**Table V. Structural Comparison of Uranium and Thorium Half-Sandwiches (Å)**

| | $(C_8H_8)UCl_2(NC_5H_5)_2$ | $(C_8H_8)ThCl_2(OC_4H_8)_2$ |
|---|---|---|
| M–C | 2.684 | 2.72 |
| M–Cl | 2.644 | 2.686 |
| $r_M$ | 1.05 | 1.09 |
| $r_{COT}$ | 1.63 | 1.63 |
| $r_{Cl}$ | 1.59 | 1.60 |

THF was removed in vacuo, and the orange solid was dissolved in 150 mL of toluene. The solution was filtered and then concentrated and cooled to afford 1.21 g (92%) of orange crystals. $^1H$ NMR (toluene-$d_8$, 30 °C): −29.6 (s, 13.1 Hz, 8 H), −10.0 (s, 6.6 Hz, 12 H), 10.2 (s, 3.5 Hz, 2 H). Visible (THF): 382 (sh), 458, 531 (sh), 572 (sh). IR (Nujol): 1355 s, 1288 s, 1201 m, 1145 m, 1075 m, 1010 m, 990 s, 984 sh, 870 m, 850 m, 805 m, 763 s, 710 m, 665 m, 650 s, 600 m, 580 m, 550 w. Anal. Calcd for $C_{18}H_2O_4U$: C, 40.01; H, 4.10. Found: C, 40.33; H, 3.98.

**Crystal Structures.** The air-sensitive crystals, sealed inside quartz capillaries, were mounted on a modified Picker FACS-1 automated diffractometer equipped with a molybdenum X-ray tube ($\lambda(K\alpha_1) = 0.709\,30$ Å) and an oriented graphite monochromator. A set of $\theta$–$2\theta$ scanned intensities were collected and processed. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares. Anisotropic thermal parameters were assigned to all non-hydrogen atoms and isotropic thermal parameters to the hydrogen atoms. In the $(C_8H_8)UCl_2(NC_5H_5)_2$ complex, the hydrogen atomic parameters were all refined in an unrestrained manner. In the $(C_8H_8)UCl_2(CH_3COCHCOCH_3)_2$ complex, the hydrogen atomic parameters were restrained to their estimated values because the data would not support an unrestrained refinement. Atomic scattering factors for all atoms were taken from values in ref 24. The experimental details of the data collection and the least-squares refinements are tabulated in Table IV.

**Supplementary Material Available:** Listings of crystal data, thermal parameters, H atom positional parameters, additional bond distances and angles, and least-squares planes and additional ORTEP views for 3 and 4 (10 pages); listings of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

(24) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2, pp 71–102.

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# Application of the Fenske–Hall Molecular Orbital Method to the Calculation of $^{13}C$ NMR Shifts in Organometallic Compounds: Correlation between Calculated $\sigma_p$ Values and the Observed Chemical Shift, $\delta$

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The nonparameterized Fenske–Hall molecular orbital (MO) approach and the Ramsey sum-over-states approximation are employed to establish that the sign and magnitude of the "paramagnetic" term of the nuclear shielding have excellent correlation with observed $^{13}C$ NMR shifts in a wide variety of shielding environments in six transition-metal organometallic compounds. In this context it is presumed that changes in the "diamagnetic" or localized charge density term are relatively unimportant in molecules of this type. A detailed analysis of the molecular orbital contributions in the prototype complex $(CO)_5CrC(OCH_3)(CH_3)$—a system in which shift values range over 300 ppm—yields an unambiguous picture of the key contributions to a particular $^{13}C$ resonance. An examination of individual terms in the sum-over-states expression demonstrates the importance of three factors: the symmetry requirements of the angular momentum operators, the energetic position of ligand MO's in relation to the metal d orbitals, and the energy difference between filled and unfilled MO's containing atomic character of the carbon atom of interest.

## Introduction

The nuclear magnetic resonance experiment is unique in its ability to directly provide reaction mechanistic and kinetic data as well as stereochemical and conformational information. Despite the voluminous literature devoted to the experiment and its applications,[1] it has remained difficult to develop a reliable theoretical treatment for calculating shielding factors for large molecular systems of interest. Though the analysis of information such as coupling constants, line widths, and relaxation times is

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(1) For a comprehensive treatment of NMR spectroscopy see: Sohar, P. *Nuclear Magnetic Resonance Spectroscopy*; CRC Press: Boca Raton, FL, 1983; Vols. I–III.

**Chart I**
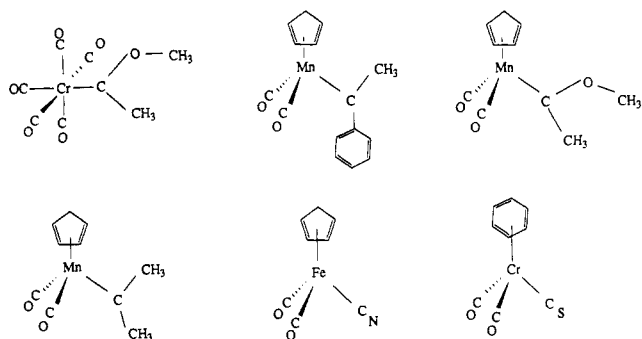
necessary for the full application of the technique, the chemical shift, $\delta$, is the parameter of greatest interest.

The quantum-mechanical treatment of the NMR phenomenon was developed a number of years ago. Ramsey,[2] and later Pople,[3] used a perturbational approach in expressing the molecular wave function in a magnetic field in terms of ground- and excited-state functions. This leads to the equation for shielding often written

$$\sigma = \sigma_d + \sigma_p \qquad (1)$$

The "diamagnetic" term, $\sigma_d$, depends on the ground-state wave function and is frequently thought of as a localized charge density term, whereas $\sigma_p$, the "paramagnetic" term, depends on ground- and excited-state wave functions and consequently may include contributions from atoms relatively distant in the molecule, far from the magnetic center of interest. In the NMR spectra of atoms larger than hydrogen, it is well recognized that the importance of changes in $\sigma_p$ far exceeds that of changes in the diamagnetic term.[4]

In light of the Fenske-Hall method's successful application to problems in transition-metal organometallic chemistry,[5] the calculation of NMR shielding terms with use of this approximate molecular orbital approach was considered. Though rigorous calculations with the inclusion of configuration interaction would be necessary to achieve the accuracy needed to predict unknown chemical shifts, the computational effort needed to solve all of the integrals for an organometallic compound of even moderate size would be formidable. In addition, a workable model that could be easily utilized and interpreted would be unattainable in a method that required large basis sets and numerous contributions from a variety of excited states. It was hoped that a semiquantitative model with a minimal basis set could provide an explanation for characteristic regions of shifts or explain a seemingly anomalous shift.

For our study of $^{13}C$ NMR chemical shifts, the transition-metal organometallic systems listed in Table I and illustrated in Chart I have been chosen. Three of the molecules, $(CO)_5CrC(OCH_3)CH_3$, $(\eta^6\text{-}C_6H_6)Cr(CO)_2CS$, and $(\eta^5\text{-}C_5H_5)(CO)_2MnC(OCH_3)(CH_3)$, were selected because they have been the subject of previous molecular orbital studies by our group and as a result have orbital interactions with which we are quite familiar.[6] The remaining

(2) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699.

(3) (a) Pople, J. A. *J. Chem. Phys.* **1963**, *37*, 53. (b) Pople, J. A. *J. Chem. Phys.* **1963**, *37*, 60.

(4) (a) Saika, A.; Slichter, C. P. *J. Chem. Phys.* **1954**, *22*, 26. (b) Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803. (c) Mahnke, H.; Sheline, R. K.; Spiess, H. W. *J. Chem. Phys.* **1974**, *61*, 55.

(5) (a) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768. (b) Fenske, R. F. *Pure Appl. Chem.* **1971**, *27*, 61. For applications see for example: (c) Fenske, R. F.; DeKock, R. L. *Inorg. Chem.* **1970**, *9*, 1053. (d) Lichtenberger, D. L.; Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1973**, *12*, 702. (e) Czech, P. T.; Gladysz, J. A.; Fenske, R. F. *Organometallics* **1989**, *8*, 1806.

**Table I. Observed $^{13}C$ Chemical Shifts, Calculated Paramagnetic Contributions to the Chemical Shift, and Natural Atomic Population on the Carbon Center of Interest**

| molecule | position | $\delta$(obs) | $\sigma_p$(calc) | population | ref |
|---|---|---|---|---|---|
| $(CO)_5CrC(OCH_3)$- $CH_3$ | methyl | 49.1 | −54.95 | 6.14 | a |
| | methoxy | 67.2 | −58.79 | 5.72 | |
| | cis CO | 217.6 | −114.54 | 5.89 | |
| | trans CO | 223.6 | −118.12 | 5.89 | |
| | carbene | 362.2 | −158.41 | 5.87 | |
| $(\eta^6\text{-}C_6H_6)Cr(CO)_2$- (CS) | ring | 99.3 | −83.25 | 5.96 | b |
| | carbonyl | 231.5 | −119.53 | 5.87 | |
| | thiocarbonyl | 346.3 | −154.13 | 6.11 | |
| $(\eta^5\text{-}C_5H_5)Fe(CO)_2$- (CN) | ring | 85.9 | −80.06 | 5.95 | c |
| | cyano | 154.7 | −96.53 | 6.14 | |
| | carbonyl | 211.1 | −121.88 | 5.89 | |
| $(\eta^5\text{-}C_5H_5)(CO)_2$- $MnC(CH_3)_2$ | methyl | 52.3 | −55.98 | 6.05 | d |
| | ring | 90.0 | −81.48 | 6.00 | |
| | carbonyl | 233.3 | −123.88 | 5.96 | |
| | carbene | 372.8 | −201.37 | 6.13 | |
| $(\eta^5\text{-}C_5H_5)(CO)_2$- $MnC(OCH_3)$- $(CH_3)$ | methyl | 46.0 | −51.28 | 6.12 | e |
| | methoxy | 62.6 | −55.58 | 5.76 | |
| | ring | 88.5 | −81.17 | 6.00 | |
| | carbonyl | 234.4 | −125.85 | 5.99 | |
| | carbene | 339.2 | −159.71 | 5.96 | |
| $(\delta^5\text{-}C_5H_5)(CO)_2$- $MnC(C_6H_5)$- $(CH_3)$ | methyl | 68.4 | −57.18 | 6.02 | f |
| | ring | 90.6 | −80.18 | 6.05 | |
| | phenyl 4 | 118.9 | −91.98 | 5.93 | |
| | phenyl 3 | 125.3 | −92.91 | 5.97 | |
| | phenyl 2 | 127.3 | −89.63 | 6.01 | |
| | phenyl 1 | 167.0 | −91.98 | 5.97 | |
| | carbonyl | 232.9 | −126.00 | 5.94 | |
| | carbene | 363.7 | −190.76 | 6.22 | |

*$^a$Structure: Schubert, U. *Coord. Chem. Rev.* **1984**, *558* 261. NMR: Connor, J. A.; Jones, E. M.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Dalton Trans.* **1972**, 2419. *$^b$Structure: Saillard, J. Y.; Grandjean, D.; Caillet, P.; LeBeuze, A. *J. Organomet. Chem.* **1980**, *190*, 371. NMR: Cozak, D.; Butler, I.; Baibich, I. O. *J. Organomet. Chem.* **1979**, *169*, 381. *$^c$Structure: idealized. NMR: Farnell, L. F.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc. D* **1971**, 1078. *$^d$Structure: Friedrich, P.; Besl, G.; Fischer, E. O.; Huttner, G. *J. Organomet. Chem.* **1977**, *139*, C68. NMR: Fischer, E. O.; Clough, R. L.; Besl, G., Kreissl, F. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 543. *$^e$Structure: Schubert, U. *Organometallics* **1982**, *1*, 1085. NMR: Fischer, E. O.; Besl, G. *J. Organomet. Chem.* **1978**, *157*, C33. *$^f$Structure: Reference a. NMR: Reference d.*

molecules in the list were chosen in order to cover a wide range of different shielding environments and $^{13}C$ chemical shift values.

## Theoretical Considerations

The molecular orbital calculations were completed on a VAX 8650 computer using the Fenske-Hall approximate MO method.[5a] Interatomic distances and angles were idealized from X-ray crystallographic data in the references listed after Table I. A minimal basis set was employed in these calculations. Clementi's free-atom double-$\zeta$ Hartree-Fock-Slater type orbitals[7] were used for the second-row elements. Only the 2p functions on each atom were kept in the double-$\zeta$ form; the 1s and 2s functions were curve-fit to a single-$\zeta$ form with use of the maximum overlap criterion.[8] $X\alpha$-SW calculations were performed on sulfur, chromium, manganese, and iron by following the method of Herman and Skillman.[9] For these atoms, a basis of orthogonalized STO's that maximize overlap with the $X\alpha$-SW eigenfunctions

(6) (a) Lichtenberger, D. L.; Fenske, R. F. *Inorg. Chem.* **1976**, *15*, 2015. (b) Block, T. F.; Fenske, R. F.; Casey, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 441.

(7) Clementi, E.; Ramondi, D. L. *J. Chem. Phys.* **1963**, *38*, 2686.

(8) Radtke, D. D. Ph.D. Thesis, University of Wisconsin—Madison, 1966.

(9) Herman, F.; Skillman, S. *Atomic Structure Calculations*; Prentice Hall: Englewood Cliffs, NJ, 1963.

was created.[10] The STO functions of these atoms were of single-$\zeta$ form, except for the valence p orbitals on sulfur and the valence d orbitals on the transition metals, all of which were double-$\zeta$ form. The hydrogen 1s exponent was set at 1.16. The exponents for the transition-metal valence s and p orbitals were set at 2.0. These functions are less diffuse than atomic results but are found to describe bonding in organometallic complexes more accurately.[11] In addition, we have made use of the natural population analysis of Weinhold and co-workers.[12] The procedure provides an alternative to the Mulliken population analysis, eliminating the overlap partitioning problem of this traditional scheme.[13]

The solution of the sum-over-states expression for the paramagnetic term of the chemical shift requires the evaluation of matrix elements for the $1/r$, $L$, and $L/r^3$ operators (see eqs 2 and 3). Our approach utilizes the same Slater-type atomic orbital basis functions that are used in the Fenske-Hall MO calculations. For the evaluation of $\sigma_p$ for a particular carbon atom in a molecule, the operators were centered on that atom. The computer programs for our study are adapted from those used by Freier et al. in a X$\alpha$-SW study of the ^{13}C NMR shifts of some small organic molecules.[14] As in that study, a mixed analytical–numerical integration is performed.[14,15]

All integrals associated with the matrix elements for the $L$ operator were calculated, while for the matrix elements of the $L/r^3$ operator, all integrals except three-center terms were evaluated. The operators employed are those obtained from the standard $x$, $y$, and $z$ components of the angular momentum operators by multiplying by $i$. Once the atomic orbital results are calculated, a simple transfer to a molecular orbital basis is performed with use of the coefficients associated with the appropriate Fenske–Hall eigenvectors.

A bridge needs to be made between the calculated paramagnetic contribution to nuclear shielding, $\sigma_p$, and the reported values of ^{13}C chemical shifts, $\delta$(obs). Since $\delta = \sigma(\text{ref}) - \sigma(\text{sample})$, it follows from eq 1 that $\delta(\text{calc}) = [\sigma_d(\text{ref}) - \sigma_d(\text{sample})] + [\sigma_p(\text{ref}) - \sigma_p(\text{sample})]$. For convenience, $\sigma_p(\text{ref})$ is chosen to be zero and the first bracketed term is assumed to be constant. As a result, our $\delta(\text{calc})$ value is proportional to $-\sigma_p(\text{sample})$.

## General Considerations

When the LCAO approximation is applied to Ramsey's equations, the sum-over-states expression for the diamagnetic and the paramagnetic term result:

$$\sigma_d{}^n = \frac{\mu_0 e^2}{12\pi m} \sum_{j=1}^{occ} \left\langle \Phi_j \left| \frac{1}{r} \right| \Phi_j \right\rangle \tag{2}$$

$$\sigma_p{}^n = (-\mu_0 e^2/8\pi m^2) \sum_j^{occ} \sum_k^{unocc} [\langle \Phi_j | L_n | \Phi_k \rangle \times$$

$$\langle \Phi_k | L_n/r^3 | \Phi_j \rangle + \langle \Phi_j | L_n/r^3 | \Phi_k \rangle \langle \Phi_k | L_n | \Phi_j \rangle ] / (E_k - E_j) \tag{3}$$

(10) (a) Bursten, B. E.; Fenske, R. F. *J. Chem. Phys.* **1977**, *67*, 3138. (b) Bursten, B. E.; Jensen, J. R.; Fenske, R. F. *J. Chem. Phys.* **1978**, *68*, 3320.

(11) (a) Fenske, R. F.; Radtke, D. D. *Inorg. Chem.* **1968**, *7*, 479. (b) Fenske, R. F. *Pure Appl. Chem.* **1988**, *60*, 1153.

(12) (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (b) Rives, A. B.; Weinhold, F. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1980**, *14*, 201; **1981**, *15*, 555. (c) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (d) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 99.

(13) The NBO procedure has been modified for use in conjunction with Fenske–Hall MO calculations. Applications of this adaptation can be found in the following: (a) Harris, H. A.; Kanis, D. R.; Dahl, L. F. Submitted for publication. (b) Kanis, D. R.; Fenske, R. F. Submitted for publication. (c) Kanis, D. R. Ph.D. Thesis, University of Wisconsin—Madison, 1988.

(14) The programs have been used previously in conjunction with X α–SW wave functions that had been projected onto a STO basis. (a) Freier, D. G.; Fenske, R. F.; Xiao-Zeng, You, *J. Chem. Phys.* **1983**, *7*, 3526. (b) Fenske, R. F. Proceedings of IUCCP Symposium. In *Organometallic Compounds, Synthesis, Structure and Theory*; Shapiro, B., Ed.; Texas A&M Press: College Station, TX, Vol. 1, pp 305–333. (c) Freier, D. G. Ph.D. Thesis, University of Wisconsin—Madison, 1981.

(15) (a) Pitzer, R. M.; Kern, C. W.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 267. (b) Harriman, J. E. *Theoretical Foundations of Electron Spin Resonance*; Academic: New York, 1978.

**Chart II**
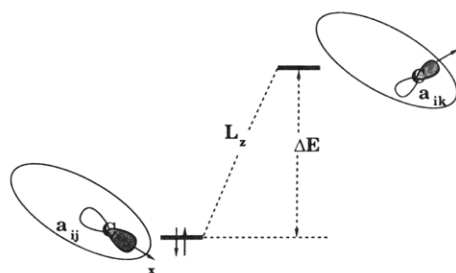


where $n$ spans $x$, $y$, and $z$, whereas the indices $j$ and $k$ span the filled and unfilled molecular orbitals, respectively.[16] Due to the fact that the angular momentum operators in the paramagnetic term (3) require angular dependence of the wave function, an analysis of ^{1}H NMR spectra can ignore contributions to $\delta$ due to this term. That is, since hydrogen p orbitals are essentially unpopulated, the solution of the integrals in (3) yields only trivial contributions to the overall shift. As a result, localized $\sigma_d$-type concepts such as the inductive effect can be used successfully in the study of proton NMR spectra. In addition, since variations in charge on a hydrogen atom in a molecule are small, the range of ^{1}H spectra is relatively narrow.

In rigorous calculations on small molecules,[4] it has been demonstrated that the diamagnetic and paramagnetic terms are of the same order in magnitude but are opposite in sign. Calculations of (2) and (3) with Fenske–Hall wave functions agree with this finding. The calculated chemical shift then becomes the sensitive difference between two large numbers, thus making the correlation of observed shifts, $\delta$, with calculated $\sigma$ values extremely tenuous. In our basis it was found, however, that values of $\sigma_d$ have *no* correlation with observed $\delta$ values. These results correspond with the observations of Nakatsuji, who, in an ab initio study of transition-metal NMR spectra, demonstrated that the chemical shifts are almost completely determined by the valence MO contributions to the paramagnetic term.[17] If one goes on to make the approximation that changes in the electron population of a carbon atom and its related $\sigma_d$ value are relatively small, the chemical shift becomes a function of only the paramagnetic contribution.[18] Such an assumption is not rigorous. It can only be justified on the basis of its ability to correlate the experimental chemical shifts with the calculated $\sigma_p$ values and the chemical insight that is obtained by consideration of the nature of the relevant orbitals involved. The remainder of this paper is devoted to precisely this task.

In the sum-over-states description, the representations of excited-state wave functions by virtual molecular orbitals are, of course, very rough approximations, especially for the very high lying orbitals. It is only the inverse dependence on $\Delta E$, the energy difference between the filled and empty orbitals, that enables the use of the approximation. Analysis of (3) indicates that there are a total of three criteria that must be simultaneously satisfied for a

(16) For a detailed discussion and derivation of these equations see: Ando, I.; Webb, G. A. *Theory of NMR Parameters*; Academic: New York, 1983.

(17) (a) Nakatsuji, H.; Kanda, K.; Ehdo, K.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 4653. (b) Kanda, K.; Nakatsuji, H.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 5888.

(18) Many authors have expressed severe reservations that any theoretical approach will correlate ^{13}C NMR shifts for carbon atoms bound to transition metals: (a) Evans, J.; Norton, J. R. *Inorg. Chem.* **1974**, *13*, 3042. (b) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: New York, 1981. These concerns focus on the treatment of the diamagnetic or $1/r$ term.

specific interaction to make an important contribution to $\sigma_p$. First is the aforementioned $\Delta E$ $(E_k - E_j)$ term. It will be demonstrated that this term is always small for the most significant contributions to the $\sigma_p$ values of carbon atoms with large downfield shifts. Second, due to the $1/r^3$ dependence of the $L/r^3$ operator, the contributions of the atomic p functions on the magnetic center of interest to both the filled and unfilled levels must be significant. Finally, the orbitals involved must be of proper symmetry. The last condition can be appreciated by noting that for the $L_z$ operator on an isolated carbon atom only the terms $\langle C\ 2p_y|L_z|C\ 2p_x \rangle$ and $\langle C\ 2p_x|L_z|C\ 2p_y \rangle$ are nonzero. However, it should not be overlooked that contributions to a molecular matrix element $\langle \Phi_k|L_n|\Phi_j \rangle$ can arise from terms on atomic centers other than the carbon atom of interest, such as $\langle [C\ 2p_y](2)|L_z(1)|[C\ 2p_x](2) \rangle$, where $L_z(1)$ refers to the operator placed on carbon center 1 while the carbon functions are centered at carbon center 2. Such interactions are particularly important in systems where the contributions by centers 1 and 2 are equal by the symmetry of the molecule. As summarized in Chart II, showing $\langle C\ 2p_x|L_z|C\ 2p_y \rangle$, only high-lying filled and low-lying unfilled MO's with large C 2p coefficients $(a_{ij}, a_{ik})$ having the proper symmetry will contribute to $\sigma_p$. Hence, a significant fraction of terms in the double sum in (3) are negligible.

## A Prototype Calculation: $(CO)_5CrC(OCH_3)CH_3$

In order to illustrate the factors that influence the various degrees of shielding at a carbon nucleus, we now examine one molecule that contains a number of carbon nuclei over a wide range of shift values. The chromium Fischer carbene complex $(CO)_5CrC(OCH_3)CH_3$ has five distinct resonances in its $^{13}C$ NMR spectrum.[19] The reported values of the chemical shifts, $\delta$(obs), the calculated paramagnetic contribution, $\sigma_p$, and the calculated natural atomic population of each unique carbon are listed in Table I. The comparison of $\delta$(obs) with $\delta$(calc) is displayed in Figure 1 and is excellent, considering the approximations that have been made. The peaks that appear farthest upfield at $\delta$ 49.1 and 67.2 ppm are the resonances from the methyl and methoxy carbons, respectively. The cis and trans CO peaks appear at $\delta$ 217.6 and 223.6 ppm, in the normal region for transition-metal carbonyl carbons. Finally, another 140 ppm downfield at $\delta$ 362.3 ppm, the peak for the carbene carbon appears. Note that, in contrast to the excellent correlation with the calculated paramagnetic contribution, the diamagnetic term, as reflected in the natural atomic charges, shows no correlation to the observed shift values.

It should be noted that the slope of the best-fit line in Figure 1 is significantly greater than 1. This can be attributed to two factors that overestimate the magnitude of $\Delta E$. First, the use of a limited basis set as in the Fenske–Hall approach leads to a much larger spread of energies (especially in the unfilled levels) than those of more exact methods with larger basis sets. Second, our approach uses the term $\Delta E = \epsilon_k - \epsilon_j$ rather than the more accurate expression $\Delta E = \epsilon_k - \epsilon_j - J_{jk} + 2K_{jk}$, where $J$ and $K$ are the Coulomb and exchange integrals, respectively. The second expression is the Hartree–Fock approximation to the energy separation of the orbitals $\Phi_j$ and $\Phi_k$. This expression for $\Delta E$ is not appropriate in connection with Fenske–Hall calculations, since the method does not split the degeneracy of atomic orbitals with the same $l$ value
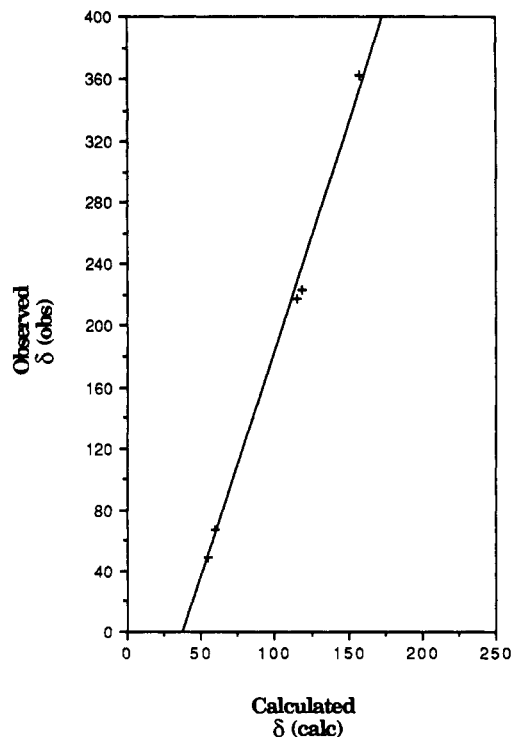
(19) (a) Fischer, E. O.; Maasbol, A. *Chem. Ber.* 1967, *100*, 2445. (b) Conner, J. A.; Jones, E. M.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Dalton Trans.* 1972, 2419.



**Figure 1.** Correlation of $\delta$(obs) and $\delta$(calc) for the five unique carbon atoms in $(CO)_5CrC(OCH_3)CH_3$ as listed in Table I. The equation of the straight line is $y = -67.125 + 3.384x$. $R = 0.992$.

on the basis of their self-consistent orbital populations. Due to the inverse dependence of $\Delta E$ on the calculated $\sigma_p$ value, the use of a limited basis set and the neglect of the Coulomb and exchange corrections result in a low paramagnetic contribution and a slope greater than 1.

The partial molecular orbital diagram of $(CO)_5CrC(OCH_3)CH_3$ is presented in Figure 2. From $\Delta E$ considerations alone we are able to get a rough idea of which carbon atoms will have large or small paramagnetic terms. For example, as shown in Figure 2, some of the lowest lying molecular orbitals in the valence description of the molecule are essentially bonds containing atomic character on the methyl and methoxy carbons. The MO diagram indicates that the antibonding counterparts are among the most destabilized or high-lying orbitals. The resultant $\Delta E$ terms are very large and diminish the nonzero matrix elements in the numerator of eq 3, producing small $\delta$(calc) values, corresponding to the high-field region of an NMR spectrum.

A more subtle observation can be made from the Fenske–Hall sum-over-states calculations. Due to the greater charge, and hence larger $e^- - e^-$ repulsions on the methyl carbon as compared to those on the methoxy carbon, the diagonal terms of the methyl carbon p orbitals lie about 2 eV higher in energy than the methoxy p orbitals. This difference has little consequence on the energy of the filled MO's; however, the unfilled orbitals that contain methoxy carbon p character appear about 10–15 eV below the region where the methyl antibonding orbitals first appear. Thus, the smaller $\Delta E$ values between coupled MO's containing methoxy carbon character yield slightly larger paramagnetic contributions than those for the methyl carbon.

A detailed analysis of contributions to $\sigma_p$ for carbonyl ligands indicates that over 90% of the paramagnetic term for a carbonyl carbon is accounted for by couplings between $\sigma$-type molecular orbitals to $\pi^*$-type carbonyl orbitals. That is, the most dominant terms result from the matrix elements of molecular orbitals that contain sig-

**Chart III**



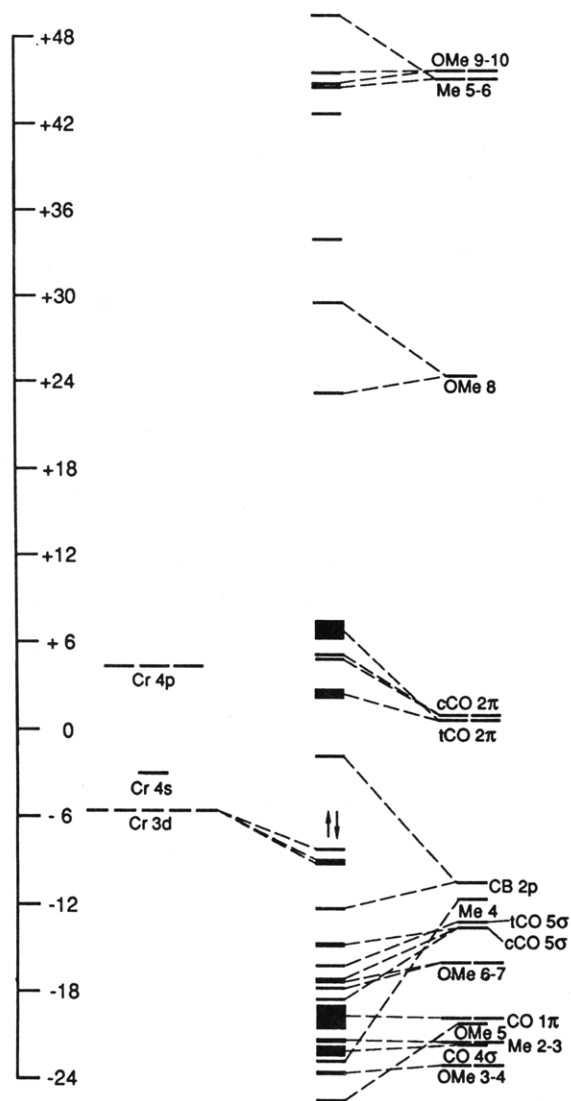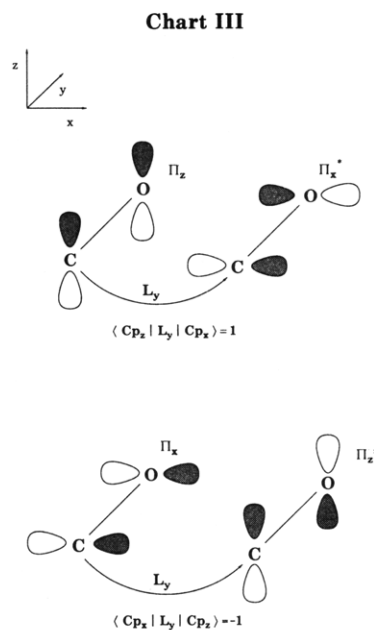**Figure 2.** Molecular orbital diagram for $(CO)_5CrC(OCH_3)(CH_3)$.

nificant bond-axis p character and are coupled, or "rotated", by the $L$ operator into unfilled $\pi^*$-type molecular orbitals containing perpendicular carbon p character. The MO diagram shows that the $\Delta E$ term will be substantially smaller than in the methyl and methoxy cases detailed above. In general, CO $\pi^*$ interactions are among the energetically lowest unfilled orbitals in molecules of this type. It should be noted that our references to "$\sigma$"- and "$\pi$"-type molecular orbitals refer to simple "one-electron" symmetry MO descriptions and not to multielectron state nomenclature.

The reason $\pi-\pi^*$ couplings do not contribute to a large degree can be illustrated by considering an isolated CO ligand. As shown in Chart III, a nonzero filled $p_x$–unfilled $p_z$ interaction is accompanied by a filled $p_z$–unfilled $p_x$ coupling that is equal in magnitude but opposite in sign. In the free CO species, all of the possible local and nonlocal contributions of $L$ and $L/r^3$ to $\sigma_p$ will be negated by such a degenerate interaction as a result of the symmetry of the orbitals in tandem with the symmetry of the operator. Though individual terms with small $\Delta E$ values may yield large nonzero couplings, the doubly degenerate nature of the $\pi$ interactions in the CO ligand prevents $\pi-\pi^*$ couplings from contributing to $\sigma_p$.

Upon interaction with a transition-metal carbene complex, the symmetry of the carbonyl is changed, and the degeneracy of the above example is broken. Though this change is not great, and the resultant $\pi-\pi^*$ terms are small, the differences in the observed $^{13}C$ shifts between the cis and trans CO's in $(CO)_5CrC(OCH_3)CH_3$ can be traced to this interaction. The cis and trans carbonyl carbon atoms have different relationships to the metal d orbitals as well as the carbene ligand in that a cis carbonyl carbon maintains a "symmetry equivalent" partner on the other side of the molecule that undergoes the same rotation upon each $L_n$ operation. In a mechanism analogous to that in the free CO example, most nonzero couplings will be counteracted by a concomitant interaction of opposite sign. The trans carbonyl carbon is not related to the carbene carbon in the same way. This fact is illustrated in the molecular orbital results. Due to the differing donor–acceptor properties of the carbene ligand as compared to those of CO (stronger $\sigma$ donor, weaker $\pi$ acceptor), the trans carbonyl carbon p orbitals are found 0.15 eV above the cis carbon p orbital diagonal terms. This seemingly small difference affects the character of the unfilled orbitals of the compound. Some trans carbon p character (about 5.8%) appears in the LUMO of the complex, whereas cis CO $\pi^*$ character first appears more than 4 eV above the LUMO. Ultimately it is the symmetry "unique" character of the trans carbon that allows nonzero $\pi-\pi^*$ terms to contribute and yield an observed downfield shift of 6 ppm. These effects are similar to the "antipodal" substituent effects seen in boride and carboride cages and analyzed via the sum-over-states method in another paper by this group.[20]

The most *deshielded* resonance, in the classical language, belongs to the carbene carbon and it appears 362.3 ppm downfield from the TMS standard. As a result, the sum-over-states approach should yield a large, negative $\sigma_p$(calc). As shown in Figure 2, the $\Delta E$ terms of the carbene carbon have the smallest values in the molecule. In fact, the LUMO of the molecule contains about 60% carbene carbon p character ($\pi$ with respect to the metal), and it is energetically isolated from the next nearest unfilled level by about 4.5 eV. When the LUMO is coupled with the filled $Cr-C_{carbene}$ $\sigma$ orbitals near $-12$ eV, the large matrix elements that result account for over 67% of the carbene's $\sigma_p$. Note that traditional shielding arguments which es-

(20) Fehlner, T. P.; Czech, P. T.; Fenske, R. F. Submitted for publication.
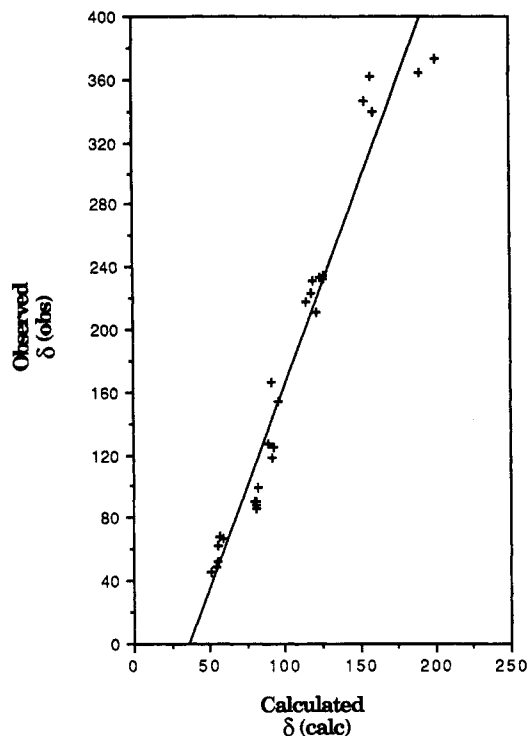
**Figure 3.** General correlation of δ(obs) and δ(calc) for the organometallic compounds given in Table I. The equation of the straight line is $y = -93.723 + 2.566x$. $R = 0.976$.

sentially focus on local electron density are not valid; the carbene carbon is no more positive than a carbonyl carbon.

Since an organometallic compound of this size and range of $^{13}C$ shifts could be treated with reasonable success despite all the approximations that were made, we decided to extend our study to include other first-row transition-metal complexes with some variation of metal and ligands involved.

## General Correlation

Standard Fenske–Hall calculations utilizing only geometric structure and AO wave functions as input have been carried out on six organometallic species. The "normal" range of $^{13}C$ chemical shifts in these molecules spans over 400 ppm downfield from the TMS standard at a value of δ 0. Table I lists the reported values of $^{13}C$ chemical shifts, δ(obs), the calculated paramagnetic contribution to the chemical shift, $\sigma_p$, and the natural population of the 28 chemically different carbon atoms in the series. Figure 3 shows the comparison of δ(obs) with δ(calc) and the linear best-fit correlation. The result is reasonable, considering that $\sigma_d$ has been ignored and only a ground-state calculation has been made. As stated earlier, the slope of the correlation is attributed to the method's description of unfilled orbitals and the $\Delta E$ term.

A qualitative ordering of paramagnetic shielding is possible via rough $\Delta E$ estimates from molecular orbital calculations, as mentioned earlier. Methyl and methoxy ligands contain some of the most stable bonds and most unstable antibonds. Thus, the denominator of (3) diminishes terms that fulfill other criteria. The $\eta^5$-$C_5H_5$ (Cp) and $\eta^6$-$C_6H_6$ rings in our group of compounds have NMR peaks in the region δ 85–100. Though the $\Delta E$ terms of these ring carbons approach the magnitude of those of methyl groups, the multiple-bond character of ring systems allows the favorable $\sigma$–$\pi^*$ couplings that are seen to give the largest contributions to $\sigma_p$. This view is supported by looking at the contributions to a ring carbon shift for each operator. If a Cp ring, for example, is found in the $x$, $y$
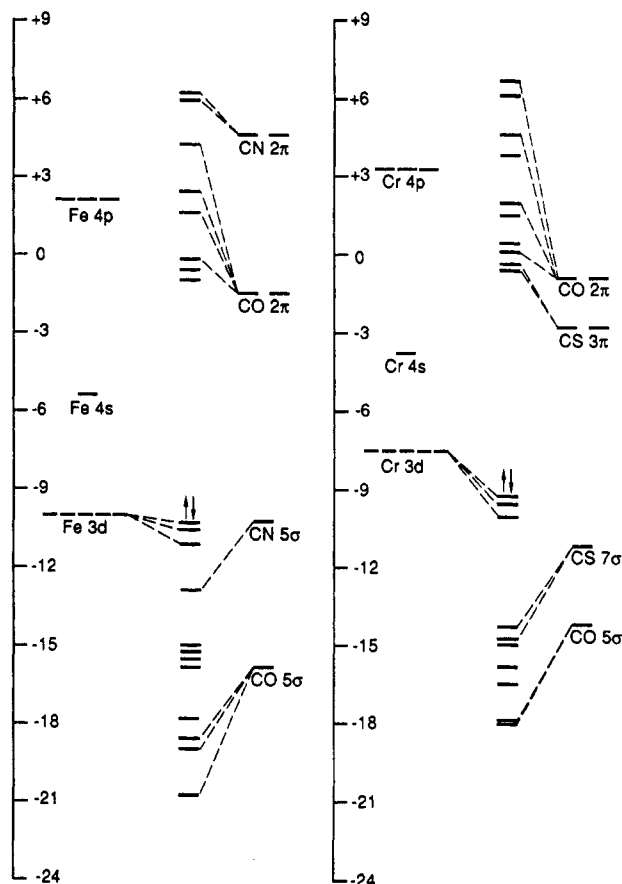


**Figure 4.** Molecular orbital diagrams for $(\eta^5$-$C_5H_5)Fe(CO)_2(CN)$ (left) and $(\eta^6$-$C_6H_6)Cr(CO)_2(CS)$ (right).

plane, the $L_x$ and $L_y$ operators are needed to rotate $\sigma$ carbon p character into the perpendicular $p_z$ orbitals of the $\pi^*$ system. Contributions from these operators account for over 80% of the $\sigma_p$ for a ring carbon. The $L_z$ and $L_z/r^3$ operators couple only $p_x$ and $p_y$ orbitals, those in the $\sigma$ and $\sigma^*$ system. These are energetically too distant to match the contributions from the other orbitals. Carbonyl carbons have already been discussed in some detail in the prototype calculation on $(CO)_5CrC(OCH_3)CH_3$. For the most part these values follow the trend.

Finally, at the lowest field region of the spectrum (>300 ppm), the carbene and thiocarbonyl resonances appear. The shifts of these carbon-containing ligands are more poorly correlated, yet they still support the premise that changes in the paramagnetic term are principally responsible for the large downfield shifts that are observed in these molecules. In addition, the calculations indicate that a detailed knowledge of how ligands interact with a transition metal and the resultant ordering of the molecular orbitals can yield a straightforward nonempirical description of the major contributions to the chemical shift. This model will help us explain why seemingly minor changes in ligand type may have extremely large influences on chemical shift values. The following example will illustrate this point.

A look at two of the compounds in our study, $(\eta^6$-$C_6H_6)Cr(CO)_2CS$ and $(\eta^5$-$C_5H_5)Fe(CO)_2CN$, will allow us to analyze the characteristic shifts of three common ligands in organometallic chemistry. The MO diagram of each species appears in Figure 4. In the chromium complex the thiocarbonyl peak is found 114.5 ppm *downfield* from the carbonyl shift. Alternatively, the cyano carbon in the iron complex appears 56.4 ppm *upfield* from the carbonyl carbon in that molecule. These results might seem curious,

considering that the electronegativity of a sulfur atom is roughly the same as that of carbon whereas nitrogen and oxygen atoms are certainly more electron withdrawing than carbon. Clearly, factors in the paramagnetic term are at work.

An earlier molecular orbital study of transition-metal thiocarbonyl complexes by our group noted the differences between the carbonyl and thiocarbonyl ligand: "The sulfur atomic functions in the CS molecule are inherently less stable than those of the corresponding oxygen atomic functions in CO. The lower stability (in a sense, the lower electronegativity) of the sulfur functions contributes additional charge to the carbon center, which in turn destabilizes the carbon functions and the carbon "lone pair" orbital, the $7\sigma$. The interaction between the carbon and sulfur p$\pi$ orbitals is also reduced, resulting in a lower $\pi^*$ orbital, the $3\pi$".[6a] In essence, a $\Delta E$ effect is responsible for the difference in shifts. We see evidence for this argument in the MO diagram in Figure 4. Filled molecular orbitals with significant thiocarbonyl p character are higher in energy than the filled Cr–CO $5\sigma$ levels. In addition, the LUMO is 23% thiocarbonyl carbon p orbital in character. The unfilled carbonyl levels are in general a little higher. An empirical comparison of chemical shifts with excitation energies has been performed,[21] but never in tandem with a molecular orbital analysis and the sum-over-states approximation.

Such a clear picture is not as easily seen in the cyano complex. The MO diagram indicates that the CN $\pi^*$ levels appear above the CO $\pi^*$ levels and that $1\pi$ and $5\sigma$ of cyanide are found above CO $1\pi$ and $5\sigma$ by roughly equal amounts of energy. Thus, a crude $\Delta E$ correlation will not hold here; rather, the large difference in $^{13}$C shift lies in the placement of the ligand orbitals in relation to the metal d levels.

Recall that the most significant contributions to the calculated paramagnetic term in carbon atoms of this type are couplings between $\sigma$ and $\pi^*$ orbitals. The filled cyano $5\sigma$ fragment orbital is roughly equal in energy to the iron 3d levels, resulting in an *even* splitting of orbital character in the final filled and unfilled molecular orbitals. Previous Fenske–Hall calculations have shown that the character of the molecular orbitals in the complex is highly sensitive

to changes in the position of the ligand diagonal terms when the metal and ligand terms are similar in energy.[11b] On the other hand, the highly stabilized CO $5\sigma$ orbitals are nearly 6 eV below the metal d levels. Thus, we expect the carbon p orbital percent character (atomic coefficients) to be much higher in Fe–carbonyl bonding interactions with the metal than in Fe–cyano bonding interactions. In the Fe–CO $\pi^*$ unfilled orbitals, the CO $2\pi$ levels are already over 8 eV higher in energy than the metal d levels; a further destabilization of 6 eV for the CN $2\pi$ levels yields only minor changes in the atomic coefficients. The larger atomic carbon coefficients in the filled MO's of the carbonyl ligand result in larger matrix elements in the numerator of eq 3, with $\Delta E$ values remaining about the same. These effects are relfected in our approach; the calculated paramagnetic term for a carbonyl carbon is clearly larger than that of the cyano carbon in $(Cp)Fe(CO)_2CN$.

## Summary

The sum-over-states approximation of the paramagnetic contribution to nuclear shielding, $\sigma_p$, has been utilized in calculations of $^{13}$C chemical shifts in a series of transition-metal organometallic complexes via Fenske–Hall wave functions and eigenvalues. The sign and magnitude of the calculated $\sigma_p$ correlates well with observed chemical shifts. Analysis of individual molecular orbital contributions to the paramagnetic term indicates the importance of the difference in energy between filled and unfilled molecular orbitals containing atomic character on the magnetic center of interest. In addition, the symmetry requirements of the $L$ and $L/r^3$ operators eliminate many interactions, resulting in a straightforward model for decomposing major contributions to $\sigma_p$. Finally, the energetic position of the ligand orbitals in relation to that of the metal d orbitals is very important to the paramagnetic term; small fluctuations can have dramatic effects on atomic characters of the final MO's and as a result the calculated $\sigma_p$. The present results not only reemphasize the inadequacy of traditional shielding arguments in the analysis of NMR spectra for atoms other than hydrogen but also direct one's attention to the key elements in the paramagnetic term that are principally responsible for the chemical shifts.

(21) (a) Griffith, J. S.; Orgel, L. E. *Trans. Faraday Soc.* **1957**, *53*, 601. (b) Freeman, R.; Murray, G. R.; Richards, R. E. *Proc. R. Soc. London, Ser. A* **1957**, *A242*, 455.