Tetrafluoroethylene versus trifluoromethylfluorocarbene complexes of cobalt carbonyl

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A B S T R A C T

The reaction of tetrafluoroethylene with $Co_2(CO)_8$ under mild conditions was reported to give $(OC)_4CoCF_2CF_2Co(CO)_4$. This compound readily undergoes decarbonylation with accompanying fluorine migration to give the trifluoromethylfluorocarbene complex $(\mu-CF_3CF)Co_2(CO)_6(\mu-CO)$ and eventually the cluster $CF_3CCo_3(CO)_9$. In order to understand the chemistry of these cobalt carbonyl complexes obtained from tetrafluoroethylene, the structures and thermochemistry of the $(C_2F_4)Co_2(CO)_n$ ($n = 8, 7, 6, 5$) systems have been investigated by density functional theory. The lowest energy $(C_2F_4)Co_2(CO)_8$ isomer is the experimentally observed $(OC)_4CoCF_2CF_2Co(CO)_4$, lying ~6 kcal/mol in energy below the isomeric $(CF_3CF)[Co(CO)_4]_2$. Loss of CO from $(OC)_4CoCF_2CF_2Co(CO)_4$ with accompanying fluorine migration to give $(\mu-CF_3CF)Co_2(CO)_6(\mu-CO)$ is essentially thermoneutral within ~1 kcal/mol. The higher energy of ~20 kcal/mol for the isomeric $(\mu-CF_2CF_2)Co_2(CO)_6(\mu-CO)$ structure, where fluorine migration has not occurred, suggests a significant activation energy for this process. 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. Such structures are possible intermediates to form $CF_3CCo_3(CO)_9$ by reaction with excess $Co_2(CO)_8$ followed by $Co(CO)_nF$ elimination.

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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→M forward σ-bonding and M→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→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→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 $(\mu\text{-}CF_3CF)Co_2(CO)_6(\mu\text{-}CO)$ in which a Co—Co bond is bridged both by a trifluoromethylfluorocarbene ligand and a CO group. In this process a fluorine atom migrates from one tetrafluoroethylene carbon to the other one to give the bridging trifluoromethylfluorocarbene ligand. This product is relatively stable, but upon reaction with excess $Co_2(CO)_8$, forms the dark purple cluster $CF_3CCo_3(CO)_9$ containing a central Co_3C tetrahedron.

An interesting feature of the experimental observations on the $C_2F_4Co_2(CO)_n$ system is the facile migration of a fluorine atom from a bridging tetrafluoroethylene ligand in the octacarbonyl $Co_2(CO)_8(\mu\text{-}C_2F_4)$ upon loss of a CO group to give a trifluoromethylfluorocarbene ligand in the heptacarbonyl $(\mu\text{-}CF_3CF)$ $Co_2(CO)_6(\mu\text{-}CO)$. We now report density functional theory studies on the structures and energetics of the $C_2F_4Co_2(CO)_n$ ($n = 8, 7, 6, 5$) systems. These include not only the experimentally known $C_2F_4Co_2(CO)_n$ ($n = 8, 7$) systems but also the unsaturated $C_2F_4Co_2(CO)_6$ and $C_2F_4Co_2(CO)_5$ 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 $CF_3CCo_3(CO)_9$ cluster (Fig. 1) from tetrafluoroethylene and $Co_2(CO)_8$ 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 $\alpha_d(C) = 0.75$,

$\alpha_d(O) = 0.85$, and $\alpha_d(F) = 1.0$ 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 $C_2F_4Co_2(CO)_n$ ($n = 8, 7, 6, 5$) 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 $C_2F_4Co_2(CO)_n$ ($n = 8, 7, 6, 5$) 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. Figs. 2 to 5 depict the optimized $C_2F_4Co_2(CO)_n$ geometries and their relative energies. All of the $C_2F_4Co_2(CO)_n$ 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. $C_2F_4Co_2(CO)_8$

A direct cobalt-cobalt bond in the octacarbonyl $C_2F_4Co_2(CO)_8$ is not required to give each cobalt atom the favored 18-electron configuration since $C_2F_4Co_2(CO)_8$ has an additional C_2F_4 ligand relative to the well-known saturated $Co_2(CO)_8$ complex [29–32]. The C_2F_4 group has two isomeric structures, namely tetrafluoroethylene, $-CF_2-CF_2-$, and trifluoromethylfluorocarbene, $:C(F)(CF_3)$. The energy difference between the free $F_2C=CF_2$ and $:C(F)-CF_3$ ligands is 41.4 kcal/mol, with the former being much more stable. Connecting two $Co(CO)_4$ units with a $-CF_2-CF_2-$ tetrafluoroethylene or a $:C(F)(CF_3)$ trifluoromethylfluorocarbene bridge gives three low-energy singlet $C_2F_4Co_2(CO)_8$ 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 $(OC)_4CoCF_2CF_2Co(CO)_4$ structure for $C_2F_4Co_2(CO)_8$ corresponding to **8S-1** or **8S-2** [8]. The structure of $(OC)_4CoCF_2CF_2Co(CO)_4$ apparently has not been determined by X-ray crystallography. The predicted long $Co{\cdots}Co$ 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.

3.2. $C_2F_4Co_2(CO)_7$

In contrast to the octacarbonyl $C_2F_4Co_2(CO)_8$, the two lowest energy structures of the heptacarbonyl $C_2F_4Co_2(CO)_7$ are the C_s
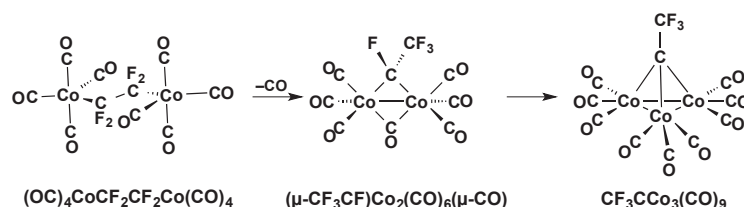
Fig. 1. The cobalt carbonyl derivatives obtained from reactions of $Co_2(CO)_8$ with tetrafluoroethylene.