phthalimide[9] yields the crystalline adduct **11**[11] (74%). The formation of **11** directly parallels the biological formation of tetrahedral intermediate **3** (Scheme I) and lends support to the mechanism[3] of Scheme I. An earlier proposed mechanism[12] for the conversion **1** + **2** → **3** invoked two steps: (a) an oxidation-reduction of **1** and **2**, yielding 2-acetylthiazolium salt plus dihydrolipoate, and (b) collapse of these intermediates, giving **3**. In our model system this possibility is ruled out by the blocking methyl group. Based on our results, we suggest that the biological generation of thioesters of coenzyme A from α-keto acids occurs via the direct reductive acylation of enzyme-bound lipoic acid by the "active aldehyde," as first formulated by Ingraham (Scheme I).[3]

Although the reactions summarized above lend further credence to the mechanisms of Scheme I, they do not directly address the involvement of the 1,2-dithiolane, lipoic acid, in the biological system. As its methyl ester, lipoic acid is completely unreactive under conditions[13] which produce thioesters from linear disulfides or from *N*-(phenylthio)phthalimide. It remains to be established whether thermodynamic or kinetic factors govern the lack of reactivity of enamine **7** toward methyl lipoate. Schmidt et al.[1d] discuss ring strain and geometrical factors which may render 1,2-dithiolanes kinetically more reactive than linear disulfides toward nucleophiles (e.g., **7**). Thermodynamic factors may then govern the stability of methyl lipoate in our model system. The enforced proximity of the thiol (thiolate) in a tetrahedral intermediate such as **3** could well drive the equilibrium **1** + **2** $\rightleftarrows$ **3** (Scheme I) toward the 1,2-dithiolane and enamine.[14,15] The position of the equilibrium should be pH dependent, however. In particular, in our model system the tertiary amine (DBU) present ensures an appreciable concentration of thiolate anion (conjugate base of intermediate **3**). At the pyruvate dehydrogenase active site, the reductive acylation of enzyme-bound lipoic acid could be driven by protonation of the dihydrolipoate intermediate (see **3**). We currently pursue a synthesis of a blocked (O-methylated) version of **3** (cf. **11**) as a model to study the facility and possible pH dependence of the conversion **3** → **1** + **2**.

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(3) The direct reductive acylation of Scheme I was first suggested by White, F. G.; Ingraham, L. L. *J. Am. Chem. Soc.* **1962,** *84*, 3109.

(4) Made by a modification of Breslow's route (ref 2b). We use *t*-BuLi (−94 °C) rather than *n*-BuLi (−78 °C) and achieve anion exchange with $AgBF_4$ (overall yield from 4-methylthiazole, 70%; mp 79-80 °C.

(5) A nitrogen stream was passed through a solution of **6** + DBU in THF and the volatile components were bubbled through a 2,4-dinitrophenylhydrazine solution in a second flask; the 2,4-dinitrophenylhydrazone of acetaldehyde, mp 161 °C, was formed in 25% isolated yield (preparative TLC); see also ref 2b. LC (C-18 reverse phase, 3:1 H_2O/CH_3CN, 1% NaOAc) of the mixture **6** + DBU shows formation of 3-benzyl-4-methylthiazolium salt (protonated ylide).

(6) The thioesters are stable to reaction conditions (see Table I).

(7) Made by benzylation of 4-methylthiazole with excess benzyl bromide at 80 °C, followed by anion exchange with $AgBF_4$, mp 89.5-91.0 °C. Satisfactory spectral data were obtained.

(8) Only a catalytic amount of DBU was used to form the ylide. Isolation was accomplished by precipitation of the phthalimide byproduct and recrystallization of **9b** (mp 138-140 °C); yield reported is of analytically pure material. Anal. Calcd for $C_{17}H_{16}NS_2BF_4$: C, 53.00; H, 4.19; N, 3.64. Found: C, 52.78; H, 4.16; N, 3.52. Satisfactory spectral data were obtained. The product **9a** was not isolated; its structure is assumed by analogy to **9b.**

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(10) Made by methylation of 2-(α-hydroxyethyl)-4-methylthiazole[2b,4] followed by benzylation and anion exchange (overall yield from 4-methylthiazole, 52%), mp 79-80 °C. Anal. Calcd for $C_{14}H_{18}NOSBF_4$: C, 50.02; H, 5.35; N, 4.17. Found: C, 50.17; H, 5.41; N, 4.18. Satisfactory spectral data were obtained.

(11) **11** had mp 176-177 °C. Anal. Calcd for $C_{20}H_{22}NOS_2BF_4$: C, 54.19; H, 5.00; N, 3.16. Found: C, 53.21, 53.23; H, 4.96, 4.95; N, 2.97, 2.96 (data from two samples of **11** recrystallized (three and six times, respectively). Satisfactory spectral data were obtained.

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(13) Reactions were monitored by GLC (4.1% SE-30 on Chromosorb G, 7 ft). No loss of methyl lipoate was detected in THF, EtOH, or *t*-BuOH with **6** plus DBU or in THF with **6** plus Et_3N. Methyl lipoate is also stable to acetaldehyde-Et_3N-3-benzyl-4-methylthiazolium tetrafluoroborate (45 °C) and to the enamine derived from methylated precursor **10.**

(14) Our thermodynamic argument is strongly supported by studies of α,ω-dithiol reducing potentials by R. P. Szajewski and G. M. Whitesides (private communication). The reducing potential of an α,ω-dithiol is strongly influenced by the size of the cyclic disulfide formed on its oxidation. Further, 1,3-dithiols are significantly more strongly reducing than simple thiols. We thank R.P.S. and G.M.W. (Massachusetts Institute of Technology) for communicating their results prior to publication.

(15) We have also reacted 1,2-dithiane, 1,2-dithiepane, and 1,2-dithiocane in our model system. The six-ring disulfide is stable to reaction conditions; the seven- and eight-ring disulfides polymerize. The polymerization may be initiated by attack of enamine 7 or thiazolium ylide **8** at the disulfide.

William H. Rastetter,* Julian Adams, John W. Frost
Larry J. Nummy, Jane E. Frommer, Kenneth B. Roberts
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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Mechanism of Photosubstitution of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ by Triphenylphosphine and Triisopropyl Phosphite. Direct Observation of a Binuclear Intermediate, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4\{P[OCH(CH_3)_2]_3\}$, a Molecule with a Carbonyl Bridge but No Metal-Metal Bond

Sir:

Very little is known about the mechanisms of photochemical reactions of polynuclear complexes containing bridging carbonyl ligands.[1] For this reason, we have been investigating the photochemistry of $Cp_2Fe_2(CO)_4$ (Cp = $\eta^5\text{-}C_5H_5$), a molecule in which the Fe-Fe unit is bridged by two carbonyls.[2] We communicate here the results of experiments that strongly suggest that the photosubstitution mechanism employed by $Cp_2Fe_2(CO)_4$ is quite different from that[3,4] of unbridged metal-metal-bonded binuclear complexes, a difference that can be attributed to the presence of the bridging groups.

Irradiation of $Cp_2Fe_2(CO)_4$ in the presence of PPh_3[1c] or $P(O\text{-}i\text{-}Pr)_3$ in cyclohexane solution at room temperature leads to quantitative or near-quantitative conversion to $Cp_2Fe_2(CO)_3(PR_3)$ (Figure 1):

$$Cp_2Fe_2(CO)_4 + PR_3 \xrightarrow{h\nu} Cp_2Fe_2(CO)_3(PR_3) + CO \quad (1)$$

$$R = Ph,\ O\text{-}i\text{-}Pr$$

Of particular mechanistic significance is our observation that photolysis of a solution of $Cp_2Fe_2(CO)_4$ and $P(O\text{-}i\text{-}Pr)_3$ in ethyl chloride (or THF) solution at −78 °C yields a yellow intermediate. Formation of this intermediate does not occur in the absence of $P(O\text{-}i\text{-}Pr)_3$. The yellow solution containing the intermediate turns green upon warming to room temperature, and infrared and electronic spectroscopic measurements show that conversion to $Cp_2Fe_2(CO)_3[P(O\text{-}i\text{-}Pr)_3]$[5] has occurred.

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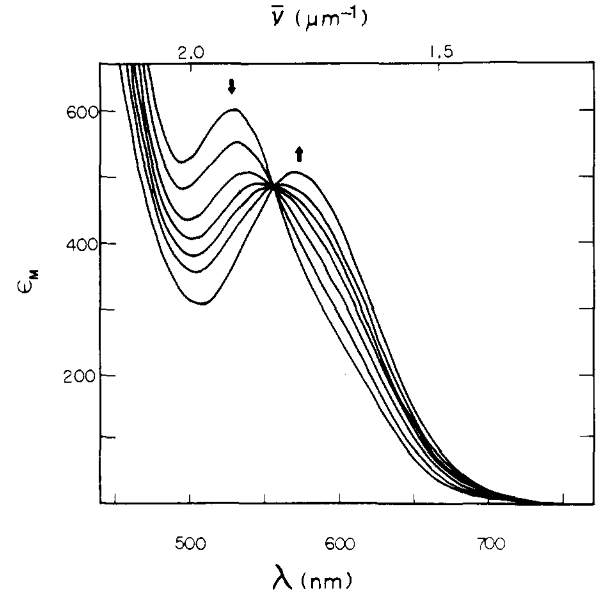
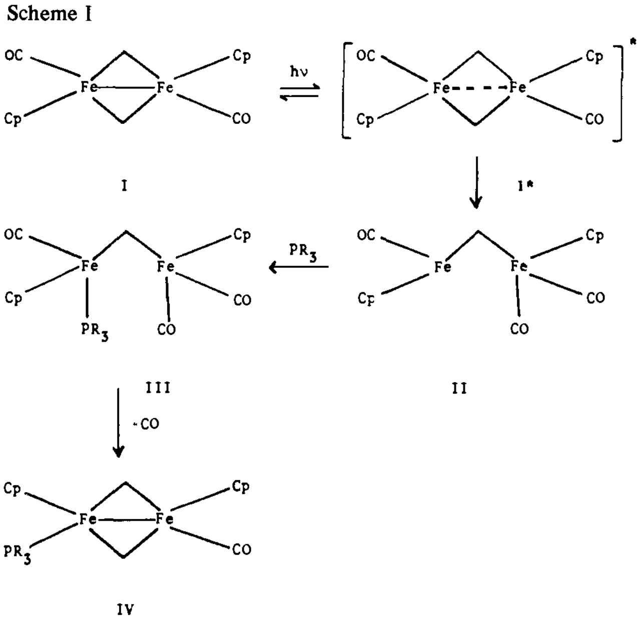


Figure 1. Spectral changes upon irradiation (λ ≥500 nm) of 1.5×10^{-3} M $Cp_2Fe_2(CO)_4$ in the presence of 0.3 M $P(O\text{-}i\text{-}Pr)_3$ in cyclohexane solution at room temperature. The disappearance quantum yield for 504-nm excitation is 0.045. A similar photoreaction is observed with PPh_3 as the entering group. In each case the same reaction is observed for 366-nm excitation. Observed conversions to $Cp_2Fe_2(CO)_3(PR_3)$ are 98 ± 2% (R = Ph) and 86 ± 5% (R = O-*i*-Pr).

Scheme I



The electronic spectrum of the yellow intermediate shows rising absorption into the ultraviolet region but no bands or shoulders are discernible between 300 and 800 nm. The important point is that the spectrum of the yellow intermediate does not have the intense $\sigma \rightarrow \sigma^*$ band of either $Cp_2Fe_2(CO)_4$ (340 nm)[6] or $Cp_2Fe_2(CO)_3[P(O\text{-}i\text{-}Pr)_3]$ (355 nm). The absence of a $\sigma \rightarrow \sigma^*$ transition in the intermediate indicates that a direct Fe–Fe bond is not present. The infrared spectrum of the yellow intermediate in THF solution at −78 °C shows a band at 1720 cm^{-1}, which is attributable to a bridging carbonyl group. We have found in addition that frozen ethyl chloride solutions containing the intermediate are EPR silent at temperatures down to 15 K.

On the basis of the evidence presented, we suggest that reaction 1 proceeds as shown in Scheme I. In this mechanistic scheme III is the yellow intermediate for R = O-*i*-Pr. It is reasonable to propose that the Fe–Fe bond is greatly weakened in the lowest $d\pi\sigma^*$ electronic excited states of $Cp_2Fe_2(CO)_4$;[1e] these excited states are collectively noted by I*. Unless significant distortion occurs in I*, the metal–metal bond will easily re-form. However, if one of the Fe–C bridging bonds breaks, an intermediate (II) is formed in which one of the Fe atoms is a 16-electron center. The coordinately unsaturated Fe can add a $P(O\text{-}i\text{-}Pr)_3$ or PPh_3 molecule to give III; upon warming, CO dissociates from III and the metal–metal bond re-forms to give the monosubstituted binuclear product. A linear Stern–Volmer plot at low PPh_3 concentrations (Figure 2) is fully consistent with the proposed mechanistic scheme.

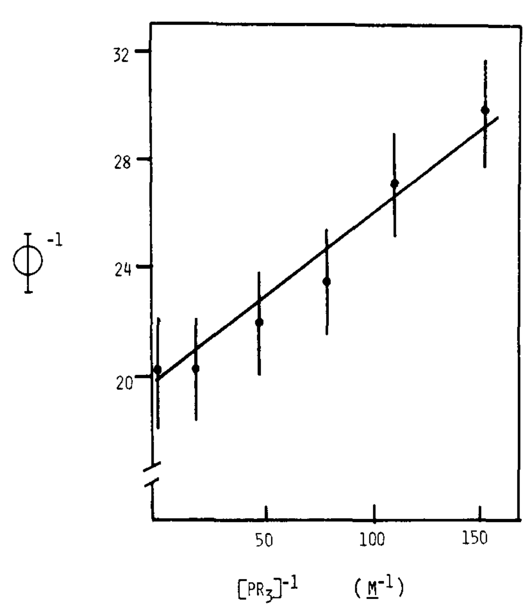


Figure 2. A Stern–Volmer plot (Φ^{-1} vs. $[PPh_3]^{-1}$) for the photoreaction of $Cp_2Fe_2(CO)_4$ with PPh_3 in toluene solution at room temperature (λ 366 nm). In benzene solution, Φ = 0.05 for 0.1 M PPh_3.[1e] Values of Φ are referenced to 0.05 as the upper limit.

It has been shown[4,7] that the photoreaction of PR_3 (R = Bu,[4] OEt,[4] Ph[7]) with $Mn_2(CO)_{10}$ yields mainly $Mn_2(CO)_8(PR_3)_2$, according to the following scheme:

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2Mn(CO)_5 \qquad (2)$$

$$Mn(CO)_5 + PR_3 \rightarrow Mn(CO)_4PR_3 + CO \qquad (3)$$

$$2Mn(CO)_4PR_3 \rightarrow Mn_2(CO)_8(PR_3)_2 \qquad (4)$$

As is observed in general for unbridged singly bonded binuclear molecules, the primary photoprocess is homolytic Mn–Mn bond cleavage;[3,4,8] this is followed by phosphine substitution in the fragment molecule, apparently by a pathway involving dissociative loss of CO.[4] If photosubstitution of $Cp_2Fe_2(CO)_4$ by PPh_3 or $P(O\text{-}i\text{-}Pr)_3$ occurred by this mechanism, we would expect to see some disubstituted product, $Cp_2Fe_2(CO)_2(PR_3)_2$.[9] Instead, the observed quantitative conversion to the monosubstituted complex is best interpreted in terms of our proposed mechanism in which all the photogenerated intermediates are binuclear species.[10]

Although it appears that the bridging CO groups in $Cp_2Fe_2(CO)_4$ play a key role in holding the two halves of the molecule together after electronic excitation, there remains the possibility that the Fe–C bridge bond in II will cleave to give mononuclear products with certain reactants. The photochemical reaction of $Cp_2Fe_2(CO)_4$ with CCl_4 to give $CpFe(CO)_2Cl$ is of interest in this regard. This reaction has been cited as evidence that the primary photoprocess upon irradiation of $Cp_2Fe_2(CO)_4$ is homolytic cleavage of the dimer to give two $CpFe(CO)_2$ fragments.[1d] However, homolytic cleavage need not be involved, as we have observed that III reacts thermally with CCl_4 to give only $CpFe(CO)_2Cl$. This result strongly suggests that mononuclear products can be formed in reactions involving II as the intermediate.

Acknowledgment. We thank Professor Mark Wrighton for sending us preprints of his papers in advance of publication. Helpful discussions with Dr. V. M. Miskowski are acknowledged. This research was supported by the National Science Foundation (CHE75-19086).

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(9) In contrast to the results for R = Ph and O-*i*-Pr, the photoreaction of $P(OMe)_3$ with $Cp_2Fe_2(CO)_4$ in cyclohexane at room temperature ($\lambda \geq 500$ nm) gives exclusively $Cp_2Fe_2(CO)_2[P(OMe)_3]_2$. This reaction does not necessarily involve homolytic cleavage, however, as we have found that III reacts thermally with $P(OMe)_3$ to give $Cp_2Fe_2(CO)_2[P(OMe)_3]_2$. Thus a pathway involving II as the intermediate is a distinct possibility. Details will be presented in a subsequent paper.

(10) It is conceivable that only monosubstituted products could result from homolytic cleavage of the Fe-Fe unit if two substituted fragments, $CpFe(CO)(PR_3)$, were sterically unable to combine to form a dimer. The Stern-Volmer plot rules out this alternative for R = Ph, however. If the fragments generated by homolysis reacted with PPh_3 by an associative pathway, then the Stern-Volmer line extrapolated from the region of high values of $[PPh_3]^{-1}$ would pass through the origin. If the fragments reacted by a dissociative mechanism, then the quantum yield would not depend on $[PPh_3]$ under the conditions used in our experiments.

David R. Tyler, Maryke A. Schmidt, Harry B. Gray*
Contribution No. 5942
Arthur Amos Noyes Laboratory
California Institute of Technology
Pasadena, California 91125

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Metamagnetic Properties of One-Dimensional Decamethylferrocenium 7,7,8,8-Tetracyano-*p*-quinodimethanide (1:1): $[Fe(\eta^5\text{-}C_5Me_5)_2]^{+}\cdot(TCNQ)^{-}\cdot$

Sir:

In the preceding paper the crystal and molecular structure of the paramagnetic decamethylferrocenium 7,7,8,8-tetracyano-*p*-quinodimethanide dimer $[(DMeFc)^{+}\cdot]_2(TCNQ_2)_2{}^{2-}$ [1a] (**1**) and one-dimensional (1 − D) $(DMeFc)^{+}\cdot(TCNQ)^{-}\cdot$ (**2**)[1b] was reported. At low temperatures **2** exhibits unusual magnetic properties which are consistent with a metamagnetic behavior.[2] A metamagnet exhibits either antiferromagnetic or ferromagnetic behavior depending on the magnitude of the applied external magnetic field. Herein we report the magnetic and Mössbauer properties of **2** and a preliminary model which describes the data.

The magnetic properties of **1**, **2**, and $DMeFc^{+}I_3{}^{-}$ (**3**) have been measured. Complex **2** obeys the Curie-Weiss expression, i.e., $\chi = c/(T - \theta)$ ($\theta = +3$ K), above 3 K, whereas **1** and **3** are similar to the ferrocenium analogue[3] and obey a simple Curie law, i.e., $\theta = 0$ K. Between 3 and 50 K the onset to ferromagnetism is observed for **2** at all magnetic fields. Below 2.5 K and at applied magnetic fields less than 1500 Oe, **2** exhibits antiferromagnetic behavior, and at applied magnetic fields greater than 1500 Oe, a ferromagnetic behavior is observed (Figure 1).

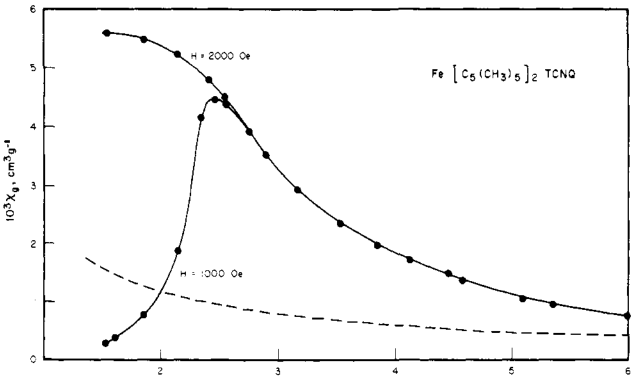

Figure 1. The magnetic susceptibility as a function of temperature between 1.5 and 6 K for **2**. The dashed line is the paramagnetism of the high temperature susceptibility extrapolated to lower temperatures. Complex **2** is antiferromagnetic below 1500 Oe and ferromagnetic above 1500 Oe.

Above 50 K the susceptibility of **2** is greater than that of **1** or **3** by one additional spin per repeat unit. The additional susceptibility arises from paramagnetic $TCNQ^{-}\cdot$ ions. This $Fe^{III}\text{-}TCNQ^{-}\cdot$ formulation results in two unpaired electrons per repeat unit and give a susceptibility in accord with the observed data. At high magnetic fields and low temperatures, the saturation moment is very close to two unpaired spins per repeat unit. This is in excellent agreement with the high temperature susceptibility. ESR data taken at 10 K do not yield any signal presumably owing to relaxation effects.[8]

The ^{57}Fe Mössbauer data taken above 4 K, **2** shows $S = 1/2$ Fe^{III}. The spectra show a single line with a quadrupole splitting of <0.3 mm s^{-1} and an isomer shift with respect to iron metal (298 K) of 0.65 (2), 0.59 (2), and 0.50 (2) mm s^{-1} at 4, 78, and 298 K, respectively. These results correspond closely to the Mössbauer data reported for ferrocenium bromide[5a] and picrate.[6b] These complexes also exhibit near-zero quadrupole splitting and isomer shifts between 0.42 and 0.58 mm s^{-1} at 78 K. In contrast decamethylferrocene, like ferrocene,[5a] exhibits a room temperature quadrupole split (2.45 mm s^{-1}) doublet at 0.42 mm s^{-1} (with respect to iron metal at 298 K).

To further confirm the metamagnetic transition the magnetic moment, σ, was obtained as a function of external magnetic field, H, at various temperatures above and below the Neél temperature, T_N, of 2.55 K (Figure 2). At lower temperatures a sharp transition is observed for **2**. The dependence of the magnetic moment on the applied field is characteristic of a metamagnet;[2,6] however, in contrast to previously reported metamagnets, e.g., $Co^{II}Cl_2$,[2a] $Fe^{II}Cl_2$,[2a] $Co^{II}(pyridine)_2Cl_2$,[2a] and $Co[PhCONHCH_2CO_2]_2\cdot 5H_2O$,[2b] **2** is not derived from an extended covalent bonding network. Long-range magnetic order presumably arises from a one-dimensional donor-acceptor interaction.

The observed metamagnetism may be understood in terms of a simple singlet-triplet model in which the Zeeman splitting γH of the triplet level may exceed the energy separation Δ between the triplet and singlet levels in zero externally applied magnetic field H. Here γ is the intrinsic moment of the triplet state. For N independent singlet-triplet assemblies, the magnetic moment induced by a field H at temperature T will be

$$\sigma = 2N\gamma[\sinh(\gamma H/kT)]/[e^{-\Delta/kT} + 1 + 2\cosh(\gamma H/kT)] \quad (1)$$

where k = Boltzmann's constant. At $T = 0$ K, eq 1 predicts an abrupt transition from a diamagnetic to a ferromagnetic state