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The binuclear cyclooctatetraene sandwich compounds $(C_8H_8)_2M_2$ of the first row transition metals: Analogues of the perpendicular dimetallocenes

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ABSTRACT

Cyclooctatetraene has been found experimentally to form the perpendicular binuclear sandwich compounds $(\eta^3,\eta^3\text{-}C_8H_8)_2Ni_2$ and $[\eta^{5,5}\text{-}(Me_3Si)_2C_8H_6]_2Ti_2$. The entire series of such cyclooctatetraene sandwich compounds $(C_8H_8)_2M_2$ has now been examined by density functional theory. Bis(pentahapto) folded $\eta^5,\eta^5\text{-}C_8H_8$ rings are found in the lowest energy $(C_8H_8)_2M_2$ derivatives of the early transition metals Ti, V, Cr, and Mn. The lowest energy Ti derivative is the singlet spin state structure $(\eta^5,\eta^5\text{-}C_8H_8)_2Ti_2$ containing two such rings with geometry close to the experimental structure for the known silylated derivative $[\eta^{5,5}\text{-}(Me_3Si)_2C_8H_6]_2Ti_2$. The lowest energy $(C_8H_8)_2M_2$ structures for V, Cr, and Mn are $(\eta^5,\eta^5\text{-}C_8H_8)M_2(\eta^3,\eta^3\text{-}C_8H_8)$ having metal–metal multiple bonds of various orders. For $(\eta^5,\eta^5\text{-}C_8H_8)V_2(\eta^3,\eta^3\text{-}C_8H_8)$ singlet and triplet spin state structures are approximately equal in energy. For $(\eta^5,\eta^5\text{-}C_8H_8)M_2(\eta^3,\eta^3\text{-}C_8H_8)$ (M = Cr, Mn) the triplet state structures are the lowest energy structures. The lowest energy $(C_8H_8)_2M_2$ structures for the later transition metals Fe, Co, Ni are triplet spin state structures for Fe and Co and a singlet spin state structure for Ni. All three such $(\eta^3,\eta^3\text{-}C_8H_8)_2M_2$ (M = Fe, Co, Ni) structures have two bis(trihapto) $\eta^3,\eta^3\text{-}C_8H_8$ rings containing uncomplexed C=C double bonds.

1. Introduction

The use of cyclooctatetraene as a ligand in transition metal chemistry dates back more than 65 years to the 1948 observation of silver complexes by Reppe and co-workers [1]. Shortly thereafter, Cope and Hochstein [2] identified three types of silver nitrate complexes of cyclooctatetraene, namely $AgNO_3{\cdot}2C_8H_8$, $AgNO_3{\cdot}C_8H_8$, and $3AgNO_3{\cdot}2C_8H_8$. The 1:1 adduct $AgNO_3{\cdot}C_8H_8$ was subsequently shown by X-ray crystallography to have an infinite chain structure with the cyclooctatetraene functioning as a bidentate chelating 1,5-diolefin with two uncomplexed C=C double bonds [3–5]. Subsequently the molecular species $(\eta^5\text{-}C_5H_5)Co(\eta^{2,2}\text{-}C_8H_8)$, synthesized from $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and cyclooctatetraene [6], was shown to have the cyclooctatetraene ligand similarly bonded as a chelating 1,5-diolefin (Fig. 1) [7]. However, the related iron tricarbonyl complex $(\eta^4\text{-}C_8H_8)Fe(CO)_3$, synthesized in 1960 by several research groups [8–11] in fairly good yield by the thermal reaction of $Fe(CO)_5$ with cyclooctatetraene, was shown to have the tetrahapto C_8H_8 ligand bonded to the iron atom as a conjugated 1,3-diene, similar to the butadiene ligand in butadiene iron tricarbonyl, $(\eta^4\text{-}C_4H_6)Fe(CO)_3$. The binuclear cyclooctatetraene iron carbonyls $(\eta^4,\eta^4\text{-}C_8H_8)[Fe(CO)_3]_2$ and a species originally reported as "$C_8H_8Fe_2(CO)_7$" but later shown [12] to be $(\eta^5,\eta^5\text{-}C_8H_8)Fe_2(CO)_5$ were isolated in this early work as low-yield byproducts from the $Fe(CO)_5$/cyclooctatetraene reaction.

The chemistry of binary cyclooctatetraene metal complexes is somewhat more recent, dating from the remarkable synthesis of the sandwich compound "uranocene," namely $(\eta^8\text{-}C_8H_8)_2U$, by Streitwieser and Müller-Westerhoff in 1968 (Fig. 2) [13]. This was followed by syntheses of similar sandwich compounds $(\eta^8\text{-}C_8H_8)_2M$ of other f-block metals, namely M = Ce [14], Th [15], Pa [16,17], Np [18], Pu [18]. However, analogous bis(octahaptocyclooctatetraene) sandwich compounds with two fully bonded $\eta^8\text{-}C_8H_8$ rings were not obtained from d-block metals. Nevertheless, several d-block metals were found to form binary

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(1,2,3,4-η^4-C_8H_8)Fe(CO)$_3$ (η^5-C_5H_5)Co(1,2,5,6-$\eta^{2,2}$-C_8H_8)

Fig. 1. Early examples of cyclooctatetraene metal complexes showing two different ways for cyclooctatetraene to use two of its four C=C double bonds for tetrahapto bonding to a transition metal.

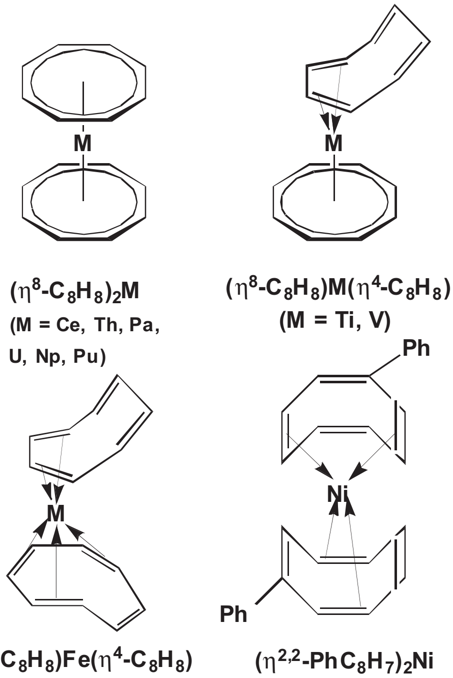
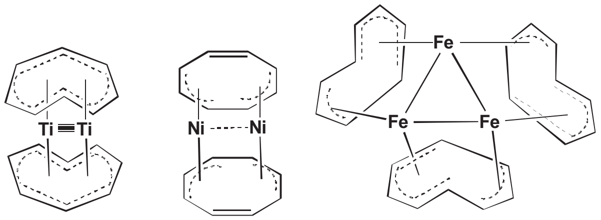


Fig. 2. Bis(cyclooctatetraene) metal complexes that have been synthesized and characterized structurally.

$(C_8H_8)_2M$ derivatives having one or two partially bonded C_8H_8 rings. These include (η^8-C_8H_8)M(η^4-C_8H_8) (M = Ti [19], V [20]) with one octahapto and one tetrahapto C_8H_8 ring and (η^6-C_8H_8)Fe(η^4-C_8H_8) [21] with one hexahapto and one tetrahapto C_8H_8 ring. Neutral $(C_8H_8)_2M$ derivatives of the first row transition metals Cr, Mn, Co, and Ni do not appear to have been to reported in the literature. However, the anion (η^4-C_8H_8)$_2$Co$^-$ has been reported [22] as well as the neutral phenylcyclooctatetraene derivative [23] ($\eta^{2,2}$-C_8H_7Ph)$_2$Ni.

Binuclear binary $(C_8H_8)_2M_2$ derivatives are known for the extreme members of the first row transition metal series (Fig. 3). The nickel derivative (η^3,η^3-C_8H_8)$_2$Ni$_2$ has been synthesized and characterized structurally by Brauer and Kruger [24]. The unsubstituted titanium derivative $(C_8H_8)_2Ti_2$ is unknown experimentally. However, the trimethylsilyl derivative [η^5,η^5-$(Me_3Si)_2C_8H_6$]$_2$Ti$_2$ has been synthesized in rather low yield from [$(Me_3Si)_2C_8H_6$]TiCl$_2$ and magnesium in the presence of $Me_3SiC{\equiv}CSiMe_3$ and shown by X-ray crystallography to have folded C_8H_8 rings [25]. Related $(C_8H_8)_2M_2$ derivatives for the remaining first row transition metals between titanium and nickel remain unknown. In addition, binuclear derivatives $(C_8H_8)_3M_2$ (M = Ti [26,27], Cr [19,28], Mo [19], W[19]) containing three cyclooctatetraene rings for two metal atoms have been synthesized and structurally characterized by X-ray crystallography. Such structures have two terminal C_8H_8 rings and one bridging C_8H_8 ring. A trinuclear binary iron derivative $(C_8H_8)_3Fe_3$ has been synthesized by Grubbs and coworkers and characterized by X-ray crystallography (Fig. 3) [29,30].



(η^5,η^5-C_8H_8)$_2$Ti$_2$ (η^3,η^3-C_8H_8)$_2$Ni$_2$ (η^5,η^3-C_8H_8)$_3$Fe$_3$

Fig. 3. Some experimentally known binuclear and trinuclear $(C_8H_8)_nM_n$ (n = 2, 3) derivatives.

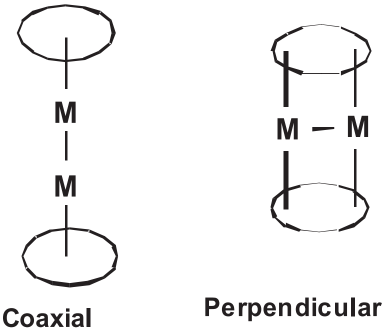


Fig. 4. Coaxial versus perpendicular dimetallocenes and related binuclear metal derivatives of planar and nearly planar cyclic hydrocarbons.

The known $(C_8H_8)_2M_2$ derivatives (M = Ti, Ni) may be regarded as analogues of perpendicular dimetallocenes but with eight-membered ring rather than five-membered ring cyclic hydrocarbon ligands (Fig. 4). The first known example of a dimetallocene was the coaxial dizincocene, (η^5-C_5H_5)Zn–Zn(η^5-C_5H_5) in which two (η^5-C_5H_5)Zn units are linked with a formal Zn–Zn bond [31,32]. Theoretical studies on $(C_5H_5)_2M_2$ systems indicate the possibility of not only such coaxial dimetallocenes but also perpendicular dimetallocenes with two bridging C_5H_5 rings [33]. Perpendicular dimetallocene structures have not yet been synthesized with cyclopentadienyl ligands. However, the benzene-palladium dication $[(C_6H_6)_2Pd_2]^{2+}$, found in $(C_6H_6)_2Pd_2(AlCl_4)_2$ and $(C_6H_6)_2Pd_2(Al_2Cl_7)_2$, first reported in 1970 [34], has the Pd–Pd axis perpendicular to the C_6 axes of the benzene rings and thus is an example of a stable species with a perpendicular dimetallocene structure.

This manuscript reports a theoretical study on the complete series of bis(cyclooctatetraene)dimetal derivatives $(C_8H_8)_2M_2$ of the first row transition metals including the experimentally realized titanium and nickel derivatives discussed above. In all cases the lowest energy structures were found to be perpendicular rather than coaxial structures. However, the hapticities of the cyclooctatetraene ligands and the nature of the metal–metal interactions were found to vary depending on the electronic requirements of the central M_2 unit.

2. Theoretical methods

Electron correlation effects were included using density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds [35–41]. The reliability of such density functional theory (DFT) methods is governed by the quality of the approximate exchange–correlation (XC) energy functional. We initially chose two DFT methods, namely, the B3LYP and the BP86 methods, which are constructed in very different ways. The B3LYP method is a hybrid HF/DFT method using a combination of the three-parameter Becke functional (B3) [42] with the Lee–Yang–Parr (LYP) generalized gradient correlation functional [43]. This method