Tetrafluoroethylene Versus Trifluoromethylfluorocarbene Complexes of Cobalt Carbonyl

Jialuo He,^a Guoliang Li,^{*a,b,c} Qian-shu Li,^a Yaoming Xie,^c and R. Bruce King,^{*a,c}

^aMOE Key Laboratory of Theoretical Chemistry of the Environment, Center for Computational Quantum Chemistry, South China Normal University, Guangzhou 510006, P. R. China

^bGuangzhou Key Laboratory of Materials for Energy Conversion and Storage, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, P. R. China

^cDepartment of Chemistry and Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602, USA

e-mails: rbking@chem.uga.edu and glli@scnu.edu.cn

ABSTRACT

The reaction of tetrafluoroethylene with $\text{Co}_2(\text{CO})_8$ under mild conditions is reported to give $(\text{OC})_4\text{CoCF}_2\text{CF}_2\text{Co}(\text{CO})_4$. This compound readily undergoes decarbonylation with accompanying fluorine migration to give the trifluoromethylfluorocarbene complex $(\mu\text{-CF}_3\text{CF})\text{Co}_2(\text{CO})_6(\mu\text{-CO})$ and eventually the cluster $\text{CF}_3\text{CCo}_3(\text{CO})_9$. In order to understand the chemistry of these cobalt carbonyl complexes obtained from tetrafluoroethylene, the structures and thermochemistry of the $(\text{C}_2\text{F}_4)\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6, 5$) systems have been investigated by density functional theory. The lowest energy $(\text{C}_2\text{F}_4)\text{Co}_2(\text{CO})_8$ isomer is the experimentally observed $(\text{OC})_4\text{CoCF}_2\text{CF}_2\text{Co}(\text{CO})_4$, lying ~ 6 kcal/mol in energy below the isomeric $(\text{CF}_3\text{CF})[\text{Co}(\text{CO})_4]_2$. Loss of CO from $(\text{OC})_4\text{CoCF}_2\text{CF}_2\text{Co}(\text{CO})_4$ with accompanying fluorine migration to give $(\mu\text{-CF}_3\text{CF})\text{Co}_2(\text{CO})_6(\mu\text{-CO})$ is essentially thermoneutral within ~ 1 kcal/mol. The higher energy of ~ 20 kcal/mol for the isomeric $(\mu\text{-CF}_2\text{CF}_2)\text{Co}_2(\text{CO})_6(\mu\text{-CO})$ structure, where fluorine migration has not occurred, suggests a significant activation energy for this process. Further loss of CO from $(\mu\text{-CF}_3\text{CF})\text{Co}_2(\text{CO})_6(\mu\text{-CO})$ gives low-energy $(\mu\text{-CF}_3\text{CF})\text{Co}_2(\text{CO})_n(\mu\text{-CO})$ isomers ($n = 5, 4$) containing Co=Co multiple bonds and/or vacant coordination sites. Such structures are possible intermediates to form $\text{CF}_3\text{CCo}_3(\text{CO})_9$ by reaction with excess $\text{Co}_2(\text{CO})_8$ followed by $\text{Co}(\text{CO})_n\text{F}$ elimination.

Keywords: Tetrafluoroethylene, Trifluoromethylfluorocarbene, Cobalt carbonyls, Structures, Density functional theory

1. Introduction

The chemistry of metal-olefin complexes dates back nearly 200 years to the synthesis of the ethylene-platinum complex $K[(\eta^2-C_2H_4)PtCl_3]$ by Zeise in 1827. The nature of the olefin-metal bonding in this complex and subsequently discovered related metal-olefin complexes remained obscure for more than a century until Dewar [1] and Chatt [2] developed a model for the bonding of olefins to transition metals. This model was originally interpreted to include the following two components: (1) A σ -type bond involving donation of the electron pair in the carbon-carbon π -bond of the olefin to an empty metal hybrid orbital and (2) A π -type bond involving back donation of electron density from filled metal d orbitals into empty olefin π^* antibonding orbitals. In this way the olefin-metal bond may be considered as analogous to the metal-carbon bond in metal carbonyls, which also involves synergistic $C \rightarrow M$ forward σ -bonding and $M \rightarrow C$ π -back-bonding.

An important feature of metal carbonyl chemistry is the stabilization of low formal oxidation states by removal of metal electron density through the strong $M \rightarrow C$ back-bonding [3]. Thus binary zerovalent metal carbonyls such as $Cr(CO)_6$ and $Fe(CO)_5$ are stable species. Highly fluorinated olefins might also be expected to stabilize low formal oxidation states of transition metals, since the strongly electron-withdrawing fluorine atoms should enhance similar metal $\rightarrow$ ligand back-bonding. With this in mind Watterson and Wilkinson [4] investigated the reaction of $Fe_3(CO)_{12}$ with tetrafluoroethylene. The air-stable white crystalline product was originally formulated as $(C_2F_4)_2Fe(CO)_3$ and believed to be derived from $Fe(CO)_5$ by substitution of two CO groups with tetrafluoroethylene ligands. However, further study of this complex indicated that two tetrafluoroethylene ligands had coupled to form a ferracyclopentane derivative $(CF_2)_4Fe(CO)_4$ containing a five-membered C_4Fe ring [5,6].

Early workers, particularly Haszeldine and coworkers [7,8], also investigated the reaction of tetrafluoroethylene with $Co_2(CO)_8$. Under mild conditions the initial product is a yellow solid formulated as $(OC)_4CoCF_2CF_2Co(CO)_4$ in which each tetrafluoroethylene carbon atom forms a σ -bond to the cobalt atom of a $Co(CO)_4$ unit (Fig. 1). This solid reversibly loses CO under mild conditions to give a red product shown to be $(\mu-CF_3CF)Co_2(CO)_6(\mu-CO)$ in which a Co-Co bond is bridged both by a trifluoromethyl-fluorocarbene ligand and a CO group. In this process a fluorine atom migrates from one tetrafluoroethylene carbon to the other one to give the bridging trifluoromethyl-fluorocarbene ligand. This product is relatively stable, but upon reaction with excess

$\text{Co}_2(\text{CO})_8$, forms the dark purple cluster $\text{CF}_3\text{CCo}_3(\text{CO})_9$ containing a central Co_3C tetrahedron.

Fig. 1. The cobalt carbonyl derivatives obtained from reactions of $\text{Co}_2(\text{CO})_8$ with tetrafluoroethylene.

An interesting feature of the experimental observations on the $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ system is the facile migration of a fluorine atom from a bridging tetrafluoroethylene ligand in the octacarbonyl $\text{Co}_2(\text{CO})_8(\mu\text{-C}_2\text{F}_4)$ upon loss of a CO group to give a trifluoromethylfluorocarbene ligand in the heptacarbonyl $(\mu\text{-CF}_3\text{CF})\text{Co}_2(\text{CO})_6(\mu\text{-CO})$. We now report density functional theory studies on the structures and energetics of the $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6, 5$) systems. These include not only the experimentally known $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7$) systems but also the unsaturated $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ and $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_5$ systems suggested by the 18-electron rule to be candidates for systems with formal double and triple cobalt-cobalt bonds, respectively. Such species may be relevant as intermediates for the formation of the $\text{CF}_3\text{CCo}_3(\text{CO})_9$ cluster (Fig. 1) from tetrafluoroethylene and $\text{Co}_2(\text{CO})_8$ under relatively vigorous conditions.

2. Theoretical Methods

Electron correlation effects have been included to some degree using density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds [9-15]. This research used three DFT methods. The B3LYP method is an HF/DFT hybrid method combining Becke's three-parameter functional [16] with the Lee-Yang-Parr generalized gradient correlation functional [17]. The BP86 method is a pure DFT method combining Becke's 1988 exchange functional [18] with Perdew's 1986 gradient correlation functional [19]. The newer generation M06-L method uses a meta-GGA functional proposed by Zhao and Truhlar [20]. The M06-L method appears particularly suitable for applications in transition metal chemistry [21,22]. Since the three DFT methods predict similar results in the present work, we discuss mainly the M06-L results in the text. The B3LYP and BP86 results are listed in the Supporting Information.

All-electron double- ζ plus polarization (DZP) sets were used. For carbon, oxygen, and fluorine atoms, the DZP basis sets are obtained from Huzinaga-Dunning-Hay [23-25] contracted double- ζ Gaussian basis sets by adding a set of pure spherical harmonic d-like polarization functions with orbital exponents $\alpha_d(\text{C}) = 0.75$, $\alpha_d(\text{O}) = 0.85$, and $\alpha_d(\text{F}) = 1.0$ using the contraction scheme (9s5p1d/4s2p1d). For cobalt, the DZP basis set, designated as (14s11p6d/10s8p3d), uses the Wachters' primitive set [26] augmented by two sets of p functions and one set of d functions and contracted following Hood, Pitzer and Schaefer [27].

The $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6, 5$) structures were fully optimized using the B3LYP/DZP, BP86/DZP, and M06-L/DZP methods. Harmonic vibrational frequency analyses were also carried out at the same levels. All computations were carried out using the Gaussian 09 program [28].

For each $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6, 5$) system, both tetrafluoroethylene and trifluoromethylfluorocarbene structures were optimized considering both singlet and triplet spin state structures. All of the triplet structures were found to have higher energies than the corresponding singlet structures, so only the singlet structures are considered in detail in this paper. Figures 2 to 5 depict the optimized $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ geometries and their relative energies. All of the $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ structures are designated as **nS-m**, where **n** is the number of CO groups, **m** orders the structures according to their relative energies, and **S** refers to the singlet spin state.

3. Results and Discussion

3.1. $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$

A direct cobalt-cobalt bond in the octacarbonyl $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ is not required to give each cobalt atom the favored 18-electron configuration since $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ has an additional C_2F_4 ligand relative to the well-known saturated $\text{Co}_2(\text{CO})_8$ complex [29-32]. The C_2F_4 group has two isomeric structures, namely tetrafluoroethylene, $-\text{CF}_2-\text{CF}_2-$, and trifluoromethylfluorocarbene, $:\text{C}(\text{F})(\text{CF}_3)$. **The energy difference between the free $\text{F}_2\text{C}=\text{CF}_2$ and $:\text{C}(\text{F})-\text{CF}_3$ ligands is 41.4 kcal/mol, with the former being much more stable.** Connecting two $\text{Co}(\text{CO})_4$ units with a $-\text{CF}_2-\text{CF}_2-$ tetrafluoroethylene or a $:\text{C}(\text{F})(\text{CF}_3)$ trifluoromethylfluorocarbene bridge gives three low-energy singlet $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ structures **8S-1**, **8S-2**, and **8S-3** (Fig. 2). The *trans*-tetrafluoroethylene structure **8S-1** is the lowest energy isomer, with the *cis*-tetrafluoroethylene structure **8S-2** lying 5.3 kcal/mol above **8S-1**. The trifluoromethylfluorocarbene structure **8S-3** has a somewhat higher energy (6.4 kcal/mol) than **8S-1**. This is consistent with the assignment based on the ^{19}F NMR

spectrum of a $(\text{OC})_4\text{CoCF}_2\text{CF}_2\text{Co}(\text{CO})_4$ structure for $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ corresponding to **8S-1** or **8S-2** [8]. The structure of $(\text{OC})_4\text{CoCF}_2\text{CF}_2\text{Co}(\text{CO})_4$ apparently has not been determined by X-ray crystallography. The predicted long $\text{Co}\cdots\text{Co}$ distances of 5.009 Å in **8S-1**, 4.109 Å in **8S-2**, and 3.616 Å in **8S-3**, are consistent with the absence of a direct Co-Co bond. However, all cobalt atoms in these structures nevertheless have the favored 18-electron configurations.

Fig. 2. Three optimized $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ structures. In Figures 2 to 5, all of the distances are reported in Å and the numbers under each structure are the relative energies (in kcal/mol) given by the M06-L/DZP method.

3.2. $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$

In contrast to the octacarbonyl $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$, the two lowest energy structures of the heptacarbonyl $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ are the C_s structures **7S-1** and **7S-2** having a bridging trifluoromethylfluorocarbene group (Fig. 3), with **7S-2** being energetically higher by only 2.1 kcal/mol. In addition to the bridging $\mu\text{-CF}_3\text{CF}$ ligand, **7S-1** and **7S-2** also have a bridging $\mu\text{-CO}$ group and direct Co-Co bonds of lengths 2.458 and 2.465 Å, respectively, both of which can be considered as formal single bonds. Thus, in both **7S-1** and **7S-2**, each

cobalt atom has the favored 18-electron configuration. Structures **7S-1** and **7S-2** may be derived from the familiar doubly bridged $\text{Co}_2(\text{CO})_8$ structure by replacing one of the bridging CO groups with a bridging CF_3CF group. However, the Co–Co distances of $\sim 2.46 \text{ \AA}$ in **7S-1** or **7S-2** are significantly shorter than the experimental Co–Co distance of $2.53 \text{ \AA}$ in the doubly bridged $\text{Co}_2(\text{CO})_8$ isomer as determined by X-ray crystallography [30]. The difference between the $(\mu\text{-CF}_3\text{CF})\text{Co}_2(\text{CO})_6(\mu\text{-CO})$ structures **7S-1** and **7S-2** is the orientation of the CF_3 group in their bridging $\mu\text{-CF}_3\text{CF}$ ligand relative to their bridging $\mu\text{-CO}$ group. Our results herein are consistent with the experimental observation from the 1:3 relative intensity pattern in the ^{19}F NMR spectrum indicating that $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ has a bridging CF_3CF group rather than a bridging tetrafluoroethylene ligand [8].

Fig. 3. Three optimized $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ structures.

The third $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ tetrafluoroethylene structure **7S-3** lies 18.6 kcal/mol in energy above **7S-1** (Fig. 3). In **7S-3**, the two $\text{Co}(\text{CO})_3$ fragments are connected by a bridging $-\text{CF}_2\text{-CF}_2-$ tetrafluoroethylene group, a bridging CO group, and a Co–Co bond of length $2.551 \text{ \AA}$, which is interpreted as a formal single bond. Thus, in **7S-3** both cobalt

atoms also have the favored 18-electron configuration. The Co–Co bond in **7S-3** is ~ 0.1 Å longer than those in **7S-1** and **7S-2**, apparently because of the different geometries of the $-\text{CF}_2\text{CF}_2-$ and $:\text{C}(\text{F})(\text{CF}_3)$ bridges.

3.3. $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$

The hexacarbonyl $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$, like the heptacarbonyl $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$, has two low-energy trifluoromethylfluorocarbene stereoisomers **6S-1** and **6S-2** lying within ~ 1 kcal/mol in energy (Fig. 4). The corresponding tetrafluoroethylene isomer **6S-3** is a relatively high-energy structure at 15.9 kcal/mol in energy above **6S-1**. All three $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ structures can be generated from the corresponding $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ structures by removal of a terminal CO group. Thus, both structures **6S-1** and **6S-2** have their two cobalt atoms connected by a bridging $:\text{C}(\text{F})(\text{CF}_3)$ trifluoromethylfluorocarbene group and a bridging CO group, while in **6S-3** the two cobalt atoms are connected by a bridging $-\text{CF}_2\text{CF}_2-$ tetrafluoroethylene group and a bridging CO group.

Fig. 4. Three optimized $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ structures.

The Co=Co distances in **6S-1** and **6S-2** are 2.393 and 2.365 Å, respectively, while in **6S-3** the cobalt-cobalt distance is 2.464 Å. These Co=Co distances are ~0.07 to 0.10 Å shorter than those in corresponding $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ structures, so they all can be considered as the formal double bonds required to give each cobalt atom the favored 18-electron configuration. However, the unsymmetrical distribution of the terminal CO groups on the cobalt atoms in each of these $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ structures means that the cobalt atom bonded to three terminal CO groups bears a formal positive charge and the cobalt atom bonded to only two terminal CO groups bears a formal negative charge.

3.4. $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_5$

Four low-energy singlet structures were found for the pentacarbonyl $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_5$, namely the trifluoromethylfluorocarbene structures **5S-1** and **5S-2** and the tetrafluoroethylene structures **5S-3** and **5S-4** (Fig. 5). Structures **5S-1**, **5S-2**, and **5S-4** can be derived from the $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ structures **6S-1**, **6S-2**, and **6S-3**, respectively, by removing a terminal CO group from the cobalt atom bearing three terminal CO groups. Thus, both **5S-1** and **5S-2** have their two cobalt atoms connected by a bridging $:\text{C}(\text{F})(\text{CF}_3)$ trifluoromethylfluorocarbene group and a bridging CO group, while in **5S-4** the two cobalt atoms are connected by a $-\text{CF}_2\text{CF}_2-$ tetrafluoroethylene bridge and a CO bridge. However, using the M06-L method for the optimization of the tetrafluoroethylene structure **5S-4** led to another tetrafluoroethylene structure **5S-3**, in which the tetrafluoroethylene group is bonded to only one cobalt atom and the two cobalt atoms are connected with two bridging CO groups. **This is consistent with the fact that the M06-L method favors π -bond structures over σ -bond structures whenever there is a reasonable energetic choice.** Again, the trifluoromethylfluorocarbene structures **5S-1** and **5S-2** have lower energies, with the tetrafluoroethylene structures **5S-3** and **5S-4** lying **13.0 and 18.6 kcal/mol (B3LYP), respectively**, above **5S-1**. The cobalt-cobalt distances in **5S-1**, **5S-2**, and **5S-3** of ~2.3 Å and in **5S-4** of ~2.4 Å, are all shorter than those of the Co=Co double bonds in the corresponding $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ structures. Although interpretation of the Co≡Co interactions as formal triple bonds might be reasonable based on the shorter distances, the difference of only ~0.1 Å between these distances in otherwise equivalent $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ and $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_5$ structures is relatively small. An alternative interpretation of the Co=Co bonds in the pentacarbonyl $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_5$ structures as formal double bonds with one of the cobalt atoms having only a 16-electron configuration seems reasonable in view of an apparent gap in the coordination sphere on

one of the cobalt atoms. Such a gap is apparent on the right-hand cobalt atom in structures **5S-1**, **5S-2**, and **5S-3** as depicted in Fig. 5.

Fig. 5. Four optimized $C_2F_4Co_2(CO)_5$ structures. The distances and the relative energies for structure **5S-4** are given by the B3LYP/DZP method. Using the M06-L method, the optimization of **5S-4** leads to **5S-3** (see text).

3.5. The $\nu(CO)$ and $\nu(CF)$ vibrational frequencies

Table 1 lists the harmonic vibrational $\nu(CO)$ and $\nu(CF)$ frequencies for the $C_2F_4Co_2(CO)_n$ ($n = 8, 7, 6, 5$) complexes obtained by the BP86 method, which has been shown to approximate more closely the experimental results than other DFT methods [33,34] and thus are discussed below. All of the terminal $\nu(CO)$ frequencies for all $C_2F_4Co_2(CO)_n$ ($n = 8, 7, 6, 5$) structures fall in the expected 1992 to 2088 cm^{-1} range. The bridging $\nu(CO)$ frequencies, ranging from 1880 to 1901 cm^{-1} , are more than 90 cm^{-1} lower than the terminal $\nu(CO)$ frequencies, which is typical for metal carbonyl derivatives. The $\nu(CF)$ frequencies are predicted to be much lower from 966 to 1144 cm^{-1} .

Table 1 The $\nu(\text{CO})$ and $\nu(\text{CF})$ vibrational frequencies (in cm^{-1}) and infrared intensities (in km/mol , given in parentheses) of the $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6, 5$) complexes at the BP86/DZP level of theory.

Structure	$\nu(\text{CO})^a$	$\nu(\text{CF})$ and $\nu(\text{CC})^b$
8S-1	2010(0), 2016(0), 2018(1741), 2019(1345), 2021(868), 2023(0), 2076(709), 2088(0)	913(0), 1039(227), 1041(0), 1051(195), 1122(0)
Exp.^c	2008s, 2016m, 2050vs, 2055s, 2087s, 2110m, 2116s	1050s
8S-2	2001(297), 2005(1099), 2021(1029), 2022(0), 2026(576), 2026(926), 2078(452), 2088(48)	912(133), 990(4), 1024(38), 1043(215), 1085(236)
8S-3	1992(258), 2002(593), 2016(524), 2017(1254), 2019(209), 2022(707), 2068(820), 2085(30)	834(73), 974(90), 1084(97), 1123(150), 1162(175)
7S-1	<i>1880(415)</i> , 2017(4), 2018(8), 2026(1077), 2029(1215), 2052(1322), 2084(77)	889(122), 1042(144), 1095(120), 1136(222), 1201(196)
Exp.^c	<i>1866</i> , 2019m, 2060vs, 2067vs, 2087vs, 2119m, 2122s	912s, 1010s, 1026s, 1136s, 1177s, 1256s
7S-2	<i>1881(444)</i> , 2013(1), 2020(0), 2024(1011), 2028(1308), 2052(1327), 2083(58)	904(139), 1012(137), 1104(131), 1132(191), 1213(211)
7S-3	<i>1880(421)</i> , 2015(11), 2017(12), 2030(828), 2032(1177), 2054(1309), 2085(136)	887(258), 1000(81), 1052(81), 1080(152), 1188(324)
6S-1	<i>1896(434)</i> , 2005(458), 2021(578), 2025(827), 2038(1407), 2076(158)	909(133), 1034(158), 1094(112), 1134(199), 1216(214)
6S-2	<i>1898(460)</i> , 2006(441), 2016(622), 2024(815), 2039(1450), 2075(120)	902(108), 1059(158), 1101(136), 1118(138), 1207(305)
6S-3	<i>1893(446)</i> , 2006(214), 2019(602), 2025(711), 2041(1426), 2076(227)	899(240), 1002(82), 1059(80), 1076(169), 1201(353)
5S-1	<i>1883(517)</i> , 1995(379), 2005(1071), 2022(1679), 2055(59)	897(102), 1062(174), 1099(123), 1144(194), 1205(202)
5S-2	<i>1883(532)</i> , 1992(407), 2005(1013), 2021(1733), 2054(55)	904(116), 1063(149), 1111(133), 1132(169), 1209(241)
5S-3	<i>1887(515)</i> , <i>1901(406)</i> , 2006(676), 2024(1646), 2055(247)	751(164), 1048(170), 1161(157), 1170(85), 1410(444)
5S-4	<i>1881(465)</i> , 2004(359), 2009(711), 2028(1437), 2063(350)	820(160), 966(124), 1074(81), 1118(155), 1207(395)

^a The *italic* font means a bridging CO group.

^b The smallest and the largest frequencies in this column are the mixtures of the C-C bond vibration and the C-F bond vibrations.

^c Ref. [8].

3.6. Thermochemistry

Table 2 reports the carbonyl dissociation energies for the following processes:

Table 2 Energies (kcal/mol) for carbonyl dissociation of the lowest-energy $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6$) structures. (a) Classical dissociation energy ΔE ; (b) $\Delta E + \text{ZPVE}$ (zero-point vibrational energy corrections); (c) ΔG_{298} : Gibbs free dissociation energy at 298.15 K.

	M06-L/DZP		
	ΔE	$\Delta E + \text{ZPVE}$	ΔG_{298}
$\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ (8S-1) $\rightarrow$ $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ (7S-1) + CO	1.3	-0.1	-11.3
$\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ (8S-1) $\rightarrow$ $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ (7S-3) + CO	19.9	18.3	7.8
$\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ (7S-1) $\rightarrow$ $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ (6S-1) + CO	29.5	27.3	16.7
$\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ (6S-1) $\rightarrow$ $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_5$ (5S-1) + CO	36.8	34.2	23.6
	BP86/DZP		
	ΔE	$\Delta E + \text{ZPVE}$	ΔG_{298}
$\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ (8S-1) $\rightarrow$ $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ (7S-1) + CO	4.0	2.6	-6.8
$\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ (8S-1) $\rightarrow$ $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ (7S-3) + CO	21.1	19.4	10.4
$\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ (7S-1) $\rightarrow$ $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ (6S-1) + CO	28.4	26.1	15.3
$\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ (6S-1) $\rightarrow$ $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_5$ (5S-1) + CO	37.4	34.8	24.5
	B3LYP/DZP		
	ΔE	$\Delta E + \text{ZPVE}$	ΔG_{298}
$\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ (8S-1) $\rightarrow$ $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ (7S-1) + CO	6.9	5.7	-3.7
$\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ (8S-1) $\rightarrow$ $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ (7S-3) + CO	24.1	22.5	13.4
$\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ (7S-1) $\rightarrow$ $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ (6S-1) + CO	22.7	20.5	9.9
$\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ (6S-1) $\rightarrow$ $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_5$ (5S-1) + CO	32.0	29.4	18.8

The dissociation energy for the loss of one CO group from $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ (**8S-1**) to give $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ (**7S-1**), in which a fluorine migration has occurred to convert a CF_2CF_2 bridge to a CF_3CF bridge, is only 1.3 kcal/mol (M06-L), 4.0 kcal/mol (BP86), or 6.9 kcal/mol (B3LYP), suggesting that this process is essentially thermoneutral. However, the CO dissociation energy to convert $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ (**8S-1**) to the higher energy $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ isomer **7S-3**, retaining the CF_2CF_2 bridge without fluorine migration, is appreciable at 19.9 kcal/mol (M06-L), 21.1 kcal/mol (BP86), or 24.1 kcal/mol (B3LYP). This provides an estimate of the significant activation energy to convert **8S-1** to **7S-1** and thus can account for the ability to isolate **8S-1** under ambient conditions. However, the near thermoneutrality of the loss of one CO group from **8S-1** to **7S-1** is consistent with the experimentally observed facile conversion of $(\text{OC})_4\text{CoCF}_2\text{CF}_2\text{Co}(\text{CO})_4$ to $(\mu\text{-CF}_3\text{CF})\text{Co}_2(\text{CO})_6(\mu\text{-CO})$ in essentially quantitative yield by removing the liberated CO in vacuum at $\sim 40^\circ\text{C}$ [8]. In contrast to $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_8$ (**8S-1**), the carbonyl dissociation energies for the lowest energy $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ and $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ isomers are substantial at 29.5 and 36.8 kcal/mol (M06-L), 28.4 and 37.4 kcal/mol (BP86), or 22.7 and 32.0 kcal/mol

(B3LYP). These are comparable to the experimental dissociation energies of 27, 41, and 37 kcal/mol for $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Cr}(\text{CO})_6$, respectively [35], suggesting the viability of both $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ and $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_6$ toward CO dissociation. The zero-point vibrational energy (ZPVE) corrections decrease the carbonyl dissociation energies of the lowest-energy $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6$) structures by ~ 2 kcal/mol (Table 2). Table 2 also shows that the Gibbs free energy changes at 298.15 K for the carbonyl dissociation of the lowest-energy $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6$) structures are lower the corresponding electronic energy changes by 10~12 kcal/mol. This may be caused by the entropy increases of these dissociation processes.

3.7. Natural Bond Orbital (NBO) Analysis

Table 3. The Wiberg bond indices (WBI) of the Co-Co bonds by natural bond orbital (NBO) analysis for the optimized singlet $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6, 5$) structures.

Structure	Co-Co (Å)	Formal bond order	WBI (Co-Co)
8S-1	5.009	0	0.02
8S-2	4.109	0	0.01
8S-3	3.616	0	0.03
7S-1	2.458	1	0.12
7S-2	2.465	1	0.11
7S-3	2.551	1	0.11
6S-1	2.394	2	0.15
6S-2	2.365	2	0.12
6S-3	2.464	2	0.13
5S-1	2.324	2	0.21
5S-2	2.324	2	0.20
5S-3	2.302	2	0.17

Table 3 lists the Wiberg bond indices (WBIs) for the cobalt-cobalt interactions in the singlet $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6, 5$) derivatives. The WBI values were found to be relatively small compared with the formal bond orders. This is a consequence of the delocalization of the cobalt-cobalt interactions through multicenter bonding as studied by Ponec using domain averaged Fermi holes [36] and subsequently discussed by Green, Green, and Parkin [37]. For example, the WBI for the formal Fe–Fe single bond in triply bridged $\text{Fe}_2(\text{CO})_9$ was found to be only 0.11 [38]. In the present study, the WBI values for the analogous formal Co–Co single bonds in the $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_7$ structures were similarly

low, ranging from 0.11 to 0.12. The WBIs for the Co=Co double bonds in the $C_2F_4Co_2(CO)_6$ and $C_2F_4Co_2(CO)_5$ structures were found to be from 0.12 to 0.21, which are roughly twice of those for the Co–Co single bond. The WBIs for the absence of bonding in the $C_2F_4Co_2(CO)_8$ structures were found to be <0.03 . Generally, the relative WBI values are consistent with the bond orders assigned based on the cobalt-cobalt distances and electron counting.

4. Conclusions

The lowest energy $(C_2F_4)Co_2(CO)_8$ isomer is the experimentally observed $(OC)_4CoCF_2CF_2Co(CO)_4$ structure **8S-1** with two $Co(CO)_4$ units bridged by a $-CF_2CF_2-$ tetrafluoroethylene unit in which each $Co(CO)_4$ unit is bonded to a different carbon atom. The isomeric $(CF_3CF)[Co(CO)_4]_2$ structure is energetically less favorable by ~ 6 kcal/mol, presumably because of steric hindrance from two $Co(CO)_4$ units bonded to the same carbon atom.

A feature of the known $(OC)_4CoCF_2CF_2Co(CO)_4$ octacarbonyl structure is the facility of CO loss to give a heptacarbonyl $(\mu-CF_3CF)Co_2(CO)_6(\mu-CO)$ isomer in which fluorine migration has occurred to convert a CF_2CF_2 ligand into a CF_3CF ligand. This process, as modeled by the CO dissociation from **8S-1** to **7S-1**, is essentially thermoneutral, predicted to require only ~ 1 kcal/mol in energy. However, this process appears to have a significant activation energy of ~ 20 kcal/mol as indicated by the higher energy of the $(\mu-CF_2CF_2)Co_2(CO)_6(\mu-CO)$ structure **7S-3**, containing an intact bridging CF_2CF_2 ligand.

Further loss of CO from $(\mu-CF_3CF)Co_2(CO)_6(\mu-CO)$ gives low-energy $(\mu-CF_3CF)Co_2(CO)_n(\mu-CO)$ isomers ($n = 5, 4$) containing Co=Co multiple bonds and/or vacant coordination sites. These are well-situated to bind to an additional $Co_2(CO)_8$ molecule, either by addition to a Co=Co multiple bond or a vacant cobalt coordination site. Elimination of $Co(CO)_4F$ from the resulting tetranuclear cobalt complex of stoichiometry $(\mu-CF_3CF)Co_4(CO)_{14}$ would give a species $CF_3CCo_3(CO)_{10}$. Such a species could readily lose a CO group with formation of an additional Co–Co bond to lead to the observed very stable Co_3C tetrahedral cluster $CF_3CCo_3(CO)_9$. A process of this type can account for the experimentally observed [8] formation of $CF_3CCo_3(CO)_9$ upon treatment of $(\mu-CF_3CF)Co_2(CO)_6(\mu-CO)$ with excess $Co_2(CO)_8$.

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Supporting Information

Table S1: Total energies and relative energies for optimized low-energy structures of the $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6, 5$) complexes at the M06-L/DZP, B3LYP/DZP and BP86/DZP levels; Table S2: Vibrational frequencies and infrared intensities for optimized low-energy structures of the $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6, 5$) complexes at the BP86/DZP level; Table S3: Cartesian coordinates for optimized low-energy structures of the $\text{C}_2\text{F}_4\text{Co}_2(\text{CO})_n$ ($n = 8, 7, 6, 5$) complexes at the M06-L/DZP, B3LYP/DZP and BP86/DZP levels; complete Gaussian 09 reference.

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