to observe that the symmetric C–F stretching mode has changed very little in frequency from 1063 cm^{-1} for $CF_3Mn(CO)_5$ to 1052 cm^{-1} for $CF_3Mn(CO)_4^-$, whereas the frequency of the degenerate C–F stretching mode of E-type symmetry has decreased from 1043 cm^{-1} for $CF_3Mn(CO)_5$ to 945 cm^{-1} for $CF_3Mn(CO)_4^-$.

Ligand Displacement Reaction Mechanism. The square-based pyramidal $CF_3Mn(CO)_4^-$ ion reacts with NO to produce $CF_3Mn(CO)_3(NO)^-$ with loss of CO. The proposed association mechanism for the ligand displacement reaction is shown in Scheme IV.

It is suggested that the reaction of NO with the 17 e$^-$ $CF_3Mn(CO)_4^-$ ion (VII) involves an approach of NO to a singly occupied orbital on the apical site to form an 18 e$^-$ intermediate (VIII) having a bent Mn–NO bond (1 e$^-$ donor) followed by loss of equatorial carbonyl trans to NO, with charge transfer from nitrogen to metal forming a linear Mn–N–O bond (3 e$^-$ donor). It has been previously shown that several metal nitrosyl carbonyl compounds (e.g. $V(CO)_5(NO)$, $Mn(CO)_4(NO)$, and $Co(CO)_3(NO)$) undergo ligand displacement reactions via an associative (S_N2) pathway involving a bent metal nitrosyl intermediate.[44] Lionel et al.[45] have observed the electron paramagnetic resonance spectrum of $Mn(CO)_4(NO)^-$ doped in $Cr(CO)_6$ single crystals suggesting that the Mn–N–O moiety is bent. These observations support the proposed associative mechanism for the ligand displacement reaction. The resulting ion is formally an 18 e$^-$ complex and presumed to have a trigonal-bipyramidal structure with a linear Mn–NO in the equatorial position.[46] Frenz et al.[47] have determined the crystal structure of $Mn(CO)_4(NO)$, revealing that the nitrosyl group is in an equatorial position in the trigonal-bipyramidal structure and the Mn–CO and Mn–NO bonds are linear. $Mn(CO)_5^-$ also has a trigonal-bipyramidal structure in the solid state.[48]

Conclusion

The CF_3 migratory decarbonylation reaction of $CF_3COMn(CO)_4^-$ yielding $CF_3Mn(CO)_4^-$ with loss of CO is observed in the gas phase. The structures of the reactant and product ions are elucidated by employing various mass spectrometric techniques. The kinetic studies of decomposition of $CF_3COMn(CO)_4^-$ show that the CF_3 migration occurs with a small barrier either prior to or in concert with decarbonylation.

The CF_3 group bonded to a transition-metal center is an ideal infrared chromophore to investigate the infrared photochemistry of organometallic complexes. These studies yield information related to the structure and reaction mechanisms of coordinatively unsaturated organometallic intermediates. It will be of further experimental and theoretical interest to see how the C–F stretching frequencies vary with the number and variety of ligand substituents in complexes containing metal-bonded CF_3 groups.

Acknowledgment. S.K.S. acknowledges the assistance of J. W. Park for the synthesis and J. E. Hanson for the FT-IR spectra. We also acknowledge the support of the National Science Foundation (Grant No. CHE87-11567) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

---

[44] Basolo, F. *Inorg. Chim. Acta* **1985**, *33*, 100.

[45] Lionel, T.; Morton, J. R.; Preston, K. F. *J. Phys. Chem.* **1982**, *86*, 367.

[46] Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* submitted for publication.

[47] Frenz, B. A.; Enemark, J. H.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 1288.

[48] Frenz, B. A.; Ibers, J. A. *Inorg. Chem.* **1972**, *11*, 1109.

Infrared Multiphoton Dissociation Spectrum of $CF_3Mn(CO)_3(NO)^-$

Seung Koo Shin and J. L. Beauchamp*

Contribution No. 7952 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. *Received August 9, 1989*

Abstract: An infrared multiphoton dissociation spectrum of $CF_3Mn(CO)_3(NO)^-$ has been obtained with Fourier transform ion cyclotron resonance spectroscopy combined with a line-tunable continuous wave CO_2 laser in the 925–1085 cm^{-1} wavelength range. The trifluoromethyl group in the anion shows two absorption maxima at 1045 and 980 cm^{-1}. The peak at 1045 is assigned as a C–F stretch of A_1-type symmetry and the peak at 980 cm^{-1} is ascribed to a C–F stretch of E-type symmetry. It is quite interesting to observe that the symmetric C–F stretching mode changes little in frequency from 1063 cm^{-1} for $CF_3Mn(CO)_5$ to 1045 cm^{-1} for $CF_3Mn(CO)_3(NO)^-$, while the C–F stretching frequency of E-type symmetry decreases from 1043 cm^{-1} for the 18 e$^-$ neutral precursor to 980 cm^{-1} for the 18 e$^-$ anion. Comparison with the infrared multiphoton dissociation spectrum of $CF_3Mn(CO)_4^-$ ion reveals that the degenerate C-F stretch of E-type symmetry increases from 945 cm^{-1} for the 17 e$^-$ $CF_3Mn(CO)_4^-$ to 980 cm^{-1} for the 18 e$^-$ $CF_3Mn(CO)_3(NO)^-$, whereas the symmetric C–F stretching bands overlap with each other within experimental uncertainties. Variations of the electron density and hybridization in the σ donor orbital of the CF_3 ligand due to the different d orbital splittings of the complexes may be responsible for the distinctive C–F stretching frequencies observed in $CF_3Mn(CO)_5$ (18 e$^-$), $CF_3Mn(CO)_4^-$ (17 e$^-$), and $CF_3Mn(CO)_3(NO)^-$ (18 e$^-$).

Spectroscopic study of molecular ions has been of great experimental interest in recent years.[1-3] Various techniques have been employed to obtain information about the structures, vibrational and electronic spectra, and photodissociation dynamics of molecular ions.[2] Recent developments in high-resolution infrared spectroscopy made it possible to study the individual vibration–rotation levels of relatively simple ions such as HD^+, HeH^+, CH^+, and H_3^+.[2,3] However, there have been only a few experimental observations of infrared spectra of organometallic ions in the gas phase.

We have recently explored the technique of multiphoton dissociation[4] using a low-power CO_2 laser to obtain infrared fre-

---

[1] In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. 3.

[2] *Molecular Photodissociation Dynamics*; Ashfold, M. N. R., Baggott, J. E., Eds.; The Royal Society of Chemistry: London, 1987.

[3] *Molecular Ions: Spectroscopy, Structure, and Chemistry*; Miller, T. A., Bondybey, V. E., Eds.; North-Holland Publishing: Amsterdam, 1983.

[4] (a) Thorne, L. R.; Beauchamp, J. L. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. 3, p 42 and earlier references therein. (b) Hanratty, M. A.; Paulsen, C. M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 5074. (c) Lupo, D. W.; Quack, M. *Chem. Rev.* **1987**, *87*, 181 and earlier references therein. (d) Watson, C. H.; Baykut, G.; Eyler, J. R. In *Fourier Transform Mass Spectrometry*; Buchanan, M. V. Ed.; American Chemical Society: Washington, DC, 1987; p 140. (e) Schulz, P. A.; Sudbo, A. S.; Krajnovich, D. J.; Kwok, H. S.; Shen, Y. R.; Lee, Y. T. *Annu. Rev. Phy. Chem.* **1979**, *30*, 379.

0002-7863/90/1512-2066$02.50/0

quencies for the C–F stretching modes of the CF_3 ligand in organometallic anions.[5] The infrared multiphoton dissociation spectrum of $CF_3Mn(CO)_4^-$ ion exhibits two infrared absorption maxima at 1052 and 945 cm^{-1}. The peaks at 1052 and 945 cm^{-1} were assigned as C–F stretches of A_1- and E-type symmetry, respectively, from comparisons with results for CF_3X molecules. In going from an 18 e^- neutral precursor $CF_3Mn(CO)_5$ to a 17 e^- ion $CF_3Mn(CO)_4^-$, the nondegenerate C–F stretching mode changes little in frequency (from 1063 to 1052 cm^{-1}), while the degenerate C–F stretch of E-type symmetry decreases about 100 cm^{-1} (from 1043 to 945 cm^{-1}).

It has been previously observed that NO substitution in place of an equatorial CO increases an axial C–O stretching force constant in trigonal-bipyramidal $LM(CO)_4$ complexes and the negative charge in anionic complexes reduces the C–O stretching force constant.[6] This relationship is in accord with the observed decrease of the C–F stretching frequencies in going from $CF_3Mn(CO)_5$ to the $CF_3Mn(CO)_4^-$ ion.[5] In light of this empirical observation, NO substitution in place of an equatorial CO is expected to increase the C–F stretching frequencies in $CF_3Mn(CO)_3(NO)^-$ compared with those in $CF_3Mn(CO)_4^-$.

In the present paper, we have investigated the infrared multiphoton dissociation of the 18 e^- ion $CF_3Mn(CO)_3(NO)^-$ to see how each C–F stretching mode varies with NO substitution.

Experimental Section

Experimental techniques associated with Fourier transform ion cyclotron resonance spectroscopy[7] and its modification for infrared photochemistry have been previously described in detail.[5] Briefly, the anion of interest is formed by the ligand displacement reaction of $CF_3Mn(CO)_4^-$ ion generated from the dissociative electron attachment[8] of $CF_3Mn(CO)_5$ with nitric oxide as shown in reactions 1 and 2. All ions

$$CF_3Mn(CO)_5 + e^- \rightarrow CF_3Mn(CO)_4^- + CO \quad (1)$$

$$CF_3Mn(CO)_4^- + NO \rightarrow CF_3Mn(CO)_3(NO)^- + CO \quad (2)$$

except $CF_3Mn(CO)_3(NO)^-$ were removed from a trapping ICR cell[9] by using a series of ion ejection pulses after 1-s delay from an initial isolation of $CF_3Mn(CO)_4^-$ ion in 10:1 mixtures of (trifluoromethyl)manganese pentacarbonyl and nitric oxide with a total pressure of 1.0×10^{-5} Torr. The $CF_3Mn(CO)_3(NO)^-$ ion is unreactive with $CF_3Mn(CO)_5$ and NO. The isolated ion of interest is irradiated with the unfocused output of a line-tunable continuous wave CO_2 laser (Apollo Lasers Model 550A). The infrared spectrum of the $CF_3Mn(CO)_3(NO)^-$ ion is obtained by monitoring the extent of photodissociation as a function of laser wavelength with laser fluence of 160 mJ/cm^2. Irradiation of $CF_3Mn(CO)_3(NO)^-$ results in loss of CO yielding $CF_3Mn(CO)_2(NO)^-$ (reaction 3). The subsequent photodissociation of $CF_3Mn(CO)_2(NO)^-$ with loss of CO (reaction 4) followed by the NO substitution reaction results in the formation of the $CF_3Mn(NO)_2^-$ ion (reaction 5).

$$CF_3Mn(CO)_3(NO)^- + h\nu \rightarrow CF_3Mn(CO)_2(NO)^- + CO \quad (3)$$

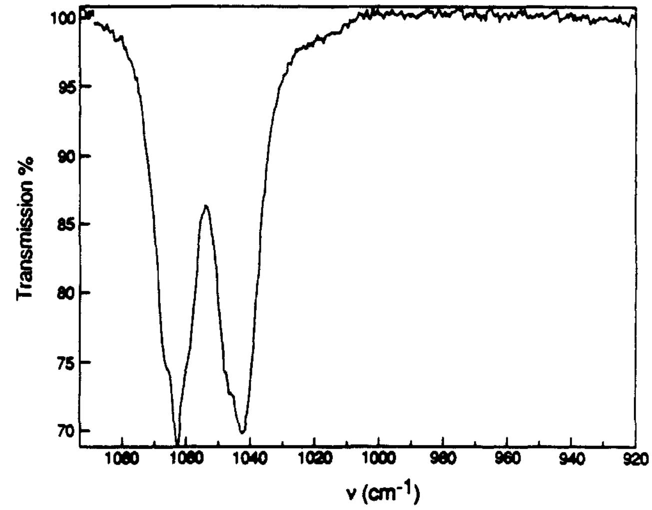
$$CF_3Mn(CO)_2(NO)^- + h\nu \rightarrow CF_3Mn(CO)(NO)^- + CO \quad (4)$$

$$CF_3Mn(CO)(NO)^- + NO \rightarrow CF_3Mn(NO)_2^- + CO \quad (5)$$

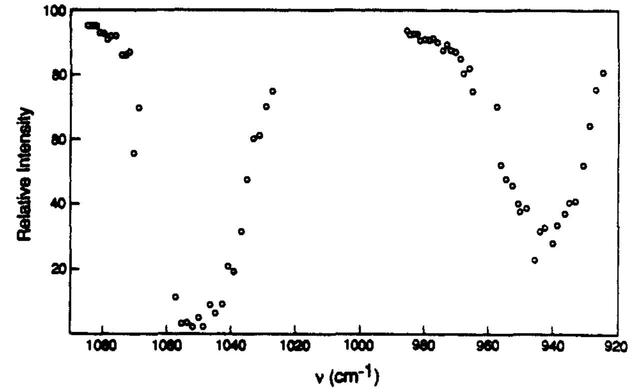
Results and Discussion

The infrared absorption spectrum of the neutral precursor, $CF_3Mn(CO)_5$, is shown in Figure 1a. The infrared multiphoton dissociation spectra of $CF_3Mn(CO)_4^-$ and $CF_3Mn(CO)_3(NO)^-$ are presented in Figure 1, spectra b and c, respectively, for comparison. The difference in intensity of the spectra of the CO and NO substituted complexes reflects different experimental conditions and not the oscillator strengths of the CF_3 groups. The peaks at 1045 and 980 cm^{-1} in Figure 1c are assigned as a C–F stretch of A_1-type symmetry and that of E-type symmetry, respectively, from comparisons with results for $CF_3Mn(CO)_4^-$.[5]

(a) $CF_3Mn(CO)_5$



(b) CF_3 Mn $(CO)_4^-$



(c) CF_3 Mn $(CO)_3$ $(NO)^-$

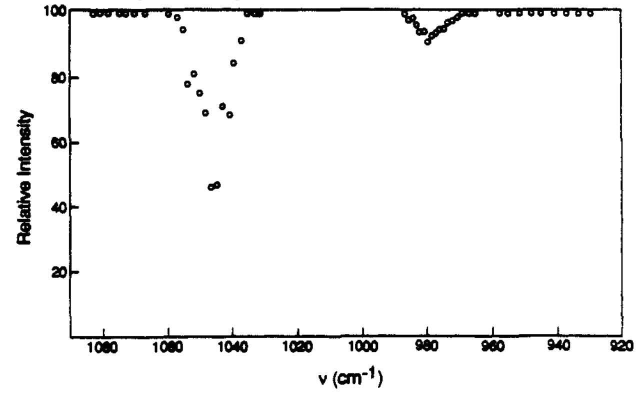


Figure 1. The infrared absorption spectra of the CF_3 group in (a) (trifluoromethyl)manganese pentacarbonyl and photodissociation spectra of (b) $CF_3Mn(CO)_4^-$ and (c) $CF_3Mn(CO)_3(NO)^-$ over the CO_2 laser spectral range. Data points for photodissociation spectra of $CF_3Mn(CO)_3(NO)^-$ are the ratio (in percentage) of the intensity of $CF_3Mn(CO)_3(NO)^-$ to the total ion intensity $[CF_3Mn(CO)_3(NO)^- + CF_3Mn(CO)_2(NO)^- + CF_3Mn(NO)_2^-]$ as a function of wavelength. The mass-selected ion of interest is irradiated for 20 ms at 8 W cm^{-2}.

Comparison of the infrared spectrum of $CF_3Mn(CO)_5$ (Figure 1a) with the infrared multiphoton dissociation spectra of $CF_3Mn(CO)_4^-$ (Figure 1b) and $CF_4Mn(CO)_3(NO)^-$ (Figure 1c) leads to the interesting observation that the C–F stretching frequencies of the anionic species have decreased from those of the neutral molecule. Whereas the decrease in the nondegenerate C–F stretching frequency is small, the degenerate C–F stretching frequency responds more sensitively to changes in total charge

---

[5] Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc.*, to be submitted.

[6] Timney, J. A. *Inorg. Chem.* **1979**, *18*, 2502.

[7] (a) Buchanan, M. V.; Comisarow, M. B. In *Fourier Transform Mass Spectrometry*; Buchanan, M. V., Ed.; American Chemical Society: Washington, DC, 1987; p 1. (b) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316. (c) Lehman, T. A.; Bursey, M. M. *Ion Cyclotron Resonance Spectrometry*; Wiley: New York, 1976. (d) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527. (e) Baldeschwieler, J. D. *Science* **1968**, *159*, 263.

[8] (a) Foster, M. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1975**, *31*, 1975. (b) Woodin, R. L.; Foster, M. S.; Beauchamp, J. L. *J. Chem. Phys.* **1980**, *72*, 4223. (c) Squires, R. R. *Chem. Phys.* **1987**, *87*, 623.

[9] Comisarow, M. B. *Int. J. Mass. Spectrom. Ion Phys.* **1981**, *37*, 251.

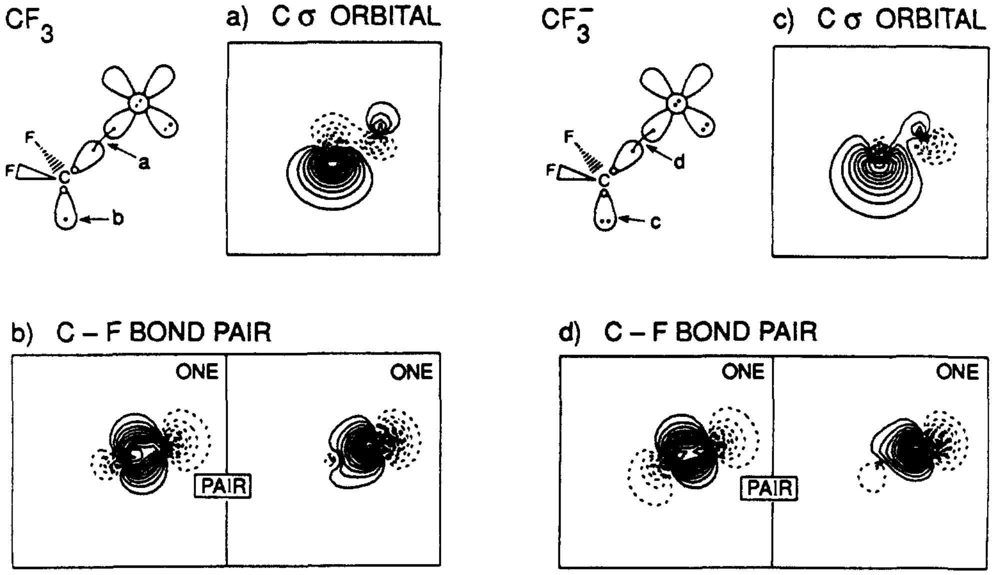
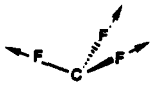


Figure 2. The GVB(3/6)-PP valence orbitals for the CF_3 radical and the CF_3^- ion: (a) the nonbonding carbon σ orbital (singly occupied) for the radical; (b) the C–F bond pair for the radical; (c) the nonbonding carbon σ natural orbital (doubly occupied) for the ion; (d) the C–F bond pair for the ion. The schematic representation shows the coupling of the carbon and fluorine orbitals. The p orbitals are represented by a normal two-lobed shape if in the plane and a circle if perpendicular to the plane. Each lobe orbital is denoted by a single lobe with a small circle at one end. The line connecting the carbon lobe and fluorine p orbitals indicates that singly occupied orbitals on two centers are coupled into a bonding pair. Orbitals with one dot and two dots represent the singly and doubly occupied orbitals, respectively. Solid lines and short dashes indicate positive and negative amplitudes, respectively. The increment between contours is 0.05 au. (For more details, see: Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Phys.* **1973**, *6*, 368.).

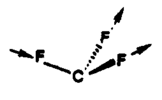
of the molecule and ligand substituents.

The decrease of the C–F stretching frequencies for the anionic species may be due to an increase of the electron density in the carbon σ-donor orbital of the CF_3 group in the anionic species. In order to illustrate the hybridization changes at carbon in the C–F bond orbitals and σ-donor orbital due to the negative charge, the GVB[10] one-electron C–F bond orbitals and carbon nonbonding σ orbitals are presented in Figure 2 for the CF_3 radical and CF_3^- ion. Analyses of Mulliken populations[11] for both radical and anion quantify the hybridization and charge transfer in the C–F bonds and carbon nonbonding σ orbital [charge population: C (5.27) and F (9.24) for the radical; C (5.96) and F (9.35) for the ion]. The CF_3^- ion has visibly more p character at the C–F bond carbon than the radical (36% s and 64% p for the radical; 100% p for the ion). This increase of carbon p character in the C–F bond orbitals of the CF_3^- ion would increase the C–F bond distance and decrease the C–F stretching force constant.

Moreover, since a contraction of one C–F bond would increase the carbon s character of the contracting bond and induce a concurrent increase of the carbon p character of the other two C–F bonds, it would tend to be more easily accompanied by an extension than the contraction of the other two bonds resulting in E-type vibration.[12] Therefore, one would expect that changes of hybridization during vibration could be more effective for the degenerate E-type vibration than the symmetric vibration. This qualitative explanation is in agreement with the observation that the anionic species have lower C–F stretching frequencies than the neutral and the E symmetry vibration decreasing more than the A_1 symmetry vibration. Previous observation of changes in the C–F stretching frequencies from the CF_3 radical[13] (C_{3v}: $\nu_s(A_1) = 1084\ cm^{-1}$ and $\nu_s(E) = 1252\ cm^{-1}$) to the CF_3^+ ion[13] (D_{3h}: $\nu_s(A') = 1125\ cm^{-1}$ and $\nu_s(E') = 1667\ cm^{-1}$) shows that the positive ion has the higher C–F stretching frequencies than the radical and the E-type stretch increases about 410 cm^{-1}, while the A_1-type stretch mode varies by only about 40 cm^{-1}. This result also supports the proposed explanation.



A_1



E

The observed increase of the degenerate C–F stretching frequency of E-type symmetry for $CF_3Mn(CO)_3(NO)^-$ compared with that of $CF_3Mn(CO)_4^-$ may afford the possibility of differentiating their structures. The structure of the d^7 complex $CF_3Mn(CO)_4^-$ is presumed to be a square-based pyramidal with CF_3 in the basal plane, from comparisons with results for other five-coordinate d^6 and d^7 complexes. An infrared spectroscopic study of the five-coordinate d^6 complex, $CH_3COMn(CO)_4$, in methane matrix at 12 K indicates the square-based pyramidal structure with an η^1-acetyl bonding.[14] Spectroscopic studies of the five-coordinate d^7 complex, $Mn(CO)_5$, generated in $Cr(CO)_6$ crystals or in low-temperature solid matrices, support a square-pyramidal structure with C_{4v} point group.[15] Extended Hückel calculations by Elian and Hoffman[16] also suggested the square-pyramidal structure for the five-coordinate d^7 complex carrying its odd electron in a relatively high-lying directional orbital oc-

---

(10) The generalized valence bond (GVB) method describes each valence bond with two natural orbitals: Bobrowicz, F. W.; Goddard, W. A., III In *Methods of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977, Chapter 4. The geometry of r(C–F) = 1.332 Å and ∠(F–C–F) = 109° from experimental values for CHF_3 is used for the GVB calculation (Ghosh, S. N.; Trambarulo, R.; Gordy, W. *J. Chem. Phys.* **1952**, *20*, 605.).

(11) Mulliken populations were obtained by summing over the electron populations of each s, p, and d basis function on carbon within each natural orbital for each GVB pair. Although this analysis tends to be basis dependent, relative trends and comparisons are expected to be reliable. Valence double-ζ plus polarization basis sets for carbon and fluorine are used: Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Chapter 1.

(12) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; Dover: New York, 1955; pp 180–181.

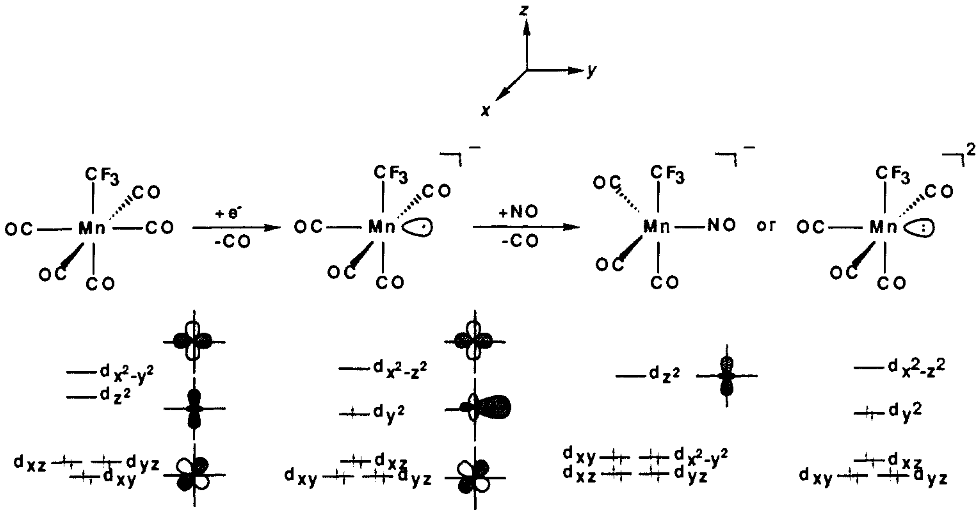
(13) Prochaska, F. T.; Andrews, L. *J. Am. Chem. Soc.* **1978**, *100*, 2102.

(14) Hitam, R. B.; Narayanaswamy, R.; Rest, A. J. *J. Chem. Soc. Dalton Trans.* **1983**, 615.

(15) (a) Hughey, J. L.; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *125*, C49. (b) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259. (c) Church, S. P.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7515. (d) Symons, M. C. R.; Sweany, R. L. *Organometallics* **1982**, *1*, 834. (e) Fairhurst, S. A.; Morton, J. R.; Perutz, R. N.; Preston, K. F. *Organometallics* **1984**, *3*, 1389. (f) Howard, J. A.; Morton, J. R.; Preston, K. F. *Chem. Phys. Lett.* **1981**, *83*, 226. (g) Lionel, T.; Morton, J. R.; Preston, K. F. *Chem. Phys. Lett.* **1981**, *81*, 17.

(16) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

Scheme I



cupying an empty apical site. The d orbital splitting schemes for $CF_3Mn(CO)_4^-$ are shown in Scheme I along with those for $CF_3Mn(CO)_5$, $CF_3Mn(CO)_3(NO)^-$, and $CF_3Mn(CO)_4^{2-}$. The choice of axis is arbitrary.

In going from the octahedral d^6 complex $CF_3Mn(CO)_5$ to the square-pyramidal d^7 complex $CF_3Mn(CO)_4^-$, the number of electrons occupying the nonbonding directional orbital (d_{y^2}) increases and the C–F stretching frequencies decrease. Assuming that the $CF_3Mn(CO)_3(NO)^-$ ion has a square-based pyramidal structure would lead to d orbital splittings similar to $CF_3Mn(CO)_4^{2-}$ bearing its nonbonding lone pair electrons in a directional d_{y^2} orbital occupying an empty apical site. If the NO substituted ion is analogous to square-pyramidal $CF_3Mn(CO)_4^{2-}$,[17] one would expect that the C–F stretching frequencies of $CF_3Mn(CO)_4^{2-}$ would decrease due to its doubly occupied d_{y^2} orbital. However, this expectation, which resulted from viewing $CF_3Mn(CO)_3(NO)^-$ as a square-pyramidal $CF_3Mn(CO)_4^{2-}$, is inconsistent with the observed increase of the degenerate C–F stretching frequency. Therefore, it is quite reasonable to suggest that the structure of $CF_3M(CO)_3(NO)^-$ is different from square pyramidal.

The d^8 complex $CF_3Mn(CO)_3(NO)^-$ is considered to have a trigonal-bipyramidal structure with a linear Mn–NO in the equatorial position from comparison with the structures of the five-coordinate d^8 complexes $Mn(CO)_4(NO)$ and $Mn(CO)_5^-$. Frenz et al.[17] have determined the crystal structure of $Mn(CO)_4(NO)$, revealing that the nitrosyl group is in an equatorial position in the trigonal-bipyramidal structure and the Mn–CO and Mn–NO bonds are linear. $Mn(CO)_5^-$ is also trigonal bipyramidal in the solid state.[18]

The trigonal-bipyramidal d^8 complex $CF_3Mn(CO)_3(NO)^-$ has an unoccupied d_{z^2} orbital that can easily accommodate the electron density on the σ-donor orbital of the CF_3^- ligand. This electron delocalization would reduce the charge population on carbon in the CF_3^- ligand and lead to concurrent decrease of carbon p character in the C–F bond orbitals resulting in the increase of the C–F stretching force constant. Since the degenerate C–F stretch of E-type symmetry changes more effectively with changes of hybridization as noted earlier, the E-type C–F stretching frequency is expected to increase more readily than the A_1-type vibration. The observed increase of the E-type C–F stretching frequency in $CF_3Mn(CO)_3(NO)^-$ is in agreement with the expectation from the trigonal-bipyramidal structure.

The above arguments support our contention that NO substitution in place of CO induces a structural change from square pyramidal for $CF_3Mn(CO)_4^-$ to trigonal bipyramidal for $CF_3Mn(CO)_3(NO)^-$.

In conclusion, infrared photochemistry of organometallic intermediates containing the CF_3 group directly bonded to metal is explored with Fourier transform ion cyclotron resonance spectroscopy. The C–F stretching shift, which is sensitive to the net charge of the complex and ligand substituents, is used to differentiate the structures of intermediates. It will be of further experimental and theoretical interest to see how each C–F stretch mode varies with ligand substituents and the coordination number.

Acknowledgment. We acknowledge the support of the National Science Foundation (Grant No. CHE87-11567) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

---

(17) Frenz, B. A.; Enemark, J. H.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 1288.

(18) Frenz, B. A.; Ibers, J. A. *Inorg. Chem.* **1972**, *11*, 1109.