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Density Functional Calculations of 19-Electron Organometallic Molecules. A Comparison of Calculated and Observed Anisotropic Hyperfine Coupling Constants for the $CpCo(CO)_2^-$ Anion. Implications for Determining Orbital Spin Populations from EPR Data

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Abstract: The anisotropic hyperfine coupling constants for a 19-electron organometallic complex, $CpCo(CO)_2^-$, were calculated using the B3LYP density functional in conjunction with several all-electron basis sets. The calculated hfc constants are generally within 10% of the experimental values as determined by EPR. The calculated wave function indicates that the unpaired electron has a much lower occupancy of the cobalt d_{yz} orbital (0.17−0.31) than the value of 0.56 obtained from the EPR data. It is concluded that the traditional method of calculating atomic orbital spin populations from EPR hyperfine coupling constants, which neglects spin polarization and covalency effects, should be used with caution when applied to organometallic systems. No significant structural changes occur in the ligands of $CpCo(CO)_2^-$ as a result of having to accommodate an extra electron.

Introduction

Nineteen-electron organometallic adducts, formed by the reaction of 2-electron donor ligands with 17-electron radicals (eq 1), are important intermediates in many organometallic radical reactions.[1−6]

$$\underset{17e^-}{ML_n} + L' \rightleftharpoons \underset{19e^-}{ML_nL'} \qquad (1)$$

$ML_n = CpMo(CO)_3, CpW(CO)_3, CpFe(CO)_2, Mn(CO)_5, Co(CO)_4$

$L' = PR_3, P(OR)_3$, etc.

These molecules are of interest because organometallic molecules with more than 18 valence electrons are still rare. Nineteen-electron adducts are exceptionally reactive, and for that reason their electronic structures have not been studied in detail. In particular, the question of "where" the unpaired electron is located in the adduct molecules is still a matter of interest. It has been suggested that the ligands distort in some molecules in order to accommodate the additional electron. For example, an $\eta^5 \rightarrow \eta^4$ ring slippage or a bent CO ligand would convert a 19-electron structure to an 18-electron structure (Figure 1). Because the adducts are so short-lived, such structural changes are difficult to observe spectroscopically, but they have been inferred from reactivity patterns in a few cases. For example, electrochemical reduction of $Cr(CO)_6$ in the presence of a hydrogen atom donor gave $Cr(CO)_5CHO^-$.[7] The pathway in Scheme 1 was proposed. Note that, in this scheme, the "19-electron complex" has a bent CO ligand[8] (formally a one-electron donor), and this gives the metal center an 18-electron count. Astruc, however, has cautioned against using reactivity to interpret ground-state electronic structures.[1] His work showed that the spin density in the transition state can be very different from that in the ground state.

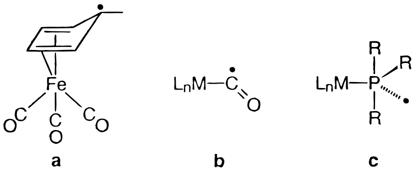
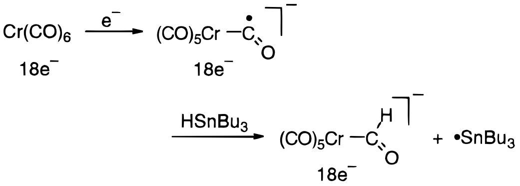


Figure 1. Alternative structures for 19-electron organometallic complexes in which the ligand distorts in order to accommodate the extra electron: (a) a slipped Cp ring; (b) a bent CO ligand; and (c) a trigonal bipyramidal phosphoranyl ligand.

Scheme 1



As part of a project to examine the electronic structure of 19-electron complexes in more detail, we carried out density functional theory (DFT) calculations on $CpCo(CO)_2^-$, **1**. This molecule was selected for an initial study because it is small enough to be treated at a reasonably high level of theory and because its published EPR parameters are also available as a computational target.[9] In addition, EPR data on the closely

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[1] Astruc, D. *Chem. Rev. (Washington, D.C.)* **1988**, *88*, 1189.

[2] Geiger, W. E. *Acc. Chem. Res* **1995**, *28*, 351.

[3] Tyler, D. R. *J. Organomet. Chem. Libr.* **1990**, *22*, 338.

[4] Tyler, D. R.; Mao, F. *Coord. Chem. Rev.* **1990**, *97*, 119.

[5] Tyler, D. R. *Acc. Chem. Res* **1991**, *24*, 325.

[6] Tyler, D. R. in *Aqueous Organometallic Chemistry and Catalysis*; NATO ASI Ser., Ser. 3, 1995; p 47.

[7] Narayanan, B. A.; Kochi, J. K. *J. Organomet. Chem.* **1984**, *272,* C49−C53.

[8] Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 4087.

[9] Symons, M. C. R.; Bratt, S. W. *J. Chem. Soc., Dalton Trans.* **1979**, 1739.

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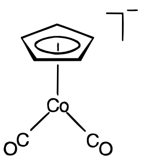

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related $Cp^{\#}Co(CO)_2^-$ ($Cp^{\#} = \eta^5$-C_5Ph_5), **2**, have been published.[10] The goals of this project were to determine the distribution of the unpaired electron in **1**, to determine whether any geometry changes take place due to its presence, and to see whether DFT could reproduce the experimental anisotropic hyperfine coupling constants. The most important point to come from this study is that the traditional method of calculating spin populations from EPR data, which works reasonably well for many organic π-radicals,[11] yields a chemically unreasonable result for **1**. The traditional method has recently been shown to fail in the case of the inorganic compound TiF_3.[12]

Methods

Computational Approach. Density functional theory has been successful in modeling systems containing a transition metal[12−20] and in calculating hyperfine coupling (hfc) constants for radicals,[12,13,20−29] including radical anions.[13,26−29] We therefore applied it to the calculation of the anisotropic hfc constants for **1**. We chose to calculate only the anisotropic components, rather than the isotropic ones, because the latter are too sensitive to the construction of the basis set and the choice of functional.[23,29]

The Hamiltonian governing the most important interactions in the EPR experiment in which a single unpaired electron interacts with a single nucleus is written as[11]

$$\hat{\mathrm{H}} = \mu_{\mathrm{B}}\mathbf{B}\cdot\mathbf{g}\cdot\hat{\mathbf{S}} + \hat{\mathbf{S}}\cdot\mathbf{A}\cdot\hat{\mathbf{I}} - \mu_{\mathrm{N}}g_{\mathrm{N}}\mathbf{B}\cdot\hat{\mathbf{I}} \tag{2}$$

where the first term describes the interaction of the unpaired electron with the applied magnetic field (electronic Zeeman term), the second governs the interaction of the electronic and nuclear spins (hyperfine term), and the last is the nuclear Zeeman term. **S** and **I** are the electron and nuclear spin operators, respectively, g_{N} is the nuclear g-factor, μ_{B} and μ_{N} are the bohr and nuclear magnetons, respectively, **B** represents the applied magnetic field, and **g** and **A** are the g and hyperfine coupling tensors, respectively. The **A** tensor is composed of isotropic and anisotropic parts

$$\mathbf{A} = A_0\mathbf{1} + \mathbf{T} \tag{3}$$

where **1** denotes the unity matrix, and **T** is the anisotropic hyperfine coupling tensor, which is traceless. The anisotropic hfc tensor elements for nucleus k may be calculated to first-order according to[12,25]

$$T_{ij}^{k} = \frac{\mu_0}{4\pi} g_{\mathrm{e}}\mu_{\mathrm{B}}g_{\mathrm{N}}\mu_{\mathrm{N}} \sum_{m}\sum_{a,b}\sum_{\mu,\nu} P_{\mu\nu}{}^{\alpha-\beta}\langle\phi_{\mu}^{a}|D_{ij}^{k}|\phi_{\nu}^{b}\rangle \tag{4}$$

where i and j range over the x, y, and z directions, μ_0 is the permeability constant, and $P^{\alpha-\beta}$ is the spin density matrix. The sum is performed over all occupied molecular orbitals m, for all nuclei a and b, for all atomic orbitals μ and ν. The coupling between the electron and nuclear spins is a dipole−dipole interaction, and is described by the operator D_{ij}:

$$D_{ij} = \frac{3r_ir_j - r^2\delta_{ij}}{r^5} \tag{5}$$

Because the dipolar coupling operator has the same angular form as the electric field gradient operator, the multiple sum in eq 4 is sometimes written as $\partial E_i/\partial q_j$, which is a spin-based electric field gradient.[23,27,28] It is evaluated by contracting the spin density (rather than the charge density) with the electronic component of the electric field gradient integrals.[30]

Calculations were performed using Gaussian 94.[31] Molecular properties were calculated using a variety of basis sets (using five real d and seven real f orbitals) in conjunction with the B3LYP hybrid and BLYP density functionals.[32−35] Tight convergence criteria were employed during the SCF for single-point calculations, and the default fine integration grid (75 radial shells, 302 angular points, pruned) was retained. Spin con-

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(10) Connelly, N. G.; Geiger, W. E.; Lane, G. A.; Raven, S. J.; Rieger, P. H. *J. Am. Chem. Soc.* **1986**, *108*, 6219.

(11) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance*; Wiley: New York, 1994.

(12) Belanzoni, P.; Baerends, E. J.; van Asselt, S.; Langewen, P. B. *J. Phys. Chem.* **1995**, *99*, 13094.

(13) Aarnts, M. P.; Wilms, M. P.; Peelen, K.; Fraanje, J.; Goubitz, K.; Hartl, F.; Stufkens, D. J.; Baerends, E. J.; Vlcek, A. *Inorg. Chem.* **1996**, *35*, 5468.

(14) Holthausen, M. C.; Mohr, M.; Koch, W. *Chem. Phys. Lett.* **1995**, *240*, 245.

(15) Hu, C.-H.; Chong, D. P. *Chem. Phys. Lett.* **1996**, *262*, 733.

(16) Hertwig, R. H.; Hrusak, J.; Schroeder, D.; Koch, W.; Schwarz, H. *Chem. Phys. Lett.* **1995**, *236*, 194.

(17) Holthausen, M. C.; Fiedler, A.; Schwarz, H.; Koch, W. *J. Phys. Chem.* **1996**, *100*, 6236.

(18) Adamo, C.; Lelj, F. *J. Chem. Phys.* **1996**, *103*, 10605.

(19) Barone, V. *Chem. Phys. Lett.* **1995**, *233*, 129.

(20) Barone, V. *J. Phys. Chem.* **1995**, *99*, 11659.

(21) Barone, V. In *Recent Advances in Density Functional Methods, Part 1*; Chong, D. P., Ed.; World Scientific: Singapore, 1995.

(22) Barone, V. *Theor. Chim. Acta* **1995**, *91*, 113.

(23) Adamo, C.; Barone, V.; Fortunelli, A. *J. Chem. Phys.* **1995**, *102*, 384.

(24) Engels, B.; Eriksson, L. A.; Lunell, S. *Adv. Quantum Chem.* **1996**, *27*, 297.

(25) Malkin, V. G.; Malkina, O. L.; Eriksson, L. A.; Salahub, D. R. in *Modern Density Functional Theory*; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995.

(26) Lim, M. H.; Worthington, S. E.; Dulles, F. J.; Cramer, C. J. In *Chemical Applications of Density Functional Theory*; Laird, B. B., Ross, R. B., Ziegler, T., Eds.; ACS Symposium Series 629, American Chemical Society: Washington, DC, 1996.

(27) O'Malley, P. J.; Collins, S. J. *Chem. Phys. Lett.* **1996**, *259*, 296.

(28) O'Malley, P. J. *Chem. Phys. Lett.* **1996**, *262*, 797.

(29) Eriksson, L. A.; Malkina, O. L.; Malkin, V. G.; Salahub, D. R. *J. Chem. Phys.* **1996**, *100*, 5066.

(30) Gaussian 94 calculates the electric field gradient (EFG) at the nuclei if one specifies "Prop=EFG IOp(6/17=2, 6/26=4)" in the route section. Iop 6/17=2 specifies that the spin density is to be used, and 6/26=4 specifies that only the electronic component of the integrals is to be calculated. Because the units of ∂E/∂q are usually given in bohr^{-3}, a conversion factor of $a_0{}^3$ (the bohr radius) is needed in the denominator to give T_{ij} in SI units. Hyperfine coupling units are unfortunately given variously as gauss, millitesla, megahertz, and $\mathrm{cm}^{-1}\cdot 10^{-4}$. To convert the above into these units, one multiplies by $10^4/(g_e\mu_B)$, $10^3/(g_e\mu_B)$, $1/(10^6h)$, and $100/(hc)$, respectively.

(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision D.4*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(32) The B3LYP functional employed in Gaussian 94 is slightly different from the one proposed by Becke in ref 34. The form actually used is given in Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(33) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(34) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(35) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

tamination of the final wave function was estimated by the value of S^2, which varied from 0.76 to 0.90. These values are higher than for pure doublets, for which $S^2 = 0.75$, and also somewhat higher than values reported for other DFT calculations on doublet systems. This matter is discussed further below.

Two basis sets were employed for the geometry optimizations. The first, denoted here as SV66, consisted of the 6-31+G(d′)[36] basis for C, H, and O and the 6-311G* basis for Co.[37,38] The second basis set, DZVP2+, was the valence double-ζ plus polarization set taken from the work of Godbout et al.[39] This basis set was developed especially for DFT calculations. It includes one set of p polarization functions on H and one set of d polarization functions on C and O. One set of diffuse s and p functions on C and O were added, with exponents equal to one-third of the most diffuse component of the same shell. Finally, the TZVP+ basis, also from Godbout et al.,[39,40] is triple-ζ for H, C and O and also contains the above polarization functions for these elements. One set of diffuse s and p functions were added to C and O as above. For cobalt, a single function was decontracted from the last contractions of the s, p, and d shells to produce a triple-ζ basis, which was then supplemented with one set of diffuse s, p, and d functions (with exponents chosen as above) and one f function with exponent equal to 1.0.

Experimental EPR Approach. One of the goals of this study was to determine the location of the unpaired electron in the $CpCo(CO)_2^-$ molecule by examining the optimized LCAO-MO wave function for the unpaired electron (the SOMO), and compare this to the spin populations on cobalt calculated from the EPR data. It is important to note that EPR does not measure atomic spin densities in molecules; these are not observables. What is actually measured is the hyperfine coupling of the unpaired electron to the nuclei. The atomic spin populations are then *calculated* by comparing the observed hfc to the theoretical (calculated) maximum coupling that would be observed for the isolated atom. The determination of the maximum hfc proceeds as follows: the value of $\langle r^{-3}\rangle$ (related to the integral in eq 4) is first calculated from an optimized atomic wave function for an electron in a pure atomic orbital on an isolated atom with a particular electronic configuration. In practice, values of $\langle r^{-3}\rangle$ are usually taken from a known tabulation.[41] The maximum hfc is then calculated according to eq 6:

$$T_{\mathrm{calc}} = \frac{\mu_0}{4\pi} f g_e \mu_B g_N \mu_N \langle r^{-3}\rangle \tag{6}$$

where f is an angular factor whose value depends upon whether the electron is in a p, d, or f orbital.[41] The value thus obtained represents the maximum possible coupling for an unpaired electron in that atom. (A slightly different equation is used for the isotropic coupling for an electron in an s orbital.[11]) The population of this atomic orbital in a molecule is then commonly calculated as[42,43]

$$P = T_{\mathrm{obs}}/T_{\mathrm{calc}} \approx c^2 \tag{7}$$

where c is the atomic orbital coefficient in the LCAO-MO wave function. More sophisticated methods, which take into account, for example, spin−orbit coupling, have been employed,[10,44] but these also normally include a term that depends on the *calculated* value of $\langle r^{-3}\rangle$ for the isolated atom. For cobalt, this quantity varies in the literature from 4.648 27 bohr^{-3} [45] to 6.71 bohr^{-3},[41] and it depends sensitively on the assumed electronic configuration for the atom. Because the electronic state of a transition metal in a molecule often corresponds to an excited state of the isolated atom,[37,46] the ground-state atomic configuration is inappropriate for representing the metal atom in a molecule. But it is also dangerous to use any single electronic configuration of a free atom or ion for molecular calculations because this requires that $\langle r^{-3}\rangle$ be the same for all molecules in which the atom is assumed to have that configuration.

The critical assumption made in many EPR studies of organometallic compounds is that the spin distribution in the molecule is identical with the unpaired electron distribution (the SOMO). This is tantamount to neglecting spin polarization. In eq 4, this would mean that all of the spin density matrix elements, $P^{\alpha-\beta}$, are essentially zero for all molecular orbitals except for the SOMO, i.e., the α and β spins cancel for all closed shells. Another assumption that is often made is that covalent contributions, i.e., integrals of the form $\langle\phi^a|D^k|\phi^k\rangle$ in eq 4, where $a \neq k$, are assumed to be negligibly small. These assumptions are often justified for planar organic molecules in which the unpaired electron is localized in a carbon p-orbital, and the calculation of atomic spin populations based on EPR data then becomes much easier, because eq 4 can be drastically simplified. It is questionable, however, to make these same assumptions in the case of molecules containing a transition metal. Doing so has recently been shown to produce erroneous estimates of the SOMO composition in TiF_3.[12] They may not be generally valid for organometallics such as **1**.

Results and Discussion

Location of the Unpaired Electron. Calculations showed that the energy of the $CpCo(CO)_2^-$ molecule was insensitive to the orientation of the Cp ring. This is consistent with the known low barrier to internal rotation (0.07 kcal/mol) for the neutral parent of **1**.[47] The calculated energy difference between the two optimized structures with C_s symmetry (structures **I** and **II** below) was 0.04 kcal/mol at most, and the energy of a molecule with an optimized C_1 geometry was only 0.16 kcal/mol higher.[48] Connelly et al.[10] made arguments favoring structure **I** for molecule **2**, while electron diffraction data on the neutral parent of **1** slightly favored structure **II**.[49] Because

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[36] Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193. The 6-31+G-(d′) basis differs from the more popular 6-31+G* in that the exponents for the d polarization functions on C and O are taken from the 6-311G basis set, and are different from each other, whereas in 6-31+G*, the d orbital exponents for C and O are identical.

[37] Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377.

[38] Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

[39] Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.

[40] The DZVP2 and TZVP basis sets were 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, USA, 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.

[41] Morton, J. R.; Preston, K. F. *J. Magn. Res.* **1978**, *30*, 577.

[42] Atkins, P. W.; Symons, M. C. R. *The Structure of Inorganic Radicals*; Elsevier: Amsterdam, 1967.

[43] Symons, M. *Chemical and Biochemical Aspects of Electron-Spin Resonance Spectroscopy*; Wiley: New York, 1978.

[44] Rieger, P. H. In *Organometallic Radical Processes*; Trogler, W. C., Ed., Elsevier: Amsterdam, 1990.

[45] Huzinaga, S., Ed.; Elsevier: Amsterdam, 1984.

[46] Sargent, A. L.; Hall, M. B. *J. Comput. Chem.* **1991**, *12*, 923.

[47] Roehrig, M. A.; Chen, Q.-Q.; Haubrich, S. T.; Kukolich, S. G. *Chem. Phys. Lett.* **1991**, *183*, 84.

Table 1. Observed and Calculated Cobalt Anisotropic Hyperfine Coupling Constants[a] for **1** and **2**

	exptl values	structure **I**			structure **II**			
		SV66	DZVP2+	TZVP+	SV66	DZVP2+	DZVP2+[b]	TZVP+
compd **1**	−90.5	−89.6 (1)	−93.2 (3)	−90.9 (<1)	−89.5 (1)	−93.1 (3)	−77.7 (14)	−90.7 (<1)
	45.2	44.8 (1)	46.6 (3)	45.4 (<1)	44.7 (1)	46.5 (3)	38.8 (14)	45.3 (<1)
compd **2**	−85.0	−90.2 (6)	−93.8 (10)	−91.5 (8)	−90.1 (6)	−93.7 (10)	−78.2 (8)	−91.3 (7)
	28.8	38.2 (33)	43.8 (52)	40.2 (40)	38.1 (32)	36.2 (26)	21.3 (26)	33.8 (17)
	56.1	51.8 (8)	49.9 (11)	51.2 (9)	51.8 (8)	57.2 (2)	56.5 (1)	57.2 (2)
compd **2**[c]	−85.0	−90.2 (6)	−93.8 (10)	−91.5 (8)	−90.1 (6)	−93.7 (10)	−78.2 (8)	−91.3 (7)
	42.5	45.0 (6)	46.9 (10)	45.7 (8)	45.0 (6)	46.7 (10)	38.9 (8)	45.5 (7)
% cobalt d_{yz} or d_{xz} in SOMO	compd 1: 56 compd 2: 54	17	31	23	17	31	28	23
% CO orbitals in SOMO		20	30	30	18	26	29	27
% Cp orbitals in SOMO		63	37	43	65	41	35	46
spin contamination $\langle S^2 \rangle$		0.8994	0.8455	0.8856	0.8989	0.8443	0.7611	0.8839

[a] Units for the hyperfine coupling are $\mathrm{cm^{-1}\cdot 10^{-4}}$. The hfc data for **1** were originally reported in units of gauss; they have been converted to $\mathrm{cm^{-1}\cdot 10^{-4}}$ (using the reported **g** values of 2.005 and 2.004 for A parallel and A perpendicular, respectively) for comparison to the reported values for **2**. Numbers in parentheses are percent deviation from the experimental values. [b] Calculated using the BLYP functional. [c] The two smaller hfc values have been averaged.[50]

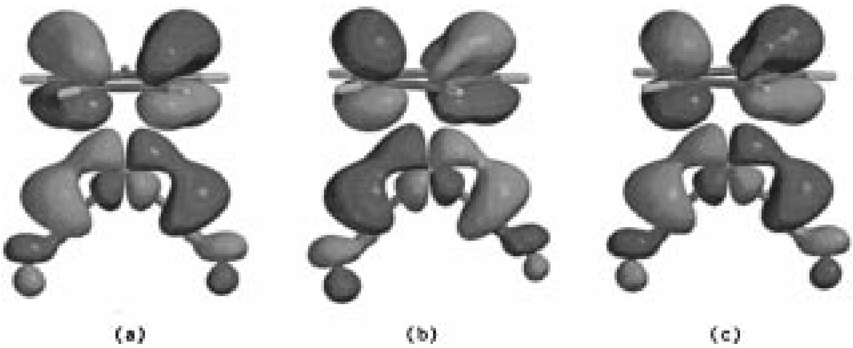
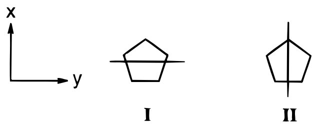


Figure 2. Plots of the SOMO for **1**: (a) B3LYP/TZVP+/structure **I**; (b) B3LYP/TZVP+/structure **II**; and (c) B3LYP/SV66/structure **II**.

the potential energy surface with respect to rotation of the Cp ring is nearly flat, the position of the true minimum along this coordinate is sensitive to the choice of basis set. Instead of performing expensive frequency calculations on every optimized structure to verify that it was a true minimum with respect to rotation of the Cp ring, all calculations were carried out on both C_s structures.



Assuming structure **I**, the d_{yz} orbital occupancy for cobalt was calculated from EPR data to be 0.56 for **1**[9] and 0.54 for **2**.[10] (If structure **II** had been assumed, the dominant metal orbital would have been d_{xz}.) Table 1 shows the results of DFT calculations on **1** compared to the experimental EPR data for **1** and **2**. Not surprisingly, the experimental anisotropic hfc constants for **1** and **2** are very similar.[50] As Table 1 shows, the contribution of the cobalt d orbital to the SOMO is about 30% at most. An examination of the SOMO for all calculations showed that, in most cases, the unpaired electron is approximately evenly distributed over the metal, the Cp ring, and the two CO ligands (Table 1 and Figure 2).

Although the calculated hfc constants in Table 1 agree very well with the experimental values for either **1** or **2** (usually within 10%), the percent cobalt d_{yz} or d_{xz} character in the SOMO (0.17−0.31) is always much less than that calculated according to eq 7 (≈0.55). The hfc constants were not very sensitive to changing the geometry from **I** to **II**, but they were somewhat sensitive to the choice of basis set, which was expected.

Figure 2 shows SOMO plots for the TZVP+/structure **I**, TZVP+/structure **II**, and SV66/structure **II** molecules, respectively.[51] As expected, the SOMO is mostly M−L antibonding, but the energies of the SOMO (−0.08−0.06 eV calculated with the B3LYP functional, 1.0 eV calculated with BLYP) indicate that occupation of the SOMO is not strongly destabilizing.

If the unpaired electron in **1** is so delocalized, it is perhaps surprising that the anisotropic hfc is so large. This situation is not adequately treated by the traditional method of analysis described above (eqs 6 and 7). Belanzoni et al.[12] described in detail several simplifications in the traditional method that render it invalid in cases such as this. All of the effects on the hfc due to interactions of the metal orbitals with the ligand orbitals are usually ignored, but for transition metal compounds they can be significant. Spin polarization of doubly occupied orbitals by the unpaired electron is also ignored. This effect can either increase or decrease the hfc.[12] An examination of the values

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(48) The C_1 structure was optimized using the SV66 basis set. The Cp ring remained very nearly planar, and the Co−C−O bond angles were 172° and 174°. The hfc constants were −91.8, 38.5, and 53.2 $\mathrm{cm^{-1}\cdot 10^{-4}}$, nearly identical with those of the two C_s structures using the same basis set.

(49) Beagley, B.; Parrott, C. T.; Ulbrecht, V.; Young, G. G. *J. Mol. Struct.* **1979**, *52*, 47.

(50) The EPR spectrum of **1** was originally interpreted assuming axial **g** and **A** tensors, but because the molecule has at most C_s symmetry, the tensors cannot be strictly axial. The spectrum of **2** is similar to that of **1**, but it was interpreted as nonaxial, so the T_x and T_y components for **2** were averaged in Table 1 to allow a rough comparison with the perpendicular component for **1**. Due to the different interpretations of the two EPR spectra, one set of data cannot be preferred over the other for comparison to the calculated hfc values.

(51) The orbital plots were generated using Spartan (Wavefunction, Inc.) based upon wave functions calculated by Gaussian 94. Because Spartan cannot handle f basis functions, the Gaussian calculations were redone without using an f function on cobalt. The results were identical with those performed with f functions.

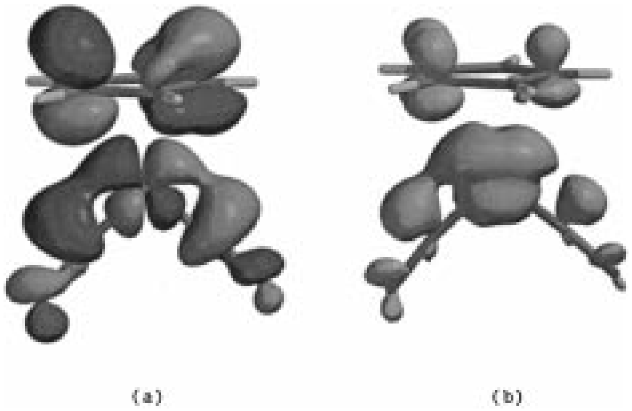

Figure 3. (a) Plot of the SOMO for **1** and (b) plot of the spin density for **1**. Both calculated using B3LYP/DZVP2+/structure **II**.

of the individual electric field gradient integrals for **1** was not possible due to software limitations, so the contribution from covalent terms could not be determined. However, a plot of the spin density in **1** (Figure 3) shows that there is in fact significant spin polarization of all of the cobalt d orbitals, increasing the amount of spin density around cobalt beyond that due to the nominally unpaired electron in the SOMO. A Mulliken spin population analysis also indicated that the spin density on the cobalt atom was in the range 0.61−1.12. Although a Mulliken population analysis by itself is not always reliable when applied to organometallics, the high values for **1** calculated here are consistent with the value of 0.56 calculated from the EPR data. However, it is evident that the spin distribution in **1** is not the same as the unpaired electron distribution (the SOMO). The calculations suggest that estimates of orbital populations from EPR data on organometallic molecules can produce erroneous results due to the neglect of spin polarization.

Recently the electron affinity for the neutral parent of **1** was reported, based on a negative-ion photoelectron spectroscopic study.[52] An upper bound of 0.86 ± 0.2 eV was determined for the adiabatic electron affinity (EA). The investigators also tried to calculate the EA according to EA = E(anion) − E(neutral). This requires optimizing the geometry of both species to allow for relaxation. Due to problems of SCF convergence with the anion radical (**1**), the investigators had to assume that the geometries of the two species were identical, even though the spectroscopic data indicated that the geometries were "significantly different". As shown above, the error thus introduced is negligible, because the energy difference between structures **I** and **II** is small. However, zero-point energies are not negligible. Using structure **I** for the neutral species and structure **II** for the anion, we calculated the EA to be 0.74 eV. When corrections for zero-point energies were included, the EA became 0.88 eV. This compares favorably with the experimental upper bound of 0.86 eV and provides an additional check on the quality of the DFT wave function.

Geometrical Deformations. The geometry of **1** was optimized in both structures **I** and **II** using the SV66 and DZVP2+ basis sets. The change in basis had little effect on the geometry, and the hfc parameters changed by only a few percent, remaining in good agreement with the experimental values. Single-point calculations on the two DZVP2+ structures were also carried out using the much larger TZVP+ basis. Again, the experimental hfc values were reproduced well (Table 1). The calculations showed that the structure of the ligands did not change much due to the presence of the extra electron. The Cp ring remained planar, and the Co−C−O bond angles were nearly linear (172−176°), except for the BLYP/VDZP2+ structure, in which one Co−C−O angle was 169°.

Spin Contamination. Most of the wave functions in Table 1 contain a greater amount of spin contamination than is usual for DFT treatments of doublet systems. It is possible to project the primary contaminating state (a quartet in this case) out of a wave function,[53] but the resulting wave function is not a self-consistent solution to the Hamiltonian. In general, molecular properties calculated with such a wave function should be viewed with caution.[54,55]

Unrestricted Hartree−Fock wave functions are known to display a high degree of spin contamination and have also been shown to overestimate spin polarization.[56] Spin polarization is a consequence of the exchange interaction, and it can strongly affect the magnitude of hyperfine coupling. A hybrid density functional like B3LYP, which includes some Hartree−Fock exchange, should be expected to allow more spin polarization and spin contamination than a "pure" functional like BLYP. Structure **II** was therefore reoptimized using the BLYP functional, which does not contain any Hartree−Fock exchange term, and the DZVP2+ basis. This reduced the value of $\langle S^2\rangle$, as expected, and reduced the magnitude of all of the hfc parameters somewhat, but they all remained in good agreement with experiment.

It is not yet known how to calculate $\langle S^2\rangle$ exactly for a DFT wave function.[57] The values reported in Table 1 were calculated by Gaussian 94 using the formula for a Hartree−Fock wave function:[58]

$$\langle S^2\rangle = S(S+1) + n_\beta - \sum_{\alpha,\beta}\langle\phi^\alpha|\phi^\beta\rangle^2 \tag{8}$$

where the sum is over all occupied spin−orbitals. Pople et al.[56] and Perdew et al.[59] have pointed out that when this formula is used with DFT orbitals, the last two terms should not be expected to cancel. When the numbers of α and β electrons differ, their effective potentials must be different, which means that their spatial distributions will be different, so their overlaps will not be unity. Thus the term "contamination" is inappropriate when applied to such DFT wave functions. What is unknown at this point is what amount of "spin contamination" is correct for a given system. In view of this, the larger values of $\langle S^2\rangle$ for the B3LYP wave functions for **1** do not necessarily indicate that the wave functions are of inferior quality.

Conclusions

Density functional theory has been successful in predicting the magnetic properties of organic molecules, and our results and others[12−20] indicate that it is able to model organometallics as well. The calculations on **1** showed that the metal d orbital contribution to the SOMO (about 30% at most) is not nearly as high as that calculated from the experimental EPR data (about

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[52] Campbell, J. M.; Martel, A. A.; Chen, S.-P.; Waller, I. M. *J. Am. Chem. Soc.* **1997**, *119*, 4678.

[53] Andrews, J. S.; Jayatilaka, D.; Bone, R. G. A.; Handy, N. C.; Amos, R. D. *Chem. Phys. Lett.* **1991**, *183*, 423.

[54] Nandi, P. K.; Kar, T.; Sannigrahi, A. B. *J. Mol. Struct. (THEOCHEM).* **1996**, *362*, 69.

[55] Wittbrodt, J. M.; Schlegel, H. B. *J. Chem. Phys.* **1996**, *105*, 6574.

[56] Pople, J. A.; Gill, P. M. W.; Handy, N. C. *Int. J. Quantum Chem.* **1995**, *56*, 303.

[57] Wang, J.; Becke, A. D.; Smith, V. H., Jr. *J. Chem. Phys.* **1995**, *102*, 3477.

[58] Douglas J. Fox, Gaussian, Inc., personal communication.

[59] Perdew, J. P.; Savin, A.; Burke, K. *Phys. Rev. A.* **1995**, *51*, 4531.

55%).[60] The discrepancy is mostly attributable to the neglect of spin polarization in the EPR analysis. The degree of hyperfine coupling to a metal nucleus is not related to the localization on that nucleus as simply as eq 7 suggests. In fact, the magnitude of hfc can be quite large even though the SOMO is delocalized.

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Supporting Information Available: Tables of calculated bond lengths and angles for **1** and of calculated ∂E/∂q values and structures (1 page). See any current masthead page for ordering and Internet access instructions.

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(60) If the metal contribution to the SOMO is only 30% or less, one may question whether the term “19-electron complex” should apply. There is, of course, no sharp dividing line between 19-electron complexes and what have come to be called “$18+\delta$ complexes”.[5] In these latter molecules, the unpaired electron is essentially ligand localized (SOMO $<$ 10% metal character, say). The distinction is important in terms of reactivity. The $18+\delta$ complexes are typically less reactive than 19-electron adducts because the electron is delocalized over the many atoms of a ligand. Our computational results and the marginal inertness of the $CpCo(CO)_2^-$ molecule suggest that it is a borderline 19-electron complex.