Inorg. Chem. **1981**, *20*, 2540-2543

Contribution from the Departments of Chemistry, Brown University, Providence, Rhode Island 02912, and the University of Otago, Dunedin, New Zealand

Paramagnetic Organometallic Molecules. 11.[1] The $SFeCO_2(CO)_9^{-}\cdot$ Radical Anion and the Electronic Structure of Capped M_3 Clusters

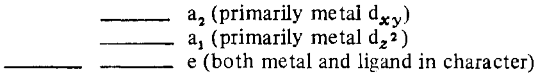
BARRIE M. PEAKE,[2a] PHILIP H. RIEGER,*[2b] BRIAN H. ROBINSON,*[2a] and JIM SIMPSON[2a]

Received September 18, 1980

The first reversible reduction wave at −0.24 V vs. Ag/AgCl for $SFeCo_2(CO)_9$ corresponds to the formation of a radical anion. This radical anion can be produced by electrochemical, alkali metal, or naphthalenide reduction and has been studied by ESR methods. Frozen solution ESR spectra were interpreted in terms of anisotropic **g** and cobalt hyperfine tensors. One component of the hyperfine tensor is parallel to the principal axes of the two equivalent cobalt nuclei, but the other two are orientated ±18° relative to the g-tensor axes. Information on the electronic structure from this spectrum is compared with that for homometallic CCo_3 and SCo_3. The replacement of Co by Fe results in admixture of Co $3d_{z^2}$ character into the primarily $3d_{xy}$ antibonding orbital; approximately 60% of the spin density resides on the two cobalt atoms. The electrochemical behavior of $(CO)_5Cr{\cdot}SFeCo_2(CO)_9$ and $SFeCo_2(CO)_8[P(OMe)_3]$ is also described.

Introduction

A number of structurally related complexes containing a common capped trimetallic cluster core XM_3 have been known for some time although their rich chemistry is only beginning to emerge. By far the most examples are found in cobalt chemistry[3] where the capping group X may be a single group 5 or 6 atom[4,5] or a group 3 or 4 atom which retains a functional group[6,7] (an exception is $AlCo_3(CO)_9$).[8] In either case the capping group formally contributes three electrons to cluster bookkeeping. As a consequence of the odd-electron contribution, certain clusters of this type[4,5] are paramagnetic, namely, when X = PR, S, Se, Te, with a stereochemically active electron pair on the capping atom. These clusters can therefore act as Lewis bases toward acceptors such as $Cr(CO)_5$[9] and BF_3.[10] Conversely, clusters such as $AlCo_3(CO)_9$ should be strong Lewis acids. Typically, the geometry of the capped clusters allows a distorted octahedral ligand coordination around each metal atom, and the overall symmetry is C_{3v}.[3,5,7,11] In this sense they are closely related to the noncapped cluster $M_3(CO)_{12}$. If only the five 3d orbitals per cobalt atom in a XCo_3 unit are taken as the basis set then it can be easily shown from symmetry arguments that the bonding symmetry orbitals are $a_1(d_{z^2}, d_{yz}, d_{x^2-y^2})$ and $e(d_{xz}, d_{xy})$ and the antibonding orbitals $a_2^*(d_{xy}, d_{xz})$ and $e^*(d_{x^2-y^2}, d_{yz}, d_{z^2})$. A similar result emerges if the molecular orbitals are constructed from three $Co(CO)_3$ fragments. For this purpose C_s local symmetry about each metal atom is required and the 3d, 4s, and 4p metal orbitals used as the basis set. Combination of each set of frontier orbitals, two a'(d_{z^2} and a sp_z hybrid) and $a''(d_{xz})$ under C_{3v} gives a series of e, a_1, or a_2 levels. Early work by Strouse and Dahl[5] on the $SCo_3(CO)_9$ cluster suggested the LUMO orbital in trimetallic clusters was $a_2^*(d_{xz})$ and primarily metal in character, and this has been confirmed by more recent spectroscopic[12] and theoretical studies.[13] The exact ordering of the upper e and a_1 levels has been calculated by Schilling and Hoffmann[13] as shown in **1**.



1

The tricobalt carbon cluster is the most thermodynamically and kinetically stable representative of the capped clusters, and its organic[11,14] and organometallic chemistry[11] gives an insight into the electronic makeup of capped clusters. It is clear that this cluster can function as an electron reservoir via push–pull interactions involving the apical substituent on the capping carbon atom.[11,14,15] These interactions are responsible for the stabilization of positively charged carbon centers in the apical substituent and are discussed by Schilling and Hoffman.[16] An important result from the work on the neutral cluster/radical anion couples[17,18] is the insensitivity of the upper bonding orbitals to the type of apical substituent (even when a mesomeric-type interaction is not possible) and to the coordination environment of the cobalt atoms, whereas the a_2^* is relatively unaffected by these factors. This rather suggests that the highest bonding molecular orbital is the e rather than the a_1 as in **1**.

Transition-metal complexes which evidence extended interactions in the solution and the solid state display many interesting and unusual properties.[19] Part of our research program involved the synthesis of clusters containing multiple capped trimetallic units, in which the push–pull interactions of multiple clusters can be coupled to varying degrees. In order to interpret the resulting spectroscopic data, it was necessary to understand the HOMO and LUMO structure of XM_3 clusters in more detail. We have shown[20] that this detail can be gleaned from the frozen-solution ESR spectra of cluster radical anions, and this treatment is utilized in this paper for the clusters SCo_3, CCo_3 and $SFeCo_2$. The latter molecule is of considerable interest since the question of how the distribution of spin density and orbital character differs in iso-

---

(1) Part 10: C. M. Kirk, P. N. Lindsay, B. M. Peake, B. H. Robinson and J. Simpson, submitted for publication in *Inorg. Chem.*

(2) (a) University of Otago. (b) Brown University.

(3) H. Vahrenkamp, *Struct. Bonding (Berlin)*, **32**, 1 (1977).

(4) (a) A. Vizi-Orosz, G. Palyi, and L. Marko, *J. Organomet. Chem.*, **60**, C25 (1973). (b) L. Marko and B. Marko, *Inorg. Chim. Acta*, **14**, L39 (1975).

(5) C. E. Strouse and L. F. Dahl, *Discuss. Faraday Soc.*, **47**, 93 (1969).

(6) P. W. Sutton and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 261 (1967).

(7) G. Schmidt, *Angew. Chem.*, **90**, 417 (1978).

(8) K. E. Schwarzhaus and H. Steiger, *Angew. Chem., Int. Ed., Engl.* **11**, 535 (1972).

(9) R. Richter and H. Vahrenkamp, *Angew. Chem.*, **90**, 474 (1978).

(10) B. H. Robinson, unpublished work.

(11) B. R. Penfold and B. H. Robinson, *Acc. Chem. Res.*, **6**, 73 (1973).

(12) B. M. Peake, B. H. Robinson, J. Simpson, and D. J. Watson, *Inorg. Chem.*, **16**, 405 (1977).

(13) B. E. R. Schilling and R. Hoffmann, *J. Am. Chem. Soc.*, **101**, 3456 (1979).

(14) D. Seyferth, *Adv. Organomet. Chem.*, **14**, 97 (1976).

(15) (a) D. C. Miller and T. B. Brill, *Inorg. Chem.*, **17**, 240 (1978). (b) B. Stutte, V. Batzel, R. Boese and G. Schmid, *Chem. Ber.*, **111**, 1603 (1978).

(16) B. E. R. Schilling and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 6274 (1978).

(17) A. M. Bond, B. M. Peake, B. H. Robinson, J. Simpson, and D. J. Watson, *Inorg. Chem.*, **16**, 410 (1977).

(18) A. M. Bond, P. Dawson, B. M. Peake, B. H. Robinson, and J. Simpson, *Inorg. Chem.*, **16**, 2199 (1977).

(19) L. V. Interrante, *ACS Symp. Ser.*, **No. 5** (1974).

(20) B. M. Peake, P. H. Rieger, B. H. Robinson, and J. Simpson, *J. Am. Chem. Soc.*, **102**, 156 (1980).

0020-1669/81/1320-2540$01.25/0

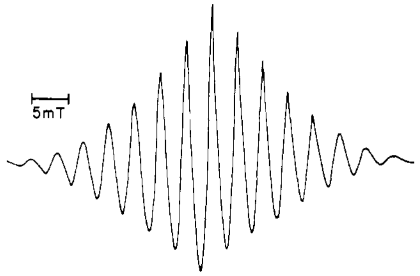


Figure 1. ESR spectrum of $SFeCo_2(CO)_9^{-}\cdot$ in THF solution at −20 °C.

structural homonuclear and heteronuclear clusters has not been posed previously.

Experimental Section

The clusters CCo_3,[6] SCo_3,[5] $SFeCo_2$,[21,22] $(CO)_5Cr{\cdot}SFeCo_2(CO)_9$,[9] and $SFeCo_2(CO)_{9-x}[P(OPh)_3]_x$[23] were synthesized by literature methods. Radical anions were produced by the methods previously described[12] and the ESR spectra recorded on a Varian E-4 spectrometer equipped with a variable-temperature accessary. The electrochemical measurements were made on PAR equipment similar to that already described.[17]

Results

Electrochemistry of $SFeCo_2(CO)_9$ Compounds. The dc polarogram of $SFeCo_2(CO)_9$ in acetone shows three waves at −0.24, −0.92, and −1.75 V vs. Ag/AgCl. The first two waves are electrochemically reversible one-electron reductions ($E_{1/4} - E_{3/4} = 55$ mV); the third wave is less well-defined with a smaller diffusion current. Cyclic voltammetry on Pt or Hg, and ac polarography, confirmed that the first wave is due to an uncomplicated reversible reduction to the radical anion.

$$SFeCo_2(CO)_9 + e^- = SFeCo_2(CO)_9^{-}\cdot$$

Reduction to the anion can also be carried out successfully with the use of chemical agents such as sodium and sodium naphthalenide. The half-life of the $SFeCo_2(CO)_9^{-}\cdot$ radical anion is only on the order of 1 min at ambient temperatures compared to several hours for the most stable $YCCo_3(CO)_9^{-}\cdot$ radical anions. The second wave is chemically completely irreversible on the cyclic voltammetry time scale, and it gives rise to an anodic absorption peak at −0.7 V on Hg (−0.6 V on Pt). An extra reduction peak at −1.1 V is observed only at scan rates greater than 0.5 V s^{-1}. It is suggested that these irreversible processes are due to fragmentation of the $SFeCo_2(CO)_9$ molecule; there is no evidence for a dianion $SFeCo_2(CO)_9$ analogous to the CCo_3 series.[17,18] Electrode reactions involving $SFeCo_2$ and other sulfur-containing clusters are characterized by strong absorption phenomena and the electron transfer is slower than with CCo_3 compounds. Electron transfer in the latter compounds is most probably via the carbonyl groups,[1,17,18] but we suggest, because of the lone pair on the sulfur and the affinity of Pt and Hg for chalconides, that electron transfer in $SFeCo_2$ clusters is via the apical sulfur atom.

This thesis receives support from the observation that the strong absorption phenomena were absent in the electrode reaction of the adduct $(CO)_5Cr{\cdot}SFeCo_2(CO)_9$. The first reduction potential for this adduct was virtually identical with that of $SFeCo_2(CO)_9$ but only quasi-reversible electrochemically. Replacement of a CO by a phosphite ligand produced the expected shift to more negative potential (for $SFeCo_2(CO)_8P(OPh)_3$, $E_{1/2} = -0.86$ V vs. Ag/AgCl).

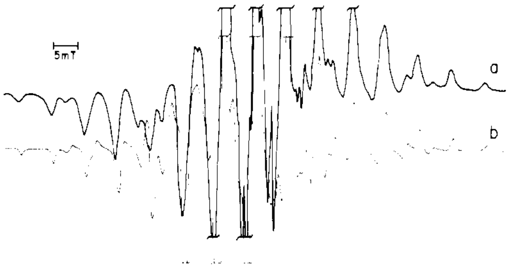


Figure 2. ESR spectrum of frozen THF solution of $SFeCo_2(CO)_9^{-}\cdot$: (a) experimental spectrum; (b) simulated spectrum.

ESR Spectrum of $SFeCo_2(CO)_9^-$. The ESR spectrum of $SFeCo_2(CO)_9^{-}\cdot$, produced either by sodium reduction or electrolytically in THF solution, shows the expected 15 hyperfine lines resulting from coupling with two equivalent cobalt nuclei; see Figure 1. Although the g value is temperature independent within experimental error, $\langle g\rangle = 2.0137 \pm 0.0015$, the cobalt hyperfine coupling constant $|\langle a\rangle| = 3.44 \pm 0.01$ mT at 273 K is slightly temperature dependent in the temperature range −60 to +20 °C with a temperature coefficient $d|\langle a\rangle|/dt = -0.34\ \mu T\ K^{-1}$.

The ESR spectrum of a frozen THF solution of $SFeCo_2(CO)_9^{-}\cdot$ is shown in Figure 2a. The most prominent features of the spectrum are nearly equally spaced and have similar shapes. These features correspond to the largest hyperfine tensor component for which the principal axes for the two cobalt nuclei are nearly parallel or collinear. After corrections are made for the small second-order shifts[20,24] (by using estimates of the other two hyperfine tensor components), these lines may be fitted to obtain $g_1 = 2.0115 \pm 0.0015$ and $|a_1| = 6.60 \pm 0.01$ mT. Several features are observed in the spectrum which can be assigned to another series of 15 lines. These correspond to the second largest hyperfine tensor component; however, because the spacings vary and the lines differ somewhat in shape, this component corresponds to principal tensor axes which are not parallel for the two cobalt nuclei. Under these circumstances, the line positions are functions not only of g_2 and a_2 but also of g_3, a_3, and the angle α which relates the principal axes of the hyperfine tensors.[20]

In a single crystal oriented with the principal axes corresponding to a_1 perpendicular to the magnetic field, the resonant field at a particular azimuthal angle ϕ is given to first order by eq 1; m_1 and m_2 are the nuclear spin quantum numbers,

$$B = h\nu/g\mu_B - m_1b_+ - m_2b_- \qquad (1)$$

and g and $b_\pm$ are given by eq 2 and 3. In the frozen-solution

$$g = (g_2^2 \cos^2 \phi + g_3^2 \sin^2 \phi)^{1/2} \qquad (2)$$

$$b_\pm = [a_2^2 \cos^2 (\phi \pm \alpha) + a_3^2 \sin^2 (\phi \pm \alpha)]^{1/2} \qquad (3)$$

spectrum, spectral features are expected at field positions corresponding to values of ϕ which maximize and minimize B for a given set of quantum numbers m_1 and m_2. When $m_1 = m_2$, these extrema occur at $\phi = 0$ and 90°, but when $m_1 \neq m_2$, extrema occur at other angles. Thus, variations are expected in line spacings, and degenerate lines corresponding to a given value of $M = m_1 + m_2$ split into components with spacings roughly proportional to $|m_1 - m_2|$. In fact, several features are observed in the frozen solution spectrum of $SFeCo_2(CO)_9^{-}\cdot$ which result from just such splitting. Thus two $M = -3$ features are observed; one feature corresponds to quantum numbers $-{}^7/_2, +{}^1/_2$ and the other to the unresolved pair $-{}^5/_2, -{}^1/_2$ and $-{}^3/_2, -{}^3/_2$. Similarly two $M = -2$ features are observed which can be assigned to $-{}^5/_2, +{}^1/_2$ and $-{}^3/_2, -{}^1/_2$;

---

(21) S. A. Khattab, L. Marko, G. Bor, and B. Marko, *J. Organomet. Chem.*, **18** 373 (1964).

(22) D. L. Stevenson, C. H. Wei, and L. F. Dahl, *J. Am. Chem. Soc.*, **93**, 6027 (1971).

(23) R. Rossetti, G. Gervasio, and P. L. Stanghellini, *J. Chem. Soc. D*, 222 (1978).

(24) N. M. Atherton and C. J. Winscom, *Inorg. Chem.*, **12**, 383 (1973).

Table I. ESR Parameters for $YCCo_3(CO)_9$ Radical Anions

Y	$\langle g\rangle^a$	$g_\parallel{}^b$	$g_\perp{}^c$	$\langle a\rangle$/mT^d	$a_\parallel$/mT^d	$a_\perp$/mT^e
H	2.011	2.002	2.016	−3.46	−7.36	−1.51
F^f	2.015	2.005	2.020	−3.70	−7.63	−1.74
C_2H_5	2.013	2.000	2.020	−3.59	−7.58	−1.60
C_6H_5	2.013	1.996	2.022	−3.58	−7.90	−1.42
C_6F_5	2.016	2.004	2.022	−3.52	−7.92	−1.32

[a] ±0.001. [b] ±0.002. [c] Computed from $\langle g\rangle$ and $g_\parallel$ by using eq 4. [d] ±0.01 mT. [e] Computed from $\langle a\rangle$ and $a_\parallel$ by using eq 5. [f] $\langle a^F\rangle = 1.2$ mT.

the expected third $M = -2$ feature with quantum numbers $-^7/_2$, $+^3/_2$ is shifted to higher field and is obscured by an adjacent a_1 feature. The spacing between these features is very sensitive to the angle α and can be used to estimate this angle quite reliably. Computer simulations confirmed the assignments and were used to refine parameter estimates. The best fit simulation shown in Figure 3b corresponds to $\alpha = 18°$, $|a_2| = 5.36$ mT, $|a_3| = 1.55$ mT, $g_2 = 2.013_5$, $g_3 = 2.016_1$. The simulation proved to be rather insensitive to g_3 and a_3, and these parameters were in practice computed from the isotropic parameters with the use of eq 4 and 5.

$$\langle g\rangle = (g_1 + g_2 + g_3)/3 \qquad (4)$$

$$\langle a\rangle = (a_1 + a_2 + a_3)/3 \qquad (5)$$

ESR Spectrum of $YCCo_3(CO)_9^{-}\cdot$. Spectra of frozen THF solutions of the $YCCo_3(CO)_9$ radical anions were obtained at 133 K. The spectrum of the Y = C_6H_5 anion, which is typical, has been published.[25] All spectra clearly indicate one large hyperfine tensor component, comparable in magnitude (~7.6 mT) to the splitting found by Strouse and Dahl[5] for $SCo_3(CO)_9$ doped in $SFeCo_2(CO)_9$ single crystals when the threefold axis was aligned parallel within the magnetic field. Most of the 22 parallel features were well resolved and easily identified in the frozen-solution spectra. Analysis with small second-order corrections[20,24] gave the value of $g_\parallel$ and $a_\parallel$ in Table I; features due to the other two hyperfine components were almost completely unresolved. Both components must be small compared with $a_\parallel$, and it is reasonable to assume that they are equal and given by $a_\perp = (3\langle a\rangle - a_\parallel)/2$, with $\langle a\rangle$ extrapolated to 166 K, the freezing point of THF. These values of $a_\perp$ are also given in Table I. Since the lines of the frozen-solution spectrum were typically ~2 mT wide, it is not surprising that the perpendicular features were unresolved.

Discussion

A comparison of the potential for the one-electron reduction of $SFeCo_2(CO)_9$ with those for the CCo_3 series[18] reveals that the replacement of one Co by Fe, and sulfur for carbon, has had little effect. In fact, the $SFeCo_2(CO)_9{}^{0/-}$ couple is exactly comparable to the $FCCo_3(CO)_9{}^{0/-}$ couple (−0.28 V); that is, the CCo_3 cluster with the most electron-withdrawing apical substituent. The electronegativities of C and S are very similar so the removal of charge from the trimetal unit most likely arises from the more effective Co–S orbital overlap compared to Co–C overlap; this raises the energy of the a_1 HOMO. It is interesting that the involvement of the lone pair on the sulfur atom in adduct formation (as $(CO)_5Cr\cdot SFeCo_2(CO)_9$) does not seem to perturb the redox orbitals of the $SFeCo_2$ cluster. In contrast, coordination of a donor ligand to the basal Co_3 unit lowers the energy of the HOMO and increases the reduction potential.

The frozen-solution ESR spectrum of the $SFeCo_2(CO)_9$ radical anion was analyzed in terms of two equivalent cobalt nuclei with hyperfine tensors given by eq 6. Here we have

$$\mathbf{a} = |-6.60 - 5.36 + 1.55|\ \mathrm{mT} \qquad (6)$$

chosen signs consistent with an assumed negative isotropic coupling constant. The first component of the hyperfine tensor corresponds to parallel principal axes for the two nuclei, but the second and third components correspond to principal axes orientated at ±18° relative to the corresponding **g** tensor axes. Neglecting spin–orbit contributions to the hyperfine tensor, the dipolar contributions can be computed by using eq 7 to

$$b_i = a_i - \langle a\rangle \qquad (7)$$

$$\mathbf{b} = |-3.13 - 1.89 + 5.02|\ \mathrm{mT} \qquad (8)$$

obtain eq 8. This dipolar tensor can be obtained from many different combinations of cobalt 3d orbitals, all of which lead to eq 9. With the parameter P, given by eq 10, equal to 30.2

$$\mathbf{b} = |-0.353 - 0.213 + 0.566| P\rho^{3d} \qquad (9)$$

$$P = g_e g_N \mu_B \mu_N \langle r^{-3}\rangle \qquad (10)$$

mT,[26] eq 8 and 9 lead to the cobalt 3d spin density, $\rho^{3d} = 0.294$.

The isotropic cobalt coupling is the sum of terms arising from polarization of inner shell s orbitals and contributions from 4s character in the MO containing the unpaired electron. Since the 4s character must be zero in the a_2 orbital of $SCo_3(CO)_9$ (vide infra), we can use the experimental isotropic coupling constant, −3.09 mT, and the 3d spin density estimated for this radical, $\rho^{3d} = 0.25$, to estimate the polarization contribution to $\langle a\rangle$ in $SFeCo_2(CO)_9^{-}\cdot$. A single 4s electron is expected[26] to produce an isotropic coupling of 212 mT. Thus we estimate a 4s spin density of about 0.001 on each cobalt. There may be a small unobservable cobalt 4p contribution to the molecular orbital, but it appears that about 60% of the spin density resides on the two cobalt atoms.

Under the C_s symmetry of $SFeCo_2(CO)_9$, symmetry restrictions on MO composition are nearly absent, and so a detailed assignment of the atomic orbital composition of the LUMO is not possible in the unique sense achieved for the $R_2C_2Co_2(CO)_6$ radical anions.[20] However, arguing from the starting point of the isoelectronic $SCo_3(CO)_9$ radical, we can make a plausible assignment. In the latter case, the unpaired electron occupies an a_2 MO delocalized over the tricobalt plane and composed primarily of cobalt $3d_{xy}$ contributions.[5] If we assume that the LUMO in $SFeCo_2(CO)_9$ is still in the trimetal plane, then the unique axis, common to the hyperfine tensors and to the **g** tensor, must again be the z axis perpendicular to the plane. As any admixture of d_{xz} or d_{yz} would shift the principal hyperfine tensor axes away from the z axis, these orbitals can be excluded from further consideration. Furthermore, since the z axis corresponds to the larger negative component of the hyperfine tensor, 3d combinations are restricted to 19.1% d_{z^2} and 80.4% of some mixture of d_{xy} and $d_{x^2-y^2}$. The angle $\alpha = 18°$ then fixes the $d_{xy}/d_{x^2-y^2}$ ratio given a choice of x and y axes in the trimetal plane. We chose the local x axes as directed toward the center of the M_3 triangle. The Co–Co vector, from which α is measured, is orientated at 30° relative to the x axes so that the major hyperfine tensor axis is at either 12 or 48° with respect to the x axis. In the reference radical $SCo_3(CO)_9$, where the 3d contribution is entirely d_{xy} in this coordinate system, this angle is 45° so that the choice of 48° seems logical. With this choice, the 3d contributions to the LUMO are 19.1% d_{z^2}, 80.0% d_{xy}, and 0.9% $d_{x^2-y^2}$.

It is interesting that these Co 3d contributions amount to an atomic orbital with a shape very close to d_{z^2}. This conclusion is in fact obvious from the dipolar tensor where the major component is positive. Indeed, if the hyperfine tensor

---

(25) B. M. Peake, P. H. Rieger, B. H. Robinson, and J. Simpson, *Inorg. Chem.*, **18**, 1000 (1979).

(26) J. R. Morton and K. F. Preston, *J. Magn. Reson.*, **30**, 577 (1978).

Table II. $SFeCo_2(CO)_9$ LUMO Composition

	z^2	xz	yz	xy	x^2-y^2	total 3d
			Experimental Values			
Fe	0	0			0	
Co	0.056	0	0	0.235	0.003	0.294
			Theoretical Values[a]			
Fe	0	0	0.001	0.152	0	0.153
Co	0.008	0.003	0.001	0.168	0.001	0.181

[a] Extended Hückel MO calculations by Fisel and Hoffmann.[27]

axes are used as local axes with z chosen as the major axis, then the atomic orbital contribution is uniquely described as 99.6% d_{z^2}, 0.4% $d_{x^2-y^2}$.

Two features of our conclusions are qualitatively reproduced by extended Hückel molecular orbital calculations by Fisel and Hoffmann:[27] the cobalt 3d contribution to the LUMO is predominantly d_{xy} with a significant admixture of d_{z^2}, and the cobalt 3d contributions are about 20% greater than those of the iron. Detailed comparison of our results with these calculations shows less satisfactory agreement (Table II). Thus the calculated total metal 3d contribution to the LUMO is 0.52 whereas our estimate is 0.59 on the two cobalt atoms alone. Since this comparison rests on the reliability of the parameter P, it should perhaps not be taken too seriously. The composition of the cobalt 3d contributions, however, is more reliably determined from the dipolar hyperfine tensor, and this is matched only very roughly by the MO calculations. Fisel and Hoffmann find[27] the cobalt 3d contributions to be 92.7% d_{xy}, 4.5% d_{z^2}, 1.6% d_{xz}, 0.7% d_{yz}, and 0.4% $d_{x^2-y^2}$. A hybrid orbital of this composition would result in the dipolar hyperfine tensor of eq 11, where the principal axes are rotated from the

$$\mathbf{b} = |-0.513 + 0.038 + 0.474|P\rho^{3d} \qquad (11)$$

local Cartesian axes through the Eulerian angles $\phi = 21°$, $\theta = 7°$, and $\chi = -64°$. The discrepancy between eq 9 and 11 comes almost entirely from the d_{xy}/d_{z^2} ratio. The small admisture of d_{xz} and d_{yz} makes little difference to the dipolar tensor, and the 7° tip of the tensor principal axis from the local z axis might not be experimentally detectable.

Comparison of the Orbital Character of XCo_3 Clusters. We are now in a position to compare the electronic structures of the capped trimetallic clusters CCo_3, SCo_3, and $SFeCo_2$. The ESR spectrum of $SCo_3(CO)_9$ was obtained a decade ago by Strouse and Dahl,[5] who studied both hexane solutions and $SCo_3(CO)_9$ diluted in a single crystal of $SFeCo_2(CO)_9$. The spectrum was analyzed to obtain axially symmetric **g** and hyperfine tensors with $a_{\parallel} = -7.43$ mT and $a_{\perp} = 0.92$ mT, where the signs were based on an assumed negative isotropic coupling $\langle a \rangle = -3.09$ mT. Strouse and Dahl concluded that the unpaired electron occupies an orbital of a_2 symmetry which, if the threefold axis is labeled z, is primarily cobalt $3d_{xy}$ in character. This assignment was based on arguments which relied in part on the magnitude of the parameter P (eq 10), but the same conclusion may be reached by a slightly different line of reasoning. The three cobalt nuclear hyperfine tensors have a common major tensor axis (corresponding to $a_{\parallel}$), necessarily the z axis. The identification of $a_{\parallel}$ with the threefold axis was of course experimentally determined in the single-crystal ESR study but a tensor axis common to all three tensors is symmetry required to be the threefold axis. The major axes for d_{xz} and d_{yz} are y and x axes, respectively, so that involvement of these two atomic orbitals may be neglected. The dipolar hyperfine tensor, computed according to eq 7, where spin–orbit contributions to the a_i are assumed negligible has $b_{\parallel} = -4.34$ mT, $b_{\perp} = +2.17$ mT. The negative value of b excludes d_{z^2}, leaving a choice between $a_2(d_{xy})$ and $a_1(d_{x^2-y^2})$ orbitals. From MO arguments, we expect the a_1 orbital to be strongly metal–metal bonding and filled while the a_2 orbital is strongly antibonding and is the logical candidate for the half-filled orbital. More detailed MO theory calculations by Teo et al.[28] and more recently by Schilling and Hoffmann[13] are in agreement with this assignment. If the unpaired electron occupies a MO composed of cobalt $3d_{xy}$ contributions, then $b_{\parallel}$ should be given by (12). If we take $P = 30.2$ mT, then

$$b_{\parallel} = -\tfrac{4}{7}P\rho^{3d} \qquad (12)$$

$\rho^{3d} = 0.25$. The remaining 25% of the spin density must then be distributed among cobalt $4p_y$ and various ligand orbital contributions to the molecular orbital. Compared with 3d, 4p contributions to the dipolar hyperfine tensor are expected to be negligible because of the smaller value of $\langle r^{-3} \rangle$.

Comparing $SFeCo_2(CO)_9^{-}\cdot$ with $SCo_3(CO)_9$, we see that the replacement of cobalt by iron results in a significant admixture of cobalt $3d_{z^2}$ into the primarily $3d_{xy}$ antibonding orbital. The $3d_{xy}$ contribution from cobalt is only slightly reduced (from 0.25 to 0.24) with the $3d_{z^2}$ contribution (0.056) amounting to a net gain in cobalt spin density. Since the ligand contributions would not be expected to change markedly, it seems likely that the iron 3d contributions are significantly smaller, perhaps as low as 0.15 or half the cobalt spin density.

The isotropic and anisotropic cobalt hyperfine coupling constants for $YCCo_3(CO)_9^{-}\cdot$, Table I, are very similar to the corresponding parameters for the $SCo_3(CO)_9$ radical[5] $\langle a \rangle = -3.09$ mT, $a = -7.43$ mT. Thus the arguments outlined above may be applied to show that the unpaired electron occupies a molecular orbital of a_2 symmetry and largely cobalt d_{xy} character. The dipolar couplings for Y = C_6H_5 and C_6F_5 are nearly identical with that for $SCo_3(CO)_9$ and lead to similar estimates of the 3d spin density on cobalt ($\rho^{3d} = 0.25$). For Y = H, F, and C_2H_5, on the other hand, b is significantly smaller in magnitude, leading to $\rho^{3d} = 0.23$; the reason for this difference is not apparent.

Acknowledgment. We thank Professor Roald Hoffmann for the unpublished results of his extended Hückel calculations on $SFeCo_2(CO)_9$. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. $SFeCo_2(CO)_9^{-}\cdot$, 77845-72-8; $SFeCo_2(CO)_9$, 22364-22-3; $HCCo_3(CO)_9^{-}\cdot$, 51900-20-0; $C_2H_5CCo_3(CO)_9^{-}\cdot$, 61024-68-8; $C_6H_5CCo_3(CO)_9^{-}\cdot$, 61024-80-4; $(CO)_5Cr\cdot SFeCo_2(CO)_9$, 66523-73-7; $SFeCo_2(CO)_8P(OPh)_3$, 65966-72-5.

---

(27) R. Fisel and R. Hoffmann, personal communication.

(28) B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *Inorg. Chem.*, **14**, 3103 (1975).