Reactivity of Gas-Phase Niobium Clusters toward Several Cyclic Hydrocarbons

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The reaction of small niobium metal clusters, Nb_x (x = 2–15), made by laser evaporation of solid niobium within a supersonic nozzle beam, with cyclohexane (C_6H_{12}), cyclohexene (C_6H_{10}), and 1,3-cyclohexadiene (C_6H_8) is investigated in a fast flow reactor. No reaction products are observed for the saturated cyclohexane molecule under our conditions. However, the unsaturated compounds show differing degrees of dehydrogenation dependent on the size of the parent niobium cluster. For clusters of three or fewer niobium atoms, dehydrogenation to form $Nb_xC_6H_6$ (presumably a benzene compound) is observed. Further dehydrogenation to form $Nb_xC_6H_{2y}$ (y = 2, 1, and 0) is observed for clusters with $x \geq 4$. These results are compared with previous results for reactions with benzene under similar conditions. All the results can be rationalized in terms of the relative stabilities of the reactants and products for the different reactions involved.

Introduction

The method of laser vaporization[1] of a solid target within a pulsed supersonic nozzle has been shown to generate isolated clusters consisting of $2-10^2$ atoms with densities sufficiently high for spectroscopic and mass analysis.[2,3] Several studies thus far have used this technique of cluster synthesis in molecular beams to examine the electronic and magnetic properties through measurements of their ionization potentials[3] and magnetic moments.[4] The chemistry of clusters has also been examined through experiments on their relative reactivity and kinetics in a fast flow reactor.[5,6] In order to better understand the factors that determine the observed reactivity of the different cluster sizes, we studied the reaction of niobium clusters (Nb_x) with different organic compounds. The isotopic purity of niobium leads to a simple mass spectrum with only one mass peak for each cluster size. In addition, the niobium clusters are known to have ionization potentials below the photon energy of an ArF excimer laser.

The reaction of benzene with niobium clusters has recently been reported.[7] The conversion of $Nb_xC_6H_6$ to Nb_xC_6 was followed as a function of the size of the cluster. Under the conditions used

in that study, the observation of a threshold for this dehydrogenation reaction at x = 4 with an observed maximum of reactivity at x = 5 and 6 and minimum at x = 8 and 10 could be explained in terms of the relative stability of the benzene and the different Nb_x clusters.[7]

In this work organic reactants with different relative stabilities with respect to benzene are reacted with niobium clusters. The cyclic hydrocarbons, cyclohexane, cyclohexene, and 1,3-cyclohexadiene are used. It is found that, under our conditions, unsaturated carbon–carbon bonds seem to be required to observe reactions with niobium clusters. Once again, a number of observations are found that can be described in terms of the relative stabilities of the reactants and the different products formed.[7]

Experimental Section

The experiment involves the generation of niobium metal clusters by laser vaporization[8] (5 mJ of 355-nm light) of a solid niobium rod in the midst of a helium pulse. The metal atom plume formed from the rod is entrained and quenched in the helium pulse where condensation/nucleation results in cluster formation. The clusters are then expanded into our fast flow reactor tube where a pulse of reactant gas mixture overlaps with the metal cluster beam. The reactant is pulsed into the stream of clusters such that the overlap and mixing with the metals are maximized. The average density in the reactor region is calculated to be ~200 Torr in helium with a 1–2% reactant concentration. The retention time for the metals in the reactor is measured to be ~120 μs. The cluster mixture is then expanded into a high-vacuum system where a sudden decrease in density halts all but unimolecular reactions from occurring.

Detection of the cluster products is done using an ArF excimer laser to photoionize the species for the time-of-flight (TOF) mass analysis. The laser energy is kept to a 50-μJ, unfocused 2-mm-diameter beam to assure that only single-photon ionization occurs, thereby minimizing multiphoton fragmentation of the reaction products.[9] The resulting ions are then accelerated down a 1.7-m TOF mass spectrometer and collected on a multichannel plate ion detector. The signal is then amplified, digitized, and stored as a mass spectrum on a VAX 11/780 computer.

The appearance of new product peaks from the addition of reactant mixtures is monitored by alternately using a control reactant which consists of only pure helium kept at the same pressure as the helium reactant mixture. This allows for a comparison between the bare niobium cluster distribution and the new distribution formed when the reactant species are introduced into the reactor. The observed cluster distribution can be centered

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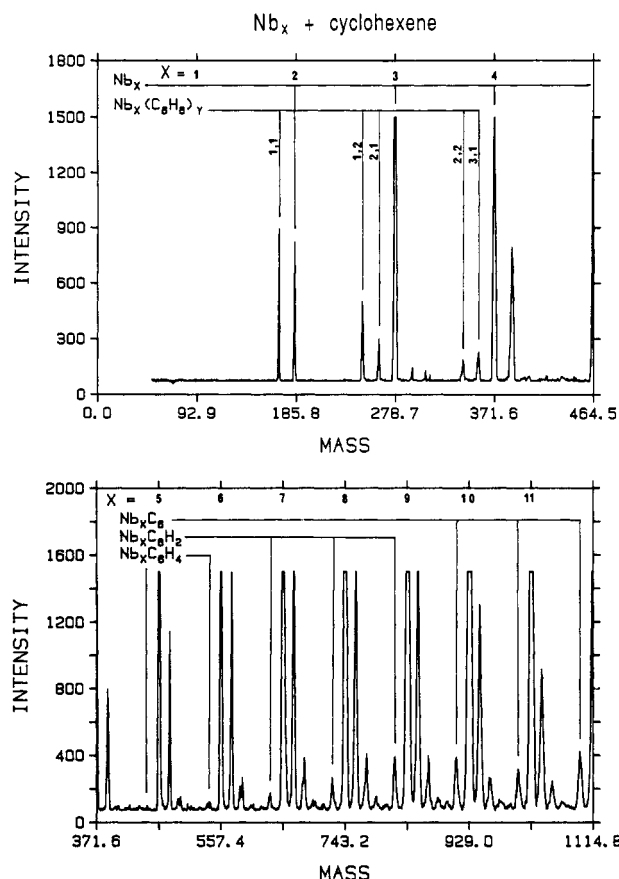(9) St. Pierre, R. J.; Chronister, E. L.; El-Sayed, M. A. *J. Phys. Chem.,* in press.

Figure 1. Shown is an expanded view of the TOF photoionization mass spectrum of niobium clusters reacted with cyclohexene (C_6H_{10}). The upper portion of the figure shows the small cluster region, i.e., fewer than four niobium atoms in the cluster. Simple adsorption of the reactant compound to any of the metal clusters is not detected. Instead, reactions occur which result in single and multiple units of a benzene-like species bound to these smaller clusters, i.e., $Nb_x(C_6H_6)_y$. In the larger cluster region shown below we observe products of the form $Nb_xC_6H_y$ with (y = 4, 2, or 0). It is found that the amount of dehydrogenation increases as the niobium cluster size increases up to about Nb_{10}.
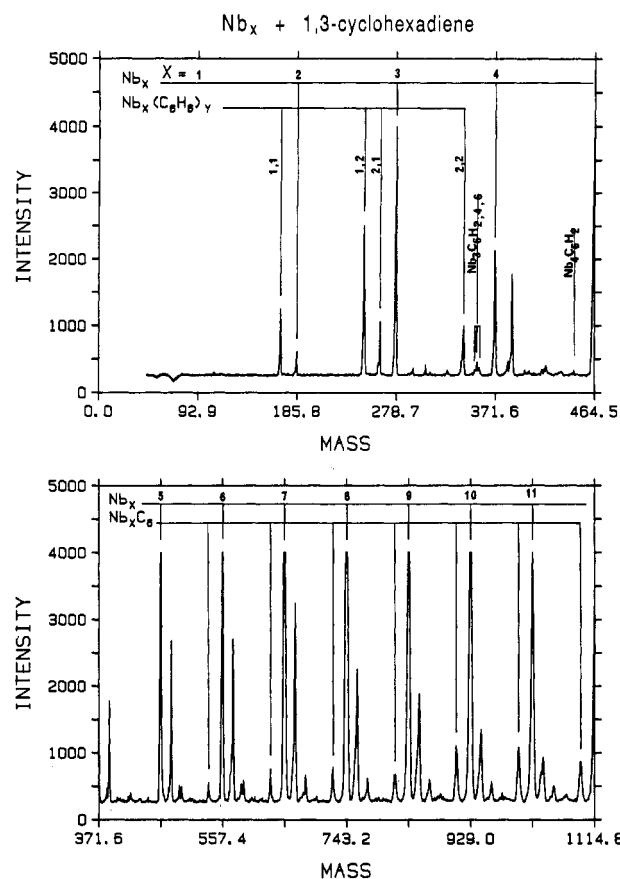

Figure 2. Shown is an expanded view of the TOF photoionization mass spectrum of niobium clusters reacted with 1,3-cyclohexadiene (C_6H_8). The upper portion of the figure shows the small cluster region, i.e., four or fewer niobium atoms in the cluster. We again do not observe any cluster adducts with the reactant molecule, but again we see products of the form $Nb_x(C_6H_6)_y$, as well as further dehydrogenated products. The Nb_3 parent cluster shows the product peaks $Nb_3C_6H_6$, $Nb_3C_6H_4$, and $Nb_3C_6H_2$, and the major product of Nb_4 is $Nb_4C_6H_2$. In the larger cluster region (>5 niobium atoms) shown below, the 1,3-cyclohexadiene appears completely converted to a Nb_xC_6 product species.

around Nb_7 as the most intense peak by setting the appropriate deflection voltages on the TOF mass spectrometer. A peak for Nb_1 should not seen since its ionization potential (6.8 eV) is higher than the 6.4-eV energy of the ArF laser photons. Typically, satellite peaks to higher mass of each Nb_x peak can occur and are Nb_xO_y oxide species resulting from oxygen impurities in the metal sample region.

Results

When cyclohexane (1.4% in helium) was mixed with the niobium clusters formed in our fast flow reactor, it yielded a spectrum identical with our control in which only helium was mixed into the reaction tube. Since no new peaks appeared and the shape of the niobium cluster distribution was relatively unchanged, it suggests that cyclohexane does not adsorb well on these clusters; i.e., a minimum of a double bond may be required to cause physisorption or chemisorption prior to further reactions on these metal clusters. However, the possibility of there being reactions or chemisorption products cannot be entirely ruled out. If the ionization potential of the reaction products has been increased relative to that of the bare cluster, above the 6.4-eV energy of the ArF laser photons, the species will not be photoionized or detected.

Cyclohexene (1.3%) and 1,3-cyclohexadiene (1.4%) were then mixed into the reactant gas pulse under similar conditions to that used for cyclohexane and benzene.[7,9] The spectra with the unsaturated reactant molecules show definite new product peaks as a result of reaction with the parent niobium clusters. An expanded view of the cyclohexene spectrum is shown in Figure 1. The upper portion of the figure shows the region from Nb_1 through Nb_4. For

the Nb_x clusters with x = 1–3, the cyclohexene has chemisorbed and reacted to form a C_6H_6 species. Product peaks corresponding to $Nb_x(C_6H_6)_1$ are observed for x = 1, 2, and 3 while $Nb_x(C_6H_6)_2$ species are observed for x = 1 and 2. In the lower portion of the figure, the region from Nb_4 to Nb_{15} is shown. If one carefully measures the mass values of the product peaks, the degree of dehydrogenation of cyclohexene is seen to gradually progress as the niobium cluster size increases. Niobium clusters with x = 4 and 5 show $Nb_xC_6H_4$ as the dominant mass peaks while clusters with x = 6, 7, and 8 have $Nb_xC_6H_2$ as their major products. In the region from Nb_9 to Nb_{15} the cyclohexene is completely dehydrogenated and Nb_xC_6 products are dominantly observed.

Figure 2 shows a similar view of the mass spectrum resulting from a reaction with Nb_x and 1,3-cyclohexadiene. Again, the niobium atom and dimer show the $Nb_xC_6H_6$ product peak as the major product. These niobium clusters also show $Nb_x(C_6H_6)_2$ products. The Nb_3 parent cluster clearly shows the product peaks $Nb_xC_6H_6$, $Nb_xC_6H_4$, and $Nb_xC_6H_2$, the most intense being $Nb_xC_6H_4$. The major product of Nb_4 is $Nb_xC_6H_2$ although the peak intensity is low. For the rest of the larger niobium clusters with x = 5–15, the cyclohexadiene appears completely converted to a Nb_xC_6 product species.

In the case of both cyclohexene and 1,3-cyclohexadiene, several similar observations can be made. A strong product peak for the niobium atom adducts is observed in both spectra. Also, no evidence for adsorption of the parent molecular species is seen on any of the clusters regardless of its size. Also, the larger niobium clusters (especially Nb_8 and Nb_{10}) show no $Nb_xC_6H_6$ products which were observed when benzene was reacted with these clusters. The niobium oxide clusters present in our control
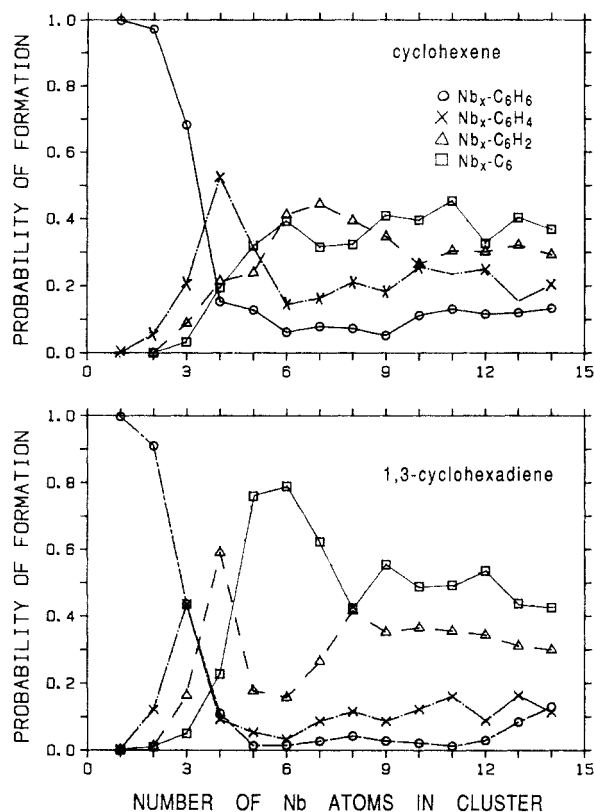
Figure 3. Intensities of the products Nb_x-C_6H_6, -C_6H_4, -C_6H_2, and -C_6 are all plotted simultaneously as a function of the niobium cluster size, x, for both cyclohexene and 1,3-cyclohexadiene and are normalized to the total observed product intensity for a particular niobium cluster size. It can be seen that for small x $Nb_xC_6H_6$ products dominate but that successively larger niobium clusters show correspondingly more dehydrogenation of their most abundant product species.

spectra (a ubiquitous impurity) do not appear to react with either of these hydrocarbon compounds and were previously found to be unreactive toward benzene.[7]

Discussion

From the above results it can be seen that the reactivity of the niobium cluster distribution toward the reactants cyclohexene and 1,3-cyclohexadiene appears to have three different reactivity regions.

Region 1. The observed chemistry of the smaller Nb_x clusters with $x \leq 3$ is dominated by the appearance of products of the form $Nb_x(C_6H_6)_y$ with $y = 1$ and 2. Products of this type were also observed for the reaction of benzene[7] with small niobium clusters, suggesting benzene as the identity of the C_6H_6 species.

Region 2. The intermediate cluster size region, Nb_x with $x = 4$–8, shows reaction products which are of the form $Nb_xC_6H_y$ with $y = 4, 2$, and 0. This region shows the progression toward complete dehydrogenation.

Region 3. For the larger clusters, $x \geq 9$, the most dominant hydrocarbon adduct is Nb_xC_6, indicating complete dehydrogenation of the molecular reactant.

Figure 3 shows the intensities for products of the form $Nb_xC_6H_y$ with $y = 6, 4, 2$, or 0, for the reactions of niobium with cyclohexene and cyclohexadiene. The intensities of the products Nb_x-C_6H_6, -C_6H_4, -C_6H_2, and -C_6 are all plotted simultaneously as a function of the niobium cluster size, x, and are normalized to the total observed intensity for that niobium cluster size.

The important conclusions that can be drawn from the results obtained under our experimental conditions can be summarized as follows:

1. At least one double bond in the hydrocarbon ring is required in order to observe niobium–hydrocarbon adducts. This seems to indicate a role for the unsaturated double bonds (π electrons) for the adsorption (and further reaction) of these hydrocarbons on niobium clusters.
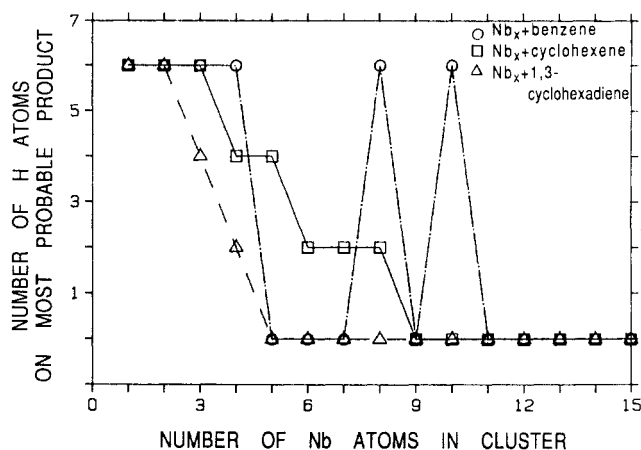

Figure 4. Gross features of the cluster-induced dehydrogenation of cyclohexene and 1,3-cyclohexadiene are shown by plotting the number of hydrogens found on the most abundant product peak as a function of niobium cluster size. Also included are the results for benzene dehydrogenation from a previous publication.

2. For niobium clusters of fewer than three niobium atoms, $Nb_xC_6H_6$ and $Nb_x(C_6H_6)_2$ are strongly detected. These types of products are observed for the reaction of both cyclohexene and 1,3-cyclohexadiene. They are also observed for the reaction when benzene is used.[7] These two observations suggest that the C_6H_6 on these clusters is a benzene-like adduct.

3. For the reaction with cyclohexene and 1,3-cyclohexadiene, Nb_xC_6 is observed weakly for $x = 3$ and increases gradually for larger niobium clusters. This trend can be seen in Figure 3 for both cyclohexene and cyclohexadiene. Figure 4 displays the gross features of the dehydrogenation process by plotting the number of hydrogens found on the most abundant product peak as a function of niobium cluster size. Figure 4 is easily derived from Figure 3 by simply finding the most probable product for each cluster size; included also are the results for benzene from our previous work.[7] For the benzene reaction,[7] a sharp threshold is observed at $x \geq 5$ for the dominant production of Nb_xC_6 except for clusters Nb_8 and Nb_{10} which show dominant $Nb_xC_6H_6$ products.[7] Contrary to the benzene results, $Nb_xC_6H_6$ products are never observed as dominant products for $x > 4$ in the reactions of cyclohexene and 1,3-cyclohexadiene with the larger niobium clusters. This indicates that these reactions most likely do not proceed via the formation of an intermediate benzene-like adduct $Nb_xC_6H_6$.

4. From Figure 3 it can be seen that there is a trend in the appearance of the different dehydrogenated product peaks with increasing niobium cluster size. In the case of benzene,[7] there is evidence of a sharp threshold for the conversion of $Nb_xC_6H_6$ to Nb_xC_6. The appearance of the intermediate $Nb_xC_6H_{2y}$ product peaks may be due to slower dehydrogenation reaction rates. This suggests that a chain dehydrogenation process with successive loss of molecular hydrogen is possible for cyclohexene and 1,3-cyclohexadiene. It is interesting that the total dehydrogenation of 1,3-cyclohexadiene becomes dominant at $x = 5$ just like for benzene, as shown in Figure 4. This might be a result of the fact that with six carbon atoms and five Nb atoms, sufficient Nb–C bonds can be formed to drive the reaction.

Points 2, 3, and 4 can best be explained in terms of the relative stability of the reactants and products. For smaller clusters, benzene simply chemisorbs,[7] while cyclohexene and 1,3-cyclohexadiene seem to react to form a benzene-like adduct. This behavior might thus be explained by the relative stability of the benzene structure. A minimum of five Nb atoms in the cluster are needed before $Nb_xC_6H_6$ is no longer the dominant product species in the reaction with benzene while fewer than five niobium atoms are needed to observe $Nb_xC_6H_y$ products for reactions with cyclohexene and 1,3-cyclohexadiene. The stability of the aromatic benzene ring may require the formation of more Nb–C bonds to make that reaction thermodynamically more favorable. In addition, the evolution of additional H_2 molecules in the reactions

of niobium clusters with cyclohexene and 1,3-cyclohexadiene makes both the energy and the entropy contribution to the free energy even more favorable for the dehydrogenation reaction. These two factors, the lack of aromatic stability and the increased entropy change, appear to lessen the effect of the relative stability of the Nb_8 and Nb_{10} structures on their reactivity with cyclohexene and 1,3-cyclohexadiene. There is no distinct minimum reactivity for these cluster sizes with cyclohexene and 1,3-cyclohexadiene as was observed for benzene.

Before closing, we would like to point out some obvious difficulties with the interpretations used in this field in general: (1) As we pointed out previously,[7,9] it is difficult to differentiate between neutral thermal reactions (which is generally assumed) in the reactor and a one-photon photochemical reaction induced during the detection process (or a combination). (2) The internal temperature of these clusters before, during, or after the reaction is not known. (3) The ions formed in the plasma by the vapor-ization laser are not completely neutralized prior to their arrival at the reactor. Due to the large ion–molecule reaction cross section, small amounts of unneutralized ions could greatly contribute to the neutral distribution of the organometallic species, which upon ionization with the excimer laser can be detected. (4) Finally, the name "cluster" probably does not apply to these compounds, in particular when the number of atoms in a cluster is as small as it is in our system. All these compounds have relatively strong chemical bonds so they are actually molecules; for the pure metal clusters they are homonuclear polyatomics, and for their reaction products with organic compounds they are organometallic compounds. However, the word cluster here is useful in differentiating this type of work from other kinds in the field of chemical reactivity.

New Predictions for Singlet–Triplet Gaps of Substituted Carbenes

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Recent thermodynamic analysis by Carter and Goddard suggested the best previous ab initio predictions of substituted carbene singlet–triplet splittings were in error by 3 to 17 kcal/mol. Herein we report a new approach for correlation-consistent calculations [based on generalized valence bond with configuration interaction] which yields accurate but simple wave functions. Applying the method to the singlet–triplet splittings of CH_2, $CH(SiH_3)$, CF_2, CCl_2, CHF, and CHCl leads to good agreement (within 3 kcal/mol) with available experimental results.

Considerable uncertainty exists in the values of singlet–triplet energy splittings in substituted carbenes, with CF_2 being the only heterocarbene for which an experimental ΔE_{ST} has been reported.[1] These values are crucial for understanding the chemistry expected for such carbenes, since singlet carbenes are known to undergo concerted, stereospecific reactions, while triplet carbenes are typically involved in stepwise, nonstereospecific chemistry.[2] Carter and Goddard[3] recently suggested a means of extracting the singlet–triplet splittings ($\Delta E_{ST} = E_{singlet} - E_{triplet}$) in halogenated carbenes, from a thermochemical analysis of bond strength trends in substituted olefins and methanes. However, the estimates obtained from this analysis were in serious disagreement (up to 17 kcal/mol) with the best previous ab initio theoretical predictions of ΔE_{ST}.[4–6] In order to test the reliability of these empirical predictions[3] and to assess the accuracy of previous theoretical results, we developed a new theoretical approach practical for large substituents on carbenes (X and Y on CXY). Herein we report the first results from this new ab initio technique.[7]

Elements of the method include generalized valence bond correlations for the bonds to carbon (C–X and C–Y bonds) and the nonbonding σ orbital in singlet carbene [thus, GVB(3/6) for describing these three electron pairs with six orbitals and perfect singlet pairing].[8] The perfect pairing restriction is relaxed by performing a restricted configuration interaction (RCI) calculation which allows all three occupations of two electrons in two orbitals for each correlated pair (leading to 27 configurations for singlet carbene, before accounting for symmetry). This self-consistent RCI wave function (using only 20–25 spin eigenfunctions) provides an excellent approximation (within 0.5 kcal/mol) to the full CI result (involving ~220 000 spin eigenfunctions) for the singlet–triplet splitting in methylene.[9]

For electronegative substituents with lone pairs (e.g. F, Cl), it is critical to allow charge-transfer (CT) configurations, in which π donation from the ligand lone pairs to the partially empty $p\pi$ orbital on carbon is allowed simultaneous with σ CT from carbon to the ligand. Thus, to the RCI wave function above (which allows σ CT), we include simultaneous excitations from the $p\pi$ lone pairs on X and Y to the C $p\pi$ orbital. When optimized self-consistently, this RCI*ΠCI(opt) wave function yields excellent results for CF_2

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