The relative probabilities of reaction (a) to reaction (a′) should be given directly by the ratio of trimethylsilane to isobutane obtained when *tert*-butyltrimethylsilane is photolyzed in the presence of oxygen. No alternative intramolecular mechanism for the formation of either product appears possible. Table I shows that the yield of isobutane is approximately twice that of trimethylsilane. This strongly suggests that reaction (a′) predominates over reaction (a).

While the driving force for the production of Si-C unsaturation is not probed directly by our experiments, there is clear evidence that this species must be the single most important even electron product in the photolysis of $(CH_3)_3SiC(CH_3)_3$, $i\text{-}C_4H_{10}$, the saturated cofragment of $(CH_3)_2SiCH_2$, is produced in yield equal to that of $i\text{-}C_4H_8$, and in other examples where the ratio of saturation to unsaturation can be compared (Table I) the unsaturated product yield is equal to two–three times that of its saturated cofragment. Thus, we conclude that the failure to isolate $(CH_3)_2SiCH_2$ must be due to its reactivity rather than some intrinsic barrier to its formation.

Similar conclusions have been reached based on pyrolysis studies.[8,9]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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Theoretical Model for the 4-Fe Active Sites in Oxidized Ferredoxin and Reduced "High-Potential" Proteins. Electronic Structure of the Analogue $[Fe_4S^*_4(SCH_3)_4]^{2-}$

Sir:

Active sites of the 1-, 2-, and 4-Fe types are now established in Fe-S redox proteins[1,2] and synthetic analogues for each have been characterized.[3,4] For the 4-Fe sites $[Fe_4S^*_4(S\text{-}Cys)_4]$ in ferredoxin (Fd) and high-potential (HP) proteins, whose structures are known,[2,5,6] the protein-analogue stereochemical[7] and electronic[8] correlation $Fd_{red} \equiv HP_{ox} \equiv [Fe_4S^*_4(SR)_4]^{2-}$ is well established. Electronic structures of these clusters have previously been described by a qualitative symmetry-factored MO model[7a,9] Here we present preliminary electronic structural results for the simplest known analogue,[7a] $[Fe_4S^*_4(SCH_3)_4]^{2-}$, obtained by the recently developed SCF-Xα-SW method.[10,11]

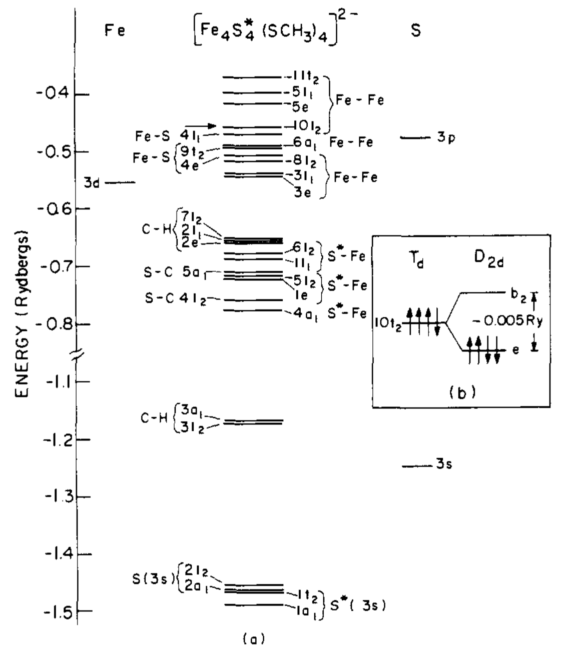

Figure 1. (a) SCF-Xα-SW orbital energies of $[Fe_4S^*_4(SCH_3)_4]^{2-}$ in T_d symmetry and (b) splitting of highest occupied orbital ($10t_2$) in D_{2d} symmetry. Fe and S free-atom energy levels obtained by SCF-Xα method.

In the present model overall perfect T_d analogue symmetry was imposed (Fe-S*, 2.27; Fe-S, 2.25; S-C, 1.83;[7] and C-H, 1.12 Å) and the actual D_{2d} $Fe_4S^*_4S_4$ cluster symmetry[7] considered a perturbation. The energies of the highest occupied and first few unoccupied orbitals are shown in Figure 1a,[12] from which emerge the following points. (1) The number and character of occupied orbitals suggest that each Fe atom has the effective fractional valence state $Fe^{2.5+}$; discrete integral valence states are not spectroscopically detectable in $[Fe_4S^*_4(SR)_4]^{2-}$.[13] (2) The electronic inequivalence of S* and S atoms is emphasized by the findings that the charge localized in sulfur atomic regions averages 54.3 and 36.7% in the S*-Fe and Fe-S orbitals, respectively, a behavior attributable to the influence of the electropositive metal in the structural fragments $S^*\text{-}Fe_3$ and Fe-S-C. (3) The band of levels between −0.55 and −0.35 Ry corresponds to orbitals ("Fe-Fe") predominantly Fe 3d-like in character and orbitals ("Fe-S") with almost equal amounts of Fe-3d and S-3p character. However, the Fe-Fe levels are not purely metallic in nature, as compared with the orbitals of an isolated tetrahedral Fe_4 cluster having the same Fe-Fe interatomic distance. The Fe-Fe orbitals in $[Fe_4S^*_4(SCH_3)_4]^{2-}$ have S 3p-like components ranging from only 3% S and 1% S* in the most metallic occupied bonding orbital (3e) to as much as 25% S and 12% S* in the least metallic unoccupied antibonding orbital (5e). Therefore, the Fe-S interactions are quite covalent. This is in contrast to earlier SCF-Xα-SW calculations for the simpler prototype cluster, $[Fe_4S^*_4(SH)_4]^{2-}$, which gave results suggesting an almost purely metallic 3d-like band of levels separated in energy well above two bands of almost pure S (3p) and S* (3p) character.[14] However, these earlier results are unphysical because Fe-Fe antibonding orbitals holding 12 electrons were occupied in place of two S*-Fe bonding orbitals of t_2 symmetry, whose nearly degenerate eigenvalues were inadvertently missed in the computational procedure. Recent (unpublished) calculations for $[Fe_4S^*_4(SH)_4]^{2-}$, with the proper occupancy, are qualita-

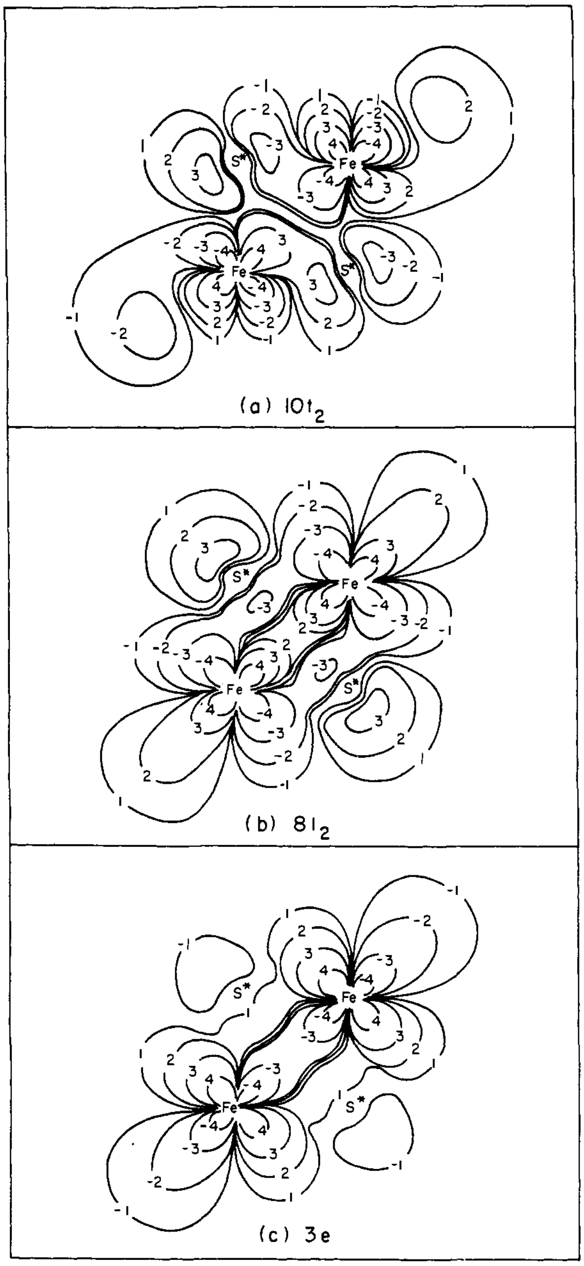

Figure 2. Contour maps, plotted in $Fe_2S^*_2$ plane (cube face), for the (a) $10t_2$, (b) $8t_2$, and (c) 3e orbital wave functions of $[Fe_4S^*_4(SCH_3)_4]^{2-}$. Sign of contour indicates sign of wave function.

tively consistent with the 4-Fe bonding model presented in this communication, in analogy to the similarity of hydrogen- and methyl-terminated models for oxidized rubredoxin recently published by Norman.[15] (4) The highest occupied level ($10t_2$) in $[Fe_4S^*_4(SCH_3)_4]^{2-}$ (ground state configuration ... $(4t_1)^6(10t_2)^4$) is predominantly tetrametal antibonding in character, with S and S* contributions to the orbital charge amounting to 18 and 7%, respectively.[15] A contour map of the $10t_2$ orbital wavefunction plotted in a $Fe_2S^*_2$ plane (cube face, Figure 2a) reveals the 3d-like lobes centered on the Fe nuclei, polarized by in-plane and out-of-plane covalent interactions with S* and S 3p-like components, respectively. The interactions between metal d orbitals and sulfur p orbitals offer support for the model proposed for spin delocalization and attendant ^{1}H NMR contact shifts of $[Fe_4S^*_4(SR)_4]^{2-}$ [8b] Also shown in Figure 2 are the heavily tetrametal $8t_2$ and 3e orbitals which illustrate the net Fe–Fe bonding.

Optical absorption spectra for the series $[Fe_4S^*_4(SR)_4]^{2-}$ (R = alkyl)[8c] are somewhat red-shifted but otherwise are similar to those of HP_{red} and Fd_{ox} and are dominated by intense features near 295 nm (4.20 eV) and 418 nm (2.97 eV), additional incompletely resolved bands at intermediate energies, and a low intensity shoulder at ~650 nm (1.91 eV). We assign the intense peaks and fine structure between these peaks to "charge-transfer" excitations from the band of predominantly sulfur-like levels lying between −0.68 and −0.78 Ry to the partially unoccupied tetrametal level $10t_2$. The top ($6t_2$) and bottom ($4a_1$) of the sulfur band are separated from the $10t_2$ level by the energies 2.98 and 4.32 eV, which (neglecting orbital relaxation) are remarkably close to the energies, 2.97 and 4.20 eV, of the principal absorption peaks. The low intensity shoulder at ~1.91 eV is assigned to "d → d" electronic transitions between the occupied and unoccupied tetrametal ("Fe–Fe") levels.

Analogue structures (R = CH_2Ph, Ph)[7] exhibit D_{2d} symmetry and those of HP_{red}[6] and Fd_{ox}[5] sites are D_{2d} or lower, a matter previously attributed (in the absence of a detailed electronic model) to the Jahn–Teller effect.[6a,9] The degeneracy of the highest partially occupied orbital ($10t_2$) indicates the likelihood of a Jahn-Teller distortion of the $[Fe_4S^*_4(SCH_3)_4]^{2-}$ and related clusters from the perfectly cubic (T_d) structure to a lower symmetry geometry. SCF-Xα-SW electronic-structure calculations for the simpler $[Fe_4S^*_4(SH)_4]^{2-}$ cluster, carried out in both T_d and D_{2d} geometries,[16] suggest a lower total energy for the distorted cube and a splitting of t_2 levels into e and b_2 levels. This splitting, however, amounts to no more than approximately 0.005 Ry (0.068 eV). If the distortion of the cube lowers the degeneracy of the $10t_2$ orbital of $[Fe_4S^*_4(SCH_3)_4]^{2-}$ (Figure 1b), then a "closed-shell" electronic configuration is attained. This results in zero net spin and is consistent with the observed low-temperature magnetic properties of analogues[8a] and HP_{red}.[8d] The paramagnetism observed at higher temperatures[8,a,b,d,17] can be explained in the present model by the excitation of electrons across the very small e → b_2 energy gap and population of $b_2\uparrow$ states. Lastly, this model suggests that the species $[Fe_4S^*_4(SR)_4]^- \equiv HP_{ox}$ would have the $(10t_2)^3$ configuration and hence, in the simplest approximation, not be subject to Jahn-Teller distortions. At this point we can only observe that the HP_{ox} site is marginally more symmetric than the HP_{red} site,[6] and that the cluster volume contraction in the process $HP_{red} \rightarrow HP_{ox}$ is, as suggested,[6a] partially accountable in terms of electron removal from an Fe–Fe antibonding orbital (the $10t_2$ orbital or its components in lower symmetry).

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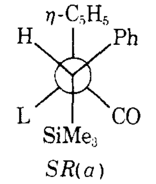
A Demonstration of Controlled Asymmetric Induction in Organoiron Chemistry. Suggestions Concerning the Specification of Chirality in Pseudotetrahedral Metal Complexes Containing Polyhapto Ligands

Sir:

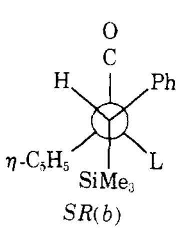
Catalysis by chiral transition metal complexes of the addition of, for instance, hydrogen and silanes to prochiral olefins and ketones often results in induction of asymmetry into the reaction products.[1,2] Although the reasons for such stereoselectivity are not, in general, understood, analogy with a number of well-studied, stoichiometric, stereoselective organic reactions[3-5] suggests that steric control may be very important in determining the relative free energies of formation of diastereomeric products, intermediates, and/or activated complexes.

We have recently shown,[6] using ^{1}H NMR spectroscopy, that steric effects strongly influence the relative energies of the staggered conformations of the compounds η^5-$C_5H_5FeCOLCH_2R$ (L = tertiary phosphine donors; R = Ph, $SiMe_3$). It was demonstrated that the order of decreasing ligand steric requirements is η^5-C_5H_5 > L > CO and $SiMe_3$ > Ph, and that the low energy rotamers, i.e., those in which the bulky η^5-C_5H_5 and R groups are mutually trans, are 550–700 cal mol^{-1} more stable than the other two rotamers when L = PPh_3 and R = Ph, 900–1500 cal mol^{-1} when L = PPh_3 and R = $SiMe_3$.

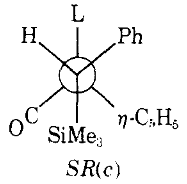
Armed with these data, we decided to study the diastereomeric relationships between a chiral metal entity, η^5-$C_5H_5Fe^*COL$–, and a chiral organic entity, –$C^*HPhSiMe_3$, both with ligands of quite different but clearly understood steric requirements. A compound of the type η^5-$C_5H_5FeCOLCHPhSiMe_3$ should exist as two diastereomerically related pairs of enantiomers, each diastereomer existing as three staggered rotamers.



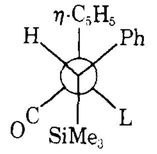
SR(*a*)



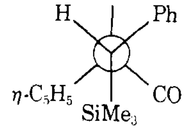
SR(*b*)



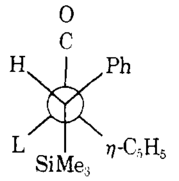
SR(*c*)



RR(*a*)



RR(*b*)



RR(*c*)

The enantiomeric *RS* and *SS* isomers would also exist, of course. (Suggestions concerning a convention for specifying the chirality of these stereoisomers will be discussed below.)

By analogy with similar primary alkyl complexes,[6] it is reasonable to expect that the most stable rotamer of each diastereomer would be that in which bulky η^5-C_5H_5 and $SiMe_3$ groups are mutually trans, i.e., *SR*(a) and *RR*(a) and their enantiomers. Furthermore, it is possible to predict that *SR*(a) should be somewhat more stable than *RR*(a), as the small CO is gauche to both the Ph and the $SiMe_3$ groups in the former, while L is gauche to Ph and $SiMe_3$ in the latter. Thus the *RS–SR* stereoisomers may be expected to be somewhat more stable than the *RR–SS* stereoisomers.

Identification of *RS-SR* and *RR-SS* diastereomers should be possible using ^{1}H NMR spectroscopy, as the α-hydrogen of the coordinated alkyl group is gauche to L in *SR*(a) but trans to L in *RR*(a). Thus, if the barriers to rotation about the iron-carbon bonds are sufficiently high that individual rotamers can be distinguished in the NMR spectrum, then $^3J_{PH}$ for *SR*(a) should be less than $^3J_{PH}$ for *RR*(a).[6] If on the other hand, barriers to rotations are sufficiently low that time-averaged spectra are obtained, then the observed $^3J_{PH}$ of *SR* should decrease with decreasing temperature, while that of *RR* should increase.[6]

Treatment of racemic η^5-$C_5H_5FeCOLI$ (L = PPh_3, $P(OPh)_3$) with racemic $Me_3SiPhCHMgBr$ at 35° in 2:1 benzene-ethyl ether solution gave stable products of the formula η^5-$C_5H_5FeCOLCHPhSiMe_3$[7] (L = PPh_3 (**1**), $P(OPh)_3$ (**2**)). Surprisingly, the ^{1}H NMR spectra (Table I)

Table I. Chemical Shift and Coupling Constant Data

Compound		α-CH	η^5-C_5H_5	SiMe	Ph
1	^{1}H[a]	δ 1.40, $^3J_{PH}$ = 7.7 Hz	δ 4.37, J_{PH} = 1.5 Hz	δ 0.30	δ ~7.15
2		δ 2.24, $^3J_{PH}$ = 10.1 Hz	δ 4.07, J_{PH} = 1.0 Hz	δ 0.33	δ ~7.14
3		δ 2.13, $^3J_{PH}$ = 10.5 Hz	δ 4.30, J_{PH} = 1.0 Hz	δ 0.35	δ ~7.14
2	^{13}C[b]	δ 2.9, $J_{PC} \approx$ 18 Hz[c]	δ 82.84, J_{PC} = 1.5 Hz	δ 2.27	δ 121–157
3		δ 1.6, $J_{PC} \approx$ 18 Hz[c]	δ 82.70, J_{PC} = 1.4 Hz	δ 2.20	δ 121–157

[a] In C_6D_6 solution. [b] In $CDCl_3$ solution, in ppm downfield from internal TMS. [c] Doublet partially obscured by stronger MeSi resonance.