



Methylborabenzene ligands in binuclear iron carbonyl derivatives: High spin states and iron–iron multiple bonding[☆]

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ABSTRACT

The experimentally known methylborabenzene iron carbonyl $(C_5H_5BCH_3)_2Fe_2(CO)_4$ and its decarbonylation products $(C_5H_5BCH_3)_2Fe_2(CO)_n$ ($n = 3, 2$) have been studied by density functional theory for comparison with their cyclopentadienyl analogs. The lowest energy $(\eta^6-C_5H_5BCH_3)_2Fe_2(CO)_4$ structures are the experimentally known singlet doubly bridged *cis*-($\eta^6-C_5H_5BCH_3$)₂Fe₂(CO)₂(μ-CO)₂ and the corresponding *trans* isomer similar to the corresponding $(\eta^5-C_5H_5)_2Fe_2(CO)_2(\mu-CO)_2$ system. Also the triplet triply bridged $(\eta^6-C_5H_5BCH_3)_2Fe_2(\mu-CO)_3$ is the lowest energy tricarbonyl structure similar to the cyclopentadienyl system. However, significant differences between the methylborabenzene and cyclopentadienyl derivatives are found in the dicarbonyl systems. A singlet $(\eta^5-C_5H_5)_2Fe_2(\mu-CO)_2$ structure with a short Fe≡Fe distance of ~2.1 Å was previously found to be the lowest energy structure in the cyclopentadienyl system. An analogous methylborabenzene structure $(\eta^6-C_5H_5BCH_3)_2Fe_2(\mu-CO)_2$ is found as the lowest energy singlet structure. However, an unsymmetrical quintet $(\eta^6-C_5H_5BCH_3)_2Fe_2(CO)_2(\eta^6-C_5H_5BCH_3)$ structure is predicted to lie ~22 kcal/mol below this singlet structure. The existence of this low-energy, high-spin $(\eta^6-C_5H_5BCH_3)_2Fe_2(CO)_2$ structure makes $(\eta^6-C_5H_5BCH_3)_2Fe_2(\mu-CO)_3$ disfavored with respect to disproportionation into $(\eta^6-C_5H_5BCH_3)_2Fe_2(\mu-CO)_4 + (\eta^6-C_5H_5BCH_3)_2Fe_2(\mu-CO)_2$ unlike its cyclopentadienyl analog.

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1. Introduction

The ability of cyclopentadienyl rings to form stable complexes with transition metals was first demonstrated in 1951 by the discovery of ferrocene having a sandwich structure with the iron atom between two parallel planar rings [1,2]. Subsequently dibenzenechromium was synthesized showing that a pair of benzene rings could also sandwich a metal atom to give a stable compound [3]. In addition, numerous compounds having only a single cyclopentadienyl or benzene ring bonded to a metal atom were also synthesized shortly after the discoveries of ferrocene and dibenzenechromium. Cyclopentadienyl metal carbonyls were found to be

particularly important as readily available starting materials for the syntheses of many organometallic compounds of the first row transition metals ranging from vanadium to nickel [4,5]. Also numerous arene-chromium tricarbonyls were synthesized by simple thermal reactions of Cr(CO)₆ with diverse arene derivatives [6–10].

The development of the transition metal chemistry of heterocycles related to the cyclopentadienyl and benzene ligands occurred considerably later, owing to initial synthetic challenges in obtaining the required heterocyclic starting materials. In this connection the borabenzene ligand C₅H₅BH and its ring substitution products are of particular interest because of its relationship to both the cyclopentadienyl and benzene ligands. Thus a neutral borabenzene ligand, like the neutral cyclopentadienyl radical, can donate its five π electrons to a transition metal atom. However, the six-membered BC₅ ring of borabenzene is sterically equivalent to the C₆ ring of benzene.

The chemistry of borabenzene metal complexes dates back to the 1971 discovery by Herberich and co-workers of the ring expansion of cobaltocene with alkyl- or arylidihaloboranes to give the paramagnetic complex $(\eta^6-C_5H_5BR)_2Co$, in which the central cobalt atom has a 19-electron configuration [11]. These cobalt complexes (Fig. 1)

[☆] This paper is dedicated to Prof. Vladimir Bregadze on the occasion of his 75th birthday in recognition of the leading role that he has played in Russian organometallic chemistry including the chemistry of deltahedral metallaboranes.

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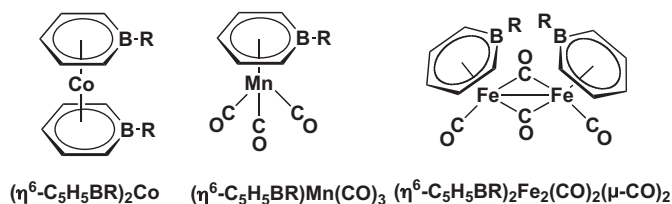


Fig. 1. Some borabenzene metal complexes (R = CH₃ or C₆H₅ in the systems that have been studied most extensively).

were found to serve as reagents to prepare borabenzene complexes of a variety of other metals by ligand transfer reactions. Some of the first borabenzene metal carbonyl complexes prepared by this method include *cis*-($\eta^6\text{-C}_5\text{H}_5\text{BR}$)₂Fe₂(CO)₂($\mu\text{-CO}$)₂ and ($\eta^6\text{-C}_5\text{H}_5\text{BR}$)Mn(CO)₃ [12,13]. Shortly after the original synthesis of borabenzene derivatives by ring expansion of cobaltocene, an alternative approach to borabenzene derivatives was developed by Ashe and coworkers [14] using the ring closure of 1,4-pentadiyne with an R₂SnH₂ derivative to give a stannabenzene derivative following by displacement of the tin with RBX₂. Much later, a simpler route to borabenzene metal complexes was developed using the ring closure of 2,4-pentadienylboranes [15]. A large number of borabenzene metal complexes have been prepared of diverse metals using these methods [16,17]. Borabenzene transition metal complexes have become of interest as olefin polymerization catalysts [18].

The general objective of the research discussed in this paper is the comparison of isoelectronic binuclear cyclopentadienyl, benzene, and borabenzene metal carbonyl derivatives including unsaturated derivatives where metal–metal multiple bonding might be expected to occur. The iron carbonyl system ($\eta^6\text{-C}_5\text{H}_5\text{BCH}_3$)₂Fe₂(CO)_n (*n* = 4, 3, 2) was chosen for this study since the corresponding cyclopentadienyl iron carbonyl system ($\eta^5\text{-C}_5\text{H}_5$)₂Fe₂(CO)_n (*n* = 4, 3, 2) has been studied extensively both experimentally and theoretically [19]. Furthermore the iron carbonyl derivative *cis*-($\eta^6\text{-C}_5\text{H}_5\text{BCH}_3$)₂Fe₂(CO)₂($\mu\text{-CO}$)₂ has been synthesized by thermal reactions of ($\eta^6\text{-C}_5\text{H}_5\text{BCH}_3$)₂Co with Fe₂(CO)₉ or Fe(CO)₅ [12] and structurally characterized by X-ray crystallography [20]. The related binuclear hexamethylbenzene manganese carbonyl complex ($\eta^6\text{-Me}_6\text{C}_6$)₂Mn₂(CO)₂($\mu\text{-CO}$)₂ has been synthesized and structurally characterized by X-ray crystallography [21,22]. In addition, its decarbonylation to give ($\eta^6\text{-Me}_6\text{C}_6$)₂Mn₂(CO)_n (*n* = 3, 2) has been studied theoretically [23].

Extensive experimental work has been done on unsaturated binuclear cyclopentadienyl iron carbonyl derivatives. Thus the saturated ($\eta^5\text{-C}_5\text{H}_5$)₂Fe₂(CO)₂($\mu\text{-CO}$)₂ is known to undergo photochemical decarbonylation to give an unusual stable triplet state

structure ($\eta^5\text{-C}_5\text{H}_5$)₂Fe₂($\mu\text{-CO}$)₃ [24–26]. The corresponding pentamethylcyclopentadienyl derivative has been characterized structurally by X-ray crystallography and shown to have a short Fe=Fe distance of 2.265 Å, interpreted as the formal double bond required to give both iron atoms the favored 18-electron configuration [27]. However, the two unpaired electrons in this triplet state structure are assumed to lie in two π “half-bond” components of this Fe=Fe double bond analogous to the O=O double bond in the normal (triplet) dioxygen.

Further decarbonylation of ($\eta^5\text{-C}_5\text{H}_5$)₂Fe₂(CO)₂($\mu\text{-CO}$)₂ is also interesting. Thus pyrolysis of ($\eta^5\text{-C}_5\text{H}_5$)₂Fe₂(CO)₂($\mu\text{-CO}$)₂ at ~100 °C leads to the very stable tetranuclear cluster ($\eta^5\text{-C}_5\text{H}_5$)₄Fe₄($\mu_3\text{-CO}$)₄ containing a central Fe₄ tetrahedron with each face capped by a face-bridging carbonyl group [28]. Theoretical studies on ($\eta^5\text{-C}_5\text{H}_5$)₂Fe₂(CO)_n (*n* = 4, 3, 2) derivatives [19] suggest the intermediacy of an unsaturated ($\eta^5\text{-C}_5\text{H}_5$)₂Fe₂($\mu\text{-CO}$)₂ with a short Fe=Fe distance of ~2.13 Å consistent with the formal triple bond required to give each iron atom the favored 18-electron configuration.

The richness of the experimental decarbonylation chemistry of ($\eta^5\text{-C}_5\text{H}_5$)₂Fe₂(CO)₂($\mu\text{-CO}$)₂ suggests that the isoelectronic ($\eta^6\text{-C}_5\text{H}_5\text{BCH}_3$)₂Fe₂(CO)₂($\mu\text{-CO}$)₂ might also have interesting decarbonylation chemistry. In order to explore this possibility a theoretical study of ($\eta^6\text{-C}_5\text{H}_5\text{BCH}_3$)₂Fe₂(CO)_n (*n* = 4, 3, 2) derivatives was undertaken using density functional methods similar to those used in previously reported theoretical studies of the related ($\eta^5\text{-C}_5\text{H}_5$)₂Fe₂(CO)_n [19] and ($\eta^6\text{-C}_6\text{H}_6$)₂Mn₂(CO)_n [23] systems. The methyl substituent on the borabenzene ligand was chosen as the simplest alkyl substituent in a ($\eta^6\text{-C}_5\text{H}_5\text{BR}$)₂Fe₂(CO)₂($\mu\text{-CO}$)₂ derivative that has been synthesized.

2. Theoretical methods

Density functional theory (DFT) including electron correlation effects is a powerful computational tool that has been successfully used in organotransition metal chemistry [29–35]. Three DFT

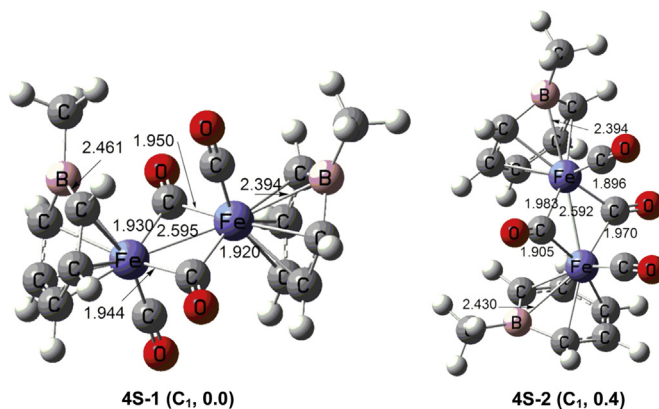


Fig. 2. The geometries for the two (C₅H₅BCH₃)₂Fe₂(CO)₄ structures optimized with the B3LYP* method. The numbers in parentheses are relative energies (ΔE , in kcal/mol).

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