H_6)$-2T, NLMO-1 of represent the non-coordinated exocyclic C—C π-bond, NLMO-2~3 are the two metal-alkene interactions, NLMO-4 represents the possible metal-aromatic interaction of Cr-C_3 and Mn-C_3, and NLMO-5~7 are the metal-aromatic interactions of Cr-C_5H_5 and Mn-C_5H_5. NLMO-8~10 of $CpCr(C_6H_6)$-2Q are three single d-electrons located on Cr atom. While NLMO-8 of $CpMn(C_6H_6)$-2T represents a lone pair of d-electrons, and NLMO-9~10 are two single d-electrons located on Mn atom. Cr atom adopt 15- and Mn atom adopt 16-electron configurations.

3.2.3. $CpFe(C_6H_6)$, $CpCo(C_6H_6)$ and $CpNi(C_6H_6)$

The ground states of $CpFe(C_6H_6)$ and $CpCo(C_6H_6)$ are the η^4-coordinated doublet $CpFe(C_6H_6)$-1D and singlet $CpCo(C_6H_6)$-1S, which are 10.9 and 8.7 kcal/mol lower than the quartet $CpFe(C_6H_6)$-2Q and triplet $CpCo(C_6H_6)$-2T, respectively. For NLMO-1 of $CpFe(C_6H_6)$-1D and $CpCo(C_6H_6)$-1S represent the non-coordinated exocyclic C—C π-bond, NLMO-2~3 are the two metal-alkene interactions, NLMO-4 represent the possible metal-aromatic