

Density Functional Theory Calculations on 19-Electron Organometallic Complexes: The $\text{Mn}(\text{CO})_5\text{Cl}^-$ Anion. The Difference between Unpaired Electron Density and Spin Density Due to Spin Polarization

Dale A. Braden and David R. Tyler*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403-1253

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The anisotropic hyperfine coupling (hfc) constants for the 19-electron $\text{Mn}(\text{CO})_5\text{Cl}^-$ complex, **1**, and for the 17-electron $\text{Mn}(\text{CO})_4\text{Cl}^-$ complex, **2**, were calculated using density functional theory (DFT). The calculated hfc values for **1** are in good agreement with the experimental ones reported in two EPR studies, which were not able to distinguish between **1** and **2**. The Mn–CO(axial) bond dissociation energy in **1** was calculated to be 19 kcal/mol, which shows that **1** is stable to loss of axial CO. These data indicate that the species observed in the EPR experiments was the 19-electron complex, **1**. The unpaired electron population of the manganese d_z^2 orbital indicated by the SOMO of the DFT wave function (ca. 0.2–0.3) is significantly less than that obtained from the two EPR analyses (0.49, 0.63), which neglected spin polarization. The calculations show that spin polarization in **1** causes the spin density (as measured by EPR) to differ significantly from the unpaired electron density (SOMO). It is concluded that neglect of spin polarization in the EPR analysis of open-shell transition metal compounds may lead to an overestimate of the unpaired electron population on the metal. The standard method for estimating atomic orbital populations by ratioing the observed hfc in a molecule to the atomic hfc is not reliable for organometallic compounds.

Introduction

Our interest in 19-electron organometallic complexes has led us to pursue reliable computational methods for investigating their electronic structures. In particular, our studies have focused on using density functional theory (DFT) to answer the question of “where” the unpaired electron is located in these molecules.¹ Spectroscopic and reactivity studies suggest that 19-electron complexes can be roughly divided into two categories, those where the 19th valence electron has substantial metal character and those where the 19th electron is primarily ligand based (so-called $18+\delta$ complexes).^{2,3} One of the intriguing results of our calculational studies, however, is the finding that complexes of the former type may not have as much metal character as they are generally attributed with. For example, we showed¹ that the amount of metal character (ca. 30%) for the unpaired electron in the 19-electron $\text{CpCo}(\text{CO})_2^-$ complex was not as large as that calculated from the EPR anisotropic hyperfine coupling constants (56%).⁴ The discrepancy was shown to be attributable to the neglect of spin polarization in the EPR analysis. While such neglect is generally acceptable in the study of organic radicals, for which spin polarization is known to be small, our results suggest that it cannot be neglected in the EPR analysis of organometallic radicals. Spin

polarization arises because the unpaired electron polarizes the electron spins in doubly occupied orbitals with the consequence that the α and β spin orbitals adopt different spatial distributions. EPR is sensitive to the spin density in a molecule, and so a key point is that the spin density is not necessarily the same as the “unpaired electron density”.⁵ In terms of orbitals, this latter quantity is described by the singly occupied molecular orbital (SOMO).

To check on the generality of the results obtained in our $\text{CpCo}(\text{CO})_2^-$ study¹ (namely that many 19-electron complexes have considerably less metal character than attributed to them by EPR), we carried out calculations on the $\text{Mn}(\text{CO})_5\text{Cl}^-$ molecule, a putative 19-electron complex obtained by γ -irradiation of $\text{Mn}(\text{CO})_5\text{Cl}$ in either a single crystal⁶ or in a $\text{Cr}(\text{CO})_6$ matrix⁷ at low temperature. An additional goal of this study was to find out if DFT calculations could determine if it was $\text{Mn}(\text{CO})_5\text{Cl}^-$ or $\text{Mn}(\text{CO})_4\text{Cl}^-$ that was observed in the EPR experiments. The uncertainty arose because electron addition to $\text{Mn}(\text{CO})_5\text{Cl}$ gives the 19-electron anion, **1**, which might lose axial CO to give the 17-electron anion, **2** (eq 1). Because there is no hyperfine coupling to ^{12}C , the EPR experiments could not determine if the observed spectrum was that of **1** or **2**. A final goal was to see if DFT could predict the experimentally observed

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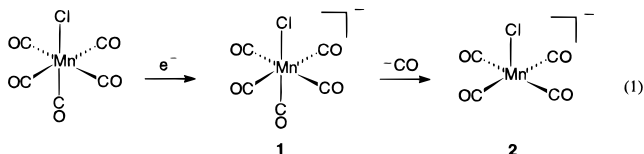
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anisotropic hfc constants for both the Mn and Cl nuclei. The calculation of the hfc for both nuclei is a more challenging test of DFT than the calculation of the hfc in CpCo(CO)₂⁻, for which hfc was only observable to the cobalt nucleus.



Computational Methods

Calculations were performed using Gaussian 94.⁸ The anisotropic hyperfine coupling constants, T_{ii} , were calculated from the eigenvalues of the spin density-based electric field gradient tensor according to⁹

$$T_{ii} = \frac{\mu_0}{4\pi} g^{\mu_B} g^{\mu_N} \frac{\partial E_i}{\partial q_i} \quad (2)$$

where μ_0 is the vacuum permeability, g and g_N are the g factors for the radical and the nucleus of interest, respectively, and μ_B and μ_N are the corresponding magnetons. Full details are available in an earlier publication.¹ Because the g -values for the radical observed in the EPR experiments^{6,7} were nearly identical to the free electron g -value of 2.0023, the latter was used in eq 2. The values of the nuclear g factors were taken from a recent tabulation.¹⁰ The calculated anisotropic hfc values for chlorine were corrected for the fact that the two naturally occurring isotopes for chlorine, ³⁵Cl and ³⁷Cl, have different nuclear g factors and occur in a 3:1 ratio.

The primary basis set¹¹ (I) used in this study was from the work of Ahlrichs et al.¹² A d function was added to C, O, and Cl, with exponents of 0.8, 1.2, and 0.75, respectively. An extra s function was added to Cl, as recommended,¹² along with a diffuse p function, with exponents equal to one-third of the most diffuse function in the same shell. Two p functions were added to Mn, with exponents as for the 4s shell, as recommended. Finally, the d shell was decontracted somewhat, resulting in a 842111/63111/21111 contraction scheme. A larger basis (II) was created by adding one set of diffuse s and p functions to all atoms, and a diffuse d function to Mn, all with exponents equal to one-third of the most diffuse function in the same shell. An f function with exponent equal to 2.195 was added to Mn.¹³ Finally, the atomic natural orbital basis

set of Roos et al.^{14,15} (III) was employed as a check because it has a much larger number of primitive functions per shell and a different contraction scheme from the Ahlrichs basis sets. Basis set III consisted of a (10s6p3d)/[5s4s3p] general contraction for C and O, a (13s10p4d)/[6s5p4d] general contraction for Cl, and a (17s12p9d4f)/[7s6p5d4f] general contraction for Mn.

Three density functionals, B3LYP, BLYP, and BPW91, as implemented in Gaussian 94, were also employed.^{16–20} Full geometry optimizations using basis set I were performed on **1** and **2**, which were constrained to C_{4v} symmetry. Subsequent vibrational frequency calculations showed that the geometry for **1** was at a true minimum on the potential energy surface, but the geometry for **2** was at a first-order saddle point, requiring a reduction in symmetry to C_{2v} . Another geometry optimization on **2** under a C_{2v} symmetry constraint achieved a true minimum. Single-point calculations were carried out on the B3LYP/I structure for **1** using basis sets II and III. The bond dissociation energy for loss of CO from **1** was calculated using the B3LYP functional and basis set I and includes zero-point energies, but was not corrected for basis set superposition error.

The underlying assumption in this computational approach is that if the anisotropic hfc values can be calculated reasonably accurately from the electron spin density, then the associated wave function will give meaningful information about the distribution of the unpaired electron (SOMO).

Results and Discussion

γ -Irradiation of Mn(CO)₅Cl at low temperature in either a Cr(CO)₆ matrix⁷ or as a single crystal⁶ led to the formation of a species identified as either **1** or the CO-loss product, **2** (eq 1). If both **1** and **2** have C_{4v} symmetry, they would be difficult to distinguish from each other on the basis of their EPR spectra because there is no hyperfine coupling to ¹²C nuclei (for which $I = 0$) to establish the presence of the axial ligand. The experimental hfc tensor is essentially axial (i.e., two of the eigenvalues are the same, or very nearly so; see Table 1). This situation arises when the molecule contains a rotational axis of 3-fold or higher symmetry. The calculated optimum geometry for **1** has C_{4v} symmetry, so the calculated hfc tensor for this molecule is axial. In contrast, calculations showed that loss of the axial CO ligand from **1** causes a distortion to C_{2v} symmetry in **2**, in which the pairs of opposing equatorial ligands are bent upward and downward, respectively (Cl–Mn–C angles $\sim 85^\circ$ and $\sim 105^\circ$; see Figure 1). Because the distortion is so pronounced, the hfc tensor shows a marked departure from axial symmetry, and the resulting hfc constants differ from the experimental values (Table 1). This suggests that **2** was not the species observed in the EPR experiments.²¹

Symons et al. examined the EPR spectrum of **1** that had been labeled with ¹³CO in order to be able to detect

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(9) HFC values are reported here in units of gauss. Because $\partial E/\partial q$ is given in atomic units, a conversion factor of $10^4/(g_{\mu_B} a_0^3)$ is required, where a_0 is the Bohr radius.

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(11) The basis set was obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0 (<http://www.emsl.pnl.gov:2080/forms/basisform.html>), as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.

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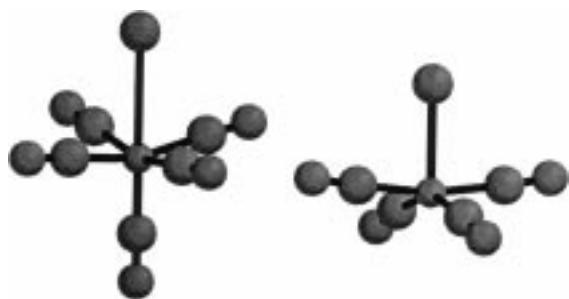
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Table 1. Anisotropic Hyperfine Coupling Constants (G) for Mn, Cl, and ^{13}C (axial) in **1 and **2** and Orbital Occupations**

| | exptl values | | calculated values for $\text{Mn}(\text{CO})_5\text{Cl}^-$ | | | | | | | calculated values ^c for $\text{Mn}(\text{CO})_4\text{Cl}^-$ | |
|---------------------------------|--------------------------|----------------|---|----------------|----------------|-----------------------|-----------------------|----------------|----------------|---|--------------------------|
| | ref 7 | ref 6 | B3LYP/I | B3LYP/II | B3LYP/III | B3LYP ^a /I | B3LYP ^a /I | BLYP/I | BPW91/I | B3LYP/I | BLYP/I |
| Mn hfc | 62.8, -31.1, -31.7 | 69.2, -34.6 | 63.3, -31.6 | 64.0, -32.0 | 62.0, -31.0 | 70.6, -35.3 | 68.1, -34.1 | 53.1, -26.6 | 50.2, -25.1 | 67.2, -14.6, -52.6 | 67.2, -12.5, -54.7 |
| Cl hfc | 16.9, -7.7, -9.3 | 12.9, -6.5 | 27.6, -13.8 | 27.8, -13.9 | 26.3, -13.2 | 22.9, -11.5 | 17.9, -8.9 | 33.0, -16.5 | 34.0, -17.0 | 1.6, 1.4, -3.0 | 0.2, ~0, -0.2 |
| $^{13}\text{C}_{\text{ax}}$ hfc | | not obsd | 0.9, -0.5 | 0.9, -0.4 | 0.9, -0.4 | 1.1, -0.5 | 0.8, -0.4 | 1.0, -0.5 | 0.9, -0.4 | | |
| %Mn- d_z^2 in SOMO | 49 | 63 | 21 | 19 | 29 | 24 | 24 | 19 | 17 | 7 | 10 |
| %Mn (total) in SOMO | | | 35 | 37 | 31 | 36 | 37 | 32 | 33 | 44 | 36 |
| %Cl in SOMO | | | 33 | 32 | 33 | 35 | 31 | 32 | 33 | 28 | 26 |
| %CO in SOMO | | | 31 | 31 | 36 | 28 | 32 | 36 | 34 | 28 | 34 |

^a The B3LYP functional for this calculation used a value of 0.30 for the Hartree–Fock exchange coefficient, α_0 . ^b Single-point calculation using the B3LYP/I structure in a spherical solvent cavity of radius 4.5 Å and a dielectric constant of 5. ^c Calculated for the C_{2v} structure.

**Figure 1.** The B3LYP/I optimized geometries of **1** and **2**.⁴⁵

hfc to the axial CO ligand.²² They observed no hyperfine coupling to the axial carbon and concluded that either the hfc was unresolvably small (less than 4 G)²² or the axial CO had been lost. Table 1 shows that, for all functionals, the calculated hfc to the axial carbon in **1** is 1 G or less and thus too small to have been resolved.

According to the calculations, the unpaired electron occupies an orbital that is bonding with respect to the Mn–CO(axial) group (Figure 1), which makes it less likely that this ligand is lost on formation of the 19-electron complex. In agreement with this qualitative argument, the bond dissociation energy for loss of axial CO from **1** was calculated to be 19 kcal/mol. (Note that because coupling to a chlorine nucleus was observed, there was no loss of chloride ligand.) This calculated Mn–CO(ax) bond energy is acceptable in comparison to the very few known experimental M–CO bond strengths for 18-electron organometallic compounds containing a first-row transition metal, which are in the range 25–41 kcal/mol.²³ In summary, the calculated bond dissociation energy of **1** shows that it is thermodynamically stable with respect to loss of axial CO. The calculated Mn–CO(axial) bond dissociation energy and

the close agreement between the calculated and observed hfc constants strongly support the identification of **1** with the species observed in the EPR spectra.

The EPR researchers also expressed some doubt about the sign of the total hfc constants for chlorine.^{6,7} In ref 7 the possibilities considered were (46.2, 21.6, 20.0) and (46.2, -21.6, -20.0), for which the isotropic couplings are calculated to be 29.3 and 1.5 G, respectively.²⁴ Both EPR research groups favored all positive signs.²⁵ Isotropic hfc values are difficult to calculate accurately because they are especially sensitive to the basis set description of the electron density near the nuclei.^{26–29} In the case of **1**, however, the accuracy of the calculation was sufficient to distinguish between the two very different values for the isotropic hfc. The isotropic hfc constants calculated with the B3LYP functional using all three basis sets were in the range 22–23 G, thus supporting the previous researchers' choice of all positive signs for the total hfc tensor eigenvalues for chlorine.

Table 1 shows that the hfc values for Mn in **1** calculated with the B3LYP functional agree with the observed values. The calculated hfc constants for Cl are higher than the observed values, but the magnitude of the observed hfc is small, and the absolute error between the B3LYP values and those from ref 7 is less than 11 G. The hfc values for Cl were not improved using the larger basis sets, and we conclude that the lack of close agreement between the calculated and observed hfc is not due to a deficiency of the basis set.

The effect of the density functional on the hfc constants was also examined. As shown in Table 1, the hfc values calculated with the hybrid B3LYP functional agree better with the observed values than those calculated with the "pure" functionals BPW91 or BLYP.

(24) Using the data from ref 6, the isotropic hfc values would be 25.9 and 0 G, respectively.

(25) The reasons for this choice are somewhat vague. They are based either on the reasonableness of calculated orbital populations for **1** or by comparison to hyperfine data for molecular halogen anions. See refs 6 and 7.

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(21) The C_{2v} structure was calculated to be only 0.7 kcal/mol lower in energy than the C_{4v} structure. Because of the existence of a lower symmetry structure of nearly identical energy, the observed hfc tensor should be nonaxial.

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This is due to the admixture of Hartree–Fock exchange into B3LYP, which tends to enhance spin polarization.³⁰ The optimum value found by Becke for a_0 , the coefficient controlling the amount of Hartree–Fock exchange in the total functional, was 0.20.¹⁷ When a_0 was increased to 0.30, the hfc values for **1** changed significantly relative to those obtained with the standard B3LYP functional, increasing the hfc for Mn and decreasing it for Cl. Some recent studies emphasize the need for including a substantial amount of Hartree–Fock exchange,^{31–33} while others indicate that only a minimal amount is required.^{34,35} Spin polarization is an exchange phenomenon, and the inclusion of Hartree–Fock exchange in density functional theory³⁶ appears to be necessary for modeling open-shell organometallics in which spin polarization is significant. Because the three parameters in B3LYP were optimized by fitting them to experimental data for the G2 molecule set,¹⁷ which contains no transition metals, it is likely that the optimum values for transition metal compounds are different. In the case of **1**, increasing the amount of Hartree–Fock exchange in the B3LYP functional improves the hfc values for Cl, but the hfc values for Mn become worse, so the small discrepancy between theory and experiment cannot be reduced by adjusting the amount of Hartree–Fock exchange in the density functional.

The discrepancy between the experimental and calculated hfc values for Cl might also be due to neglect of matrix effects in the calculations. The EPR experiments were carried out using two different matrixes. In one study,⁶ a single crystal of $\text{Mn}(\text{CO})_5\text{Cl}$ was irradiated with γ -rays, while in the other study,⁷ $\text{Mn}(\text{CO})_5\text{Cl}$ was doped into $\text{Cr}(\text{CO})_6$ and then irradiated. In the more polar medium ($\text{Mn}(\text{CO})_5\text{Cl}$), the hfc to Mn is greater and the hfc to Cl is smaller than in the less polar $\text{Cr}(\text{CO})_6$ matrix (Table 1). This indicates a shift of spin density from Cl to Mn as the environment becomes more polar. The calculated hfc values are in better agreement with the experimental values obtained in the nonpolar $\text{Cr}(\text{CO})_6$ matrix. This is expected because the “environment” in the calculation is a vacuum. To model the effect of a low-dielectric medium such as $\text{Cr}(\text{CO})_6$, a single-point calculation was carried out on **1** using the optimized B3LYP/I structure in a spherical solvent cavity of radius 4.5 Å and uniform dielectric constant equal to 5.³⁷ As indicated by the results in Table 1, the deviation of the calculated hfc values from the experimental values in ref 7 is less than 10% for both Mn and Cl. This close agreement justifies an examination of the

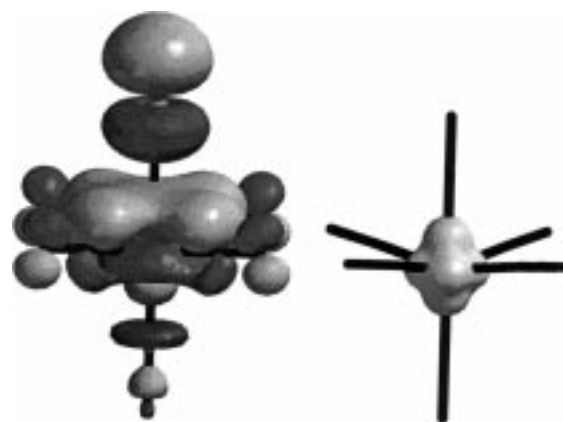


Figure 2. Calculated at the B3LYP/I level for **1**: (a) the SOMO; (b) the α spin density isosurface ($0.003 \text{ e}^-/\text{bohr}^3$) resulting from subtracting the SOMO electron density from the total spin density.⁴⁵

SOMO in order to determine the location of the unpaired electron in **1**.

Included in Table 1 are the unpaired electron populations for the metal and ligand orbitals based on the LCAO coefficients for the singly occupied molecular orbital (SOMO) and the corresponding values calculated from the EPR data. Although the B3LYP hfc values for **1** are in good agreement with the observed values, the population of the Mn d_z^2 orbital indicated by the SOMO (ca. 0.2–0.3) does not agree with the high values of ca. 0.5–0.6 calculated from the EPR data. Atomic orbital populations are usually calculated from the measured hfc constants by assuming that the spin distribution in the molecule is determined by the unpaired electron only. The observed hfc is compared to the maximum coupling that would be observed for the isolated atom of interest, and it is assumed that the attenuation of the hfc in the molecule is due to delocalization of the unpaired electron onto other atoms.^{1,38–41} The presence of additional spin density due to spin polarization is often assumed to be negligible in organometallic systems because it is often very small in organic radicals.³⁸ This assumption sometimes leads to unrealistically high occupations of metal orbitals in transition metal compounds (e.g., 0.56 for $\text{Co}_{d_{yz}}$ in $\text{CpCo}(\text{CO})_2^-$,⁴ 0.70 for Ti_{4s} in TiF_3 ,⁴² 0.67 for Co_{3d} in Cp_2Co).⁴³ The difference between the unpaired electron density and the spin density due to spin polarization in **1** is shown in Figure 2. Figure 2a shows the SOMO (unpaired electron distribution) and Figure 2b shows the spin density that results from subtracting the density of the SOMO from the total spin density. The excess α spin density is localized around the Mn atom, and it is clearly not isotropic (i.e., confined to s orbitals). This accounts for the high observed anisotropic hfc. The

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plot of the SOMO shows that the unpaired electron is not as localized on the metal atom as the EPR analyses indicated.

Conclusions

The DFT calculations support the conclusion that the species observed in the EPR studies was the 19-electron complex, **1**, and not the 17-electron complex resulting from the loss of the axial CO ligand, **2**. The calculated bond dissociation energy for Mn–CO(axial) and the hfc values for **1** are all consistent with this view.

The calculations also indicate that the neglect of spin polarization in the EPR analysis leads to an overestimate of the unpaired electron population of the manganese d_z^2 orbital. The SOMO shows that the unpaired electron is in fact delocalized throughout the entire molecule and is approximately equally distributed among the five CO ligands (considered as a group), the chlorine atom, and the metal atom, with the metal d_z^2

orbital having an occupancy of about 0.2–0.3. There is significant additional spin density, however, which is due to spin polarization. The calculations presented here and elsewhere^{1,44} indicate that spin polarization can be of considerable magnitude in compounds containing a transition metal. The determination of orbital populations in organometallic compounds by EPR should therefore be viewed with caution if spin polarization is neglected.

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