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A Binuclear Trimethylenemethane Cobalt Carbonyl Providing the First Example of a Low-Energy Perpendicular Structure with Acyclic Hydrocarbon Ligands

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Abstract

Trimethylenemethane (TMM) has long been known as a ligand in metal carbonyl complexes such as [η^4-$(CH_2)_3C$]Fe$(CO)_3$ and [η^4-$(CH_2)_3C$]Cr$(CO)_4$. The prospects for synthesizing currently unknown TMM complexes of cobalt carbonyl have been explored by a density functional theory study of the binuclear complexes $[(CH_2)_3C]_2Co_2(CO)_n$ (n = 2, 3, 4, 5, 6). The dicarbonyl is unexpectedly found to favor by more than ~12 kcal/mol a perpendicular structure [μ-$(CH_2)_3C]_2Co_2(CO)_2$ with bridging η^4-TMM ligands, terminal CO groups, and a relatively short Co-Co distance of ~2.29 Å. This is the first example of an energetically favorable perpendicular binuclear metal complex structure having bridging acyclic hydrocarbon ligands. The other viable species is $[(CH_2)_3C]_2Co_2(CO)_4$, which is a substitution product of the well-known $Co_2(CO)_8$ with terminal η^4-TMM ligands. Similar to $Co_2(CO)_8$, doubly bridged and unbridged $[(CH_2)_3C]_2Co_2(CO)_4$ structures have approximately equal energies within ~2 kcal/mol and predicted Co–Co distances of ~2.5 and ~2.7 Å, respectively. Carbonyl-rich $[(CH_2)_3C]_2Co_2(CO)_n$ (n = 5, 6) structures are also found with dihapto η^2-TMM ligands. However, these are predicted to be unstable with respect to CO dissociation to give $[(CH_2)_3C]_2Co_2(CO)_4$.

1. Introduction

An important recent development in organometallic chemistry has been the synthesis of the first dimetallocenes in which a pair of metal atoms is sandwiched between two planar carbocyclic rings. This area of chemistry was stimulated by the 2004 discovery of dizincocene $(\eta^5\text{-}Me_5C_5)_2Zn_2$ in which a pair of zinc atoms is sandwiched between two parallel $\eta^5\text{-}Me_5C_5$ rings so that the Zn-Zn bond axis is collinear with the C_5 rotation axes of the rings.[1,2] Shortly after this original report a theoretical study[3] on the late transition metal dimetallocenes $(C_5H_5)_2M_2$ (M = Zn, Cu, Ni) predicted not only coaxial dimetallocene structures but also perpendicular structures, particularly $(C_5H_5)_2Cu_2$ (Figure 1). In the perpendicular dimetallocene structures, the rings function as bridging ligands across a metal-metal bond, rather than as terminal ligands, bonded solely to a single metal atom. After recognition of the possibility of perpendicular dimetallocenes from this theoretical study, the benzenepalladium(II) complexes $(\mu\text{-}C_6H_6)_2Pd_2(AlCl_4)_2$ and $(C_6H_6)_2Pd_2(Al_2Cl_7)_2$, which were originally synthesized by Allegra and coworkers in 1970,[4] were recognized as relatives to perpendicular dimetallocenes with bridging benzene rings rather than cyclopentadienyl rings.

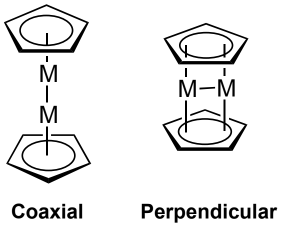


Figure 1. Coaxial and perpendicular dimetallocenes.

A question of interest is whether analogues of perpendicular metallocenes can be synthesized containing bridging acyclic hydrocarbon ligands rather than bridging planar cyclic hydrocarbon rings. We have now discovered that density functional theory (DFT) predicts an interesting low-energy perpendicular $[\mu\text{-}(CH_2)_3C]_2Co_2(CO)_2$ structure with a bridging acyclic trimethylenemethane ligand. This perpendicular structure lies more than 12 kcal/mol below the next lowest energy $[\mu\text{-}(CH_2)_3C]_2Co_2(CO)_2$ structure, which is also a perpendicular structure but with a different orientation of the bridging trimethylenemethane ligands. The lowest energy coaxial $[(CH_2)_3C]_2Co_2(CO)_2$ structure is found to lie more than 19 kcal/mol higher in energy than the lowest energy isomeric perpendicular $[\mu\text{-}(CH_2)_3C]_2Co_2(CO)_2$ structure. These energetic considerations make the perpendicular $[\mu\text{-}(CH_2)_3C]_2Co_2(CO)_2$ structure a promising synthetic objective.

This unexpected discovery of a low-energy perpendicular $[\mu\text{-}(CH_2)_3C]_2Co_2(CO)_2$ structure arose during a theoretical study of the structures and energetics of $[(CH_2)_3C]_2Co_2(CO)_n$ complexes derived from the pairwise substitution of CO groups in $Co_2(CO)_8$ by a trimethylenemethane (TMM) ligand. Interest in TMM began in 1948 with a hypothesis attributed to Moffitt in a paper by Coulson[5] that the central carbon atom in TMM has a significantly greater π bond order than the outer carbon atoms. TMM was first detected experimentally as a product of the photochemical decomposition of 4,5-dihydro-4-methylene-3H-pyrazole [6] or 3-methylenecyclobutanone at –185°C. [7] Subsequent electron spin resonance (ESR) studies of TMM confirmed the theoretical prediction of the triplet ground state with the planar geometry of this highly reactive species.[8] The planarity of the TMM ligand makes it a suitable acyclic ligand for perpendicular binuclear transition metal structures analogous to dimetallocenes. In addition a series of bis(trimethylenemethane) complexes $[(CH_2)_3C]_2M$ of the first row transition metals has been studied theoretically as analogues of the metallocenes.[9]

In 1966 Pettit and co-workers[10] reported the synthesis of the first metal complex of TMM, namely the iron tricarbonyl derivative, $[\eta^4\text{-}(CH_2)_3C]Fe(CO)_3$ (**A** in Figure 2), by the dechlorination of 3-chloro-(2-chloromethyl)propene $CH_2{=}C(CH_2Cl)_2$ with $Fe_2(CO)_9$ at room temperature. This synthesis parallels an analogous synthesis of (cyclobutadiene)iron tricarbonyl (**B** in Figure 2) that they reported earlier that year.[11] The synthesis of the iron tricarbonyl derivative of the isoelectronic butadiene (**C** in Figure 2) was reported much earlier in 1930 by Reihlen and co-workers as a product from the reaction of $Fe(CO)_5$ with butadiene in a sealed vessel.[12] The umbrella shape of the TMM ligand in its iron tricarbonyl complex was originally characterized by electron diffraction studies in the gas phase[13] and much later by X-ray crystallography in the solid state.[14,15] Theoretical studies on such structures were subsequently reported by Hoffmann and co-workers.[16] Since then, a variety of transition-metal complexes possessing a TMM ligand have been synthesized.[17,18,19,20]

Substitution products of $Co_2(CO)_8$ such as $[(CH_2)_3C]Co_2(CO)_6$ and $[(CH_2)_3C]_2Co_2(CO)_4$ in which CO groups are replaced pairwise by TMM ligands are unknown. However, related $Co_2(CO)_8$ derivatives in which CO groups are replaced pairwise by other types of four-electron donor hydrocarbon ligands are known. Thus the binuclear bis(butadiene)dicobalt tetracarbonyl $(\eta^4\text{-}C_4H_6)_2Co_2(CO)_4$ (**D** in Figure 2) was first reported in 1961[21] and has been structurally characterized by X-ray crystallography. [22] In addition, the binuclear (tetramethylcyclobutadiene)cobalt carbonyl $(\eta^4\text{-}Me_4C_4)_2Co_2(CO)_4$ has been synthesized, albeit in relatively low yield, and characterized by elemental analysis, mass spectrometry, and infrared ν(CO) frequencies (**E** in Figure 2).[23]

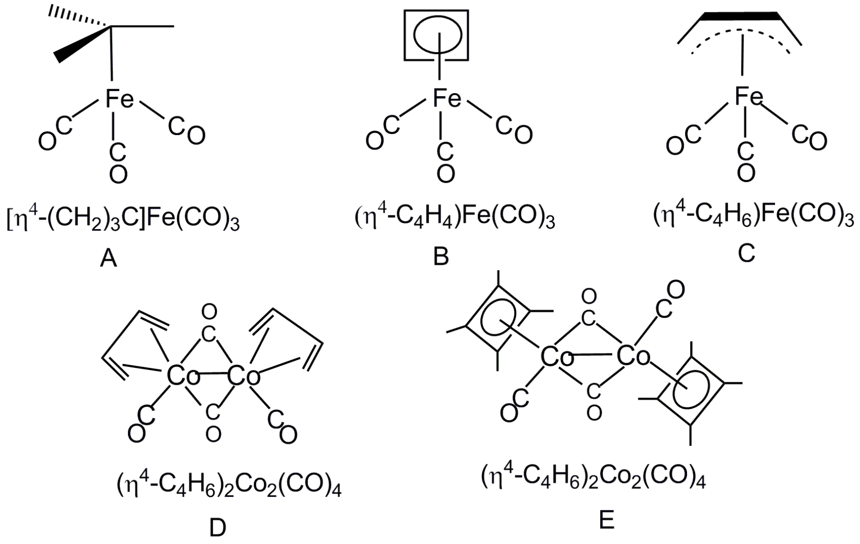


Figure 2. Comparison of the known iron tricarbonyl complexes of trimethylenemethane (**A**), cyclobutadiene (**B**), and butadiene (**C**) as well as the known binuclear bis(butadiene)dicobalt tetracarbonyl (**D**) and bis(tetramethylcyclobutadiene)dicobalt tetracarbonyl (**E**).

This paper reports theoretical studies on the complete series of binuclear trimethylenemethane cobalt carbonyls $[(CH_2)_3C]_2Co_2(CO)_n$ (n = 2, 3, 4, 5, 6). The dicarbonyl $[(CH_2)_3C]_2Co_2(CO)_2$ is of particular interest in representing the first example of a perpendicular binuclear metal derivative with bridging acyclic hydrocarbon ligands analogous to a perpendicular dimetallocene with bridging cyclopentadienyl ligands. The species $[(CH_2)_3C]_2Co_2(CO)_n$ (n = 3, 4) are substitution products of $Co_2(CO)_n$ (n = 7, 8) with terminal TMM ligands. The carbonyl-rich $[(CH_2)_3C]_2Co_2(CO)_n$ (n = 5, 6) provide examples of structures in which the TMM ligands are only partially bonded to the metal atoms in order to prevent the Co atoms from exceeding the favored 18-electron configuration. However, the tendency for TMM to bond fully to a metal atom as a tetrahapto ligand makes these carbonyl richest structures disfavored with respect to CO elimination.

2. Theoretical Methods

Four DFT methods were adopted for this work. The popular B3LYP method combines the three-parameter Becke functional (B)[24] with the Lee-Yang-Parr generalized gradient correlation functional (LYP).[25] The BP86 method combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional (P86).[26,27] These two DFT methods predict different singlet-triplet splittings. Usually B3LYP prefers high-spin states, while BP86 prefers low-spin states. Therefore, Reiher et al.[28,29] suggested a new functional, namely B3LYP*, with less exact exchange functional (15%), which can reproduce the better relative energies for different spin states. This B3LYP* method is the third method used in the present work. The fourth functional is a hybrid meta-GGA DFT method, M06-L, developed by Truhlar et al.[30] The M06-L functional was constructed using three strategies, namely constraint satisfaction, modeling the exchange-correlation hole, and empirical fitting. Truhlar et al. suggests M06-L for transition metal compounds. The four DFT methods agree well with each other for the geometries, while the M06-L method predicts the relative energies closer to experiment. Thus, we adopt the energy orderings predicted by the M06-L method, but list the results from all four methods in the Supporting Information.

Double-ζ plus polarization (DZP) basis sets have been adopted to provide continuity with a body of existing research on a series of organometallic compounds. For C and O, one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$ is added to the Huzinaga-Dunning standard contracted DZ sets, designated as (9s5p1d/4s2p1d).[31,32] 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[33] is used after being augmented by two sets of p functions and one set of d functions, contracted using the method of Hood, Pitzer, and Schaefer,[34] and designated as (14s11p6d/10s8p3d).

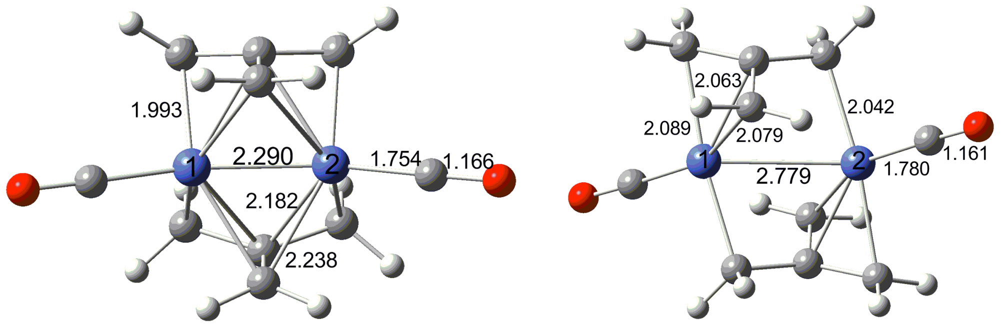
The geometries of the structures were fully optimized using the Gaussian09 program.[35] The vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The ultrafine grid, i.e., the pruned (99, 590), was used for the computation of two-electron integrals. Natural Bond Orbital (NBO) analyses[36,37] were carried out using the DZP M06-L method.

The optimized $[(CH_2)_3C]_2Co_2(CO)_n$ (n = 2, 3, 4, 5, 6) structures are reported in Figures 3 through 8. The structures are designated **nX-m**, where **n** represents the number of carbonyl groups, **X** represents the spin state, i.e., **S** for singlets and **T** for triplets, and **m** orders the structures according to their relative energies.

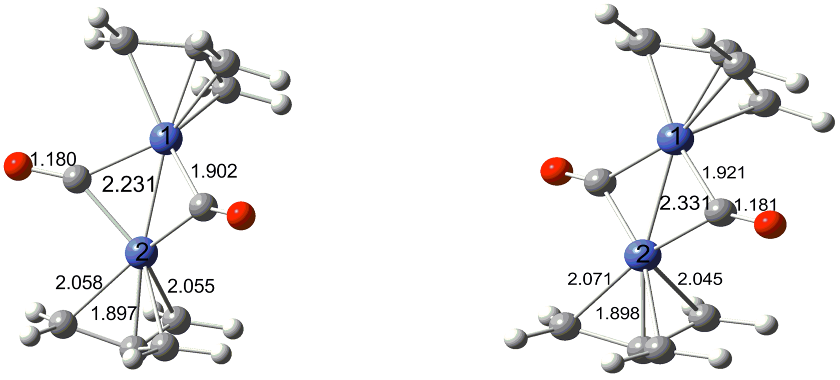
3. Results and Discussion

3.1 The $[(CH_2)_3C]_2Co_2(CO)_2$ system with low-energy perpendicular structures

For the $[(CH_2)_3C]_2Co_2(CO)_2$ system containing just two carbonyl groups, perpendicular structures are possible in which the TMM ligands bridge the pair of cobalt atoms in addition to the coaxial structures with terminal TMM ligands. In general, such perpendicular $Q_2M_2(CO)_2$ structures are of significantly higher energy than the isomeric coaxial complexes, as found in the chemistry of binuclear iron, cobalt, and nickel complexes having two cyclopentadienyl,[38,39,40] butadiene,[41] or cyclobutadiene[42,43] ligands bridging the pair of metal atoms. The $[(CH_2)_3C]_2Co_2(CO)_2$ system is exceptional since both the singlet perpendicular structure **2S-1** and the triplet perpendicular structure **2T-2** lie significantly in energy below the corresponding coaxial structures **2S-3** and **2T-4** (Figure 3 and Table S1). All four $[(CH_2)_3C]_2Co_2(CO)_2$ structures are predicted to be genuine minima with no imaginary vibrational frequencies.



2S-1 (C_{2v}, 0.0) **2T-2** (C_i, 12.6)



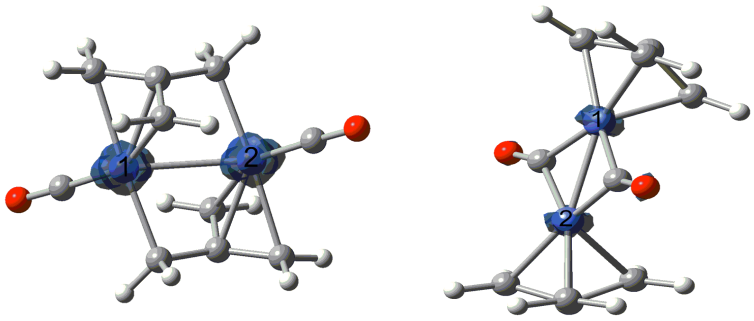
2S-3 (C_{2v}, 19.3) **2T-4** (C_{2v}, 23.6)

Figure 3. Equilibrium geometries and relative energies (kcal/mol) for the four $[(CH_2)_3C]_2Co_2(CO)_2$ structures.

The C_{2v} singlet perpendicular $[(CH_2)_3C]_2Co_2(CO)_2$ structure **2S-1** is predicted to be the global minimum (Figure 3 and Table S1). The short Co≡Co distance of 2.290 Å in **2S-1** suggests the formal triple bond required to give each cobalt atom the favored 18-electron configuration. This Co≡Co bond is bridged by a pair of carbon atoms from each TMM ligand with the C–C bond of each pair of carbon atoms perpendicular to the Co≡Co bond. The WBI of the Co≡Co interaction of 0.22 is abnormally low owing to delocalization of this interaction through the bridging carbon atoms of the TMM ligand.

The triplet perpendicular $[(CH_2)_3C]_2Co_2(CO)_2$ structure **2T-2**, lying 12.6 kcal/mol in energy above **2S-1**, has a very different configuration of the bridging TMM ligands with the two bridging carbon atoms nearly parallel to the Co-Co axis (Figure 3 and Table S1). The predicted long Co···Co distance in **2T-2** of 2.779 Å and the low WBI of 0.03 suggests a lack of significant metal-metal bonding, giving each Co atom a 15-electron configuration consistent with a binuclear triplet. The spin density in **2T-2** is delocalized over both cobalt atoms (Figure 4).

The doubly bridged coaxial singlet structure **2S-3** and triplet structure **2T-4** in which each Co atom is bonded to a single TMM ligand are both much higher energy $[(CH_2)_3C]_2Co_2(CO)_2$ structures, lying 19.3 and 23.6 kcal/mol, respectively, above **2S-1**. The short Co≡Co distance of 2.231 Å in the singlet structure **2S-3** can be interpreted as the formal triple bond required to give each cobalt atom an 18-electron configuration. However, the low WBI of 0.28 of this Co≡Co interaction suggests considerable delocalization through the bridging CO groups. The longer Co=Co distance of 2.331 Å in the triplet structure **2T-4** coupled with a smaller WBI value of 0.16 suggests the formal Co=Co double bond required to give each cobalt atom a 17-electron configuration for a binuclear triplet. Again the low WBI value of 0.16 of the Co=Co interaction suggests considerable delocalization through the bridging CO groups. The two cobalt atoms share the spin density of the two unpaired electrons (Figure 4).



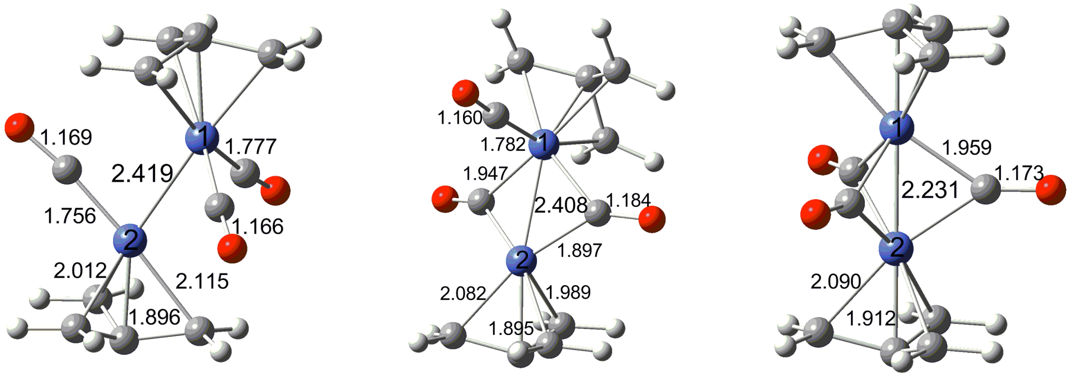
2T-2 (C_i) **2T-4** (C_{2v})

Figure 4. Spin densities for the triplet $[(CH_2)_3C]_2Co_2(CO)_2$ structures.

3.2. $[(CH_2)_3C]_2Co_2(CO)_n$ (*n* = 3, 4): substitution products of $Co_2(CO)_n$ (*n* = 7, 8)

All of the $[(CH_2)_3C]_2Co_2(CO)_n$ (*n* = 3, 4) structures found in this work contain exclusively terminal TMM ligands. They may thus be considered as substitution products of either the well-known[44,45,46] $Co_2(CO)_8$ (for *n* = 4) or the unsaturated $Co_2(CO)_7$ (for *n* = 3), which have been the subjects of a previous theoretical study.[47] In these coaxial structures, each Co atom bonds more strongly with the central carbon atom of the TMM ligand with Co-C distances of ~1.9 Å, while the three Co-C distances to the exterior TMM carbon atoms are predicted to be ~2.0 Å.

3.2.1 $[(CH_2)_3C]_2Co_2(CO)_3$. Three low-lying $[(CH_2)_3C]_2Co_2(CO)_3$ structures are found with energies within 3.3 kcal/mol, suggesting a fluxional system (Figure 5 and Table S2). The C_s unbridged $[(CH_2)_3C]_2Co_2(CO)_3$ structure **3S-1** is the global minimum. The predicted Co=Co distance of 2.419 Å suggests a formal double bond, thereby giving each cobalt atom the favored 18-electron configuration.

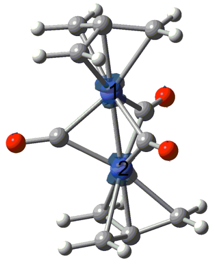


3S-1 (C_s, 0.0) **3S-2** (C_s ,1.4) **3T-3** (D_{3h}, 3.3)

Figure 5. Equilibrium geometries and relative energies (kcal/mol) for the $[(CH_2)_3C]_2Co_2(CO)_3$ structures.

The doubly bridged $[(CH_2)_3C]_2Co_2(CO)(\mu\text{-}CO)_2$ structure **3S-2** lies only 1.4 kcal/mol in energy above **3S-1** (Figure 5 and Table S2). The Co=Co distance of 2.408 Å in **3S-2** is similar to that in **3S-1** suggesting a formal double bond. This gives each cobalt atom in **3S-2** the favored 18-electron configuration with a formal positive charge on the cobalt atom bearing the terminal CO group and a formal negative charge on the other cobalt atom.

The triply bridged triplet $[(CH_2)_3C]_2Co_2(\mu\text{-}CO)_3$ structure **3T-3**, lying only 3.3 kcal/mol above **3S-1**, has relatively high D_{3h} symmetry (Figure 5 and Table S2). The Co=Co distance of 2.231 Å in **3T-3** can be interpreted as a formal double bond, shortened by the presence of the three bridging CO groups. This gives each cobalt atom in **3T-3** the favored 18-electron configuration. The two unpaired electrons leading to the triplet spin multiplicity in **3T-3** reside in two single-electron orthogonal π "half-bond" components of the Co=Co double bond, which thus is of the σ + $^2\!/_2$ π type. A similar σ + $^2\!/_2$ π Fe=Fe double bond is found in the experimentally known[48,49,50] cyclopentadienyl derivative $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3$. The corresponding permethylated derivative $(\eta^5\text{-}Me_5C_5)_2Fe_2(\mu\text{-}CO)_3$ has been shown by X-ray crystallography[51] to have an Fe=Fe distance of 2.265(1) Å, very close to the predicted 2.231 Å length of the Co=Co double bond in **3T-3**. The suggested σ + $^2\!/_2$ π Co=Co double bond in **3T-3** is supported by the equal distribution of the spin density in **3T-3** on each cobalt atom (Figure 6).



3T-3 (D_{3h})

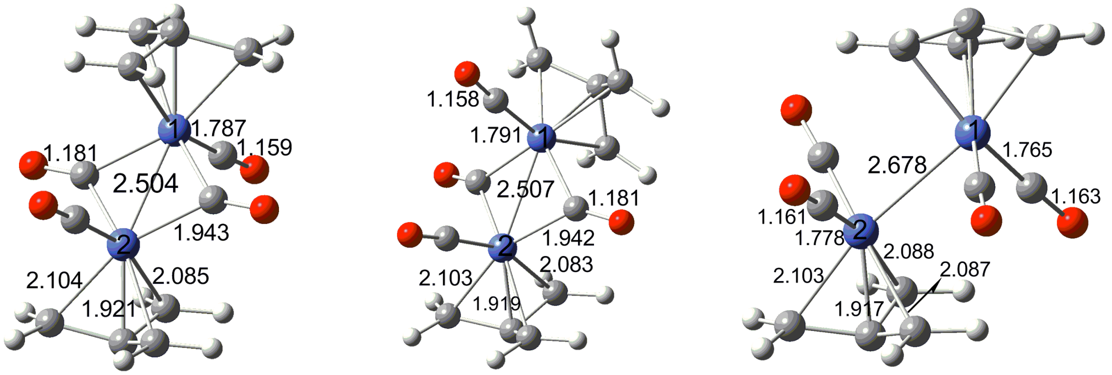
Figure 6. Spin density for the triplet $[(CH_2)_3C]_2Co_2(\mu\text{-}CO)_3$ structure.

3.2.2 $[(CH_2)_3C]_2Co_2(CO)_4$

Three low-energy singlet $[(CH_2)_3C]_2Co_2(CO)_4$ structures are found, namely the two doubly bridged structures **4S-1** and **4S-2** and one unbridged structure **4S-3** (Figure 7 and Table S3). These structures are genuine minima and lie within ~2 kcal/mol of energy suggesting a fluxional system. Triplet $[(CH_2)_3C]_2Co_2(CO)_4$ structures lie at least 30 kcal/mol above the singlet structures and thus are not discussed in this paper. The C_{2h} *trans* **4S-1** structure lies only 0.4 kcal/mol below the C_{2v} *cis* structure **4S-2.** The predicted Co–Co distance in **4S-1** of 2.504 Å is reasonably close to the 2.559(3) Å experimental Co–Co distance found by X-ray crystallography in the related 1,3-cyclohexadiene complex $(\eta^4\text{-}C_6H_8)_2Co_2(CO)_2(\mu\text{-}CO)_2$.[52] The predicted Co–Co distance in **4S-2** of 2.507 Å is very close to that in **4S-1**. These Co–Co distances as well as the WBIs of 0.12 for **4S-1** and **4S-2** suggest formal single bonds, thereby giving each cobalt atom the favorable 18-electron configuration.

The unbridged $[(CH_2)_3C]_2Co_2(CO)_4$ structure **4S-3**, lying only 1.7 kcal/mol in energy above **4S-1**, possesses the same *trans* configuration as **4S-1** (Figure 7 and Table

S3). The Co–Co distance of 2.678 Å in the unbridged structure **4S-3** is ~0.2 Å longer than that in the doubly bridged structures **4S-1** and **4S-2**. A similar effect was noted experimentally by X-ray crystallography in $Co_2(CO)_8$ for which the doubly bridged isomer[44,45,46] was found to have a Co–Co distance of 2.530 Å in contrast to the Co–Co distance of 2.700 Å for the unbridged isomer[53] stabilized in a C_{60} matrix. Despite the longer Co–Co distance in **4S-3** relative to that in **4S-1** and **4S-2**, the WBI of 0.18 for the Co–Co interaction in the unbridged structure **4S-3** is significantly larger than the WBI of 0.12 in the doubly bridged structures **4S-1** and **4S-2**. This is a demonstration of the reduction of the effective Co–Co bond order by interaction with the bridging CO groups leading to multicenter bonding as discussed in more detail by Ponec, Green, and their collaborators in recent papers.[54,55]

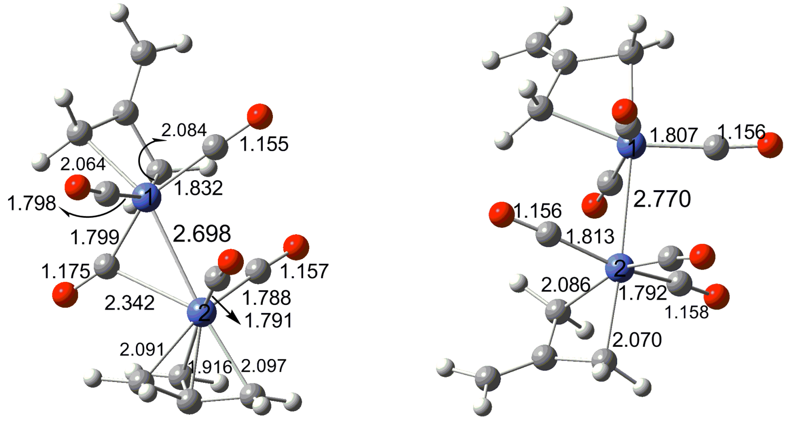


4S-1 (C_{2h}, 0.0) **4S-2** (C_{2v}, 0.4) **4S-3** (C_2, 1.7)

Figure 7. Equilibrium geometries and relative energies (kcal/mol) for the $[(CH_2)_3C]_2Co_2(CO)_4$ structures.

3.3 Carbonyl-rich structures $[(CH_2)_3C]_2Co_2(CO)_n$ (n = 5, 6): examples of dihapto trimethylenemethane ligands

In 1962 Murdoch and Weiss found a dihapto butadiene ligand in the mononuclear $(\eta^2\text{-}C_4H_6)Fe(CO)_4$ complex and a bis(dihapto) butadiene ligand in the binuclear complex $(\eta^2,\eta^2\text{-}C_4H_6)Fe_2(CO)_8$.[56] For this reason we explored possible carbonyl-rich species containing dihapto TMM ligands. Thus one singly bridged singlet spin state $[\eta^2\text{-}(CH_2)_3C][\eta^4\text{-}(CH_2)_3C]Co_2(\mu\text{-}CO)(CO)_4$ structure **5S** was found for the pentacarbonyl $[(CH_2)_3C]_2Co_2(CO)_5$ having one tetrahapto η^4-TMM ligand and one dihapto η^2-TMM ligand. The Co–Co distance of 2.698 Å in **5S** coupled with a WBI of 0.12 indicates a formal single bond to provide each cobalt atom with the favored 18-electron configuration. Only a single singlet unbridged structure **6S** was found for the carbonyl-richer hexacarbonyl [η^2-$(CH_2)_3C]_2Co_2(CO)_6$, (Figure 8 and Table S4). Structure **6S** has two dihapto η^2-TMM ligands and a predicted Co−Co distance of 2.770 Å. The long Co−Co bond distance with a WBI of 0.12 in **6S** corresponds to a weak formal single bond, giving each cobalt atom the favored 18-electron configuration.



5S (*C*$_1$) **6S** (*C*$_2$)

Figure 8. Equilibrium geometries for the carbonyl-rich $[(CH_2)_3C]_2Co_2(CO)_5$ and $[(CH_2)_3C]_2Co_2(CO)_6$ structures.

3.4 NBO Analysis

Table 1 lists the Co–Co distances, the formal Co–Co bond orders, the natural charges for the cobalt atoms, and Co electron configurations for all of the structures reported in this article. In general, a decrease in the number of carbonyl groups bonded to a given cobalt atom increases its positive natural charge, since increased electron density arising from σ-donation from the CO groups to the cobalt atom is not completely balanced by π back bonding from the cobalt atom to the CO π* antibonding orbitals. For $[(CH_2)_3C]_2Co_2(CO)_3$, with an unsymmetrical distribution of carbonyl groups between the two cobalt atoms, the Co1 atoms with more carbonyls in **3S-1** and **3S-2** have lower positive charges of 0.14 to 0.17 relative to the 0.37 to 0.47 positive charges on the Co2 atoms. A similar situation occurs in the $[(CH_2)_3C]_2Co_2(CO)_5$ structure **5S**.

The Wiberg Bond Indices (WBIs) in Table 1 of the Co–Co bonds are shown to correlate with the formal bond order suggested by the Co–Co distances and electron counting. Thus the WBIs for the Co–Co single bonds are in the range 0.12 to 0.18. The high WBI values of 0.20 and 0.16 for **3S-1** and **2T-4** can be interpreted as formal Co=Co double bonds. The still higher WBI values of 0.22 and 0.28 for **2S-1** and **2S-3** can be interpreted as formal Co≡Co triple bonds. The very low WBI of 0.03 indicates the lack of significant Co-Co bonding for **2T-2**. These WBI values are consistent with those in our previous theoretical studies where formal Fe–Fe single bonds were found to have values of 0.12 to 0.19.[57] Also the relatively low WBIs for the Co-Co interactions are reduced even more by interaction of the Co-Co bonds with the bridging CO groups leading to multicenter bonding.[54,55]

Table 1. Co-Co distances, NPA natural charges, Co electron configurations, the formal Co-Co bond orders, and WBIs for the $[(CH_2)_3C]_2Co_2(CO)_n$ (n = 2, 3, 4, 5, 6) structures using the M06-L method. Global minima structures are in bold type.

		Co-Co distance	Co natural charge		Co electron configuration		Formal bond order	WBI for Co-Co
			Co1	Co2	Co1	Co2		
2S-1	**C_{2v}**	**2.290**	**0.33**	**0.33**	**18**	**18**	**3**	**0.22**
2T-2	C_i	2.779	0.63	0.63	15	15	0	0.03
2S-3	C_{2v}	2.231	0.38	0.38	18	18	3	0.28
2T-4	C_{2v}	2.331	0.43	0.43	17	17	2	0.16
3S-1	**C_s**	**2.419**	**0.14**	**0.37**	**18**	**18**	**2**	**0.20**
3S-2	C_s	2.408	0.17	0.47	18	16	1	0.15
3T-3	D_{3h}	2.231	0.25	0.25	17	17	1	0.12
4S-1	**C_{2h}**	**2.504**	**0.19**	**0.19**	**18**	**18**	**1**	**0.12**
4S-2	C_{2v}	2.507	0.19	0.19	18	18	1	0.12
4S-3	C_2	2.678	0.18	0.18	18	18	1	0.18
5S	**C_1**	**2.698**	**0.10**	**0.18**	**18**	**18**	**1**	**0.12**
6S	**C_2**	**2.770**	**0.09**	**0.09**	**18**	**18**	**1**	**0.12**

3.5 Thermochemistry

The thermochemistry of the $[(CH_2)_3C]_2Co_2(CO)_n$ system suggests that the perpendicular $[\mu\text{-}(CH_2)_3C]_2Co_2(CO)_2$ structure **2S-1** is a viable synthetic objective. Thus the predicted carbonyl dissociation energy of 18.6 kcal/mol required to go from $[(CH_2)_3C]_2Co_2(CO)_3$ (**3S-1**) to $[(CH_2)_3C]_2Co_2(CO)_2$ (**2S-1**) is much smaller than the 40.8 kcal/mol energy required to go from $[(CH_2)_3C]_2Co_2(CO)_4$ (**4S-1**) to $[(CH_2)_3C]_2Co_2(CO)_3$ (**3S-1**) (Table 2). The latter dissociation energy is similar to the experimental CO dissociation energies of 41 kcal/mol and 37 kcal/mol for the simple metal carbonyls $Fe(CO)_5$ and $Cr(CO)_6$, respectively.[58] Furthermore, the formation of $[(CH_2)_3C]_2Co_2(CO)_2$ (**2S-1**) by disproportionation of $[(CH_2)_3C]_2Co_2(CO)_3$ (**3S-1**) into **2S-1** + $[(CH_2)_3C]_2Co_2(CO)_4$ (**4S-1**) is an exothermic process by ~20 kcal/mol (Table 3). This also supports the viability of $[(CH_2)_3C]_2Co_2(CO)_2$ (**2S-1**) as a synthetic objective.

The thermochemical information in Tables 2 and 3 also provide insights into the viability of other $[(CH_2)_3C]_2Co_2(CO)_n$ derivatives. Carbonyl dissociation from the carbonyl-rich species $[(CH_2)_3C]_2Co_2(CO)_n$ (n = 5, 6) is a slightly exothermic process by 2 to 4 kcal/mol indicating that these species are disfavored. This suggests that conversion of a partially bonded dihapto η^2-TMM ligand to a fully bonded tetrahapto η^4-TMM ligand with loss of a carbonyl group is an exothermic process. On the other hand $[(CH_2)_3C]_2Co_2(CO)_4$, as a substitution product of the stable $Co_2(CO)_8$, is a viable species as indicated by its high CO dissociation energy around ~40 kcal/mol (Table 2) and its endothermic disproportionation energy into $[(CH_2)_3C]_2Co_2(CO)_5$ + $[(CH_2)_3C]_2Co_2(CO)_3$ also of ~40 kcal/mol (Table 3).

Table 2. Dissociation energies (kcal/mol) for the successive removal of carbonyl groups from $[(CH_2)_3C]_2Co_2(CO)_n$

$[(CH_2)_3C]_2Co_2(CO)_3$ (**3S-1**) → $[(CH_2)_3C]_2Co_2(CO)_2$ (**2S-1**) + CO	18.6
$[(CH_2)_3C]_2Co_2(CO)_4$ (**4S-1**) → $[(CH_2)_3C]_2Co_2(CO)_3$ (**3S-1**)+ CO	40.8
$[(CH_2)_3C]_2Co_2(CO)_5$ (**5S**) → $[(CH_2)_3C]_2Co_2(CO)_4$ (**4S-1**) + CO	–2.8
$[(CH_2)_3C]_2Co_2(CO)_6$ (**6S**) → $[(CH_2)_3C]_2Co_2(CO)_5$ (**5S**) + CO	–4.3

Table 3. Energies (kcal/mol) for the disproportionation reactions $2[(CH_2)_3C]_2Co_2(CO)_n \rightarrow [(CH_2)_3C]_2Co_2(CO)_{n+1} + [(CH_2)_3C]_2Co_2(CO)_{n-1}$

$2[(CH_2)_3C]_2Co_2(CO)_3$(**3S-1**) → $[(CH_2)_3C]_2Co_2(CO)_4$(**4S-1**)+ $[(CH_2)_3C]_2Co_2(CO)_2$(**2S-1**)	–22.2
$2[(CH_2)_3C]_2Co_2(CO)_4$(**4S-1**) → $[(CH_2)_3C]_2Co_2(CO)_5$(**5S**)+ $[(CH_2)_3C]_2Co_2(CO)_3$(**3S-1**)	43.6
$2[(CH_2)_3C]_2Co_2(CO)_5$(**5S**) → $[(CH_2)_3C]_2Co_2(CO)_6$(**6S**)+ $[(CH_2)_3C]_2Co_2(CO)_4$(**4S-1**)	1.5

3.6 Vibrational Frequencies

Table 4 exhibits the ν(CO) frequencies and their infrared intensities for all of the $[(CH_2)_3C]_2Co_2(CO)_n$ (n = 2, 3, 4, 5, 6) structures. These were predicted by the BP86 method, which has been shown to predict ν(CO) frequencies close to the experimental fundamental frequencies. The terminal ν(CO) frequencies range from 1938 to 2053 cm^{-1}, while the bridging ν(CO) frequencies are significantly lower ranging from 1805 to 1900 cm^{-1} in accord with expectation. The significantly lower ν(CO) frequencies for bridging relative to terminal carbonyls are consistent with the longer C-O distances. Thus the C-O distances are ~1.16 and 1.18 Å for the bridging and terminal carbonyls, respectively, implying lower effective C–O bond orders in the bridging carbonyls relative to terminal carbonyls.

Table 4. ν(CO) Frequencies for the $[(CH_2)_3C]_2Co_2(CO)_n$ structures using the BP86 method. Bridging ν(CO) frequencies are in bold type.

2S-1	C_{2v}	1957 (B$_2$, 1669), 1967 (A$_1$, 227)
2T-2	C_i	1968 (A$_u$, 1945), 1986 (A$_g$, 0)
2S-3	C_{2v}	**1841 (B$_1$, 871), 1858 (A$_1$, 152)**
2T-4	C_{2v}	**1805 (B$_1$, 805), 1822 (A$_1$, 31)**
3S-1	C_s	1938 (A’, 689), 1946 (A’’, 647), 1977 (A’, 101)
3S-2	C_s	**1809 (A’’, 733), 1848 (A’, 52)**, 1993 (A’, 633)
3T-3	D_{3h}	**1868 (E’, 703), 1868 (E’, 703), 1900 (A1’, 0)**
4S-1	C_{2h}	**1826 (A$_u$, 768), 1862 (A$_g$, 0)**, 1990 (B$_u$, 1220), 2002 (A$_g$, 0)
4S-2	C_{2v}	**1823 (B$_1$, 751), 1860 (A$_1$, 32)**, 1987 (B$_2$, 176), 2017 (A$_1$, 1047)
4S-3	C_2	1959 (B, 119), 1968 (A, 940), 1978 (B, 882), 2011 (A, 194)
5S	C_1	**1830 (A, 526), 1896 (A, 196)**, 1991 (A, 694), 2010 (A, 629), 2032 (A, 412)
6S	C_2	1971 (A, 147), 1985 (B, 804), 1999 (B, 180), 2001 (A, 863), 2005 (B, 901), 2053 (A, 317)

4. Conclusion

The lowest energy $[(CH_2)_3C]_2Co_2(CO)_2$ structure by more than 12 kcal/mol is a perpendicular structure with terminal CO groups and bridging tetrahapto $(CH_2)_3C$ ligands. This structure is stable towards CO dissociation with a CO dissociation energy of ~20 kcal/mol. In addition, the disproportionation of $[(CH_2)_3C]_2Co_2(CO)_3$ to give $[(CH_2)_3C]_2Co_2(CO)_4 + [(CH_2)_3C]_2Co_2(CO)_2$ is an exothermic process by ~20 kcal/mol.

Another viable binuclear TMM cobalt carbonyl is the tetracarbonyl $[(CH_2)_3C]_2Co_2(CO)_4$ for which doubly bridged and unbridged structures have approximately equal energies within ~2 kcal/mol suggesting a fluxional system. This can be regarded as a substitution product of $Co_2(CO)_8$ in which two TMM ligands replace four terminal carbonyl groups. Carbonyl-rich $[(CH_2)_3C]_2Co_2(CO)_n$ (n = 5, 6) structures with dihapto η^2-TMM ligands are also found. However, they are not viable species since CO dissociation from them to give eventually $[(CH_2)_3C]_2Co_2(CO)_4$ is a slightly exothermic process by ~2 kcal/mol.

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Supporting Information. Tables S1 to S4: Co-Co distances (Å), total energies (E, in hartree), relative energies (ΔE, in kcal/mol) and spin expectation values $\langle S^2 \rangle$ for all structures by the four DFT methods. Tables S5 to S16: Atomic coordinates of the optimized structures for the all structures; Tables S17 to S28: Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for all structures.

Literature References

1 I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* 2004, **305**, 1136-1138.

2 Y. Wang, B. Quillan, P. Wei, H. Wang, X. J. Yang, Y. Xie, R. B. King, P. v. R. Schleyer, H. F. Schaefer, G. H. Robinson, *J. Am. Chem. Soc.,* 2005, **127**, 11944-11945.

3 Y. Xie, H. F. Schaefer, R. B. King, *J. Am. Chem. Soc.,* 2005, **127**, 2818-2819.

4 G. Allegra, G. Tettamanti Casagrande, A. Immirzi, L. Porri, G. Vitulli, *J. Am. Chem. Soc.,* 1970, **92**, 289-293.

5 C. A. Coulson, *J. Chim. Phys. Physicochim. Biol.,* 1948, **45**, U247-248.

6 P. Dowd, *J. Am. Chem. Soc.,* 1966, **88**, 2587-2589.

7 P. Dowd, K. Sachdev, *J. Am. Chem. Soc.,* 1967, **89**, 715-716.

8 J. H. Davis, W. A. Goddard III, *J. Am. Chem. Soc.,* 1976, **98**, 303-304.

9 Q. Fan, H. Feng, W. Sun, H. Li, Y. Xie, R. B. King, H. F. Schaefer, *New J. Chem.,* 2013, **37**, 1545-1553

10 G. F. Emerson, K. Ehrlich, W. P. Giering, P. C. Lauterbur, *J. Am. Chem. Soc.,* 1966, **88**, 3172-3173.

11 G. F. Emerson, L. Watts, R. Pettit, *J. Am. Chem. Soc.,* 1965, **87**, 131-133.

12 H. Reihlen, A. Gruhl, G. Hessling, O. Pfrengle, *Liebigs Ann. Chem.,* 1930, **482**, 161.

13 A. Almenningen, A. Haaland, K. Wahl, *Acta Chem. Scand.,* 1969, **23**, 1145-1150.

14 W. Tam, D. F. Eaton, J. C. Calabrese, I. D. Williams, Y. Wang, A. G. Anderson, *Chem. Mater.,* 1989, **1**, 128-140.

15 L. J. Farrugia, C. Evans, M. Tegel, *J. Phys. Chem. A* 2006, **110**, 7952-7961.

16 D. J. Tantillo, B. K. Carpenter, R. Hoffmann, *Organometallics* 2001, **20**, 4562-4564.

17 R. Aumann, J. Uphoff, *Angew. Chem. Int. Ed.,* 1987, **26**, 357-359.

18 R. S. Lokey, N. S. Mills, A. L. Rheingold, *Organometallics* 1989, **8**, 1803-1805.

19 G. E. Herberich, T. P. Spaniol, *J. Chem. Soc., Dalton Trans,*. 1993, 2471-2476.

20 G. C. Bazan, G. Rodriguez, B. P. Cleary, *J. Am. Chem. Soc.,* 1994, **116**, 2177-2178.

21 E. O. Fischer, P. Kuzel, H. P. Fritz, *Z. Naturforsch.,* 1961, **16b**, 138-139.

22 R. O. Jones, E. N. Maslen, *Z. Kristallogr*., 1966, **123**, 330-337.

23 M. R. Cook, P. Härter, P. L. Pauson, J. Šraga, *J. Chem. Soc., Dalton Trans.,* 1987, 2757-2760.

24 A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648-5652.

25 C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, **37**, 785-789.

26 A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098-3100.

27 J. P. Perdew, *Phys. Rev. B* 1986, **33**, 8822-8824.

28 M. Reiher, O. Salomon, B. A. Hess, *Theor. Chem. Acc.,* 2001, **107**, 48-55.

29 O. Salomon, M. Reiher, B. A. Hess, *J. Chem. Phys.,* 2002, **117**, 4729-4737.

30 Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.,* 2008, **120**, 215-241.

31 T. H. Dunning, *J. Chem. Phys.,* 1970, **53**, 2823-2833.

32 S. Huzinaga, *J. Chem. Phys.,* 1965, **42**, 1293-1302.

33 A. J. H. Wachters, *J. Chem. Phys.,* 1970, **52**, 1033-1036.

34 D. M. Hood, R. M. Pitzer, H. F. Schaefer, *J. Chem. Phys.* 1979, **71**, 705-712.

35 Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

36 *NBO 5.0.* E. D. Glendening, J, K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2001.

37 K. B. Wiberg, *Tetrahedron* 1968, **24**, 1083-1096.

38 H. Wang, Y. Xie, R. B. King, H. F. Schaefer, *Inorg. Chem.,* 2006, **45**, 3384-3392.

39 H. Wang, Y. Xie, R. B. King, H. F. Schaefer, *J. Am. Chem. Soc.,* 2005, **127**, 11646-11651.

40 H. Wang, Y. Xie, R. B. King, H. F. Schaefer, *Inorg. Chem.,* 2006, **45**, 5621-5629.

41 Q. C. Fan, H. Feng, W. G. Sun, Y. Zeng, Y. Xie, R. B. King, *Inorg. Chim. Acta.,* 2012, **388**, 22-32.

42 H. Wang, Y. Xie, R. B. King, H. F. Schaefer, *Organometallics* 2008, **27**, 3113-3123.

43 H. Wang, Y. Xie, R. B. King, H. F. Schaefer, Organometallics 2007, **26**, 1393-1401.

44 G. G. Sumner, H. P. Klug, L. E. Alexander, *Acta Cryst.,* 1964, **17**, 732-742.

45 P. C. Leung, P. Coppens, *Acta Cryst. B* 1983, **39**, 535-542.

46 D. Braga, F. Grepioni, P. Sabatino, A. Gavezzotti, *J. Chem. Soc. Dalton Trans.,* 1992, 1185-1191.

47 J. P. Kenny, R. B. King, H. F. Schaefer, *Inorg. Chem.,* 2001, **40**, 900-911.

48 J. V. Caspar, T. J. Meyer, *J. Am. Chem. Soc.,* 1980, **102**, 7794-7795.

49 R. H. Hooker, K. A. Mahmoud, A. J. Rest, *J. Chem. Soc., Chem. Commun.,* 1983, 1022-1024.

50 A. F. Hepp, J. P. Blaha, C. Lewis, M. S. Wrighton, Organometallics 1984, **3**, 174-177.

51 J. P. Blaha, B. E. Bursten, J. C. Dewan, R. B. Frankel, C. L. Randolph, B. A.Wilson, M. S. Wrighton, *J. Am. Chem. Soc.,* 1985, **107**, 4561-4562.

52 F. S. Stephens, *J. Chem. Soc., Dalton Trans.,* 1972, 1752-1754.

53 T. Y. Garcia, J. C. Fettinger, M. M. Olmstead, A. L. Balch, *Chem. Comm.,* 2009, 7143-7145.

54 R. Ponec, G. Lendvay, J. Chaves, *J. Comput. Chem.,* 2008, **29**, 1387-1398.

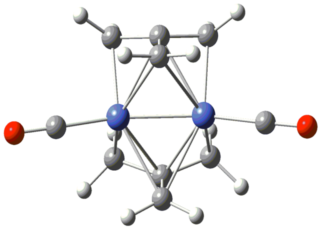
55 J. C. Green, M. L. H. Green, G. Parkin, *Chem. Commun.,* 2012, **48**, 11481-11503.

56 H. D. Murdoch, E. Weiss, *Helv. Chim. Acta,,* 1962, **137**, 1156-1161.

57 Y. Zeng, S. J. Wang, H. Feng, Y. Xie, R. B. King, H. F. Schaefer, *New J. Chem.,* 2011, **35**, 920-929.

58 L. S. Sunderlin, D. Wang, R. R. Squires, *J. Am. Chem. Soc.,* 1993, **115**, 12060-12070.

Table of Contents Figure



$[(CH_2)_3C]_2Co_2(CO)_2$