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Unsaturation in Binuclear (Cyclobutadiene)cobalt Carbonyls with Axial and Perpendicular Structures: Comparison with Isoelectronic Binuclear Cyclopentadienyliron Carbonyls

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The binuclear (cyclobutadiene)cobalt carbonyls $(\eta^4\text{-}C_4H_4)_2Co_2(CO)_n$ ($n = 1-4$) have been studied by density functional theory (DFT) using the B3LYP and BP86 methods. The singlet doubly bridged and unbridged isomers of $(\eta^4\text{-}C_4H_4)_2Co_2(CO)_4$ are nearly degenerate, suggesting a highly fluxional system similar to the experimentally known and closely related $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^4\text{-diene})_2Co_2(CO)_4$ systems. The global minimum of $(C_4H_4)_2Co_2(CO)_3$ is the doubly bridged singlet isomer $(\eta^4\text{-}C_4H_4)_2Co_2(CO)(\mu\text{-}CO)_2$, in contrast to the isoelectronic $(C_5H_5)_2Fe_2(CO)_3$, where the global minimum is the triply bridged triplet isomer $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3$, analogous to dioxygen. A related triply bridged triplet isomer of $(C_4H_4)_2Co_2(CO)_3$ is also found, but at 9.6 kcal/mol (B3LYP) or 5.1 kcal/mol (BP86) above the global minimum. The $(C_4H_4)_2Co_2(CO)_2$ system behaves analogously to the corresponding $(C_5H_5)_2Fe_2(CO)_2$ system in that its lowest energy structure is the doubly bridged isomer $(\eta^4\text{-}C_4H_4)_2Co_2(\mu\text{-}CO)_2$ with a short cobalt−cobalt distance suggestive of the Co≡Co triple bond required to give both cobalt atoms the favored 18-electron configuration. Both axial and perpendicular metallocene structures are found for $(C_4H_4)_2Co_2(CO)$, including a low-energy $(\eta^4\text{-}C_4H_4)_2Co_2(\eta^2\text{-}\mu\text{-}CO)$ structure with a four-electron-donor bridging CO group and a cobalt−cobalt distance suggestive of a Co≡Co triple bond.

1. Introduction

No binuclear (cyclobutadiene)metal carbonyls of the type $(\eta^4\text{-}C_4H_4)_2M_2(CO)_n$ with unsubstituted cyclobutadiene rings on both metal atoms have been synthesized. However, the binuclear (tetramethylcyclobutadiene)cobalt carbonyl derivative $(\eta^4\text{-}Me_4C_4)_2Co_2(CO)_4$ has been synthesized in relatively low yield and characterized by elemental analysis, mass spectrometry, and infrared ν(CO) frequencies.[1] It is presumed to have a trans doubly bridged structure (Figure 1), but this has not been confirmed by X-ray crystallography. Related $(\eta^4\text{-diene})_2Co_2(CO)_4$ complexes are known[2] with other dienes such as butadiene, 1,3-cyclohexadiene (Figure 1), and norbornadiene. In addition, the binuclear cyclobutadiene complex $(\eta^4\text{-}C_4H_4)Co_2(CO)_6$ (Figure 1), i.e. $(\eta^4\text{-}C_4H_4)Co(CO)_2Co(CO)_4$, is known,[3,4] in which only one of the two cobalt atoms bears a cyclobutadiene ring. In $(\eta^4\text{-}C_4H_4)Co_2(CO)_6$ the Co−Co bond distance is 2.673(1) Å, consistent with the metal−metal single bond required for the favored 18-electron configuration for both cobalt atoms. This compound is thus best considered as a close relative of $(\eta^4\text{-}C_4H_4)Co(CO)_2I$ in which the iodine is replaced by a $Co(CO)_4$ group functioning as a pseudohalogen.

This paper reports our density functional theory (DFT) studies on the binuclear (cyclobutadiene)cobalt carbonyls $(\eta^4\text{-}C_4H_4)_2Co_2(CO)_n$ ($n = 1-4$) using methods similar to our recent DFT studies on binuclear cyclopentadienylmetal carbonyl derivatives.[5−7] In addition to the possibility of comparing the resulting structures with the isoelectronic $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_n$ ($n = 1-4$)[5] and confirming the structure proposed[1] for $(\eta^4\text{-}Me_4C_4)_2Co_2(CO)_4$, there is a reasonable chance of synthesizing unsaturated permethyl derivatives predicted by our study from $(\eta^4\text{-}Me_4C_4)Co(CO)_2I$. The latter compound has been shown to be a useful and readily available synthon for the preparation of numerous (tetramethylcyclobutadiene)cobalt derivatives.[8]

2. Theoretical Methods

For carbon and oxygen the double-ς plus polarization (DZP) basis set used here adds 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 is designated (9s5p1d/4s2p1d).[9,10] For H, a set of p polarization functions $\alpha_p(H) = 0.75$ is added to the Huzinaga−Dunning DZ sets. 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 by following the method of Hood et al., and designated (14s11p6d/10s8p3d).[11,12] Thus, for $(C_4H_4)_2Co_2(CO)$,

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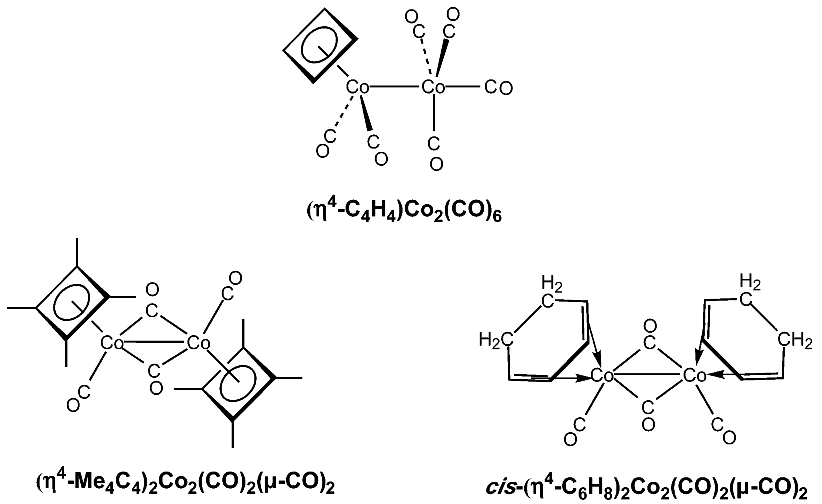
$(\eta^4\text{-}C_4H_4)Co_2(CO)_6$

$(\eta^4\text{-}Me_4C_4)_2Co_2(CO)_2(\mu\text{-}CO)_2$

$cis\text{-}(\eta^4\text{-}C_6H_8)_2Co_2(CO)_2(\mu\text{-}CO)_2$

Figure 1. Some known binuclear (diene)cobalt carbonyl derivatives.

$(C_4H_4)_2Co_2(CO)_2$, $(C_4H_4)_2Co_2(CO)_3$, and $(C_4H_4)_2Co_2(CO)_4$, there are 288, 318, 348, and 378 contracted Gaussian functions, respectively.

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.[13−20] Two DFT methods were used in this study. The first method is the hybrid B3LYP method, which incorporates Becke's three-parameter exchange functional (B3) with the Lee, Yang, and Parr (LYP) correlation functional.[21,22] The second approach is the BP86 method, which marries Becke's 1988 exchange functional (B) with Perdew's 1986 correlation functional.[23,24] It has been noted that the BP86 method may be somewhat more reliable than the B3LYP method for the type of organometallic systems considered in this paper.[25,26]

The geometries of all of the structures were fully optimized using both the DZP B3LYP and DZP BP86 methods. The harmonic vibrational frequencies were determined at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were 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.[27]

In the search for minima using all currently implemented DFT methods, low-magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in the DFT computations. Thus, all imaginary vibrational frequencies with a magnitude of less than $100i$ cm^{-1} are considered insignificant and are neglected in the analysis.[28,29] Therefore, we do not always follow such low imaginary vibrational frequencies.

3. Results and Discussion

3.1. Molecular Structures. 3.1.1. $(C_4H_4)_2Co_2(CO)_4$. Four possible isomers of $(C_4H_4)_2Co_2(CO)_4$, namely doubly CO bridged cis and trans isomers as well as unbridged cis and trans isomers, were used as starting points for optimization with the B3LYP and BP86 methods. The optimized structures are shown in Figure 2, and the optimized structural parameters are presented in Tables 1 and 2 for the singlet and triplet isomers, respectively. For singlet $(C_4H_4)_2Co_2(CO)_4$, four stable isomers were obtained, namely the C_{2h} trans-unbridged isomer **Ia-s**, the C_{2h} trans doubly bridged isomer **Ib-s,** the C_{2v} cis doubly bridged isomer **Ic-s**, and the C_2 cis-unbridged isomer **Id-s**. For the triplet, the cis and trans unbridged isomers of $(C_4H_4)_2Co_2(CO)_4$ are not stationary points but dissociate to $(C_4H_4)Co(CO)_2$ units upon optimization.

In the B3LYP method, the four singlet structures have very similar energies (within 1.6 kcal/mol), thereby predicting a highly fluxional system. This is in accord with experimental results[30] on related $(\eta^4\text{-diene})_2Co_2(CO)_2(\mu\text{-}CO)_2$ derivatives in solution. In the BP86 method, the trans and cis doubly bridged isomers (**Ib-s** and **Ic-s**, respectively) have energies within 0.4 kcal/mol. The corresponding unbridged isomers **Ia-s** and **Id-s** are significantly higher in energy at 7.7 and 9.1 kcal/mol, respectively, above the global minimum **Ib-s**. The triplet doubly bridged structures **Ie-t** and **If-t** are higher in energy than the corresponding singlet structures by more than 30 kcal/mol in each case (Table 2).

The Co−Co distances predicted for the singlet dibridged isomers $(\eta^4\text{-}C_4H_4)_2Co_2(CO)_2(\mu\text{-}CO)_2$, namely **Ib-s** and **Ic-s**, fall in the range 2.50−2.53 Å, similar to the 2.56 Å Co−Co distance

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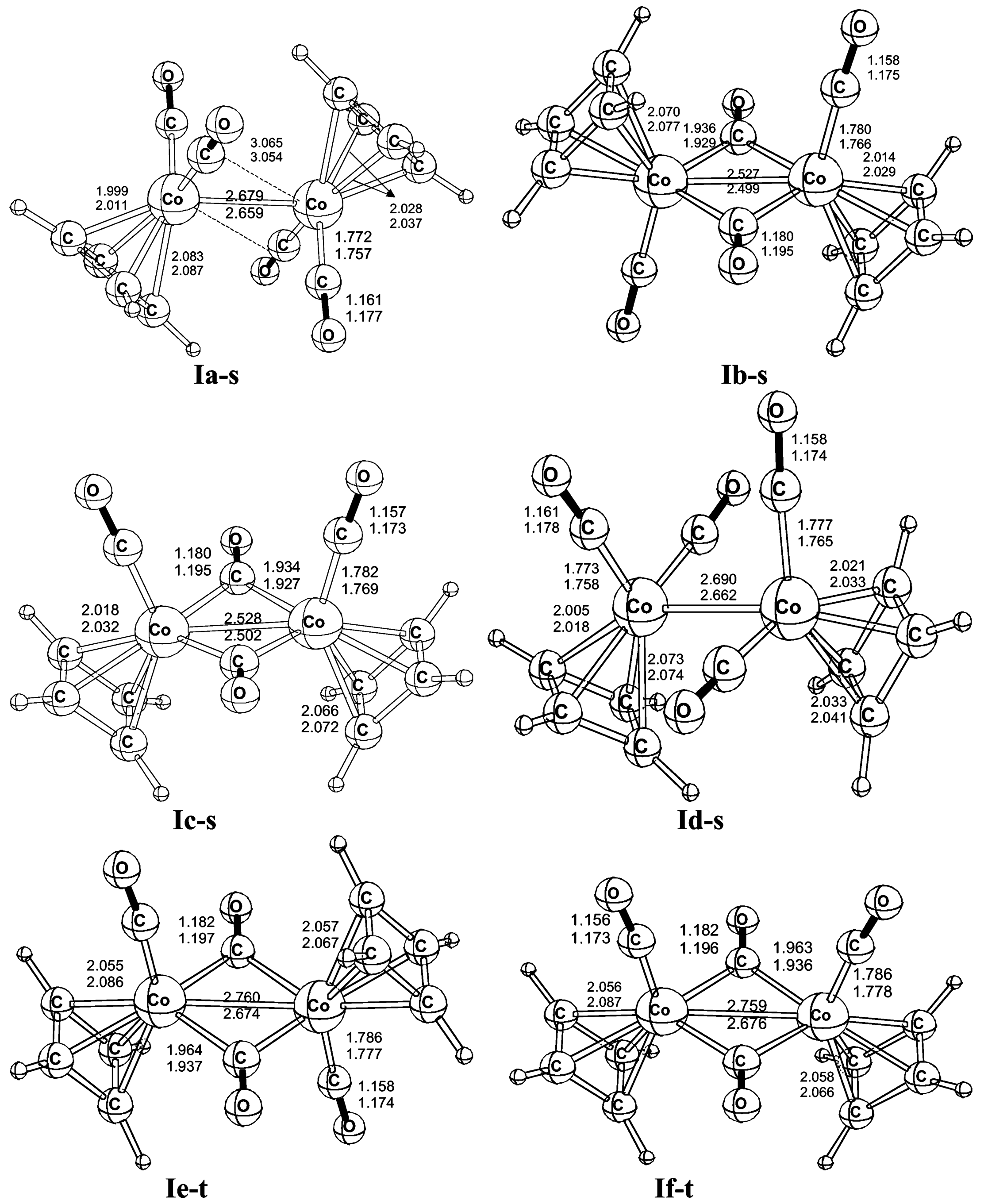

Ia-s **Ib-s**

Ic-s **Id-s**

Ie-t **If-t**

Figure 2. Optimized geometries for the $(C_4H_4)_2Co_2(CO)_4$ isomers (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 Singlet State $(C_4H_4)_2Co_2(CO)_4$ Isomers

	trans-$(C_4H_4)_2Co_2(CO)_4$ **Ia-s** (C_{2h})		*trans*-$(C_4H_4)_2Co_2(CO)_2(\mu\text{-}CO)_2$ **Ib-s** (C_{2h})		*cis*-$(C_4H_4)_2Co_2(CO)_2(\mu\text{-}CO)_2$ **Ic-s** (C_{2v})		*cis*-$(C_4H_4)_2Co_2(CO)_4$ **Id-s** (C_2)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Co−Co	2.679	2.659	2.527	2.499	2.528	2.502	2.690	2.662
Co−C	1.772	1.757	1.936	1.929	1.934	1.927	1.777	1.765
			1.780	1.766	1.782	1.769	1.773	1.758
C−O	1.161	1.177	1.180	1.195	1.180	1.195	1.158	1.174
			1.158	1.175	1.157	1.173	1.161	1.178
−*E*	3 528.666 89	3 529.187 27	3 528.666 29	3 529.199 61	3 528.666 23	3 529.198 96	3 528.664 43	3 529.185 11
Δ*E*	0.0	7.7	0.4	0.0	0.4	0.4	1.5	9.1
imaginary frequency	none	18*i*	none	none	none	18*i*	none	none

found by X-ray crystallography[31] for the 1,3-cyclohexadiene complex $(\eta^4\text{-}C_6H_8)_2Co_2(CO)_2(\mu\text{-}CO)_2$ (Figure 1). The Co−Co distances in the unbridged singlet isomers $(\eta^4\text{-}C_4H_4)_2Co_2(CO)_4$, namely **Ia-s** and **Id-s**, fall in the range 2.66−2.69 Å. similar to the experimentally observed 2.67 Å distance[4] for the unbridged Co−Co single bond in $(\eta^4\text{-}C_4H_4)Co(CO)_2Co(CO)_4$ (Figure 1).

Table 2. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for the Triplet State $(C_4H_4)_2Co_2(CO)_4$ Isomers

	trans-$(C_4H_4)_2Co_2(CO)_2$-(μ-CO)$_2$ (**Ie-t** (C_{2h}))		*cis*-$(C_4H_4)_2CO_2(CO)_2$-(μ-CO)$_2$ (**If-t** (C_{2v}))	
	B3LYP	BP86	B3LYP	BP86
Co−Co	2.760	2.674	2.759	2.676
Co−C	1.964	1.937	1.963	1.936
	1.786	1.777	1.786	1.778
C−O	1.182	1.197	1.182	1.196
	1.158	1.174	1.156	1.173
−*E*	3 528.616 38	3 529.146 74	3 528.615 75	3 529.145 60
Δ*E*[a]	31.7	33.2	32.1	33.9
imaginary frequency	none	none	15*i*	21*i*, 15*i*

[a] Relative to the lowest energy singlet isomer.

This lengthening of a metal−metal bond by about 0.15 Å upon repositioning two bridging CO groups is typically observed in systems of this type.[5] Furthermore, the Co−Co distances in the dibridged triplet isomers **Ie-t** and **If-t** fall in the range 2.67−2.76 Å, which is about 0.2 Å longer than the Co−Co distances in the corresponding dibridged singlet isomers **Ib-s** and **Ic-s**, respectively.

3.1.2. $(C_4H_4)_2Co_2(CO)_3$. Isomers of $(C_4H_4)_2Co_2(CO)_3$ having three, two, or one bridging CO groups have been studied (Figure 3 and Table 3). The singly bridged singlet isomer $(C_4H_4)_2Co_2(CO)_2(\mu\text{-CO})$ collapses to the triply bridged isomer $(C_4H_4)_2Co_2(\mu\text{-CO})_3$ (**IIb-s** in Figure 3), which is a transition state with the large imaginary vibrational frequencies 213*i* and 97*i* cm^{-1} (B3LYP) or 42*i* cm^{-1} (BP86). Following the 213*i* cm^{-1} (B3LYP) or 42*i* cm^{-1} (BP86) imaginary frequency leads to the doubly bridged isomer $(C_4H_4)_2Co_2(CO)(\mu\text{-CO})_2$ (**IIa-s**), which is found to be a genuine minimum without imaginary frequencies. The singly and doubly bridged triplet isomers of $(C_4H_4)_2Co_2(CO)_3$ collapse to the triply bridged isomer (**IIc-t**), which is 9.6 kcal/mol (B3LYP) or 5.1 kcal/mol (BP86) above the doubly bridged singlet global minimum **IIa-s**. The **IIc-t** structure is found to be a genuine minimum with only very small imaginary frequencies at 24*i* and 20*i* cm^{-1} (B3LYP) or 20*i* and 17*i* cm^{-1} (BP86). This structure is analogous to the experimentally known triplet $(\eta^5\text{-}Me_5C_5)_2Fe_2(\mu\text{-CO})_3$ structure with an Fe═Fe double bond similar to the double bond in dioxygen.[32] However, unlike $(C_5H_5)_2Fe_2(\mu\text{-CO})_3$, the triplet triply bridged structure **IIc-t** for $(C_4H_4)_2Co_2(\mu\text{-CO})_3$ is not the global minimum but lies 9.6 kcal/mol (B3LYP) or 5.1 kcal/mol (BP86) above the global minimum $(\eta^4\text{-}C_4H_4)_2Co_2(CO)(\mu\text{-CO})_2$ (**IIa-s**).

The cobalt−cobalt bond distance for the doubly bridged structure **IIa-s** is 2.429 Å (B3LYP) or 2.387 Å (BP86), which is longer than that in the triply bridged structure **IIc-t** (2.252 Å by B3LYP or 2.245 Å by BP86) but consistent with the Co═Co double bond required to give both metal atoms the favored 18-electron configuration.

3.1.3. $(C_4H_4)_2Co_2(CO)_2$. Four structures were optimized for $(C_4H_4)_2Co_2(CO)_2$ (Figure 4 and Table 4), namely singlet and triplet doubly CO bridged structures as well as structures without bridging CO groups. The lowest energy singlet and triplet isomers of $(C_4H_4)_2Co_2(CO)_2$, namely **IIIa-s** and **IIIb-t**, respectively, have coaxial structures, $(C_4H_4)_2Co_2(\mu\text{-CO})_2$, with two bridging CO ligands. The other two isomers for $(C_4H_4)_2Co_2(CO)_2$ found in this work, namely singlet **IIIc-s** and triplet **IIId-t**, have perpendicular metallocene-like structures with two terminal CO ligands similar to that computed for the carbonyl-free dimetallocenes Cp_2M_2 (M = Cu, Ni)[33] and perpendicular ⊥−$Cp_2Co_2(CO)_2$.[6] In both **IIIc-s** and **IIId-t** two carbon atoms of each cyclobutadiene ring bridge the cobalt−cobalt bond. The doubly CO bridged coaxial structures **IIIa-s** and **IIIb-t** lie lower in energy than the perpendicular structures of corresponding multiplicities **IIIc-s** and **IIId-t**, respectively, by 16.0 and 3.6 kcal/mol (B3LYP) or 21.6 and 24.0 kcal/mol (BP86), respectively. Furthermore, the energies of the singlet structures are lower than those of the triplet structures (Table 4). Thus, the predicted global minimum for $(C_4H_4)_2Co_2(CO)_2$ is the singlet C_{2v} structure **IIIa-s** with two symmetric bridging CO ligands.

The theoretical cobalt−cobalt distance in the singlet structure **IIIa-s** is only 2.216 Å (B3LYP) or 2.188 Å (BP86). The cobalt−cobalt distance is 0.098 Å (B3LYP) or 0.106 Å (BP86) longer for the corresponding triplet structure **IIIb-t** than that in structure **IIIa-s**. This is consistent with a Co═Co double bond in the triplet structure as compared with a Co≡Co triple bond in the singlet structure. The cobalt−cobalt distance in the triplet unbridged structure **IIId-t** at 2.458 Å (B3LYP) or 2.437 Å (BP86) is ∼0.155 Å (B3LYP) or 0.115 Å (BP86) longer than the cobalt−cobalt distance in the singlet unbridged structure **IIIc-s** at 2.303 Å (B3LYP) or 2.322 Å (BP86).

3.1.4. $(C_4H_4)_2Co_2(CO)$. Optimizations have been carried out on triplet and singlet $(C_4H_4)_2Co_2(CO)$ structures in which the single CO group is either bridging or terminal. Two types of stationary points are obtained (Table 5 and Figure 5). One type is the cisoid dimetallocene structure with a bridging CO ligand, exemplified by **IVa-s** and **IVb-t**. This dimetallocene bends because of its single CO bridge. The unusual bridging η^2-μ-CO group in the $(C_4H_4)_2Co_2(CO)$ isomers **IVa-s** and **IVb-t** can be considered to be a formal 4-electron donor to the pair of metal atoms, since it bonds to one of the metal atoms as a normal 2-electron-donor linear CO ligand and to the other metal atom through an electron pair from an C−O π bond. Such 4-electron-donor CO groups are characterized by unusually short Co−O distances, namely 2.000 Å (B3LYP) or 2.001 Å (BP86) in **IVa-s** and 2.032 Å (B3LYP) in **IVb-t.** Note that since the bridging CO groups in **IVa-s** and **IVb-t** are 4-electron donors, the Co≡Co bond order needs to be only 3 rather than 4 for both cobalt atoms to have the favored 18-electron configuration.

The other structures for $(\mu\text{-}C_4H_4)_2Co_2(CO)$, namely **IVc-s** and **IVd-t**, are perpendicular metallocene structures[33] with the metal−metal bond axis parallel or nearly parallel to the cyclobutadiene rings and a terminal CO ligand bonded to one of the metal atoms. In structures **IVc-s** and **IVd-t**, each cobalt atom is bonded to a portion of each cyclobutadiene ring, in contrast to structures **IVa-s** and **IVb-t**, in which each metal atom is bound to only one of the cyclobutadiene rings.

The results for $(C_4H_4)_2Co_2(CO)$ are strongly dependent on the method used (B3LYP or BP86). Thus, the structure of the triplet $(C_4H_4)_2Co_2(\mu\text{-CO})$ with one CO bridge is different in the B3LYP and BP86 methods (**IVb-t**). For the singlet, the energy of the optimized coaxial structure **IVa-s** is slightly higher than that of the perpendicular structure **IVc-s** by 0.6 kcal/mol (BP86). For the triplet, the energy of the optimized coaxial structure **IVb-t** is higher than that of the perpendicular structure **IVd-t** by 6.3 kcal/mol by BP86, whereas the relative energies are inverted in the B3LYP method. Thus, according to the BP86 optimization results, the triplet bridged structure **IVb-t** has the lowest energy among the four optimized structures and is the

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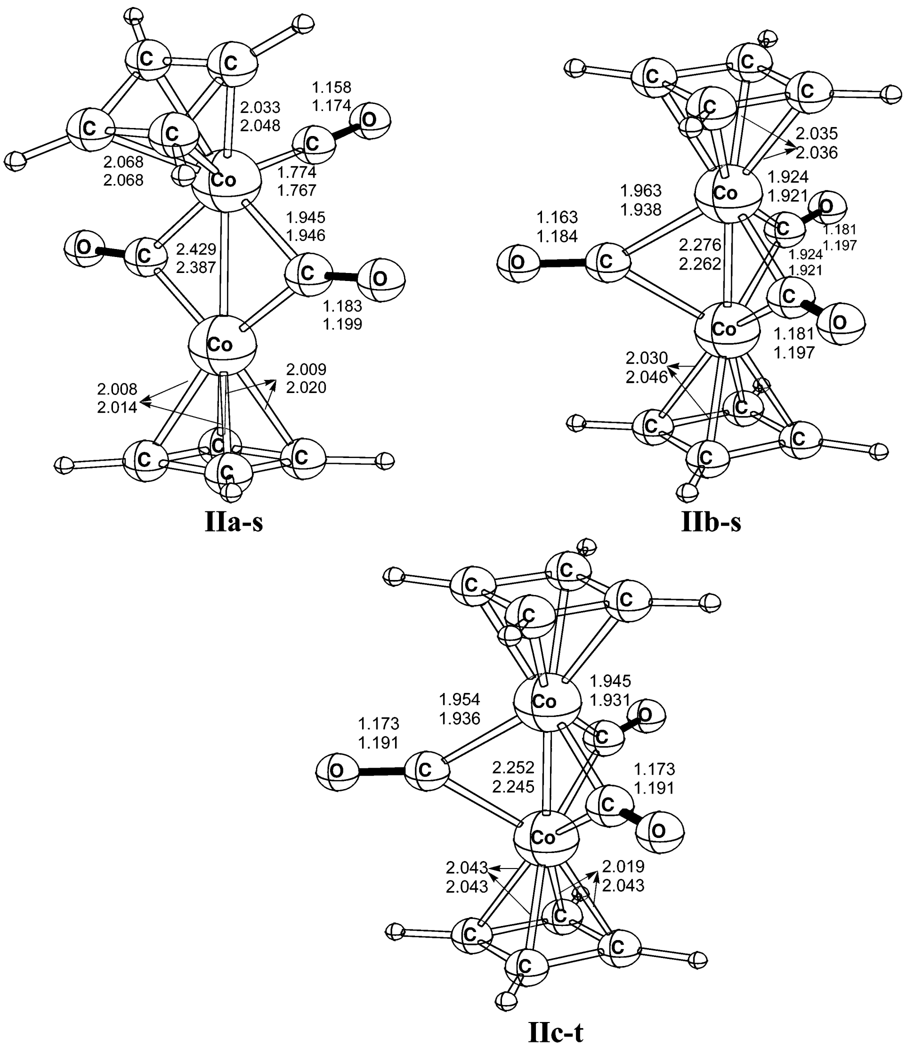


Figure 3. Optimized geometries for $(C_4H_4)_2Co_2(CO)_3$ (bond distances are in Å).

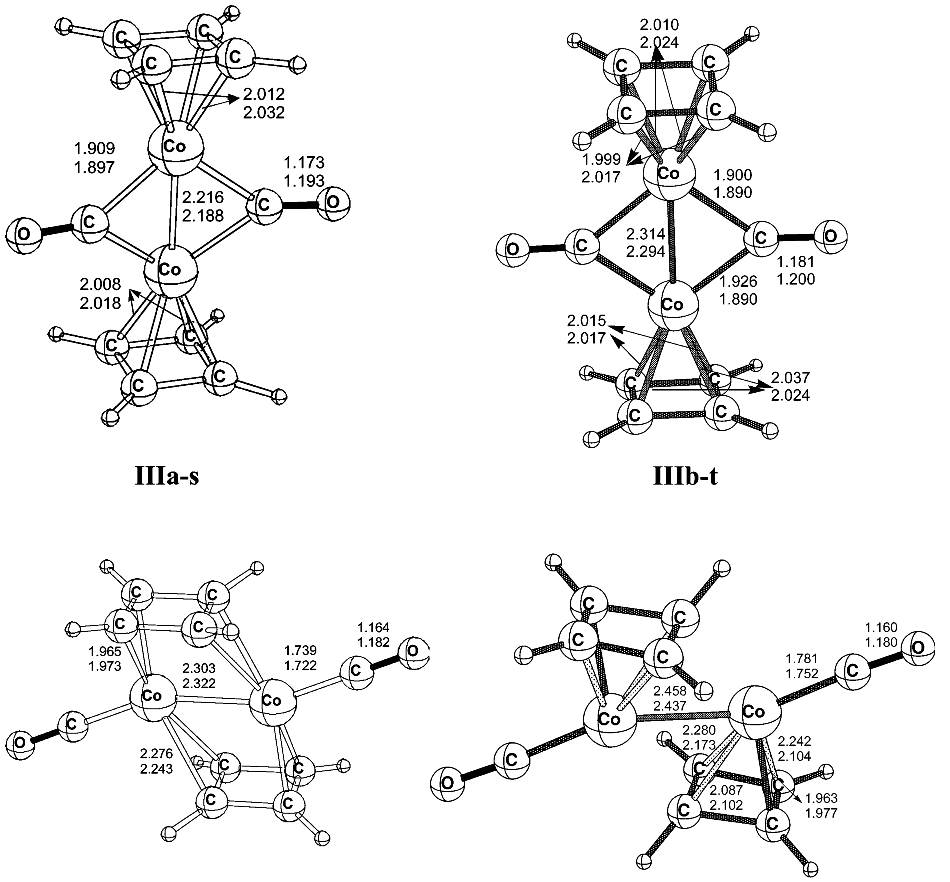
Table 3. Bond Distances (in Å), Total Energies (*E* in Hartree) and Relative Energies (Δ*E* in kcal/mol) for the Singlet and Triplet State $(C_4H_4)_2Co_2(CO)_3$ Isomers

	$(C_4H_4)_2Co_2(CO)(\mu\text{-}CO)_2$ (**IIa-s** (C_s))		$(C_4H_4)_2Co_2(\mu\text{-}CO)_3$ (**IIb-s** (C_{2v}))		$(C_4H_4)_2Co_2(\mu\text{-}CO)_3$ (**IIc-t** (C_{2v}))	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Co−Co	2.429	2.387	2.276	2.262	2.252	2.245
Co−C	1.945	1.946	1.924	1.921	1.954	1.936
	1.774	1.767	1.963	1.938	1.945	1.931
C−O	1.183	1.199	1.181	1.197	1.173	1.191
	1.158	1.174	1.163	1.184	1.173	1.191
−*E*	3 415.277 50	3 415.802 08	3 415.255 54	3 415.793 68	3 415.262 18	3 415.793 98
Δ*E*	0.0	0.0	13.8	5.3	9.6	5.1
imaginary frequency	none	none	213*i*, 97*i*	42*i*	24*i*, 20*i*	20*i*, 17*i*

global minimum or close to the minimum with only a small imaginary vibrational frequency (49*i* cm^{-1} in BP86). The next lowest lying structure for $(C_4H_4)_2Co_2(CO)$ at 6.3 kcal/mol above the global minimum **IVb-t** is the triplet structure **IVd-t** with a terminal CO group, which is a genuine minimum without any imaginary vibrational frequencies. The cobalt−cobalt distance in the triplet bridged structure **IVb-t** is 2.220 Å, which is shorter than the cobalt−cobalt distance in the triplet unbridged structure **IVd-t** at 2.328 Å. The other two minima are the singlet structures **IVa-s** and **IVc-s** with cobalt−cobalt distances of 2.461 and 2.323 Å, respectively.

3.2. Comparison of the Structures of $(C_4H_4)_2Co_2(CO)_n$ and $Cp_2Fe_2(CO)_n$ ($n = 1-4$). Table 6 compares the global minimum structures for $(C_4H_4)_2Co_2(CO)_n$ and $Cp_2Fe_2(CO)_n$ ($n = 1-4$) using the BP86 method. Table 6 also includes the formal metal−metal bond orders, assuming that the favored 18-electron metal configurations are approached as closely as possible.

The cobalt−cobalt distances in the $(C_4H_4)_2Co_2(CO)_n$ ($n = 2-4$) derivatives are seen to correlate with the number of bridging CO groups and the formal cobalt−cobalt bond order required to give both cobalt atoms the favored 18-electron configuration, similar to the iron−iron distances in the corresponding structures of $Cp_2Fe_2(CO)_n$ ($n = 1-4$).[5] Thus, each unit increase in the formal cobalt−cobalt bond order is predicted to shorten the cobalt−cobalt bond distances by roughly 0.1 Å, in accord with the known crystal structures of $Cp_2Fe_2(CO)_n$ ($n = 3, 4$). Similarly, each additional bridging CO group for a $(C_4H_4)_2Co_2(CO)_n$ ($n = 2-4$) derivative shortens the cobalt−cobalt bond distances by roughly 0.1 Å. In the $(C_4H_4)_2Co_2(CO)$ global minimum isomer **IVb-t** the carbonyl group is a four-



IIIa-s **IIIb-t**

IIIc-s **IIId-t**

Figure 4. Optimized geometries for $(C_4H_4)_2Co_2(CO)_2$ (bond distances are in Å).

Table 4. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for the Singlet and Triplet Electronic States of $(C_4H_4)_2Co_2(CO)_2$

	$(C_4H_4)_2Co_2(\mu\text{-}CO)_2$ (**IIIa-s** (C_{2v}))		$(C_4H_4)_2Co_2(\mu\text{-}CO)_2$ (**IIIb-t** (C_s))		$(\mu\text{-}C_4H_4)_2Co_2(CO)_2$ (**IIIc-s**(C_{2h}))		$(\mu\text{-}C_4H_4)_2Co_2(CO)_2$ (**IIId-t** (C_i))	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Co−Co	2.216	2.188	2.314	2.294	2.303	2.322	2.458	2.437
Co−C	1.909	1.897	1.900	1.890	1.739	1.722	1.781	1.752
C−O	1.173	1.193	1.181	1.200	1.164	1.182	1.160	1.180
−*E*	3 301.902 21	3 302.414 66	3 301.891 67	3 302.405 21	3 301.876 67	3 302.380 21	3 301.885 91	3 302.367 02
Δ*E*	0.0	0.0	6.6	5.9	16.0	21.6	10.2	29.9
imaginary frequency	none	40*i*, 37*i*	none	none	24*i*	46*i*, 42*i*	none	73*i*

Table 5. Bond Distances (in Å), Total Energies (*E* in Hartree) and Relative Energies (Δ*E* in kcal/mol) for the Singlet and Triplet Electronic States of $(C_4H_4)_2Co_2(CO)$

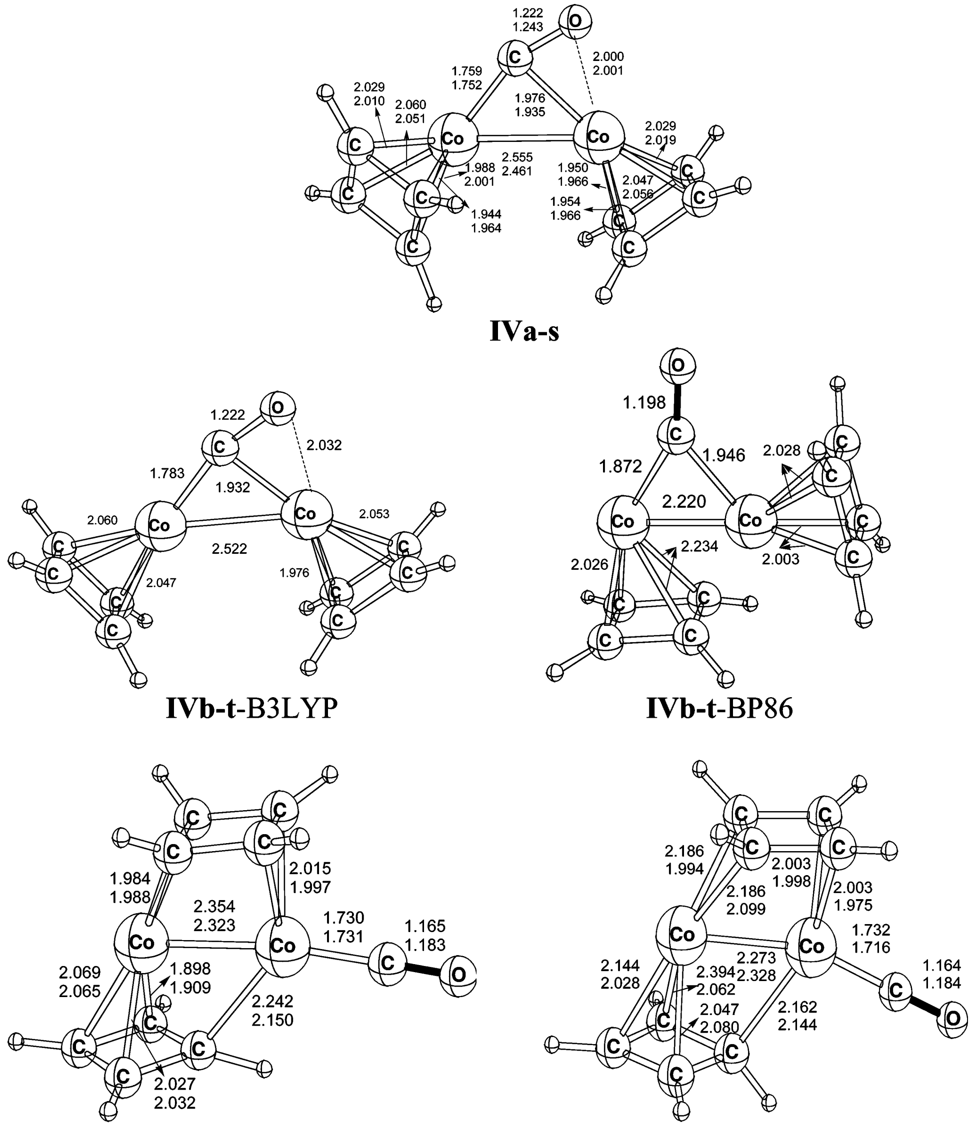
	$(C_4H_4)_2Co_2(\mu\text{-}CO)$ (**IVa-s** (C_1))		$(C_4H_4)(\mu\text{-}C_4H_4)Co_2(\mu\text{-}CO)$ (**IVb-t** (C_s))		$(\mu\text{-}C_4H_4)_2Co_2(CO)$ (**IVc-s** (C_1))		$(\mu\text{-}C_4H_4)_2Co_2(CO)$ (**IVd-t** (C_1))	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Co−Co	2.555	2.461	2.522	2.220	2.354	2.323	2.273	2.328
Co−C	1.759	1.752	1.783	1.872	1.730	1.731	1.732	1.716
	1.976	1.935	1.932	1.946				
C−O	1.222	1.243	1.222	1.198	1.165	1.183	1.164	1.184
−*E*	3 188.481 32	3 188.972 48	3 188.481 60	3 188.983 77	3 188.481 24	3 188.973 51	3 188.502 95	3 188.973 65
Δ*E*	13.6	7.1	13.4	0.0	13.6	6.4	0.0	6.3
imaginary frequency	none	none	63*i*, 28*i*	49*i*	none	43*i*	none	none

electron-donor η^2-μ-CO group so that a Co≡Co triple bond rather than a Co$\overset{4}{—}$Co quadruple bond is required to give both cobalt atoms the favored 18-electron configuration. This is consistent with the cobalt−cobalt distance of 2.220 Å in **IVb-t**, which is ~0.03 Å *longer* than the Co≡Co distance of 2.188 Å in the global minimum **IIIa-s** of $(C_4H_4)_2Co_2(CO)_2$, which clearly requires a formal Co≡Co triple bond for both metal atoms to have the favored 18-electron configuration.

3.3. Dissociation Energies. Table 7 reports the dissociation energies of the single carbonyl dissociation steps

$$(C_4H_4)_2Co_2(CO)_n \rightarrow (C_4H_4)_2Co_2(CO)_{n-1} + CO$$

In determining these dissociation energies, the fragments were allowed to relax.



IVa-s

IVb-t-B3LYP

IVb-t-BP86

IVc-s

IVd-t

Figure 5. Optimized geometries for $(C_4H_4)_2Co_2(CO)$ (bond distances are in Å).

Table 6. Bond Distances (in Å) and Formal Metal−Metal Bond Orders for the Global Minima of $(C_4H_4)_2Co_2(CO)_n$ and $Cp_2Fe_2(CO)_n$ (n = 1−4)

	isomer	state	no. of bridging COs	M−M	M−C	C−O	formal M−M bond order
$(C_4H_4)_2Co_2(CO)_4$	**Ib-s**	^1A_g	2	2.499	1.929/1.766	1.195/1.175	1
$Cp_2Fe_2(CO)_4$	**Ia**	$^1A'$	2	2.540	1.922/1.745	1.201/1.180	1
$(C_4H_4)_2Co_2(CO)_3$	**IIa-s**	$^1A_1$	2	2.387	1.946/1.767	1.199/1.174	2
$Cp_2Fe_2(CO)_3$	**IIa**	$^3B_1$	3	2.264	1.920/1.922	1.198	2
$(C_4H_4)_2Co_2(CO)_2$	**IIIa-s**	$^1A_1$	2	2.188	1.897	1.193	3
$Cp_2Fe_2(CO)_2$	**IIIa**	$^1A_1$	2	2.120	1.906	1.198	3
$(C_4H_4)_2Co_2(CO)$	**IVb-t**	$^3A'$	1	2.220	1.872/1.946	1.198	3[a]
$Cp_2Fe_2(CO)$ (B3LYP)	**IVa**	$^1A_1$	1	2.219	1.899	1.185	4

[a] Since the CO group in this isomer of $(C_4H_4)_2Co_2(CO)$ is a 4-electron donor (see text), only a Co≡Co triple bond is required to give each metal atom the favored 18-electron configuration.

The predicted dissociation energy of one CO group from $(C_4H_4)_2Co_2(CO)_4$ is 37.7 kcal/mol (B3LYP) or 44.1 kcal/mol (BP86). Further dissociation of a CO group from $(C_4H_4)_2Co_2(CO)_3$ to give $(C_4H_4)_2Co_2(CO)_2$ requires a similar energy of 29.3 kcal/mol (B3LYP) or 37.8 kcal/mol (BP86). However, the next CO dissociation process, namely the $(C_4H_4)_2Co_2(CO)_2$ dissociation process to $(C_4H_4)_2Co_2(CO)$ + CO, requires the much higher energy of 57.7 kcal/mol (B3LYP) or 65.1 kcal/mol (BP86). Thus, $(C_4H_4)_2Co_2(CO)_2$ appears to be very stable with respect to extrusion of a carbonyl ligand. This suggests an energy barrier for a pair of cobalt atoms to form a bond of formal order higher than 3. Comparison of the dissociations of $(C_4H_4)_2Co_2(CO)_2$ and $Co_2(CO)_6$, both with formal Co≡Co triple bonds, suggests that the single carbonyl dissociation energy for $Co_2(CO)_6$ to $Co_2(CO)_5$, namely 52.9 kcal/mol (B3LYP) or 53.0 kcal/mol (BP86),[34] is similar to that of $(C_4H_4)_2Co_2(CO)_2$ to $(C_4H_4)_2Co_2(CO)$.

3.4. Vibrational Frequencies. The harmonic vibrational frequencies and their infrared intensities for all of the structures

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[34] Kenny, J. P.; King, R. B.; Schaefer, H. F., III. *Inorg. Chem.* **2001**, *40*, 900.

Table 7. Dissociation Energies (kcal/mol, Zero-Point Energy Corrected Values in Parentheses) for the Successive Removal of Carbonyl Groups from $(C_4H_4)_2Co_2(CO)_4$ and $Co_2(CO)_8$[a,b]

	B3LYP	BP86
$(C_4H_4)_2Co_2(CO)_4$ (**Ib-s**) → $(C_4H_4)_2Co_2(CO)_3$ (**IIa-s**) + CO	37.7 (35.1)	44.1 (41.4)
$(C_4H_4)_2Co_2(CO)_3$ (**IIa-s**) → $(C_4H_4)_2Co_2(CO)_2$ (**IIIa-s**) + CO	29.3 (26.6)	37.8 (35.1)
$(C_4H_4)_2Co_2(CO)_2$ (**IIIa-s**) → $(C_4H_4)_2Co_2(CO)$ (**IVb-t**) + CO	57.7 (54.0)	65.1 (62.0)
$Co_2(CO)_8 \rightarrow Co_2(CO)_7$ + CO	18.2	35.6
$Co_2(CO)_7 \rightarrow Co_2(CO)_6$ + CO	18.8	22.9
$Co_2(CO)_6 \rightarrow Co_2(CO)_5$ + CO	52.9	53.0

[a] All results reported here refer to the lowest energy structures of $(C_4H_4)_2Co_2(CO)_n$ (BP86). [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.

Table 8. Metal Carbonyl ν(CO) Frequencies (in cm^{-1}) Predicted for the $(C_4H_4)_2Co_2(CO)_n$ ($n = 1-4$) Isomers[a]

	B3LYP	BP86
	$(C_4H_4)_2Co_2(CO)_4$	
Ia-s (C_{2h})	**2049 (a, 1604)**^{t}	**1962 (a, 1367)**^{t}
	2082 (a, 0)^{t}	1998 (a, 0)^{t}
	2033 (b, 0)^{t}	1948 (b, 0)^{t}
	2040 (b, 1254)^{t}	**1966 (b, 971)**^{t}
Ib-s (C_{2h})	1936 (a$_g$, 0)	1856 (a$_g$, 0)
	2081 (a$_g$, 0)^{t}	1992 (a$_g$, 0)^{t}
	1896 (a$_u$, 1181)	**1830 (a$_u$, 917)**
	2068 (b$_u$, 1596)^{t}	**1979 (b$_u$, 1377)^{t}**
Ic-s (C_{2v})	1937 (a$_1$, 0)	1858 (a$_1$, 2)
	2099 (a$_1$, 1467)^{t}	**2011 (a$_1$, 1195)^{t}**
	1898 (b$_1$, 1182)	**1833 (b$_1$, 919)**
	2071 (b$_2$, 323)^{t}	**1984 (b$_2$, 314)^{t}**
Id-s (C_2)	2042 (a, 154)^{t}	1955 (a, 145)^{t}
	2103 (a, 1229)^{t}	**2017 (a, 986)^{t}**
	2040 (b, 1136)^{t}	**1959 (b, 1111)^{t}**
	2052 (b, 589)^{t}	**1972 (b, 267)^{t}**
Ie-t (C_{2h})	1884 (a$_g$, 0)	1816 (a$_g$, 0)
	2077 (a$_g$, 0)^{t}	1983 (a$_g$, 0)^{t}
	1877 (a$_u$, 802)	**1804 (a$_u$, 692)**
	2064 (b$_u$, 1884)^{t}	**1970 (b$_u$, 1621)^{t}**
If-t (C_{2v})	1886 (a$_1$, 5)	1817 (a$_1$, 0)
	2094 (a$_1$, 1575)^{t}	**2001 (a$_1$, 1295)^{t}**
	1879 (b$_1$, 806)	**1805 (b$_1$, 693)**
	2066 (b$_2$, 533)^{t}	**1975 (b$_2$, 436)^{t}**
	$(C_4H_4)_2Co_2(CO)_3$	
IIa-s (C_s)	1918 (a′, 19)	1840 (a′, 19)
	2077 (a′, 913)^{t}	**1990 (a′, 748)^{t}**
	1884 (a″, 1242)	**1816 (a″, 987)**
IIc-t (C_{2v})	**1939 (a$_1$, 954)**	**1854 (a$_1$, 758)**
	1973 (a$_1$, 4)	1889 (a$_1$, 7)
	1936 (b$_2$, 1017)	**1850 (b$_2$, 803)**
	$(C_4H_4)_2Co_2(CO)_2$	
IIIa-s (C_{2v})	1957 (a$_1$, 31)	1863 (a$_1$, 74)
	1939 (b$_2$, 1297)	**1844 (b$_2$, 987)**
IIIb-t (C_s)	1902 (a′, 3)	1814 (a′, 0)
	1890 (a″, 1269)	**1801 (a″, 949)**
IIIc-s (C_{2h})	2052 (a$_g$,0)^{t}	1960 (a$_g$, 0)^{t}
	2033 (b$_u$, 2539)^{t}	**1945 (b$_u$, 1956)^{t}**
IIId-t (C_i)	2068 (a$_g$, 0)^{t}	1961 (a$_g$, 0)^{t}
	2052 (a$_u$, 2542)^{t}	**1937 (a$_u$, 2445)^{t}**
	$(C_4H_4)_2Co_2(CO)$	
IVa-s (C_1)	**1704 (440)**^{f}	**1608 (313)**^{f}
IVb-t (C_s)	**1694 (a′, 583)**^{f}	**1828 (a′, 604)**
IVc-s (C_1)	**2039 (1360)^{t}**	**1948 (1075)^{t}**
IVd-t (C_1)	**2045 (1125)^{t}**	**1937 (1145)^{t}**

[a] Infrared intensities are given in parentheses and are in km/mol; infrared-active CO frequencies are given in boldface type. The superscript "t" implies a terminal CO stretching frequency; the superscript "f" implies a η^2-μ-CO bridging frequency. All of the other reported frequencies correspond to bridging CO groups.

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. In general, the vibrational frequencies determined by the BP86 functional have been found to be closer to experiment than those determined by the B3LYP functional.[25,35]

The predicted ν(CO) frequencies for the $(C_4H_4)_2Co_2(CO)_n$ ($n = 1-4$) 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 predicted ν(CO) stretching frequencies are listed in Table 8 for all of the $(C_4H_4)_2Co_2(CO)_n$ ($n = 1-4$) species investigated in this work. In general, the ν(CO) frequencies predicted by the BP86 functional are 60−100 cm^{-1} lower than those predicted by the B3LYP functional and are significantly closer to the experimental values. Furthermore, 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. This same trend is found for the $(C_4H_4)_2Co_2(CO)_n$ ($n = 1-4$) derivatives studied in this work, where the bridging ν(CO) frequencies fall in the range 1889−1801 cm^{-1} and the terminal ν(CO) frequencies fall in the range 2017−1937 cm^{-1} (BP86). Similar observations concerning bridging and terminal ν(CO) frequencies were made in our previous work with $Cp_2Fe_2(CO)_n$ ($n = 1-4$)[5] and $Cp_2Co_2(CO)_n$ ($n = 1-3$)[6] derivatives.

The lowest ν(CO) frequencies found in this work, namely 1704 cm^{-1} (B3LYP) or 1608 cm^{-1} (BP86) for **IVa-s** and 1694 cm^{-1} (B3LYP) for **IVb-t**, arise from the unusual η^2-μ-CO four-electron-donor bridging CO group in isomers of $(C_4H_4)_2Co_2(CO)$, in which the C═O π-bond is involved in the bonding to one of the cobalt atoms. Such π-bonding of a bridging CO group is expected to lower the effective carbon−oxygen bond order, thereby leading to an unusually low ν(CO) frequency.

The one point of comparison of the calculated ν(CO) frequencies in Table 8 with experiment is with the reported ν(CO) frequencies[1] of 1978 s and 1785 s cm^{-1} for $(\eta^4\text{-}Me_4C_4)_2Co_2(CO)_4$, presumed to have a trans doubly bridged structure analogous to **Ib-s** (Figures 1 and 2 and Table 1). The calculated strong ν(CO) infrared frequencies for *trans*-$(\eta^4\text{-}C_4H_4)_2Co_2(CO)_2(\mu\text{-}CO)_2$ (**Ib-s**) are 1979 and 1830 cm^{-1}, which agree well with the experimental values for $(\eta^4\text{-}Me_4C_4)_2Co_2(CO)_4$ when the electron-releasing effects of the methyl substituents are considered. For this reason tetramethylcyclobutadiene derivatives are expected to exhibit ν(CO) frequencies somewhat lower than those for the corresponding unsubstituted cyclobutadiene derivatives. Thus, our calculations support the assignment of the trans doubly bridged structure for $(\eta^4\text{-}Me_4C_4)_2Co_2(CO)_2(\mu\text{-}CO)_2$ suggested approximately 20 years ago.[1]

4. Summary

The singlet doubly bridged and unbridged isomers of $(\eta^4\text{-}C_4H_4)_2Co_2(CO)_4$ have closely separated energies, suggesting a highly fluxional system similar to the experimentally known and closely related $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^4\text{-diene})_2Co_2(CO)_4$ systems. The global minimum of $(C_4H_4)_2Co_2(CO)_3$ is the singlet doubly bridged isomer $(\eta^4\text{-}C_4H_4)_2Co_2(CO)(\mu\text{-}CO)_2$, in contrast to the isoelectronic $(C_5H_5)_2Fe_2(CO)_3$, where the global minimum is the triply bridged triplet isomer $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3$, analo-

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(35) Xie, Y.; Schaefer, H. F.; King, R. B. *Spectrochim. Acta, Part A* **2005**, *A61*, 1693.

gous to dioxygen. A related triply bridged triplet isomer of $(C_4H_4)_2Co_2(\mu\text{-}CO)_3$ is also found, but at 9.6 kcal/mol (B3LYP) or 5.1 kcal/mol (BP86) above the global minimum. The $(C_4H_4)_2Co_2(CO)_2$ system behaves analogously to the corresponding $(C_5H_5)_2Fe_2(CO)_2$ system in that its lowest energy structure is the doubly bridged isomer $(\eta^4\text{-}C_4H_4)_2Co_2(\mu\text{-}CO)_2$, with a short cobalt−cobalt distance suggestive of the Co≡Co triple bond required to give both cobalt atoms the favored 18-electron configuration. Both axial and perpendicular metallocene structures are found for $(C_4H_4)_2Co_2(CO)$, including a low-energy $(\eta^4\text{-}C_4H_4)_2Co_2(\eta^2\text{-}\mu\text{-}CO)$ structure with a four-electron donor bridging CO group and a cobalt−cobalt distance suggestive of a Co≡Co triple bond.

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Supporting Information Available: Complete tables of harmonic vibrational frequencies for $(C_4H_4)_2Co_2(CO)_n$ ($n = 1-4$) isomers (Tables S1−S17). This material is available free of charge via the Internet at http://pubs.acs.org.

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