the predicted maximum in the susceptibility *vs.* temperature curve. Using data taken above 80°K and fitting it with the Ising model, Campbell, *et al.*, have calculated values of $J = -47$ cm^{-1} and $g = 2.09$. These parameters agree well with our values of -45 cm^{-1} and 2.07. This large value of J for these methyl-substituted quinoxaline complexes may be indicative of a magnetic interaction taking place through bridging quinoxaline ligands rather than through chloride ions. Antiferromagnetic J values for chloride-bridged complexes of known structures appear to be small (less than -20 cm^{-1}) for most cases and are larger ($\simeq 45$ cm^{-1}) only when both bond distances are small as in CuCl$_2$.[14] The magnetism of the complex (pyrazine)-Cu(NO$_3$)$_2$, known to consist of linear chains in which a pyrazine molecule acts as a bridging ligand,[16] has been studied in this laboratory. Experimental results[17] show a maximum in the susceptibility at $\simeq 9$°K, indicating a weak antiferromagnetic interaction. This weaker interaction may mean that a fused-ring compound such as quinoxaline has available more electron density for the transmission of the spin–spin coupling

across the bridging ligand. The interaction would be further enhanced by the electron-donating methyl groups. Hyde, *et al.*,[18] have calculated $J \simeq -20$ cm^{-1} for the unsubstituted quinoxaline complex which is also thought to contain bridging quinoxaline ligands. Since their calculations were based on a small number of data points taken above 77°K, a more careful study of the magnetism is necessary.

(2,3-Diphenylquinoxaline)$_2$CuCl$_2$.—The deviation from Curie–Weiss behavior for this complex probably represents a very weak ferromagnetic coupling of spins on neighboring copper atoms. The ferromagnetic nature of the coupling is evident from the field dependence of susceptibility, from a positive intercept at ~ 2°K in the $1/\chi_{m'}$ plot, and from the magnetization which is plotted as a function of H/T in Figure 6. The calculated curves for spins, $S = 1$ and $^1/_2$, were generated by Brillouin functions.[19] A comparison of the experimental and calculated curves shows the complex to be more easily magnetized at certain fields and temperatures than a complex with a pure doublet ground state.

(16) A. Santoro, A. D. Mighell, and C. W. Reimann, *Acta Crystallogr., Sect. B,* **26**, 979 (1970).

(17) J. F. Villa and W. E. Hatfield, *J. Amer. Chem. Soc.,* **93**, 4081 (1971).

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Electronic Structure and Bonding in Methyl- and Perfluoromethyl(pentacarbonyl)manganese

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Using approximate molecular orbital calculations, we have investigated the electronic structure and bonding of CH$_3$Mn(CO)$_5$ and CF$_3$Mn(CO)$_5$. The appearance of an unexpected additional band in the photoelectron spectra can explain both the apparent reversal in the b$_2$ and e bands of the methyl compound and the increased intensity of the first band in the perfluoromethyl compound. Other experimental evidence, such as the carbon–fluorine force constant of the CF$_3$ group, for which dπ(metal)–σ^*(CF$_3$) back-bonding has been proposed as an explanation, can be understood in terms of σ donation from an antibonding CF$_3$ orbital and energy stabilization due to the effect of charges on neighboring atoms. The influence of the CX$_3$ ligands on the metal ionization potentials and on the carbonyl force constants can also be interpreted in terms of these two effects.

Introduction

Recently there has been considerable interest in the bonding of the methyl and perfluoromethyl groups to transition metals. Evans, *et al.*, have reported the photoelectron (pe) spectra of methyl and perfluoromethylmanganese pentacarbonyl compounds.[1] These workers interpreted the spectra in terms of the changes one would expect relative to the octahedral complex Mn(CO)$_6$$^+$. If one assumes that methyl and perfluoromethyl act essentially as σ donors and that the idealized symmetry, C_{4v}, is applicable, the loss of the π-acceptor ability in the sixth position in going from Mn-(CO)$_6$$^+$ to Mn(CO)$_5$L should split the upper t$_{2g}$^{6} level into b$_2$e^4 with the e level at higher energy, *i.e.*, lower ionization potential, than the b$_2$ level. On the basis of intensity arguments Evans, *et al.*, suggested that the

expected order is correct for CF$_3$Mn(CO)$_5$ but that the order is reversed for CH$_3$Mn(CO)$_5$.

A controversial aspect of the bonding by the perfluoromethyl ligand involves the ability of this ligand to accept π-electron density by the interaction of its empty σ^* orbitals with the filled dπ metal orbitals. Thus, from an approximate force constant analysis of the perfluoromethyl infrared spectra, Cotton and Wing concluded that the perfluoromethyl group is a good π-electron acceptor.[2] In addition, the greater stability and shorter metal–carbon bond lengths observed for fluoroalkyl complexes relative to alkyl complexes are also cited as evidence favoring the strong π-electron accepting ability of fluoroalkyl groups.[3-5]

(1) S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, *Discuss. Faraday Soc.,* **No. 47**, 112 (1969).

(2) F. A. Cotton and R. M. Wing, *J. Organometal. Chem.,* **9**, 511 (1967).

(3) P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.,* **1**, 143 (1964).

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However, from the carbonyl force constants Graham concluded that methyl and perfluoromethyl are equally poor π-electron acceptors.[6]

In previous work we have indicated that it is possible to correlate our approximate molecular orbital calculations with infrared and photoelectron spectra.[7] Using a similar procedure, we have calculated the electronic structure of methyl- and perfluoromethyl(pentacarbonyl)manganese with the hope of elucidating the cause of the apparent reversal of the e and b_2 levels in $CH_3Mn(CO)_5$, the degree of π-electron acceptor ability or back-bonding ability of the perfluoromethyl group in $CF_3Mn(CO)_5$, and the nature of the electronic structure and bonding of both of these compounds.

Computational Considerations

Theory.—The computational procedure employed is similar to that used in previous studies of the manganese pentacarbonyl halides and hydride.[7] The basis for our procedure can be understood through the application of various well-known approximations to the Hartree–Fock–Roothaan (HFR) operator.[8-10] It may be useful to present a simple conceptual rationalization to acquaint the reader with the essential features of our method and with approximations not employed in our previous work.

Since the HFR operator is a one-electron operator, whose application yields the energy of an electron moving in the average field of the other electrons and nuclei, we can write a model one-electron operator, F, as a kinetic energy operator plus a potential energy operator for each center in the system. This equation

$$F = -\frac{1}{2}\nabla^2 + \sum_C V_C \qquad (1)$$

assumes that we can assign the electron density to the appropriate center; we do so through the use of the Mulliken population analysis,[11] which will be used for all of the population analysis in this work.

We use this approximate operator to generate matrix elements between atomic basis functions and obtain our final wave function by solving self-consistently the Hartree–Fock–Roothaan equations with our approximate matrix elements. Using eq 1, the diagonal matrix element for function χ_a (on center A) becomes

$$F_{aa} = \left(\chi_a\left|-\frac{1}{2}\nabla^2 + V_A\right|\chi_a\right) + \sum_{C\neq A}(\chi_a|V_C|\chi_a) \qquad (2)$$

The first term in eq 2, which is the atomic orbital energy, ϵ_a, of an electron in function χ_a, can be calculated using Slater's average of configuration approach.[12] Thus

$$\epsilon_a = \left(\chi_a\left|-\frac{1}{2}\nabla^2\right|\chi_a\right) + (\chi_a|-Z_A/r_A|\chi_a) + \sum_{i\neq a}^A n_i g_{ia} + (n_a - 1)g_{aa} \qquad (3)$$

(6) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).
(7) R. F. Fenske and R. L. DeKock, *ibid.*, **9**, 1053 (1970).
(8) R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeny, *ibid.*, **5**, 951 (1966).
(9) R. F. Fenske and D. D. Radtke, *ibid.*, **7**, 479 (1968).
(10) K. G. Caulton and R. F. Fenske, *ibid.*, **7**, 1273 (1968).
(11) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841 (1955).
(12) J. C. Slater, "Quantum Theory of Atomic Structure," Vol. I, McGraw-Hill, New York, N. Y., 1960, p 322.

The first two terms are the kinetic energy and nuclear attraction energy, respectively. The summation is over all other atomic orbitals on center A (including core orbitals), n_i is the Mulliken population of orbital χ_i,[11] and g_{ia} is Slater's average of the configuration electrostatic repulsion integral.[12]

The second term in eq 2 describes the influence of each of the other centers (nuclei and electrons) on the diagonal matrix element. As in our previous work V_C is represented by a point charge, where the charge on center C, q_C, is calculated *via* the Mulliken populations[11]

$$q_C = Z_C - \sum_i^C n_i \qquad (4)$$

where Z_C is the bare nuclear charge and the sum includes all valence and core functions on center C. A second point-charge approximation can be made on the charge distribution of χ_a.[13] The final expression for the diagonal term then becomes

$$F_{aa} = \epsilon_a + \sum_{C\neq A}(-q_C)(1/R_{AC}) \qquad (5)$$

where ϵ_a is evaluated according to eq 3, q_C according to eq 4, and $1/R_{AC}$ is the potential energy of two unit point charges at a distance R_{AC} from each other.

In order to evaluate the off-diagonal matrix element between two different centers one first adds and subtracts a kinetic energy operator from equation 1. After grouping appropriate terms together, one obtains the equation for the off-diagonal term

$$F_{ab} = \left(\chi_a\left|-\frac{1}{2}\nabla^2 + V_A\right|\chi_b\right) + \left(\chi_a\left|-\frac{1}{2}\nabla^2 + V_B\right|\chi_b\right) - \left(\chi_a\left|-\frac{1}{2}\nabla^2\right|\chi_b\right) + \sum_{C\neq A,B}(\chi_a|V_C|\chi_b) \qquad (6)$$

We now assume that the function χ_a is an eigenfunction of the operator $-\frac{1}{2}\nabla^2 + V_A$ with eigenvalue ϵ_a,[10,14] an approximation closely related to that used by Goeppert-Mayer and Sklar.[15] The last term in eq 6 consists of the three-center interactions and is calculated by employing the Mulliken and point-charge approximations.[7,13] With these approximations the final expression for the two-center off-diagonal term becomes

$$F_{ab} = (\chi_a|\chi_b)(\epsilon_a + \epsilon_b) - \left(\chi_a\left|-\frac{1}{2}\nabla^2\right|\chi_b\right) - \frac{1}{2}(\chi_a|\chi_b)\sum_{C\neq A,B}(q_C/R_{AC} + q_C/R_{BC}) \qquad (7)$$

where $(\chi_a|\chi_b)$ and $(\chi_a|-\frac{1}{2}\nabla^2|\chi_b)$, the overlap and kinetic energy integrals, are evaluated exactly. The remaining terms in eq 7 are calculated as they were for the diagonal term, eq 6.

The HFR formalism includes matrix elements of the type $F_{aa'}$, where χ_a and $\chi_{a'}$ are two functions on the same center. In terms of our operator, eq 1, this one-center off-diagonal term can be written as

$$F_{aa'} = \left(\chi_a\left|-\frac{1}{2}\nabla^2 + V_A\right|\chi_{a'}\right) + \sum_{C\neq A}(\chi_a|V_C|\chi_{a'}) \qquad (8)$$

Since χ_a and $\chi_{a'}$ are orthonormal and are assumed to

(13) I. H. Hillier, *J. Chem. Soc. A*, 878 (1969).
(14) H. Basch and H. B. Gray, *Inorg. Chem.*, **6**, 639 (1967).
(15) M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

be eigenfunctions of the operator $(-1/2\nabla^2 + V_A)$, the first term vanishes. In order to be consistent with the use of the Mulliken and point-charge approximation for the three-center terms the last summation will be set equal to zero. Hence all one-center off-diagonal terms are set equal to zero.

There are several general points about this method which should be emphasized. First, it does not involve the use of any adjustable or empirical parameters; the final results depend only on the choice of basis function and on the internuclear distances both of which are chosen in a consistent nonarbitrary fashion. Second, the method includes the effects of all neighboring atoms in determining the energetic placement of the levels. Third, it is invariant to a rotation of the local coordinate system on each atom. Fourth, the modifications of our previous procedure were accepted only after extensive calculations showed that they had only minor effects on the eigenvalues and eigenvectors.

Procedure.—The formulas for the matrix elements given above are used to calculate the approximate HFR matrix. We then proceed to solve the complete HFR equation[16]

$$FC = SC\epsilon \quad (9)$$

where S is the overlap matrix, C is the eigenvector matrix, and ϵ is the diagonal eigenvalue matrix. In order to solve this equation, we transform the F, S, and C matrices such that eq 9 becomes a simple eigenvalue problem which can be solved by standard techniques.[17]

Since the F matrix depends on the C matrix through the Mulliken populations, eq 9 must be solved iteratively. Initially the matrix $S^{-1/2}$[18] is used as the transformation matrix, but for each subsequent cycle it is advantageous to use the vectors from the previous cycle. This procedure yields an almost diagonal F' matrix, for which the Jacobi method of diagonalization is extremely fast.

For each iteration new Mulliken populations must be calculated to generate the new F matrix. In order to prevent oscillations we found it necessary to damp each new input population.[19] Although damping proved to be a satisfactory way of reaching a self-consistent solution, the rate of convergence to this solution can be improved by using a modification of Aitken's δ^2 extrapolation[20] on every third cycle in place of the damping procedure. Aitken's method, which is a general mathematical extrapolation technique, does not guarantee conservation of the total number of electrons in the system (*i.e.*, it will not preserve the trace of the density matrix in an orthonormal basis); consequently it was necessary to modify Aitken's technique to guarantee this condition. The appropriate expressions are

$$n_k^{i+1} = m_k^i - (p_k^i - z^i|p_k^i|)/(1 + |z^i|) \quad (10)$$

where

$$p_k^i = (m_k^{i-1} - m_k^i)^2/(m_k^{i-2} - 2m_k^{i-1} + m_k^i) \quad (11)$$

$$z^i = \sum_k p_k^i / \sum_k |p_k^i| \quad (12)$$

and n_k^i and m_k^i are the input and output populations for the lth cycle.

We have written a series of three computer programs for this calculational procedure, and we have merged these into a single package in order to prevent errors in handling data and to allow for their uninterrupted execution. This single package can perform a complete molecular orbital calculation on any system regardless of its symmetry, the only restriction being the size of the computer.[21] Because the iterations consume most of the computer time for a calculation, both the prediagonalization of the F matrix and the modified extrapolation procedure are important in keeping this time within a reasonable bound. The calculations reported here were iterated as described until $|n_k^i - m_k^i|$ for each orbital χ_k was less than 0.001.

Basis Functions.—Atomic basis functions optimized for the free atom of appropriate charge and configuration were employed. Clementi's double-ζ functions were used for the carbon, oxygen, and fluorine atoms.[22] The 2s functions were curve fit to single-ζ form while being held orthogonal to a similarly constructed 1s function. The 2p functions were used in their original double-ζ form except for the carbon(1+) function, which was curve fit to double-ζ form from the four-ζ function of Clementi.[23] The curve fitting was based on the maximum overlap criterion.[24,25] The hydrogen exponent of 1.16 corresponds to the minimum energy exponent for methane.[26] The manganese 1s–3d functions were taken from the results of Richardson, *et al.*[25] The 3d function corresponds to a 3d^6 configuration of Mn$^+$. The 4s and 4p functions were constructed by maximizing their overlap with the carbonyl carbon atom.[9,24]

Bond Distances and Angles.—Because the exact structural parameters of the compounds are unknown, bond distances and bond angles have been estimated from those of similar compounds. The final distances used for these calculations are given in Table I. All

TABLE I
BOND DISTANCES (Å)

Bond	CH₃Mn-(CO)₅	CF₃Mn-(CO)₅	Bond	CH₃Mn-(CO)₅	CF₃Mn-(CO)₅
C–O	1.128	1.128	Mn–CX₃	2.15	2.10
Mn–CO$_{ax}$	1.82	1.82	C–X	1.096	1.34
Mn–CO$_{eq}$	1.85	1.85			

carbon–oxygen bond distances were taken to be the same as that in free CO.[27] This is consistent with the observation[28] that the changes in carbonyl bond lengths are small for bond orders in the range of 2–3. The manganese–carbon bond lengths for the carbonyls were drawn from the reported bond lengths for HMn-(CO)₅.[29] The manganese–carbon distance for the methyl was calculated from the covalent radii of Mn,

(16) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

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(20) A. Ralston, "A First Course in Numerical Analysis," McGraw-Hill, New York, N. Y., 1965, p 348.

(21) Using one 65K memory module of the Univac 1108 we can handle up to 124 valence basis functions on up to 45 different centers.

(22) E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964).

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(24) D. D. Radtke, Ph.D. Thesis, University of Wisconsin, 1966.

(25) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(26) W. J. Hehre, R. F. Stewart, and J. A. Pople, *ibid.*, **51**, 2657 (1969).

(27) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950.

(28) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965).

(29) S. J. LaPlaca, W. C. Hamilton, J. A. Ibers, and A. Davison, *ibid.*, **8**, 1928 (1969).

1.38 Å,[30] and of the sp³ carbon, 0.77 Å. This procedure is also applicable to the known manganese–pentacarbonyl–hydride and –halide distances.[7] The manganese–carbon distance for the perfluoromethyl was assumed to be 0.05 Å shorter than that for the methyl. This is consistent with the shortening that is observed in similar iron complexes.[6] The manganese carbonyl framework was taken to have octahedral geometry since the deviations from this should be small.[29] The methyl and perfluoromethyl groups were assumed to have tetrahedral angles and bond distances appropriate to the corresponding iodine compound.[31]

Results and Discussion

Free Ligands.—After the calculations have reached self-consistency, it is convenient to transform the final results from a basis of free-atom orbitals to a basis of free-ligand orbitals. This procedure reduces the myriad changes in the populations of orbitals on individual atoms making up each ligand to changes only in populations of ligand orbitals which are important in bonding to the metal. We will transform the carbonyl ligands using the free-CO basis, while for the methyl and perfluoromethyl we will use the CX_3^- basis orbitals. We should emphasize that this choice is arbitrary, and it would make very little difference if we had chosen the CX_3^+ basis orbitals instead.

In Table II we have listed the eigenvalues, per cent

TABLE II
PER CENT CHARACTER, EIGENVALUES, AND OVERLAP
POPULATIONS OF THE MOLECULAR ORBITALS
FOR CO, CH_3^-, AND CF_3^-

Group	Orbital	s(C)	p(C)	s(X)	p(X)	Eigenvalue, eV	Overlap population[a]
CO	5σ	34.5	47.8	1.0	16.7	−13.79	−0.128
	2π	...	66.8	...	33.2	0.28	−0.478
CH_3^-	$2a_1$	54.0	1.0	45.0	...	−14.81	+0.146
	$3a_1$	6.4	91.8	1.8	...	2.74	−0.0002
	$2e$	...	50.7	49.3	...	57.15	−0.717
CF_3^-	$4a_1$	21.1	0.1	7.5	71.3	−13.55	+0.050
	$5a_1$	1.4	15.9	0.0	82.7	−9.20	+0.048
	$6a_1$	13.5	66.0	0.1	20.5	5.44	−0.107
	$6e$	...	73.0	6.6	20.4	38.40	−0.397

[a] This is the overlap population between carbon and one of the other atoms for a single electron occupying the molecular orbital.

character, and overlap populations for the orbitals which will be important in metal–ligand bonding. These orbitals include the highest filled and lowest unfilled orbitals of the free ligands, and for CH_3^- and CF_3^- several of the lower orbitals which are capable of σ donation. It appears that the remaining ligand orbitals are unfavorable for bonding on the basis of either energy or overlap and that they remain essentially unaffected in form when the ligand bonds.

All of these ligands form a σ bond by donating electron density from their "lone-pair" orbital. For CO this corresponds to the antibonding 5σ MO. For CH_3^- and CF_3^- the lone-pair orbital is a linear combination of the various a_1 MO's. The exact combination will depend on the group to which it is bonding. An important difference between these two ligands

can be seen in the character of their highest filled a_1 MO. For the methyl ion it is essentially a nonbonding p orbital while for the perfluoromethyl it is strongly antibonding and contains considerably more s character.

In addition to a σ bond many ligands can form π bonds to a transition metal by accepting electron density into their unfilled orbitals. The carbonyl group back-bonds in this manner using its low-energy 2π orbitals. From the results in Table II we expect that the methyl and perfluoromethyl groups will be much weaker π-electron acceptors since they have no low-energy unfilled orbitals.

Photoelectron Spectra of the Complexes.—Within the limitations of the assumptions implicit in Koopmans' theorem,[32] one can correlate the eigenvalues of a molecular orbital calculation with vertical ionization potentials (IP) obtained by pe spectroscopy. If one considers the metal–ligand bonding of $CF_3Mn(CO)_5$ and $CH_3Mn(CO)_5$ as analogous to that of $HMn(CO)_5$, an identical splitting and intensity pattern might be expected. One need only postulate that the reduction from true C_{4v} symmetry in the perfluoromethyl and methyl complexes does not drastically alter the degeneracy of the e level and that both of these ligands exhibit essentially no π-acceptor ability relative to the carbonyl groups. The pe spectrum of $CF_3Mn(CO)_5$ exhibits two bands at 9.20 and 10.30 eV with an intensity ratio of 3:1, which the initial investigators[1] took as an indication that the e level was indeed above the b_2. However, in the pe spectrum of $CH_3Mn(CO)_5$ the bands at 8.46 and 9.10 eV have an approximate intensity ratio of 1:2. This intensity ratio was interpreted by the original workers[1] as arising from a reversal of the ground-state e and b_2 levels in $CH_3Mn(CO)_5$. There are, in fact, several alternatives available to explain this unusual intensity pattern.

1. Intensities might not be an acceptable criterion for relative orbital degeneracy. Relative intensities are known to involve more than orbital degeneracy; nevertheless, the degeneracy does appear to play a substantial role in the determination of intensity.[33] Thus, the complete reversal of the intensities seems unlikely.

2. Koopmans' theorem might be violated due to substantially different relaxation energies[34] for the e and b_2 levels in forming the respective excited states of the ion. For $CH_3Mn(CO)_5$ our eigenvectors show a great deal of similarity in the e and b_2 orbitals; the e is 68% metal 3d and 30% carbonyl 2π and the b_2 is 60% metal 3d and 38% carbonyl 2π. Because of this similarity it is reasonable to expect rather similar relaxation energies rather than drastically different ones; nevertheless one cannot entirely rule out this latter possibility.

3. Different correlation or relativistic energies could invert the ionic states. Here again the similarity in character of the e and b_2 orbitals mitigates against this possibility. In addition, relativistic energy differences should be small for valence electron IP's.[35]

4. A true reversal of the e and b_2 levels could exist

(30) M. J. Bennet and R. Mason, *Nature (London)*, **205**, 760 (1965).
(31) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 18** (1965).
(32) T. Koopmans, *Physica*, **1**, 104 (1933).
(33) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970, p 33.
(34) A. Rosen and I. Lindgren, *Phys. Rev.*, **136**, 176 (1968).
(35) W. G. Richards, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 419 (1969).

in the ground state of $CH_3Mn(CO)_5$ compared to $HMn(CO)_5$ and $CF_3Mn(CO)_5$. This is the postulate of the original authors.[1] As shown by Figure 1, our results do not indicate that such a reversal is present; rather they suggest a fifth possible interpretation.
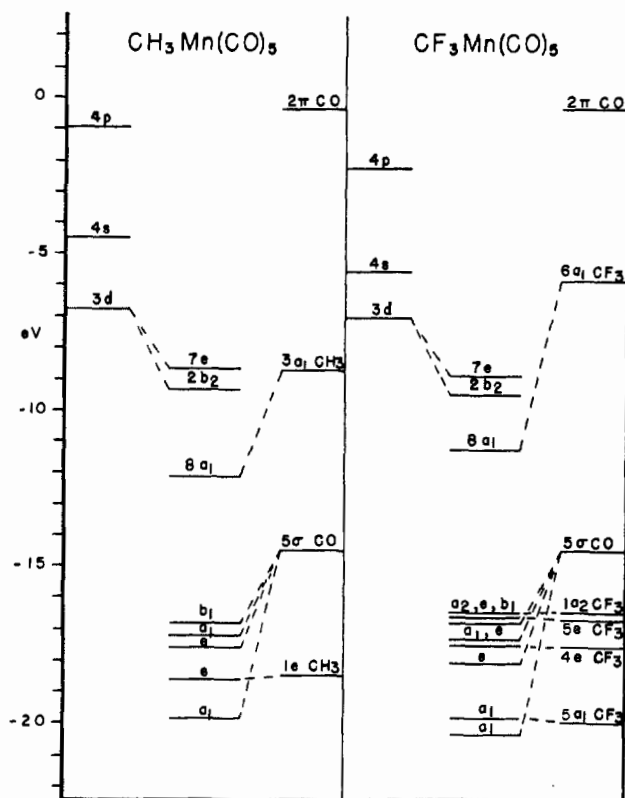

Figure 1.—Energy levels for $CH_3Mn(CO)_5$ and $CF_3Mn(CO)_5$. For clarity, the three uppermost levels were numbered analogous to those of $HMn(CO)_5$,[7] even though C_{4v} symmetry is not present in these compounds The ligand levels are labeled in accord with their localized symmetry prior to bonding in the complex.

5. The interference of an additional ionization band whose energy is sufficiently similar to that of the bands in question could result in an apparent inversion of the intensity ratios. Superposition of two levels has been previously observed in pe spectra. For example, in CH_2F_2 two bands whose theoretical eigenvalues differ by 1.5 eV are found to overlap to such an extent that under low resolution they appear as one band.[36] Such overlap requires that the additional orbital have different relaxation and/or correlation energy and probably a different bonding character. Furthermore, since the orbital character would not be the same, the simple intensity ratios need no longer apply. If the highest filled a_1 level in $CH_3Mn(CO)_5$ possessed a relaxation and correlation energy which was larger than those of the e and b_2 levels by 2.5 eV, then the ionization energy of an electron from the a_1 level would be similar to that of a b_2 electron and a superposition of the two bands would occur. Furthermore, the same arguments applied to $CF_3Mn(CO)_5$ would result in a superposition of the a_1 band with the e band causing an increase in its apparent intensity relative to the b_2 band. Thus, this single hypothesis explains both the

(36) B. P. Pullen, T. A. Carlson, W. E. Moddeman, G. K. Schweitzer, W. E. Bull, and F. A. Grimm, *J. Chem. Phys.*, **53**, 768 (1970).

apparent level reversal in $CH_3Mn(CO)_5$ and the high intensity for the first band in $CF_3Mn(CO)_5$.

A reason to be self-critical of our hypothesis is the accidental degeneracy in the *two* molecules, the a_1 first with the b_2 and next with the e. Examination of the spectra,[37] Figure 2, does not exclude our hypothesis;
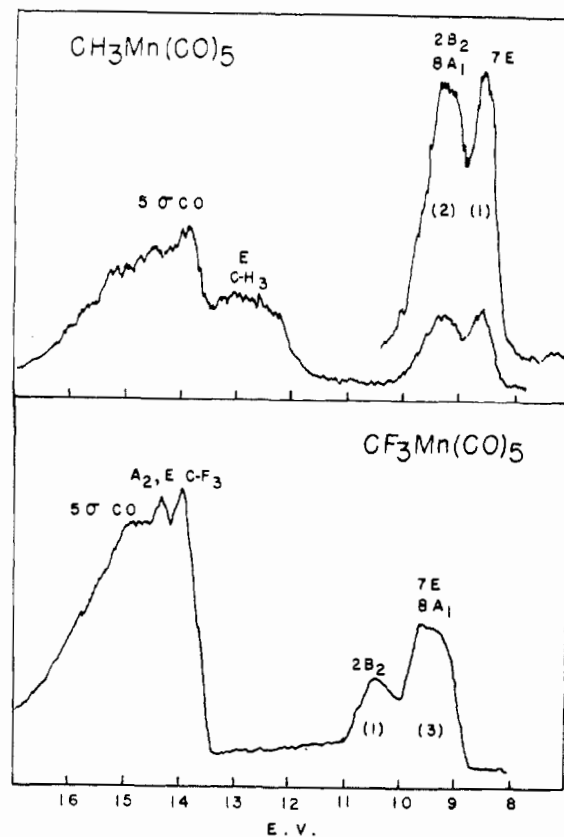

Figure 2.—Photoelectron spectra of $CH_3Mn(CO)_5$ and $CF_3Mn(CO)_5$ (see ref 37).

indeed one can convince oneself of its probability. Since the experimental method used to obtain the spectra involved a single slow scan of the energy region, further study, particularly with the newer data-accumulating techniques could prove helpful either by locating the a_1 bands in some other region or by more clearly defining the presence of multiple bands in accord with our hypothesis. Another experiment which would provide a test of our hypothesis would be to study the series of complexes in which the hydrogens of the methyl group are successively replaced by fluorines.

The pe spectra at higher energies consist of broad overlapping bands. Because our eigenvalues are the result of approximate methods and, more particularly, because a ground-state calculation does not include the relaxation and correlation effects in the excited ion, it is not possible to make a direct correspondence between the calculated eigenvalues and the observed IP's. Nevertheless, we are able to achieve band assignments and quantitative correlations with the pe values. This is accomplished by comparative calculations which correct for relaxation, correlation, and other effects which distinguish the ground-state orbital

(37) The authors gratefully acknowledge copies of the spectra supplied by the authors of ref 1.

energy from the IP. For example, from experimental results on HCF_3 the IP of an electron in the $1a_2$ molecular orbital, a nonbonding fluorine orbital, is 15.5 eV,[36,38] while from our calculated results the value is 18.1 eV. The difference between these values results in a scaling constant of 2.6 eV to be applied to the analogous orbital in $CF_3Mn(CO)_5$. Similar scaling constants are obtained for the metal–carbon σ bonds from $Cr(CO)_6$ and for the carbon–hydrogen bond of the CH_3 group from CH_4. These scaling constants, which are summarized in Table III, can be applied to both localized

TABLE III

SCALING CONSTANTS FOR BANDS IN THE PHOTOELECTRON
SPECTRA FROM KNOWN COMPOUNDS

Compound	Level	IP, eV Calcd	IP, eV Obsd	Scaling constant, eV
$Cr(CO)_6$	$e(5\sigma)$	17.6	14.2[a]	3.4
HCH_3	$1t_2$	20.8	14.0[b]	6.8
HCF_3	$1a_2$	18.1	15.5[b]	2.6
	$5e$	18.2	16.2[b]	2.0

[a] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970, p 361. [b] References 36 and 38.

and delocalized molecular orbitals as long as they have a principal component corresponding to the fragment. Their application to our calculated orbital energies for $CH_3Mn(CO)_5$ and $CF_3Mn(CO)_5$ yields estimates of the IP's which are compared with the experimental values in Table IV. The band assignments are labeled in the spectra[37] presented in Figure 2.

TABLE IV

PREDICTED AND OBSERVED BANDS IN THE PHOTOELECTRON
SPECTRA OF $CH_3Mn(CO)_5$ AND $CF_3Mn(CO)_5$

Compound	Level	IP, eV Calcd	IP, eV Obsd[a]
$CH_3Mn(CO)_5$	$7e$	8.7	8.5
	$2b_2$	9.3	9.1
	$8a_1$	(9.7)	9.1
	$e(CH_3)$	11.8	12.6
	$5\sigma(CO)$	13.4–16.5	13.8–16.5
$CF_3Mn(CO)_5$	$7e$	8.8	9.2
	$8a_1$	(8.8)	9.2
	$2b_2$	9.4	10.3
	$5\sigma(CO)$	13.5–17.0	14.0–17.0
	$a_2(CF_3)$	14.3	14.5
	$e(CF_3)$	14.4	14.5

[a] Reference 1.

It is of interest to note that, whereas the eigenvalues of Figure 1 would appear to suggest that the pe bands due to ionization of the electrons in the carbon–hydrogen bonds of the methyl group would be "buried" in the bands due to metal–carbonyl bonding electrons, the application of the above procedure clearly places the IP of the methyl group at a lower value than that of the carbonyl group. Similarly, our method superimposes the ionization energies of the electrons of the perfluoromethyl group on the leading edge of the carbonyl bands. These observations are in complete accord with the original interpretation of the spectra by Evans, *et al.*[1]

Our ability to correlate the observed and calculated IP's by the method outlined above suggests that the

interpretations of pe spectra are amenable to approximate molecular orbital calculations. The technique does stress the importance of *comparative* calculations rather than direct reliance upon orbital energies. It is very encouraging that the scaling constants appear to be transferable from simple to more complex systems. Further work in this area is presently in progress in our laboratory.

The Carbonyl Bond.—The factors which contribute to the strength of the carbon–oxygen bond in carbonyl complexes have been the subject of some discussion.[39,40] Considerable use has been made of force constants determined by the Cotton–Kraihanzel method[41] as a means of estimating the relative bond strength within the carbonyl group. Recent studies in our laboratories[42] have indicated that the vibrational force constants of octahedrally coordinated metal carbonyl complexes can be correlated with the Mulliken populations of the 5σ and 2π orbitals of the carbonyl group. Both the 5σ and 2π carbonyl orbitals are antibonding in character so that the greater their occupancy the weaker the carbon–oxygen bond. The orbital occupations and the Cotton–Kraihanzel force constants[6] for CH_3Mn-$(CO)_5$ and $CF_3Mn(CO)_5$ are presented in Table V.

TABLE V

CARBONYL ORBITAL OCCUPANCIES AND FORCE CONSTANTS

	Occupancies 5σ	Occupancies 2π	Force constants,[a] mdyn/Å
	$CH_3Mn(CO)_5$		
Cis	1.381	0.468	16.82
Trans	1.360	0.549	16.11
	$CF_3Mn(CO)_5$		
Cis	1.366	0.466	17.34
Trans	1.343	0.532	16.59

[a] Reference 6.

The absence of a π-acceptor ligand opposite the trans carbonyl results in a substantial increase of electron occupancy in the 2π orbitals of the trans carbonyl relative to those of the cis carbonyl. It should be noted that the trans carbonyl group becomes a somewhat better σ donor in accord with the well-known synergic effect[43] but that the strengthening of the carbon–oxygen bond due to σ donation is overcome by the $3d\pi$–2π back-donation so that the combined effects produce a weaker bond and a smaller force constant.

In comparing the 5σ and 2π orbitals of CH_3Mn-$(CO)_5$ with those of $CF_3Mn(CO)_5$, one finds that the carbonyl groups of the latter species have less electron occupancy in accord with the observed increase in force constants. In this paper we are content to illustrate the accord between force constants and orbital occupations in a qualitative way. In a future publication[42] we shall present quantitative correlations between these variables for a variety of mono- and disubstituted metal carbonyl complexes.

CX₃ Ligand Bonding.—In terms of the Mulliken population the back-bonding ability of a ligand increases

(39) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(40) D. J. Darensbourg and T. L. Brown, *ibid.*, **7**, 959 (1968).

(41) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

(42) M. B. Hall and R. F. Fenske, submitted for publication in *Inorg. Chem.*

(43) L. E. Orgel, "An Introduction to Transition-Metal Chemistry," Wiley, New York, N. Y., 1960, p 137.

(38) C. R. Brundle, M. B. Robin, and H. Basch, *J. Chem. Phys.*, **53**, 2196 (1970).

with increasing occupancy of the virtual orbitals of the proper symmetry. The virtual orbitals of CH_3^- and CF_3^- contain only 0.006 and 0.012 electron, respectively, a small amount compared to the 2π carbonyl occupancies listed in Table V, which indicates that these ligands are not good π-electron acceptors.

Because of the arguments in favor of back-bonding in CF_3^- groups,[2,5,6] we carried out additional calculations with basis sets on the carbon atom expanded to include either carbon 3p or 3d orbitals. These basis functions were added in the hope of lowering the position of the σ^* orbitals allowing them to have a stronger interaction with the $3d\pi$ metal orbitals. However, this procedure failed to improve the back-bonding ability of the perfluoromethyl group. We could only conclude that the perfluoromethyl ligand cannot be considered a good π-electron acceptor, which accords with Graham's analysis of the carbonyl force constants.[6] If such a conclusion is correct, it is necessary to look for other explanations for the various experimental observations usually rationalized by invoking back-bonding arguments.

The evidence usually cited falls into three categories. First, the shorter metal–carbon bond which is observed for the perfluoroalkyl groups compared to alkyl groups is interpreted as evidence of multiple bonding, where in addition to the σ metal bond the perfluoroalkyl has a π metal bond due to its π-electron acceptor ability.[5] Second, the weaker C–F bonds in $CF_3Mn(CO)_5$ compared to those in ICF_3 are cited as indicative of $3d\pi$ to σ^* electron transfer, where this π-electron acceptance weakens the C–F bond because the σ^* is strongly antibonding in this region.[2] Third, the increased thermal stability of perfluoroalkyls is taken as evidence of a stronger metal–carbon bond due to the perfluoromethyl back-bonding ability.[4,5] Implicit in all of these interpretations is the general assumption that differences in π bonding are the only important differences between the bonding of alkyl and perfluoroalkyl ligands.

The common assumption that CX_3^- bonds through an sp^3 hybrid has proven useful in describing carbon and hydrogen bonds, but this description may not be applicable to systems such as $CX_3Mn(CO)_5$. To examine this assumption we may compare the $H–CH_3$ bond in CH_4 with the $Mn–CH_3$ bond in $CH_3Mn(CO)_5$. The methyl group in CH_4 bonds to the hydrogen through both its $3a_1$ and $2a_1$ orbitals in such a way that the C–H bond is essentially an sp^3 hybrid and 1s hydrogen bond as expected. However, the manganese atom bonds to the carbon atom only through the $3a_1$ orbital, the $2a_1$ remaining isolated and nonbonding. Similarly in HCF_3 the H–C bond occurs between the hydrogen orbitals and a sp^3 type hybrid formed from a linear combination of the perfluoromethyl $4a_1$, $5a_1$, and $6a_1$ orbitals, but in $CF_3Mn(CO)_5$ the Mn–C bond occurs between the manganese orbitals and the $6a_1$ alone, the $5a_1$ and $4a_1$ orbitals remaining isolated. Thus, the Mn–C bonds will be considerably different from the H–C bonds and the Mn–CX_3 bonds will be different for different X while the H–CX_3 bonds will be similar for all X.

In qualitative arguments it is also common to neglect the effect of the charges on the surrounding ligand atoms, but these may be particularly important in

comparing ligands such as CH_3 and CF_3. Our calculations indicate that the fluorines withdraw electron density from the carbon atom leaving it substantially more positive than the carbon atom in the methyl group. This high positive charge then stabilizes the manganese levels in the perfluoromethyl complex relative to those in the methyl complex. The negative fluorines are further from the metal and will only compensate for part of the positive charge on the carbon. The influence of the surrounding atoms is an independent contribution to the value of the diagonal term and cannot be classified as uniquely due to either a σ- or π-bonding effect.

On the basis of the σ bonding and energetic differences just mentioned, it is possible to interpret the experimental observations concerning the methyl and perfluoromethyl complexes without invoking π backbonding. The observed metal–carbon bond shortening[5] can easily be explained in terms of the differences in the highest filled a_1 orbitals of methyl and perfluoromethyl. Because the $6a_1$ orbital of perfluoromethyl has considerably more carbon 2s character than the $3a_1$ orbital of methyl, the electron density in this σ-bonding orbital is concentrated closer to the carbon atom. Thus, in forming a bond with manganese the perfluoromethyl group will naturally approach closer than the methyl group. It is interesting to note that the bond shortening of 0.05 Å observed for the perfluoromethyl compared to the methyl ligand is substantially smaller than the bond shortening frequently associated with metal–ligand π interactions. For example, metal–carbonyl bonds are about 0.2 Å shorter than expected for metal–carbon single bonds;[44] similarly the strong π acceptor PF_3 forms metal–ligand bonds that are 0.15 Å shorter than those for $P(CH_3)_3$.[45] These results lend credence to interpreting the smaller degree of bond shortening for perfluoroalkyl groups in terms of differences in the character of the σ bond alone.

The weaker carbon–fluorine bonds in $CF_3Mn(CO)_5$ compared to those in ICF_3[2] can also be explained in terms of differences in σ bonding. In discussing the free ligands we emphasized that the $6a_1$ orbital of the perfluoromethyl is antibonding in the C–F region and that this means the smaller the $6a_1$ occupancy the stronger the bond. Since essentially all of the electron density donated by CF_3^- comes from this orbital, its electron occupation will be a determining factor in the relative force constants in these systems. In Table VI we have listed the force constants[2] and the

TABLE VI
C–F FORCE CONSTANTS AND ORBITAL OCCUPANCIES
FOR ICF_3 AND $CF_3Mn(CO)_5$

Compound	$6a_1$ occupancy	Force constant,[a] mdyn/Å
ICF_3	0.93	5.9
$CF_3Mn(CO)_5$	1.07	4.6

[a] Reference 2.

calculated occupancies of the $6a_1$ orbital for both ICF_3 and $CF_3Mn(CO)_5$. One can see immediately that the weaker C–F bonds of $CF_3Mn(CO)_5$ correspond to

(44) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 331–336.

(45) B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, **9**, 2403 (1970).

the larger $6a_1$ occupancy. Although the differences in $6a_1$ occupation may appear small, our results for carbonyl force constants[41] would suggest that the differences observed here are sufficient to explain the smaller force constants for $CF_3Mn(CO)_5$ without any need to invoke back-bonding arguments.

It is becoming evident that an increase in thermal stability of a complex does not necessarily imply stronger bonds. For example, it was recently pointed out[45] that $HCo(CO)_4$ is considerably less stable than $HCo(PF_3)_4$ but that the mass spectral studies[46] indicate that the Co–C and Co–P bond energies are equal. This suggests that the greater stability of perfluoroalkyl complexes is insufficient evidence for back-bonding in these systems; rather, it may be due to several contributions including the steric factors inherent in the larger ligand. One contribution that seems to have been overlooked is the stabilization of the metal levels due to the potentials of the neighboring atoms. Examination of the contributions to the diagonal term in the F matrix indicates that, relative to the CH_3 group, the charge distribution within the CF_3 group stabilizes the metal levels by 2.7 eV. This energy can contribute to the overall thermal stability of the molecule in two ways. First, it lowers the metal levels leading to an increased IP and possibly increased excitation energies, so that the perfluoro complex will be more stable with respect to decomposition by these routes. Second, the lower metal levels can form stronger bonds with *all* the ligands.

From the previous discussion it should be clear that one of the most important differences between the perfluoromethyl and methyl groups lies in the differences between their "lone-pair" orbitals. Especially significant is the fact that these orbitals are not true lone pairs but involve contributions from other atoms in the ligand. Hence, the degree of electron donation from these orbitals affects the bonding in the rest of the ligand. We should point out that the possibility of important σ-bonding differences between alkyls and perfluoroalkyls was recognized early,[4] but the consequences of this possibility seem to have been neglected in favor of interpretations involving π back-bonding. Our results indicate that the major differences are due to the σ- rather than the π-bonding effects.

Effect of the CX_3 Ligands.—The differences between the methyl and perfluoromethyl groups discussed

above can also be used to interpret the effects of these ligands on the electronic structure and bonding in the rest of the manganese complex. It is common to explain the effects of exchanging one ligand for another in terms of differences in their σ-electron-donating or π-electron-accepting ability. Thus, Evans and coworkers[1] interpreted the similarity in the "metal" e and b_2 IP's of $CF_3Mn(CO)_5$ and $IMn(CO)_5$ (9.20, 10.30 and 9.57, 10.37 eV, respectively) as due to essentially equivalent σ-donor strength of the CF_3 and I ligands. Our calculations also show a similarity in the "metal" IP's of these compounds, but they indicate that this similarity is not achieved by their equivalent σ-donor strength. A Mulliken population analysis of our final results suggests that the perfluoromethyl group is a considerably stronger σ donor than the iodide, donating 0.20 electron more with most of this density going into the $3d_{z^2}$ orbitals. The destabilization due to the increased donation is then compensated for by the stabilizing influence of the carbon atom's high positive charge. It is the balance between these two effects which leads the perfluoromethyl complex to have IP's similar to those of the iodide complex.

This example suggests that the electron-donating strength of the perfluoromethyl group may be underestimated whenever the stabilizing influence of its carbon atom is neglected. Another example of this problem is provided by Graham's analysis of the force constants. In his analysis all effects which isotropically result in a change in the metal levels are included in the category of σ effects. Since the potential due to the ligand affects the metal levels in an essentially isotropic fashion, it is automatically lumped together with the σ-donor effect. Thus, when there is a strong stabilization due to the charge on the ligand, this type of analysis will interpret the stabilization as an electron-withdrawing effect.

These are just some of the problems one can encounter in interpreting experimental results when one neglects the effect of the potential of the neighboring atoms on the energy of the metal orbitals. The effects of the potentials due to the charges on nieghboring atoms are particularly important when one is comparing ligands which have substantially different charges on their constituent atoms.

(46) F. E. Saalfield, M. V. McDowell, S. K. Gondal, and A. G. Mac Diarmid, *J. Amer. Chem. Soc.*, **90**, 3684 (1968).