The hapticity of cyclooctatetraene in its first row mononuclear transition metal carbonyl complexes: Several examples of octahapto coordination

Hongyan Wang [a,*], Quan Du [b], Yaoming Xie [c], R. Bruce King [c,*], Henry F. Schaefer III [c]

[a] College of Sciences, Southwest Jiaotong University, Chengdu 610031, PR China
[b] School of Physics and Chemistry and Research Center for Advanced Computation, Xihua University, Chengdu 610039, PR China
[c] Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602, USA

ARTICLE INFO

ABSTRACT

The two cyclooctatetraene metal carbonyls that have been synthesized are the tetrahapto derivative $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ and the hexahapto derivative $(\eta^6\text{-}C_8H_8)Cr(CO)_3$ using the reactions of cyclooctatetraene with $Fe(CO)_5$ and with $fac\text{-}(CH_3CN)_3Cr(CO)_3$, respectively. Related $C_8H_8M(CO)_n$ (M = Ti, V, Cr, Mn, Fe, Co, Ni; n = 4, 3, 2, 1) species have now been investigated by density functional theory in order to explore the scope of cyclooctatetraene metal carbonyl chemistry. In this connection, the existence of octahapto $(\eta^8\text{-}C_8H_8)M(CO)_n$ species is predicted as long as the central metal M does not exceed the 18-electron configuration by receiving eight electrons from the $\eta^8\text{-}C_8H_8$ ring. Thus the lowest energy structures $(\eta^8\text{-}C_8H_8)Ti(CO)_n$ (n = 3, 2, 1), $(\eta^8\text{-}C_8H_8)M(CO)_n$ (M = V, Cr; n = 2, 1), and $(\eta^8\text{-}C_8H_8)Mn(CO)$ all have octahapto $\eta^8\text{-}C_8H_8$ rings. An exception is $(\eta^6\text{-}C_8H_8)Fe(CO)$, with a hexahapto $\eta^6\text{-}C_8H_8$ ring and thus only a 16-electron configuration for the iron atom. Hexahapto $(\eta^6\text{-}C_8H_8)M(CO)_n$ structures are predicted for the known $(\eta^6\text{-}C_8H_8)Cr(CO)_3$ as well as the unknown $(\eta^6\text{-}C_8H_8)Ti(CO)_4$, $(\eta^6\text{-}C_8H_8)V(CO)_3$, $(\eta^6\text{-}C_8H_8)Mn(CO)_2$, and $(\eta^6\text{-}C_8H_8)Fe(CO)_2$ with 18, 18, 17, 17, and 18 electron configurations, respectively, for the central metal atoms. There are two types of tetrahapto $C_8H_8M(CO)_n$ complexes. In the 1,2,3,4-tetrahapto $(\eta^4\text{-}C_8H_8)M(CO)_n$ complexes two adjacent C=C double bonds, forming a 1,3-diene unit similar to butadiene, are bonded to the metal atom. In the 1,2,5,6-tetrahapto $(\eta^{2,2}\text{-}C_8H_8)M(CO)_3$ derivatives two non-adjacent C=C double bonds of the C_8H_8 ring are bonded to the metal atom. The known $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ is a 1,2,3,4-tetrahapto complex. The unknown isomeric 1,2,5,6-tetrahapto complex $(\eta^{2,2}\text{-}C_8H_8)Fe(CO)_3$ is predicted to lie ~15 kcal/mol above $(\eta^4\text{-}C_8H_8)Fe(CO)_3$. The related 1,2,5,6-tetrahapto complexes $(\eta^{2,2}\text{-}C_8H_8)Cr(CO)_4$, $(\eta^{2,2}\text{-}C_8H_8)Mn(CO)_4$, $[(\eta^{2,2}\text{-}C_8H_8)Mn(CO)_3]^-$, $(\eta^{2,2}\text{-}C_8H_8)Co(CO)_2$, and $(\eta^{2,2}\text{-}C_8H_8)Ni(CO)_2$ are all predicted to be low-energy structures.

© 2009 Published by Elsevier B.V.

1. Introduction

The chemistry of cyclooctatetraene metal carbonyl derivatives dates back to the first synthesis of cyclooctatetraene-iron tricarbonyl, $C_8H_8Fe(CO)_3$ in 1959 independently by three research groups, namely Manuel and Stone in the USA [1,2], Rausch and Schrauzer in the USA [3], and Nakamura and Hagihara in Japan [4]. Thus, the simple thermal reaction of $Fe(CO)_5$ with cyclooctatetraene proceeds readily in good yield to give $C_8H_8Fe(CO)_3$ as an air-stable, red sublimable solid. However, because of the non-routine nature of X-ray crystallography at that time, the structure of $C_8H_8Fe(CO)_3$ was initially an enigma. Thus the proton NMR spectra of $C_8H_8Fe(CO)_3$ under ambient conditions exhibited only a single sharp resonance for the eight protons of the C_8H_8 ring. Taken at

face value, this would seem to imply that the C_8H_8 ring is an octahapto ligand, as suggested by Cotton in a 1960 theoretical study [5] shortly after the discovery of $C_8H_8Fe(CO)_3$. However, the iron atom in $C_8H_8Fe(CO)_3$ would then have an unfavorable 22-electron configuration by receiving eight electrons from an $\eta^8\text{-}C_8H_8$ ring and six electrons from the three carbonyl groups in addition to the original eight electrons of the neutral iron atom.

The problem of the structure of $C_8H_8Fe(CO)_3$ was readily solved when an X-ray structure determination in 1961 by Dickens and Lipscomb [6] showed that only four carbon atoms of the C_8H_8 ring were located within bonding distance of the iron atom leaving effectively two uncomplexed C=C double bonds (Fig. 1). Thus the C_8H_8 ring functioned only as a tetrahapto ligand, donating only four electrons to the iron atom. This gives the iron a favorable 18-electron configuration, by receiving only four electrons from the $\eta^4\text{-}C_8H_8$ ring as well as the six electrons from the three carbonyl groups and the original eight electrons of the neutral iron atom. However, a new dilemma arose, namely how to reconcile
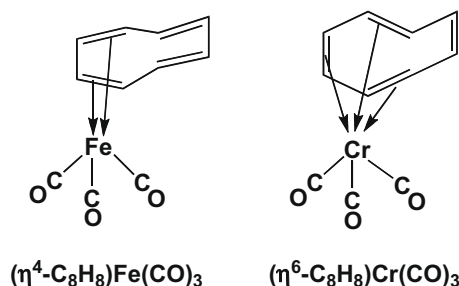
Fig. 1. A comparison of the structures of the original cyclooctatetraene metal carbonyls to show the difference between the tetrahapto ring in $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ and the hexahapto ring in $(\eta^6\text{-}C_8H_8)Cr(CO)_3$.

the single C_8H_8 proton NMR resonance in $C_8H_8Fe(CO)_3$ with the obvious four non-equivalent pairs of hydrogen atoms in the tetrahapto structure (Fig. 1). This second dilemma was resolved when the technology of taking NMR spectra at low temperatures became available. Thus the proton NMR spectrum of $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ at $-150\,°C$ showed the expected non-equivalence of the four protons on carbon atoms bonded to the iron atom and the four protons on the carbon atoms of the two uncomplexed C=C double bonds [7,8]. The temperature dependence of the NMR spectrum of $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ was found to be reversible since these low temperature proton resonances of the C_8H_8 ring coalesced into a single peak upon warming to room temperature. The single proton NMR peak in $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ at ambient temperature was interpreted as indicating motion of the $Fe(CO)_3$ moiety around the C_8H_8 ring faster than the time scale of the NMR measurement, i.e., a stereochemical non-rigid system colloquially known as a "ring whizzer" in the early days. Cotton coined the more elegant term "fluxional" to describe such behavior [9]. Thus $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ is of historical interest in representing one of the first examples of a fluxional organometallic molecule. In fact, this early research on $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ was a key impetus in the development of the concept of fluxionality. Also $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ is one of the first examples of a metal complex of an unsaturated hydrocarbon in which the unsaturated network of the hydrocarbon is only partially bonded to the metal atom. This was a key structure to motivate Cotton to develop the "hapto" nomenclature for olefin–metal complexes to indicate how much of the unsaturated system is actually directly bonded to the metal atom [10].

The other example of an isolable $C_8H_8M(CO)_n$ derivative of a first row transition metal is the chromium derivative $(\eta^6\text{-}C_8H_8)Cr(CO)_3$. The synthesis of $(\eta^6\text{-}C_8H_8)Cr(CO)_3$ is more difficult than that of $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ since it does not arise from the simple thermal reaction of $Cr(CO)_6$ with cyclooctatetraene. Instead it is necessary to convert $Cr(CO)_6$ to a $fac\text{-}L_3Cr(CO)_3$ derivative with weakly bonded L ligands, e.g. L = NH_3 [11] or CH_3CN [12], so the reaction with cyclooctatetraene can occur under much milder conditions than would be possible with $Cr(CO)_6$. Furthermore, $(\eta^6\text{-}C_8H_8)Cr(CO)_3$ is more air-sensitive and reactive than $(\eta^4\text{-}C_8H_8)Fe(CO)_3$.

The two compounds $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ and $(\eta^6\text{-}C_8H_8)Cr(CO)_3$ discovered more than 40 years ago still remain the only examples of mononuclear cyclooctatetraene first row transition metal complexes that have been isolated. Other possibilities that might have been anticipated from the 18-elecron rule such as $(\eta^8\text{-}C_8H_8)Ti(CO)_3$, $(\eta^6\text{-}C_8H_8)Ti(CO)_4$, $(\eta^4\text{-}C_8H_8)Cr(CO)_4$, $(\eta^2\text{-}C_8H_8)Ni(CO)_3$, and $(\eta^4\text{-}C_8H_8)Ni(CO)_2$ remain unknown experimentally. In order to evaluate the possibilities in this area we have performed a comprehensive theoretical study of the first row transition metal $C_8H_8M(CO)_n$ derivatives (M = Ti, V, Cr, Mn, Fe, Co, Ni; n = 4, 3, 2, 1) using density functional theory methods. This paper reports our results in this area.

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 [13–27]. 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) with the Lee, Yang, and Parr (LYP) correlation functional [28,29]. The second approach is the BP86 method, which marries Becke's 1988 exchange functional (B) with Perdew's 1986 correlation functional [30,31]. It has been noted that the BP86 method may be somewhat more reliable than the B3LYP method for the types of organometallic systems considered in this paper [32–34].

For carbon and oxygen, the double-ζ plus polarization (DZP) basis set used here (9s5p/4s2p) adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$ to the Huzinaga–Dunning standard contracted DZ sets [35,36]. For the first row transition metals Ti to Ni in our loosely contracted DZP basis set, the Wachters' primitive set is used, but augmented by two sets of p functions and one set of d functions and contracted following Hood et al., and designated (14s11p6d/10s8p3d) [37,38].

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 were evaluated analytically as well. All of the computations were carried out with the GAUSSIAN 94 program [39] 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. All of the computations were performed without symmetry constraints.

Low magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in standard DFT computations. Thus imaginary vibrational frequencies with magnitudes less than $50i\,cm^{-1}$ are considered questionable, and thus were not always pursued in the optimizations [40–42].

The geometries of the complexes $(C_8H_8)M(CO)_n$ (n = 4, 3, 2, 1) (M = Ti, V, Cr, Mn, and Fe) and $(C_8H_8)M(CO)_n$ (n = 3, 2, 1) (M = Co, and Ni) were optimized. The stationary point geometries are shown in Figs. 1–7, with all C–C bond distances given in angstroms. The stationary points are designated as Mn-m where M is the atomic symbol of the central metal atom, n is the number of carbonyl groups, and m orders the structures by relative energies when two isomeric structures were found. In the tables ΔE_{diss} for $C_8H_8M(CO)_n$ indicates the energy required to lose a carbonyl group from $C_8H_8M(CO)_n$ to give the lowest energy $C_8H_8M(CO)_{n-1}$ derivative.

3. Results

3.1. Titanium complexes

For $(C_8H_8)Ti(CO)_4$, three stationary points with η^4, η^6, and η^8 coordination of C_8H_8 ring have been optimized (Fig. 2 and Table 1). The global minimum is the hexahapto complex $(\eta^6\text{-}C_8H_8)Ti(CO)_4$ (**Ti4-1**) with a 18-electron titanium configuration. The octahapto structure $(\eta^8\text{-}C_8H_8)Ti(CO)_4$ (**Ti4-2**), lies 0.9 kcal/mol (B3LYP) or 2.1 kcal/mol (BP86) above **Ti4-1**. The 1,2,5,6-tetrahapto structure $(\eta^{2,2}\text{-}C_8H_8)Ti(CO)_4$ (**Ti4-3**) lies at significantly higher energies, namely 14.3 kcal/mol (B3LYP) or 17.2 kcal/mol (BP86) above **Ti4-1**. The titanium atom in structure **Ti4-3** is approximately octahedral being coordinated to the four carbonyl groups and
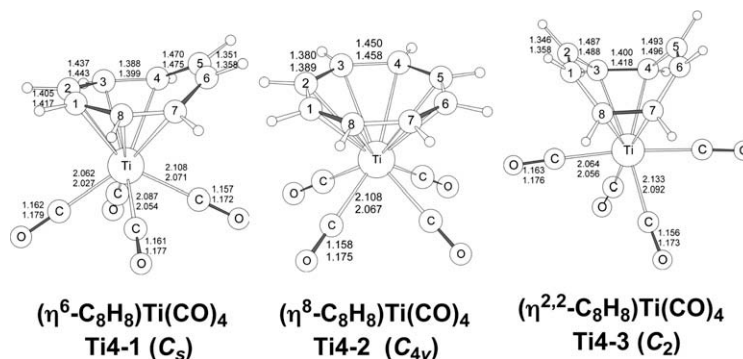
Fig. 2. The optimized $(C_8H_8)Ti(CO)_4$ structures. In Figs. 2–13 the upper distances were obtained by the B3LYP method and the lower distances by the BP86 method.
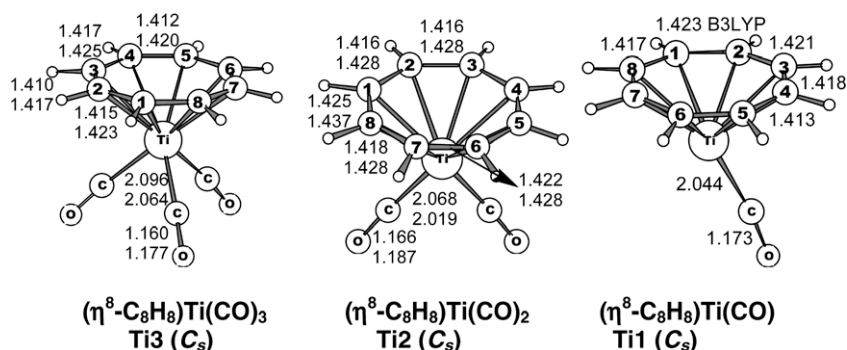
Fig. 3. The optimized structures for $(C_8H_8)Ti(CO)_n$ (n = 3, 2, 1).
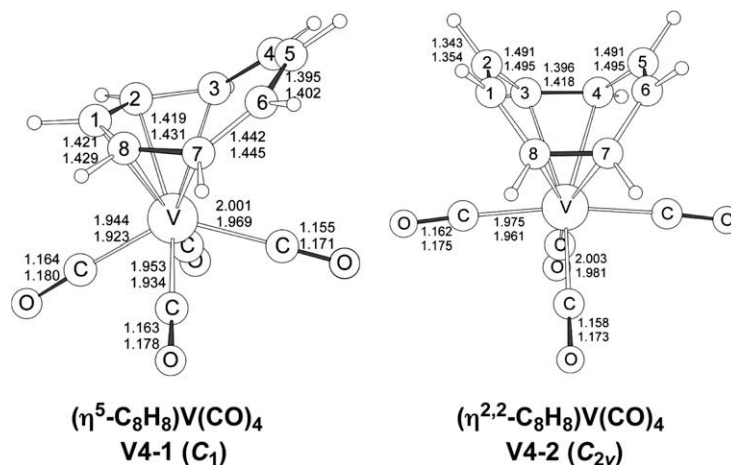
Fig. 4. Optimized structures of $C_8H_8V(CO)_4$.
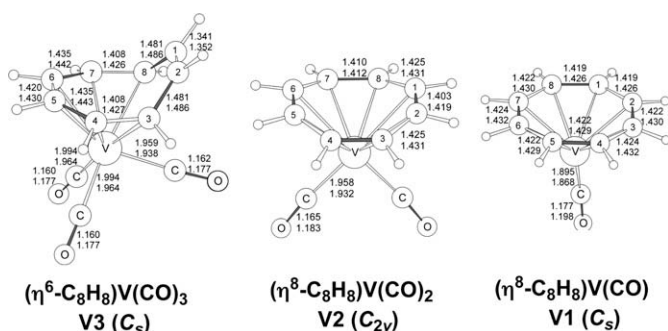
Fig. 5. The optimized structures for $(C_8H_8)V(CO)_n$ (n = 3, 2, 1).

two opposite C=C double bonds of the C_8H_8 ring. This gives the central titanium atom only a 16-electron configuration, which might account for the relatively high energy of **Ti4-3**.

Successive removal of carbonyl groups from the $(C_8H_8)Ti(CO)_4$ global minimum structure leads to stationary points for $(C_8H_8)Ti(CO)_3$ (**Ti3**), $(C_8H_8)Ti(CO)_2$ (**Ti2**), and $(C_8H_8)Ti(CO)$ (**Ti1**) (Fig. 3 and Table 2). All of these structures have octahapto C_8H_8 rings and are genuine minima without imaginary frequencies. The predicted dissociation energy of one CO group from $(\eta^6\text{-}C_8H_8)Ti(CO)_4$ (**Ti4-1**) to form $(\eta^8\text{-}C_8H_8)Ti(CO)_3$ (**Ti-3**) is −1.7 kcal/mol (B3LYP) or 4.0 kcal/mol (BP86), indicating that **Ti4-1** is unstable with respect to loss of a carbonyl group to give $(\eta^8\text{-}C_8H_8)Ti(CO)_3$ (**Ti3**). One of the driving forces of this reaction is the conversion of a hexahapto $\eta^6\text{-}C_8H_8$ ring with one uncomplexed C=C double bond to a fully
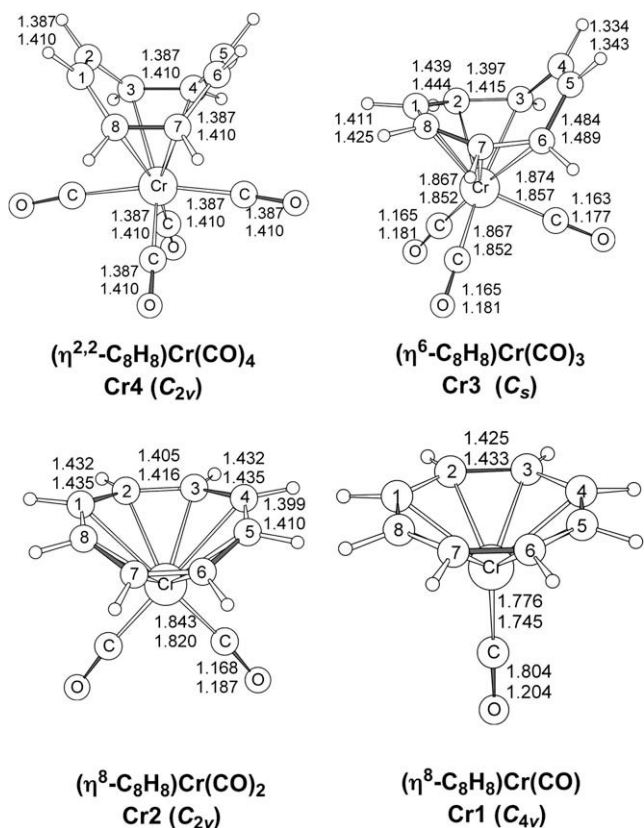
Fig. 6. The optimized structures of $C_8H_8Cr(CO)_n$ (n = 4, 3, 2, 1).
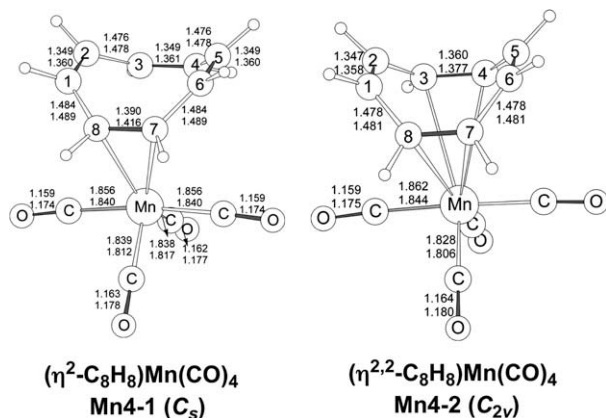
Fig. 7. Optimized structures of $C_8H_8Mn(CO)_4$.

bonded octahapto η^8-C_8H_8 ring. Further dissociation of CO groups from (η^8-C_8H_8)Ti(CO)$_3$ (**Ti3**) is predicted to require energies >20 kcal/mol indicating that (η^8-C_8H_8)Ti(CO)$_3$ is reasonably stable towards carbonyl loss. Despite this predicted stability of (η^8-C_8H_8)Ti(CO)$_3$, it has not yet been reported in the literature.

3.2. Vanadium complexes

The $C_8H_8V(CO)_4$ structures analogous to the (C_8H_8)Ti(CO)$_4$ structures discussed above were used as starting points for optimization with the B3LYP and BP86 methods. Three optimized (C_8H_8)V(CO)$_4$ structures were found. The structures (η^5-C_8H_8)V(CO)$_4$ (**V4-1**) and ($\eta^{2,2}$-C_8H_8)V(CO)$_4$ (**V4-2**) have real vibrational frequencies confirming that they are genuine minima on the energy surface (Fig. 4 and Table 3). The pentahapto structure (η^5-C_8H_8)V(CO)$_4$ (**V4-1**) is the global minimum. The 1,2,5,6-tetrahapto structure ($\eta^{2,2}$-C_8H_8)V(CO)$_4$ (**V4-2**) lies only 0.2 kcal/mol (B3LYP) or 5.8 kcal/mol (BP86) in energy above the **V4-1** global minimum, suggesting a highly fluxional system. The octahapto structure (η^8-C_8H_8)V(CO)$_4$ is a transition state with a large imaginary vibrational frequency of 217i cm^{-1} (B3LYP) or 223i cm^{-1} (BP86). Following the corresponding normal mode leads to the global minimum (η^5-C_8H_8)V(CO)$_4$ (**V4-1**).

The loss of one CO group from (η^5-C_8H_8)V(CO)$_4$ (**V4-1**) gives the hexahapto structure (η^6-C_8H_8)V(CO)$_3$ (**V3**) with a 17-electron vanadium configuration (Fig. 5 and Table 4). The predicted energy for this CO dissociation process is 9.6 kcal/mol (B3LYP) or 17.5 kcal/mol (BP86). This CO dissociation energy ΔE_{diss} from (η^5-C_8H_8)V(CO)$_4$ is thus significantly higher than the CO dissociation from (C_8H_8)Ti(CO)$_4$ discussed above. Further dissociation of a CO group from (η^6-C_8H_8)V(CO)$_3$ to give (η^8-C_8H_8)V(CO)$_2$ requires an energy of 20.1 kcal/mol (B3LYP) or 26.4 kcal/mol (BP86). The next CO dissociation process, namely the dissociation of (η^8-C_8H_8)V(CO)$_2$ to (η^8-C_8H_8)V(CO) + CO, requires a slightly higher energy of 30.0 kcal/mol (B3LYP) or 38.8 kcal/mol (BP86).

3.3. Chromium complexes

A stable 1,2,5,6-tetrahapto structure ($\eta^{2,2}$-C_8H_8)Cr(CO)$_4$ (**Cr4**) was found as a genuine minimum without any imaginary vibrational frequencies (Fig. 6 and Table 5). In this structure the $\eta^{2,2}$-C_8H_8 ligand may be regarded as a chelating diolefin so that the chromium atom in **Cr4** is approximately octahedral with the favored 18-electron configuration as in the unsubstituted Cr(CO)$_6$. A similar chelating diolefin ligand is found in the related 1,5-cyclooctadiene complex ($\eta^{2,2}$-C_8H_{12})Cr(CO)$_4$ [43]. The octahapto structure (η^8-C_8H_8)Cr(CO)$_4$ is a transition state with a large imaginary vibrational frequency not shown here. In this respect, chromium is analogous to vanadium.

Successive loss of carbonyl groups from ($\eta^{2,2}$-C_8H_8)Cr(CO)$_4$ (**Cr4**) gives first the hexahapto structure (η^6-C_8H_8)Cr(CO)$_3$ (**Cr3**) and then the octahapto structure (η^8-C_8H_8)Cr(CO)$_2$ (**Cr2**), retaining the favored 18-electron configuration by complexing a new C=C double bond from the C_8H_8 ring to compensate for each carbonyl loss (Fig. 6 and Table 5). The predicted energies required for this CO loss are 16.2 kcal/mol (B3LYP) or 18.7 kcal/mol (BP86) for the conversion of ($\eta^{2,2}$-C_8H_8)Cr(CO)$_4$ (**Cr4**) to (η^6-C_8H_8)Cr(CO)$_3$ (**Cr3**) and then the much larger energy of 34.6 kcal/mol (B3LYP) or 39.8 kcal/mol (BP86) for the conversion of (η^6-C_8H_8)Cr(CO)$_3$ (**Cr3**) to (η^8-C_8H_8)Cr(CO)$_2$ (**Cr2**). The further dissociation of CO from (η^8-C_8H_8)Cr(CO)$_2$ (**Cr2**) to give the 16-electron complex (η^8-C_8H_8)Cr(CO) (**Cr1**)

Table 1
Bond distances (in Å), HOMO–LUMO energy gaps (Egap in eV), total energies (E in hartree), and relative energies (ΔE in kcal/mol) for the (C_8H_8)Ti(CO)$_4$ structures.

	Ti4-1 (C_s)		Ti4-2 (C_{4v})		Ti4-3 (C_2)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Ti–C_8H_8 (ave.)	2.694	2.693	2.603	2.602	2.830	2.793
Egap	1.94	0.78	2.12	0.92	2.00	0.75
−Energy	1612.56007	1612.70445	1612.55860	1612.70118	1612.53721	1612.67699
ΔE	0.0	0.0	0.9	2.1	14.3	17.2
Imaginary frequencies	None	None	None	None	None	34i

Table 2
Bond distances (in Å), HOMO–LUMO energy gaps (Egap in eV), total energies (E in hartree), dissociation energies (ΔE_{diss} in kcal/mol) for the $(C_8H_8)Ti(CO)_n$ (n = 3, 2, 1) structures.

	$(\eta^8\text{-}C_8H_8)Ti(CO)_3$ Ti3 (C_s)		$(\eta^8\text{-}C_8H_8)Ti(CO)_2$ Ti2 (C_s)		$(\eta^8\text{-}C_8H_8)Ti(CO)$ Ti1 (C_s)
	B3LYP	BP86	B3LYP	BP86	B3LYP
Ti–C$_8$H$_8$ (ave.)	2.445	2.437	2.351	2.322	2.342
Egap	2.30	0.95	1.89	0.51	1.79
−Energy	1499.23416	1499.37080	1385.86877	1385.99905	1272.49489
ΔE_{diss}	23.1	27.9	28.4	–	–
Imaginary frequencies	None	None	None	None	None

Table 3
Bond distances (in Å), HOMO–LUMO energy gaps (Egap in eV), total energies (E in hartree), and relative energies (ΔE in kcal/mol) for the $(C_8H_8)V(CO)_4$ structures.

	V4-1 (C_1)		V4-2 (C_{2v})	
	B3LYP	BP86	B3LYP	BP86
V–C$_8$H$_8$ (ave.)	2.81	2.76	2.84	2.84
Egap	3.23	2.00	4.10	2.72
−Energy	1707.10548	1707.28491	1707.10516	1707.27572
ΔE	0.0	0.0	0.2	5.8
Imaginary frequencies	None	None	None	None
$\langle S^2 \rangle$	0.78	0.76	0.76	0.75

Table 4
Bond distances (in Å), HOMO–LUMO energy gaps (Egap in eV), total energies (E in hartree), dissociation energies (ΔE_{diss} in kcal/mol) for the $(C_8H_8)V(CO)_n$ (n = 3–1) structures.

	$(C_8H_8)V(CO)_3$ V3 (C_s)		$(C_8H_8)V(CO)_2$ V2 (C_{2v})		$(C_8H_8)V(CO)$ V1 (C_s)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
V–C$_8$H$_8$ (ave.)	2.518	2.492	2.363	2.357	2.281	2.269
Egap	3.58	2.10	3.08	1.47	3.26	1.08
−Energy	1593.76155	1593.92982	1480.40080	1480.56051	1367.02438	1367.17151
ΔE_{diss}	20.1	26.4	30.0	38.8	–	–
Imaginary frequencies	None	None	None	None	12i	10i
$\langle S^2 \rangle$	0.77	0.75	0.79	0.76	0.78	0.82

Table 5
Bond distances (in Å), HOMO–LUMO energy gaps (Egap in eV), total energies (E in hartree), dissociation energies (ΔE_{diss} in kcal/mol) for the $(C_8H_8)Cr(CO)_n$ (n = 4, 3, 2,1) structures.

		$(C_8H_8)Cr(CO)_4$ Cr4 (C_{2v})	$(C_8H_8)Cr(CO)_3$ Cr3 (C_s)	$(C_8H_8)Cr(CO)_2$ Cr2 (C_{2v})	$(C_8H_8)Cr(CO)$ Cr1 (C_{4v})
Cr–C$_8$H$_8$ (ave.)	B3LYP	2.812	2.518	2.317	2.212
	BP86	2.759	2.493	2.311	2.195
Egap	B3LYP	4.14	3.49	3.15	3.63
	BP86	2.66	2.02	1.41	1.28
−E	B3LYP	1807.59246	1694.23802	1580.85420	1467.47312
	BP86	1807.79619	1694.43908	1581.04842	1467.65107
ΔE_{diss}	B3LYP	16.2	34.6	32.9	–
	BP86	18.7	39.8	44.0	–
Imaginary frequency		None	None	None	None

requires almost the same energy of 32.9 kcal/mol (B3LYP) or 44.0 kcal/mol (BP86).

The hexahapto complex $(\eta^6\text{-}C_8H_8)Cr(CO)_3$ (**Cr3**) has been synthesized [11,12] but its crystal structure, as determined by X-ray diffraction, is not reported in the literature. The BP86 method predicts v(CO) frequencies of 1980, 1934, and 1911 cm^{-1}, which are very close to the experimental values of 1996, 1940, and 1912 cm^{-1} determined experimentally in cyclohexane solution [11].

3.4. Manganese complexes

Optimization of the 1,2,5,6-tetrahapto complex $(\eta^{2,2}\text{-}C_8H_8)$Mn(CO)$_4$ (**Mn4-2** in Fig. 7 and Table 6) leads to a large imaginary vibrational frequency of 100i cm^{-1} (B3LYP) or 117i cm^{-1} (BP86).

Table 6
Bond distances (in Å), HOMO–LUMO energy gaps (Egap in eV), total energies (E in hartree), and relative energies (ΔE in kcal/mol) for the $(C_8H_8)Mn(CO)_4$ structures.

	Mn4-1 (C_s)		Mn4-2 (C_{2v})	
	B3LYP	BP86	B3LYP	BP86
Mn–C$_8$H$_8$ (ave.)	3.29	3.22	3.29	3.13
Egap	3.36	1.65	2.93	1.07
−Energy	1914.09738	1914.31813	1914.09138	1914.31024
ΔE	0.0	0.0	3.8	5.0
Imaginary frequencies	None	None	100i	117i
$\langle S^2 \rangle$	0.78	0.76	0.77	0.76

Following the corresponding normal mode leads to rupture of one of the olefin–manganese bonds to give the dihapto derivative

Fig. 8. Optimized structures of $[C_8H_8Mn(CO)_3]^z$ ($z = 0, -1$).
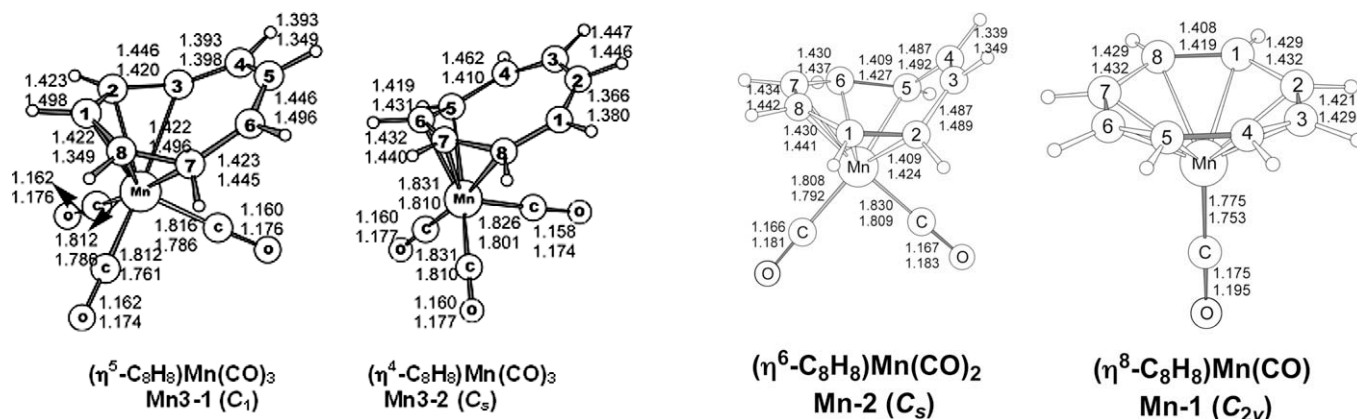
Fig. 9. Optimized structures for $(C_8H_8)Mn(CO)_n$ ($n = 2, 1$).

with the B3LYP and BP86 methods. Both $(\eta^4\text{-}C_8H_8)Mn(CO)_3$ and $(\eta^{2,2}\text{-}C_8H_8)Mn(CO)_3$ optimized structures were found. The structures $(\eta^4\text{-}C_8H_8)Mn(CO)_3$ (**Mn3-2**) and $(\eta^{2,2}\text{-}C_8H_8)Mn(CO)_3$ (**Mn3-3**) with the 17-electron configuration have real vibrational frequencies confirming that they are genuine minima on the energy surface (Fig. 8 and Table 7). The tetrahapto structure $(\eta^4\text{-}C_8H_8)Mn(CO)_3$ (**Mn3-2**) and the 1,2,5,6-tetrahapto structure $(\eta^{2,2}\text{-}C_8H_8)Mn(CO)_3$ (**Mn3-3**) lie 7.3 and 12.3 kcal/mol (B3LYP) or 8.5 and 14.5 kcal/mol (BP86) in energy, respectively, above the **Mn3-1** global minimum.

The anion $[C_8H_8Mn(CO)_3]^-$ isoelectronic with the known $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ was also investigated (Fig. 8). A 1,2,5,6-tetrahapto structure $[(\eta^{2,2}\text{-}C_8H_8)Mn(CO)_3]^-$ was found, which has the favored 18-electron configuration. This contrasts with the known [6] 1,2,3,4-tetrahapto structure for $(\eta^4\text{-}C_8H_8)Fe(CO)_3$.

Further loss of a carbonyl group from $(\eta^5\text{-}C_8H_8)Mn(CO)_3$ (**Mn3-1** in Fig. 8) requires a significantly higher energy of 31.0 kcal/mol (B3LYP) or 38.8 kcal/mol (BP86) and leads to a hexahapto complex $(\eta^6\text{-}C_8H_8)Mn(CO)_2$ (**Mn2** in Fig. 9) with a 17-electron manganese configuration. The next CO dissociation process, namely that of the hexahapto complex $(\eta^6\text{-}C_8H_8)Mn(CO)_2$ (**Mn2**) to the octahapto complex $(\eta^8\text{-}C_8H_8)Mn(CO)$ (**Mn1** in Fig. 9 and Table 8), requires the much higher energy of 42.9 kcal/mol (B3LYP) or 52.4 kcal/mol (BP86). The conversion of a hexahapto $\eta^6\text{-}C_8H_8$ ligand in **Mn2** into an octahapto $\eta^8\text{-}C_8H_8$ ligand in **Mn1** balances the carbonyl loss so that the 17-electron manganese configuration is retained in **Mn1**.

3.5. Iron complexes

A dihapto $(\eta^2\text{-}C_8H_8)Fe(CO)_4$ structure (**Fe4** in Fig. 10 and Table 9) is found without any imaginary vibrational frequencies analogous to the $(\eta^2\text{-}C_8H_8)Mn(CO)_4$ structure **Mn4** (Fig. 8). This structure is analogous to known $(\eta^2\text{-olefin})Fe(CO)_4$ derivatives [47,48] and

$(\eta^2\text{-}C_8H_8)Mn(CO)_4$ (**Mn4-1**) as the real global minimum with an energy 3.8 kcal/mol (B3LYP) or 5.0 kcal/mol (BP86) below the stationary point $(\eta^{2,2}\text{-}C_8H_8)Mn(CO)_4$ (**Mn4-2**). The manganese atom in $(\eta^2\text{-}C_8H_8)Mn(CO)_4$ has a 17-electron configuration.

Loss of a carbonyl group from $(\eta^2\text{-}C_8H_8)Mn(CO)_4$ (**Mn4-1** in Fig. 7) gives the pentahapto structure $(\eta^5\text{-}C_8H_8)Mn(CO)_3$ (**Mn3-1**) structure with a local 18-electron environment for the manganese atom (Fig. 8) similar to the very stable [44–46] $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ but with an unpaired electron on the uncomplexed carbon atoms. This CO loss from **Mn4-1** requires only the very small energy of 4.8 kcal/mol (B3LYP) or 3.9 kcal/mol (BP86) suggesting $(\eta^2\text{-}C_8H_8)Mn(CO)_4$ to be unstable towards carbonyl loss. This is not surprising since in the dihapto complex $(\eta^2\text{-}C_8H_8)Mn(CO)_4$ (**Mn4-1**) there are three uncomplexed C=C double bonds in the C_8H_8 ring available for intramolecular displacement of a carbonyl group.

The $(C_8H_8)Mn(CO)_3$ structures analogous to the $(C_8H_8)Fe(CO)_3$ structures were also used as starting points for optimization

Table 7
Bond distances (in Å), HOMO–LUMO energy gaps (Egap in eV), total energies (E in hartree), and dissociation energies (ΔE_{diss} in kcal/mol) for the $(C_8H_8)Mn(CO)_n$ ($n = 3$–1) structures.

	Mn3-1 (C_1)		Mn3-2 (C_s)		Mn3-3 (C_s)		Mn3$^-$	
	B3LYP	BP86	B3LYP	B3LYP	B3LYP	BP86	B3LYP	BP86
Mn–C$_8$H$_8$ (ave.)	2.706	2.696	2.899	2.908	2.676	2.640	2.248	2.229
Egap	4.02	2.47	3.43	2.09	3.45	2.08	3.82	2.53
$-E$	1800.76114	1800.98467	1800.74945	1800.97114	1800.74151	1800.96163	1573.98586	1574.18494
ΔE	0.0	0.0	7.3	8.5	12.3	14.5	–	–
ΔE_{diss}	31.0	38.8	23.7	30.3	18.7	24.3	–	–
Imaginary frequency	None	None	None	10i	None	None	None	None
$\langle S^2 \rangle$	0.78	0.76	0.77	0.76	0.76	0.75	0.86	0.79

Table 8
Bond distances (in Å), HOMO–LUMO energy gaps (Egap in eV), total energies (E in hartree), dissociation energies (ΔEdiss in kcal/mol) for the $(C_8H_8)Mn(CO)_n$ ($n = 2$ and 1) structures.

	$(C_8H_8)Mn(CO)_2$ **Mn2** (C_s)		$(C_8H_8)Mn(CO)$ **Mn1** (C_{2v})	
	B3LYP	BP86	B3LYP	BP86
Mn–C_8H_8 (ave.)	2.386	2.367	2.248	2.229
Egap	3.79	2.07	2.82	0.74
$-E$	1687.38294	1687.59567	1573.98586	1574.18494
ΔE_{diss}	42.9	52.4	–	–
Imaginary frequency	None	None	None	None
$\langle S^2 \rangle$	0.84	0.77	0.86	0.79

has the favored 18-electron configuration. Two energetically low-lying structures were found for $(C_8H_8)Fe(CO)_3$ (Fig. 10 and Table 9). The global minimum is the 1,2,3,4-tetrahapto structure (η^4-C_8H_8)Fe(CO)$_3$ **Fe3-1** found experimentally by X-ray crystallography [6]. The other structure is the 1,2,5,6-tetrahapto structure ($\eta^{2,2}$-C_8H_8)Fe(CO)$_3$, which lies 14.0 kcal/mol (B3LYP) or 15.5 kcal/mol (BP86) above the global minimum **Fe3-1**. Both $C_8H_8Fe(CO)_3$ structures are the genuine minima without the imaginary vibrational frequencies. The CO dissociation energy for the conversion of (η^2-C_8H_8)Fe(CO)$_4$ (**Fe4**) into (η^4-C_8H_8)Fe(CO)$_3$ (**Fe3-1**) is rather low at 8.4 kcal/mol (B3LYP) or 8.8 kcal/mol (BP86) consistent with the experimentally observed direct formation of (η^4-C_8H_8)Fe(CO)$_3$ from cyclooctatetraene and iron carbonyls without the observation of any (η^2-C_8H_8)Fe(CO)$_4$ intermediate.

The predicted structure for (η^4-C_8H_8)Fe(CO)$_3$ (**Fe3-1**) is close to that found experimentally by X-ray diffraction [6]. Thus the bond-

ing Fe–C distances to the "inner" and "outer" carbons of the 1,2,3,4-η^4-C_8H_8 unit in **Fe3-1** are predicted to be 2.11 Å (B3LYP) or 2.07 Å (BP86) and 2.32 Å (B3LYP) or 2.25 Å (BP86) as compared with experimental values of 2.05 Å and 2.18 Å, respectively, determined by the original X-ray diffraction study reported in 1961 [6]. No subsequent X-ray crystal structure determinations on (η^4-C_8H_8)Fe(CO)$_3$ have been reported using more modern methods. The predicted v(CO) frequencies (BP86) for (η^4-C_8H_8)Fe(CO)$_3$ are 2016, 1967, and 1956 cm^{-1} as compared with experimental values of 2047, 1992, and 1978 cm^{-1} in CS$_2$ solution [2].

A hexahapto structure (η^6-C_8H_8)Fe(CO)$_2$ (**Fe2-1** in Fig. 11) with the favored 18-electron configuration is predicted to be the global minimum for $C_8H_8Fe(CO)_2$. A higher energy 1,2,5,6-tetrahapto structure ($\eta^{2,2}$-C_8H_8)Fe(CO)$_2$ lies 18.4 kcal/mol (B3LYP) or 17.5 kcal/mol (BP86) above this global minimum. The dissociation energy ΔE_{diss} for loss of a carbonyl group from (η^4-C_8H_8)Fe(CO)$_3$ (**Fe3-1**) to give (η^6-C_8H_8)Fe(CO)$_2$ (**Fe2-1**) is relatively high at 38.3 kcal/mol (B3LYP) or 41.7 kcal/mol (BP86). Further carbonyl loss from (η^6-C_8H_8)Fe(CO)$_2$ (**Fe2-1**) also requires a rather high energy of 35.1 kcal/mol (B3LYP) or 42.7 kcal/mol (BP86) and gives a hexahapto complex (η^6-C_8H_8)Fe(CO) (**Fe1**) with a 16-electron configuration for the iron atom.

3.6. Cobalt complexes

A trihapto structure **Co3** (Fig. 12 and Table 10) is found for $C_8H_8Co(CO)_3$ in which the environment of the cobalt atom is very similar to the well-known trihaptoallyl derivative [49,50] (η^3-C_3H_5)Co(CO)$_3$. However, this leaves an unpaired electron on the uncomplexed carbon atoms of the C_8H_8 ring.

$(\eta^2$-$C_8H_8)Fe(CO)_4$
Fe4 (C_s)

$(\eta^4$-$C_8H_8)Fe(CO)_3$
Fe3-1 (C_s)

$(\eta^{2,2}$-$C_8H_8)Fe(CO)_3$
Fe3-2 (C_s)

Fig. 10. Optimized structures of $C_8H_8Fe(CO)_n$ ($n = 4, 3$).

Table 9
Bond distances (in Å), HOMO–LUMO energy gaps (Egap in eV), total energies (E in hartree), relative energies (ΔE in kcal/mol), dissociation energies (ΔEdiss in kcal/mol) for the $(C_8H_8)Fe(CO)_n$ ($n = 4, 3, 2, 1$) structures.

		Fe4 (C_s)	**Fe3-1** (C_s)	**Fe3-2** (C_s)	**Fe2-1** (C_s)	**Fe2-2** (C_1)	**Fe1** (C_1)
Fe–C_8H_8 (ave.)	B3LYP	3.642	2.841	2.629	2.359	2.519	2.274
	BP86	3.619	2.862	2.598	2.352	2.503	2.265
Egap	B3LYP	4.08	3.45	4.42	3.86	2.70	3.48
	BP86	2.36	2.06	2.80	2.28	1.51	1.49
$-E$	B3LYP	2026.83824	1913.49619	1913.47381	1800.10656	1800.07721	1686.72205
	BP86	2027.08467	1913.74339	1913.71875	1800.34971	1800.32177	1686.95444
ΔE	B3LYP	0.0	0.0	14.0	0.0	18.4	0.0
	BP86	0.0	0.0	15.5	0.0	17.5	0.0
ΔE_{diss}	B3LYP	8.4	38.3	42.6	35.1	16.6	–
	BP86	8.8	41.7	43.8	42.7	25.2	–
Imaginary frequency		None	None	None	None	None	None

Fig. 11. Optimized structures of $C_8H_8Fe(CO)_n$ ($n = 2, 1$).

Fig. 12. Optimized structures of $C_8H_8Co(CO)_n$ ($n = 3, 2, 1$).

Two tetrahapto structures were found for $C_8H_8Co(CO)_2$. The 1,2,5,6-tetrahapto derivative ($\eta^{2,2}$-$C_8H_8)Co(CO)_2$ (**Co2-1** in Fig. 12 and Table 10) is the global minimum. The cobalt atom in **Co2-1**

can be considered to be tetrahedrally coordinated to the two C_8H_8 double bonds and the two carbonyl groups and has a 17-electron configuration. The 1,2,3,4-tetrahapto derivative (η^4-C_8H_8)Co

Table 10
Bond distances (in Å), HOMO–LUMO energy gaps (Egap in eV), total energies (E in hartree), relative energies (ΔE in kcal/mol), dissociation energies (ΔE_{diss} in kcal/mol) for the $(C_8H_8)Co(CO)_n$ (n = 3, 2, 1) structures.

		Co3 (C_1)	**Co2-1** (C_s)	**Co2-2** (C_1)	**Co2⁻**	**Co1-1** (C_1)	**Co1-2** (C_{4v})
Co–C₈H₈ (ave.)	B3LYP	3.073	2.644	2.793	2.908	2.541	2.376
	BP86	3.360	2.532	2.798	2.916	2.477	2.314
Egap	B3LYP	2.65	4.76	2.56	3.10	4.24	1.91
	BP86	1.14	3.14	1.51	1.87	2.25	0.28
$-E$	B3LYP	2032.53759	1919.18405	1919.17818	1919.24636	1805.80079	1805.77953
	BP86	2032.79439	1919.41810	1919.42248	1919.49894	1806.02541	1806.00816
ΔE	B3LYP	0.0	0.0	3.7	–	0.0	13.3
	BP86	0.0	0.0	2.8	–	0.0	10.8
ΔE_{diss}	B3LYP	15.6	34.3	43.9			
	BP86	30.8	41.1	54.6			
Imaginary frequencies		None	None	None	None	None	None
$\langle S^2 \rangle$	B3LYP	0.86	0.80	0.85	0.00	0.85	1.18
	BP86	0.77	0.76	0.76	0.00	0.78	0.77

$(CO)_2$ (**Co2-2**) lies 3.7 kcal/mol (B3LYP) or 2.8 kcal/mol (BP86) above this global minimum. Thus the relative energy order of the 1,2,5,6-tetrahapto and 1,2,3,4-tetrahapto structures for $C_8H_8Co(CO)_2$ is the opposite of that for $C_8H_8Fe(CO)_3$ discussed above. The carbonyl dissociation energy ΔE_{diss} for the conversion of (η^3-$C_8H_8)Co(CO)_3$ (**Co3**) to ($\eta^{2,2}$-$C_8H_8)Co(CO)_2$ (**Co2-1**) is rather high at 15.6 kcal/mol (B3LYP) or 30.8 kcal/mol (BP86).

Since the cobalt atoms in the tetrahapto derivatives ($\eta^{2,2}$-$C_8H_8)Co(CO)_2$ (**Co2-1** in Fig. 12) and (η^4-$C_8H_8)Co(CO)_2$ (**Co2-2**) have only 17-electron configurations, the $[(C_8H_8)Co(CO)_2]^-$ anion was also investigated hoping to obtain a tetrahapto derivative with an 18-electron configuration. However, the optimized structure of the anion, namely $[(\eta^3$-$C_8H_8)Co(CO)_2]^-$ (**Co2⁻**) is predicted to have a trihapto η^3-C_8H_8 ligand similar to that in the tricarbonyl (η^3-$C_8H_8)Co(CO)_3$ (**Co3** in Fig. 12) and thus a 17-electron cobalt configuration. The coordination of the cobalt is approximately square planar to the two carbonyl groups and the midpoints of the C–C bonds in the trihapto allyl portion of the η^3-C_8H_8 ring.

Two structures for the monocarbonyl $C_8H_8Co(CO)$ were optimized. The lowest energy structure ($\eta^{2,2}$-$C_8H_8)Co(CO)$ (**Co1-1** in Fig. 12) has a 1,2,5,6-tetrahapto ring similar to that in ($\eta^{2,2}$-$C_8H_8)Co(CO)_2$ (**Co2-1**). The carbonyl dissociation energy ΔE_{diss} of **Co2-1** to give **Co1-1** is rather high at 34.3 kcal/mol (B3LYP) or 41.1 kcal/mol (BP86) (Table 10). The higher energy structure of the monocarbonyl, namely (η^8-$C_8H_8)Co(CO)$ (**Co1-2**) at 13.3 kcal/mol (B3LYP) or 10.8 kcal/mol (BP86), has an octahapto η^8-C_8H_8 ring and thus a 20-electron configuration for the central cobalt atom.

3.7. Nickel complexes

The dihapto structure (η^2-$C_8H_8)Ni(CO)_3$ (**Ni3** in Fig. 13 and Table 11) is predicted for the tricarbonyl. The nickel has the favored 18-electron configuration and tetrahedral coordination similar to the well-known [51,52] $Ni(CO)_4$. Loss of a carbonyl group from **Ni3** requires 13.7 kcal/mol (B3LYP) or 15.9 kcal/mol to give the 1,2,5,6-tetrahapto derivative ($\eta^{2,2}$-$C_8H_8)Ni(CO)_2$ (**Ni2-1** in Fig. 13 and Table 11). A higher energy 1,2,3,4-tetrahapto (η^4-$C_8H_8)$ $Ni(CO)_2$ structure **Ni2-2** is also predicted at 9.5 kcal/mol (B3LYP) or 8.9 kcal/mol (BP86) above the **Ni2-1** global minimum. Both tetrahapto $C_8H_8Ni(CO)_2$ derivatives **Ni2-1** and **Ni2-2** have the favored 18-electron nickel configuration. Further dissociation of a carbonyl group from ($\eta^{2,2}$-$C_8H_8)Ni(CO)_2$ (**Ni2-1** in Fig. 13) requires 30.8 kcal/mol (B3LYP) or 35.5 kcal/mol (BP86) to give ($\eta^{2,2}$-$C_8H_8)Ni(CO)$ (**Ni1**) with retention of the 1,2,5,6-tetrahapto C_8H_8 ligand. The nickel atom in **Ni1** has a 16-electron configuration similar to that in a number of tricoordinate Ni(0) complexes.
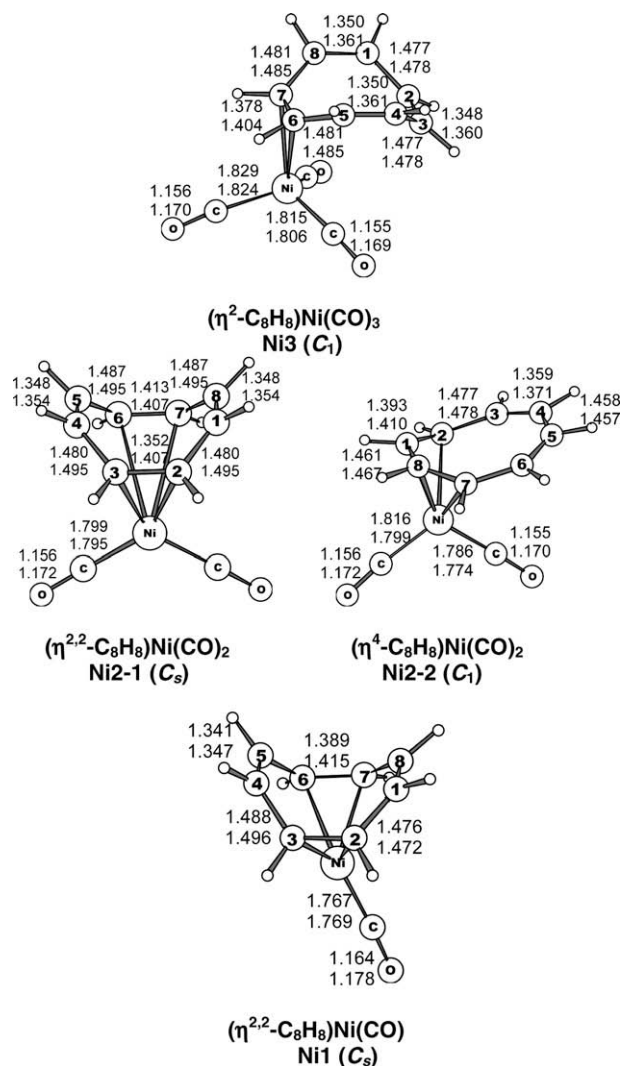

Fig. 13. Optimized structures of $C_8H_8Ni(CO)_n$ (n = 3, 2, 1).

4. Discussion

Metal tricarbonyl complexes of cyclic hydrocarbons of the type (η^n-$C_nH_n)M(CO)_3$ with the favored 18-electron configurations are known to be stable for all ring sizes from three to seven as exemplified by (η^3-$Ph_3C_3)Co(CO)_3$ [53], (η^4-$C_4H_4)Fe(CO)_3$ [54,55], (η^5-

Table 11
Bond distances (in Å), HOMO–LUMO energy gaps (Egap in eV), total energies (E in hartree), relative energies (ΔE in kcal/mol), dissociation energies (ΔE_{diss} in kcal/mol) for the $(C_8H_8)Ni(CO)_n$ (n = 3–1) structures.

	Ni3 (C_1)		Ni2-1 (C_s)		Ni2-2 (C_1)		Ni1 (C_s)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Ni–C$_8$H$_8$ (ave.)	3.360	3.268	2.919	2.566	2.839	2.820	2.509	2.448
Egap	3.76	2.24	4.21	2.90	2.52	1.21	3.80	2.28
$-E$	2158.09863	2158.34837	2044.74816	2044.99572	2044.73297	2044.98158	1931.37037	1931.61184
ΔE	0.0	0.0	0.0	0.0	9.5	8.9	0.0	0.0
ΔE_{diss}	13.7	15.9	30.8	35.5	21.3	26.7	–	–
Imaginary frequency	None	None	None	None	None	None	None	None

$C_5H_5)Mn(CO)_3$ [44–46], $(\eta^6-C_6H_6)Cr(CO)_3$ [56,57], and $(\eta^7-C_7H_7)$ $V(CO)_3$ [58]. The next member of this series is $(\eta^8-C_8H_8)Ti(CO)_3$ (see **Ti3** in Fig. 3), which has not yet been synthesized. We predict this to be a stable compound with a reasonably high CO dissociation energy (ΔE_{diss}) of 25 ± 3 kcal/mol. Furthermore, loss of a carbonyl group from the tetracarbonyl $(\eta^6-C_8H_8)Ti(CO)_4$ to give $(\eta^8-C_8H_8)Ti(CO)_3$ is predicted to be essentially thermoneutral within ~4 kcal/mol. The reason why $(\eta^8-C_8H_8)Ti(CO)_3$ has not yet been synthesized may relate to the lack of a suitable neutral titanium carbonyl derivative to react with cyclooctatetraene analogous to the methods used to synthesize the known compounds [1–4,11,12] $(\eta^6-C_8H_8)Cr(CO)_3$ and $(\eta^4-C_8H_8)Fe(CO)_3$. Reactions such as that between the known [59] $Ti(CO)_6^{2-}$ and cyclooctatetraene in the presence of a mild oxidizing agent such as Ag$^+$, Hg^{2+}, etc., might provide a route to $(\eta^8-C_8H_8)Ti(CO)_3$.

This study predicts the existence of octahapto $(\eta^8-C_8H_8)M(CO)_n$ derivatives as long as the central metal M does not exceed the favored 18-electron configurations by receiving eight electrons from the $\eta^8-C_8H_8$ ring. Thus the lowest energy structures for $(\eta^8-C_8H_8)$ $Ti(CO)_n$ (n = 3, 2, 1), $(\eta^8-C_8H_8)M(CO)_n$ (M = V, Cr; n = 2, 1), and $(\eta^8-C_8H_8)Mn(CO)$ all have octahapto $\eta^8-C_8H_8$ rings. An exception is $(\eta^6-C_8H_8)Fe(CO)$, with a hexahapto $\eta^6-C_8H_8$ ring and thus only a 16-electron configuration. In fact, no $C_8H_8Fe(CO)_n$ structures were found with octahapto $\eta^8-C_8H_8$ rings.

A hexahapto $\eta^6-C_8H_8$ ring with an uncomplexed double bond is found in the known [11,12] compound $(\eta^6-C_8H_8)Cr(CO)_3$ obtained by reactions of suitable fac-$L_3Cr(CO)_3$ derivatives (e.g., L = NH$_3$ or CH$_3$CN) with cyclooctatetraene. Hexahapto structures are also predicted for $(\eta^6-C_8H_8)Ti(CO)_4$, $(\eta^6-C_8H_8)V(CO)_3$, $(\eta^6-C_8H_8)Mn(CO)_2$, and $(\eta^6-C_8H_8)Fe(CO)_2$ with 18, 17, 17, and 18 electron configurations, respectively, for the central metal atoms.

The tetrahapto $C_8H_8M(CO)_n$ complexes are particularly interesting since two types of tetrahapto metal complexes are observed (Fig. 14). A 1,2,3,4-tetrahapto cyclooctatetraene ring, designated as $\eta^4-C_8H_8$, has four adjacent carbon atoms bonded to the metal atom with six of the C_8H_8 carbon atoms being approximately coplanar. The remaining four carbon atoms form a 1,3-diene unit, which can bond to a second metal atom as in the binuclear complex $(\eta^{4,4}-C_8H_8)[Fe(CO)_3]_2$, which is another product from the reaction of cyclooctatetraene with iron carbonyl [1–4]. However, in the 1,2,5,6-tetrahapto complexes, designated as $\eta^{2,2}-C_8H_8$, the carbon atoms from two non-adjacent double bonds are bonded to the me-

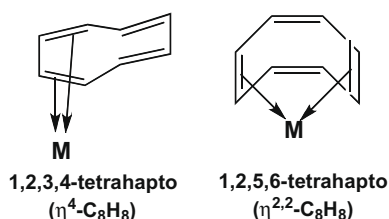tal atom so that the conformation of the C_8H_8 ring remains in the tub form as is the case for free cyclooctatetraene. None of the 1,2,5,6-tetrahapto $(\eta^{2,2}-C_8H_8)M(CO)_n$ derivatives predicted in this research has been synthesized. However, there are other examples of stable 1,2,5,6-tetrahapto cyclooctatetraene metal complexes that have been isolated such as $(\eta^5-C_5H_5)Co(\eta^{2,2}-C_8H_8)$, obtainable from the reaction of $(\eta^5-C_5H_5)Co(CO)_2$ with cyclooctatetraene [60]. For $C_8H_8Fe(CO)_3$ the experimentally unknown 1,2,5,6-tetrahapto $(\eta^{2,2}-C_8H_8)Fe(CO)_3$ structure is predicted to lie ~18 kcal/mol above the experimentally known [6] 1,2,3,4-tetrahapto $(\eta^4-C_8H_8)Fe(CO)_3$ structure.

A few dihapto $\eta^2-C_8H_8$ derivatives are predicted. However, these compounds are predicted to lose CO easily since a dihapto $\eta^2-C_8H_8$ ligand has three uncomplexed C=C double bonds available to displace carbonyl groups from the central metal atom. The dihapto nickel complex $(\eta^2-C_8H_8)Ni(CO)_3$ (**Ni3** in Fig. 13) has the favorable 18-electron configuration. However, because of the three uncomplexed double bonds on the $\eta^2-C_8H_8$ ligand, the CO dissociation energy from $(\eta^2-C_8H_8)Ni(CO)_3$ (**Ni3**) to give the 1,2,5,6-tetrahapto complex $(\eta^{2,2}-C_8H_8)Ni(CO)_2$ (**Ni2-1**) is rather low at ~14 ± 2 kcal/mol. The other dihapto $\eta^2-C_8H_8$ complex is the manganese complex $(\eta^2-C_8H_8)Mn(CO)_4$ (**Mn4-1** in Fig. 7), which has a 17-electron configuration for the manganese atom. The CO dissociation energy of **Mn4-1** to give $(\eta^5-C_8H_8)Mn(CO)_3$ (**Mn3-1** in Fig. 8) of ~4 kcal/mol is even lower than that of **Ni3**.

The $C_8H_8M(CO)_n$ derivatives of the transition metal of odd atomic number, namely vanadium, manganese, and cobalt, clearly have an odd number of electrons and thus have the expected doublet spin state with an unpaired electron. In most of these derivatives the doublet spin state is reflected in a 17-electron configuration of the central metal atom. However, there are some examples of optimized $C_8H_8M(CO)_n$ structures in which an odd number of carbon atoms are bonded to a transition metal of odd atomic number, i.e., a structure with odd hapticity of the C_8H_8 ring. In these structures the unpaired electron must necessarily reside within the group of uncomplexed carbon atoms in the C_8H_8 ring so that the transition metal actually has the favored 18-electron configuration. Typically the local environment of the odd-numbered transition metal in these structures is an 18-electron configuration similar to that of a stable organometallic compound of the same metal. Thus the pentahapto $\eta^5-C_8H_8$ structures $(\eta^5-C_8H_8)V(CO)_4$ (**V4-1** in Fig. 4) and $(\eta^5-C_8H_8)Mn(CO)_3$ (**Mn3-1** in Fig. 8) correspond to the very stable well-known cyclopentadienylmetal carbonyls [44,61] $(\eta^5-C_5H_5)V(CO)_4$ and $(\eta^5-C_5H_5)Mn(CO)_3$, respectively. Similarly, the trihapto $(\eta^3-C_8H_8)Co(CO)_3$ (**Co3** in Fig. 12) corresponds to the stable trihaptoallyl cobalt carbonyl [49,50] $(\eta^3-C_5H_5)Co(CO)_3$.

Acknowledgments

Fig. 14. The two different types of tetrahapto cyclooctatetraene metal complexes.

Appendix A. Supplementary material

Tables S1–S7: Metal–carbon distances for the $(C_8H_8)M(CO)_n$ structures; Tables S8–S41: Harmonic vibrational frequencies for the $(C_8H_8)M(CO)_n$ structures; complete Gaussian reference (Ref. [39]). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.008.

References

[1] T.A. Manuel, F.G.A. Stone, Proc. Chem. Soc. London (1959) 90.
[2] T.A. Manuel, F.G.A. Stone, J. Am. Chem. Soc. 82 (1960) 366.
[3] M.D. Rausch, G.N. Schrauzer, Chem. Ind. (1959) 957.
[4] A. Nakamura, N. Hagihara, Bull. Chem. Soc. Jpn. 32 (1959) 880.
[5] F.A. Cotton, J. Chem. Soc. (1960) 400.
[6] B. Dickens, W.N. Lipscomb, J. Am. Chem. Soc. 83 (1961) 4862.
[7] F.A. Cotton, A. Davison, J.W. Faller, J. Am. Chem. Soc. 88 (1966) 4507.
[8] C.E. Keller, B.A. Shoulders, R. Pettit, J. Am. Chem. Soc. 88 (1966) 4760.
[9] F.A. Cotton, Acc. Chem. Res. 1 (1968) 257.
[10] F.A. Cotton, J. Am. Chem. Soc. 90 (1968).
[11] C.G. Kreisler, A. Maasbol, F.A.L. Anet, H.D. Kaesz, S. Winstein, J. Am. Chem. Soc. 88 (1966) 3444.
[12] R.B. King, J. Organomet. Chem. 8 (1967) 139.
[13] A.W. Ehlers, G. Frenking, J. Am. Chem. Soc. 116 (1994) 1514.
[14] B. Delly, M. Wrinn, H.P. Lüthi, J. Chem. Phys. 100 (1994) 5785.
[15] J. Li, G. Schreckenbach, T. Ziegler, J. Am. Chem. Soc. 117 (1995) 486.
[16] V. Jonas, W. Thiel, J. Phys. Chem. 102 (1995) 8474.
[17] T.A. Barckholtz, B.E. Bursten, J. Am. Chem. Soc. 120 (1998) 1926.
[18] S. Niu, M.B. Hall, Chem. Rev. 100 (2000) 353.
[19] P. Macchi, A. Sironi, Coord. Chem. Rev. 238 (2003) 383.
[20] J.-L. Carreon, J.N. Harvey, Phys. Chem. Chem. Phys. 8 (2006) 93.
[21] M. Bühl, H. Kabrede, J. Chem. Theory Comput. 2 (2006) 1282.
[22] T. Ziegler, J. Autschbach, Chem. Rev. 105 (2005) 2695.
[23] M.P. Waller, M. Bühl, K.R. Geethanakshmi, D. Wang, W. Thiel, Chem. Eur. J. 13 (2007) 4723.
[24] P.G. Hayes, C. Beddie, M.B. Hall, R. Waterman, T.D. Tilley, J. Am. Chem. Soc. 128 (2006) 428.
[25] M. Bühl, C. Reimann, D.A. Pantazis, T. Bredow, F. Neese, J. Chem. Theory Comput. 4 (2008) 1449.
[26] 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.
[27] S. Ye, T. Tuttle, E. Bill, L. Simkhorich, Z. Gross, W. Thiel, F. Neese, Chem. Eur. J. 14 (2008) 10839.
[28] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[29] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[30] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
[31] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.
[32] See especially: F. Furche, J.P. Perdew, J. Chem. Phys. 124 (2006) 044103.
[33] H.Y. Wang, Y. Xie, R.B. King, H.F. Schaefer, J. Am. Chem. Soc. 127 (2005) 11646.
[34] H.Y. Wang, Y. Xie, R.B. King, H.F. Schaefer, J. Am. Chem. Soc. 128 (2006) 11376.
[35] T.H. Dunning, J. Chem. Phys. 53 (1970) 2823.
[36] S. Huzinaga, J. Chem. Phys. 42 (1965) 1293.
[37] A.J.H. Wachters, J. Chem. Phys. 52 (1970) 1033.
[38] D.M. Hood, R.M. Pitzer, H.F. Schaefer, J. Chem. Phys. 71 (1979) 705.
[39] M.J. Frisch et al., GAUSSIAN 94, Revision B.3, Gaussian Inc., Pittsburgh, PA, 1995.
[40] H. Jacobsen, T. Ziegler, J. Am. Chem. Soc. 118 (1996) 4631.
[41] J.M.L. Martin, C.W. Bauschlicher, A. Ricca, Comput. Phys. Commun. 133 (2001) 189.
[42] B.N. Papas, H.F. Schaefer, J. Mol. Struct. 768 (2006) 175.
[43] E.O. Fischer, W. Fröhlich, Chem. Ber. 92 (1959) 2995.
[44] E.O. Fischer, R. Jira, Z. Naturforsch. 9b (1954) 618.
[45] A.F. Berndt, R.E. Marsh, E. Richard, Acta Crystallogr. 16 (1963) 119.
[46] P.J. Fitzpatrick, Y. Le Page, J. Sedman, I.S. Butler, Inorg. Chem. 20 (1981) 2852.
[47] E. Weiss, K. Stark, J.E. Lancaster, H.D. Murdoch, Helv. Chim. Acta 46 (1963) 288.
[48] H.D. Murdoch, E. Weiss, Helv. Chim. Acta 46 (1963) 1588.
[49] R.F. Heck, D.S. Breslow, J. Am. Chem. Soc. 82 (1960) 750.
[50] R. Seip, Acta Chem. Scand. 26 (1972) 1966.
[51] L. Mond, C. Langer, F. Quincke, J. Chem. Soc. 57 (1890) 749.
[52] J. Ladell, B. Post, I. Fankuchen, Acta Crystallogr. 5 (1952) 795.
[53] T. Chiang, R.C. Kerber, D.S. Kimball, J.W. Lauher, Inorg. Chem. 18 (1979) 1687.
[54] G.F. Emerson, L. Watts, R. Pettit, J. Am. Chem. Soc. 87 (1965) 131.
[55] P.D. Harvey, W.P. Schaefer, H.B. Gray, D.F.R. Gilson, I.S. Butler, Inorg. Chem. 27 (1988) 57.
[56] E.O. Fischer, K. Öfele, Chem. Ber. 90 (1957) 2532.
[57] P. Corradini, G. Allegra, J. Am. Chem. Soc. 81 (1959) 2271.
[58] R.P.M. Werner, S.A. Manastyrskyj, J. Am. Chem. Soc. 83 (1961) 2023.
[59] K.M. Chi, S.R. Frerichs, S.B. Philson, J.E. Ellis, J. Am. Chem. Soc. 110 (1988) 303.
[60] A. Nakamura, N. Hagihara, Bull. Chem. Soc. Japan 33 (1960) 425.
[61] E.O. Fischer, S. Vigoureux, Chem. Ber. 91 (1958) 2205.