



Diverse bonding modes of the pentalene ligand in binuclear cobalt carbonyl complexes



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ABSTRACT

The 2007 synthesis of the hexamethylpentalene complex *cis*-(η^5, η^5 -C₈H₆Me₆)Co₂(CO)₄ by O'Hare and coworkers makes of interest a theoretical study of the unsubstituted binuclear pentalene cobalt carbonyls (C₈H₆)Co₂(CO)_n (*n* = 6, 5, 4, 3). In this connection an unbridged unsubstituted *cis*-(η^5, η^5 -C₈H₆)Co₂(CO)₄ structure analogous to the experimental hexamethyl structure is found to be the lowest energy (C₈H₆)Co₂(CO)₄ structure. Furthermore, this (C₈H₆)Co₂(CO)_n structure is predicted to be the product from reactions of pentalene derivatives with cobalt carbonyls based on the thermochemistry of CO dissociation energies in the sequence *n* = 6 → 5 → 4 → 3 → 2. The low-energy structures for the unsaturated (C₈H₆)Co₂(CO)_n (*n* = 3, 2) derivatives also have the pentalene ligand bonded to each cobalt as a pentahapto ligand. They may be derived from either this unbridged *cis*-(η^5, η^5 -C₈H₆)Co₂(CO)₄ structure or a doubly CO-bridged variation thereof by removal of one or two CO groups. The carbonyl-rich (C₈H₆)Co₂(CO)_n (*n* = 6, 5) structures, which may be considered as precursors to *cis*-(η^5, η^5 -C₈H₆)Co₂(CO)₄, illustrate considerable diversity of bonding modes of the pentalene ligand to the central Co₂ unit. Structures without direct Co–Co bonds are found exhibiting either *cis* or *trans* stereochemistry in which trihapto allylic and/or pentahapto cyclopentadienylic subunits are bonded to Co(CO)₃ and Co(CO)₂ moieties, respectively. In addition, (C₈H₆)Co₂(CO)_n (*n* = 6, 5) structures exhibiting *cis* stereochemistry are found in which C=C bonds of a butadiene or fulvene subunit of the pentalene ligand replace CO groups in Co₂(CO)₈, retaining the formal Co–Co single bond.

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1. Introduction

One of the simplest planar bicyclic non-benzenoid hydrocarbons as a possible ligand for binuclear metal carbonyl complexes is pentalene, the lower homolog of naphthalene consisting of two fused five-membered rings. However, the instability of pentalene under ambient conditions [1,2] precludes the synthesis of pentalene metal carbonyl complexes by the direct reaction of pentalene with metal carbonyls. Nevertheless, the use of dihydropentalene as a reagent has allowed the synthesis of a number of metal carbonyl complexes such as the binuclear derivatives *cis*-(η^5, η^5 -C₈H₆)Fe₂(CO)₅ [3], *trans*-(η^5, η^5 -C₈H₆)[M(CO)₃]₂ (M = Mn, Re) [4], and Ru₂(MMe₃)₂(CO)₄(C₈H₆)(E = Si, Ge) [5]. Within the last few years the chemistry of pentalene metal complexes has expanded with the development

by O'Hare and coworkers [6] of methods for the synthesis of permethylpentalene precursors in quantity. This has allowed the synthesis of the stable hexamethylpentalene metal carbonyl complexes [7] *cis*-(η^5, η^5 -C₈H₆Me₆)Fe₂(CO)₅ and *cis*-(η^5, η^5 -C₈H₆Me₆)Co₂(CO)₄ (Fig. 1) [7].

The synthesis of O'Hare's cobalt complex *cis*-(η^5, η^5 -C₈H₆Me₆)Co₂(CO)₄ from the stable permethylpentalene isomer 1,3,4,5,6-pentamethyl-2-methylene-1,2-dihydropentalene requires the loss of four CO groups from the Co₂(CO)₈ reagent used as the cobalt source [7]. Thus more carbonyl-rich species such as (C₈R₆)Co₂(CO)_n (*n* = 6, 5; R = Me) are possible intermediates in this reaction. In order to obtain some insight into the nature of these possible intermediates and relevant thermochemistry leading to the experimentally observed (C₈R₆)Co₂(CO)₄ tetracarbonyl product, the structures of the more carbonyl-rich species have now been investigated using density functional theory. In order to simplify the computational aspects of this work and allow investigation of a more extensive variety of (pentalene)Co₂(CO)_n derivatives, the

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unsubstituted derivatives $(C_8H_6)Co_2(CO)_n$ ($n = 6, 5, 4, 3$) were used rather than the hexamethylpentalene derivatives synthesized by O'Hare and coworkers [7]. This study leads to the prediction of facile CO loss from the carbonyl-rich $(C_8H_6)Co_2(CO)_n$ ($n = 6, 5$) derivatives to proceed only to the tetracarbonyl stage $(C_8H_6)Co_2(CO)_4$. However, further CO loss from the tetracarbonyl $(C_8H_6)Co_2(CO)_4$ to give the still unknown tricarbonyl $(C_8H_6)Co_2(CO)_3$ is predicted to be difficult. This theoretical result is consistent with the experimental synthesis of *cis*-(η^5, η^5 - C_8Me_6) $Co_2(CO)_4$ from $Co_2(CO)_8$ and the hexamethylpentalene isomer [7].

The nature of the metal–metal bonding in these binuclear hexamethylpentalene iron and cobalt carbonyl complexes is an interesting question. If the pentalene ligand simply divides its eight π -electrons equally between the pair of metal atoms, then each metal atom in *cis*-(η^5, η^5 - C_8Me_6) $Fe_2(CO)_5$ and *cis*-(η^5, η^5 - C_8Me_6) $Co_2(CO)_4$ has the favored 18-electron configuration [8–12] if there is a single bond between the pair of metal atoms. Furthermore, the experimental metal–metal bond distances of 2.69 Å for the diiron complex and 2.68 Å for the dicobalt complex are reasonable for metal–metal formal single bonds. However, O'Hare and coworkers suggest the absence of metal–metal bonding in these complexes based on small atom overlap populations [7]. In order to provide more insight into the metal–metal bonding or lack thereof in these systems, we have included a study of the Wiberg bond indices (WBIs) for the cobalt–cobalt interactions in the $(C_8H_6)Co_2(CO)_n$ ($n = 6, 5, 4, 3$). This method confirms the essentially negligible direct cobalt–cobalt bonding suggested by O'Hare and coworkers for $(C_8R_6)Co_2(CO)_4$ on the basis of a low value of the atom–atom overlap population [7].

2. Theoretical methods

Electron correlation effects were considered by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds [13–19]. Thus two DFT methods were used in this study. The first functional is the B3LYP method, which is the hybrid HF/DFT method using a combination of the three-parameter Becke functional (B3) with the Lee–Yang–Parr (LYP) generalized gradient correlation functional [20]. The other DFT method used in the present paper is BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86) [21]. In the present study, the B3LYP and BP86 methods agree with each other fairly well in predicting the structural characteristics of the $(C_8H_6)Co_2(CO)_n$ complexes. However, in some cases, the B3LYP and BP86 methods predict quite different singlet–triplet splittings [22]. This discrepancy has been thoroughly studied by Reiher et al. [23] They have proposed a new parametrization for the B3LYP functional, named B3LYP*, which provides electronic state orderings in agreement with experiment [24]. In this study, we also adopted the B3LYP* method in case the B3LYP and BP86 methods predict quite different singlet–triplet splittings.

Previous work shows that the $\nu(CO)$ vibrational frequencies predicted by the BP86 method are closer to the experimental values without using any scaling factors [25,26]. This concurrence may be accidental, since the theoretical vibrational frequencies predicted by BP86 are harmonic frequencies, whereas the experimental fundamental frequencies are anharmonic.

All computations were performed using double- ζ plus polarization (DZP) basis sets. The DZP basis sets used for carbon and oxygen add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$ to the standard Huzinaga–Dunning contracted DZ sets [27,28] and are designated (9s5p1d/4s2p1d). For hydrogen, a set of p polarization functions

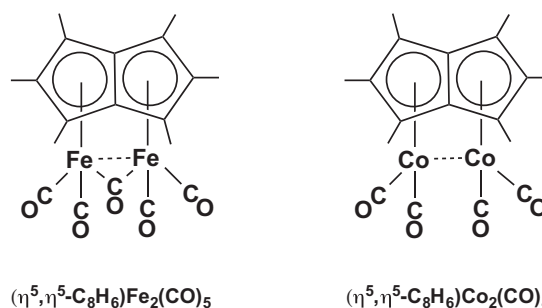


Fig. 1. Structures of the pentalene iron and cobalt carbonyl complexes. The hexamethylpentalene analogue was synthesized by O'Hare and coworkers [7] and structurally characterized by X-ray diffraction.

$\alpha_p(H) = 0.75$ is added to the Huzinaga–Dunning DZ set. The loosely contracted DZP basis set for cobalt is the Wachters primitive set [29] augmented by two sets of p functions and a set of d functions and contracted following Hood, Pitzer, and Schaefer [30], designated (14s11p6d/10s8p3d). The geometries of all structures were fully optimized using the DZP B3LYP and DZP BP86 methods. The vibrational frequencies and the corresponding infrared intensities were determined analytically. All of the computations were carried out with the GAUSSIAN 09 program [31], exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically [32].

3. Results

3.1. Molecular structures

3.1.1. $(C_8H_6)Co_2(CO)_6$

Seven low-lying structures (six singlet structures and one triplet structure) were found for $(C_8H_6)Co_2(CO)_6$. The four lowest-lying singlet structures and one low-lying triplet structure are discussed in this paper (Fig. 2 and Tables 1 and 2). All four singlet spin state structures belong to the C_1 point group.

The $C_8H_6Co_2(CO)_6$ structure **6S-1**, with six terminal CO groups and a terminal tetrahapto pentalene ligand, is the global minimum (Fig. 2 and Table 1). Two CO groups are bonded to the cobalt atom bearing the terminal pentalene ligand whereas four CO groups are bonded to the other cobalt atom. The predicted Co–Co distance of 2.781 Å (BP86) or 2.806 Å (B3LYP) in **6S-1** suggests a formal single bond, thereby giving both Co atoms the favored 18-electron configuration.

The $C_8H_6Co_2(CO)_6$ structure **6S-2**, lying 4.5 kcal/mol (BP86) or 7.5 kcal/mol (B3LYP) above **6S-1**, has six terminal CO groups and a bridging pentalene ligand bonded as a trihapto ligand to each cobalt atom (Fig. 2 and Table 1). This bis(trihapto) mode of bonding of the pentalene ligand to the pair of cobalt atoms in **6S-2** leaves an uncomplexed C=C double bond with a relatively short C=C distance of 1.377 Å (BP86) or 1.361 Å (B3LYP) compared with the other C–C bonds in the pentalene ligand. The *trans* stereochemistry of **6S-2** leads to a very long Co...Co distance of 5.135 Å (BP86) or 5.120 Å (B3LYP), clearly indicating the absence of a direct cobalt–cobalt bond. The local environment of each cobalt atom in **6S-2** is similar to that in the well-known [33,34] allylcobalt tricarbonyl (η^3 - C_3H_5) $Co(CO)_3$ giving each cobalt atom the favored 18-electron configuration. The $(C_8H_6)Co_2(CO)_6$ structure **6S-3**, lying 11.7 kcal/mol (BP86) or 11.0 kcal/mol (B3LYP) above **6S-1**, is closely related to structure **6S-2**, but with *cis* rather than *trans* stereochemistry of the cobalt atoms relative to the pentalene ligand. However, in **6S-3** the uncomplexed C=C double bond is the pair of carbon atoms shared by both rings of the pentalene ligand.

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