



Variable hapticity of the cyclooctatetraene ring in sandwich compounds of the first row transition metals

Hao Feng^a, Hongyan Wang^{b,*}, Yaoming Xie^c, R. Bruce King^{c,**}, Henry F. Schaefer III^c

^aSchool of Physics and Chemistry and Research Center for Advanced Computation, Xihua University, Chengdu 610039, PR China

^bCollege of Physical Science and Technology, Southwest Jiaotong University, Chengdu 610031, China

^cDepartment of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, GA 30602, USA

ARTICLE INFO

Article history:

Received 10 May 2010

Received in revised form

5 July 2010

Accepted 6 July 2010

Available online 14 July 2010

Keywords:

Cyclooctatetraene

Sandwich compounds

Density functional theory

Transition metals

ABSTRACT

Density functional theory methods (B3LYP and BP86) indicate that the preferred structures for such early transition metal derivatives are $(\eta^8\text{-C}_8\text{H}_8)\text{M}(\eta^4\text{-C}_8\text{H}_8)$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}$) with one octahapto $\eta^8\text{-C}_8\text{H}_8$ ring and one tetrahapto $\eta^4\text{-C}_8\text{H}_8$ ring. In such structures only 12 of the 16 carbon atoms of the two C_8H_8 rings are bonded to the metal, leading to 16-, 17-, and 18-electron complexes, respectively, in accord with the experimentally known structures for the Ti and V derivatives. The preferred structures for the Mn and Fe derivatives are $(\eta^6\text{-C}_8\text{H}_8)\text{M}(\eta^4\text{-C}_8\text{H}_8)$ ($\text{M} = \text{Mn}, \text{Fe}$) with one hexahapto and one tetrahapto C_8H_8 ring and thus having 17- and 18-electron configurations, respectively, in accord with experimental data on the iron complex. The lowest energy structure for the cobalt complex is $(\eta^4\text{-C}_8\text{H}_8)\text{Co}(\eta^{2,2}\text{-C}_8\text{H}_8)$ with two different types of tetrahapto C_8H_8 rings and a 17-electron metal configuration. The nickel complex $(\text{C}_8\text{H}_8)_2\text{Ni}$ appears to prefer a structure with a 16-electron configuration and two trihapto C_8H_8 rings, similar to the known $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$ rather than a bis(tetrahapto) structure with the favored 18-electron configuration. These theoretical studies indicate that in $(\text{C}_8\text{H}_8)_2\text{M}$ derivatives of the first row transition metals, the number of carbon atoms in the pair of C_8H_8 rings involved in the bonding to the central metal atom gives the metal atoms 16-, 17-, or 18-electron configurations.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The landmark 1951 discovery of ferrocene [1,2], $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$, in which an iron atom is sandwiched between two cyclopentadienyl rings, almost immediately raised the question as to whether transition metals could be sandwiched between carbocyclic rings of other sizes. In this connection the subsequent 1955 discovery of dibenzenechromium [3], $(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}$, showed that benzene rings, as well as cyclopentadienyl rings, could serve as the “bread” for metal sandwich compounds.

The synthesis of analogous $(\eta^8\text{-C}_8\text{H}_8)_2\text{M}$ sandwich compounds (Fig. 1) containing two fully bonded octahapto cyclooctatetraene rings has not been achieved with any of the d-block transition metals. The reasons for this are clear from considerations of formal oxidation state and the 18-electron rule. Thus in $(\eta^8\text{-C}_8\text{H}_8)_2\text{M}$ complexes the planar $\eta^8\text{-C}_8\text{H}_8$ ring is the 10 π -electron $\text{C}_8\text{H}_8^{2-}$

dianion corresponding to a formal +4 metal oxidation state. The earliest first row transition metal with an accessible +4 formal oxidation is titanium. However, such a $(\eta^8\text{-C}_8\text{H}_8)_2\text{Ti}$ complex with octahapto C_8H_8 rings has an unfavorable 20-electron configuration. As a result the bis(octahapto) complexes $(\eta^8\text{-C}_8\text{H}_8)_2\text{M}$ are only known for the f-block metals ($\text{M} = \text{Ce}$ [4], Th [5], Pa [6,7], U [8], Np [9], Pu [9]) with accessible +4 formal oxidation states for which the 18-electron rule is no longer applicable.

Among the first row transition metals a bis(cyclooctatetraene) titanium derivative, $(\eta^8\text{-C}_8\text{H}_8)\text{Ti}(\eta^4\text{-C}_8\text{H}_8)$, was reported in 1966 as a product from reactions of titanium alkoxides with aluminum alkyls in the presence of excess cyclooctatetraene [10]. A subsequent X-ray structural study [11] showed that one of the C_8H_8 rings is fully bonded as an octahapto ligand, but the other C_8H_8 is bonded through only four of the eight carbon atoms as a 1,2,3,4-tetrahapto ligand similar to the cyclooctatetraene ligand [12] in $(\eta^4\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$, discovered a few years earlier by three independent research groups (Fig. 1) [13–16]. An analogous vanadium compound $(\eta^8\text{-C}_8\text{H}_8)\text{V}(\eta^4\text{-C}_8\text{H}_8)$ has also been synthesized and structurally characterized [17]. In addition, a bis(cyclooctatetraene)iron derivative $(\eta^6\text{-C}_8\text{H}_8)\text{Fe}(\eta^4\text{-C}_8\text{H}_8)$ (Fig. 1) is known [18] in which one of the C_8H_8 rings is a tetrahapto ring, such as in $(\eta^4\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$ and $(\eta^8\text{-C}_8\text{H}_8)\text{M}(\eta^4\text{-C}_8\text{H}_8)$

* Corresponding author.

** Corresponding author.

E-mail addresses: wanghyxx@yahoo.com (H. Wang), rbking@chem.uga.edu (R.B. King).

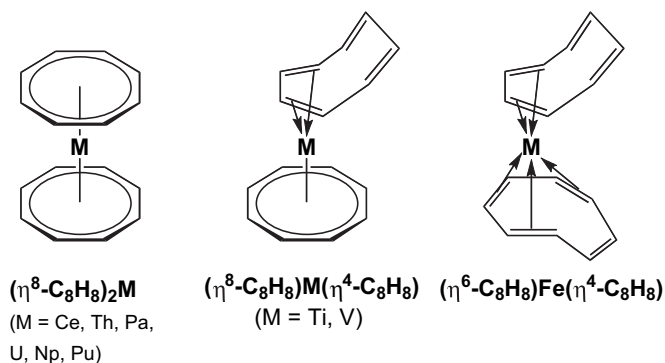


Fig. 1. The three structure types of the known $(\text{C}_8\text{H}_8)_2\text{M}$ derivatives.

(M = Ti, V), but the other C_8H_8 ring is a hexahapto ring as in $(\eta^6\text{-C}_8\text{H}_8)\text{Mo}(\text{CO})_3$. The iron atom in $(\eta^6\text{-C}_8\text{H}_8)\text{Fe}(\eta^4\text{-C}_8\text{H}_8)$ has the favored 18-electron configuration. However, the titanium and vanadium atoms in their $(\eta^8\text{-C}_8\text{H}_8)\text{M}(\eta^4\text{-C}_8\text{H}_8)$ derivatives have 16- and 17-electron configurations, respectively. Neutral $(\text{C}_8\text{H}_8)_2\text{M}$ derivatives of the first row transition metals Cr, Mn, Co, and Ni do not appear to have been reported in the literature. However, the anion $(\eta^4\text{-C}_8\text{H}_8)_2\text{Co}^-$ has been reported [19] as well as the neutral phenylcyclooctatetraene derivative [20] $(\eta^{2,2}\text{-C}_8\text{H}_7\text{Ph})_2\text{Ni}$. Both of these latter complexes have cyclooctatetraene rings bonded to the metals as tetrahapto ligands thereby leading to the favored 18-electron configuration.

This paper explores the scope of the $(\text{C}_8\text{H}_8)_2\text{M}$ derivatives of the first row transition metals using density functional theory methods. These methods are found to predict correctly the experimentally observed structures for the known Ti [10], V [17], and Fe [18] derivatives. New structures are predicted for the $(\text{C}_8\text{H}_8)_2\text{M}$ derivatives of the other metals, namely Cr, Mn, Co, and Ni.

2. Theoretical methods

Electron correlation effects were included by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds [21–35]. Two DFT methods were used in this study. The first functional is the hybrid B3LYP method, which incorporates

Becke's three-parameter exchange functional (B3) [36] with the Lee, Yang, and Parr (LYP) correlation functional [37]. The second approach is the BP86 method, which marries Becke's 1988 exchange functional (B) [38] with Perdew's 1986 correlation functional [39]. It has been noted that the BP86 method may be somewhat more reliable than B3LYP for the type of organometallic systems considered in this paper [40,41].

For carbon the double- ζ plus polarization (DZP) basis set used here adds one set of pure spherical harmonic d functions with an orbital exponent $\alpha_d(\text{C}) = 0.75$ to the Huzinaga–Dunning standard contracted DZ sets, and is designated (9s5p1d/4s2p1d) [42,43]. For H, a set of p polarization functions with $\alpha_p(\text{H}) = 0.75$ is added to the Huzinaga–Dunning DZ sets. For the first row transition metals Ti through Ni, in our loosely contracted DZP basis set, the Wachters' primitive set is used augmented by two sets of p functions and one set of d functions, contracted following Hood et al., and designated (14s11p6d/10s8p3d) [44,45].

The geometries of all of the structures were fully optimized using both the DZP B3LYP and DZP BP86 methods. The harmonic vibrational frequencies were determined at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities are evaluated analytically as well. All of the computations were carried out with the Gaussian 94 program [46] in which the fine grid (75,302) is the default for evaluating integrals numerically, and the tight (10^{-8} hartree) designation is the default for the energy convergence. For the open shell structures the unrestricted method is used in the Gaussian program. In this method the spin orbitals have different spatial orbitals for alpha and beta spins. The unrestricted determinants generated from these orbitals are not eigenfunctions of $\langle S^2 \rangle$ and thus they do not describe a pure spin state. In this way the expectation value of $\langle S^2 \rangle$ determines the spin contamination.

In the search for minima, low magnitude imaginary vibrational frequencies are suspect, because of significant limitations in the numerical integration procedures used in standard DFT computations [47]. Thus imaginary vibrational frequencies with magnitudes less than 50 cm^{-1} are considered questionable, and in many cases we do not follow the eigenvectors corresponding to imaginary frequencies less than 50 cm^{-1} in search of another minimum [48]. In this work the larger grid (99,590) is used to remove the very small imaginary vibrational frequencies. None of the final structures reported in this paper exhibited any imaginary vibrational frequencies.

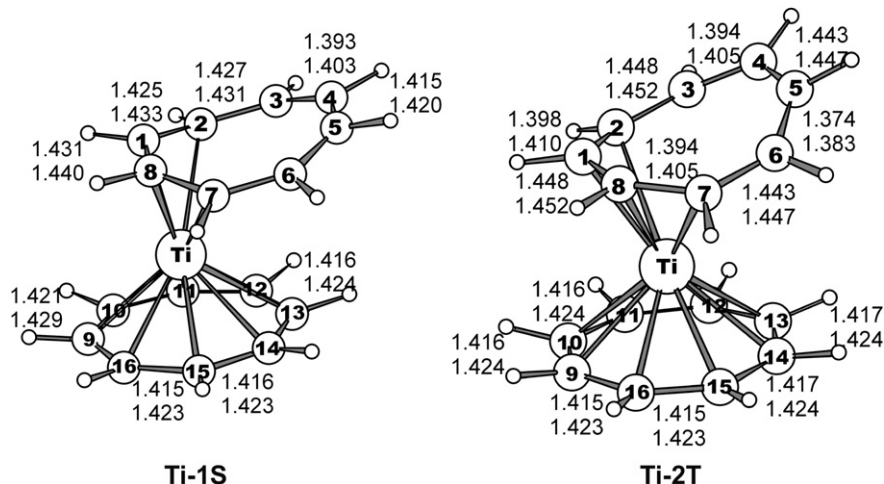


Fig. 2. Optimized geometries for the $\text{Ti}(\text{C}_8\text{H}_8)_2$ structures. In Figs. 2–8 the upper distances were obtained by the B3LYP method and the lower distances by the BP86 method.

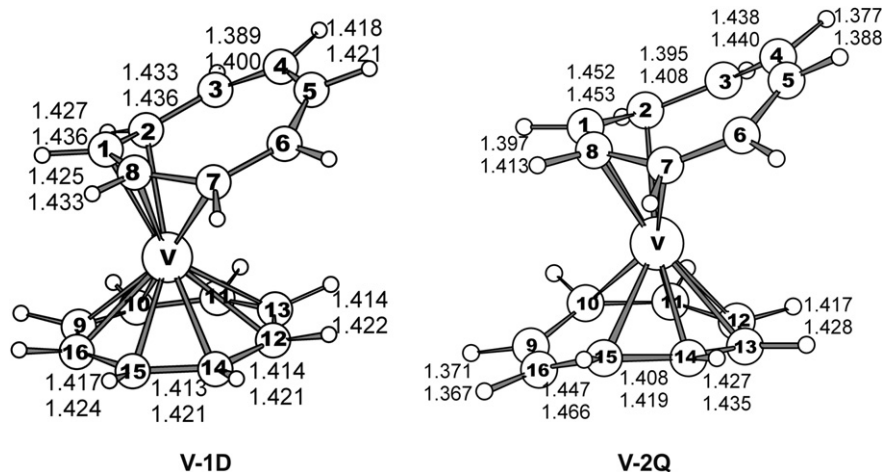


Fig. 3. Optimized geometries for the $(C_8H_8)_2V$ structures.

3. Results

3.1. Molecular structures

The geometries of the complexes $M(C_8H_8)_2$ ($M = Ti, V, Cr, Mn, Fe, Co,$ and Ni) were optimized in their lowest energy electronic singlet and triplet states for $Ti, Cr, Fe,$ and Ni , and doublet and quartet states for $V, Mn,$ and Co . The stationary point geometries of the energetically low-lying species of $M(C_8H_8)_2$ are shown in Figs. 2–8, with all C–C bond distances given in Ångströms. Unless otherwise indicated, all structures are predicted to be genuine minima with no imaginary vibrational frequencies.

3.1.1. $Ti(C_8H_8)_2$

The global minimum of $Ti(C_8H_8)_2$ (**Ti-1S**) is a singlet ($\eta^8-C_8H_8$) $Ti(\eta^4-C_8H_8)$ structure with one octahapto and one tetrahapto C_8H_8 ring as indicated by the $Ti-C$ distances (Fig. 2 and Table 1). This structure is very similar to the experimentally known structure [10]. The C=C distances between the uncomplexed carbon atoms in the $\eta^4-C_8H_8$ ring of **Ti-1S** are 1.393 Å (B3LYP) or 1.403 Å (BP86), which are appreciably shorter than the other carbon–carbon distances and consistent with uncomplexed double bonds. The higher energy triplet ($\eta^8-C_8H_8$) $Ti(\eta^4-C_8H_8)$ structure at 9.5 kcal/

mol (B3LYP) or 18.4 kcal/mol (BP86) above the global minimum **Ti-1S** has a similar bonding mode for the two C_8H_8 rings. Both the singlet and triplet ($\eta^8-C_8H_8$) $Ti(\eta^4-C_8H_8)$ structures thus have a 16-electron titanium configuration, similar to the well-known [49] ($\eta^5-C_5H_5$) $Ti(\eta^7-C_7H_7)$.

3.1.2. $V(C_8H_8)_2$

The optimized structure **V-1D** for doublet $V(C_8H_8)_2$ (Fig. 3 and Table 2) corresponds rather closely to the singlet structure **Ti-1S** (Fig. 2) found for $(C_8H_8)_2Ti$ with one octahapto and one tetrahapto C_8H_8 ring, i. e. ($\eta^8-C_8H_8$) $V(\eta^4-C_8H_8)$. This structure is known experimentally [17] and has a 17-electron configuration about the vanadium atom, analogous to the well-known ($\eta^5-C_5H_5$) $V(\eta^7-C_7H_7)$ [50,51]. A higher energy quartet structure **V-2Q** found for $(C_8H_8)_2V$ at 16.2 kcal/mol (B3LYP) or 25.8 kcal/mol (BP86) above **V-1D** (Fig. 3) is ($\eta^6-C_8H_8$) $V(\eta^4-C_8H_8)$, with one hexahapto and one tetrahapto C_8H_8 ring corresponding to a 15-electron metal configuration.

3.1.3. $Cr(C_8H_8)_2$

The global minimum for $(C_8H_8)_2Cr$ was found to be the singlet structure ($\eta^4-C_8H_8$) $Cr(\eta^8-C_8H_8)$ (**Cr-1S** in Fig. 4) with a tilted $\eta^4-C_8H_8$ ring and a planar $\eta^8-C_8H_8$ ring similar to the corresponding Ti and V compounds **Ti-1S** (Fig. 2) and **V-1D** (Fig. 3), respectively. In

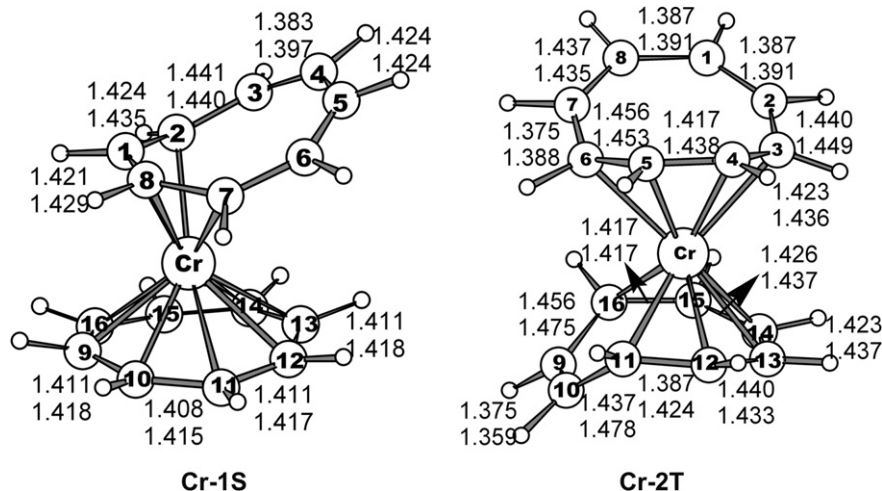


Fig. 4. Optimized geometries for the $(C_8H_8)_2Cr$ structures.

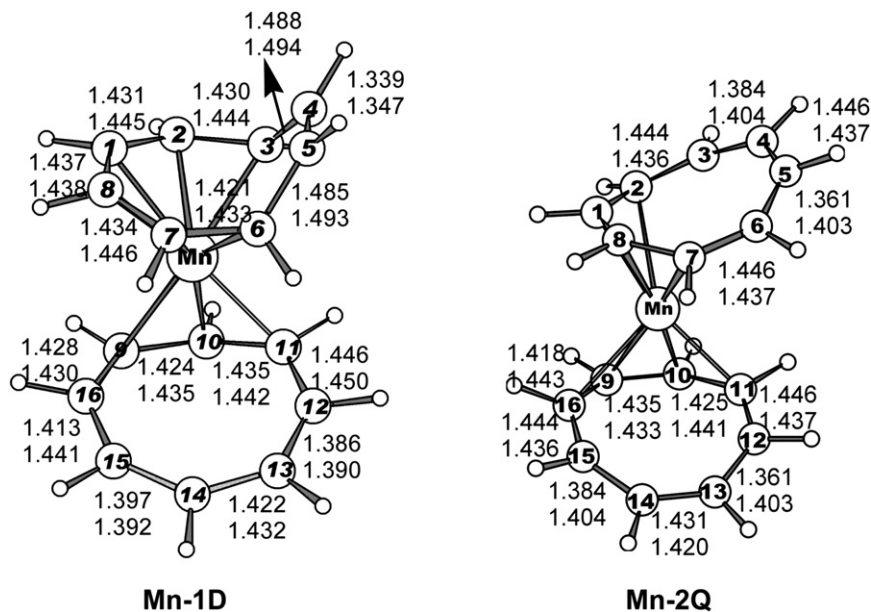


Fig. 5. Optimized geometries for the $(C_8H_8)_2Mn$ structures.

$(\eta^4-C_8H_8)Cr(\eta^8-C_8H_8)$ the chromium atom has the favored 18-electron configuration. The average Cr–C bond distances predicted for **Cr-1S** are 2.306 Å (B3LYP) or 2.301 Å (BP86) for the octahapto C_8H_8 ligand, which are somewhat shorter than the corresponding M–C distances in the corresponding titanium and vanadium derivatives $(\eta^4-C_5H_5)M(\eta^8-C_8H_8)$ (M = Ti, V) discussed above.

The higher energy triplet structure $(\eta^4-C_8H_8)Cr(\eta^6-C_8H_8)$ (**Cr-2T** in Fig. 4) is predicted by the BP86 method to have a tetrahapto $\eta^4-C_8H_8$ ring and a hexahapto $\eta^6-C_8H_8$ ring and lies 11.7 kcal/mol (BP86) above the global minimum **Cr-1S**. A different triplet structure $(\eta^4-C_8H_8)_2Cr$ with two tetrahapto rings is predicted by the B3LYP method as indicated by the Cr–C bond lengths. The relative energy between this B3LYP triplet structure and the singlet global minimum **Cr-1S** is predicted to be 21.7 kcal/mol. However, there is significant spin contamination in the B3LYP optimization of triplet $(C_8H_8)_2Cr$ as indicated by an $\langle S^2 \rangle$ value of 3.18 as compared with the ideal $\langle S^2 \rangle$ value of 2 for a triplet (Table 3). The pure DFT method BP86 does much better in this regard with $\langle S^2 \rangle = 2.12$.

3.1.4. $Mn(C_8H_8)_2$

For $Mn(C_8H_8)_2$ (Fig. 5 and Table 4), the doublet structure **Mn-1D** is predicted by the BP86 method to be $(\eta^6-C_8H_8)Mn(\eta^4-C_8H_8)$ with one hexahapto and one tetrahapto C_8H_8 ring leading to a 17-electron metal configuration. The two uncomplexed carbon atoms of the $\eta^6-C_8H_8$ ring in **Mn-1D** (C4 and C5 in Fig. 5) have Mn–C distances of ~ 3.0 Å (Table 2). Furthermore, the C=C distance between these carbon atoms is 1.339 Å (B3LYP) or 1.347 Å (BP86), which is appreciably shorter than the other carbon–carbon distances and consistent with an uncomplexed double bond. The quartet structure **Mn-2Q** is a bis(tetrahapto) derivative $(\eta^4-C_8H_8)_2Mn$. Two of the C=C distances in the chain of four uncomplexed carbon atoms in the $\eta^4-C_8H_8$ rings of **Mn-2Q** are 1.38 Å and 1.36 Å (Fig. 5), corresponding to double bonds in a *cis* butadienoid unit. The BP86 method predicts **Mn-2Q** to lie 0.8 kcal/mol above the doublet **Mn-1D** whereas the less reliable B3LYP method predicts **Mn-2Q** to lie 17.5 kcal/mol below the doublet **Mn-1D**. However, there is significant spin contamination in the B3LYP optimizations of $(C_8H_8)_2Mn$ as indicated by $\langle S^2 \rangle$ values of

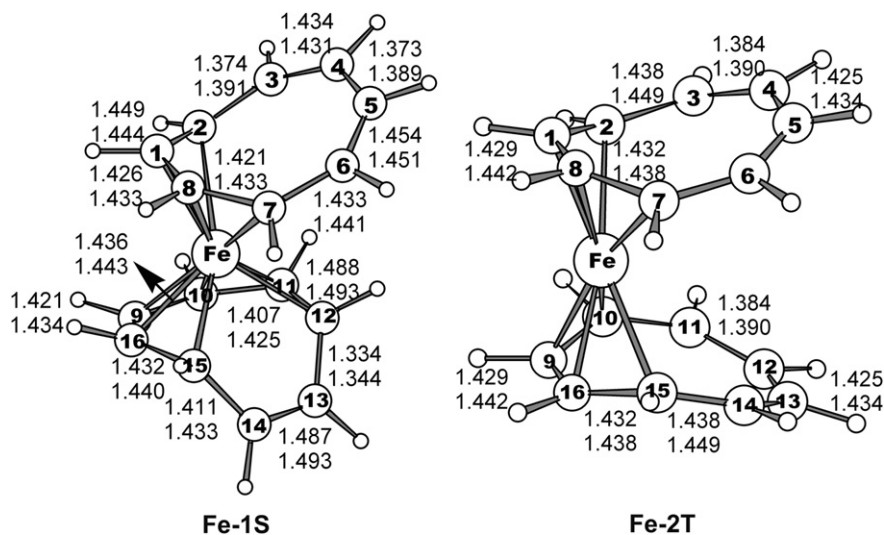


Fig. 6. Optimized geometries for the $(C_8H_8)_2Fe$ structures.

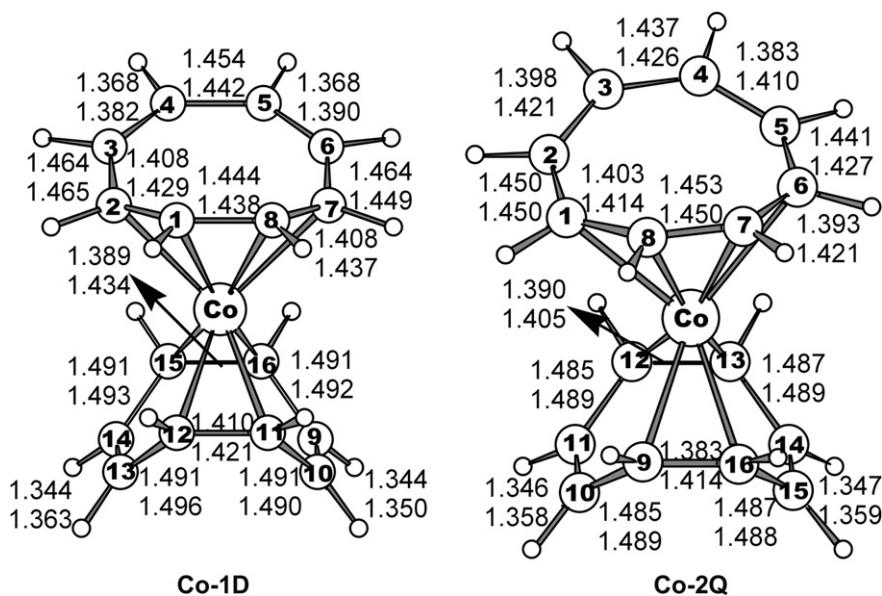


Fig. 7. Optimized geometries for the $(C_8H_8)_2Co$ structures.

1.69 and 4.42 versus the ideal values of 0.75 and 3.75 for the doublet and quartet, respectively. For this reason we consider the BP86 results for $(C_8H_8)_2Mn$ to be more reliable than the B3LYP results.

3.1.5. $Fe(C_8H_8)_2$

The optimized singlet $Fe(C_8H_8)_2$ structure **Fe-1S** (Fig. 6 and Table 5) has one hexahapto and one tetrahapto C_8H_8 ring leading to the

favored 18-electron metal configuration. This structure is known experimentally [18]. The predicted C=C distance between the uncomplexed carbon atoms in **Fe-1S** is 1.334 Å (B3LYP) or 1.344 Å (BP86). The triplet structure **Fe-2T** is a bis(tetrahapto) structure ($\eta^4-C_8H_8)_2Fe$ with two uncomplexed C=C double bonds on the two rings leading to a 16-electron configuration. The spin contamination in the triplet structure **Fe-2T** is significant by the B3LYP

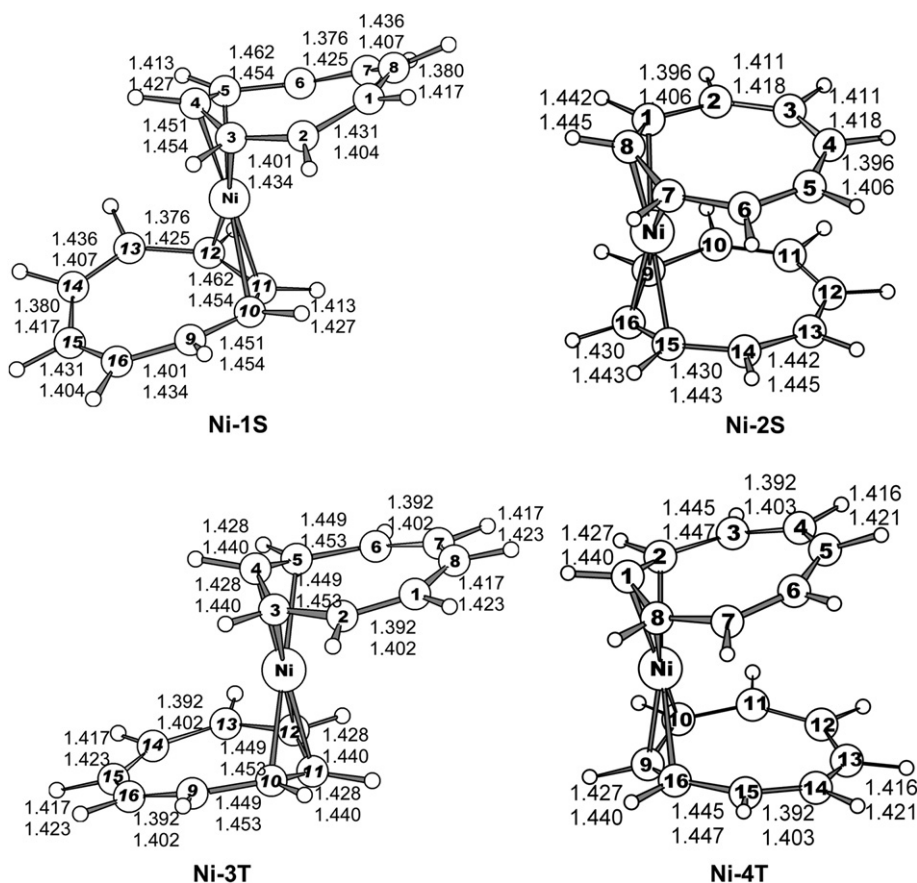


Fig. 8. Optimized geometries for the $(C_8H_8)_2Ni$ structures.

Table 1

Bond distances (in Å), total energies (E in Hartree), relative energies (ΔE in kcal/mol), HOMO–LUMO gaps, and spin expectation values ($\langle S^2 \rangle$) for the $(C_8H_8)_2Ti$ structures.

	Ti-1S (C_2)		Ti-2T (C_1)	
	B3LYP	BP86	B3LYP	BP86
^a M–C ₈ H ₈	2.35	2.36	2.44	2.41
^b M–C ₈ H ₈	2.36	2.36	2.38	2.38
–HOMO(α)	0.1752	0.15599	0.16873	0.11697
–LUMO(α)	0.0696	0.10757	0.03189	0.06111
Gap/eV	2.87	1.32	3.72	1.52
– E	1468.83523	1468.95540	1468.82015	1468.92604
ΔE	0.0	0.0	9.5	18.4
$\langle S^2 \rangle$	0.00	0.00	2.02	2.01

^a Average upper bonded M–C₈H₈ ring distance.

^b Average lower bonded M–C₈H₈ ring distance.

Table 2

Bond distances (in Å), total energies (E in Hartree), relative energies (ΔE in kcal/mol), HOMO–LUMO gaps, and spin expectation values ($\langle S^2 \rangle$) for the $(C_8H_8)_2V$ structures.

	V-1D (C_1)		V-2Q (C_1)	
	B3LYP	BP86	B3LYP	BP86
^a M–C ₈ H ₈	2.29	2.29	2.37	2.32
^b M–C ₈ H ₈	2.34	2.33	2.33	2.31
–HOMO	0.17340	0.14979	0.16916	0.14808
–LUMO	0.06953	0.09405	0.06289	0.08719
Gap/eV	2.83	1.52	2.89	1.66
– E	1563.34357	1563.49025	1563.31774	1563.44912
ΔE	0.0	0.0	16.2	25.8
$\langle S^2 \rangle$	0.86	0.80	3.82	3.79

^a Average upper bonded M–C₈H₈ ring distance.

^b Average lower bonded M–C₈H₈ ring distance.

method, i.e., an $\langle S^2 \rangle$ value of 2.46 versus the ideal 2. Thus the BP86 calculations for $(C_8H_8)_2Fe$ should be considered to be the more reliable. With the BP86 method, the global minimum is the singlet structure **Fe-1S**, which is predicted to lie 12.5 kcal/mol below the triplet structure **Fe-2T**.

3.1.6. $Co(C_8H_8)_2$

The optimized structures for both the doublet and quartet spin states of $(C_8H_8)_2Co$ were found to have two non-equivalent tetrahapto C_8H_8 ligands (Fig. 7 and Table 6). One of the tetrahapto C_8H_8 ligands has four adjacent carbon atoms within bonding distance of the central cobalt atom, similar to the $\eta^4-C_8H_8$ ligands in the $(\eta^8-C_8H_8)M(\eta^4-C_8H_8)$ structures of the early transition metals Ti, V, and Cr (**Ti-1S**, **V-1D**, and **Cr-1S** in Figs. 2–4, respectively). The other tetrahapto C_8H_8 ligand in the $(C_8H_8)_2Co$ structures has two non-adjacent C=C double bonds of the C_8H_8 ring bonded to the cobalt atom and thus may be considered as a 1,2,5,6 or $\eta^{2,2}$ tetrahapto ligand. Such a $\eta^{2,2}-C_8H_8$ tetrahapto ligand is found experimentally in the known compound $(\eta^5-C_5H_5)Co(\eta^{2,2}-C_8H_8)$. The relative

Table 3

Bond distances (in Å), total energies (E in Hartree), relative energies (ΔE in kcal/mol), HOMO–LUMO gaps, and spin expectation values ($\langle S^2 \rangle$) for the $(C_8H_8)_2Cr$ structures.

	Cr-1S (C_2)		Cr-2T (C_1)	
	B3LYP	BP86	B3LYP	BP86
^a M–C ₈ H ₈	2.23	2.23	2.27	2.21
^b M–C ₈ H ₈	2.31	2.30	2.56	2.24
–HOMO	0.17037	0.11857	0.17723	0.15056
–LUMO	0.07163	0.10034	0.11796	0.09014
Gap/eV	2.69	0.50	1.61	1.64
– E	1663.75385	1663.93126	1663.78842	1663.94851
ΔE	0.0	0.0	21.7	11.7
$\langle S^2 \rangle$	0.00	0.00	3.18	2.12

^a Average upper bonded M–C₈H₈ ring distance.

^b Average lower bonded M–C₈H₈ ring distance.

Table 4

Bond distances (in Å), total energies (E in Hartree), relative energies (ΔE in kcal/mol), HOMO–LUMO gaps, and spin expectation values ($\langle S^2 \rangle$) for the $(C_8H_8)_2Mn$ structures.

	Mn-1D (C_1)		Mn-2Q (C_2)	
	B3LYP	BP86	B3LYP	BP86
^a M–C ₈ H ₈	2.16	2.12	2.26	2.19
^b M–C ₈ H ₈	2.16	2.13	2.26	2.19
–HOMO	0.18713	0.16251	0.17056	0.15511
–LUMO	0.09111	0.09761	0.10387	0.10663
Gap/eV	2.61	1.77	1.81	1.32
– E	1770.28549	1770.48580	1770.31337	1770.48462
ΔE	17.5	0.0	0.0	0.8
$\langle S^2 \rangle$	1.69	0.82	4.42	3.94

^a Average upper bonded M–C₈H₈ ring distance.

^b Average lower bonded M–C₈H₈ ring distance.

energy of the quartet ($\eta^4-C_8H_8$)Co($\eta^{2,2}-C_8H_8$) structure **Co-2Q** is predicted to be 5.7 kcal/mol (B3LYP) or 15.8 kcal/mol (BP86) above the corresponding doublet global minimum **Co-1D**. The BP86 value is considered to be more reliable, owing to significant spin contamination in the B3LYP optimization of **Co-1D**.

3.1.7. $Ni(C_8H_8)_2$

The singlet and triplet *cis* and *trans* $(C_8H_8)_2Ni$ structures are of the type $(\eta^3-C_8H_8)_2Ni$ with two trihapto C_8H_8 ligands as clearly indicated by their Ni–C distances (Fig. 8 and Table 7). The nickel atoms in all four structures have 16-electron configurations with a nickel environment very similar to the well-known [52]bis(η^3 -allyl)nickel, $(\eta^3-C_3H_5)_2Ni$. The singlet *trans* structure **Ni-1S** is the global minimum. The singlet *cis* structure **Ni-2S** is close in energy to the corresponding *trans* structure. For the triplet $(C_8H_8)_2Ni$, the *cis* structure **Ni-4T** has a higher energy than the *trans* structure **Ni-3T** by 2.4 kcal/mol (B3LYP) or 0.5 kcal/mol (BP86). The triplet *trans* structure **Ni-3T** lies 0.6 kcal/mol (B3LYP) or 10.1 kcal/mol (BP86) above the singlet global minimum **Ni-1S**.

3.2. Molecular orbital analyses

Analyses of the frontier molecular orbitals (MOs) (Fig. 9) were performed for the lowest energy $(\eta^8-C_8H_8)M(\eta^4-C_8H_8)$ structures **Ti-1S** (Fig. 2), **V-2D** (Fig. 3), and **Cr-1S**. These are seen to involve the metal d orbitals with the MO incorporating the z^2 orbital being of the highest energy. This MO is empty (i. e., the LUMO) in the 16-electron complex $(\eta^8-C_8H_8)Ti(\eta^4-C_8H_8)$, occupied by a single electron (i. e., the SOMO) in the 17-electron complex $(\eta^8-C_8H_8)V(\eta^4-C_8H_8)$, and filled by a lone pair (i. e., the HOMO) in the 18-electron complex $(\eta^8-C_8H_8)Cr(\eta^4-C_8H_8)$.

The two MOs energetically below the z^2 MO involve π -bonding of the metal *xz* and *yz* orbitals to the four adjacent carbon atoms of the tetrahapto $\eta^4-C_8H_8$ ring, with essentially no involvement of the

Table 5

Bond distances (in Å), total energies (E in Hartree), relative energies (ΔE in kcal/mol), HOMO–LUMO gaps, and spin expectation values ($\langle S^2 \rangle$) for the $(C_8H_8)_2Fe$ structures.

	Fe-1S (C_1)		Fe-2T (C_{2v})	
	B3LYP	BP86	B3LYP	BP86
^a M–C ₈ H ₈	2.14	2.15	2.20	2.15
^b M–C ₈ H ₈	2.13	2.11	2.20	2.15
–HOMO	0.17642	0.15592	0.17188	0.15617
–LUMO	0.05685	0.09144	0.10034	0.11076
Gap/eV	3.25	1.75	1.95	1.24
– E	1883.00775	1883.23676	1883.01503	1883.21680
ΔE	0.0	0.0	–4.6	12.5
$\langle S^2 \rangle$	0.00	0.00	2.46	2.01

^a Average upper bonded M–C₈H₈ ring distance.

^b Average lower bonded M–C₈H₈ ring distance.

Table 6

Bond distances (in Å), total energies (E in Hartree), relative energies (ΔE in kcal/mol), HOMO–LUMO gaps, and spin expectation values (S^2) for the $(C_8H_8)_2Co$ structures.

	Co-1D (C_1)		Co-2Q (C_1)	
	B3LYP	BP86	B3LYP	BP86
^a M–C ₈ H ₈	2.21	2.13	2.31	2.23
^b M–C ₈ H ₈	2.16	2.08	2.22	2.16
–HOMO	0.16723	0.14820	0.14961	0.12614
–LUMO	0.08584	0.09998	0.05828	0.07836
Gap/eV	2.21	1.31	2.49	1.30
– E	2002.08028	2002.30121	2002.07126	2002.27596
ΔE	0.0	0.0	5.7	15.8
$\langle S^2 \rangle$	1.08	0.78	3.79	3.77

^a Average upper bonded M–C₈H₈ ring distance.

^b Average lower bonded M–C₈H₈ ring distance.

octahapto η^8 -C₈H₈ ring (Fig. 9). Because of the bent conformation of the tetrahapto η^4 -C₈H₈ ring, this metal–ring π -bond is a “side-on” bond to a ring MO of bimodal δ symmetry, as can be seen in Fig. 9 by the lobes of the ring orbitals not overlapping with the lobes of the relevant metal d orbitals.

The next two MOs going down in energy involve δ bonding of the metal x^2-y^2 and xy orbitals to the octahapto η^8 -C₈H₈ ring with essentially no involvement of the tetrahapto ring (Fig. 9).

4. Discussion

The preferred structures for the early transition metal bis (cyclooctatetraene) derivatives are $(\eta^8-C_8H_8)M(\eta^4-C_8H_8)$ ($M = Ti, V, Cr$) in which 12 of the 16 carbon atoms of the two C₈H₈ rings are within bonding distance of the metal atom. Interestingly enough, only the titanium [10] and vanadium [17] derivatives with 16- and 17-electron metal configurations are known experimentally. The chromium complex $(\eta^8-C_8H_8)Cr(\eta^4-C_8H_8)$ remains unknown despite its favorable 18-electron metal configuration. Instead a homoleptic binuclear chromium derivative $(C_8H_8)_3Cr_2$ is known shown by an X-ray structural study [53] to have a short Cr–Cr distance interpreted as a formal quadruple bond. The mononuclear $(\eta^8-C_8H_8)M(\eta^4-C_8H_8)$ derivatives have 12 carbon atoms of the two rings within bonding distance of the metal similar to the well-known stable sandwich compounds of the types $(\eta^6-C_6H_6)_2M$ and $(\eta^5-C_5H_5)M(\eta^7-C_7H_7)$ ($M = Ti, V, Cr$).

The central metal atoms in similar hypothetical complexes $(\eta^8-C_8H_8)M(\eta^4-C_8H_8)$ of manganese and later first row transition metals would have electronic configurations greater than the favored 18-electrons. It is therefore not surprising that our theoretical studies find $(\eta^8-C_8H_8)M(\eta^4-C_8H_8)$ structures to be unfavorable for manganese and later transition metals. Structures of the type $(\eta^6-C_8H_8)M(\eta^4-C_8H_8)$ with one hexahapto and one tetrahapto C₈H₈ ring are predicted for manganese and iron to be low energy structures. The iron complex of this type $(\eta^6-C_8H_8)Fe(\eta^4-C_8H_8)$ is known experimentally [18] in accord with this theoretical prediction as well as its

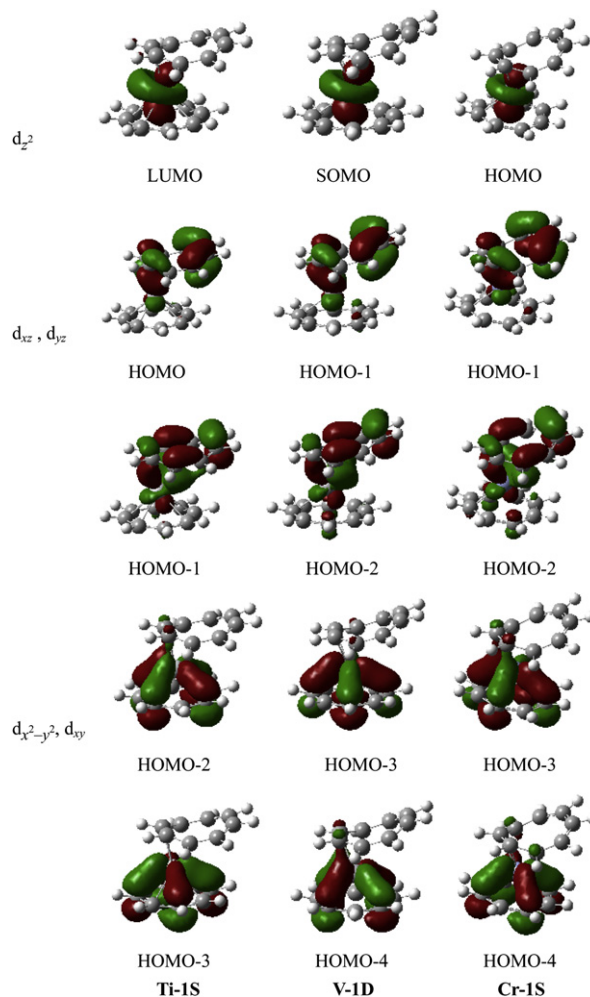


Fig. 9. The frontier molecular orbitals of the $(\eta^8-C_8H_8)M(\eta^4-C_8H_8)$ complexes **Ti-1S**, **V-1D**, and **Cr-1S**.

favorable 18-electron configuration. For manganese a quartet $(\eta^4-C_8H_8)_2Mn$ structure with two tetrahapto rings and a 15-electron manganese configuration appears to be energetically favorable as well as the doublet structure $(\eta^6-C_8H_8)Mn(\eta^4-C_8H_8)$ with a 17-electron configuration. Neither of these structures nor any other $(C_8H_8)_2Mn$ structure is known experimentally.

A 17-electron bis(tetrahapto) structure $(\eta^4-C_8H_8)Co(\eta^{2,2}-C_8H_8)$ is predicted to be the lowest energy structure for the cobalt complex $(C_8H_8)_2Co$. This structure is interesting since the two tetrahapto C₈H₈ rings are of different types. The 1,2,3,4-tetrahapto η^4 -C₈H₈ ring has four adjacent carbon atoms bonded to the cobalt

Table 7

Bond distances (in Å), total energies (E in Hartree), relative energies (ΔE in kcal/mol), HOMO–LUMO gaps, and spin expectation values (S^2) for the $(C_8H_8)_2Ni$ structures.

	Ni-1S (C_2)		Ni-2S (C_{2v})		Ni-3T (C_2)		Ni-4T (C_{2v})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
^a M–C ₈ H ₈	2.07	2.06	2.05	2.05	2.06	2.05	2.08	2.07
^b M–C ₈ H ₈	2.07	2.06	2.05	2.05	2.08	2.07	2.08	2.07
–HOMO	0.17176	0.15574	0.17004	0.15400	0.17068	0.14418	0.16623	0.14040
–LUMO	0.10457	0.11231	0.10075	0.11781	0.07345	0.09782	0.07257	0.09849
Gap/eV	1.83	1.18	1.89	0.98	2.65	1.26	2.55	1.14
– E	2127.63715	2127.87918	2127.63683	2127.87774	2127.63621	2127.86308	2127.63241	2127.86229
ΔE	0.0	0.0	0.2	0.9	0.6	10.1	3.0	10.6
$\langle S^2 \rangle$	0.00	0.00	0.00	0.00	2.09	2.03	2.10	2.03

^a Average upper bonded M–C₈H₈ ring distance.

^b Average lower bonded M–C₈H₈ ring distance.

atom similar to the cyclooctatetraene ring in the well-known [12] ($\eta^4\text{-C}_8\text{H}_8$) $\text{Fe}(\text{CO})_3$. The 1,2,5,6-tetrahapto $\eta^{2,2}\text{-C}_8\text{H}_8$ ring in ($\eta^4\text{-C}_8\text{H}_8$) $\text{Co}(\eta^{2,2}\text{-C}_8\text{H}_8)$ has two non-adjacent C=C double bonds bonded to the cobalt atom similar to the chelating diolefin 1,5-cyclooctadiene in such complexes as ($\eta^5\text{-C}_5\text{H}_5$) $\text{Cr}(1,5\text{-C}_8\text{H}_{12})$ [54]. A similar ($\eta^4\text{-C}_8\text{H}_8$) $\text{Co}(\eta^{2,2}\text{-C}_8\text{H}_8)$ structure is found for the quartet spin state but at higher energy. No (C_8H_8) $_2\text{Co}$ derivatives are known experimentally.

A bis(tetrahapto) structure ($\eta^4\text{-C}_8\text{H}_8$) $_2\text{Ni}$ (or ($\eta^4\text{-C}_8\text{H}_8$) $\text{Ni}(\eta^{2,2}\text{-C}_8\text{H}_8)$ analogous to the cobalt complex discussed above) would be expected to be very favorable for the nickel complex since it would have the favorable 18-electron configuration. However, our theoretical studies predict a bis(trihapto) complex ($\eta^3\text{-C}_8\text{H}_8$) $_2\text{Ni}$ to be the preferred structures for both the singlet and triplet spin states. Both *cis* and *trans* isomers were found for ($\eta^3\text{-C}_8\text{H}_8$) $_2\text{Ni}$ in both the singlet and triplet spin states. In all of these structures the nickel atom has a local 16-electron configuration similar to the nickel atom in the well-known [52] bis(allyl)nickel, ($\eta^3\text{-C}_3\text{H}_5$) $_2\text{Ni}$. This bis(trihapto) structure ($\eta^3\text{-C}_8\text{H}_8$) $_2\text{Ni}$ with a 16-electron metal configuration is very different from the bis(tetrahapto) structure ($\eta^4\text{-C}_8\text{H}_8$) $_2\text{Co}^-$ with an 18-electron metal configuration found experimentally for the isoelectronic bis(cyclooctatetraene)cobalt monoanion [19].

Acknowledgment

We are grateful to the China National Science Foundation (Grants 10774104 and 10974161), Sichuan Province Youth Science and Technology Foundation (2008-20-360) and the U.S. National Science Foundation (Grant CHE-0716718 and CHE-074986) for support of this work.

Appendix. Supplementary data

Complete tables of metal-carbon distances (in Å) for the M (C_8H_8) $_2$ (M = Ti, V, Cr, Mn, Fe, Co, Ni) structures (Tables S1 to S7); complete tables of vibrational frequencies for (C_8H_8) $_2\text{M}$ (M = Ti, V, Cr, Mn, Fe, Co, Ni) structures (Tables S8 to S23); complete Gaussian reference 46).

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jorganchem.2010.07.003.

References

- [1] T.J. Kealy, P.L. Pauson, *Nature* 168 (1961) 1039.
- [2] S.A. Miller, J.A. Tebboth, J.F. Tremaine, *J. Chem. Soc.* (1952) 632.
- [3] E.O. Fischer, W. Hafner, *Z. Naturforsch.* 10b (1955) 665.
- [4] A. Greco, S. Cesca, G. Bertolini, *J. Organometal. Chem.* 113 (1976) 321.
- [5] A. Streitwieser Jr., N. Yoshida, *J. Am. Chem. Soc.* 91 (1969) 7328.
- [6] D. Starks, T. Parsons, A. Streitwieser Jr., N. Edelstein, *Inorg. Chem.* 13 (1974) 1307.
- [7] J. Goffart, J. Fuger, D. Brown, G. Duyckaerts, *Inorg. Nucl. Chem. Lett.* 10 (1974) 413.
- [8] A. Streitwieser Jr., U. Müller-Westerhoff, *J. Am. Chem. Soc.* 90 (1968) 7364.
- [9] D.G. Karkaker, J.A. Stone, E.R. Jones Jr., N. Edelstein, *J. Am. Chem. Soc.* 92 (1970) 4841.
- [10] H. Breil, G. Wilke, *Angew. Chem.* 78 (1966) 942.
- [11] H. Dietrich, M. Soltwisch, *Angew. Chem. Int. Ed.* 8 (1969) 765.
- [12] B. Dickens, W.N. Lipscomb, *J. Am. Chem. Soc.* 83 (1961) 4862.
- [13] T.A. Manuel, F.G.A. Stone, *Proc. Chem. Soc. London* (1959) 90.
- [14] T.A. Manuel, F.G.A. Stone, *J. Am. Chem. Soc.* 82 (1960) 366.
- [15] M.D. Rausch, G.N. Schrauzer, *Chem. and Ind.* (1959) 957.
- [16] A. Nakamura, N. Hagihara, *Bull. Chem. Soc. Japan* 32 (1959) 880.
- [17] D. Gourier, E. Samuel, B. Bachmann, F. Hahn, J. Heck, *Inorg. Chem.* 31 (1992) 86.
- [18] G. Allegra, A. Colombo, A. Immirzi, I.W. Bassi, *J. Am. Chem. Soc.* 90 (1968) 4455.
- [19] W.W. Brennessel, V.G. Young Jr., J.E. Ellis, *Angew. Chem. Int. Ed.* 41 (2002) 1211.
- [20] W. Gausing, G. Wilke, C. Krüger, L.K. Liu, *J. Organometal. Chem.* 199 (1980) 137.
- [21] A.W. Ehlers, G. Frenking, *J. Am. Chem. Soc.* 116 (1994) 1514.
- [22] S. Chiodo, O. Kondakova, M.D. Michellini, N. Russo, E. Sicilia, A. Irigoras, J.M. Ugalde, *J. Phys. Chem. A* 108 (2004) 1069.
- [23] J. Li, G. Schreckenbach, T. Ziegler, *J. Am. Chem. Soc.* 117 (1995) 486.
- [24] V. Jonas, W. Thiel, *J. Chem. Phys.* 102 (1995) 8474.
- [25] T.A. Barckholtz, B.E. Bursten, *J. Am. Chem. Soc.* 120 (1998) 1926.
- [26] S. Niu, M.B. Hall, *Chem. Rev.* 100 (2000) 353.
- [27] P. Macchi, A. Sironi, *Coord. Chem. Rev.* 238 (2003) 383.
- [28] J.-L. Carreon, J.N. Harvey, *Phys. Chem. Phys.* 8 (2006) 93.
- [29] M. Bühl, H. Kabrede, *J. Chem. Theory Comput.* 2 (2006) 1282.
- [30] T. Ziegler, J. Autschbach, *Chem. Rev.* 105 (2005) 2695.
- [31] M.P. Waller, M. Bühl, K.R. Geethanakshmi, D. Wang, W. Thiel, *Chem. Eur. J.* 13 (2007) 4723.
- [32] P.G. Hayes, C. Beddie, M.B. Hall, R. Waterman, T.D. Tilley, *J. Am. Chem. Soc.* 128 (2006) 428.
- [33] M. Bühl, C. Reimann, D.A. Pantazis, T. Bredow, F. Neese, *J. Chem. Theory Comput.* 4 (2008) 1449.
- [34] M. Besora, J.-L. Carreon-Macedo, J. Cowan, M.W. George, J.N. Harvey, P. Portius, K.L. Ronayne, X.-Z. Sun, M. Towrie, *J. Am. Chem. Soc.* 131 (2009) 3583.
- [35] X. Zhang, H. Schwarz, *Chem. Eur. J.* 16 (2010) 5882.
- [36] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [37] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [38] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [39] J.P. Perdew, *Phys. Rev. B* 33 (1986) 8822.
- [40] X. Feng, J. Gu, Y. Xie, R.B. King, H.F. Schaefer, *J. Chem. Theor. Comput.* 3 (2007) 1580.
- [41] S. Zhao, W. Wang, Z. Li, Z.P. Liu, K. Fan, Y. Xie, H.F. Schaefer, *J. Chem. Phys.* 124 (2006) 184102.
- [42] T.H. Dunning, *J. Chem. Phys.* 53 (1970) 2823.
- [43] S. Huzinaga, *J. Chem. Phys.* 42 (1965) 1293.
- [44] A.J.H. Wachters, *J. Chem. Phys.* 52 (1970) 1033.
- [45] D.M. Hood, R.M. Pitzer, H.F. Schaefer, *J. Chem. Phys.* 71 (1979) 705.
- [46] Gaussian 94, Revision B.3. Gaussian Inc., Pittsburgh, PA, 1995, (see Supporting Information for details).
- [47] B.N. Pappas, H.F. Schaefer, *J. Mol. Struct.* 768 (2006) 175.
- [48] Y. Xie, H.F. Schaefer, R.B. King, *J. Am. Chem. Soc.* 122 (2000) 8746.
- [49] J.D. Zeinstra, J.L. De Boer, *J. Organometal. Chem.* 54 (1973) 207.
- [50] R.B. King, F.G.A. Stone, *J. Am. Chem. Soc.* 81 (1959) 5263.
- [51] G. Engebretson, R.E. Rundle, *J. Am. Chem. Soc.* 85 (1963) 481.
- [52] G. Wilke, B. Bogdanovi, *Angew. Chem.* 73 (1961) 756.
- [53] D.J. Brauer, C. Krüger, *Inorg. Chem.* 15 (1976) 2511.
- [54] R.B. King, P.M. Treichel, F.G.A. Stone, *J. Am. Chem. Soc.* 83 (1961) 3593.