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Perfluoroolefin Complexes Versus Perfluorometallacycles and Perfluorocarbene Complexes in Cyclopentadienylcobalt Chemistry

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Abstract

Fluorocarbons have been shown experimentally by Baker and coworkers to combine with the cyclopentadienylcobalt (CpCo) moiety to form fluoroolefin and fluorocarbene complexes as well as fluorinated cobaltacyclic rings. In this connection density functional theory (DFT) studies on the cyclopentadienylcobalt fluorocarbon complexes CpCo(L)(C_nF_{2n}) (L = CO, PMe_3; n = 3, 4) indicate structures with perfluoroolefin ligands to be the lowest energy structures followed by perfluorometallacycle structures and finally by structures with perfluorocarbene ligands. Thus, for the CpCo(L)(C_3F_6) (L = CO, PMe_3) complexes, the perfluoropropene structure has the lowest energy, followed by the perfluorocobaltacyclobutane structure and the perfluoroisopropylidene structure less stable by 8 to 11 kcal/mol, and the highest energy perfluoropropylidene structure less stable by more than 12 kcal/mol. For the two metal carbene structures Cp(L)Co=C(CF_3)$_2$ and Cp(L)Co=CF(C_2F_5), the former is more stable than the latter, even though the latter has Fischer carbene character. For the CpCo(L)(C_4F_8) (L = CO, PMe_3) complexes, the perfluoroolefin complex structures have the lowest energies, followed by the perfluorometallacycle structures at 10 to 20 kcal/mol, and the structures with perfluorocarbene ligands at yet higher energies more than 20 kcal/mol above the lowest energy structure. This is consistent with the experimentally observed isomerization of the perfluorinated cobaltacyclobutane complexes CpCo(PPh_2Me)(–CFR–CF_2–CF_2–) (R = F, CF_3) to the perfluoroolefin complexes CpCo(PPh_2Me)(RCF=CF_2) in the presence of catalytic quantities of HN(SO_2CF_3)$_2$. Further refinement of the relative energies by the state-of-the-art DLPNO-CCSD(T) method gives results essentially consistent with the DFT results summarized above.

1. Introduction

An important feature of transition metal coordination chemistry is the stabilization of low formal metal oxidation states by transfer of metal electron density into ligand antibonding orbitals through strong back-bonding.[1] Carbon monoxide is the classical strong back-bonding ligand leading, for example, to stable homoleptic derivatives of most of the central transition metals, as exemplified by $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, $Co_2(CO)_8$, and $Ni(CO)_4$ in the first-row transition metal series. Unsaturated fluorocarbons would appear to provide other examples of strong back-bonding ligands attracting electron density from a transition metal into ligand π^*-antibonding orbitals, because of the high electronegativity of fluorine. Such considerations led to early investigations of reactions of tetrafluoroethylene with metal carbonyls in the 1960s, when X-ray determinations of molecular structures were far from routine. The stable white crystalline product of stoichiometry $C_4F_8Fe(CO)_4$ from tetrafluoroethylene and $Fe_3(CO)_{12}$ was initially believed to be such a perfluoroolefin complex $(C_2F_4)_2Fe(CO)_3$ considered to be a substitution product of $Fe(CO)_5$ with two carbonyl groups replaced by tetrafluoroethylene ligands.[2] However, it was soon shown to be a perfluorinated ferracyclopentane metallacycle (Figure 1).[3,4] The stabilization of the two Fe–C σ-bonds of the FeC_4 metallocycle ring by Fe$\rightarrow$C back bonding into the π^*-antibonding orbitals of the C–F bond labilizes the fluorine atoms on the carbon atoms directly bonded to the iron atom through "no-bond" resonance structures (Figure 2). On the other hand, as pointed out by Grushin et al. in their review article, more recent studies have reported rather weak π-acceptor properties of CF_3 ligands so that back-bonding into the C-F σ-anti-bonding orbitals is suggested to play a minor role compared to electrostatic effects.[5]

The reaction of tetrafluoroethylene with $Co_2(CO)_8$ was also found not to give a fluoroolefin complex.[6,7] Instead an adduct $(OC)_4CoCF_2CF_2Co(CO)_4$ was formed in which a tetrafluoroethylene unit adds across the Co–Co bond of $Co_2(CO)_8$ by the formation of two Co–C σ-bonds (Figure 1). This dicobalt derivative is thus related to the trifluoromethyl derivative $CF_3Co(CO)_4$, which is a stable liquid distillable at ~100°C in contrast to the unstable hydrocarbon analogue $CH_3Co(CO)_4$.[8] Under mild conditions $(OC)_4CoCF_2CF_2Co(CO)_4$ loses CO with concurrent fluorine migration to give $(\mu\text{-}CF_3CF)Co_2(CO)_6(\mu\text{-}CO)$, which under further heating undergoes a more drastic transformation to give the trinuclear $(\mu_3\text{-}CF_3C)Co_3(CO)_9$ with a trifluoromethylcarbyne ligand bridging a Co_3 triangle.

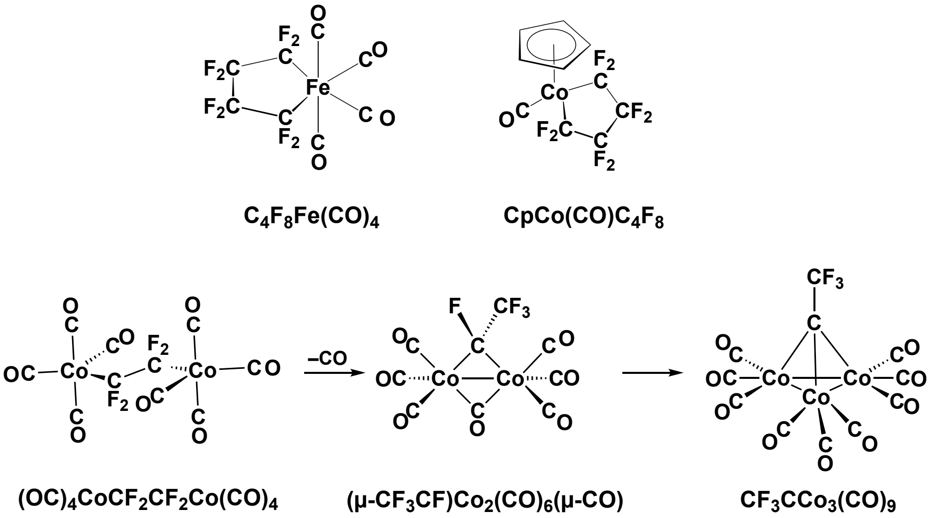


Figure 1. Iron and cobalt carbonyl derivatives obtained from tetrafluoroethylene.

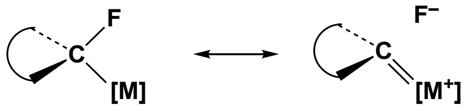


Figure 2. Strengthening of the metal-carbon bond and weakening of the carbon-fluorine bond through a "no-bond" resonance structure with a metal-carbon double bond.

The cyclopentadienylcobalt unit CpCo (Cp = η^5-C_5H_5) is isoelectronic with the $Fe(CO)_3$ unit, suggesting a certain analogy between cyclopentadienylcobalt derivatives and iron carbonyls. In this connection $CpCo(CO)_2$ was reported in 1961 to react with tetrafluoroethylene to give the cobaltacycle $CpCo(CO)(C_4F_8)$ (Figure 1).[9] This work remained rather dormant until Baker and co-workers[10] synthesized the related carbene complexes $CpCo(L){=}C(F)R_f$ (L = PPh_2Me; R_f = perfluoroalkyl) by sodium amalgam reduction of the corresponding perfluoroalkylcobalt iodides $CpCo(L)(I)R_f$ (Figure 3). Furthermore, tetrafluoroethylene addition to the Co=C carbene double bond provided a route to the four-membered ring perfluorinated cobaltacycles $CpCo(L)(CF_2CF_2CFR_f)$. These underwent rearrangement by a fluorine shift to give isomeric perfluoroolefin complexes $CpCo(L)(CF_3C{=}CF_2R_f)$ in the presence of catalytic quantities of $HN(SO_2CF_3)_2$. This rearrangement suggests that the metal perfluoroolefin complex is a lower energy structure than the isomeric perfluorinated metallacycle. This is consistent with our recent theoretical studies on the octafluoroferracyclopentane $C_4F_8Fe(CO)_4$ and its isomers.[11]

Substitution of an $Fe(CO)_3$ unit in $C_4F_8Fe(CO)_4$ with a CpCo unit containing the more weakly back-bonding Cp ligand relative to three CO groups to give $CpCo(CO)C_4F_8$ necessarily increases the negative charge on the metal atom. Furthermore, in the CpCo fluorocarbon chemistry reported by Baker and co-workers,[10,12,13] replacing the remaining carbonyl ligand in $CpCo(CO)C_4F_8$ with a more weakly back-bonding phosphine ligand increases the negative charge on the metal atom even further. We now report the use of density functional theory methods to assess the energies of the $CpCo(L)(C_nF_{2n})$ (L = CO, PMe_3; $n = 3, 4$) perfluorinated cobaltacycles relative to their isomers with perfluoroolefin and perfluorocarbene ligands. The rearrangement of the cobaltacycle $CpCo(PR_3)(CF_2CF_2CF_2)$ to the isomeric perfluoropropene complex $CpCo(PR_3)(CF_3CF{=}CF_2)$ by a fluorine shift catalyzed by $HN(SO_2CF_3)_2$ is shown to be an energetically favored process in terms of the relative energies of the starting material and rearranged product.

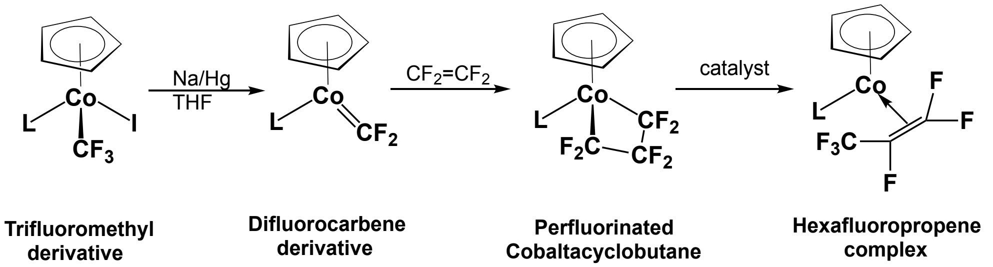


Figure 3. Examples of cyclopentadienylcobalt fluorocarbon derivatives synthesized by Baker and coworkers (L = PPh_2Me).[10]

2. Theoretical Methods

Density functional theory (DFT) methods have evolved as a practical and effective computational tool for organometallic compounds.[14,15,16,17,18,19,20,21] A newer generation density functional method, M06-L, was used in this work. The M06-L functional, which is based on a meta-GGA functional proposed by Zhao and Truhlar,[22] has been reported to give better overall performance for organometallic compounds than the first-generation functionals.[23,24] In conjunction with the M06-L method, all-electron double zeta plus polarization (DZP) basis sets and correlation-consistent polarized valence triple-ζ (cc-pVTZ) basis sets were used. For the carbon, oxygen, fluorine, and phosphorus atoms the Huzinaga-Dunning-Hay[25,26,27] contracted double-ζ Gaussian basis sets were used augmented by a set of pure spherical harmonic d-like polarization functions. For the hydrogen atoms, a set of p polarization functions was added to the Huzinaga-Dunning DZ set. The DZP basis set for cobalt begins with the Wachters' primitive set[28] and adds two sets of p functions and one set of d functions followed by contractions according to Hood et al.[29] The cc-pVTZ basis sets used for the hydrogen, carbon, oxygen, fluorine, and phosphorus atoms are given by Dunning,[30,31] while those used for the cobalt atom come from Balabanov and Peterson.[32]

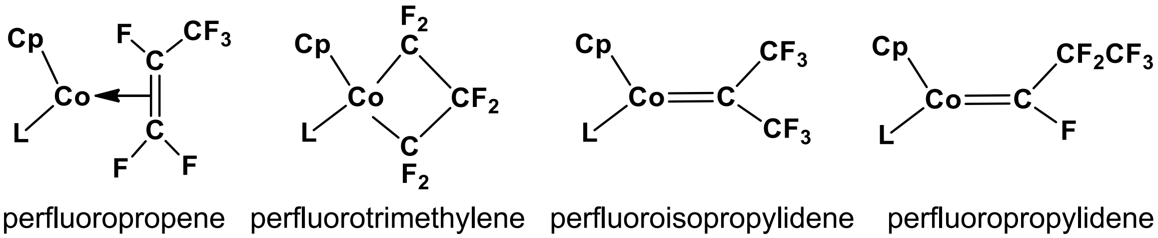
Conceivable CpCo(L)(C_3F_6) and CpCo(L)(C_4F_8) (L = CO, PMe_3) structures were fully optimized using first the M06-L/DZP method and then the M06-L/cc-pVTZ method. Harmonic vibrational frequency analyses were also carried out at the same levels of theory. Only singlet spin state structures were involved in this work. All of the M06-L computations were performed utilizing the Gaussian 09 program,[33] with the ultrafine grid for numerical integration. Both the M06-L/DZP and M06-L/cc-pVTZ computations predict similar results in the present work, so the M06-L/cc-pVTZ results are mainly used in the following discussion. A given CpCo(L)(C_3F_6) and CpCo(L)(C_4F_8) (L = CO, PMe_3) structure is designated as **L-X-n,** where **L** refers to the CO or PMe_3 ligand, **X** is C_3F_6 or C_4F_8, and **n** orders the structures according to their relative M06-L energies. For example, the lowest-energy structure of CpCo(CO)(C_3F_6) is designated as **CO-C_3F_6-1**.

Based on the M06-L/cc-pVTZ geometries, we also computed the single point energies of the lowest energy CpCo(L)(C_3F_6) and CpCo(L)(C_4F_8) (L = CO, PMe_3) structures using the state-of-the-art DLPNO-CCSD(T) method, based on domain-based local pair natural orbital coupled-cluster theory with single and double excitations and including a perturbative triples correction.[34,35] The loss of correlation energy due to the additional approximations in DEPNO-CCSD(T) was claimed to be very small (<0.05%) but the computation cost is dramatically reduced compared with the canonical CCSD(T) method.[34] Both cc-pVTZ and augmented cc-pVTZ (*aug*-cc-pVTZ) basis sets[32,36] were used in the DLPNO-CCSD(T) single point calculations. All of the DLPNO-CCSD(T) computations were performed using the ORCA program package (versions 4.1.2).[37]

3. Results and Discussion

3.1 CpCo(L)(C_3F_6) (L = CO, PMe_3)

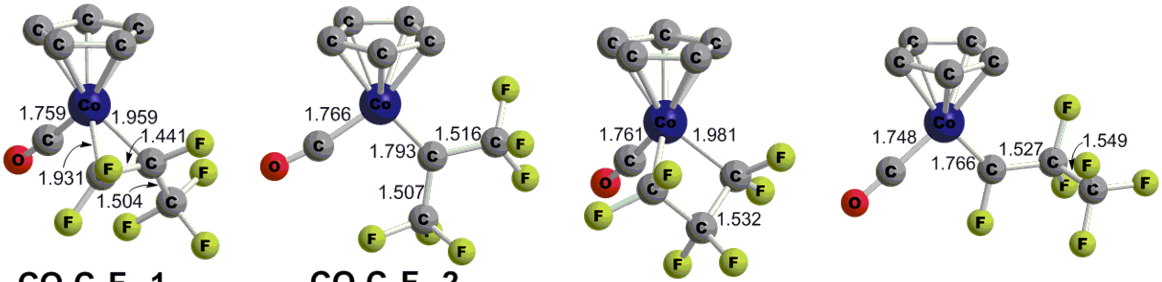
The C_3F_6 ligand can coordinate with a CpCo(L) unit four different ways, namely, $CF_2{=}CF{-}CF_3$ (perfluoropropene), $-CF_2{-}CF_2{-}CF_2-$ (perfluorotrimethylene), $=CF{-}CF_2{-}CF_3$ (perfluoropropylidene), and $=C(CF_3)_2$ (perfluoroisopropylidene), to form isomeric structures (Scheme 1).



Scheme 1. Four CpCo(L)(C_3F_6) (L = CO, PMe_3) isomeric structures with different C_3F_6 ligands.

3.1.1 CpCo(CO)(C_3F_6)

We predict isomeric CpCo(CO)(C_3F_6) structures with four different types of C_3F_6 ligands (Figure 4). The lowest energy such structure is the perfluoropropene complex CpCo(CO)(1,2-η^2-CF_2=CF–CF_3) (**CO-C_3F_6-1)** with bonding Co–CF_2 and Co–CF distances of 1.931 and 1.959 Å, respectively. The complexed C=C double bond distance of 1.441 Å in **CO-C_3F_6-1** is ~0.11 Å longer than the C=C double bond distance of 1.329 Å in uncomplexed perfluoropropene as determined by gas phase electron diffraction.[38] This indicates considerable back donation of cobalt d-electrons from the CpCo(CO) unit into the σ^* antibonding orbitals of the perfluoropropene ligand upon complexation. However, the complexed C=C distance in **CO-C_3F_6-1** is still ~0.07 Å shorter than the C–C single bond distance of 1.513 Å in uncomplexed perfluoropropene from the gas phase electron diffraction structure.



CO-C_3F_6-1 (C_1, ^{1}A, 0.0)

CO-C_3F_6-2 (C_1, ^{1}A, 8.4)

CO-C_3F_6-3 (C_s, ^{1}A', 10.6)

CO-C_3F_6-4 (C_1, ^{1}A, 12.7)

Figure 4. Optimized CpCo(CO)(C_3F_6) structures with Cp hydrogen atoms omitted for clarity. In Figures 4, 5, 7 and 8, all bond distances are in Å, and the M06-L/cc-pVTZ relative energies (in kcal/mol) are in parentheses under each structure.

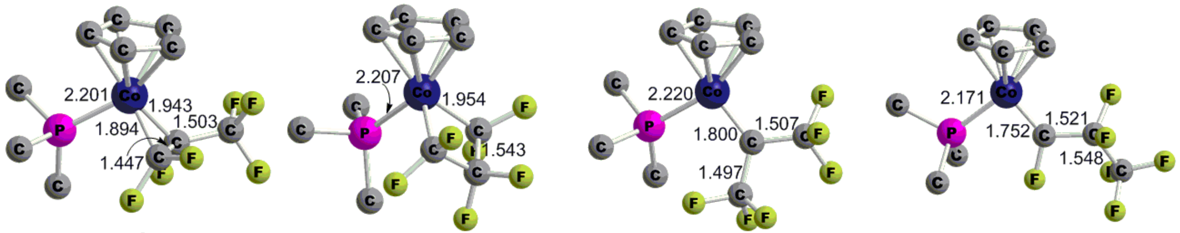
For further evaluation of the bonding situation in **CO-C_3F_6-1**, the QTAIM (quantum theory of atom in molecules) analysis[39] was carried out using the Multiwfn software.[40] In QTAIM analysis, the electron density (ρ_r) and the Laplacian of the electron density ($\nabla^2\rho_r$) at the bond critical points (BCPs) are commonly used as criteria to distinguish different types of interactions. In transition metal complexes,[41] a small ρ_r value is generally observed and $\nabla^2\rho_r$ also has a small positive value for a covalent interaction. The local electronic energy density (H_r), which is the sum of local kinetic (G_r) and potential (V_r) energy densities, can also be used to ascertain the nature of bonding in transition metal complexes.[42,43] Our QTAIM analyses obtain small values of ρ_r, small positive values of $\nabla^2\rho_r$, and the small negative values of H_r at the BCPs between the central cobalt atom and the carbon atoms in C_3F_6 (Table S5 in the Supporting Information), indicating covalent interactions between the cobalt atom and the carbon atoms. The location of the bond paths and critical points are shown in Figure S1 in the Supporting Information.

The next higher energy CpCo(CO)(C_3F_6) structure is an isomer with a perfluorinated carbene ligand, namely the perfluoroisopropylidene CpCo(CO)[=C(CF_3)$_2$] complex **CO-C_3F_6-2**, lying 8.4 kcal/mol in energy above **CO-C_3F_6-1**. The third isomer **CO-C_3F_6-3**, which exhibits the perfluorocobaltacyclobutane CpCo(CO)(1,3-η^2-CF_2–CF_2–CF_2–) structure, lies 10.6 kcal/mol in energy above **CO-C_3F_6-1** and is generated by connecting each terminal carbon atom of a perfluorotrimethylene ligand to the central cobalt, thereby giving a four-membered CoC_3 ring. The highest energy of the four isomers is the perfluoropropylidene CpCo(CO)(=CF–CF_2–CF_3) complex **CO-C_3F_6-4** lying 12.7 kcal/mol higher than **CO-C_3F_6-1**. It should be noted that the Cp(CO)Co=C(CF_3)$_2$ metal carbene is more stable than the isomeric Cp(CO)Co=CF(C_2F_5) metal carbene even though the latter has Fischer carbene character.

3.1.2 CpCo(PMe$_3$)(C$_3$F$_6$)

The same four kinds of isomeric structures are also found for the CpCo(PMe_3)(C_3F_6) complex (Figure 5), although the energy ordering of these isomers is somewhat different. The perfluoropropene CpCo(PMe_3)(1,2-η^2-CF_2=CF–CF_3) complex **PMe$_3$-C_3F_6-1** has the lowest energy, similar to the CpCo(CO)(C_3F_6) system. The bonding Co–CF_2 distance of 1.894 Å in **PMe$_3$-C_3F_6-1** is slightly shorter than the corresponding distance in **CO-C_3F_6-1** (1.931 Å), as is also the Co–CF distance. This reflects increasing back-donation from the cobalt atom into the perfluoroolefin π^* orbitals. Again, the complexed C=C double bond length (1.447 Å) in the perfluoropropene ligand of **PMe$_3$-C_3F_6-1** is shorter than the C–C single bond length (1.503 Å). The QTAIM analysis reveals the covalent interaction between the central cobalt atom and the carbon atoms of C_3F_6 ligand for **PMe$_3$-C_3F_6-1**. The locations of the bond paths between the cobalt atom and the carbon atoms are shown in Figure S1 in the Supporting Information, and the negative values of H_r at the BCPs are listed in Table S5 in the Supporting Information. The perfluorocobaltacyclobutane CpCo(PMe_3)(1,3-η^2-CF_2–CF_2–CF_2–) structure **PMe$_3$-C_3F_6-2** and the perfluoroisopropylidene CpCo(PMe_3)[=C(CF_3)$_2$] structure **PMe$_3$-C_3F_6-3** lie 9.8 and 10.9 kcal/mol, respectively, in energy above **PMe$_3$-C_3F_6-1**. Thus, the relative energies of the perfluorocobaltacyclobutane and perfluoroisopropylidene isomers in the CpCo(PMe_3)(C_3F_6) system are reversed from those in the CpCo(CO)(C_3F_6) system. The Co–CF_2 bond distance of 1.954 Å in **PMe$_3$-C_3F_6-2** is slightly shorter than the corresponding distance in **CO-C_3F_6-3** (1.981 Å), again reflecting increased back-donation in **PMe$_3$-C_3F_6-2** relative to **CO-C_3F_6-3.** However, the Co=C(CF_3)$_2$ bond distance of 1.800 Å in **PMe$_3$-C_3F_6-3** is slightly longer than the corresponding distance in **CO-C_3F_6-2** (1.793 Å). The perfluoropropylidene CpCo(PMe_3)(=CF–CF_2–CF_3) isomer **PMe_3-C_3F_6-4** has the highest energy of the four structures, as in the CpCo(CO)(C_3F_6) system. Again, the metal carbene structure Cp(PMe_3)Co=C(CF_3)$_2$ is more stable than the isomeric Cp(PMe_3)Co=CF(C_2F_5) structure even though the latter has Fischer carbene character. Our results are consistent with those demonstrated by Baker and coworkers in that the metallacycles are more stable than the metal carbenes for the CoCp(PPh_2Me)(C_3F_6) complex.[44]

In the experimentally known[10] CpCo(PPh_2Me)(η^2-CF_2–CF_2–CF_2–) complex, which has the same structure type as **PMe_3-C_3F_6-2**, the bond lengths and bond angles are R(Co–P) = 2.209 Å, R(Co–CF_2) = 1.949/1.952 Å, R(CF_2–CF_2) = 1.516/1.527 Å, ∠C-Co-C = 73°, ∠Co-C-C = 94° and ∠C-C-C = 99°.[10] Our predicted bond lengths and angles in **PMe_3-C_3F_6-2** are close to these experimental values (Figure 6).



PMe_3-C_3F_6-1 (C_1, ^{1}A, 0.0) **PMe_3-C_3F_6-2 (C_s, ^{1}A', 9.8)** **PMe_3-C_3F_6-3 (C_s, ^{1}A, 10.9)** **PMe_3-C_3F_6-4 (C_1, ^{1}A, 16.0)**

Figure 5. Optimized CpCo(PMe_3)(C_3F_6) structures with all Cp hydrogen atoms omitted for clarity.

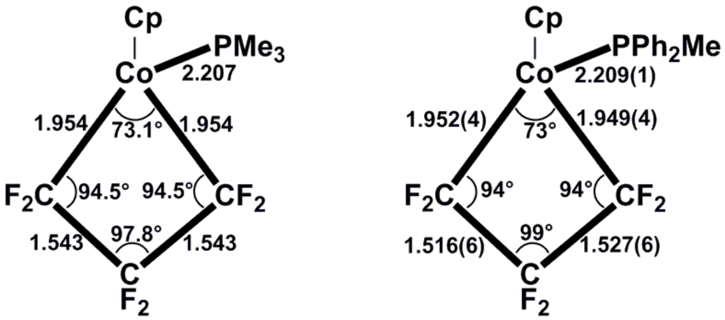
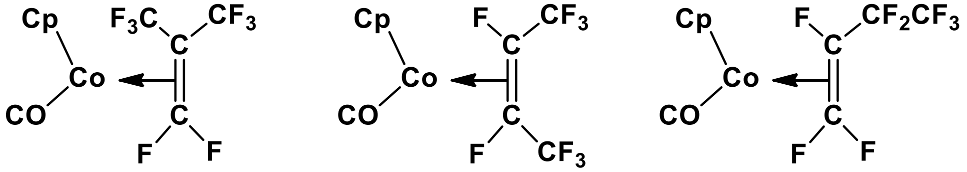


Figure 6. Comparison of the bond lengths (in Å) and bond angles (in degrees) between the experimentally known[10] perfluorocobaltacyclobutane complex CpCo(PPh_2Me)(η^2-CF_2–CF_2–CF_2–) (right) with those predicted in our work for **PMe_3-C_3F_6-2** (left).

In all of the structures with dihapto η^2-C_3F_6 ligands, including the perfluoroolefin complexes **CO-C_3F_6-1** and **PMe_3-C_3F_6-1** and the perfluorocobaltacyclobutanes **CO-C_3F_6-3** and **PMe_3-C_3F_6-2**, the Co–C distances range from 1.89 to 1.98 Å, corresponding to formal single bonds. However, in all of the η^1-C_3F_6 structures **CO-C_3F_6-2**, **CO-C_3F_6-4**, **PMe_3-C_3F_6-3**, and **PMe_3-C_3F_6-4** with perfluorocarbene ligands, the Co=C distances are shortened to 1.75 to 1.80 Å suggesting formal Co=C double bonds. In all of these CpCo(L)(C_3F_6) (L = CO, PMe_3) complexes the C_3F_6 ligands are two-electron donors, thereby giving their cobalt atoms the favored 18-electron configuration.

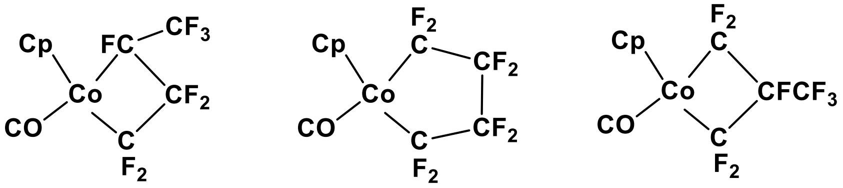
3.2 CpCo(L)(C_4F_8) (L = CO, PMe_3)

Adding one more CF_2 group to the C_3F_6 ligand gives the C_4F_8 ligand, which can have nine different arrangements, namely CF_2=CF–CF_2–CF_3 (perfluoro-1-butene), CF_3–CF=CF–CF_3 (perfluoro-2-butene), CF_2=C(CF_3)–CF_3 (perfluoro-2-methylpropene), –CF_2–CF_2–CF_2–CF_2– (perfluorotetramethylene), –CF(CF_3)–CF_2–CF_2– (perfluoro-1-methyltrimethylene), –CF_2–CF(CF_3)–CF_2– (perfluoro-2-methyltrimethylene), =CF–CF_2–CF_2–CF_3 (perfluorobutylidene), =C(CF_3)–CF_2–CF_3 (perfluoro-1-methylpropylidene), =CF–CF(CF_3)–CF_3 (perfluoro-2-methylpropylidene). Consequently, there are nine corresponding isomeric CpCo(CO)(C_4F_8) complexes (Schemes 2 to 4). The optimized geometries of these isomers are shown in Figure 7.



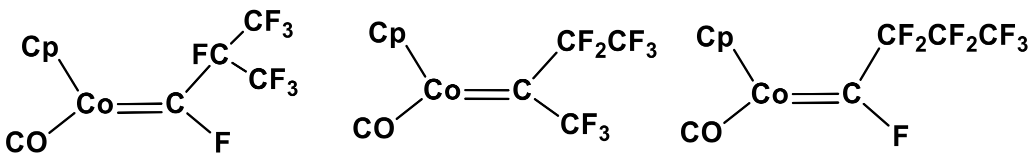
CO-C$_4$F$_8$-1 **CO-C$_4$F$_8$-2** **CO-C$_4$F$_8$-3**

Scheme 2. Three CpCo(CO)(C_4F_8) isomeric structures with different arrangements of the perfluoroolefin C_4F_8 ligand.



CO-C$_4$F$_8$-4 **CO-C$_4$F$_8$-5** **CO-C$_4$F$_8$-6**

Scheme 3. Three CpCo(CO)(C_4F_8) isomeric perfluorinated metallacycle complexes with different arrangements of the C_4F_8 ligand.

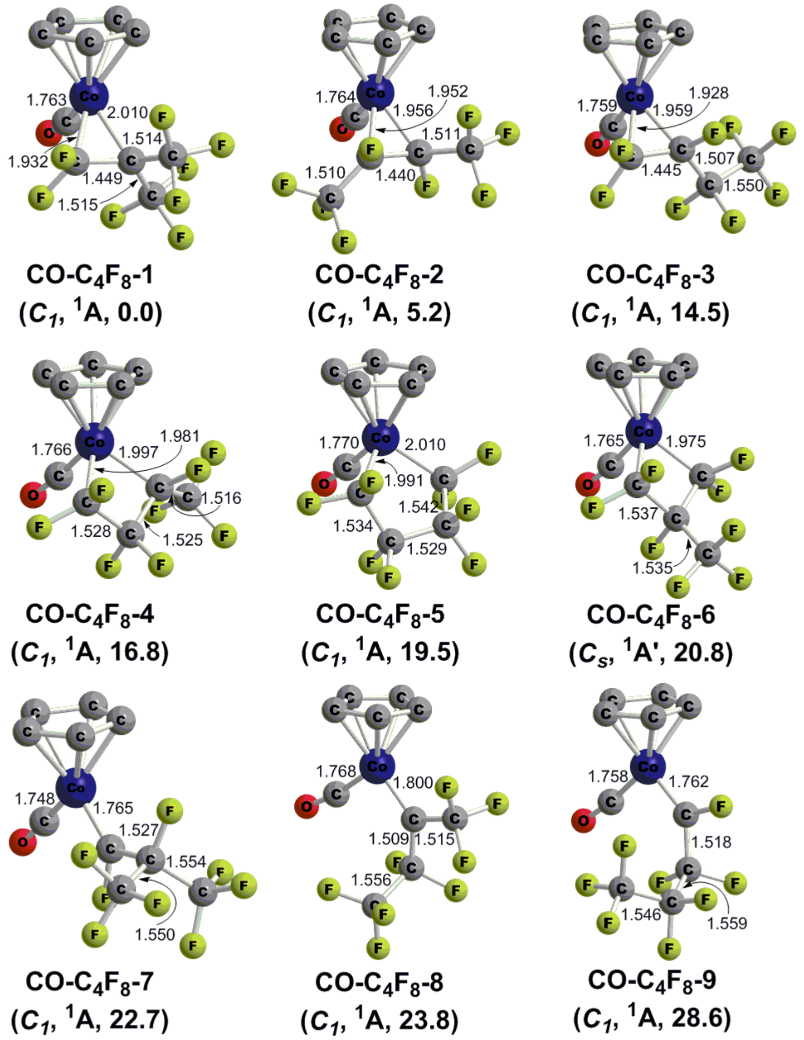


CO-C$_4$F$_8$-7 **CO-C$_4$F$_8$-8** **CO-C$_4$F$_8$-9**

Scheme 4. Three CpCo(CO)(C_4F_8) isomeric complexes with the C_4F_8 carbene ligand.

3.2.1 CpCo(CO)(C_4F_8)

In the three lowest energy CpCo(CO)(C_4F_8) complexes **CO-C_4F_8-1**, **CO-C_4F_8-2**, and **CO-C_4F_8-3** the C_4F_8 ligand is a perfluoroolefin forming a dative bond from the olefinic C=C π bond to the cobalt atom (Scheme 2). The perfluoro-2-methylpropene complex CpCo(CO)[1,2-η^2-CF_2=C(CF_3)–CF_3] (**CO-C_4F_8-1**) is the lowest energy structure followed by the perfluoro-2-butene complex CpCo(CO)(2,3-η^2-CF_3–CF=CF–CF_3) (**CO-C_4F_8-2**) and the perfluoro-1-butene complex CpCo(CO)(1,2-η^2-CF_2=CF–CF_2–CF_3) (**CO-C_4F_8-3**) at 5.2 and 14.5 kcal/mol, respectively, in energy above **CO-C_4F_8-1** (Figure 7). The Co–C distances between the cobalt atom and the carbon atoms of the C=C bonds range from 1.93 to 2.01 Å. The complexed C=C double bond distances in these three structures are ~1.44 Å, which is ~0.07 Å shorter than the C–C single bond (~1.51 Å).



CO-C_4F_8-1 (C_1, ^{1}A, 0.0)
CO-C_4F_8-2 (C_1, ^{1}A, 5.2)
CO-C_4F_8-3 (C_1, ^{1}A, 14.5)
CO-C_4F_8-4 (C_1, ^{1}A, 16.8)
CO-C_4F_8-5 (C_1, ^{1}A, 19.5)
CO-C_4F_8-6 (C_s, ^{1}A', 20.8)
CO-C_4F_8-7 (C_1, ^{1}A, 22.7)
CO-C_4F_8-8 (C_1, ^{1}A, 23.8)
CO-C_4F_8-9 (C_1, ^{1}A, 28.6)

Figure 7. The nine optimized CpCo(CO)(C_4F_8) structures with all Cp hydrogen atoms omitted for clarity.

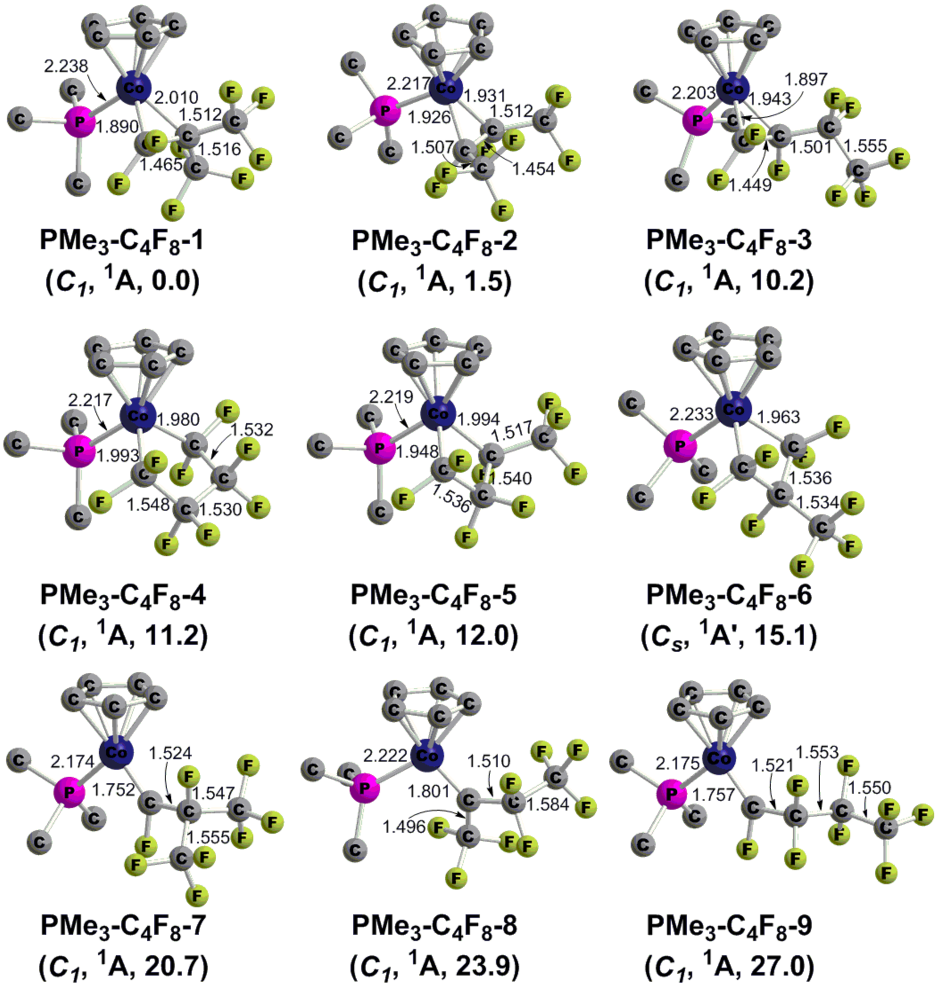
The QTAIM analysis also reveals the covalent interaction between the central cobalt atom and the carbon atoms of C_4F_8 ligand. The bond paths, critical points, and the negative values of H_r at the BCPs are shown in Figure S1 and Table S5 in Supporting Information.

The next higher energy $CpCo(CO)(C_4F_8)$ structures are the three perfluorinated cobaltacycles (Scheme 3 and Figure 7). These include the perfluorinated 1-methyl-cobaltacyclobutane complex $CpCo(CO)[1,3\text{-}\eta^2\text{-}CF(CF_3)\text{–}CF_2\text{–}CF_2\text{–}]$ (**CO-C_4F_8-4**), the perfluorinated cobaltacyclopentane complex $CpCo(CO)(1,4\text{-}\eta^2\text{-}CF_2\text{–}CF_2\text{–}CF_2\text{–}CF_2\text{–})$ (**CO-C_4F_8-5**), and the perfluorinated 2-methyl-cobaltacyclobutane complex $CpCo(CO)[1,3\text{-}\eta^2\text{-}CF_2\text{–}CF(CF_3)\text{–}CF_2\text{–}]$ (**CO-C_4F_8-6**) lying 16.8, 19.5, and 20.8 kcal/mol, respectively, in energy above **CO-C_4F_8-1**. The Co–C distances in these structures range from 1.975 to 2.010 Å.

The three $CpCo(CO)(C_4F_8)$ isomers with perfluorinated carbene ligands, namely the perfluoro-2-methylpropylidene complex $CpCo(CO)[{=}CF\text{–}CF(CF_3)\text{–}CF_3]$ (**CO-C_4F_8-7**), the perfluoro-1-methylpropylidene complex $CpCo(CO)[{=}C(CF_3)\text{–}CF_2\text{–}CF_3]$ (**CO-C_4F_8-8**) and the perfluorobutylidene complex $CpCo(CO)({=}CF\text{–}CF_2\text{–}CF_2\text{–}CF_3)$ (**CO-C_4F_8-9**) are still higher energy structures, lying at least 22 kcal/mol above **CO-C_4F_8-1** (Scheme 4 and Figure 7). The Co=C distances in these structures with perfluorocarbene ligands, ranging from 1.762 to 1.800 Å, are significantly shorter than those in the perfluoroolefin complexes and perfluorocobaltacycles. This indicates the expected Co=C double bonds rather than Co–C single bonds in the perfluorocarbene complexes.

3.2.2 $CpCo(PMe_3)(C_4F_8)$

Nine isomers of $CpCo(PMe_3)(C_4F_8)$ were found similar to $CpCo(CO)(C_4F_8)$. The lowest energy of these nine isomers are the three perfluoroolefin complexes **PMe_3-C_4F_8-1**, **PMe_3-C_4F_8-2,** and **PMe_3-C_4F_8-3** (Figure 8). In each of these three complexes the C=C double bond is coordinated to the cobalt atom. The perfluoro-2-methylpropene complex $CpCo(PMe_3)[1,2\text{-}\eta^2\text{-}CF_2{=}C(CF_3)\text{–}CF_3]$ (**PMe_3-C_4F_8-1**) is the lowest energy structure. The perfluoro-2-butene complex $CpCo(PMe_3)(2,3\text{-}\eta^2\text{-}CF_3\text{–}CF{=}CF\text{–}CF_3)$ (**PMe_3-C_4F_8-2**) and the perfluoro-1-butene complex $CpCo(PMe_3)(1,2\text{-}\eta^2\text{-}CF_2{=}CF\text{–}CF_2\text{–}CF_3)$ (**PMe_3-C_4F_8-3**) are higher energy structures, lying 1.5 and 10.2 kcal/mol, respectively, above **PMe_3-C_4F_8-1**. The Co–C distances in the three structures range from 1.89 to 2.01 Å and the C=C complexed double bond lengths are 1.45 to 1.47 Å, again ~0.05 Å shorter than the C–C single bonds. Again, the QTAIM analysis reveals the covalent interaction between the central cobalt atom and the carbon atoms of C_4F_8 ligand. The bond paths, critical points, and the negative values of H_r at the BCPs are shown in Figure S1 or Table S5 in Supporting Information.



PMe_3-C_4F_8-1
(C_1, ^{1}A, 0.0)

PMe_3-C_4F_8-2
(C_1, ^{1}A, 1.5)

PMe_3-C_4F_8-3
(C_1, ^{1}A, 10.2)

PMe_3-C_4F_8-4
(C_1, ^{1}A, 11.2)

PMe_3-C_4F_8-5
(C_1, ^{1}A, 12.0)

PMe_3-C_4F_8-6
(C_s, ^{1}A', 15.1)

PMe_3-C_4F_8-7
(C_1, ^{1}A, 20.7)

PMe_3-C_4F_8-8
(C_1, ^{1}A, 23.9)

PMe_3-C_4F_8-9
(C_1, ^{1}A, 27.0)

Figure 8. Optimized CpCo(PMe_3)(C_4F_8) structures with all Cp hydrogen atoms omitted for clarity.

The three cobaltacycle CpCo(PMe_3)(C_4F_8) isomers are higher energy structures, lying 11.2, 12.0, and 15.1 kcal/mol, respectively, above **PMe_3-C_4F_8-1**. These structures are the perfluorinated cobaltacyclopentane complex CpCo(PMe_3)(η^2-CF_2–CF_2–CF_2–CF_2–) (**PMe_3-C_4F_8-4**), the perfluorinated 1-methyl-cobaltacyclobutane complex CpCo(PMe_3)[η^2-CF(CF_3)–CF_2–CF_2–] (**PMe_3-C_4F_8-5**), and the perfluorinated 2-methyl-cobaltacyclobutane complex CpCo(PMe_3)[η^2-CF_2–CF(CF_3)–CF_2–] (**PMe_3-C_4F_8-6**). Note that for CpCo(PMe_3)(C_4F_8), the relative energies of the perfluorinated cobaltacyclopentane and 1-methyl-cobaltacyclobutane complexes are reversed.

Our optimized CpCo(PMe_3)[η^2-CF(CF_3)–CF_2–CF_2–] (**PMe_3-C_4F_8-5**) geometry is close to that of the experimental CpCo(PPh_2Me)(η^2-CF(CF_3)–CF_2–CF_2–) structure (Figure 9).[10] The Co–P, Co–CF, Co–CF_2, FC–CF_2, F_2C–CF_2 distances for the CpCo(PMe_3)[η^2-CF(CF_3)–CF_2–CF_2–] (**PMe_3-C_4F_8-5**) complex are 2.219, 1.994, 1.948, 1.540, and 1.536 Å, respectively, which are very similar to the corresponding experimental bond distances of 2.226, 1.986, 1.938, 1.537, and 1.518 Å. Our predicted FC–Co–CF_2, Co–CF–CF_2, Co–CF_2–CF_2, and FC–CF_2–CF_2 bond angles of 73.1°, 92.6°, 94.5°, and 99.6°, respectively, are also close to the experimental bond angles of 73°, 93°, 95°, and 99°.

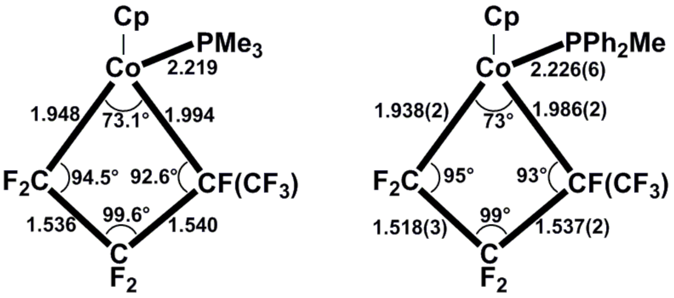


Figure 9. Optimized bond lengths (in Å) and bond angles (in degrees) for the $CpCo(PMe_3)[\eta^2\text{-}CF(CF_3)\text{–}CF_2\text{–}CF_2\text{–}]$ (**PMe_3-C_4F_8-5S**) complex (left) and their comparison with the experimental values from the $CpCo(PPh_2Me)[\eta^2\text{-}CF(CF_3)\text{–}CF_2\text{–}CF_2\text{–}]$ complex (right).[10]

The three perfluorinated carbene complex structures have even higher energies of ~20 kcal/mol above **PMe_3-C_4F_8-1**. These structures are similar to their $CpCo(CO)(C_4F_8)$ analogues, including the perfluoro-2-methylpropylidene complex $CpCo(PMe_3)[{=}CF\text{–}CF(CF_3)\text{–}CF_3]$ (**PMe_3-C_4F_8-7**), the perfluoro-1-methylpropylidene complex $CpCo(PMe_3)[{=}C(CF_3)\text{–}CF_2\text{–}CF_3]$ (**PMe_3-C_4F_8-8**) and the perfluorobutylidene complex $CpCo(PMe_3)({=}CF\text{–}CF_2\text{–}CF_2\text{–}CF_3)$ (**PMe_3-C_4F_8-9**). The Co=C bond distances in all of the η^1-C_4F_8 carbene complexes **PMe_3-C_4F_8-7, PMe_3-C_4F_8-8,** and **PMe_3-C_4F_8-9** range from 1.75 to 1.80 Å, which is ~0.2 Å shorter than the Co–C single bond distances in the other isomers, indicating Co=C double bonds in the perfluorinated carbene complexes.

The C_4F_8 ligands in these eighteen $CpCo(L)(C_4F_8)$ (L = CO, PMe_3) structures are all two-electron donors thereby giving the cobalt atoms the favored 18-electron configuration

3.3 DLPNO-CCSD(T) energies

Table 1 shows the relative energies of various $CpCo(L)(C_3F_6)$ and $CpCo(L)(C_4F_8)$ (L = CO, PMe_3) structures based on the DLPNO-CCSD(T)/cc-pVTZ// M06-L/cc-pVTZ and DLPNO-CCSD(T)/*aug*-cc-pVTZ//M06-L/cc-pVTZ computations. From Table 1 we can see that this DLPNO-CCSD(T) method predicts the same energy orders for the lowest-energy structures as those predicted by the DFT method. According to the DLPNO-CCSD(T)/*aug*-cc-pVTZ//M06-L/cc-pVTZ results for the $CpCo(CO)(C_3F_6)$ complex, the perfluoropropene structure **CO-C_3F_6-1** still has the lowest energy, with the perfluoroisopropylidene structure **CO-C_3F_6-2**, the perfluorocobaltacyclobutane structure **CO-C_3F_6-3**, and the perfluoropropylidene structure **CO-C_3F_6-4** energetically higher than **CO-C_3F_6-1** by 3.6, 11.0, and 8.6 kcal/mol, respectively. For the CpCo(PMe_3)(C_3F_6) complex, the perfluoropropene structure **PMe_3-C_3F_6-1** still has the lowest energy, with the perfluoro-cobaltacyclobutane structure **PMe_3-C_3F_6-2**, the perfluoroisopropylidene structure **PMe_3-C_3F_6-3**, and the perfluoropropylidene structure **PMe_3-C_3F_6-4** energetically higher than **PMe_3-C_3F_6-1** by 8.7, 7.4, and 11.6 kcal/mol, respectively. For the CpCo(CO)(C_4F_8) complex, the perfluoro-2-methylpropene structure **CO-C_4F_8-1** still has the lowest energy, with the other two perfluoroolefin structures **CO-C_4F_8-2** and **CO-C_4F_8-3**, the three perfluorometallacycle structures **CO-C_4F_8-4**, **CO-C_4F_8-5** and **CO-C_4F_8-6**, and the three perfluorocarbene structures **CO-C_4F_8-7**, **CO-C_4F_8-8** and **CO-C_4F_8-9** less stable than **CO-C_3F_6-1** by 5.3, 16.7, 17.6, 19.3, 22.7, 19.9, 20.8, and 27.1 kcal/mol, respectively. For the CpCo(PMe_3)(C_4F_8) complex, the perfluoro-2-methylpropene structure **PMe_3-C_4F_8-1** still has the lowest energy, with the other two perfluoroolefin structures **PMe_3-C_4F_8-2** and **PMe_3-C_4F_8-3**, the three perfluorometallacycle structures **PMe_3-C_4F_8-4**, **$PMe_3$$C_4F_8$-5** and **$PMe_3$-$C_4F_8$-6**, and the three perfluorocarbene structures **PMe_3-C_4F_8-7**, **PMe_3-C_4F_8-8** and **PMe_3-C_4F_8-9** energetically higher than **PMe_3-C_3F_6-1** by 1.7, 11.7, 9.6, 11.3, 15.8, 17.3, 22.0, and 24.2 kcal/mol, respectively. Thus, in general, the DLPNO-CCSD(T)/*aug*-cc-pVTZ//M06-L/cc-pVTZ energies are essentially consistent with the M06-L/cc-pVTZ results.

5. Summary

Density functional theory on the cyclopentadienylcobalt fluorocarbon complexes CpCo(L)(C_nF_{2n}) (Cp = η^5-C_5H_5; L = CO, PMe_3; n = 3, 4) indicate structures with perfluoroolefin ligands to be the lowest energy structures followed by perfluoro-cobaltacycle structures and finally by structures with perfluorocarbene ligands. This is consistent with the experimentally observed[10] isomerization of perfluorinated cobaltacyclobutane complexes CpCo(PPh_2Me)(–CFR–CF_2–CF_2–) (R = F, CF_3) to the perfluoroolefin complexes CpCo(PPh_2Me)(RCF=CF_2) in the presence of catalytic quantities of HN(SO_2CF_3)$_2$. Further refinement of the relative energies by the state-of-the-art DLPNO-CCSD(T) method gives results essentially consistent with the DFT results summarized above. The fundamental results from this theoretical study involving the relative stability of fluorocarbon metal complexes of different types are potentially useful in the design of catalytic systems for fluorocarbon rearrangements.

Table 1. Relative energies (in kcal/mol) for optimized low-energy structures of the CpCo(L)(C_3F_6) and CpCo(L)(C_4F_8) (L = CO, PMe_3) complexes at the DLPNO-CCSD(T)/cc-pVTZ//M06-L/cc-pVTZ and DLPNO-CCSD(T)/*aug*-cc-pVTZ//M06-L/cc-pVTZ levels of theory. The M06-L/cc-pVTZ relative energies are also shown for comparison.

Complex	Structure	M06-L/cc-pVTZ	DLPNO-CCSD(T) /cc-pVTZ //M06-L/cc-pVTZ	DLPNO-CCSD(T) /*aug*-cc-pVTZ //M06-L/cc-pVTZ
CpCo(CO)(C_3F_6)	**CO-C_3F_6-1**	0.0	0.0	0.0
	CO-C_3F_6-2	8.4	2.9	3.6
	CO-C_3F_6-3	10.6	12.1	11.0
	CO-C_3F_6-4	12.7	8.0	8.6
CpCo(CO)(C_4F_8)	**CO-C_4F_8-1**	0.0	0.0	0.0
	CO-C_4F_8-2	5.2	5.4	5.3
	CO-C_4F_8-3	14.5	17.0	16.7
	CO-C_4F_8-4	16.8	18.7	17.6
	CO-C_4F_8-5	19.5	21.2	19.3
	CO-C_4F_8-6	20.8	23.6	22.7
	CO-C_4F_8-7	22.7	19.1	19.9
	CO-C_4F_8-8	23.8	20.5	20.8
	CO-C_4F_8-9	28.6	26.8	27.1
CpCo(PMe_3)(C_3F_6)	**PMe_3-C_3F_6-1**	0.0	0.0	0.0
	PMe_3-C_3F_6-2	9.8	9.6	8.7
	PMe_3-C_3F_6-3	10.9	5.9	7.4
	PMe_3-C_3F_6-4	16.0	10.4	11.6
CpCo(PMe_3)(C_4F_8)	**PMe_3-C_4F_8-1**	0.0	0.0	0.0
	PMe_3-C_4F_8-2	1.5	1.7	1.7
	PMe_3-C_4F_8-3	10.2	11.5	11.7
	PMe_3-C_4F_8-4	11.2	11.1	9.6
	PMe_3-C_4F_8-5	12.0	12.2	11.3
	PMe_3-C_4F_8-6	15.1	16.4	15.8
	PMe_3-C_4F_8-7	20.7	16.1	17.3
	PMe_3-C_4F_8-8	23.9	21.0	22.0
	PMe_3-C_4F_8-9	27.0	23.3	24.2

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Supporting Information

Table S1: Total energies and relative energies for optimized low-energy structures of the CpCo(L)(C_3F_6) and CpCo(L)(C_4F_8) (L = CO, PMe_3) complexes at the M06-L/cc-pVTZ level; Table S2. Total energies and relative energies for optimized low-energy structures of the CpCo(L)(C_3F_6) and CpCo(L)(C_4F_8) (L = CO, PMe_3) complexes at the DLPNO-CCSD(T)/cc-pVTZ//M06-L/cc-pVTZ and DLPNO-CCSD(T)/*aug*-cc-pVTZ//M06-L/cc-pVTZ levels of theory; Table S3: Vibrational frequencies and infrared intensities for optimized low-energy structures of the CpCo(L)(C_3F_6) and CpCo(L)(C_4F_8) (L = CO, PMe_3) complexes at the M06-L/cc-pVTZ level; Table S4: Cartesian coordinates for optimized low-energy structures of the CpCo(L)(C_3F_6) and CpCo(L)(C_4F_8) (L = CO, PMe_3) complexes at the M06-L/cc-pVTZ level. Table S5: Topological data at the bond critical points for the interactions between the cobalt atom and the C=C double bond in optimized lowest-energy structures of the CpCo(L)(C_3F_6) and CpCo(L)(C_4F_8) (L = CO, PMe_3) complexes at the M06-L/cc-pVTZ level of theory. Figure S1: Bond paths for optimized lowest-energy structures of the CpCo(L)(C_3F_6) and CpCo(L)(C_4F_8) (L = CO, PMe_3) complexes at the M06-L/cc-pVTZ level of theory. Complete Gaussian 09 reference.

Literature References

[1] F. Calderazzo, in *Encyclopedia of Inorganic Chemistry*, 2nd Edition, ed. King, R. B., Wiley, Chichester, 2005, pp. 764-781.

[2] K. F. Watterson and G. Wilkinson, Perfluorolefin transition metal complexes. *Chem. and Ind.* 1959, 991-991.

[3] K. F. Watterson and G. Wilkinson, Fluorocarbon transition metal complexes. *Chem. and Ind.* 1960, 1358-1358.

[4] H. H. Hoehn, L. Pratt, K. F. Watterson and G. Wilkinson, Transition-metal fluorocarbon complexes. 1. Derivatives of perfluoro-olefins. *J. Chem. Soc.* 1961, 2738-2745.

[5] O. A. Tomashenko and V. V. Grushin. Aromatic trifluoromethylation with metal complexes. *Chem. Rev.*, 2011, **111**, 4475-4521.

[6] B. L. Booth, R. N. Haszeldine, P. R. Mitchell and J. J. Cox, Reactions of fluoro-olefins with octacarbonyldicobalt. *Chem. Commun.*, 1967, 529-530.

[7] B. L. Booth, R. N. Haszeldine, P. R. Mitchell and J. J. Cox, Metal carbonyl chemistry. Part V. Reactions of fluoro-olefins with octacarbonyldicobalt. *J. Chem. Soc. A*, 1969, 691-698.

[8] D. J. Harrison, A. L. Daniels, I. Korobkov and R. T. Baker, Tetracarbonyl-(trifluoromethyl)cobalt(I) [$Co(CO)_4(CF_3)$] as a precursor to new cobalt trifluoromethyl and difluorocarbene complexes. *Organometallics*, 2015, **34**, 4598–4604.

[9] T. D. Coyle, R. B. King, E. Pitcher, S. L. Stafford, P. M. Treichel and F. G. A. Stone, A novel heterocyclic cobalt compound. *J. Inorg. Nucl. Chem.*, 1961, **20**, 172-173.

[10] D. J. Harrison, G. M. Lee, M. C. Leclerc, I. Korobkov and R. T. Baker, Cobalt fluorocarbenes: Cycloaddition reactions with tetrafluoroethylene and reactivity of the perfluorometallacyclic products. *J. Am. Chem. Soc.*. 2013, **135**, 18296-18299.

[11] L. Huang, J. Li, J.; G. Li, Y. Xie, R. B. King and H. F. Schaefer, Alternative modes of bonding of C_4F_8 Units in mononuclear and binuclear iron carbonyl complexes. *New J. Chem.*, 2019, **43***,* 6932-6942.

[12] D. J. Harrison, S. K. Gorelsky, G. M. Lee, I. Korobkov and R. T. Baker, Cobalt fluorocarbene complexes. *Organometallics*, 2013, **32**, 12-15.

[13] G. M. Lee, A. S. C. Leung, D. J. Harrison, I. Korobkov, R. P. Hughes and R. T. Baker, Experimental and computational evidence for 1,4-diradical intermediates in reactions of cobalt fluorocarbene complexes with terminal aryl-alkynes to give metallacyclobutenes. *Organometallics*, 2017, **36**, 2853-2860.

[14] T. Ziegler and J. Autschbach, Theoretical methods of potential use for studies of inorganic reaction mechanisms. *Chem. Rev*., 2005, **105**, 2695-2722.

[15] M. Bühl and H. Kabrede, Geometries of transition-metal complexes from density-functional theory. *J. Chem. Theory Comput*., 2006, **2**, 1282-1290.

[16] M. Brynda, L. Gagliardi, P. O. Widmark, P. P. Power and B. O. Roos, A quantum chemical study of the quintuple bond between two chromium centers in [PhCrCrPh]: trans-bent versus linear geometry, *Angew. Chem. Int. Ed*., 2006, **45**, 3804-3807.

[17] N. Sieffert and M. Bühl, Hydrogen generation from alcohols catalyzed by ruthenium-triphenylphosphine complexes: multiple reaction pathways. *J. Am. Chem. Soc*., 2010, **132**, 8056-8070.

[18] P. Schyman, W. Lai, H. Chen, Y. Wang and S. Shaik, The directive of the protein: how does cytochrome P450 select the mechanism of dopamine formation? *J. Am. Chem. Soc*., 2011, **133**, 7977-7984.

[19] R. D. Adams, W. C. Pearl, Y. O. Wong, Q. Zhang, M. B Hall and J. R. Walensky, Tetrarhena-heterocycle from the palladium-catalyzed dimerization of $Re_2(CO)_8(\mu$-

SbPh$_2$)(μ-H) exhibits an unusual host–guest behavior, *J. Am. Chem. Soc.*, 2011, **133**, 12994-12997.

[20] R. R. Lonsdale, J. Olah, A. J. Mulholl and J. N. Harvey, Does compound I vary significantly between isoforms of cytochrome P450? *J. Am. Chem. Soc.*, 2011, **133**, 15464-15474.

[21] R. H. D. Lyngdoh, H. F. Schaefer and R. B. King, Metal-metal (MM) bond distances and bond orders in binuclear metal complexes of the first row transition metals titanium through zinc, *Chem. Rev.*, 2018, **118**, 11626-11706.

[22] Y. Zhao and D. G. Truhlar, A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions, *J. Chem. Phys.*, 2006, **125**, 194101-194107.

[23] Y. Zhao and D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Acc.*, 2008, **120**, 215-241.

[24] Y. Zhao and D. G. Truhlar, Density functionals with broad applicability in chemistry, *Acc. Chem. Res*. 2008, **41**, 157-167.

[25] S. Huzinaga, Gaussian-type functions for polyatomic systems. I, *J. Chem. Phys*., 1965, **42**, 1293-1302.

[26] T. H. Dunning, Gaussian basis functions for use in molecular calculations. I. Contraction of (9s5p) atomic basis sets for the first-row atoms, *J. Chem. Phys*., 1970, **53**, 2823-2833.

[27] T. H. Dunning and P. J. Hay, Methods of electronic structure theory, edited by H. F. Schaefer, Plenum, New York, 1977, Vol. 3, p. 1-27.

[28] A. J. H. Wachters, Gaussian basis set for molecular wavefunctions containing third-row atoms, *J. Chem. Phys*., 1970, **52**, 1033-1036.

[29] D. M. Hood, R. M. Pitzer and H. F. Schaefer, Electronic structure of homoleptic transition metal hydrides: TiH_4, VH_4, CrH_4, MnH_4, FeH_4, CoH_4, and NiH_4, *J. Chem. Phys*., 1979, **71**, 705-712.

[30] T. H. Dunning, Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys*., 1989, **90**, 1007-1023.

[31] D. E. Woon and T. H. Dunning, Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon, *J. Chem. Phys*., 1993, **98**, 1358-1371.

[32] N. B. Balabanov and K. A. Peterson, Systematically convergent basis sets for transition metals. I. All-electron correlation consistent basis sets for the 3d elements Sc–Zn, *J. Chem. Phys*., 2005, **123**, 064107-1-15.

[33] M. J. Frisch, et al, Gaussian 09, Revision B.01; Gaussian, Inc.; Wallingford CT, 2010 (see Supporting Information for details).

[34] C. Riplinger and F. Neese, An efficient and near linear scaling pair natural orbital based local coupled cluster method. *J. Chem. Phys.*, 2013, **138**, 034106-1-18.

[35] C. Riplinger, B. Sandhoefer, A. Hansen and F. Neese, Natural triple excitations in local coupled cluster calculations with pair natural orbitals. *J. Chem. Phys.*, 2013, **139**, 134101-1-13.

[36] R. A. Kendall, T. H. Dunning, and R. J. Harrison, Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.*, 1992, **96**, 6796-6806.

[37] F. Neese, The ORCA program system. *WIREs Comput. Mol. Sci.* 2012, **2**, 73-78.

[38] A. H. Lowrey, C. George, F. D'Antonio, and J. Karle, An electron diffraction investigation of the structure of hexafluoropropene combined with infrared and microwave spectroscopy, *J. Mol. Struct.*, 1979, **53**, 189-196.

[39] R. F. W. Bader, in *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, 1990.

[40] T. Lu and F. W. Chen, Multiwfn: a multifunctional wavefunction analyzer. *J. Comput. Chem.* 2012, **33**, 580-592.

[41] L. J. Farrugia, C. Evans and M. Tegel, Chemical bonds without "chemical bonding"? A combined experimental and theoretical charge density study on an iron trimethylenemethane complex. *J. Phys. Chem. A*, 2006, **110**, 7952-7961.

[42] D. Cremer and E. Kraka, Chemical bonds without bonding electron density—does the difference electron-density analysis suffice for a description of the chemical bond? *Angew. Chem., Int. Ed.*, 1984, **23**, 627-628.

[43] J. Georg, S. Martin, F. Bernd, H. G. Lutz, J. S. Ian and M. Mary, Unsupported Ti-Co and Zr-Co bonds in heterobimetallic complexes: a theoretical description of metal-metal bond polarity. *J. Am. Chem. Soc.*, 1998, **120**, 7239-7251.

[44] J. T. Fuller, D. J. Harrison, M. C. Leclerc, R. T. Baker, D. H. Ess and R. P. Hughes, A new stepwise mechanism for formation of a metallacyclobutane via a singlet diradical intermediate. *Organometallics*, 2015, **34**, 5210-5213.

Table of Contents Entry

Perfluoroolefin Complexes Versus Perfluorometallacycles and Perfluorocarbene Complexes in Cyclopentadienylcobalt Chemistry

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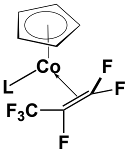
Density functional theory studies on the cyclopentadienylcobalt fluorocarbon complexes CpCo(L)(C_nF_{2n}) (Cp = η^5-C_5H_5; L = CO, Me_3P; *n* = 3, 4) indicate structures with perfluoroolefin ligands to be the lowest energy structures followed by perfluorometallacycle structures and finally by structures with perfluorocarbene ligands.



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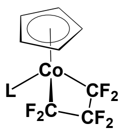
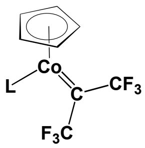


Perfluorinated Cobaltacyclobutane



Perfluorinated carbene complex