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Comparison of Complete Multi-ζ Electric Dipole Moment Matrices for π-RC$_6$H$_5$Cr(CO)$_3$ as a Test of Semiempirical MO Models

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Rigorous evaluation of the complete one-, two-, and three-center electric dipole moment matrices of a multi-ζ basis was carried out for C$_6$H$_6$Cr(CO)$_3$, FC$_6$H$_5$Cr(CO)$_3$, and H$_2$NC$_6$H$_6$Cr(CO)$_3$. The transformation of these complete operator matrices over valence orbitals into molecular orbital space allowed comparisons to be made of molecular orbitals derived from several commonly used approximations. The empirical input of Basch, Viste, and Gray was found to lead to the best answers. It was also found that the self-consistent charge criterion for convergence gave superior molecular eigenvectors whenever the latter were derived from Lowdin orthogonalizations ($C'^TC' = 1$) rather than from oblique sets ($C^TSC = 1$); *viz.*, the use of eigenvectors from the self-consistent Lowdin charge convergence led to the order of dipole moments, H$_2$NC$_6$H$_5$Cr(CO)$_3$ > C$_6$H$_6$Cr(CO)$_3$ > FC$_6$H$_5$Cr(CO)$_3$, which is in agreement with experiment. This was not the case for eigenvectors derived from the Mulliken charge convergence. It was also observed that the agreement of the Lowdin point charge moments and the more difficult to derive operator moments was much better than the agreement between the Mulliken point charge moments and the operator moments. Finally, the order of the Lowdin charges of para carbon atoms of the coordinated aryl molecules was consistent with experimental ^{13}C chemical shift values when such charges were calculated with the molecular orbital coefficient matrices which predicted the experimental moment order for RC$_6$H$_5$Cr(CO)$_3$.

Introduction

It was the premise of this study that semiempirical LCAO-MO procedures as used by inorganic chemists to investigate large, many-electron transition metal complexes should be evaluated by complete operator computations, and not by inspecting quantities such as bond orders and charges, since the latter are not operator-connected with observables. We chose the important π-aryl series, RC$_6$H$_5$Cr(CO)$_3$, where R = H, F, and NH$_2$, for this study and the electric dipole moment, μ, as the operator quantity to be investigated. Complete electric dipole moment matrices (eX, eY, eZ) were evaluated using multi-ζ AO basis sets, and these moment matrices were then transformed into the MO space of each of several commonly employed semiempirical LCAO-MO methods.

Thus, rigorous evaluation of the complete one-, two-, and three-center electric dipole moment matrices was carried out for C$_6$H$_6$Cr(CO)$_3$ (eZ), H$_2$NC$_6$H$_5$Cr(CO)$_3$, and FC$_6$H$_5$Cr-(CO)$_3$ (eX, eY, eZ). These molecules were chosen because they contain the important π-RC$_6$H$_5$–metal fragment and because the transition metal carbonyl group, (CrCO), has in the past been found to be structurally quite interesting. The choice of evaluating the electric dipole moment operator was also expected to be important, since it would indicate the relative electron density distributions in the RC$_6$H$_5$ and CO fragments. Also, for any MO model to be successful it would have to predict the experimental electric dipole moment order, so that this is the first time that the quality of ground state functions of a series of transition metal aryl-carbonyl molecules has been evaluated by constructing their complete operator matrices, {O}, in AO basis sets.

Whereas atomic charges and bond orders from Mulliken formulas, though commonly reported in the literature, are not fundamentally related to observables, the present approach does permit the evaluation of the quality of ground state functions, as generated by several semiempirical MO methods in common use, and this is done for three related transition metal molecules. In addition, it was desired to determine if state functions as derived by converging on Lowdin charges (*vide infra*) differed significantly from func-

tions resulting from converging on Mulliken charges, and this question was also answered in this study.

Computations

All computations were carried out over valence orbital basis sets, *i.e.*, 3d, 4s, and 4p for Cr and 2s and 2p for each of N, C, and F. The multi-ζ Cr functions were chosen from Richardson, *et al.*,[2] and were as follows.

$$\chi_{3d} = [0.506 N_r r^2 \exp(-4.95r) + 0.675 N_r r^2 \exp(-1.80r)] Y_d$$

$$\chi_{4s} = [-0.02145 N_r \exp(-23.39r) + 0.0736 N_r r^1 \times \exp(-8.90r) - 0.18510 N_r r^2 \exp(-4.06r) + 1.01420 N_r r^3 \exp(-1.30r)] Y_s$$

$$\chi_{4p} = [0.04483 N_r r \exp(-9.70r) - 0.16359 N_r r^2 \times \exp(-3.74r) + 1.01216 N_r r^3 \exp(-1.18r)] Y_p \quad (1)$$

Clementi's "double-ζ" orbitals were employed for nonmetal functions.[3] For example, the 2s and 2p carbon functions were

$$\chi_{2s} = [0.0155 N_r \exp(-7.96897r) - 0.27176 N_r \times \exp(-5.23090r) + 0.78907 N_r r \exp(-1.82031r) + 0.27368 N_r r \exp(-1.16782r)] Y_s$$

$$\chi_{2p} = [0.26048 N_r r \exp(-2.72625r) + 0.80168 N_r r \times \exp(-1.25572r)] Y_p \quad (2)$$

Integrals were also evaluated over the simpler single-ζ chromium functions of Carroll and McGlynn,[4] and results were compared with the above functions. Similar comparisons were also made using the single-ζ Clementi-Raimondi nonmetal functions.[5]

The several thousand one-, two-, and three-center moment

(2) (a) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962); (b) J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *J. Chem. Phys.*, **38**, 769 (1963).
(3) E. Clementi in "Tables of Atomic Functions," a supplement to E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965).
(4) D. G. Carroll and S. P. McGlynn, *Inorg. Chem.*, **7**, 1285 (1968).
(5) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(1) (a) NDEA Predoctoral Fellow; (b) American Chemical Society, Petroleum Fund Fellow.

integrals of ex, ey, and ez were next rigorously evaluated in double precision arithmetic on the IBM 370/165 of the Triangle Universities Computing Center. Integrals were checked against available literature values as derived by other computational procedures; *e.g.*, ref 6 tabulated moments for formaldehyde as derived by the Barnett-Coulson and other methods. The one- and two-center aligned moment integrals of this study were evaluated by the formulas of Kuppermann, Karplus, and Isaacson[7,8] as coded conveniently by Yeranos[9] in Fortran from Li's original MAD program.[10]

All three-center moment integrals which arose were reduced to linear combinations of two-center integrals by the identity relationships among coordinates of pairs of atoms

$$X_A = X_B + R \sin \theta \cos \phi$$

$$Y_A = Y_B + R \sin \theta \sin \phi \qquad (3)$$

$$Z_A = Z_B + R \cos \theta$$

A and B are two atomic sites, R is the distance between them, and angles θ and ϕ are clearly depicted in Figure 1 and derived from the geometry of the molecule. The use of these equations then permits one to reduce three- to two-center integrals, *e.g.*

$$\langle p_{z,C} | eX_A | p_{y,B} \rangle = \langle p_{z,C} | eX_B | p_{y,B} \rangle +$$
$$R \sin \theta \cos \phi \langle p_{z,C} | p_{y,B} \rangle \qquad (4)$$

All rotation operations were carried out in the Goldstein convention.[11]

The several tested semiempirical MO procedures, previously used at various times for transition metal complexes, differed in the manner of how the elements of the Hamiltonian matrix, F, of $(F - \epsilon S)C = 0$ were generated. For each of the five methods tested, however, diagonal metal elements were chosen as $F_{ii}^M = -\Sigma_k b_k (\text{VOIP})_k$ given by Basch, Viste, and Gray,[12] and the Wolfsberg-Helmholz expression was employed for F_{ij} with $K = 1.9$.[13] The methods were then defined by the choice of ligand elements: method I, $F_{ii}^L = -(A_i Q_L^2 + B_i Q_L + C_i)$ with coefficients from Basch, Viste, and Gray;[12] method II, $F_{ii}^L = -((B_i Q_L^2/2) + A_i Q_L + C_i)$ with coefficients from Hinze and Jaffe;[14] method III, $F_{ii}^L = -(A_i Q_L + C_i)$ with coefficients from Basch, Viste, and Gray;[12] method IV, $F_{ii}^L = -\text{VSIE}_i^{Lo} - (Q_L \times 2 \text{ eV/unit}$ charge), with VSIE^{Lo} taken from Ballhausen and Gray;[15] method V, $F_{ii}^L = -\text{VSIE}_i^{Lo}$ as given by Ballhausen and

(6) W. H. Flygare, J. M. Pochan, G. I. Kerley, T. Caves, M. Karplus, S. Aung, R. M. Pitzer, and S. I. Chan, *J. Chem. Phys.*, 45, 2793 (1966).

(7) M. Karplus, A. Kuppermann, and L. Isaacson, *J. Chem. Phys.*, 29, 1240 (1958).

(8) A. Kuppermann, M. Karplus, and L. Isaacson, *Z. Naturforsch. A*, 14, 311 (1959).

(9) W. A. Yeranos, Moment Integral Calculations (QCPE No. 82.1). Care must be taken when using this Fortran package, since it evaluates B functions by taking only ten expansion terms. This led to errors for integrals of very contracted orbitals (large ζ) or when the pair of orbitals of the integral are separated by large distances. Our B function expansions were varied in length so as to remedy this problem.

(10) W.-K. Li, private communication.

(11) H. Goldstein, "Classical Mechanics," Addison-Wesley, Reading, Mass., 1950.

(12) H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, 3, 458 (1965).

(13) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, 20, 837 (1952).

(14) J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, 84, 540 (1962); *J. Phys. Chem.*, 67, 1501 (1963).

(15) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1965, pp 120-122.
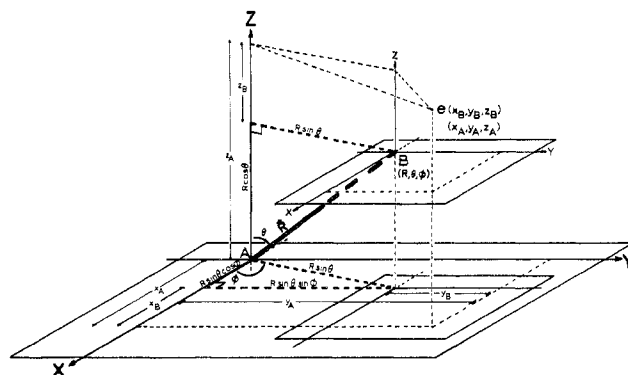

Figure 1. Relationships of the coordinates of a pair of atomic sites, A and B.

Gray.[15] Each method was used by us to derive molecular orbitals by using the self-consistent charge condition. Convergence to conventional Mulliken charges,[16] Q, *e.g.*, for atom A, was carried out in the oblique basis. Convergence

$$Q_A = Z_A - [\sum_k^{occ} (\sum_i^A N_k C_{ik}^2 + \sum_{i \, j \neq i}^A N_k C_{ik} C_{jk} S_{ij})] \qquad (5)$$

to charges derived from molecular orbitals, C', obtained from a Lowdin orthogonalized basis,[17] was also explored, where

$$C' = D[rt(D^T S D)]D^T C \qquad (6)$$

wherein $rt(M) = \{\sqrt{M_{ii}}\}$, D diagonalized the overlap matrix, S, of the oblique basis, and C contains the molecular orbital coefficients of the oblique basis.

The coordinates of atoms for $C_6H_6Cr(CO)_3$ were obtained by idealizing those of the crystallographic report of Bailey and Dahl[18] to result in the C_{3v} staggered configuration. The coordinates of the other two molecules were derived from those of this parent molecule by replacing H_A of $C_6H_5H_A$ by F and NH$_2$ (see Figure 2).

Results and Discussion

Figure 2 shows the experimentally staggered $C_6H_6Cr(CO)_3$ drawn approximately to scale, and it shows the chosen molecular $x, y,$ and z directions. Directions in the other two molecules, $FC_6H_5Cr(CO)_3$ and $H_2NC_6H_5Cr(CO)_3$, were chosen in the same way, but H_A was replaced by F and NH$_2$, respectively. Table I contains the computed dipole moments for the C_6H_6 complex using five types of state functions as obtained by the MO methods I-V described in the computational section. First, it was interesting to discover that each of the five semiempirical methods predicts the same dipole direction, $C_6H_6 \rightarrow (CO)_3$, with C_6H_6 the positive end and $(CO)_3$ the negative end. Second, the Basch-Viste-Gray empirical ligand input (method I) was found to lead to the smallest discrepancy between the computed (7.13 D) and experimental (4.31 to 5.33 D) moments, as can be seen by comparing the properly evaluated operator moments of methods I-V given in Table I. Third, it was also found by comparing the operator moments of MO procedures I and III that the polynomial term in Q^2 of $F_{ii}^L = -(A_i Q_L^2 + B_i Q_L + C_i)$ does produce a significant effect (7.13 D by procedure I, 8.52 D by method III). The operator moment of the empirical Hinze-Jaffe input (method II) was worse than the quadratic ligand expressions of Basch-

(16) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833 (1955).

(17) P.-O. Lowdin, *J. Chem. Phys.*, 18, 365 (1950).

(18) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 4, 1314 (1965).

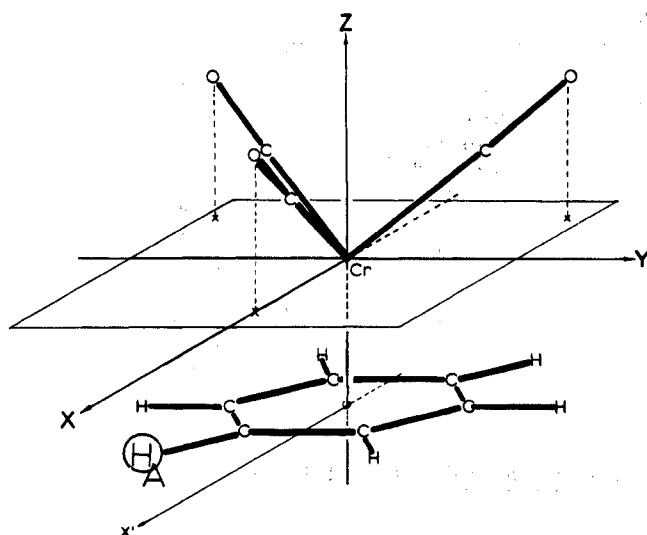**Figure 2.** Molecular Cartesian coordinates of C$_6$H$_6$Cr(CO)$_3$. The origin is Cr.

Table I. Electric Dipole Moment Results for π-(C$_6$H$_6$)Cr(CO)$_3$

Method[a]	Computed μ, D[b]	
	Operator	Mulliken charges
I	+7.13	2.45
II	+9.80	4.75
III	+8.52	3.42
IV	+11.63	7.75
V	+12.46	8.31
VI	−3.40	

Exptl μ = 4.31 to 5.33 D[c]

[a] See the computational section. [b] The direction of the positive moment +μ is C$_6$H$_6$ → (CO)$_3$ with the defined directional convention that the head of the arrow is negative. [c] W. Strohmeier and D. V. Hobe, *Z. Elektrochem.*, **64**, 945 (1960).

Viste–Gray (method I) yet better than the near-neutral ligand input of computations IV and V (Table I). The results for C$_6$H$_6$Cr(CO)$_3$ thus led us to use method I for investigating the remaining molecules, FC$_6$H$_5$Cr(CO)$_3$ and H$_2$NC$_6$-H$_5$Cr(CO)$_3$.

A fourth definitive conclusion which emerges from the study of the parent, C$_6$H$_6$Cr(CO)$_3$, was that inclusion of the three-center integrals in the operator matrix is vital. Thus, evaluation of the operator moment by method VI differed from method V only in that all three-center integrals were artificially annihilated in the former. This approximation resulted in the wrong sign of the computed dipole moment, so that the three-center integrals should be retained in such matrices. The fifth point to be made is that a simple point charge calculation of the dipole moment, with atomic charges obtained from the Mulliken population formula, leads to large errors. For example, the point charge moment was 4.75 D by method II, which is close to the experimental value (Table I), but when the same molecular orbitals were properly employed to evaluate the operator moment (9.80 D), the latter was about 4 D too large. Therefore, an "intuitively reasonable" Mulliken charge distribution need not be reasonable at all. However, it is quite interesting that each of the point charge moments also was directionally correct (Table I). The error, perhaps, resides in the equal division of the overlap population term, $2C_iC_jS_{ij}$, between a heterogeneous, oblique orbital pair, χ_i and χ_j (*vide infra*).

Several important conclusions were also drawn about the dependence of moment integral values on the choice of

metal and nonmetal AO functions. Table II contains examples of integral values evaluated with several types of functions. Numerical data such as these led us to conclude the Clementi-Raimondi[5] single-ζ functions for nonmetals (C, O, N) were as a whole nearly as good as the Clementi many-ζ functions.[3] On the other hand, the use of single-ζ metal functions,[4] obtained by matching overlap integrals with the multi-ζ kind, often did not lead to good electric dipole moment integrals. Figure 3 is a display of such multi-center integrals (Table II).

In order to decide on the desirability of employing Mulliken charge convergence or the Lowdin charge convergence, it was concluded that it was more important to computationally predict the experimental order of dipole moments for these molecules, *i.e.*, FC$_6$H$_5$Cr(CO)$_3$ < C$_6$H$_6$Cr(CO)$_3$ < H$_2$NC$_6$H$_5$Cr(CO)$_3$, than to match experimental magnitudes of these moments. As mentioned already, the empirical Basch-Viste-Gray data were employed for the F and NH$_2$ members of the series, but as soon as the operator evaluated moment for FC$_6$H$_5$Cr(CO)$_3$ was computed (7.38 D) by the convergence to Mulliken charges, it was obvious that the computations predicted the wrong order of moments, FC$_6$H$_5$Cr(CO)$_3$ > C$_6$H$_6$Cr(CO)$_3$ (Table I). The decision was then made to avoid the equal division of the population quantity $2C_iC_jS_{ij}$ between atomic orbitals χ_i and χ_j of the population analysis for an oblique basis set and its complementary molecular orbital coefficients, C. For this reason we carried out Lowdin orthogonalizations so as to be able to use density matrices, $\rho = C'^{T}C'$, for charge calculations, where C' comes from eq 6, (see the computational section). Ground state functions were then derived for these three molecules by converging to self-consistent Lowdin charges, Q'. By analogy to eq 5 one would have

$$C' = D\left[rt(D^{T}SD)\right]D^{T}C$$

$$Q_{A}' = Z_{A} - \left[\sum_{k}^{occA}\sum_{i} N_{k}C_{ik}'^{2}\right] \tag{7}$$

It is evident from Table III that this approach results in the computed moments having the experimentally known order FC$_6$H$_5$Cr(CO)$_3$ < C$_6$H$_6$Cr(CO)$_3$ < H$_2$NC$_6$H$_5$Cr(CO)$_3$. The computed magnitudes of moments, however, are too large. This agreement between the computed and experimental order of moments suggests that MO method I, which uses the Basch-Viste-Gray data, can be expected to give a relatively correct picture of molecular electron distributions of related molecules. The method was also chosen over methods II-V because it led to the least discrepancy between the magnitudes of the computed and experimental moments. In other words, this electric dipole moment result inferred that this procedure accounted reasonably well for the relative electron distribution between RC$_6$H$_5$ and (CO)$_3$ fragments.

We comment briefly on additional features inherent when converging on either Mulliken or Lowdin charges. First, the empirical data used for deriving the constants A, B, and C for VOIP's of $F_{ii}^{M} = -\sum_{k}b_{k}(\text{VOIP})_{k}$ (*vide supra*) are based on ionization energy data of atoms and their ions. These species bear *real charges* and are, therefore, fully independent of the definition of charge. Next, the practice of using these data and VOIP expressions for "atoms" or "ions" in molecules becomes a bit problematic because (i) "charges" can be fractional and (ii) "charges" are defined and not measured. It is for such reasons that we proceeded to empirically evaluate the molecular orbital coefficients, as obtained

Table II. Numerical Values of Several Two-Center and Three-Center Integrals

Integral type	Choice of chromium function	Nonmetal function	Value of integral
$\langle 2s(C)|eZ(Cr)|3d_{z^2}(Cr)\rangle$	Double ζ^a or χ^a	Single ζ^b or χ^b	+0.665
	Double ζ^a or χ^a	Multi ζ^c or χ^c	+0.668
	Single ζ^d or χ^d	Multi ζ^c or χ^c	+0.379
$\langle 2p_y(C)|eZ(Cr)|3d_{z^2}(Cr)\rangle$	χ^a	χ^b	−0.604
	χ^a	χ^c	−0.684
	χ^d	χ^c	−0.465
$\langle 2p_z(C)|eZ(Cr)|2p_z(O)\rangle$	χ^a	χ^b	−0.708
	χ^a	χ^c	−1.15
	χ^d	χ^c	−1.17
$\langle 2p_x(O)|eZ(Cr)|3d_{x^2-y^2}(Cr)\rangle$	χ^a	χ^b	0.089
	χ^a	χ^c	0.106
	χ^d	χ^c	0.050

^{a} Reference 2. ^{b} Reference 5. ^{c} Reference 3. ^{d} Reference 4.

Table III. Electric Dipole Moments (D) of $RC_6H_5Cr(CO)_3$ as Computed by the Operator Method and by the Point Charge Model

| | Operator evaluation | | Point charge model^a | | |
Molecule	Method M: Mulliken charge convergence	Method L: Lowdin charge convergence	Mulliken charges	Lowdin charges	Exptl^b
$FC_6H_5Cr(CO)_3$	7.38	8.95	3.94	6.67	4.75
$C_6H_6Cr(CO)_3$	7.13	10.2	4.66	8.07	4.95
$H_2NC_6H_5Cr(CO)_3$		10.4	3.95	7.33	5.40

^{a} The set of MO coefficients from method L of this table was used to carry out Mulliken and Lowdin population analyses. The resulting atomic charges were then employed to evaluate these point charge moments. ^{b} W. Strohmeier and D. V. Hobe, *Z. Elektrochem.*, **64**, 945 (1960).
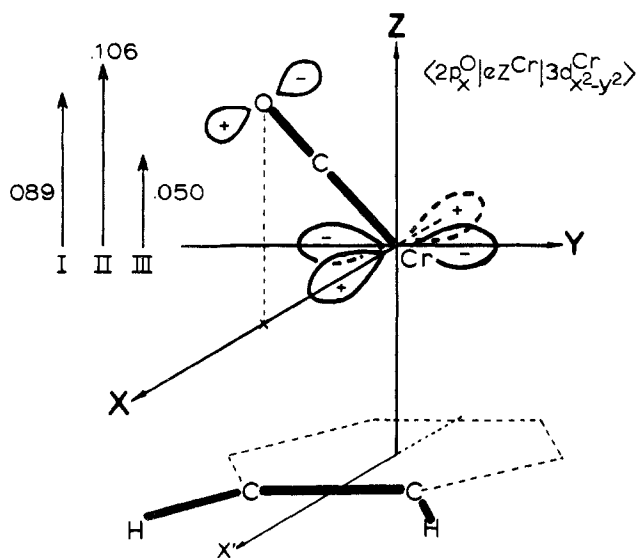

Figure 3. Three values and directions of a two-center electric dipole moment integral using several AO functions. This is integral type **4** of Table II, which also defines the functions.

Figure 4. Atom charges in $C_6H_6Cr(CO)_3$ using Mulliken (A) and Lowdin (B) convergence (see text).

by two definitions of charge, by computing operator quantities and not by inspecting the results of population analyses, but an example of the two sets of charges obtained is illustrative of the general results. Figure 4A shows several charges of atoms in $C_6H_6Cr(CO)_3$ as obtained from using C and S and converging on Mulliken charges (eq 5). Figure 4B shows charges of the same atoms after converging on Lowdin charges. These charges of the latter procedure were calculated after transforming the molecular orbital coefficient matrix, C', of orthogonal AO's (*vide supra*) to the matrix C^α of nonorthogonal AO's

$$C^\alpha = L^{-1}C'$$
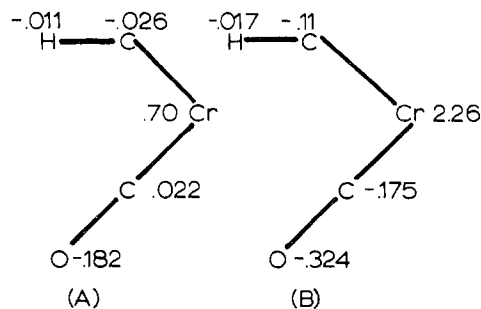
where L is the product of matrices to the left of C in eq 6.

Final Mulliken charges are, therefore, being compared assuming two different definitions of charge for the molecular orbital calculation. The general feature is that the Lowdin convergence creates a more positive metal charge and the electron density at all the other atoms increases.

There is a second property which provides another check on these wave functions. Bodner[19] recently reported ^{13}C nuclear magnetic resonance spectra of several aryl chromium tricarbonyl molecules. He found the chemical shifts of para carbon atoms of the RC_6H_5 rings were in the order $FC_6H_5 < H_2NC_6H_5$, and the shift value of C_6H_6 was less than both of these. This result implies that the electron density at the para position is $C_6H_6 < FC_6H_5 < H_2NC_6H_5$. This order of electron densities was predicted by the above MO model which also yields the correct order of dipole moments; *viz.*, the net charges at the para carbon from the Lowdin analyses are 0.047 (NH_2-), 0.060 (F–), and 0.093 (H–). The Mulliken charges derived from these Lowdin values are also correct, *i.e.*, −0.160 (NH_2-), −0.149 (F–) and −0.110 (H–). Unlike this carbon atom,[19] the ^{13}C chemical shifts of CO and of others in the ring will probably be composed of paramagnet-

(19) G. M. Bodner, University of Illinois, Urbana, private communication.

ic as well as local diamagnetic contributions. It is probably for this reason that we found the charges did not correlate well with the shift values. Whether or not these same functions also predict other molecular ground state properties reasonably well remains to be investigated. It is anticipated, however, that other properties which depend on all the molecular orbitals collectively will be reasonably well accounted for, whereas properties which are indicative of a portion or all of any one individual such orbital will most likely not fare as well.

It is very informative to also compare, using Table III, the operator moments of the three molecules, $RC_6H_5Cr(CO)_3$, with the moments computed from Mulliken and Lowdin point charges. Recall the above reference to the equal division between AO's χ_i and χ_j of overlap population $2NC_iC_jS_{ij}$ from the Mulliken population analysis and that this is avoided in the Lowdin charge calculation. The numerical results of Table III permit one to conclude that, using the Lowdin charge convergence to arrive at a set of MO coefficients, the values of the moments derived from Lowdin point charges (fourth column of numbers) are much closer to the more difficult to evaluate operator moments (second column of numbers) than are the moments derived from the simple Mulliken point charges. The better agreement derives probably from not having to cope with the quantity $2NC_iC_jS_{ij}$ when using the Lowdin procedure. However, only the order of the operator moments was the same as the order of experimental moments (Table III), so that

even the order of Lowdin point charge moments cannot be relied upon to accurately reflect changes in a series of related molecules.

Finally, it is of chemical interest to point out the computed directions of the operator dipole moments. The direction of the moment of $C_6H_6Cr(CO)_3$ has already been discussed above; i.e., benzene is the positive end and $(CO)_3$ constitutes the negative end of the dipole moment vector, which is directionally coincident with the molecular z axis, or C_3 symmetry axis (Figure 1). For the fluorobenzene derivative, $FC_6H_5Cr(CO)_3$, the resultant, or net moment, of the three moments, u_x, u_y, and u_z, was tilted ~12° away from the z axis and toward F and was in the plane which contains F, Cr, and the z axis (Figure 2). On the other hand, it was found for $H_2NC_6H_5Cr(CO)_3$ that the net moment tilted away from the latter's molecular z axis but also away from the NH_2 substituent as can be visualized from Figure 2. These directional results are consistent with the notions that F and NH_2 withdraw and donate electron density, respectively.

Photoreactions of Aminepentacarbonylmolybdenum(0) and -tungsten(0) Complexes

MARK WRIGHTON

The ligand photosubstitution processes in $M(CO)_5L$ (M = Mo and W; L = NH_3, n-$PrNH_2$, and piperidine) upon excitation with 366-, 405-, or 436-nm light have been investigated. Photosubstitution of both L and CO is found and the quantum yields are dependent on the excitation wavelength. Photosubstitution of L dominates the chemical decay paths of the excited state with CO substitution becoming more important at shorter excitation wavelengths. Photosubstitution of CO for M = Mo is generally higher than for M = W in the $M(CO)_5L$ complexes investigated. Typical quantum yields for M–L cleavage at 405 nm are of the order of 0.5 as determined by measuring the formation of $M(CO)_6$ by photolysis of $Mo(CO)_5NH_3$ or $W(CO)_5$(piperidine) in the presence of CO. Substitution yields for CO release are in the range of 10^{-2}–10^{-1} as determined by photolysis of $M(CO)_5L$ in the presence of excess L yielding $M(CO)_4L_2$ complexes. Importantly, the total reaction quantum yields are less than unity.

Introduction

Metal carbonyls are among the most photosensitive coordination compounds, and for the mononuclear binary carbonyls CO dissociation is thought to account for a large fraction of the excited state chemical decay paths.[1] Included among the most photoreactive metal carbonyls are $Mo(CO)_6$ and $W(CO)_6$ where reaction 1 is measured to occur with unit

$$M(CO)_6 \xrightarrow[\phi = 1.0]{h\nu} M(CO)_5 + CO \qquad (1)$$
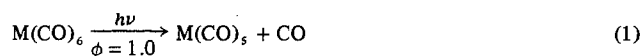
M = Mo and W

quantum efficiency as reflected in ultimate formation yields of the substituted product $M(CO)_5L$ when irradiations are

carried out in the presence of a nucleophile, L.[2] This procedure has led to an explosion of the number of derivatives of metal carbonyls since the reaction can be carried out at room temperature (or lower), and often high yields of *only* the monsubstituted complex have been obtained. Selective formation of the $M(CO)_5L$ derivative can be aided by running the reaction to small conversion to prevent competitive absorption of light by the product and/or by forming first a relatively nonphotosensitive $M(CO)_5L'$ complex followed by thermal exchange of L' by L. For many situations tetrahydrofuran has served as L' in the synthetic sequence of reactions 1-3.[3] The photosensitivity of $M(CO)_5L$ complexes

(1) M. Wrighton, *Chem. Rev.*, in press.

(2) W. Strohmeier and S. von Hobe, *Chem. Ber.*, 94, 761 (1961).

(3) W. Strohmeier, *Angew. Chem.*, 76, 873 (1964).