



Cyclic versus acyclic structures of six-carbon ligands in binuclear cobalt carbonyl derivatives: Some thermochemical observations



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ABSTRACT

Cobalt carbonyls such as $\text{Co}_2(\text{CO})_8$ are among the most frequently used catalyst precursors for the cyclotrimerization of alkynes to form benzene derivatives. In order to gain some insight regarding possible intermediates in such reactions, the species $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_n$ ($n = 6, 5, 4, 3$; $\text{R} = \text{H}, \text{F}, \text{CF}_3$) have been investigated by density functional theory. The thermochemistry of these systems is found to be very dependent on the substituent R. The lowest energy $(\text{C}_6\text{H}_6)\text{Co}_2(\text{CO})_n$ structures ($n = 6, 5, 4, 3$) by at least 8 kcal/mol all have *cis* geometries with intact benzene rings and Co–Co bonds. The benzene rings are bent for the more highly unsaturated $(\text{C}_6\text{H}_6)\text{Co}_2(\text{CO})_n$ ($n = 4, 3$) structures. The tetracarbonyl $(\text{C}_6\text{H}_6)\text{Co}_2(\text{CO})_4$ is disfavored with respect to disproportionation into $(\text{C}_6\text{H}_6)\text{Co}_2(\text{CO})_5$ and $(\text{C}_6\text{H}_6)\text{Co}_2(\text{CO})_3$. In addition, $(\text{C}_6\text{H}_6)\text{Co}_2(\text{CO})_6$ is marginally viable with respect to benzene dissociation to give $\text{Co}_2(\text{CO})_6$, which has long been recognized as an intermediate in the conversion of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$. The perfluoro and trifluoromethyl systems $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_n$ ($\text{R} = \text{F}, \text{CF}_3$; $n = 6, 5, 4, 3$) differ from $(\text{C}_6\text{H}_6)\text{Co}_2(\text{CO})_n$ in having “flyover” derivatives rather than cyclized benzene derivatives as the lowest energy structures for the tetracarbonyls $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_4$. This may relate to difficulties in the cyclization of the C_6 chain with the more hindered F and CF_3 substituents relative to hydrogen on the end carbon atoms. These “flyover” tetracarbonyl appear to be thermodynamic “sinks” consistent with the experimental isolation of $[\text{C}_6(\text{CF}_3)_6]\text{Co}_2(\text{CO})_4$ as a stable product from $\text{Co}_2(\text{CO})_8/\text{CF}_3\text{C}\equiv\text{CCF}_3$ reactions.

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1. Introduction

The [2+2+2] Reppe cyclotrimerization of alkynes leading to benzene derivatives using a variety of transition metal catalysts [1–4] has been an effective method for the synthesis of substituted arenes [5–8]. Cobalt carbonyls such as $\text{Co}_2(\text{CO})_8$ have been among the most frequently used catalyst precursors for such reactions [9–11]. So-called “flyover” $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_4$ complexes with an acyclic C_6R_6 ligand connecting the two cobalt atoms as well as a Co–Co bond (Fig. 1) have been recognized as intermediates in such cobalt carbonyl catalyzed reactions [9]. Such complexes have been isolated and characterized structurally in systems with large R substituents, e.g. $[\text{1,3,6-tBu}_3\text{C}_6\text{H}_3]\text{Co}_2(\text{CO})_4$.

A recent theoretical study [12] showed that the flyover $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_4$ compounds are the lowest energy structures only for

systems with large R groups such as those with multiple CF_3 and/or tert-butyl substituents. For systems with smaller R groups, including $(\text{C}_6\text{H}_6)\text{Co}_2(\text{CO})_4$ and $(\text{C}_6\text{Me}_6)\text{Co}_2(\text{CO})_4$, isomeric structures with a bent benzene ring bridging the two cobalt atoms were found to be lower energy structures than the corresponding “flyover” compounds (Fig. 2). However, this previous study considered only the tetracarbonyls $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_4$ ($\text{R} = \text{H}, \text{CH}_3, \text{CF}_3, \text{t-butyl}$) isomeric with the known flyover compounds. In order to gain more insight into the interaction of cobalt carbonyls with alkynes and the fate of the flyover complexes after they are formed, we have now used density functional theory methods to investigate the whole range of $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_n$ ($n = 6, 5, 4, 3$; $\text{R} = \text{CF}_3, \text{H}, \text{F}$) compounds with various numbers of carbonyl groups. A major objective of this work is the elucidation of the effects of the R substituents on the relative energies of isomeric structures with cyclic and acyclic C_6R_6 ligands. The H and F substituents were chosen to provide examples of simple monoatomic substituents of rather different electronegativities. The CF_3 substituent provides an example of a bulkier substituent known to form the stable flyover $[\text{C}_6(\text{CF}_3)_6]\text{Co}_2(\text{CO})_4$ complex [9–11,13].

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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 [14–20]. Three DFT methods were used in this study. The first functional is the popular hybrid B3LYP method, which incorporates Becke's three-parameter functional with the Lee, Yang, and Parr correlation functional [21,22]. The second approach is the BP86 method, which combines Becke's 1988 exchange functional with Perdew's 1986 correlation functional [23,24]. The BP86 method usually provides vibrational frequencies closer to the experimental values [25]. However, Reiher and coworkers have found that B3LYP favors the high-spin state and BP86 favors the low-spin state [26]. This is also true for the molecules studied in the present research so that these two DFT methods may predict global minima of different spin states. Thus we adopted a third functional in this work, namely the newer hybrid meta-GGA DFT functional, M06-L, developed by Truhlar's group [27]. This functional reflects considerable progress toward the development of improved exchange–correlation functionals that are essential for expanding the applicability of the Kohn–Sham DFT method. The M06-L functional was constructed using three strategies, namely constraint satisfaction, modeling the exchange–correlation hole, and empirical testing. The studies by Truhlar and co-workers [27] and by Gusev [28] suggest that M06-L is one of the best functionals for the study of organometallic and inorganic thermochemistry. When these three very different DFT methods agree, confident predictions can be made. For most of the structures studied in the present work, the methods agree quite well. Thus, only the M06-L geometries and energies are discussed in the present paper, while the B3LYP and BP86 results are listed in the [Supporting information](#).

For carbon and oxygen atoms, the double- ζ plus polarization (DZP) basis set used here adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(\text{C}) = 0.75$ and $\alpha_d(\text{O}) = 0.85$ to the standard Huzinaga–Dunning contracted DZ sets, and is designated (9s5p1d/4s2p1d) [29,30]. For H, a set of p polarization functions $\alpha_p(\text{H}) = 0.75$ is added to the Huzinaga–Dunning DZ sets. For cobalt, in our loosely contracted DZP basis set, the Wachters' primitive sets are used, but augmented by two sets of p functions and one set of d functions and contracted following Hood and Pitzer, and designated (14s11p6d/10s8p3d) [31,32].

The geometries of all of the structures were fully optimized using the three DFT methods. The harmonic vibrational frequencies and the corresponding infrared intensities were determined at the same levels by evaluating analytically. All of the computations were carried out with the GAUSSIAN 09 program, in which the fine grid (pruned 75, 302) is the default for evaluating integrals numerically [33]. We use default grid for B3LYP and BP86, but

use ultrafine grid (pruned 99, 590) for M06-L. The finer (120, 974) grid was used for more precise resolution of small imaginary vibrational frequencies [34]. Unless otherwise indicated, the structures reported in this paper have only real vibrational frequencies. All of the structures discussed in this paper were found to have stable wavefunctions by the M06-L method.

In the present paper each $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_6$ structure is designated as **R-xn-M**. Using this designation **R** (=H, F, CF_3) indicates the substituents on the C_6R_6 ligand; **x** indicates the structural type of the C_6R_6 ligand, i.e., **cis** indicates two cobalt atoms in the *cis* positions with respect to the benzene ring, **trans** indicates two cobalt atoms in the *trans* positions with respect to the benzene ring, and **ch** indicates a C_6R_6 chain rather than a benzene ring; **n** indicates the number of CO groups, and **M** stands for the spin multiplicity (**S** = singlet or **T** = triplet). Thus the *cis* singlet structure for $(\text{C}_6\text{H}_6)\text{Co}_2(\text{CO})_6$ is designated **H-cis6-S**.

3. Results and discussion

3.1. $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_6$ ($\text{R} = \text{CF}_3, \text{H}, \text{F}$) structures

Two types of singlet $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_6$ ($\text{R} = \text{CF}_3, \text{H}, \text{F}$) structures, i.e., *cis* and *trans*, were obtained (Fig. 3). In addition, we have tried to optimize the structures with a chain rather than cyclic C_6R_6 ligand. However, the resulting structures with a C_6R_6 chain were found to lie at least 30 kcal/mol higher in energy, and thus are not discussed in the text. In all $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_6$ structures all carbonyls are terminal groups. For $(\text{C}_6\text{H}_6)\text{Co}_2(\text{CO})_6$, the C_1 *cis* structure **H-cis6-S** with a bridging distorted benzene ring lies 8.0 kcal/mol in energy below the C_{2h} *trans* structure **H-trans6-S**. In **H-cis6-S** the cobalt atoms are in *cis* positions with respect to the η^2, η^2 - μ - C_6H_6 bridging benzene ring, which is a two-electron donor to each cobalt atom. The relatively short ~ 1.37 Å distance between the two uncomplexed carbon atoms C3 and C4 suggests a double bond. The Co–Co distance of 2.663 Å in **H-cis6-S** can be interpreted as the formal single bond required to give each cobalt atom the favored 18-electron configuration. In **H-trans6-S** the cobalt atoms are in *trans* positions with respect to the η^3, η^3 - C_6H_6 benzene ring. Each cobalt atom is directly bonded to three benzene carbon atoms. The Co–Co distance is too long to form a direct Co–Co bond. However, each cobalt atom also has the favored 18-electron configuration.

Different from $(\text{C}_6\text{H}_6)\text{Co}_2(\text{CO})_6$, the lower energy structures for $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_6$ ($\text{R} = \text{F}, \text{CF}_3$) are the C_{2h} *trans* structures **R-trans6-S** (Fig. 3). Similar to $(\text{C}_6\text{H}_6)\text{Co}_2(\text{CO})_6$, the $(\text{C}_6\text{R}_6)\text{Co}_2(\text{CO})_6$ structures with a chain rather than cyclic C_6R_6 ligand were found to lie at least 33 kcal/mol higher in energy, and are not discussed in the text. In **F-trans6-S** and **CF₃-trans6-S**, each Co atom is bonded to three carbonyl groups and three carbon atoms in the benzene ligand analogous to the well-known η^3 -allyl cobalt tricarbonyl [35–37] (η^3 - C_3H_5) $\text{Co}(\text{CO})_3$ (Fig. 4) thereby giving each Co atom the favored 18-electron configuration. The isomeric **F-cis6-S** and **CF₃-cis6-S** structures lies at 0.7 and 10.3 kcal/mol, respectively, above their *trans* isomers. Similar to **H-cis6-S**, each Co atom in **F-cis6-S** and **CF₃-cis6-S** is connected to two benzene carbon atoms leaving an uncomplexed C3=C4 double bond of ~ 1.36 Å length. The Co–Co

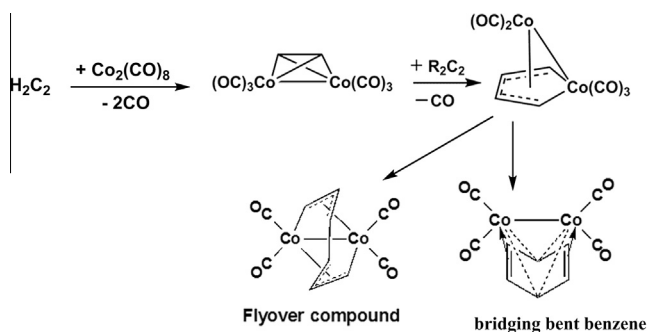


Fig. 1. Conversion of $\text{Co}_2(\text{CO})_8$ to the flyover compounds and bridging bent benzene compounds $\text{Co}_2(\text{CO})_4(\mu\text{-C}_6\text{H}_6)_2$ via the alkyne complexes $\text{Co}_2(\text{CO})_6(\mu\text{-C}_2\text{H}_2)$ and the cobaltacyclopentadiene complexes $\text{Co}_2(\text{CO})_5(\eta^4, \eta^1\text{-}\mu\text{-C}_4\text{H}_4)$.

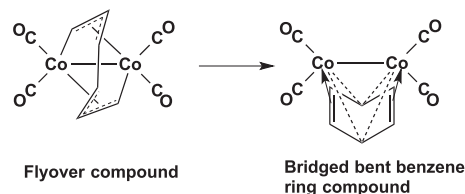


Fig. 2. A "flyover compound" and its conversion to the bridged bent benzene ring isomer.

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