Does OF$_2$ Form Stable Transition Metal Complexes? 
A Density Functional Investigation of the System (OC)$_5$Cr/OF$_2$

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Density Functional Theory (DFT) within the Local Density Approximation (LDA) was employed to calculate the reaction of OF$_2$ with the metal fragment Cr(CO)$_5$. It is demonstrated that OF$_2$ does not show simple ligand behavior but reacts with the transition metal fragment under oxidative addition, leading to a chromium oxo-complex and transforming two cis CO into fluoroformyl ligands. We calculated this reaction to proceed without any major activation barrier and to be exothermic by about 100 kcal/mol. A possible mechanism for this reaction is discussed.

Introduction

We recently discussed the σ-donor and the π-accepting behavior of simple group XV and XVI ligands bound to the metal fragment (CO)$_5$Cr and were able to provide a detailed bonding analysis, including bond energies of the metal-ligand bonds [1]. A surprising result of our study was that the very reactive fluorinated heavier chalcogen systems, SF$_2$ and SeF$_2$, show ligand behavior and act as moderate σ-donors and very powerful π-acceptors. The calculated Cr—EF$_2$ bond energies are large (BE in kcal/mol: Cr—SF$_2$ = 40.3 and Cr—SeF$_2$ = 36.9), which allowed us to speculate that it might be feasible to obtain stable complexes of SF$_2$ and SeF$_2$ using the appropriate conditions. In contrast to SF$_2$ and SeF$_2$, OF$_2$ does not show simple ligand behavior, but a more complex “reactivity” calculated with the metal fragment. For example, pure metals react with OF$_2$ to give metal oxides and metal fluorides [2a]. However, OF$_2$ "is relatively unreactive and can be mixed with H$_2$, CH$_4$, and CO without reaction, although sparking causes violent explosion" [2b].

In our calculations, we do not find that the OF$_2$ ligand stays intact upon complexation to the metal fragment, but instead we observe oxidative addition of the OF$_2$ molecule, going from a Cr$^0$-fragment to a Cr$^{1+}$-complex. Furthermore, cis-equatorial CO, activated due to complexation to the metal, is directly transformed into a fluoroformyl (FCO-)ligand. To our knowledge, there are no reports of metal-OF$_2$ complexes.

Regarding the theoretical approach, our method of choice is approximate density functional theory (DFT), which over the last decade has evolved into a powerful tool for practical applications to molecular structures and energetics of organometallic species [3a–c]. We will briefly account for the computational details of our calculations, before we discuss our findings in detail.

Computational Details

All calculations were performed utilizing the AMOL program package, developed by Baerends et al. [4a] and vectorized by Ravenek [4b]. The numerical integration was performed according to the procedure developed by te Velde et al. [4c]. The exchange factor, $\alpha_\text{ex}$, was given the usual value of 2/3. Electron correlation was treated within the Local Density Approximation (LDA) in the parametrization of Vosko et al. [4d]. The final energies were determined by adding Becke’s [4e,f] nonlocal exchange correlation as well as Perdew’s [4g] inhomogeneous gradient corrections for correlation. A double $\zeta$-STO basis set [4h], augmented by a single 3d-STO polarization function, was used for the $n$ s and $n$ p shells of carbon, oxygen and fluorine.
The $n\,s$, $n\,p$, $n\,d$, $(n+1)\,s$ and $(n+1)\,p$ shells of chromium were described by a triple $\zeta$-STO basis set. Electrons in lower shells were considered as core and treated according to the procedure of Baerends et al. [4a]. An auxiliary set [4i] of $s$, $p$, $d$, $f$ and $g$ STO functions, centered on all nuclei, was used in order to fit the molecular density and present Coulomb and exchange potentials accurately in each SCF-cycle. The geometry optimization procedure was based on the method of Versluis and Ziegler [4j]. All calculations were spin restricted.

**Results and Discussion**

1. **The molecular structures of $\text{OF}_2$ and $\text{Cr} (\text{CO})_5$**

   The molecular structure of $\text{OF}_2$ can be obtained experimentally by microwave spectroscopy. Morino and Saito [5a] determine free $\text{OF}_2$ to be bent with an $\text{F} - \text{O} - \text{F}$ angle of 103.2° and an $\text{O} - \text{F}$ bond length of 1.409 Å. Kirchhoff [5b] obtains a similar value for the bond angle, but a slightly longer $\text{O} - \text{F}$ bond length of 1.412 Å. From the theoretical point of view, $\text{O}_2\text{F}_2$-systems have been a challenging problem for *ab initio* calculations [6]. The $\text{O} - \text{F}$ bond lengths are in general significantly too short compared to the experimental values. Calculations on a high level of theory are required to satisfactorily describe the geometric structures. In an early SCF study, Rothenberg and Schaefer [7] calculated the bond length $d_{\text{O} - \text{F}}$ in free $\text{OF}_2$ to be 1.3585 Å and the angle $\angle \text{F} - \text{O} - \text{F}$ to be 102.91°. The discrepancy between the experimental and the theoretical bond length is obvious.

   It is of interest to compare the geometries obtained by *ab initio* methods with DFT results. The structure of our optimized free $\text{OF}_2$ is shown in 1. We note that our calculated bond length $d_{\text{O} - \text{F}} = 1.404$ Å as well as the bond angle $\angle \text{F} - \text{O} - \text{F} = 103.8°$ are in good agreement with the experimental values. This is especially true for the $\text{O} - \text{F}$ distance, which in our case is too short by only 0.005 Å to 0.009 Å, respectively.

   $\text{OF}_2$ indeed displays reverse polarity at the oxygen compared to other typical $\text{OR}_2$ compounds. The oxygen is slightly positively charged ($\delta_e = 0.0323$ a.u.), the fluorine atoms carry a negative charge ($\delta_f = -0.0162$ a.u.). The value for the dipole moment of $\text{OF}_2$, $\mu_{\text{OF}_2} = 0.297$ D, is rather small compared with $\text{OH}_2$, $\mu_{\text{OH}_2} = 1.85$ D, and $\text{O} (\text{CH}_3)_2$, $\mu_{\text{OMe}_2} = 1.30$ D [8]. Our calculated value for the dipole moment of $\text{OF}_2$ is 0.153 D.

   The geometry optimization of the chromium pentacarbonyl fragment resulted in a square pyramidal structure with $C_4v$ symmetry as shown in 2.

   ![Structure of $\text{OF}_2$](image)

   ![Structure of $\text{Cr} (\text{CO})_5$](image)

   The four equatorial CO are bonded to the metal with a distance $d_{\text{Cr} - \text{C}_{\text{eq}}} = 1.940$ Å. This is 0.022 Å smaller than the $\text{Cr} - \text{C}$ bond length in chromium hexacarbonyl, which we have calculated as $d_{\text{Cr} - \text{C}} = 1.962$ Å [1]. The $\text{C} - \text{O}$ bond length is with $d_{\text{C} - \text{O}_{\text{eq}}} = 1.147$ Å the same as in our calculated structure of $\text{Cr} (\text{CO})_6$. The axial CO shows with $d_{\text{C} - \text{C}_{\text{ax}}} = 1.890$ Å a significant shortening of the $\text{Cr} - \text{C}$ bond compared to $\text{Cr} (\text{CO})_6$. Furthermore, the $\text{C} - \text{O}$ distance is slightly elongated to be $d_{\text{C} - \text{O}_{\text{eq}}} = 1.151$ Å. It appears that for the axial CO ligand the increase in $\pi$-backbonding is most important.

   If the $\text{Cr} - \text{C}$ bond shortening is not accompanied by a change in the $\text{C} - \text{O}$ bond length, then one can conclude that both $\sigma$-bonding as well as $\pi$-backbonding are slightly enhanced. This is the
case for the equatorial CO ligands. Experimental IR studies of Cr(CO)₅ in a Nujol mull at 77 K [9] are in agreement with these calculated trends. Compared to Cr(CO)₆, a shift to lower wavenumbers is observed for the C–O stretching frequencies.

2. The molecular structures of \((CO)_3(OF)\_2Cr=O\) and \((CO)_2(OF)\_2Cr=O\)

The geometry optimization for the system \((CO)_3Cr(OF)\_2\) does not result in a typical Cr–OR₂ complex, in which the OR₂ ligand is weakly bonded to the metal fragment. Instead, we find that the optimized geometry can be interpreted as the outcome of an oxidative addition of OF₂, leading to an oxo-compound and transforming the two cis-equatorial CO into fluoroformyl ligands. The optimized structure of this unusual complex is displayed in 3. Complex 3 possesses a hexacoordinated Cr(d²) center in a distorted octahedral geometry. The Cr–O bond length is with \(d_{Cr-O} = 1.549\,\text Å\) about 0.02 Å to 0.05 Å shorter than Cr–O bond lengths in known pentacoordinated Cr(d²) systems [10]. The C–O bond length of the formyl unit is comparable to that of the free FCHO molecule [11] (\(d_{C-O} = 1.184\,\text Å\)). The C–F bond length is significantly elongated from \(d_{C-F} = 1.228\,\text Å\) in the free molecule to \(d_{C-F} = 1.350\,\text Å\) in the complexed FCO⁻ ligand. The most distinct feature of 3 is the CO ligand in the \(trans\) position. The metal carbon bond distance with \(d_{Cr-C_{Ir}} = 2.412\,\text Å\) is far out of range for a typical metal-carbon monoxide bond and indicates that this CO only forms a weak adduct with the metal fragment. We also note that now the C–O distance \(d_{C-O_{Ir}} = 1.125\,\text Å\) is slightly shorter than in the case of the calculated free CO. This indicates that for this particular ligand the electron donation to the metal center is most important. Since the ligand orbital involved in \(\sigma\)-bonding with the metal fragment is essentially antibonding with respect to the ligand C–O bond, an increase of electron donation will stabilize the C–O bond and thus shorten it.

As a \(\sigma\)-donor, the \(trans\) CO competes with the strong electron donors O₂⁻ and FCO⁻. As a \(\pi\)-acceptor, the \(trans\) CO cannot receive any electron density since the appropriate \(d\)-orbitals responsible for backbonding are now empty in the case of a Cr⁺⁴ system. This led us to the suggestion that the CO-ligand might be trapped in a local minimum on the energy hypersurface of the \((CO)_5Cr(OF)\_2\)-system, which prevents it from complete dissociation. We therefore optimized in addition the structure of the \((CO)_2(OCF)\_2Cr=O\) complex 4. In comparison to 3, the bond lengths of all ligands to the metal center are shortened, most prominently for the formyl ligand with a change of \(\Delta d = 0.172\,\text Å\). The interesting feature of this complex is that it adopts a tetragonal pyramidal (TP)
geometry rather than a trigonal bipyramidal (TBP) structure.

A rationale for this geometry distortion can be found by analyzing the orbital correlation diagram for the metal \(d\)-orbitals which connects these two geometries [12]. The basic motion that we follow is a decrease of the \(\angle L_{ax}-M-L_{ax}\) angle and an increase of the \(\angle L_{eq}-M-L_{eq}\) angle. For our particular system, this means that the CO groups are bent away from the oxo ligand (\(\angle CO-Cr-O>90^\circ\)), whereas the formyl groups are bent towards the oxo ligand (\(\angle FCO-Cr-O<120^\circ\)). The \(Cr^{IV}\) complex 4 possesses two empty \(d\)-orbitals, designated as \(1a'\) and \(1a''\) according to the \(C_5\) symmetry of the complex, which are available for electron donation from the oxo ligand (Fig. 1 a). Under geometry distortion, the \(1a'\) orbital will rise in energy, due to additional destabilizing \(\sigma\)-interaction with the axial ligands. Furthermore, the \(1a''\) orbital will decrease in energy since here the destabilizing interaction with the ligands is reduced (Fig. 1 b).

For a homoleptic system, the energy increase for the \(1a'\) orbital as well as the energy decrease for the \(1a''\) should be of equal size. However, our complex holds ligands of different \(\sigma\)-donor strength in equatorial and axial positions. Our previous calculations have shown CO to be only a moderate \(\sigma\)-donor [1]. It is a reasonable assumption that \(FCO^-\) is a stronger \(\sigma\)-donor than CO. This, on the other hand, implies a more drastic energetic decrease of the \(1a''\) orbital compared to the energetic increase of the \(1a'\) orbital. The geometry distortion from the trigonal bipyramid (TBP) towards the tetragonal pyramid (TP) results in an electronic structure, which might be more favorable for additional stabilizing \(\pi\)-donation from the oxo-ligand.

If we compare the total bonding energy of complex 3 with the total bonding energy of the system 4 plus free CO, we find that complex 3 is about 3.8 kcal/mol more stable than the system containing the free CO ligand as well as the free metal complex. The highly oxidized metal center might therefore be able to loosely bind to a third CO molecule.

3. The oxidative addition of \(OF_2\) to \(Cr(CO)_5\)

We investigated the course of this oxidative addition reaction by the linear transit method. As our reaction coordinate we chose the distance between the oxygen of the incoming \(OF_2\) molecule and the metal center of the \((CO)_5Cr\) fragment. We optimized the structures of the resulting complexes for four intermediate \(O-Cr\) distances. Some characteristic geometric data as well as the bonding energy compared to free \(OF_2\) plus free \(Cr(CO)_5\) (1 + 2) are given in Table I.
Table I. Some structural data for various CO-(CO)$_4$Cr-OF$_2$ complexes. The bond lengths are given in Å, the energies are reported in kcal/mol. All energies are relative to the system 1+2.

<table>
<thead>
<tr>
<th></th>
<th>d$_{Cr-O}$</th>
<th>d$_{O-F}$</th>
<th>d$_{F-Cr}$</th>
<th>d$_{Cr-Cr}$</th>
<th>d$_{O-Cr}$</th>
<th>ΔE</th>
</tr>
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<tbody>
<tr>
<td>1+2</td>
<td>∞</td>
<td>1.404</td>
<td>∞</td>
<td>1.890</td>
<td>1.151</td>
<td>0.0</td>
</tr>
<tr>
<td>3a</td>
<td>4.000</td>
<td>1.399</td>
<td>4.315</td>
<td>4.500</td>
<td>1.877</td>
<td>1.152</td>
</tr>
<tr>
<td>3b</td>
<td>3.000</td>
<td>1.400</td>
<td>3.510</td>
<td>3.579</td>
<td>1.792</td>
<td>1.154</td>
</tr>
<tr>
<td>3c</td>
<td>2.000</td>
<td>1.545</td>
<td>2.754</td>
<td>2.916</td>
<td>1.853</td>
<td>1.146</td>
</tr>
<tr>
<td>3d</td>
<td>1.562</td>
<td>2.437</td>
<td>1.656</td>
<td>2.422</td>
<td>2.286</td>
<td>1.126</td>
</tr>
<tr>
<td>3</td>
<td>1.549</td>
<td>2.852</td>
<td>1.350</td>
<td>2.816</td>
<td>2.412</td>
<td>1.125</td>
</tr>
<tr>
<td>4+CO</td>
<td>1.536</td>
<td>2.918</td>
<td>1.352</td>
<td>2.682</td>
<td>∞</td>
<td>1.131</td>
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</table>

The reaction proceeds straight forward from the products towards the final complex. We do not find any activation barrier for this reaction. As the OF$_2$ molecule approaches the metal fragment, the distance between the trans CO and the metal first becomes shorter whereas the C–O distance for the same CO slightly increases. The O–F distance of the incoming ligand decreases by about 0.005 Å. Since the electron density at the metal is polarized towards the incoming ligand, the trans CO can act as a stronger σ-donor, which leads to a shorter Cr–C$_{tr}$ distance. Concurrently, this synergetically induces a stronger ρ-backbonding, indicated in the slight elongation of the C–O bond length. Such adducts are observed for Cr–O distances between 4.0 Å and 2.5 Å and are a few kcal/mol more stable than the free systems. If the OF$_2$ molecule comes closer to the metal, the bonding situation changes. The trans CO now moves away from the metal and the O–F bond length increases. At a Cr–O distance of 2.0 Å, which would be in the range of an expected bond distance for a Cr(CO)$_5$–OF$_2$ complex, the O–F bond length is increased by 0.14 Å, compared to the free molecule. This shows how the OF$_2$ ligand accepts electron density from the metal center. Other OR$_2$ ligands like OH$_2$ and O(CH$_3$)$_2$ are not capable of any ρ-acceptance [1]. The higher difluoro chalcogenides SF$_2$ and SeF$_2$, which have been shown to be good ρ-acceptors, undergo an elongation of the S–F and Se–F bond by 0.03–0.04 Å, when coordinated to a Cr(CO)$_5$ fragment. The fact that the O–F bond stretch is about 4 times larger than for its heavier homologues indicates that the electron donation from the metal into the σ*-orbital of the OF$_2$ ligand might finally lead to a cleavage of the O–F bond. On further shortening of the Cr–O distance, the systems falls down into the steep well on the energy surface towards the final product, complex 3. The drastic rearrangement of the geometry of the complex takes place with almost no further change of the Cr–O bond length. The reaction profile together with selected geometries is shown in Fig. 2.

In Table II, the atom charges for selected atoms in various CO–(CO)$_4$Cr–OF$_2$ complexes are list-

<table>
<thead>
<tr>
<th></th>
<th>δ$_{Cr}$</th>
<th>δ$_{O}$</th>
<th>δ$_{F}$</th>
<th>δ$_{CO-eq C}$</th>
<th>δ$_{CO-eq O}$</th>
<th>δ$_{trans C}$</th>
<th>δ$_{trans O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1+2</td>
<td>0.597</td>
<td>0.032</td>
<td>-0.016</td>
<td>0.419</td>
<td>-0.526</td>
<td>0.421</td>
<td>-0.558</td>
</tr>
<tr>
<td>3a</td>
<td>0.639</td>
<td>0.010</td>
<td>-0.150</td>
<td>0.415</td>
<td>-0.529</td>
<td>0.405</td>
<td>-0.563</td>
</tr>
<tr>
<td>3b</td>
<td>0.775</td>
<td>-0.005</td>
<td>-0.007</td>
<td>0.405</td>
<td>-0.542</td>
<td>0.389</td>
<td>-0.577</td>
</tr>
<tr>
<td>3c</td>
<td>0.949</td>
<td>-0.174</td>
<td>-0.137</td>
<td>0.428</td>
<td>-0.526</td>
<td>0.410</td>
<td>-0.539</td>
</tr>
<tr>
<td>3d</td>
<td>1.295</td>
<td>-0.534</td>
<td>-0.406</td>
<td>0.563</td>
<td>-0.562</td>
<td>0.514</td>
<td>-0.436</td>
</tr>
<tr>
<td>3</td>
<td>1.525</td>
<td>-0.592</td>
<td>-0.512</td>
<td>0.794</td>
<td>-0.647</td>
<td>0.554</td>
<td>-0.436</td>
</tr>
</tbody>
</table>
It is notable that the OF$_2$ ligand at a distance 4.0 Å away from the metal fragment already induces a polarization of the electron density. Both oxygen and fluorine carry a little higher negative charge, and the metal center is slightly more positive. The trends for the \textit{trans} \textit{CO} ligand for Cr–O distances from 4.0 Å to 2.5 Å, as discussed above, are well reflected in the atom charges. The charges at the oxygen and at the carbon both become more negative. At the very short Cr–CO \textit{trans}–distances in this region, $\pi$-backbonding overcomes $\sigma$-donation. It is noteworthy that the incoming OF$_2$ also induces a small flow of density towards the ligand in the \textit{trans} position. The situation for complex 3d is particularly interesting. The charges on both the incoming oxygen as well as the incoming fluorine become significantly larger. The charge at the oxygen of the \textit{trans} \textit{CO} ligand drops from $\delta_{O,\text{tr}} = -0.539$ a.u. to $\delta_{O,\text{tr}} = -0.436$ a.u., which shows the loss of \textit{\pi}-backbonding from the metal. At the \textit{cis}-equatorial CO ligands, the negative charge at the oxygen rises, indicating that fluorine is attacking the $\pi^*$-orbital of the CO molecule. In the final product 3, the metal center is slightly less positively charged than in 3d. The \textit{trans} \textit{CO} carries a small overall positive charge, stemming from stabilizing electron donation to the metal center.

We would like to propose the following course of the reaction. The initial long range interaction between the incoming OF$_2$ and the metal fragment is a polarization of the electron density at the metal center towards the chalcogenide system, leading to the geometrical changes as discussed above. The fact that the incoming ligand is slightly tilted away from the metal fragment (see Fig. 2), indicates the formation of a $\sigma$-bond [1], which mainly involves a chalcogen based $p$-hybrid lone pair orbital of OF$_2$ and the LUMO of the Cr(CO)$_5$ fragment (Fig. 3a). However, the electron flow from the occupied $d$-orbitals at the metal into $\sigma^*$-type orbitals of OF$_2$ is to be considered the major interaction (Fig. 3b and 3c). This oxidative process eventually leads to a cleavage of the O–F bond, leaving the electron pair at the fluorine. The F atom now migrates towards a carbonyl group in \textit{cis}-position. An intermediate structure showing fluorine on its way towards CO is 3d. During this process, the fluorine atom comes in close vicinity to the positively charged metal center, which might support the migration step. Finally, the F atom attacks the CO ligand \textit{via} a $\pi^*$ orbital, inducing the formation of the FCO$^-$ ligand (Fig. 3d). The last step then is the rotation of the fluoroformyl unit into its equilibrium position.

Finally, we will briefly address the question why the heavier homologues of OF$_2$ might form stable (CO)$_5$Cr–EF$_2$ complexes and do not spontaneously undergo oxidative addition. During oxidative addition, two E–F bonds have to be broken. The energy required for this process can be estimated from thermodynamic data to be 175 kcal/mol for SF$_2$, but only 94 kcal/mol for OF$_2$ [13]. On the other hand, a very strong Cr=E bond will be formed. The bond energies for diatomic Cr=E are 103 kcal/mol for O and 79 kcal/mol for S [8]. In addition, two C=O triple bonds are transferred into two C=O double bonds and two C–F single bonds, a process for which we can estimate a gain in energy of 52 kcal/mol [14]. Although these rough estimates do not consider the further changes of the Cr(CO)$_5$-fragment, we might conclude that the process of oxidative addition should be exothermic for OF$_2$, but it should be endothermic for SF$_2$. This argument is supported by the fact that according to our calculations SF$_2$ forms a very strong metal ligand bond [1]. However, the energy required for breaking an E–F bond mainly determines whether the oxidative addition reaction might occur spontaneously or not.

![Fig. 3. Mechanism of the oxidative addition. The OF$_2$ ligand approaches the Cr(CO)$_5$ fragment and establishes a $\sigma$-bond (a). $\pi$-Backbonding into $\sigma^*$-orbitals of OF$_2$ induces the oxidative addition and the O–F bond cleavage (b+c). The F atom migrates toward a \textit{cis} CO group and attacks at C \textit{via} an antibonding $\pi^*$-orbital of CO to establish the formation of the fluoroformyl group (d).]
Conclusion

The result of our DFT study is that OF$_2$ most likely will not show ligand behavior when reacting with metal fragments. Instead, as one might have expected, OF$_2$ acts as a fluorinating and oxidizing agent. In a process of oxidative addition leading to a metal oxo compound, OF$_2$ further transforms two carbonyl ligands into formyl derivatives. We expect this reaction to proceed without any major activation barrier and to be exothermic by about 100 kcal/mol. This coordination chemistry of OF$_2$ is unique compared to other OR$_2$ derivatives, higher EF$_2$ homologues as well as the pnictogenide equivalents EF$_3$.

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