Induced Aromaticity and Electron-Count Rules for Bipyramidal and Sandwich Complexes of *s*- and *d*-Metals

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Abstract: Structures and stability of an extended series of bipyramidal, sandwich and sandwich-bipyramidal mixed complexes formed by conjugated cyclic hydrocarbons $(CH)_n$ with *s*- (Li, Na, K, Be, Mg, Ca) and *d*- (Cr, Mn, Fe) metals have been studied using DFT B3LYP/6-311+G(df,p) calculations. Stable structures of the compounds satisfy a general (**6n + 6d + 12c**) electron-count rule, where **n** stands for total number of the basal hydrocarbon rings, **d** is total number of *d*-metal centers (or separate sandwich moieties) and **c** is total number of apical metal-carbonyl groups. It is shown that stabilization of the studied polyhedral organometallic structures (induced aromaticity) is caused by filling 6π-electronic shells of basal (4-6)-membered cycles provided by donation of additional electrons from metal centers thereby acquiring closed 18-electron shells.

Keywords: Induced aromaticity, quantum-chemical calculations, sandwich compounds, bipyramidal compounds, electron-count rules.

INTRODUCTION

Aromaticity is among the most important fundamental concepts of organic and organometallic chemistry [1]. The key characteristic feature of the so-called aromatic character of a compound is enhanced thermodynamic stability, the property ensured by belonging it to a certain structural type and specific valence electron shell. Classification and quantification of various structural types of aromaticity have received much attention and were amply reviewed [1, 2]. We have previously introduced the notion of induced aromaticity [3] as a special type of stabilization of a conjugated cyclic system (initially non-aromatic or even non-existent in a free state) through interaction it with a suitable mono- or polyatomic fragment resulting in the completion of closed electronic shell of the composed system. A well-known example of this phenomenon (referred to as metalloaromaticity [4]) is a stable π-complex $(\eta^4-C_4H_4)Fe(CO)_3$ in which stabilization of the antiaromatic cyclobutadiene ring occurs *via* complexation with a $Fe(CO)_3$ group giving rise to planarization of the four-membered ring and equalization of its C-C bonds [4-6]. In a similar way, donation of electrons from the metal atoms into π-systems of the basal cycles in complexes **1 – 3** provides for the formation of three-dimensional aromatic structures attended by flattening of the cyclobutadiene [7] and cyclooctatetraene [8] rings and equalization of the CC bonds. In accordance with the principle of isolobal analogy [9] an apical irontricabonyl group in **4** can be replaced without loss of aromatic stability in the formed isostructural compound by other isolobal groups with two skeletal electrons to form, for example, stable pyramidal $(\eta^4-C_4H_4)Be$ π-complex **5** [10]. Analogously, stabilization of the three-dimensional

aromatic cyclopentadiene-based pyramidal complex **6** is achieved *via* capping the five-membered ring with a tricarbonylmanganese group [6, 11] with one skeletal electron and in the complex **7** with the univalent alkali-metal atoms [10, 12, 13]. At the same time, the replacement of the basal C_nH_n rings in sandwich and pyramidal systems with isolobal B_nH_{2n} borane fragments results in metalloboranes [6, 14, 15], which are isostructural and isoelectronic to the hydrocarbon analogues. Thus, metal-containing groups stabilize not only the aromatic forms of hydrocarbons C_nH_n, but also the aromatic *nido*-form of isoelectronic boranes B_nH_{2n}, which does not exist in the free state [6, 14].

In general, stability of various types of polyhedral organic and organometallic structures is controlled by specific electron-count rules accounting for compliance of the numbers of valence electrons and bonding MOs [16]. A classical example of such the rules is given by the 18-electron rule for transition metal coordination complexes. The electron count rules serve as convenient tools for predicting new types of chemical structures and outlining the range of potentially stable compounds. Application of these rules supported by the ideas of isolobality and induced aromaticity makes it possible to extend the search for new structural types to both organic and organometallic compounds and broadly diversify their possible thermodynamically and/or kinetically stable forms.

In the present work we report on a comparative quantum chemical computational study of electronic and spatial structures of a series of bipyramidal **8**, sandwich **9**, polysandwich **10** and mixed sandwich-bipyramidal complexes **11** of cyclopolyenes with *s*- and *d*- metal centers (M – metal atom or a metal-carbonyl group). The goal of this work is to get insight into the influence of nature of metals and length of the -M–ring-M- chain on the effects of aromatic stabilization in

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1   **2**   **3**

4   **5**   **6**   **7**

8   **9**   **10**   **11**
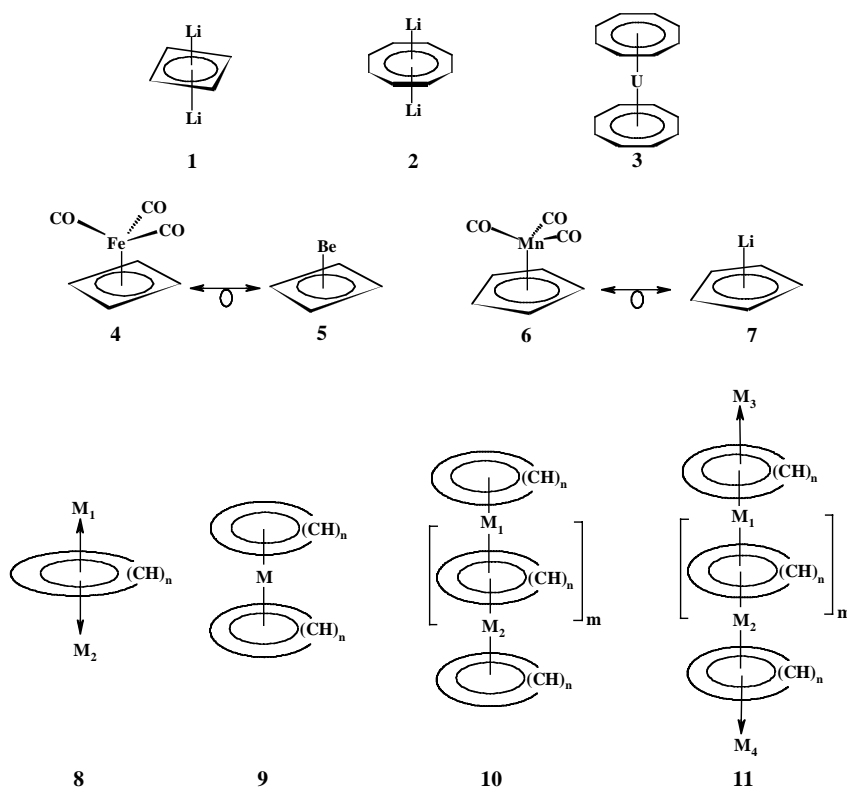
the complexes **8 – 11** and the electron-count rules determined their stability.

COMPUTATIONAL METHOD

DFT calculations were carried out using Gaussian 03 [17] with the Becke-3 parameter exchange and the Lee-Yang-Parr correlation functional (B3LYP) paired with the 6-311+G(df,p) basis set [18]. Stationary points on the potential energy surface (PES) were identified by calculating the matrix of the second derivatives (force constants), which was being carried out analytically. The aromaticity of the compounds being investigated was evaluated by calculating the NICS indices [19] at the center of the cyclic fragments. Molecular structure and molecular orbital images were generated with Chemcraft [20] program.

RESULTS AND DISCUSSION

1. Bipyramidal Complexes

Cyclobutadiene Derivatives

In the bipyramidal complexes, two additional electrons required for the completion of the aromatic 6π-electron shell of the four-membered ring of cyclobutadiene can be gained from two univalent alkali metal atoms placed into the apical positions. In accordance with the previous results [7] our calculations showed that the six-skeletal-electron bipyramidal complex **12** of D_{4h}-symmetry (Fig. **1**) corresponds to an energy minimum ($\lambda=0$; where λ is the number of negative eigenvalues of the Hessian matrix for a given stationary point) on the PES. The complex **12** is characterized by a planar conformation of the basal cycle with the equalized CC bonds, the lengths of which (1.470 Å) are intermediate between those typical for the standard single and double bonds. The apical metal atoms are distant from the center of basal

cycle for 1.735 Å. The calculated NICS index (-20.7 ppm) points to the aromatic nature of the hydrocarbon ring. In the case of sodium and potassium analogues of **12**, D_{4h}-symmetry forms do not correspond to local minima on the PESs and the bipyramidal-like structures of these compounds are distorted.

The 30-electron (sum of the numbers of π-electrons of the basal cycle and valence electrons of apical groups) d-analogues of lithium complex **12** are represented by stable bipyramidal complexes $C_4H_4Mn_2(CO)_6$ of C_{2v}-symmetry **13** and $C_4H_4V_2(CO)_8$ of D_{4h}-symmetry **14** (Fig. **1**). Stability of 30-electron complexes **13** and **14** can be explained in terms of the six interstitial electron rule [10] since each of the metallocarbonyl fragments $Mn(CO)_3$ and $V(CO)_4$ donate one electron into π-system of the basal ring providing thus for the formation of the three-dimensional aromatic 6π-electron system.

In complexes **13** and **14**, metallocarbonyl groups acquire staggered orientation with respect to the flat basal four-membered rings the CC bonds of which (1.478 – 1.480 Å in **13** and 1.476 Å in **14**) are noticeably elongated in comparison with those in lithium complex **12**. The less perfect symmetry of **13** leads to a small difference in the computed lengths of the CC bonds: those "crossed" by the CO bond of the metal tricarbonyl fragment are insignificantly (~0.02 Å) elongated in comparison with another pair. This structural feature was reported earlier for various metalcarbonyl complexes [6, 21] and was explained by the effects of orbital interactions. Distances between centers of the basal cycle and apical metal atoms are found to be 1.861 and 1.954 Å for **13** and **14**, respectively, which witnesses weakening orbital interaction between the basal and apical moieties in the tetracarbonyl complex compared to the tricarbonyl one.
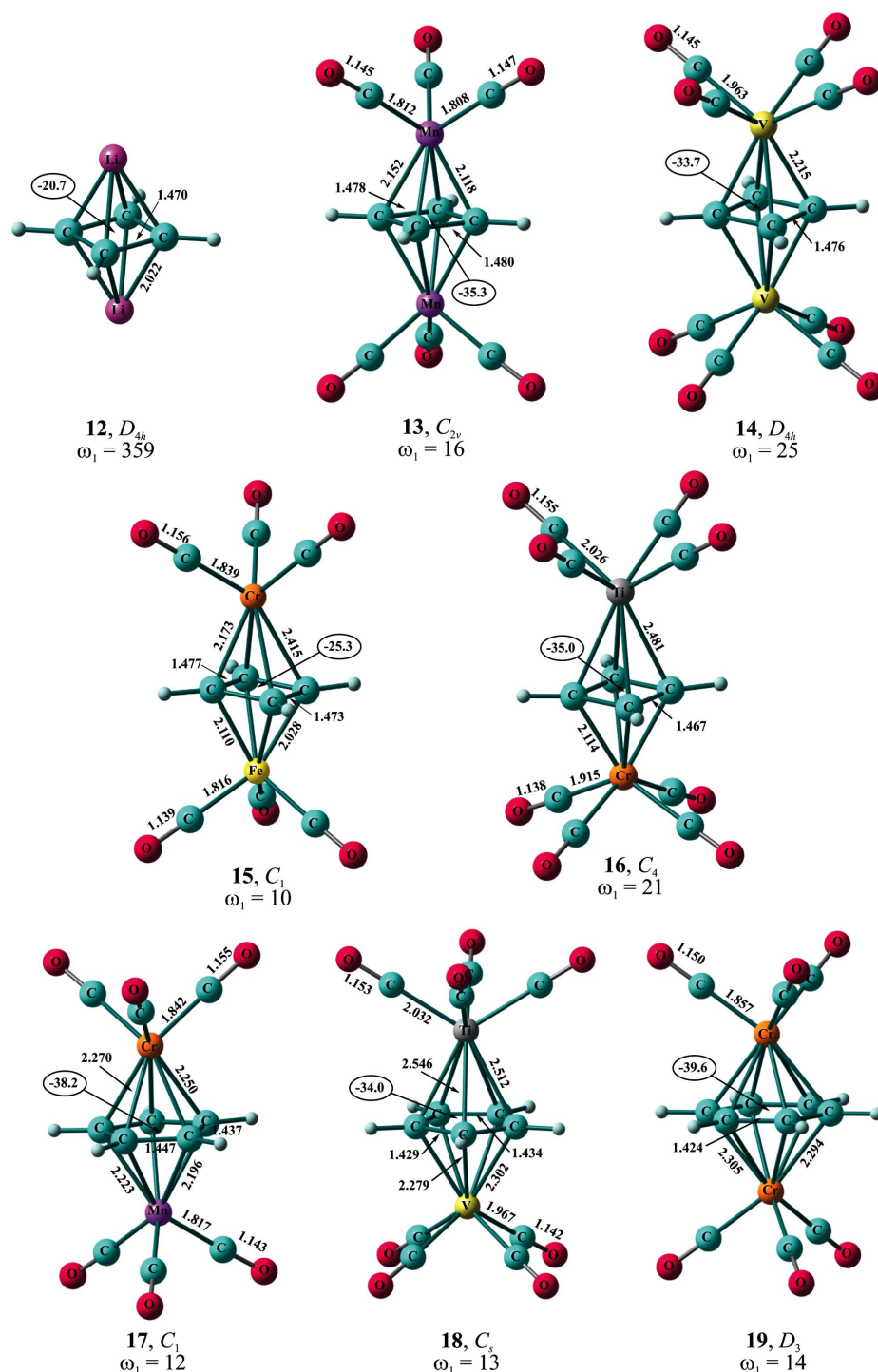
Fig. (1). Geometric characteristics (bond lengths are in angstroms) and lowest harmonic frequencies (ω_1 are in cm^{-1}) of stable ($\lambda=0$) complexes **12 – 19** calculated by the DFT B3LYP/6-311+G(df,p) method. NICS indices are shown in the oval rings.

The calculated NICS values in complexes **13** (-35.3 ppm) and **14** (-33.7 ppm) are considerably greater than that of lithium complex **12**. This finding proves enhancement of the effect of aromatic stabilization in *d*-metal-containing structures. Whereas the shapes of three filled π-orbitals of the lithium and metalcarbonyl complexes are virtually identical (see Fig. **2**), the substitution of lithium atoms by metalcarbonyl groups leads to significant lowering the energy levels of π-orbitals, and, consequently, to more expressed aromatic stabilization in thus formed compounds.

The range of stable bipyramidal metal-carbonyl complexes of cyclobutadiene can be extended to the mixed type systems, which include nonequivalent apical groups, one of which contains two skeletal electrons and another one contains no such electrons. According to the calculations performed 30-electron complexes $C_4H_4CrFe(CO)_6$ **15** and $C_4H_4TiCr(CO)_8$ **16**, in which $Fe(CO)_3$ and $Cr(CO)_4$ groups contribute each two electrons into π-systems of the basal cycles while $Cr(CO)_3$ and $Ti(CO)_4$ possess no such electrons, correspond to energy minima on the PESs (Fig. **1**). As a re-
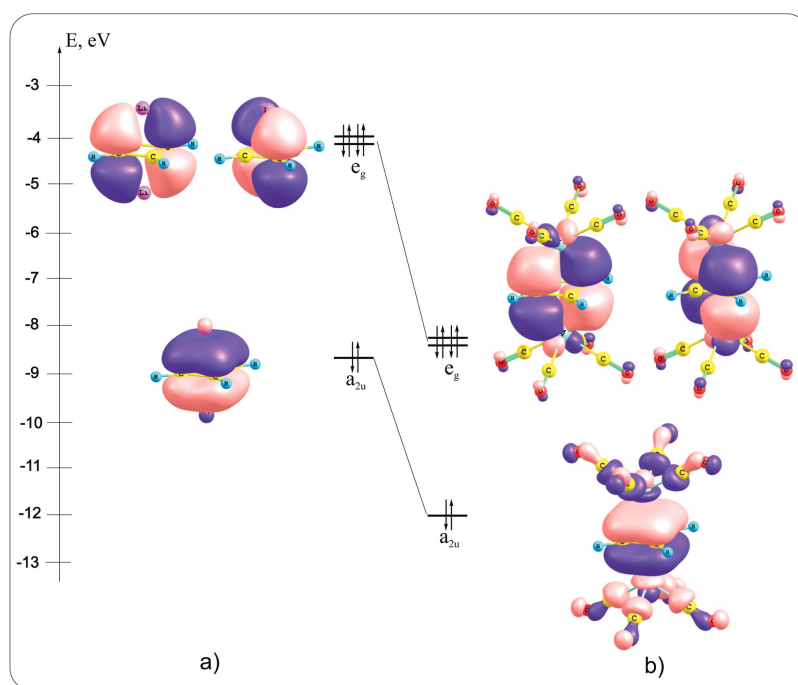
Fig. (2). Shapes and energies of the filled π-orbitals of complexes **12** (a) and **14** (b) calculated at the B3LYP/6-311+G(df,p) level of theory.

sult, centers of the donating apical groups in **15** and **16** are located closer to the basal ring than those of groups contributing no valence electrons into the π-system. The calculated distances in **15** are 1.787 (Fe) and 2.046 (Cr) Å. The distances between the basal cycle and metal atoms in complex **16** are 1.841 (Cr) and 2.254 (Ti) Å. Similar to complexes **13** and **14**, compounds **15** and **16** are characterized by the staggered orientation of apical fragments with respect to the basal cycle. The calculated NICS values for complexes **15** and **16** (-25.3 and -35.0 ppm respectively) witness the aromatic character of their basal rings.

Cyclopentadiene Derivatives

Only one additional skeletal electron is needed in order to form an aromatic 6π-electron five-membered cyclopentadienide fragment involved into a bipyramidal structure. Therefore, those bipyramidal metal-carbonyl complexes are expected to be stable, in which one of the apical groups donate a skeletal electron, while the second one contains no such electrons. The 30-electron metal-carbonyl clusters $C_5H_5CrMn(CO)_6$ **17** and $C_5H_5TiV(CO)_8$ **18** corresponding to energy minima on the PESs are pictured in Fig. (**1**). Complexes **17** and **18** are characterized by planar five-membered basal cycles, in which the calculated CC bond lengths are 1.437 – 1.447 Å (**17**) and 1.429 – 1.434 Å (**18**). As for complexes **13**, **15**, the nonequivalence of the CC bonds in the cyclopentadiene derivatives is caused by the symmetry features of complexes and effects of orbital interactions of carbonyl groups with the basal cycle. As in **15** and **16**, the π−donating metal-carbonyl groups lie closer to the basal cycle than the groups which do not contribute additional electrons into the π-system. In **17**, the calculated distances between centers of the basal cycles and metal atom are 1.841 Å (Mn) and 1.918 Å (Cr). In **18**, same type distances are 1.966 Å (V) and 2.179 Å (Ti). The NICS values (-38.2 and -34.0 ppm) calculated at the centers of the cyclopentadienyl

rings in **17** and **18**, respectively, are consistent with their significant aromatic character.

Benzene Derivatives

As in the case of cyclopentadiene derivatives, the formation of stable neutral complexes containing two apical *s*-metal atoms above a six-membered hydrocarbon basal cycle is impossible for the electron-count reasons. The aromatic benzene rings do not need additional electrons and, therefore, bipyramidal structures can be formed with the apical groups having no skeletal electrons, as exemplified by a 30-electron bipyramidal complex $C_6H_6Cr_2(CO)_6$ **19** (Fig. **1**). The complex **19** contains a planar basal cycle with the equalized CC bonds (1.424 Å). The distances between center of the basal cycle and chromium atoms (1.805 Å) are the shortest for all the carbonyl clusters examined herein and the NICS index (-39.6 ppm) has the most negative value.

It may be concluded that the wide variability of electron structure of metal-carbonyl fragments provides for manifold conditions for the formation of stable three-dimensional aromatic bipyramidal complexes of annulenes.

2. Sandwich Complexes

Cyclobutadiene Derivatives

The formation of aromatic structure of the cyclobutadiene sandwich complexes requires addition of two electrons to each of the basal cycles, and, correspondingly, the fulfillment of the 12-electron rule. Therefore, the formation of stable neutral sandwich-type structures with central *s*-metals is improbable. At the same time it is possible to comply with the requirements of the 12-electron rule by constructing sandwich-bipyramidal mixed complexes with a central alkaline earth metal atom and additional alkali metal apical atoms. According to the calculations, the 12-electron calcium complexes **20** – **22** (Fig. **3**) correspond to energy minima on the PESs. The analogous D_{4d} symmetrical sandwich com-
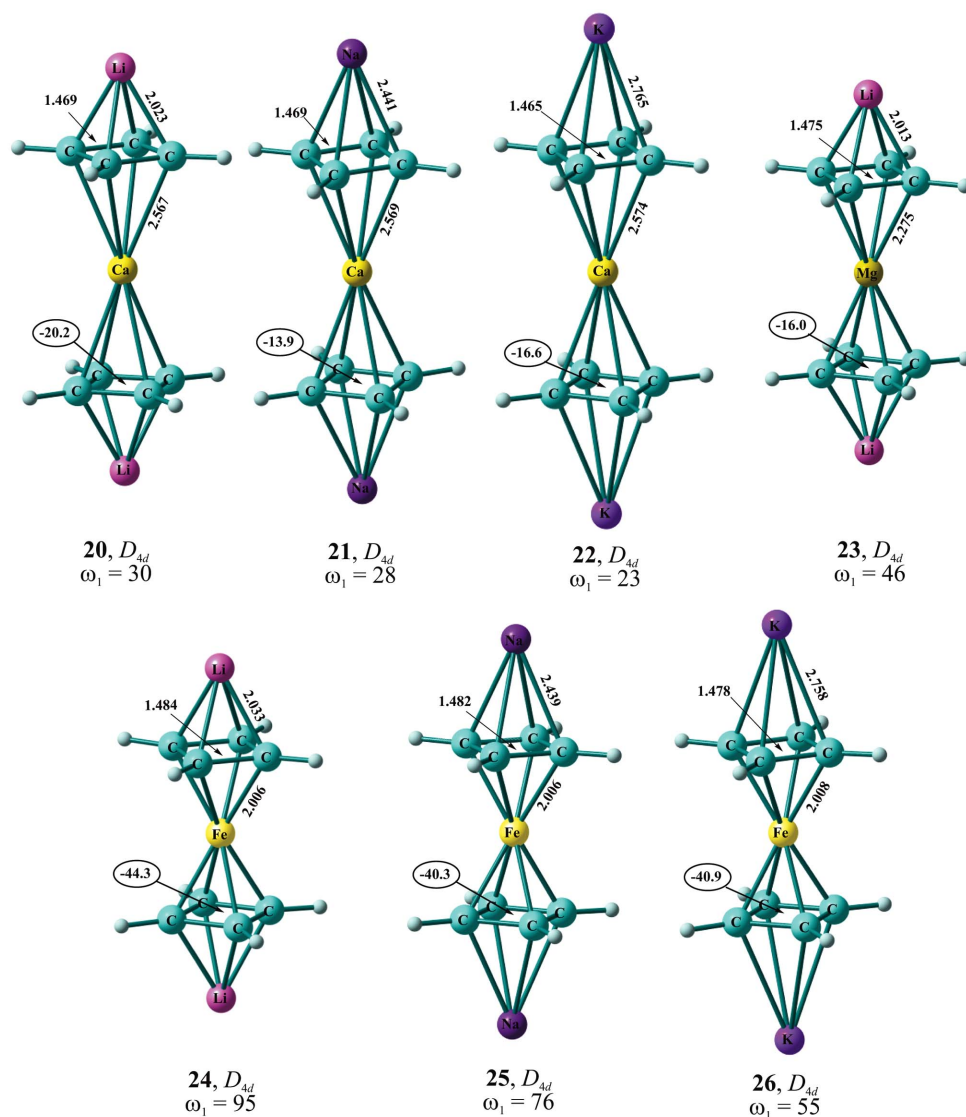
Fig. (3). Geometric characteristics (bond lengths are in angstroms) and lowest harmonic frequencies (ω_1 are in cm^{-1}) of stable ($\lambda=0$) complexes **20 – 26** calculated by the DFT B3LYP/6-311+G(df,p) method. NICS indices are shown in the oval rings.

plexes of beryllium are unstable ($\lambda=2$). For magnesium as the central atom, the only stable form found by calculations is complex **23** with apical lithium atoms.

Cyclobutadiene fragments in complexes **20 – 23** have the equalized CC bonds, whose lengths are 1.469, 1.469 and 1.465 Å for calcium complexes **20**, **21** and **22**, respectively, and 1.475 Å for magnesium complex **23**. The strength of the binding of central atom with the basal cycle in the complexes of calcium decreases from lithium to sodium and further to potassium.

Calculations indicate the aromatic nature of the basal cycles of complexes **20 – 23**: the NICS values are -20.2, -13.9, -16.6 and -16.0 ppm, respectively. Thus, as in the case of the simplest bipyramidal structure **12**, the most effective aromatic stabilization is achieved in the complex with apical lithium atoms.

Complexes **20 – 23** with the central atom of alkaline earth metal have isostructural *d*-analogs. The replacement of the central bivalent atom of calcium (magnesium) with an iron atom provides for the formation of a new group of sta-

ble compounds **24 – 26** (Fig. **3**). The calculated CC bond lengths in the hydrocarbon cycles of the iron complexes **24 – 26** (1.484, 1.482 and 1.478 Å for Li, Na, and K, respectively) are noticeably elongated compared to the complexes of calcium and magnesium. Replacement of an alkaline earth metal atom by a transition metal atom enhances the interaction of the central atom with the basal cycles, which is accompanied by substantial increase in the aromaticity of the latter: the calculated NICS values in the center of the basal cycles of complexes **24 – 26** are -44.3, -40.3, -40.9 ppm, respectively.

Replacement of the apical alkali metal atoms by suitable metal-carbonyl groups, which contain one skeletal electron, leads to stabilization of complexes **27 – 29** (Fig. **4**) including the central alkaline earth metal atom and one-electron apical groups $Mn(CO)_3$. Substitution of tricarbonyl $Mn(CO)_3$ groups by tetracarbonyl $V(CO)_4$ groups gives rise to stable complexes **30 – 32**. As in the simplest bipyramidal structures, metal-carbonyl groups provide for more effective aromatic stabilization in comparison with isolobal alkali metals atoms.
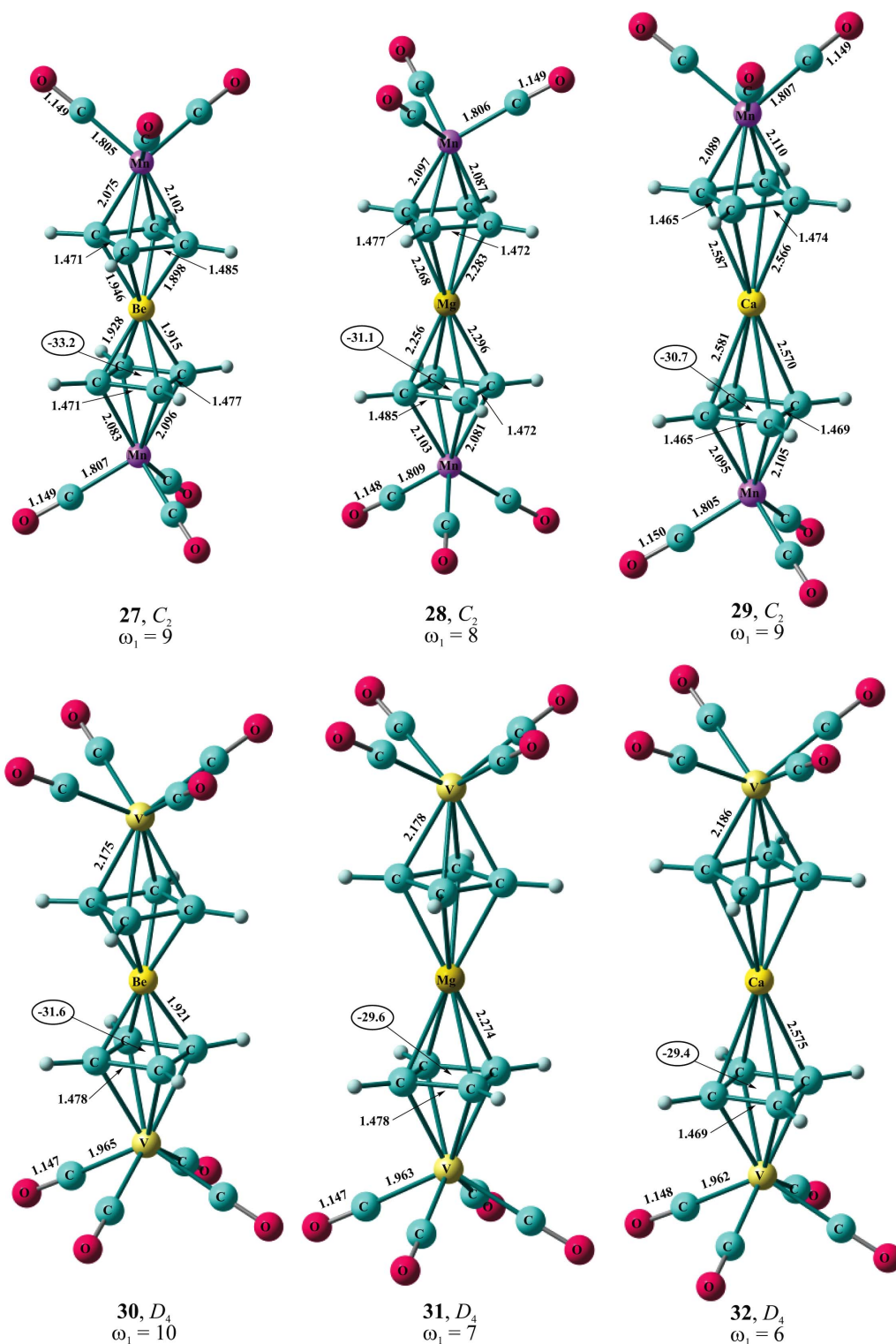
Fig. (4). Geometric characteristics (bond lengths are in angstroms) and lowest harmonic frequencies (ω_1 are in cm^{-1}) of stable ($\lambda=0$) complexes **27** – **32** calculated by the DFT B3LYP/6-311+G(df,p) method. NICS indices are shown in the oval rings.

Cyclopentadiene Derivatives

The structures of the sandwich complexes of alkaline earth metals with cyclopentadiene cycles **33** – **35** (Fig. **5**) comply with the requirements of the 12e-rule. According to the calculations performed and in agreement with previous computational studies [12, 22], high-symmetry sandwich structures of complexes of magnesium **34** and calcium **35** correspond to energy minima on the PESs.

At the same time, the stable structure of beryllocene **33** contains the central metal atom displaced from the axis connecting centers of the five-membered rings. The magnesium and calcium complexes are characterized by the equalized
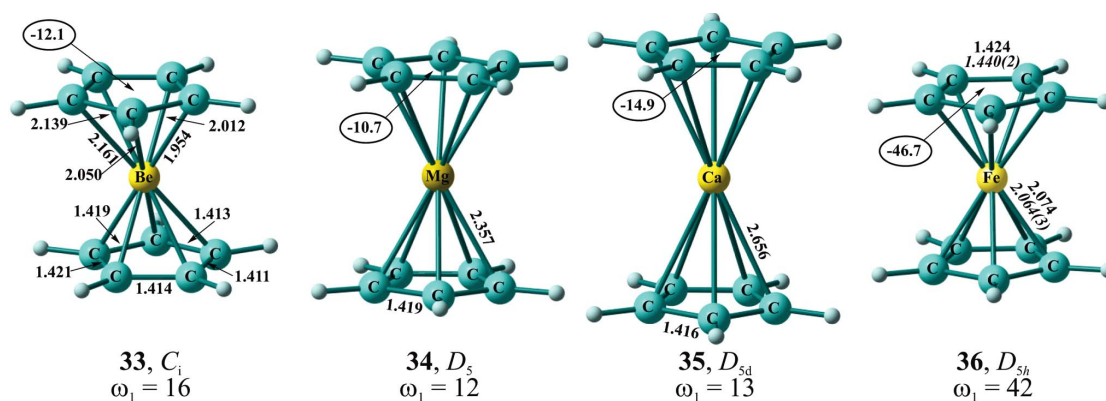
Fig. (5). Geometric characteristics (bond lengths are in angstroms) and lowest harmonic frequencies (ω_1 are in cm^{-1}) of stable ($\lambda=0$) complexes **33 – 36** calculated by the DFT B3LYP/6-311+G(df,p) method. NICS indices are shown in the oval rings. The experimental gas phase electron diffraction data [23] for ferrocene **36** are given in italics.

CC bonds with the lengths 1.419 and 1.416 Å for **34** and **35**, respectively, intermediate between the values typical of standard single and double CC bonds. The calculated NICS values in the center of the basal cycles of systems **33**, **34** and **35** are -12.1, -10.7 and -14.9 ppm, respectively, thus indicating the moderate aromatic stabilization in these complexes. The calculated geometric characteristics of ferrocene **36** (Fig. **5**), the iron *d*-analogue of complexes **33 – 35**, well agree with the electron diffraction data [23].

The shapes of filled π-MO characteristic of 12-electron π-system of complexes **35** and **36** are featured by Fig. (**6**). It may be seen that alkaline earth and iron sandwich complexes

possess almost identical π−electron systems. Replacement of *s*-metal atom by *d*-metal atom in **35** lowers the energy levels of π-orbitals and provides for the pronounced aromatic stabilization of the sandwich system accompanied by significant shortening C-Metal bonds and increase in the NICS value (-14.9 and -46.7 ppm for **35** and **36**, respectively).

From the results presented it follows that in the sandwich clusters **20 – 22** and **24 – 26**, as well as **35** and **36** the central alkaline earth metals and iron atom are structurally interchangeable. The correspondence between the 12-electron alkaline earth metal complexes and the 18-electronic iron complexes stemming from the analysis of their electron
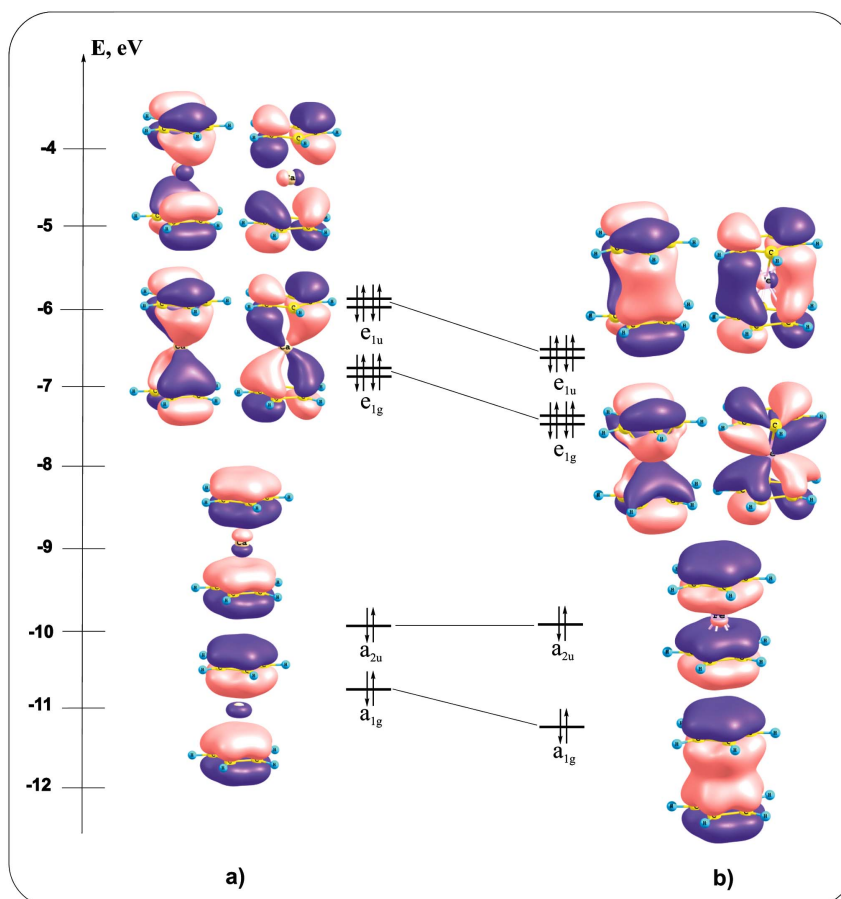

Fig. (6). Shapes and energies of filled π-orbitals of complexes **35** (**a**) and **36** (**b**) calculated at the B3LYP/6-311+G(df,p) level of theory.
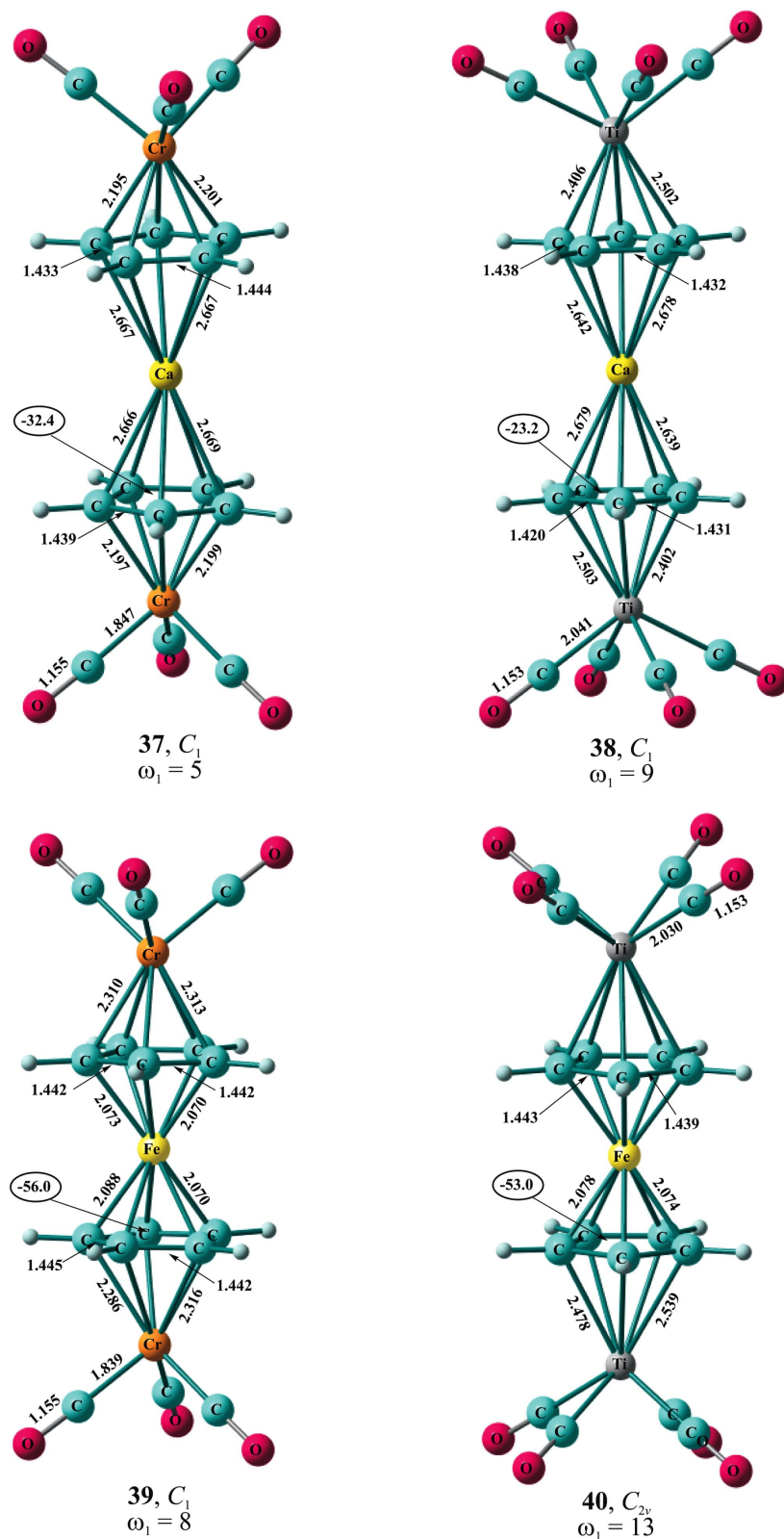
Fig. (7). Geometric characteristics (bond lengths are in angstroms) and lowest harmonic frequencies (ω_1 are in cm^{-1}) of stable (λ=0) complexes **37** – **40** calculated by the DFT B3LYP/6-311+G(df,p) method. NICS indices are shown in the oval rings.

structures is explained by that in both cases only two valence electrons take part in the formation of the composite π-systems.

The mixed sandwich-bipyramidal complexes can be formed on the basis of metallocenes **35** and **36** *via* capping them with apical metal-carbonyl groups containing no skeletal electrons, such as $Cr(CO)_3$ или $Ti(CO)_4$. The structures of

calcium complexes **37**, **38** and isostructural iron complexes **39**, **40** which exemplify such type compounds are shown in Fig. (**7**). According to the calculated values of NICS indices the apical metal-carbonyl groups considerably increase the aromatic character of **37** – **40** as compared with their precursors.

Substitution of central and apical atoms in complexes **37** – **40** by isoelectronic atoms or groups disturbs their structural type, as is the case of stable sandwich-bipyramidal lith-

ium derivatives **41**, **42** with tri- and tetracarbonyl apical groups and their isostructural manganese analogues **43**, **44** (Fig. **8**). These complexes possess same type structural features, which inherent in the simplest bipyramidal complexes **17** and **18** with the nonequivalent apical groups. Apical groups Mn(CO)$_3$ и V(CO)$_4$ donating electrons to the π-system, are closer to the basal cycle than groups Cr(CO)$_3$ or Ti(CO)$_4$ without skeletal electrons. The aromatic character of compounds **41**, **42** is augmented by substitution of alkali metal atoms by transition metal atoms.
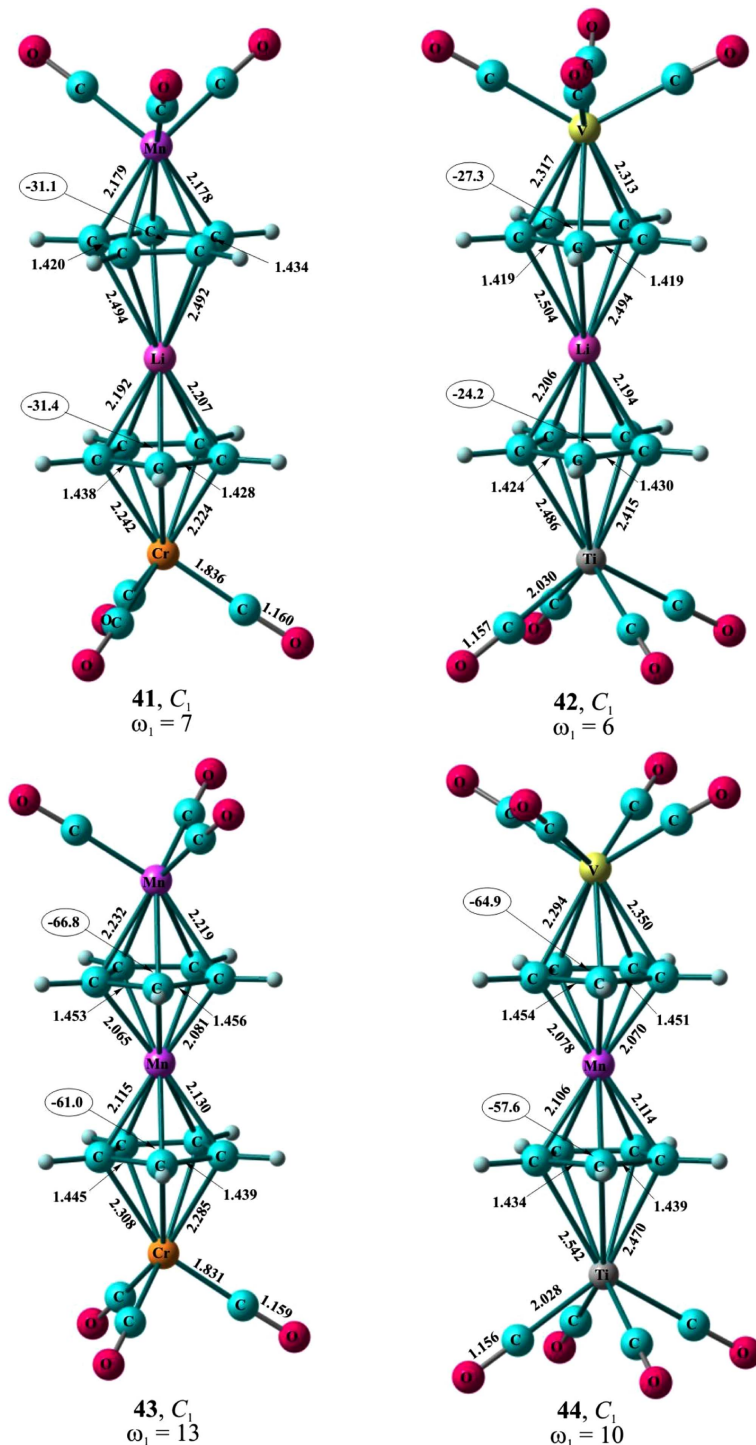

Fig. (8). Geometric characteristics (bond lengths are in angstroms) and lowest harmonic frequencies (ω_1 are in cm^{-1}) of stable (λ=0) complexes **41** – **44** calculated by the DFT B3LYP/6-311+G(df,p) method. NICS indices are shown in the oval rings.
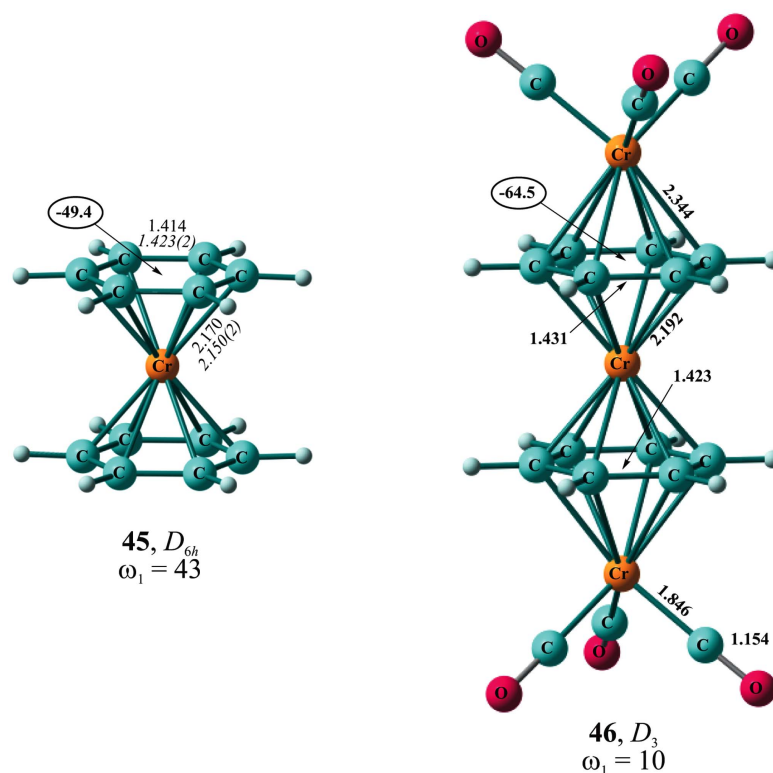
Fig. (9). Geometric characteristics (bond lengths are in angstroms) and lowest harmonic frequencies (ω_1 are in cm^{-1}) of stable (λ=0) complexes **45** and **46** calculated by the DFT B3LYP/6-311+G(df,p) method. NICS indices are shown in the oval rings. The experimental gas phase electron diffraction data [24] for chromocene **45** are given in italics.

Benzene Derivatives

The benzene basal cycles are inherently aromatic and can form stable neutral sandwich complexes with *d*-metals and organometallic groups containing no skeletal electrons like in chromocene **45** (Fig. **9**). The calculated geometry well reproduces the electron diffraction data [24].

In the same way, mixed sandwich structures bear additional apical centers without skeletal electrons. Example shown in Fig. (**9**) is represented by the 42-electron complex **46**. The appended metal-containing groups in this compound considerably increase the aromatic character as compared with the initial sandwich complex **45**.

3. Triple-Decker Sandwich Complexes

Cyclobutadiene Derivatives

Stable electrically neutral triple-decker sandwich complexes containing three aromatic 6π-electron cycles must obey to the requirements of the 18-electron rule and cannot, therefore, be formed by *s*-metals. At the same time the 18-electron rule holds true for the mixed sandwich-bipyramidal complexes with suitable apical atoms.

Shown in Fig. (**10**) are the triple-decker complexes **47** – **49** with two calcium central atoms and apical alkali metals, the structures of which correspond to energy minima on the PESs. The compounds **47** – **49** are characterized by the equalized CC bonds in the basal cycles. The calculated NICS values point to aromaticity of the cyclobutadiene fragments.

The 30-electron iron complexes **50** – **52** are *d*-analogues of the 18-electron triple-decker calcium derivatives **47** – **49**.

As is the case of double-decker structures, the aromatic character of *d*-complexes is stronger compared to the corresponding calcium complexes. As seen from Figs. (**3**) and (**10**), an increase in the chain length upon passing from double-decker calcium complexes **20** – **22** to triple-decker ones **47** – **49** does not practically affect the NICS values. In contrast to the calcium complexes, for iron complexes an increase in the chain length is accompanied by significant growth of aromaticity of the basal cycles. This finding leads to the conclusion on the formation of the integrated electronic shell encompassing the whole metalloaromatic structure.

The apical alkali metal atoms in complexes **47** – **49** can be substituted by one skeletal electron metal-carbonyl groups, such as Mn(CO)$_3$ or V(CO)$_4$, to form stable complexes **53**, **54** (Fig. **11**). As in the simpler systems, aromaticity of terminal basal cycles in these complexes is considerably higher in comparison with the alkali metal derivatives **47** – **49**.

Cyclopentadiene Derivatives

As exemplified by calcium complexes **55** – **57** (Fig. **12**), the formation of the 18-electron π-system with three cyclopentadiene cycles takes place in the mixed complexes of alkaline and alkaline earth metals. The *d*-analogues of complexes **55** – **57** are obtained *via* substitution of alkaline earth metal atoms by iron and alkali metal atoms by manganese. The structure of thus designed 30-electron thriple-decker cluster **58** corresponds to an energy minimum on the PES. The closed electron shell of the 18-electron π-system of complexes **55** and **58** is portrayed in Fig. (**13**). It can be seen that the shapes of MOs of these complexes are identical. As in all previously considered molecular systems,
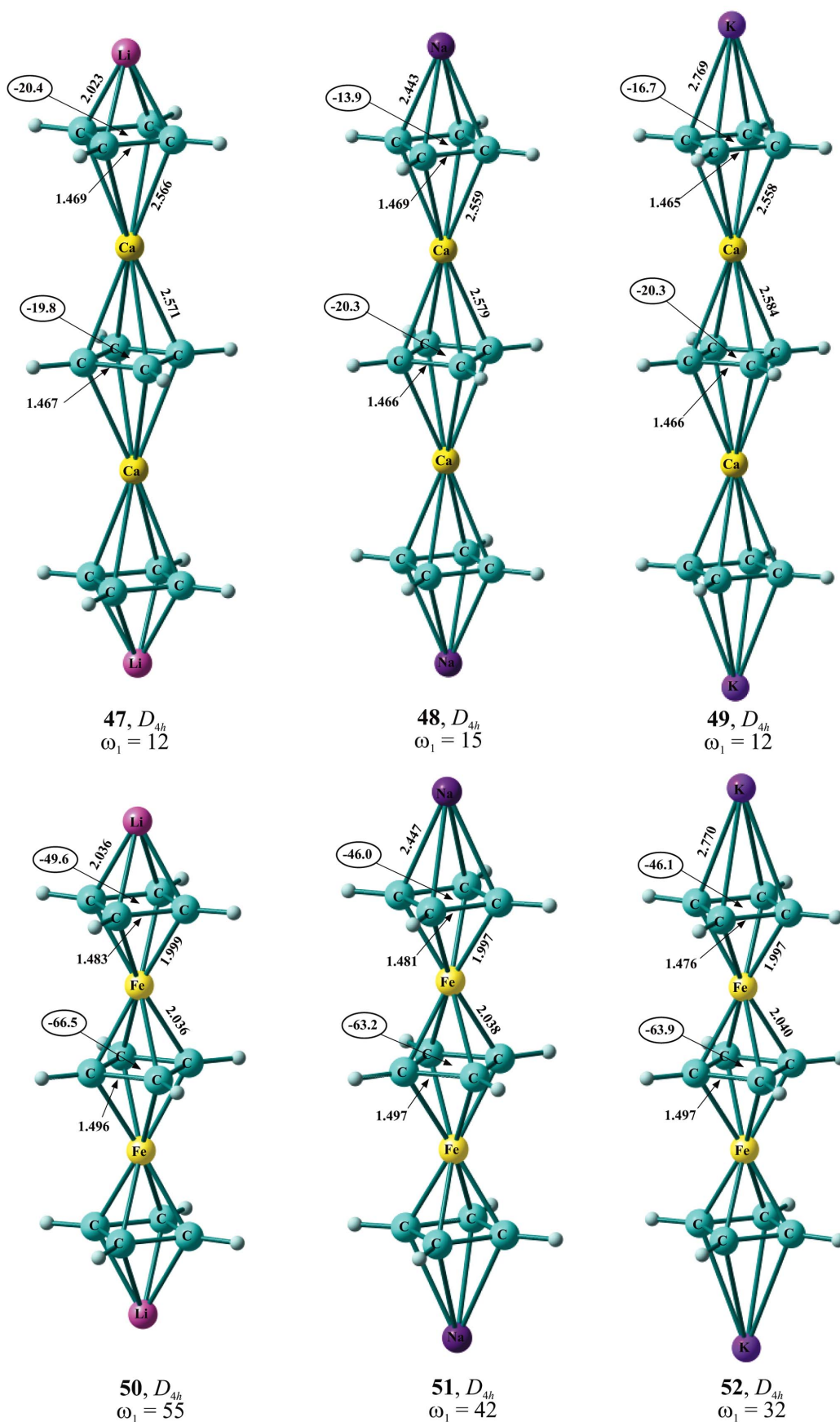
Fig. (10). Geometric characteristics (bond lengths are in angstroms) and lowest harmonic frequencies (ω_1 are in cm^{-1}) of stable (λ=0) complexes **47 – 52** calculated by the DFT B3LYP/6-311+G(df,p) method. NICS indices are shown in the oval rings.
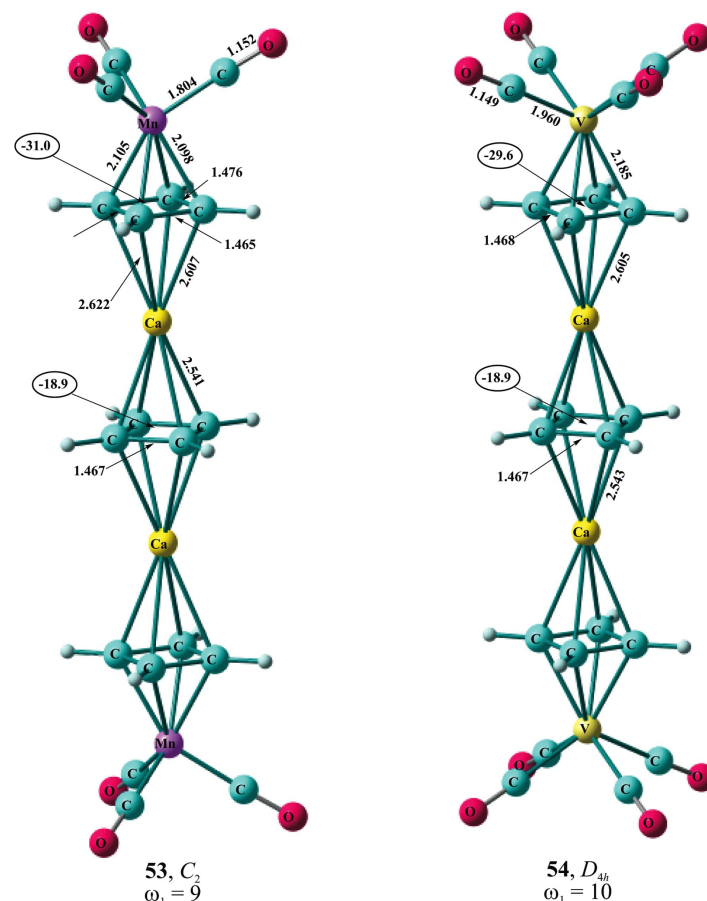
Fig. (11). Geometric characteristics (bond lengths are in angstroms) and lowest harmonic frequencies (ω_1 are in cm^{-1}) of stable (λ=0) complexes **53**, **54** calculated by the DFT B3LYP/6-311+G(df,p) method. NICS indices are shown in the oval rings.

replacement of *s*-metal atoms by *d*-metals results in strengthening of binding of the basal cycles to metal atoms and substantial increase in the aromatic character of the *d*-metal complexes, as testified by lengthening CC bonds of the basal rings, shortening the interatomic distances between metals and basal cycle and increasing NICS indices.

Stretching the ring-metal-ring chain when passing from complexes **35** to **55 – 57** does not practically affect aromatic properties of *s*-metal derivatives, whereas aromaticity of *d*-metal derivatives noticeably grows with elongation of this chain in **36** and **58**.
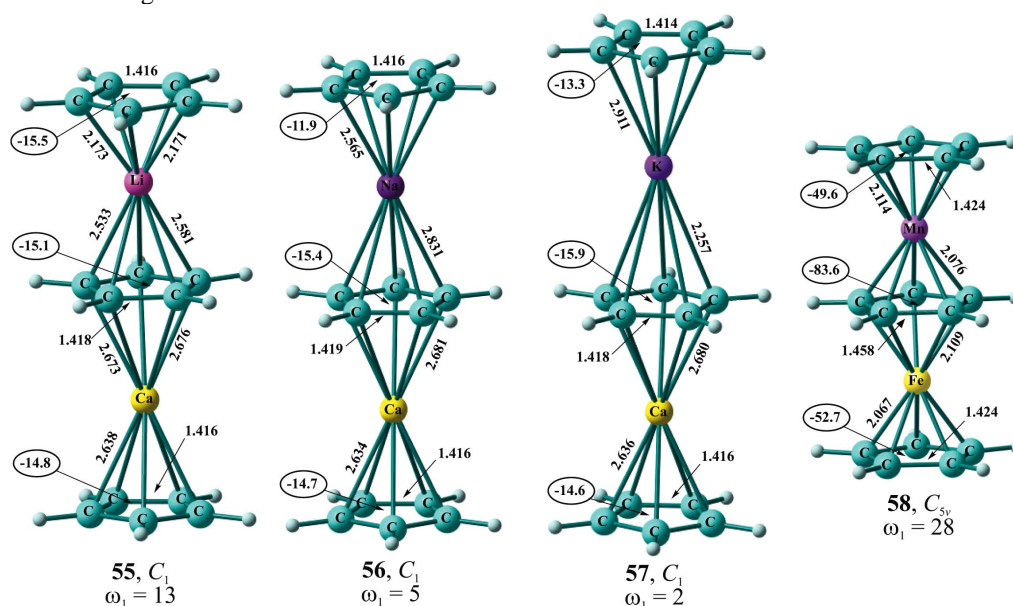

Fig. (12). Geometric characteristics (bond lengths are in angstroms) and lowest harmonic frequencies (ω_1 are in cm^{-1}) of stable (λ=0) complexes **55 – 58** calculated by the DFT B3LYP/6-311+G(df,p) method. NICS indices are shown in the oval rings.
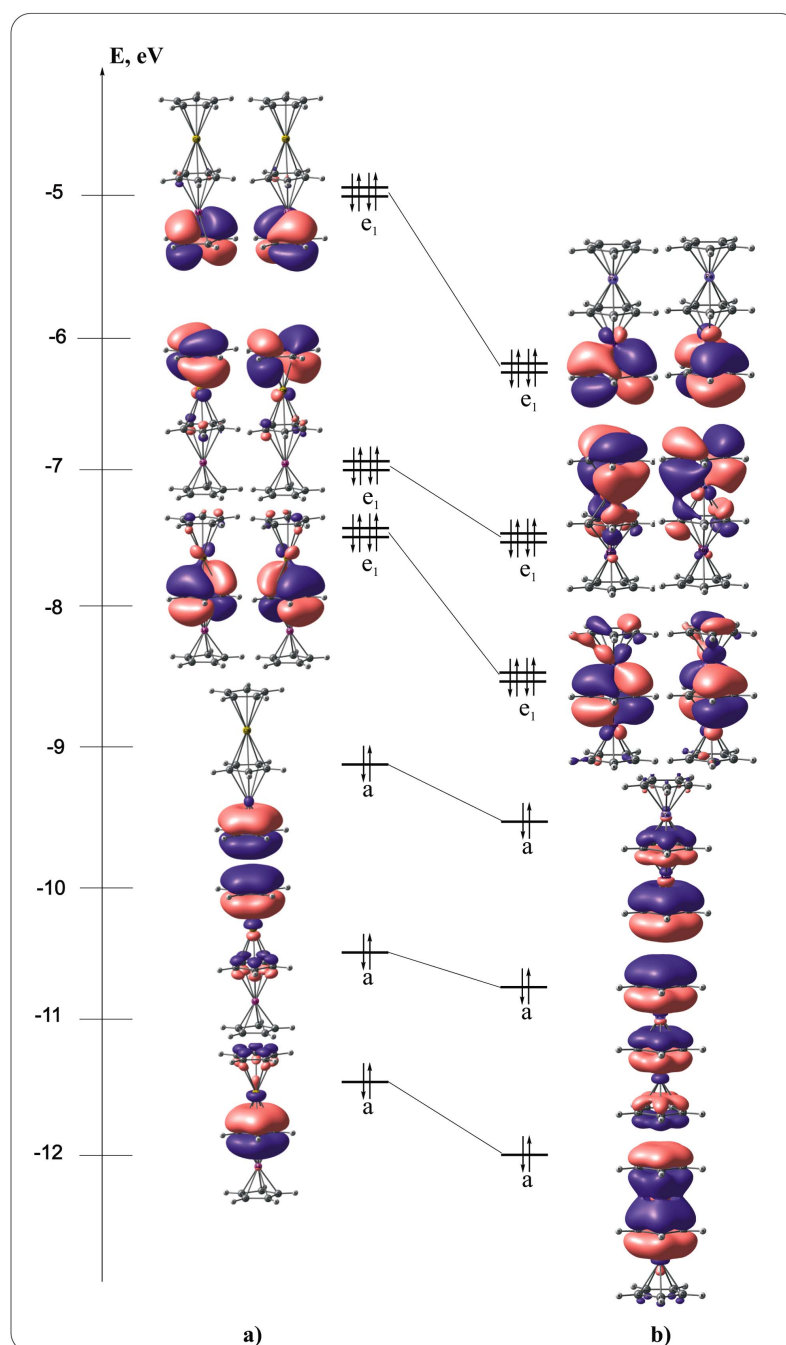
Fig. (13). Shapes and energies of filled π-orbitals of complexes **55** (**a**) and **58** (**b**) calculated at the B3LYP/6-311+G(df,p) level of theory.

Benzene Derivatives

In accordance with [25] the 30-electron triple-decker analogue of chromocene is expected to have a stable structure **59** (Fig. **14**) even more aromatic than the predecessing system **45**. The 54-electronic complex **60** demonstrates the further increase in the NICS indices conditioned by capping **59** with $Cr(CO)_3$ groups containing no skeletal electrons.

4. Multi-Decker Sandwich Complexes

Some of the multi-decker complexes based on the triple-decker sandwich compounds and mixed type sandwich systems are represented by the structures shown in Fig. (**15**). According to the calculations performed the structures of the

trinuclear four-decker sandwich clusters **61** – **63** correspond to energy minima on the PESs.

As a whole, for the multi-decker complexes, the same tendencies related to increase in aromatic properties when passing from *s*- to *d*-metal isostructural analogues and to elongation in the latter of the ring-metal-ring chains remain valid.

5. Electron-Count Rules for Bipyramidal and Sandwich Complexes of *s*- and *d*-Metals

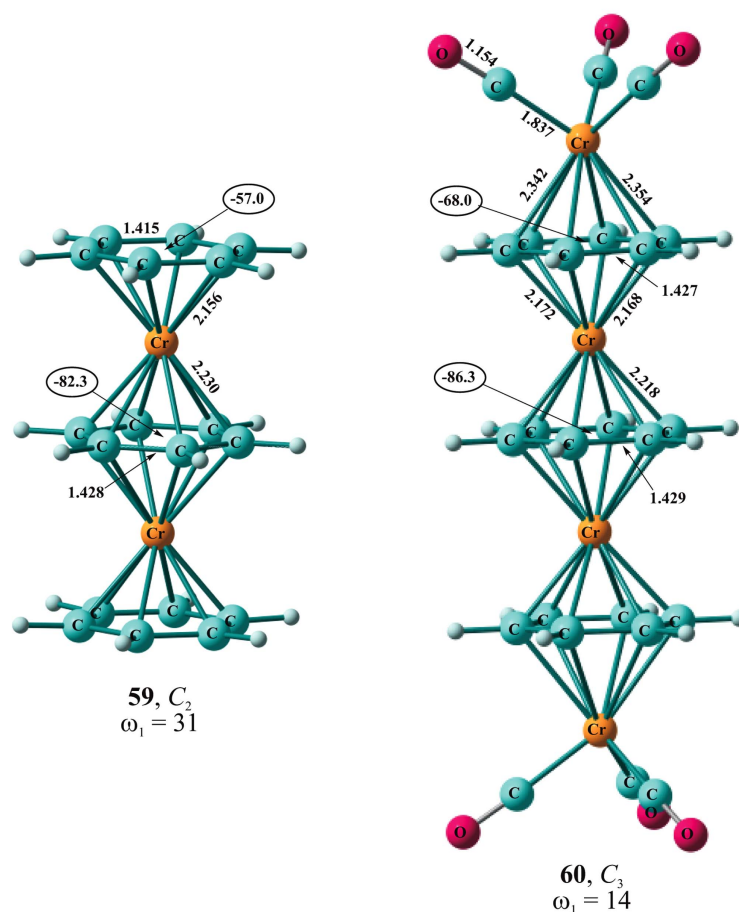For all above considered stable bipyramidal, sandwich structures formed by only *s*-metals atoms the sum (**Σ**) of

Fig. (14). Geometric characteristics (bond lengths are in angstroms) and lowest harmonic frequencies (ω_1 are in cm^{-1}) of stable ($\lambda=0$) complexes **59** calculated by the DFT B3LYP/6-311+G(df,p) method and **60** calculated by the DFT B3LYP/6-311G(df,p) method. NICS indices are shown in the oval rings.
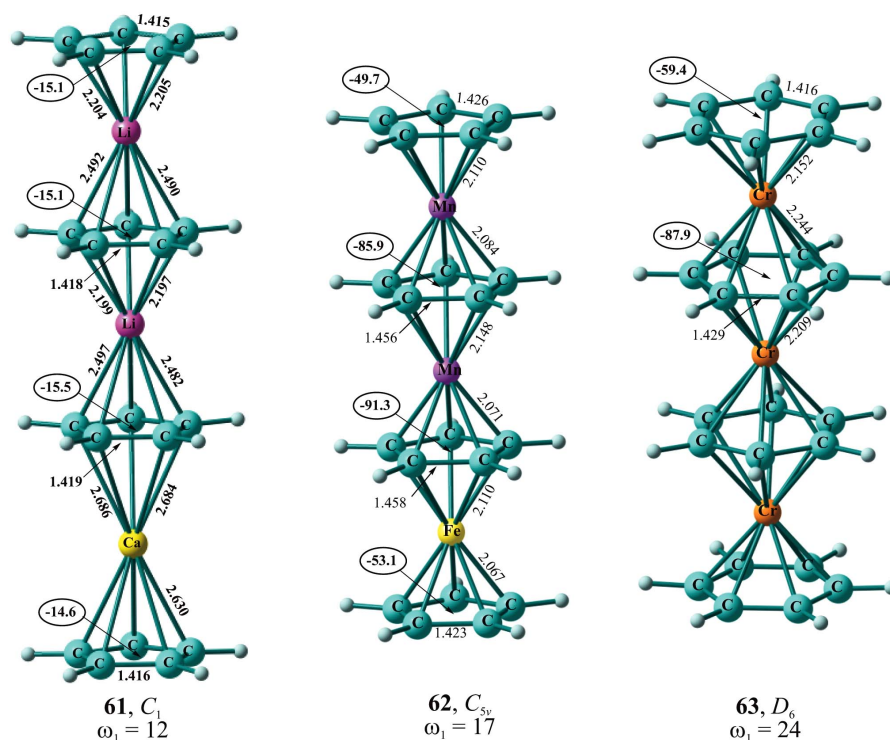

Fig. (15). Geometric characteristics (bond lengths are in angstroms) and lowest harmonic frequencies (ω_1 are in cm^{-1}) of stable ($\lambda=0$) complexes **61** – **63** calculated by the DFT B3LYP/6-311+G(df,p) method. NICS indices are shown in the oval rings.

valence electrons of metal atoms and π-electrons of basal cycles must be equal to **6n**.

$$\Sigma = 6n \quad (1)$$

(n – total number of the basal cycles)

For example, for the 6 valence electron complex **12** n = 1, for 12 valence electron complexes **20** and **35** n = 2 and for 18 valence electron complexes **47** and **55** n = 3.

Stable structures of bipyramidal [26] and polysandwich [27, 28] complexes (including their mixed derivatives [26]) composed by only *d*-metal atoms must satisfy to the rule **(2)**, according to which the sum of valence electrons of metal atoms and π-electrons of basal cycles is **12m + 6**.

$$\Sigma = 12m + 6 \quad (2)$$

(m – total number of transition metals atoms)

Thus, m = 1, 2 and 3 for the 18 valence electron complex **36**, 30 electron complexes **13**, **58** and 42 electron complexes **39** and **62**, respectively.

The electron-count rules **(1)** and **(2)** cannot be applied to the mixed type complexes containing both *s*- and *d*-metal centers. For such type systems including *s*- and *d*-metals and mixed derivatives the generalized electron-count rule **(3)** will be valid, according to which for a stable complex the sum of all valence electrons of metal atoms, apical groups and π-electrons of basal cycles is equal to **6n + 6d + 12c**.

$$\Sigma = 6n + 6d + 12c \quad (3)$$

(n –total number of hydrocarbon cycles;

d – total number of *d*-metal atoms (or separate sandwich moieties);

c – total number of metal-carbonyl groups)

Thus, there are 18 valence electrons for complex **26** (n = 2, d = 1, c = 0), 30 valence electrons for **52** (n = 3, d = 2, c = 0) and 36 valence electrons for **29** (n = 2, d = 0, c = 2).

Obviously, the rule **(1)** is a particular case of the generalized rule **(3)** under conditions d = 0, c = 0 and the rule **(2)** is derived from **(3)** for *d*-metal sandwiches with c = 0, n = d + 1 and for bipyramidal structures with n = d + 1, m = d + c.

The generalized electron-count rule **(3)** holds true also for the nonsymmetric systems including only one apical group. Thus, stable complexes **64** (n = 2, d = 1, c = 0), **65** (n

= 2, d = 0, c = 1) and **66** (n = 3, d = 0, c = 1) contains 18, 24 and 30 valence electrons, respectively.

It seems clear that the rules **(1)** – **(3)** represent an extension of well-known principles of aromaticity of organic and metal coordination compounds to the particular structural type systems. The rule **(1)** is, in fact, a consequence of the principal condition for an aromatic (4–6)-membered system to form the closed 6π-electron shell, whereas the rule **(2)** reflects requirements of the 18-electron rule for transition metal complexes with several *d*-metal centers. It should be stressed that while the rules **(1)** – **(3)** satisfactorily regulate stability of the organometal structures with (4–6)-membered basal cycles, these must be modified if applied to the systems with the larger size conjugated cycles. For stable structures of sandwich and bipyramidal *s*-metal complexes with (7–9)-membered basal cycles the rule **Σ = 10n** is applicable, since 10 is the next (after 6) term of the (4n+2) Hueckel rule. Examples of stable structures of such type are complexes **67** (20 valence electrons), **68** (30 valence electrons), **69** and **70** (40 valence electrons). According to the calculations performed in this work using B3LYP/6-311+G(df,p) method, these complexes correspond to energy minima on the PES.

At the same time, in contrast to the complexes with (4–6)-membered basal cycles, which retain their stable forms under interchanges of "sandwich" (Ca and Fe; Li and Mn) and apical (Ca and Fe(CO)₃; Li and Mn(CO)₃) centers of *s*- and *d*-metals, for systems with (7–9)-membered basal cycles this replacement leads to overflow of the *d*-metal electronic shells and deformations of the sandwich and bipyramidal structures.

CONCLUSION

The structures of multi-decker sandwich, bipyramidal and mixed complexes of *s*- and *d*-metals containing (4-6)-membered conjugated basal cycles are stabilized by donation of additional electrons from metal centers (induced aromaticity) with the formation of the closed electron shells satisfying the electron-count rule **Σ = 6n + 6d + 12c**, (where **n** – total number of hydrocarbon cycles, **d** is total number of *d*-metal centers (or separate sandwich moieties) and **c** – total number of metal-carbonyl groups). The aromatic character of the isostructural compounds formed by *d*-metals is substantially stronger than that for the *s*-metal derivatives. For the multi-decker *d*-metal compounds, lengthening the -M-ring-M-ring- chains is accompanied by increase in the aromatic

64, C_{5v} **65**, C_1 **66**, C_1

67, D_7 **68**, D_{8h} **69**, D_{8h} **70**, C_9
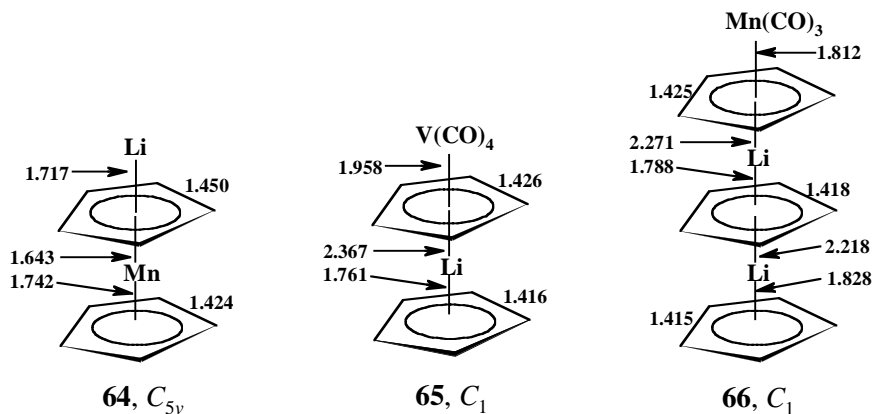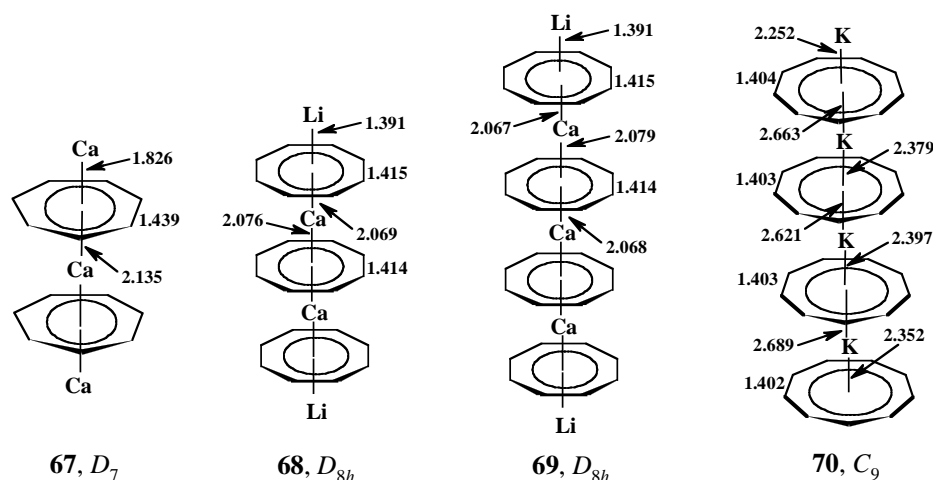
stabilization, but does not practically affect the aromatic properties of the hydrocarbon cycles of the analogous *s*-metal compounds.

REFERENCES

[1] (a) Minkin, V.I.; Glukhovtsev, M.N.; Simkin, B.Ya. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; Wiley: New York, **1994**. (b) Garrat, P.J. *Aromaticity*; Wiley: New York, **1986**. (c) Special issue on aromaticity. Schleyer P.v.R., Ed. *Chem. Rev.,* **2001**, *101*(5), 1115-1331. (d) Balaban, A.T.; Oniciu, D.C.; Katritzky, A.R. Aromaticity as a cornerstone of heterocyclic chemistry. *Chem. Rev.*, **2004**, *104*(5), 2777-2812. (e) Krygowski, T.M.; Cyrañski, M.K.; Czarnocki, Z.; Häfelinger, G.; Katritzky, A.R. Aromaticity: a theoretical concept of immense practical importance. *Tetrahedron*, **2000**, *56*(13), 1783-1796. (f) Schleyer, P.v.R.; Jiao, H. What is aromaticity? *Pure Appl. Chem.*, **1996**, *68*(2), 209-218. (g) Balaban, A.T. Is aromaticity outmoded? *Pure Appl. Chem.,* **1980**, *52* (6), 1409-1429.

[2] (a) Chen, Z.; King, R.B. Spherical aromaticity: recent work on fullerenes, polyhedral boranes, and related structures. *Chem. Rev.*, **2005**, *105*(10), 3613-3642. (b) Rzepa, H.S. Möbius aromaticity and delocalization. *Chem. Rev.*, **2005**, *105*(10), 3697-3715. (c) Boldyrev, A.I.; Wang, L-S. All-metal aromaticity and antiaromaticity. *Chem. Rev.*, **2005**, *105*(10), 3716-3757. (d) Shainyan, B.A.; Fettke, A.; Kleinpeter, E. Push−pull vs captodative aromaticity. *J. Phys. Chem. A*, **2008**, *112*(43), 10895-10903. (e) Cyrański, M.K.; Stępień, B.T.; Krygowski, T.M. Global and local aromaticity of linear and angular polyacenes. *Tetrahedron*, **2000**, *56*(49), 9663-9667. (f) Chandrasekhar, J.; Jemmis, E.D.; Schleyer, P.v.R. Double aromaticity: aromaticity in orthogonal planes. The 3,5-dehydrophenyl cation. *Tetrahedron Lett.*, **1979**, *20*(39), 3707-3710. (g) Randić, M. Aromaticity of polycyclic conjugated hydrocarbons. *Chem. Rev.*, **2003**, *103*(9), 3449-3606. (h) Kuznetsov, N.T.; Ionov, S.P.; Solntsev, K.A. *The development of the concept of aromaticity: polyhedral structure / Razvitie kontseptsii aromatichnosti: poliedricheskie struktury*; Nauka: Moscow, **2009**. (j) Strained aromatic molecules. in: *Strained hydrocarbons: beyong the van't Hoff and Le Bel hypothesis*; H. Dodziuk, Ed; Wiley-VCH: Weinheim, **2009**; Chapter 4, pp. 147-205. (k) Aihara, J.-I. Aromaticity and diatropicity. *Pure Appl. Chem.,* **1982**, *54*(5), 1115-1128. (l) Fowler, P.W.; Lillington, M.; Olson, L.P. Aromaticity, π-electron delocalization, and ring currents. *Pure Appl. Chem.*, **2007**, *79*(6), 969-979. (m) Pierrefixe, S.C.A.H.; Bickelhaupt, F.M. Aromaticity: Molecular-orbital picture of an intuitive concept. *Chem. Eur. J.*, **2007**, *13*(22), 6321-6328.

[3] Minyaev, R.M.; Minkin, V.I.; Starikov, A.G.; Gribanova, T.N. Induced aromaticity. *Russ. Chem. Bull., Int. Ed.*, **2001**, *50*(12), 2325-2335.

[4] (a) Bursten, B.E.; Fenske, R.F. Molecular orbital studies on cyclobutadienemetal complexes: the concept of metalloaromaticity. *Inorg. Chem.,* **1979**, *18*(7), 1760-1765. (b) Chinn, J.W.Jr.; Hall, M.B. Generalized molecular orbital calculations on the ground and ionic states of (η^4-cyclobutadiene)tricarbonyliron(0). *Inorg. Chem.,* **1983**, *22*(19), 2759-2766.

[5] (a) Harvey, P.D.; Schaefer, W.P.; Gray, H.B.; Gilson, D.F.R.; Butler, I.S. Structure of tricarbonyl(η^4-cyclobutadienyl)iron(0) at -45°C. *Inorg. Chem.*, **1988**, *27*(1), 57-59. (b) Davis, M.I.; Speed, C.S. Gas-phase electron diffraction studies of some iron carbonyl complexes. *J. Organomet. Chem.*, **1970**, *21*(2), 401-413. (c) Oberhammer, H.; Brune, H.A. The microwave spectrum of cyclobutadiene iron tricarbonyl. *Z. Naturforsch. A*, **1969**, *24*, 607-612. (d) Lucken, E.A.C.; Pozzi, R.; Ramaprasad, K.R. The microwave spectrum of cyclobutadiene iron tricarbonyl. *J. Mol. Struct.*, **1973**, *18*(3), 377-380. (e) Roehrig, M.A.; Wikrent, P.; Huber, S.R.; Wigley, D.E.; Kukolich, S.G. The microwave spectrum of cyclobutadiene iron tricarbonyl. *J. Mol. Spectrosc.,* **1992**, *154*(2), 355-360. (f) Schleyer, P.v.R.; Kiran, B.; Simion, D.V.; Sorensen, T.S. Does $Cr(CO)_3$ complexation reduce the aromaticity of benzene? *J. Am. Chem. Soc.*, **2000**, *122*(3), 510-513.

[6] Gribanova, T.N.; Minyaev, R.M.; Starikov, A.G.; Minkin, V.I. π-Complexes of transition metal tricarbonyls with cyclopolyenes and their boron analogs. *Russ. Chem. Bull., Int. Ed.*, **2009**, *58*(4), 691-705.

[7] (a) Zandwijk, G.; Janssen, R.A.J.; Buck, H.M. 6π Aromaticity in four-membered rings. *J. Am. Chem. Soc.*, **1990**, *112*(11), 4155-4164. (b) Balci, M.; McKee, M.L.; Schleyer, P.v.R. Theoretical study of tetramethyl- and tetra-*tert*-butyl-substituted cyclobutadiene and tetrahedrane. *J. Phys. Chem. A*, **2000**, *104*(6), 1246-1255. (c) Kleinpeter, E.; Koch, A.; Shainyan, B.A. Cyclobutadiene dianion derivatives – planar *4c,6e* or three-dimensional *6c,6e* aromaticity? *J. Mol. Struct. Theochem*, **2008**, *863*(1-3), 117-122.

[8] (a) Staley, S.W.; Grimm, R.A.; Boman, P.; Eliasson, B. Effect of ion pairing on charge transfer in the bicyclooctatetraenyl dianion. *J. Am. Chem. Soc.*, **1999**, *121*(31), 7182-7187. (b) Streitwieser, A.Jr.; Müller-Westerhoff, U. Bis(cyclooctatetraenyl)uranium (uranocene). A new class of sandwich complexes that utilize atomic f orbitals. *J. Am. Chem. Soc.,* **1968**, *90*(26), 7364-7364. (c) Streitwieser, A.Jr.; Müller-Westerhoff, U.; Sonnichsen, G.; Mares, F.; Morrell, D.G.; Hodgson, K.O.; Harmon, C.A. *J.* Preparation and properties of uranocene, di-π-cyclooctatetraeneuranium(IV). *Am. Chem. Soc.,* **1973**, *95*(26), 8644-8649.

[9] (a) Hoffmann, R. Theoretical organometallic chemistry. *Science*, **1981**, *211*(4486), 995-1002. (b) Elian, M.; Hoffmann, R. Bonding capabilities of transition metal carbonyl fragments. *Inorg. Chem.*, **1975**, *14*(5), 1058-1076. (c) Elian, M.; Chen, M.M.L.; Mingos, D.M.P.; Hoffmann, R. Comparative bonding study of conical fragments. *Inorg. Chem.*, **1976**, *15*(5), 1148-1155. (d) Schilling, B.E.R.; Hoffmann, R. M_3L_9(ligand) complexes. *J. Am. Chem. Soc.*, **1979**, *101*(13), 3456-3467.

[10] Jemmis, E.D.; Schleyer, P.v.R. Aromaticity in three dimensions. Influence of orbital compatibility on the geometry and stability of capped annulene rings with six interstitial electrons. *J. Am. Chem. Soc.*, **1982**, *104*(18), 4781-4788.

[11] (a) Cowie, J.; Hamilton, E.J.M.; Laurie, J.C.V.; Welch, A.J. The chemistry of monoanionic carbaborane ligands. Synthesis, and molecular and electronic structure of [3,3,3-(CO)$_3$-4-SMe$_2$-3,1,2-MnC$_2$B$_9$H$_{10}$], and order-of-magnitude improved structure of (η-C$_5$H$_5$)Mn(CO)$_3$. *J. Organomet. Chem.*, **1990**, *394*(1-3), 1-13. (b) Almond, M.J.; Page, E.M.; Rice, D.A.; Hagen, K.; Volden, H.V. The molecular structure of cyclopentadienyl manganese tricarbonyl determined by gas-phase electron diffraction. *J. Mol. Struct.*, **1994**, *319*, 223-230.

[12] Rayón, V.M.; Frenking, G. Structures, bond energies, heats of formation, and quantitative bonding analysis of main-group metallocenes [E(Cp)$_2$] (E=Be–Ba, Zn, Si–Pb) and [E(Cp)] (E=Li–Cs, B–Tl). *Chem. Eur. J.*, **2002**, *8*(20), 4693-4707.

[13] Mahadevi, A.S.; Sastry, G.N. A theoretical study on interaction of cyclopentadienyl ligand with alkali and alkaline earth metals. *J. Phys. Chem. B*, **2011**, DOI: 10.1021/jp109749a.

[14] (a) Greenwood, N.N. The concept of boranes as ligands. *Coord. Chem. Rev.,* **2002**, *226*(1-2), 61-69. (b) Greenwood, N.N. Metalloborane cluster compounds. *Pure Appl. Chem.,* l**983**, *55*(1), 77-87. (c) Greenwood, N.N.; Savory, C.G.; Grimes, R.N.; Sneddon, L.G.; Davison, A.; Wreford, S.S. Preparation of a stable small ferraborane, B$_4$H$_4$Fe(CO)$_3$. *J. Chem. Soc., Chem. Commun.*, **1974**, *17*, 718-718. (d) Gribanova, T.N.; Starikov, A.G.; Minyaev, R.M.; Minkin, V.I.; Siebert, M.R.; Tantillo, D.J. Sandwich compounds of transition metals with cyclopolyenes and isolobal boron analogues. *Chem. Eur. J.*, **2010**, *16*(7), 2272-2281.

[15] (a) Grimes, R.N. Structure and stereochemistry in metalloboron cage compounds. *Acc. Chem. Res.,* **1978**, *11*(11), 420-427. (b) Miller, V.R.; Grimes, R.N. Preparation of stable closo- and nido-cobaltaboranes from Na$^+$B$_5$H$_8^-$. Complexes of the formal B$_4$H$_8^{2-}$ and B$_4$H$_6^{4-}$ ligands. *J. Am. Chem. Soc.,* **1973**, *95*(15), 5078-5080. (c) Weiss, R.; Grimes, R.N. New ferraboranes. Structural analogues of hexaborane(l0) and ferrocene. A complex of cyclic B$_5$H$_{10}^-$, a counterpart of C$_5$H$_5^-$. *J. Am. Chem. Soc.,* **1977**, *99*(24), 8087-8088. (d) Weiss, R.; Grimes, R.N. Polyhedral ferraboranes derived from the B$_5$H$_8^-$ ion. Analogues of ferrocene, hexaborane(10), and nido-B$_{11}$H$_{15}$. *Inorg. Chem.,* **1979**, *18*(12), 3291-3294. (e) Grimes, R.N. Metallacarbobanes and metal-boron clusters in organometallic synthesis. *Pure Appl. Chem.,* l**982**, *54*(1), 43-58.

[16] Minkin, V.I.; Minyaev, R.M.; Zhdanov, Yu.A. *Nonclassical Structures of Organic Compounds*; Mir Publishers: Moscow, **1987**.

[17] Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A.,Jr.; Vreven, T.; Kudin, K.N.; Burant, J.C.; Millam, J.M.; Iyengar, S.S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J.E.; Hratchian, H.P.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Ayala, P.Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Zakrzewski, V.G.; Dapprich, S.; Daniels, A.D.; Strain, M.C.; Farkas, O.; Malick, D.K.; Rabuck, A.D.; Ragha-vachari, K.; Foresman, J.B.; Ortiz, J.V.; Cui, Q.; Baboul, A.G.; Clifford, S.; Cioslowski, J.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P.M.W.; Johnson, B.; Chen, W.; Wong, M.W.; Gonzalez, C.; Pople, J.A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, **2003**.

[18] (a) Becke, A.D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.,* **1993**, *98*(7), 5648-5652. (b) Becke, A.D. A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.,* **1993**, *98*(2), 1372-1377. (c) Lee, C.; Yang, W.; Parr, R.G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*, **1988**, *37*(2), 785-789. (d) Stephens, P.J.; Devlin, F.J.; Chabalowski, C.F.; Frisch, M.J. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Phys. Chem.,* **1994**, *98*(45), 11623-11627. (e) Foresman, J.B.; Frisch, E. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, **1996**.

[19] (a) Schleyer, P.v.R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N.J.R.v.E. Nucleus-independent chemical shifts: a simple and efficient aromaticity probe. *J. Am. Chem. Soc.,* **1996**, *118*(26), 6317-6318. (b) Chen, Z.; Wannere, C.S.; Corminboeuf, C.; Puchta, R.; Schleyer, P.v.R. Nucleus-independent chemical shifts (NICS) as an aromaticity criterion. *Chem. Rev.,* **2005**, *105*(10), 3842-3888.

[20] Zhurko, G. A.; Zhurko, D. A. *ChemCraft 1.6*. http://www.chemcraftprog.com

[21] Albright, T.A.; Hofmann, P.; Hoffmann, R. Conformational preferences and rotational barriers in polyene-ML$_3$ transition metal complexes. *J. Am. Chem. Soc.,* **1977**, *99*(23), 7546-7557.

[22] (a) Kaupp, M.; Schleyer, P.v.R.; Dolg, M.; Stollt, H. The equilibrium structures of monomeric Group 2 and lanthanide(II) metallocenes MCp$_2$ (M = calcium, strontium, barium, samarium, europium, ytterbium) studied by ab initio calculations. *J. Am. Chem. Soc.,* **1992**, *114*(21), 8202-8208. (b) Xie, Y.; Schaefer III, H.F.; Jemmis, E.D. Characteristics of novel sandwiched beryllium, magnesium, and calcium dimers: C$_5$H$_5$BeBeC$_5$H$_5$, C$_5$H$_5$MgMgC$_5$H$_5$, and C$_5$H$_5$CaCaC$_5$H$_5$. *Chem. Phys. Lett.*, **2005**, *402*(4-6), 414-421.

[23] Haaland, A.; Nilsson, J.E. The determination of barriers to internal rotation by means of electron diffraction. ferrocene and ruthenocene. *Acta Chem. Scand.,* **1968**, *22*(8), 2653-2670.

[24] Haaland, A. The molecular structure of gaseous dibenzene chromium (C$_6$H$_6$)$_2$Cr. *Acta Chem. Scand.,* **1965**, *19*(1), 41-46.

[25] Yasuike, T.; Yabushita, S. Ionization energies and bonding scheme of multiple-decker sandwich clusters: M$_n$(C$_6$H$_6$)$_{n+1}$. *J. Phys. Chem. A,* **1999**, *103*(23), 4533-4542.

[26] Gribanova, T.N.; Minyaev, R.M.; Minkin, V.I. Structure and stability of bipyramidal complexes of cyclopolyenes with transition metal carbonyls. *Doklady Chemistry*, **2011**, *436*(2), 23-27.

[27] Gribanova, T.N.; Minyaev.; R.M. Minkin, V.I. Multidecker transition metal sandwich compounds. *Doklady Chemistry*, **2009**, *429*(1), 258-263.

[28] Li, Q.; Yu, H.; Tang, A. Electronic structures of multi-decker transition metal sandwich complexes. *Theor. Chim. Acta,* **1986**, *70*(5), 379-389.