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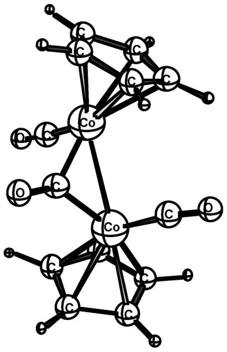

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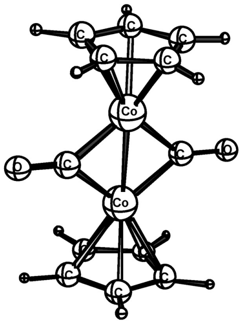

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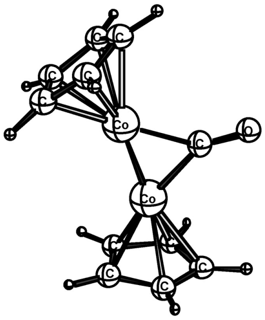

$Cp_2Co_2(CO)$

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Binuclear Cyclopentadienylcobalt Carbonyls: Comparison with Binuclear Iron Carbonyls

Hongyan Wang,[†,‡] Yaoming Xie,[‡] R. Bruce King,*[,‡] and Henry F. Schaefer, III[‡]

Contribution from the Atomic and Molecular Physics Institute, Sichuan University, Chengdu 610065, P. R. China, and Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602

Received March 24, 2005; E-mail: rbking@sunchem.chem.uga.edu

Abstract: The binuclear cyclopentadienylcobalt carbonyls $Cp_2Co_2(CO)_n$ ($n = 3, 2, 1$; Cp = η^5-C_5H_5) are studied by density functional theory using the B3LYP and BP86 functionals. The experimentally known monobridged isomer $Cp_2Co_2(CO)_2(\mu\text{-}CO)$ and the tribridged isomer $Cp_2Co_2(\mu\text{-}CO)_3$ of $Cp_2Co_2(CO)_3$ with formal Co−Co single bonds are found to be similar in energy, with the precise relative energies of the two isomers depending on the functional chosen. For $Cp_2Co_2(CO)_2$, the experimentally known coaxial isomer $Cp_2Co_2(\mu\text{-}CO)_2$ with two bridging CO groups and a formal Co═Co double bond (2.360 Å by B3LYP or 2.346 Å by BP86) is found to lie 38.2 (B3LYP) or 34.9 kcal/mol (BP86) below a perpendicular isomer $\perp$-$Cp_2Co_2(CO)_2$. Similarly, for $Cp_2Co_2(CO)$, the coaxial isomer $Cp_2Co_2(\mu\text{-}CO)$ with one bridging CO group and a formal Co≡Co triple bond (2.021 Å by B3LYP or 2.050 Å by BP86) is found to lie 9.36 (B3LYP) or 9.62 kcal/mol (BP86) below the corresponding perpendicular isomer $\perp$-$Cp_2Co_2(CO)$. This coaxial isomer $Cp_2Co_2(\mu\text{-}CO)$ is a possible intermediate in the known pyrolysis of the trimer $(\eta^5\text{-}C_5H_5)_3Co_3(\mu\text{-}CO)_3$ to give the tetranuclear complex $(\eta^5\text{-}C_5H_5)_4Co_4(\mu_3\text{-}CO)_2$. These optimized $Cp_2Co_2(CO)_n$ ($n = 3, 2, 1$) structures can be compared with the corresponding $Fe_2(CO)_{6+n}$ structures since the CpCo and $Fe(CO)_3$ groups are isolobal. In general, the metal−metal bonds are 0.09−0.22 Å shorter for the $Cp_2Co_2(CO)_n$ ($n = 3, 2, 1$) complexes than for the corresponding $Fe_2(CO)_{6+n}$ complexes. For $Fe_2(CO)_9$, the experimentally well-known $Fe_2(CO)_6(\mu\text{-}CO)_3$ isomer is shown to be very close in energy to the unknown $Fe_2(CO)_8(\mu\text{-}CO)$ isomer, with the precise relative energies depending on the basis set used.

1. Introduction

A variety of unsaturated cyclopentadienylmetal carbonyls of different types formulated with metal−metal multiple bonds[1,2] have been prepared and characterized by X-ray diffraction, including $Cp_2V_2(CO)_5$,[3,4] $Cp_2M_2(CO)_4$ (M = Cr, Mo),[5,6] and $Cp_2Mn_2(\mu\text{-}CO)_3$[7] with metal−metal triple bonds as well as $Cp_2Fe_2(\mu\text{-}CO)_3$[8] and $Cp_2M_2(\mu\text{-}CO)_2$ (M = Co, Rh)[9] with metal−metal double bonds. This suggests that there is a reasonable chance that theoretical methods can guide future quests for isolable unsaturated cyclopentadienylmetal carbonyl complexes, whose structures can be determined by unambiguous methods, notably X-ray diffraction. The unsaturation in such cyclopentadienylmetal carbonyls makes them potentially useful reactive species in transition-metal organometallic chemistry, and their chemistry could lead to the design of new and useful catalytic systems. The study of dimeric cyclopentadienylmetal carbonyls is also of interest in view of their relationship to carbonyl-free dimetallocenes, including the experimentally realized[10] $(\eta^5\text{-}Me_5C_5)_2Zn_2$ as well as the related compounds $(\eta^5\text{-}Me_5C_5)_2M_2$ (M = Cu, Ni), which have been studied by DFT methods.[11]

This paper reports our initial results in this area, namely, a study of the binuclear cyclopentadienylcobalt carbonyls $Cp_2Co_2(CO)_n$ ($n = 3, 2, 1$; Cp = an η^5-bonded cyclopentadienyl or substituted cyclopentadienyl group; η^5-C_5H_5 and η^5-Me_5C_5 are the most commonly encountered such groups). In such compounds, a CpCo group can be considered as isoelectronic and isolobal with an $Fe(CO)_3$ group, so it is relevant to compare the results reported in this paper with previous work on homoleptic binuclear iron carbonyls.[12] Thus, $Cp_2Co_2(CO)_3 \approx Fe_2(CO)_9$, $Cp_2Co_2(CO)_2 \approx Fe_2(CO)_8$, and $Cp_2Co_2CO \approx Fe_2(CO)_7$ for the three cases investigated in this paper. Since previously reported[13] computational work on $Fe_2(CO)_9$ from our group

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[†] Sichuan University.

[‡] University of Georgia.

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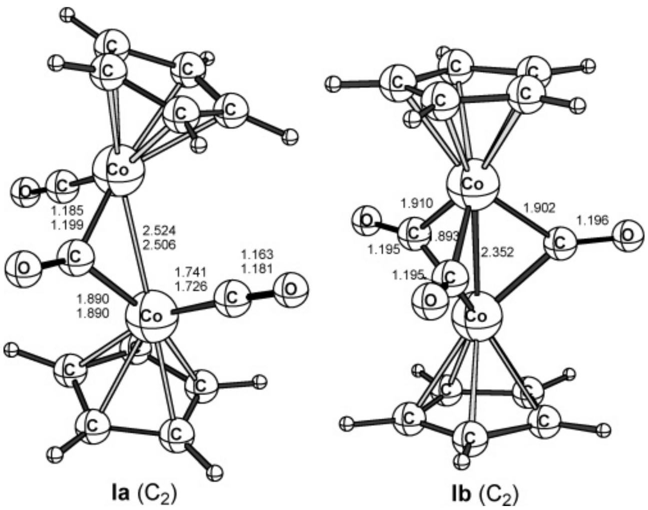
considered only the experimentally known isomer $Fe_2(CO)_6(\mu\text{-}CO)_3$ with three bridging CO groups, we have also examined alternative $Fe_2(CO)_9$ structures that have not yet been realized experimentally.

Some experimental information on binuclear cyclopentadienylcobalt carbonyls is available. Thus, photolysis of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ in solution generates the unsaturated monocarbonyl species $(\eta^5\text{-}C_5H_5)Co(CO)$, which has been identified by infrared spectroscopy in liquid krypton at 173 K.[14] At room temperature, $(\eta^5\text{-}C_5H_5)Co(CO)$ can either react with excess $(\eta^5\text{-}C_5H_5)Co(CO)_2$ to give $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_3$ or dimerize to give $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2$, therefore providing synthetic routes to two of the three $Cp_2Co_2(CO)_n$ species pursued in this paper. The dimer $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2$ is stable as a solid, but in solution, it is slowly converted to the insoluble trimer $(\eta^5\text{-}C_5H_5)_3\text{-}Co_3(CO)_3$.[15] The bond order and a simple valence bond description of the metal−metal interaction for $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2$ have been established by the Fenske Hall MO method.[16] The closely related dimeric radical anion $[(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2]^-$ was characterized structurally by Bergman and co-workers.[17] The monocarbonyl $(\eta^5\text{-}C_5H_5)_2Co_2(CO)$ is not known experimentally. However, pyrolysis of $(\eta^5\text{-}C_5H_5)_3Co_3(\mu\text{-}CO)_3$ leads to a tetranuclear complex[18] $(\eta^5\text{-}C_5H_5)_4Co_4(\mu_3\text{-}CO)_2$ through a reaction sequence that may involve dimerization of a $(\eta^5\text{-}C_5H_5)_2Co_2(CO)$ intermediate.[19]

Previous research[11] suggests two distinctly different structure types for dimetallocenes, namely, the coaxial structure found experimentally for $(\eta^5\text{-}Me_5C_5)_2Zn_2$ and an alternative structure in which the metal−metal bond axis is perpendicular to the C_5 axes of the Cp rings (designated by ⊥ in formulas). These two types of structures, in principle, can exist in dimetallocenes with added carbonyl ligands. In the present paper, both types of structures are examined theoretically for Cp_2Co_2 complexes with added CO ligands. The series of the lowest energy isomers of $Cp_2Co_2(CO)_n$ ($n = 1, 2, 3$) are explored, including both coaxial and perpendicular isomers.

2. Theoretical Methods

Basis sets have been chosen to provide continuity with a body of existing research on organometallic compounds. Fortunately, DFT methods are far less sensitive to basis set than methods such as coupled cluster theory. In this work, the double-ς plus polarization (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 Huzinaga−Dunning standard contracted DZ sets and are designated (9s5p/4s2p).[20,21] For H, a set of p polarization functions, $\alpha_p(H) = 0.75$, is added to the Huzinaga−Dunning DZ set. For Co, in our loosely contracted DZP basis set, the Wachters' primitive set is used but is augmented by two sets of p functions and one set of d functions, contracted following Hood et al., and designated (14s11p6d/10s8p3d).[22,23] For $Cp_2Co_2(CO)_3$, $Cp_2Co_2(CO)_2$, and $Cp_2Co_2(CO)$, there are 388, 358, and 328 contracted Gaussian functions, respectively.



Ia (C_2) **Ib** (C_2)

Figure 1. Optimized geometries for $Cp_2Co_2(CO)_3$ (bond distances are in Å).

Electron correlation effects were included by employing density functional theory (DFT) methods, which have been widely proclaimed as a practical and effective computational tool, especially for organometallic compounds. 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.[24,25] The second approach is the BP86 method, which marries Becke's 1988 exchange functional (B) with Perdew's 1986 correlation functional.[26,27] Both restricted and unrestricted DFT methods were used to explore the stability of the ground state with the same results.

The geometries of all structures are fully optimized with both the DZP B3LYP and DZP BP86 methods. At the same levels, the vibrational frequencies are determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities are evaluated analytically, as well. All of the computations were carried out with the Gaussian 94 program 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 with the Gaussian 94 program package.[28]

In the search for minima, low magnitude imaginary vibrational frequencies are suspicious because the numerical integration procedures used in existing DFT methods have significant limitations. Thus, when one predicts an imaginary vibrational frequency of magnitude less than $100i$ cm^{-1}, the conclusion should be that there is a minimum of energy identical to or close to that of the stationary point in question.[12] Accordingly, we do not, in general, follow the imaginary eigenvector in search of another minimum in such cases.

The optimized geometries from these computations are depicted in Figures 1−3 and Figure 5, with all bond distances given in angstroms.

3. Results and Discussion

3.1. $Cp_2Co_2(CO)_3$. There are two possible coaxial structures for $Cp_2Co_2(CO)_3$ (Figure 1 and Table 1), namely, the monobridged structure $Cp_2Co_2(CO)_2(\mu\text{-}CO)$ (**Ia**) and the tribridged

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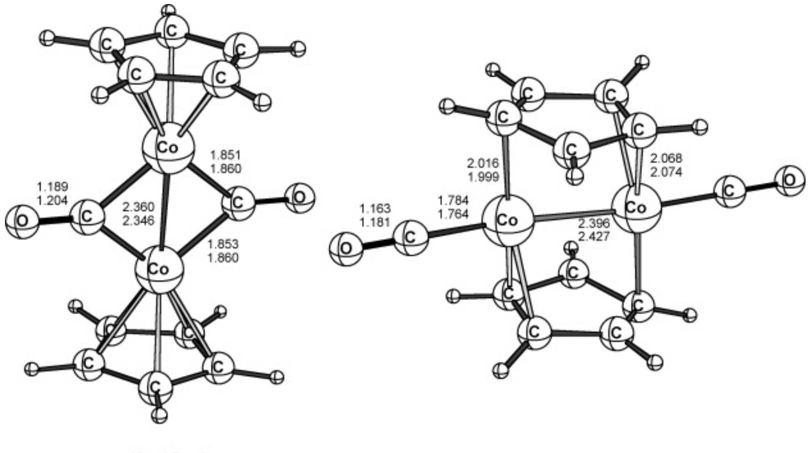
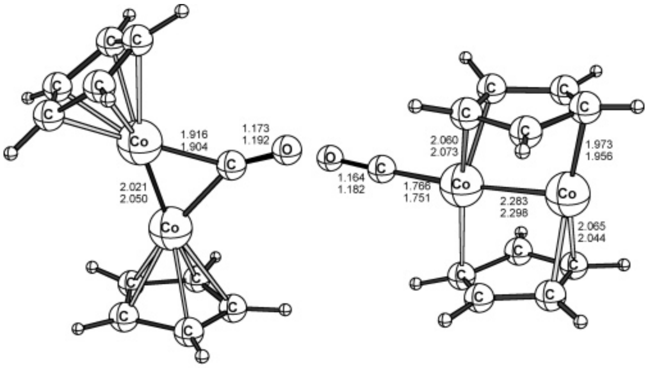


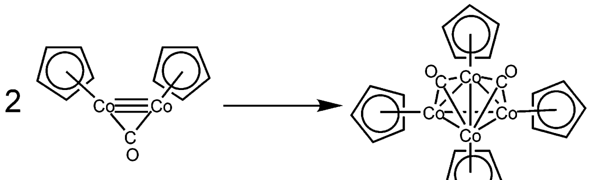
IIa (C_{2h}) **IIb** (C_{2h})

Figure 2. Optimized geometries for $Cp_2Co_2(CO)_2$ (bond distances are in Å).



IIIa (C_{2v}) **IIIb** (C_s)

Figure 3. Optimized geometries for $Cp_2Co_2(CO)$ (bond distances are in Å).



$Cp_2Co_2(\mu\text{-}CO)$ $Cp_4Co_4(\mu_3\text{-}CO)_2$

Figure 4. Dimerization of $Cp_2Co_2(\mu\text{-}CO)$ to $Cp_4Co_2(\mu_3\text{-}CO)_2$.

structure $Cp_2Co_2(\mu\text{-}CO)_3$ (**Ib**). The tribridged structure **Ib** collapses to the monobridged structure **Ia** using the B3LYP method. However, the BP86 method predicts both the monobridged and tribridged structures as stable minima with the tribridged structure lying slightly lower in energy (1.8 kcal/mol). The Co−Co bond distance for the monobridged structure **Ia** is 2.524 (B3LYP) or 2.506 Å (BP86), which is significantly longer than that in the tribridged structure **Ib** (2.352 Å by BP86). For the monobridged structure **Ia**, the two Cp rings are tilted more than those in the tribridged structure **Ib**. In both structures, the Cp ring is not strictly planar. For **Ia**, the average angle for the hydrogen atoms out of the Cp plane is about 1.4 (B3LYP) or 0.8° (BP86), whereas for **Ib**, it is 1.6° (BP86). No stable $Cp_2Co_2(CO)_3$ structure was found with the Co−Co bond perpendicular to the axis of the Cp rings.

3.2. $Cp_2Co_2(CO)_2$. There are two types of stationary points for $Cp_2Co_2(CO)_2$, both with C_{2h} symmetry (Figure 2 and Table 2). Structure **IIa** is a coaxial structure, $Cp_2Co_2(\mu\text{-}CO)_2$, with two bridging CO ligands. The unbridged coaxial structure (not shown) is not a stationary point with either B3LYP or BP86 but falls to **IIa** upon optimization. The other stationary point for $Cp_2Co_2(CO)_2$ is a structure $\perp$-$Cp_2Co_2(CO)_2$ (**IIb**) with two terminal CO ligands and with the Co−Co bond perpendicular to the axes of the Cp rings. The dibridged coaxial structure **IIa** lies lower in energy than the perpendicular structure **IIb** by 38.2 (B3LYP) or 34.9 kcal/mol (BP86).

The 18-electron rule[29] requires the metal−metal bond in $Cp_2Co_2(CO)_2$ (**IIa**) to be a formal Co═Co double bond. In this connection, the metal−metal bond distance in structure **IIa** for $Cp_2Co_2(\mu\text{-}CO)_2$ with a formal Co═Co double bond is found to be 2.360 (B3LYP) or 2.346 Å (BP86). This distance is shorter than the metal−metal bond distance in structure **Ia** for $Cp_2Co_2(CO)_2(\mu\text{-}CO)$ (2.524 Å by B3LYP or 2.506 Å by BP86), where the 18-electron rule requires only a formal Co−Co single bond. However, the situation is somewhat complicated owing to the systematic shortening of the metal−metal bond length for a given formal metal−metal bond order as the number of bridging CO groups is increased. Thus, the similarity in the computed metal−metal bond distances in isomer **IIa** for $Cp_2Co_2(\mu\text{-}CO)_2$ and isomer **Ib** for $Cp_2Co_2(\mu\text{-}CO)_3$ (2.352 Å by BP86) may relate to a balancing of the shortening of the metal−metal bond by the extra bridging CO in **Ib** with the higher formal metal−metal bond order in **IIa** (Co═Co) than in **Ib** (Co−Co). Furthermore, the Co═Co distance in the coaxial structure **IIa** for $Cp_2Co_2(\mu\text{-}CO)_2$ is shorter than that in the perpendicular structure $\perp$-$Cp_2Co_2(CO)_2$ (**IIb**) (2.396 and 2.427 Å) by 0.036 (B3LYP) or 0.081 Å (BP86). The Co−C distances to the bridging CO groups in **IIa** are 1.851 (B3LYP) and 1.860 Å (BP86), which are longer than those to the terminal CO groups in **IIb** by 0.067 (B3LYP) or 0.096 Å (BP86).

Experimental structural data are available[30] on $(\eta^5\text{-}Me_5C_5)_2Co_2(\mu\text{-}CO)_2$, where the Co═Co bond distance of 2.327 Å found by X-ray crystallography is very close to the values of 2.360 Å by B3LYP and 2.346 Å by BP86 computed here for the Co═Co distance in the closely related $(\eta^5\text{-}C_5H_5)_2Co_2(\mu\text{-}CO)_2$.

3.3. $Cp_2Co_2(CO)$. For $Cp_2Co_2(CO)$ (Figure 3 and Table 3), we predict two types of stationary points. One is the axial

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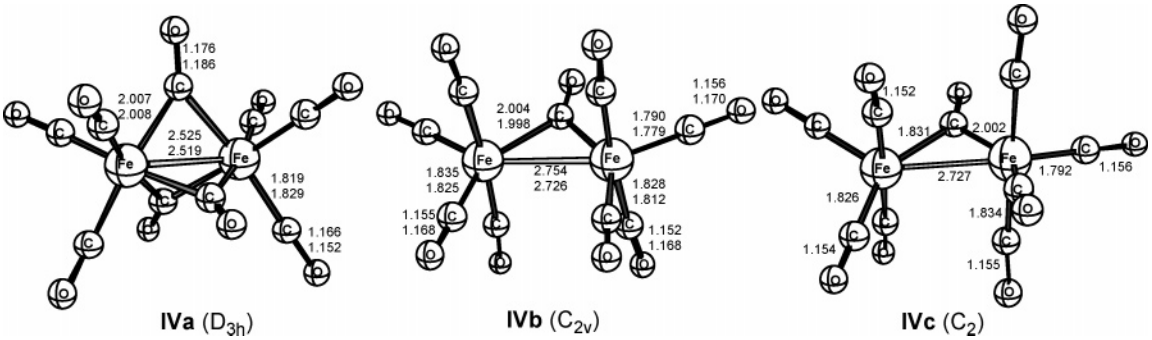

Figure 5. Optimized geometries for $Fe_2(CO)_9$ (bond distances are in Å).

Table 1. Bond Distances (in Å), Total Energies (*E*, in hartree), and Relative Energies (Δ*E*, in kcal/mol) for the Isomers of $Cp_2Co_2(CO)_3$

	$Cp_2Co_2(CO)_2(\mu\text{-CO})$ (**Ia**) (C_2)		$Cp_2Co_2(\mu\text{-CO})_3$ (**Ib**) (C_2)	
	B3LYP	BP86	B3LYP	BP86
Co−Co	2.524	2.506		2.352
Co−C (bridge)	1.890	1.890		1.910 1.893 1.902
C−O (bridge)	1.185	1.199	collapses to **Ia**	1.195 1.195 1.196
Co−C (nonbridge)	1.741	1.726		
C−O (nonbridge)	1.163	1.181		
energy	−3492.86261	−3493.36137		−3493.36424
Δ*E*	0	1.80		0
imaginary frequencies	no	no		no

Table 2. Bond Distances (in Å), Total Energies (*E*, in hartree), and Relative Energies (Δ*E*, in kcal/mol) for the Isomers of $Cp_2Co_2(CO)_2$

	$Cp_2Co_2(\mu\text{-CO})_2$ (**IIa**) (C_{2h})		$\perp\text{-}Cp_2Co_2(CO)_2$ (**IIb**) (C_{2h})	
	B3LYP	BP86	B3LYP	BP86
Co−Co	2.360	2.346	2.396	2.427
Co−C	1.852	1.860	1.784	1.764
C−O	1.189	1.204	1.163	1.181
energy	−3379.49682	−3379.99660	−3379.43592	−3379.94105
Δ*E*	0	0	38.22	34.86
imaginary frequency	11*i*	15*i*	no	5*i*

Table 3. Bond Distances (in Å), Total Energies (*E*, in hartree), and Relative Energies (Δ*E*, in kcal/mol) for the Isomers of $Cp_2Co_2(CO)$

	$Cp_2Co_2(\mu\text{-CO})$ (**IIIa**) (C_{2v})		$\perp\text{-}Cp_2Co_2(CO)$ (**IIIb**) (C_s)	
	B3LYP	BP86	B3LYP	BP86
Co−Co	2.021	2.050	2.283	2.298
Co−C	1.916	1.904	1.766	1.751
C−O	1.173	1.192	1.164	1.182
energy	−3266.07260	−3266.55780	−3266.05768	−3266.54247
Δ*E*	0	0	9.36	9.62
imaginary frequency	no	no	59*i*	97*i*

Table 4. Dissociation Energies (kcal/mol) for the Successive Removal of Carbonyl Groups from $Cp_2Co_2(CO)_3$ and $Co_2(CO)_8$ [a,b]

	B3LYP	BP86
$Cp_2Co_2(CO)_3$ (**Ib**) → $Cp_2Co_2(CO)_2$ (**IIa**) + CO	23.3	25.4
$Cp_2Co_2(CO)_2$ (**IIa**) → $Cp_2Co_2(CO)$ (**IIIa**) + CO	60.0	70.0
$Co_2(CO)_8$ → $Co_2(CO)_7$ + CO	18.2	35.6
$Co_2(CO)_7$ → $Co_2(CO)_6$ + CO	18.8	22.9
$Co_2(CO)_6$ → $Co_2(CO)_5$ + CO	52.9	53.0

[a] All results reported here refer to the lowest-energy structures of $Cp_2Co_2(CO)_n$. [b] Dissociation energies of $Co_2(CO)_8$ are taken from Kenny, J. P.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2001**, *40*, 900.

dimetallocene structure $Cp_2Co_2(\mu\text{-CO})$ (**IIIa**) with a bridging CO ligand. This dimetallocene bends with C_{2v} symmetry, owing to the CO bridge. The other structure $\perp\text{-}Cp_2Co_2(CO)$ (**IIIb**) has the metal−metal bond axis perpendicular to the original C_5 axes of the Cp rings with a terminal CO ligand bonded to one of the metal atoms. In structure **IIIb**, each cobalt atom is bonded to a portion of each Cp ring, in contrast to structure **IIIa**, in which each metal atom is bound to only one of the Cp rings. The energy of optimized coaxial structure **IIIa** is lower than that of perpendicular structure **IIIb** by 9.4 (B3LYP) or 9.6 kcal/mol (BP86). Note that this **IIIa**/**IIIb** energy separation is much less than the difference for the corresponding monocarbonyls **IIa**/**IIb**.

The metal−metal bond in the axial structure $Cp_2Co_2(\mu\text{-CO})$ (**IIIa**) is a formal Co≡Co triple bond if both cobalt atoms follow the 18-electron rule. In this connection, the Co≡Co distance of 2.021 (B3LYP) or 2.050 Å (BP86) is significantly shorter than that of either $Cp_2Co_2(CO)_2$ isomer requiring a Co═Co double bond or $Cp_2Co_2(CO)_3$ isomer requiring a Co−Co single bond to satisfy the 18-electron rule. Furthermore, the B3LYP and BP86 results show that the metal−metal distance in structure **IIIb** is longer than that in structure **IIIa** by 0.262 (B3LYP) or 0.248 Å (BP86). The Co−C distance to the bridging CO group in structure **IIIa** is longer than the Co−C distance to the terminal CO group in structure **IIIb** by 0.150 (B3LYP) and 0.153 Å (BP86).

The harmonic vibrational frequency analyses show that the axial structure **IIIa** is a genuine minimum. However, the perpendicular structure **IIIb** has a small imaginary vibrational frequency of 59*i* (B3LYP) or 97*i* cm^{-1}. Since this vibrational frequency is less than 100*i* cm^{-1}, the minimum is likely to be identical or close to that of structure **IIIb**.

The monocarbonyl $Cp_2Co_2(CO)$, unlike the dicarbonyl $Cp_2Co_2(\mu\text{-CO})_2$ and the tricarbonyl $Cp_2Co_2(CO)_2(\mu\text{-CO})$, is not known experimentally either as an isolable substance or in a low-temperature matrix. However, $Cp_2Co_2(CO)$ might well be an intermediate in the reported[19] pyrolysis of the trinuclear complex $(\eta^5\text{-}C_5H_5)_3Co_3(\mu\text{-CO})_3$ to the tetranuclear complex[18] $(\eta^5\text{-}C_5H_5)_4Co_4(\mu_3\text{-CO})_2$, which could proceed by the

Table 5. Bond Distances (in Å), Total Energies (*E*, in hartree), and Relative Energies (Δ*E*, in kcal/mol) for the Isomers of $Fe_2(CO)_9$

	$Fe_2(CO)_6(\mu\text{-}CO)_3$ (D_{3h}) **(IVa)**		$Fe_2(CO)_8(\mu\text{-}CO)$ (C_{2v}) **(IVb)**		$Fe_2(CO)_8(\mu\text{-}CO)$ (C_2) **(IVc)**	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe−Fe	2.525	2.519	2.754	2.726	2.727	
Fe−C (terminal)	1.829	1.819	1.828	1.812	1.826	collapses to the D_{3h} structure **IVa**
			1.828	1.812	1.792	
			1.790	1.779	1.832	
			1.835	1.825	1.834	
			2.004	1.998	2.002	
Fe−C (bridge)	2.008	2.007	2.004	1.998	2.002	
C−O (terminal)	1.152	1.166	1.152	1.168	1.154	
			1.152	1.168	1.155	
			1.156	1.170	1.152	
			1.155	1.168	1.155	
C−O (bridge)	1.176	1.186	1.179	1.191	1.179	
∠ C−Fe−C (terminal)	96.4	95.9	87.5	87.0	89.7	
∠ Fe−C−O (bridge)	177.5	176.9	136.6	137.0	137.1	
energy	−3547.78742	−3548.31362	−3547.78977	−3548.30486	−3547.79076	
Δ*E*	2.10	0	0.62	5.50	0	
imaginary frequency	no	no	18*i* (a_2)	21*i* (a_2)	no	

following sequence of reactions:

$$Cp_3Co_3(CO)_3 \rightarrow Cp_2Co_2(CO) + CpCo(CO)_2 \qquad (1a)$$

$$2\ Cp_2Co_2(CO) \rightarrow Cp_4Co_4(CO)_2 \qquad (1b)$$

The second step (eq 1b and Figure 4) involves the dimerization of $Cp_2Co_2(CO)$ and would be analogous to the dimerization of an alkyne to a tetrahedrane. A stable $Cp_2Co_2(\mu\text{-}CO)$ derivative might be isolable by pyrolysis of a $Cp_3Co_3(CO)_3$ derivative with bulky substituents on the Cp ring to inhibit the dimerization of $Cp_2Co_2(CO)$ to $Cp_4Co_4(CO)_2$ observed with the η^5-C_5H_5 derivative. A mechanism for the pyrolysis of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ through a similar dimerization of a $Co_2(CO)_6$ intermediate, possibly with a Co≡Co triple bond similar to that suggested for $Cp_2Co_2(CO)$ (**IIIa**) in this paper, has been suggested on the basis of kinetic studies.[31,32]

3.4. Dissociation Energies. Table 4 reports the dissociation energies in terms of the single carbonyl dissociation step

$$Cp_2Co_2(CO)_n \rightarrow Cp_2Co_2(CO)_{n-1} + CO \qquad (2)$$

The predicted dissociation energy of one CO group from $Cp_2Co_2(CO)_3$ is 23.3 kcal/mol with B3LYP and 25.4 kcal/mol with BP86. In sharp contrast, the $Cp_2Co_2(CO)_2$ dissociation process to $Cp_2Co_2(CO)$ + CO requires 60.0 kcal/mol with B3LYP and 70.0 kcal/mol with BP86. Thus, $Cp_2Co_2(CO)_2$ appears to be very stable with respect to extrusion of a carbonyl ligand. Comparison of $Cp_2Co_2(CO)_3$ and $Co_2(CO)_8$ suggests that the single carbonyl dissociation energies for $Co_2(CO)_8$ and $Co_2(CO)_7$ are close to that of $Cp_2Co_2(CO)_3$, and that of $Co_2(CO)_6$ approaches that of $Cp_2Co_2(CO)_2$.

3.5. $Fe_2(CO)_9$. The well-known $Fe_2(CO)_9$ was included in a previous DFT study[13] on the molecular structures of the three known neutral homoleptic iron carbonyls. However, only the experimentally known structure $Fe_2(CO)_6(\mu\text{-}CO)_3$, confirmed by X-ray crystallography,[33,34] was considered for $Fe_2(CO)_9$. We therefore investigated as part of the current research an alternative structure for $Fe_2(CO)_9$ with a single bridging CO group, namely, $Fe_2(CO)_8(\mu\text{-}CO)$, analogous to the known[35] structure for $Os_2(CO)_9$, for comparison with the known[19] $Cp_2Co_2(CO)_2(\mu\text{-}CO)$ structure predicted above. In this connection, the B3LYP functional predicts three distinct singlet structures for $Fe_2(CO)_9$, namely, two monobridged structures and one tribridged structure (Figure 5 and Table 5). The lowest energy of these three structures is actually the unknown monobridged structure $Fe_2(CO)_8(\mu\text{-}CO)$ (**IVc**) with C_2 symmetry rather than the known D_{3h} tribridged isomer $Fe_2(CO)_6(\mu\text{-}CO)_3$. The more symmetrical C_{2v} monobridged structure **IVb** is slightly higher in energy by 0.62 kcal/mol and has a very small imaginary vibrational frequency (18*i*). Following the corresponding vibration mode leads to structure **IVc**.

The BP86 functional leads to different results for $Fe_2(CO)_9$ than the B3LYP functional since it predicts only two structures for $Fe_2(CO)_9$, namely, **IVa** and **IVb**. A variety of subtle evidence (see, for example, ref 13) suggests that the BP86 method is somewhat more reliable than the B3LYP method for transition-metal-containing systems. The monobridged C_2 structure **IVc** found using the B3LYP functional converts into the conventional tribridged structure **IVa** upon optimization with the BP86 functional. The monobridged structure **IVb** is higher in energy than the tribridged structure **IVa** by 5.5 kcal/mol with the BP86 functional. Furthermore, structure **IVb** has a small imaginary vibrational frequency (18*i* cm^{-1} by B3LYP or 21*i* cm^{-1} by BP86). Following the corresponding imaginary vibration mode leads to the structure **IVa**. A similar result was reported by Hunstock, Mealli, Calhorda, and Reinhold,[36] who used a DFT functional closely related to BP86 in the Amsterdam Density Functional (ADF) program package to compute the monobridged C_{2v} isomer $Fe_2(CO)_8(\mu\text{-}CO)$ (**IVb**) to be 3.3 kcal/mol above the D_{3h} global minimum $Fe_2(CO)_6(\mu\text{-}CO)_3$ (**IVa**).

The Fe−Fe bond distance (2.525 and 2.519 Å) in the tribridged structure **IVa** is shorter than that in the monobridged structure **IVb** (2.754 and 2.726 Å for B3LYP and BP86, respectively) by 0.229 (B3LYP) or 0.207 Å (BP86). The Fe−C distance to the bridging CO groups is 2.008 (B3LYP) or 2.007

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Table 6. Metal Carbonyl ν(CO) Frequencies Predicted for the $Cp_2Co_2(CO)_n$ (n = 1, 2, 3) Isomers (infrared intensities in parentheses are in km/mol; infrared-active frequencies are given in bold type)

		B3LYP	BP86	exp.[a]
$Cp_2Co_2(CO)_3$	**Ia** (C_2)	**1893 (a, 583)**	**1821 (a, 477)**	**1812 (3700)**
		2052 (a, 2)	1964 (a, 4)	
		2036 (b, 1415)	**1951 (b, 1090)**	**1965 (6500)**
	Ib (C_2)		**1828 (a, 684)**	
			1883 (a, 0)	
			1829 (b, 701)	
$Cp_2Co_2(CO)_2$	**IIa** (C_{2h})	1900 (a_g, 0)	1826 (a_g, 0)	
		1853 (b_u, 1189)	**1793 (b_u, 930)**	**1792 (8400)**
	IIb (C_{2h})	2042 (a_g, 0)	1951 (a_g, 0)	
		2025 (b_u, 2582)	**1939 (b_u, 1965)**	
$Cp_2Co_2(CO)$	**IIIa** (C_{2v})	**1971 (a_1, 786)**	**1870 (a_1, 581)**	
	IIIb (C_s)	**2031 (a', 1212)**	**1941 (a', 923)**	

[a] Experimental data taken from Anderson, F. R.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 112.

Table 7. Comparison of the Analogous Dicyclopentadienyldicobalt Carbonyls $Cp_2Co_2(CO)_n$ (n = 3, 2, 1) with the Diiron Carbonyls $Fe_2(CO)_{6+n}$ (BP86 functional: ΔE in kcal/mol, M−M in Å)

diiron carbonyl[a]	ΔE	Fe–Fe	Cp_2Co_2 carbonyl	ΔE	Co–Co
$Fe_2(CO)_6(\mu\text{-}CO)_3$	0.0	2.519	$Cp_2Co_2(\mu\text{-}CO)_3$	0.0	2.352
$Fe_2(CO)_8(\mu\text{-}CO)$	5.5	2.726	$Cp_2Co_2(CO)_2(\mu\text{-}CO)$	1.8	2.506
$Fe_2(CO)_6(\mu\text{-}CO)_2$	0.0	2.447	$Cp_2Co_2(\mu\text{-}CO)_2$	0.0	2.346
$Fe_2(CO)_6(\mu\text{-}CO)$	0.0[b]	2.137	$Cp_2Co_2(\mu\text{-}CO)$	0.0	2.050

[a] Structures for the $Fe_2(CO)_8$ and $Fe_2(CO)_7$ isomers are taken from Xie, Y.; Schaefer, H. F.; King, R. B. *J. Am. Chem. Soc.*, **2000**, *122*, 8746. [b] This structure is not a genuine minimum, as indicated by a large imaginary frequency at 487*i*.

Å (BP86) in **IVa**, which is only very slightly longer than that in **IVb** by 0.004 (B3LYP) or 0.009 Å (BP86).

3.6. Vibrational Frequencies. The harmonic vibrational frequencies and their infrared intensities for all of the structures have been evaluated by the B3LYP and BP86 methods. Complete reports of the vibrational frequencies and infrared intensities are given in the Supporting Information. These results have been used to determine if a structure is a genuine minimum.

The predicted ν(CO) frequencies for the $Cp_2Co_2(CO)_n$ (n = 1, 2, 3) isomers are of particular interest since any future experimental work to detect such species is likely to rely on the relatively strong ν(CO) frequencies for initial product characterization. The ν(CO) stretching frequencies are listed in Table 6 for all $Cp_2Co_2(CO)_n$ (n = 1, 2, 3). In general, the ν(CO) frequencies predicted by the BP86 method are 60−100 cm^{-1} lower than those computed by the B3LYP method. The ν(CO) infrared frequencies computed by the BP86 functional are in very close agreement with the experimental[37] ν(CO) infrared frequencies in methylcyclohexane for $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2(\mu\text{-}CO)$ and $(\eta^5\text{-}C_5H_5)_2Co_2(\mu\text{-}CO)_2$ (Table 6).

In transition-metal carbonyl chemistry, the ν(CO) frequencies of typical symmetrical two-electron donor bridging CO groups are well-known to occur 150−200 cm^{-1} below the ν(CO) frequencies of terminal CO groups in a given type of metal carbonyl derivative. In this connection, the two bridging CO groups in $Cp_2Co_2(\mu\text{-}CO)_2$ (**IIa**) are seen to exhibit a low infrared-active ν(CO) frequency of 1853 (B3LYP) or 1793 cm^{-1} (BP86). For $Cp_2Co_2(\mu\text{-}CO)_3$ (**Ib**), the infrared-active ν(CO) frequency for the bridging CO groups is higher, namely, 1893 (B3LYP) or 1821 cm^{-1} (BP86).

3.7. Comparison of Analogous $Fe(CO)_3$ and CpCo Derivatives. The isolobal/isoelectronic analogy between $Fe(CO)_3$ and CpCo units suggests a comparison of the structures and energies of $Cp_2Co_2(CO)_n$ and $Fe_2(CO)_{6+n}$ derivatives with the same number of bridging CO groups. In all cases, the metal−metal bonds were found to be shorter by 0.09−0.22 Å for the Cp_2Co_2 derivatives relative to those of the corresponding $Fe_2(CO)_6$ derivatives (Table 7), with the shortening increasing as the number of carbonyl groups increases. This can be rationalized by the fact that replacing three CO ligands with a more weakly back-bonding $\eta^5\text{-}C_5H_5$ ring in going from an $Fe_2(CO)_6$ derivative to the corresponding Cp_2Co_2 derivative increases the electron density on the metal atoms (and thus the number of electrons available for metal−metal bonding).

The lowest-energy isomer computed for $Fe_2(CO)_7$ in our previous work[12] does not have a structure analogous to $Cp_2Co_2(\mu\text{-}CO)$ (**IIIa**), with a single symmetrical bridging CO group, but instead has a structure with two semibridging CO groups similar to the structure for $Cp_2V_2(CO)_5$ determined by X-ray diffraction.[3,4] In this earlier study,[12] the $Fe_2(CO)_6(\mu\text{-}CO)$ analogue to $Cp_2Co_2(\mu\text{-}CO)$ (**IIIa**) was computed not to be a genuine minimum but instead a saddle point with a large imaginary vibrational frequency (487*i* cm^{-1}). This latter structure was used for comparison in Table 7 with our currently computed structure **IIIa** for $Cp_2Co_2(\mu\text{-}CO)$.

4. Summary

For $Cp_2Co_2(CO)_3$ and $Fe_2(CO)_9$, the monobridged isomers $Cp_2Co_2(CO)_2(\mu\text{-}CO)$ and $Fe_2(CO)_8(\mu\text{-}CO)$, respectively, are predicted by DFT methods to have energies (within 6 kcal/mol) very similar to those of the corresponding tribridged isomers $Cp_2Co_2(\mu\text{-}CO)_3$ and $Fe_2(CO)_6(\mu\text{-}CO)_3$, consistent with the fact that the monobridged isomer $Cp_2Co_2(CO)_2(\mu\text{-}CO)$ and the tribridged isomer $Fe_2(CO)_6(\mu\text{-}CO)_3$ are the species found experimentally. For the unsaturated species $Cp_2Co_2(CO)_2$ and $Cp_2Co_2(CO)$, with formal Co═Co double and Co≡Co triple bonds, respectively, the coaxial isomers are more stable than the perpendicular isomers. The BP86 computations give ν(CO) frequencies for $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2(\mu\text{-}CO)$ and $(\eta^5\text{-}C_5H_5)_2Co_2(\mu\text{-}CO)_2$ within 15 cm^{-1} of the experimental fundamentals. The monocarbonyl $(\eta^5\text{-}C_5H_5)_2Co_2(\mu\text{-}CO)$ predicted in this work is not yet known. However, the formation of $(\eta^5\text{-}C_5H_5)_4Co_4(\mu_3\text{-}CO)_2$ from the pyrolysis of $Cp_3Co_3(CO)_3$ observed experimentally may involve dimerization of a $(\eta^5\text{-}C_5H_5)_2Co_2(\mu\text{-}CO)$ intermediate.

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Supporting Information Available: Complete tables of harmonic vibrational frequencies for $Cp_2Co_2(CO)_n$ (n = 3, 2, 1) (Tables S1−S6) and three $Fe_2(CO)_9$ isomers (Tables S8−S10); Co−Co bond distances (in Å), total energies (E, in hartree), relative energies (ΔE, in kcal/mol), and number of imaginary vibrational frequencies (Nimg) for $Cp_2Co_2(CO)_n$ (n = 3, 2, 1) (Table S7).

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