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$CoCF_3^+$ Is Really ($FCo^+\cdots F_2C$)

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Summary: Gas-phase ion chemistry studies and density functional calculations reveal that the structure of $CoCF_3^+$ *is really a* [$FCo^+\cdots F_2C$] *ion−dipole complex with electrostatic bonding between* FCo^+ *and* CF_2*. The reactions of* $CoCF_3^+$ *with* C_3−C_7 *alkanes, alkenes, and other reagents, such as benzene, water, and acetonitrile, yield predominantly* CF_2 *displacement products. This represents the first case of gas-phase C−F activation by bare cobalt ions.*

Introduction

Previous studies have shown that the reactivity of a metal ion in the gas phase can be dramatically altered by the presence of a ligand.[1−5] In this paper we report on CF_3 as a ligand. CF_3, the fluorine-containing analog of methyl radical, is a stable functional group of most hydrofluorocarbons (HFCs), including CF_3CF_2H, CF_3CFH_2, and CF_3CH_3. However, in contrast to CH_3, little is known about the effect of CF_3 on the reactivity of bare metal ions. Since fluorine has the greatest electronegativity, it exhibits a strong electron-withdrawing effect. On the other hand, fluorine is also a good π-electron donor to carbon π-systems, due to the similar size of its lone-pair 2p orbital to that of carbon. Thus, the effect of fluorine substitution is a combination of inductively withdrawing and π donating.[6] In particular, Halle, Armentrout, and Beauchamp have studied the effects of fluorine substitution on carbene stability, as well as the metathesis reactions of fluorinated olefins with $NiCH_2^+$ and $NiCF_2^+$.[5] They determined that $D^0(Ni^+{-}CF_2) = 47 \pm 7$ kcal/mol, which is substantially lower than $D^0(Ni^+{-}CH_2) = 86 \pm 6$ kcal/mol. On a related topic, C−F activation by metal centers in solution,[8−10] on surfaces,[11] and in the gas phase[12−15] has attracted a great deal of interest due to the very strong C−F bond and the high electronegativity of fluorine. In this study, we report on the gas-phase reactions of $CoCF_3^+$ with small aliphatic alkanes and alkenes, as well as with benzene, water, and acetonitrile. These reactions, together with density functional calculations and the corresponding thermochemistry, indicate that $CoCF_3^+$ is really the ion−dipole complex [$FCo^+\cdots F_2C$].

Results and Discussion

While $CoCF_3^+$ was first assumed to consist of a trifluoromethyl−Co^+ structure **1**, it soon became apparent that it might instead be a fluoro−difluorocarbene structure **2**. Collision-induced dissociation (CID) and sustained off-resonance irradiation (SORI) yield difluorocarbene loss as the major fragmentation pathway over the range of kinetic energies studied (5−80 eV in laboratory coordinates for CID and 3−5 eV for SORI), suggestive of a possible fluoro−difluorocarbene structure **2**. For comparison, CID and SORI of $CoCH_3^+$ yield $Co^{+\,2,3}$ exclusively by loss of an intact CH_3. Even stronger evidence for structure **2** is the reactions of $CoCF_3^+$ with L = alkanes, alkenes, benzene, water, and acetonitrile, which generally result in a prominent CF_2 displacement product, $CoFL^+$. These results strongly suggest that CF_3 is not an intact ligand in this case and that the CF_2 group is bound weakly to Co^+, in contrast to the Co^+−methyl structure of $CoCH_3^+$.[2,3]

$Co^+{-}CF_3$ **1**

$F{-}Co^+\cdots F_2C$ **2**

The primary reactions of $CoCF_3^+$ with alkanes and alkenes are summarized in Table 1. Like Co^+ and $CoCH_3^+$, $CoCF_3^+$ is unreactive with methane and ethane. Reactions with propane and other linear and branched alkanes up to C_7, however, yield the displacement products $F{-}Co^+{-}(C_nH_{2n+2})$ as the predominant products, except for the reactions with 2-methylpropane and 2-methylbutane. CID of these product ions yields FCo^+ exclusively, indicating that the alkane remains intact on the metal center. The displacement reaction implies that $D^0(FCo^+{-}F_2C) \le D^0(FCo^+{-}C_3H_8)$. While the latter value is not known, $D^0(Co^+{-}C_3H_8) = 30.9 \pm 1.4$ kcal/

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Table 1. Percentage Abundance of Primary Products Observed in the Reactions of $CoCF_3^+$ with Various Alkanes and Alkenes

alkane or alkene	neutral lost	products	rel %
methane		no reaction	
ethane		no reaction	
propane	CF_2	$CoF(C_3H_8)^+$	100
n-butane	CH_4	$CoCF_3(C_3H_6)^+$	75
	CF_2	$CoF(C_4H_{10})^+$	18
		$CoCF_3(C_4H_{10})^+$	7
2-methylpropane	$CoCF_3H$	$C_4H_9^+$	70
	CH_4	$CoCF_3(C_3H_6)^+$	18
	CF_2	$CoF(C_4H_{10})^+$	12
n-pentane	CF_2	$CoF(C_5H_{12})^+$	100
2-methylbutane	$CoCF_3H$	$C_5H_{11}^+$	71
	CF_2	$CoF(C_5H_{12})^+$	29
2,2-dimethylpropane	CF_2	$CoF(C_5H_{12})^+$	71
		$CoCF_3(C_5H_{12})^+$	29
n-hexane	CF_2	$CoF(C_6H_{14})^+$	100
n-heptane	CF_2	$CoF(C_7H_{16})^+$	100
ethene	CF_2	$CoF(C_2H_4)^+$	100
propene	CF_2	$CoF(C_3H_6)^+$	92
	CF_3H	$Co(C_3H_5)^+$	8
1-butene	CF_2	$CoF(C_4H_8)^+$	93
	CF_3H	$Co(C_4H_7)^+$	7
isobutene	CF_2	$CoF(C_4H_8)^+$	94
	CF_3H	$Co(C_4H_7)^+$	6
cis-2-butene	CF_2	$CoF(C_4H_8)^+$	100
1,3-butadiene	CF_2	$CoF(C_4H_6)^+$	100

mol[29] provides a useful estimate. Interestingly, the hydride abstraction products $i\text{-}C_4H_9^+$ and $i\text{-}C_5H_{11}^+$, which are stable tertiary carbocations, are dominant for the reactions of $CoCF_3^+$ with 2-methylpropane and 2-methylbutane, respectively. Formation of $i\text{-}C_4H_9^+$ suggests that $D^0(CoCF_3^+{-}H^-) > D^0(C_4H_9^+{-}H^-) = 376.1$ kcal/mol.[30] For comparison, $CoCH_3^+$ reacts with alkanes larger than ethane by initial C−H insertion, followed by CH_4 and H_2 loss to yield Co(allyl)$^+$ species.[2]

Pseudo-first-order kinetics are observed for the reactions of $CoCF_3^+$ with propane, *n*-butane, *n*-pentane, *n*-hexane, and *n*-heptane. For example, the kinetics plot of $CoCF_3^+$ with *n*-heptane at $\sim 2.5 \times 10^{-7}$ Torr is shown in Figure 1. [A] is reactant ion intensity after time *t*, and [A_0] is obtained by summing the intensities of the reactant ion and product ions at each time. The slopes of the pseudo-first-order plots are used with the calibrated reactant pressure to obtain the observed rate constants, k_{obs}. The Langevin rate constants, k_L, are also calculated to determine reaction efficiencies.[31] The values obtained for k_{obs}, k_L, and the reaction efficiencies are listed in Table 2. The linear pseudo-first-order kinetics observed for each of the reactions suggest, although not unequivocally, that the $CoCF_3^+$ ions are thermalized and consist of one isomeric structure. As the polarizability of the alkane increases, the reaction rates and efficiencies between $CoCF_3^+$ and the alkane increase dramatically. These results are again consistent with a weakly bound $FCo^+{\cdots}F_2C$ complex.

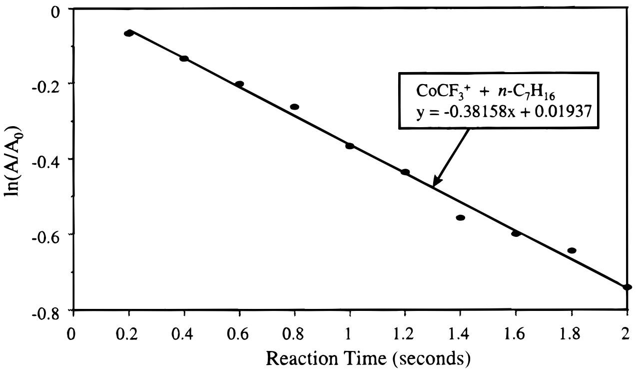

Figure 1. Pseudo-first-order plot of the reaction of $CoCF_3^+$ with *n*-heptane at 2.5×10^{-7} Torr.

Table 2. Rate Constants and Calculated Reaction Efficiencies for the Reactions of $CoCF_3^+$ with Various Linear Alkanes[a]

reagent	k_{obs}	k_L	reaction efficiency
propane	1.3×10^{-12}	1.0×10^{-9}	0.1%
n-butane	4.8×10^{-12}	1.1×10^{-9}	0.5%
n-pentane	5.9×10^{-11}	1.1×10^{-9}	5.4%
n-hexane	2.0×10^{-10}	1.1×10^{-9}	17%
n-heptane	2.6×10^{-10}	1.2×10^{-9}	22%

[a] Rate constants have the units of cm^3 molecule^{-1} s^{-1}.

Table 3. Bond Lengths and Bond Angles for the Optimized Geometries of $CoCF_3^+$ Using DFT with the Standard Effective Core Potential for Co^+ and the Dunning−Hay Double-ζ Basis Set for C and F[a]

species	bond length (Å)		bond angle (deg)	
$CoCF_3^+$	C−F(1)	1.291	F(1)−C−F(2)	100.2
	C−F(2)	1.629	C−F(2)−Co	155.0
	Co−F(2)	1.948	F(2)−Co−F(3)	179.4
	Co−F(3)	1.726		

[a] See Figure 2.

The reactions of $CoCF_3^+$ and alkenes are also dominated by CF_2 displacement, in contrast to those of $CoCH_3^+$, which proceed by initial elimination of methane to form an activated π-allyl complex.[3] CID of the $CoFL^+$ product ions gives FCo^+ as the major fragment and loss of HF as the minor fragment. The CF_2 displacement reaction of $CoCF_3^+$ with ethene suggests that $D^0(FCo^+{-}F_2C) < D^0(FCo^+{-}C_2H_4) \approx D^0(Co^+{-}C_2H_4) = 42.9 \pm 1.6$ kcal/mol.[29,32]

In addition, we have performed density functional calculations on $CoCF_3^+$. Four possible structures **3**−**6**

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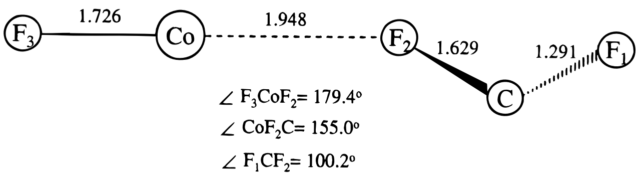
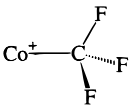


Figure 2. Optimized geometry of $CoCF_3^+$ with Becke-3-LYP using the standard effective core potential for Co^+ and the Dunning−Hay double-ζ basis set for C and F. All distances are given in Å.

were proposed as the starting structures in this calculation. Only structure **4** is found to be a true minimum,



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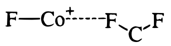

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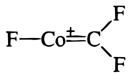

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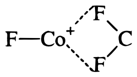

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while the other minimum structures of $CoCF_3^+$ were not detected. The ground state of Co^+ is found to be ^3F. Spin contamination is small in all of the calculations and the deviation of $\langle S^2\rangle$ is less than 1%. The optimized parameters are presented in Table 3, and the optimized structure is shown in Figure 2. The optimized $CoCF_3^+$ exhibits C_s symmetry with a Co−F(3) distance of 1.726 Å and a slightly elongated CF_2 unit bound to Co through F(2) by a distance of 1.948 Å. The Mulliken population analysis gives the charge distribution as follows: $q = +1.117$ for Co, $q = +0.578$ for C, $q = +0.015$ for F(1), $q = -0.326$ for F(2), $q = -0.383$ for F(3). The calculated binding energy of FCo^+-F_2C is 30.9 kcal/mol, which is in accordance with the experimental limit to a first approximation of 30.9 ± 1.4 kcal/mol. Interestingly, Paulino and Squires have reported a similar finding for CF_2Cl^-, where the evidence points to a carbene−halide anion structure consisting of a free carbene moiety bound electrostatically through carbon to Cl^- with nearly a full −1 charge on Cl atom.[33,34] In a similar vein, recent theoretical calculations by Schleyer and coworkers indicate that AH_3^+ is actually $HA^+\cdots H_2$ for A = Sn and Pb, while CH_3^+ and SiH_3^+ are strongly bound D_{3h} structures.[35] Likewise, our calculations indicate that $CoCF_3^+$ is a $[FCo^+\cdots F_2C]$ ion−dipole complex.

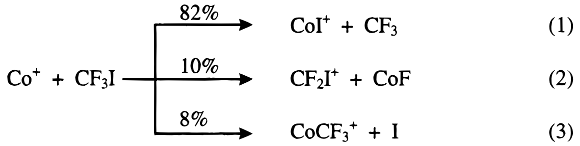
Conclusions

Upon fluorine substitution, the structure and reactivity of $CoCF_3^+$ are dramatically different compared to $CoCH_3^+$. Both experimental and theoretical results show that the structure of $CoCF_3^+$ corresponds to a $[FCo^+\cdots F_2C]$ ion−dipole complex. The weak bonding between FCo^+ and CF_2 leads to predominant displacement of CF_2 by alkanes, alkenes, and other reagents. In contrast, our recent experiments and calculations indicate that $CoCF_2^+$ corresponds to a $Co^+{=}CF_2$ structure with $D^0(Co^+-CF_2)$ bracketed as 49 ± 7 kcal/mol and calculated at 50.4 kcal/mol.[36] Thus, the bonding, bond strength, and reactivity of these two difluorocarbene complexes are quite different. To the best of our knowledge, this is also the first case of gas-phase C−F activation by bare Co^+. Currently, we are examining the structural integrity of CF_3 bound to other metal ions, such as the first- and second-row transition metals.

Experimental Section

All of the experiments were performed with a Nicolet (now Finnigan FT/MS, Madison, WI) prototype FTMS-1000 Fourier transform mass spectrometer, equipped with a Walker Scientific 15-in. electromagnet maintained at 1 T.[7] Laser desorption ionization was used to generate Co^+ from the pure metal foil by focusing the 1064 nm wavelength of a Quanta-Ray Nd:YAG laser on the metal target.[16] Argon was present at a static background pressure of ~1.0×10^{-5} Torr, serving as a cooling gas to thermalize the ions prior to reactions, as well as the collision gas in collision-induced dissociation (CID)[17] and sustained off-resonance irradiation (SORI)[18] experiments.

In analogy to the synthesis of $CoCH_3^+$ from CH_3I,[19] laser-desorbed Co^+ was reacted with trifluoromethyl iodide, which was pulsed into the cell via a General Valve Series 9 solenoid pulsed valve.[20] This yielded three products, CoI^+, CF_2I^+, and $CoCF_3^+$, reactions 1−3. The desired $CoCF_3^+$ was then isolated by using swept double-resonance ejection techniques[21] and cooled 400 ms prior to further reaction.



For the kinetics study, the alkane neutrals were introduced into the cell through a Varian leak valve and the reaction time was varied between 200 ms and 2 s. The pressure of the neutral reagent was kept at ~2.5×10^{-7} Torr, and Ar was used as the cooling gas at a total pressure of ~1.0×10^{-5} Torr. The pressure of the alkane neutral was measured using standard procedures for calibrating the ion gauge for the sensitivity toward the alkane.[22] The uncertainty in the pressure introduces an error of ±30% into the measurement of the absolute reaction rate constants, while the relative reaction rate constants are more reliable. The branching ratios of primary product ions are reproducible to within ±10%.

Theoretical calculations were carried out first at the Hartree−Fock level for full geometry optimization of $CoCF_3^+$ using the standard effective core potential[23] for Co^+, and the Dunning−Hay double-ζ basis set for C and F atoms.[24] In order to treat the effect of electron correlation, all of the calculations were repeated using DFT with Becke-3-LYP for the exchange correlation functional.[25] This functional has three fitted parameters and includes the Hartree−Fock exchange term. Although this functional is not exact,[26] it gives relatively accurate results for bond dissociation energies and geometries of transition metal compounds.[27] Corrections for zero point energy have been taken into account, as well as different spin configurations for Co^+ including ^3F and ^5F states. All of the calculations were performed with the Gaussian 94/DFT program package.[28]

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