3357

encounters a lower energetic barrier whereas in Mb ligand rebinding energetics are instantaneously those of the steady-state system.

Indeed, measurements of ligand binding energetics using temperature-dependent transient absorption techniques have established that the final barrier to ligand binding (i.e., the barrier encountered at the heme) is much larger for Mb than Hb.[16] On the basis of recent studies of ν_{Fe-His} in a large variety of R- and T-state hemoglobins, it was concluded that the variation in ν_{Fe-His} originates primarily from a protein induced tilt of the proximal histidine (within its own plane) with respect to the heme plane.[7-9,13] An increase in the tilt, which decreases ν_{Fe-His}, increases the barrier for ligand binding by making it energetically more costly to move the iron into the heme plane and thus inhibits geminate rebinding. Given the above correlation and the lower value of ν_{Fe-His} in the transient Mb species over the time course of geminate rebinding relative to Hb transients, it is possible that the reduced geminate yield,[14] the increased off rates, and the net lower affinity of Mb relative to R-state HbA[15] do not result from differences in the average steady-state tertiary structures about the heme but arise primarily from differences in the dynamics of heme–protein interactions in these proteins.

Registry No. Heme, 14875-96-8.

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Acylation of Dienyliron Anions. Selective Formation of Exo or Endo Acyl Substituted Iron Diene Complexes

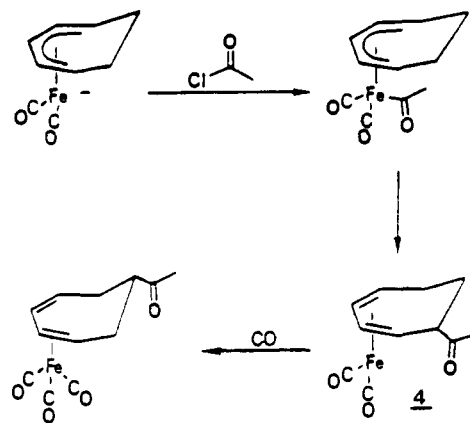Gregory M. Williams* and Duane E. Rudisill

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(Diene)iron Tricarbonyl complexes are among the more successful stoichiometric organotransition-metal reagents developed for organic synthesis. As their cationic dienyl salts, Fe(CO)$_3$ dienes react with a wide array of nucleophiles at the terminal carbon of the pentadienyl ligand, exo to the metal center.[1] In contrast, the complementary route, functionalization of iron dienes by *electrophiles*, has seen only limited development.[2-4] In this paper we report that anions derived from tricarbonyl(cycloheptatriene)iron react with acetyl chloride to provide acyl-substituted tricarbonyliron dienes. Furthermore, by controlling re-

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Scheme I

action conditions it is possible to change the nature of the iron anions such that *either* exo or endo (Acdiene)Fe(CO)$_3$ complex can be formed as the major product.

The conversion of (η^5-dienyl)iron tricarbonyl cations to their neutral iodo analogues is accomplished by reaction with potassium iodide.[5] The cycloheptadienyliodoiron species **1** is known to undergo rapid one-electron reduction to produce a metal–metal bonded dimer which is isoelectronic with [(C$_5$H$_5$)Fe(CO)$_2$]$_2$. We find that prolonged reaction between **1** and Na/Hg (THF, 7% HMPA, 25 °C, 4 h) produces a new species which we suggest is the anion (η^5-C$_7$H$_9$)Fe(CO)$_2$ (**2**).[6] Anion **2** reacts with acetyl chloride (1.3 equiv); subsequent treatment with CO (1 atm, 24 h) provides an acyl-substituted (diene)Fe(CO)$_3$ complex **3** (eq 1). Species **3** can be isolated in 45% yield as air-stable yellow

$$(1)$$
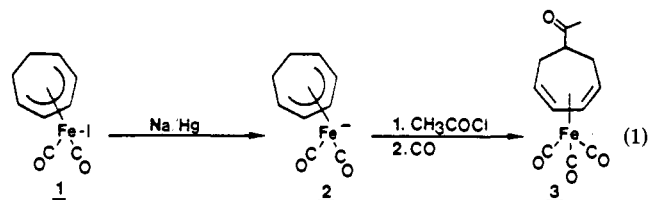
crystals. An X-ray diffraction study shows that **3** is a *symmetrical* iron diene with the acetyl group on the endo face of the coordinated diene. Proton and carbon NMR are in full accord with the proposed structure.[7]

We suggest that initial acylation of **2** occurs at the metal center to give an (η^1-acetyl)iron intermediate (Scheme I). The acyl group undergoes reductive migration to the terminal carbon of the pentadienyl ligand to provide C-5 endo-substituted (acyldiene)iron **4**. Migration of the Fe(CO)$_3$ fragment, presumably through an allyliron hydride intermediate, places the *endo*-acetyl at C-6. Steric effects could account for the isomerization of **4** to **3**. Little is known about the conformation of coordinated cycloheptadienes; however, for **3**, the ring adopts a boat conformation. Furthermore, Pearson has argued (on the basis of ^{1}H NMR data) that (5-*exo*-C$_7$H$_9$X)Fe(CO)$_2$(PR$_3$) species also prefer the boat conformation and that boat–chair interconversion should be facile.[8] If this is also the case for 5-endo-substituted species such as **3**, then steric interaction between acetyl and Fe(CO)$_3$ in the boat conformation could drive the isomerization.

Three other products have been isolated from the reaction shown in eq 1. Two of these, (cycloheptadiene)iron tricarbonyl and the known exo–exo carbon–carbon bound dimer of (C$_7$H$_{10}$)Fe(CO)$_3$ probably arise from one-electron reduction of **1**. These two products are likely derived from radical intermediates which react

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(6) IR (THF, cm^{-1}) 1980 s, 1950 s, 1887 m, 1766 s, 1716 m. The complexity of the spectrum is consistent with significant ion pairing interactions, as are common for metal carbonyl anions. For a related example, see: Pannell, K. H.; Jackson, D. *J. Am. Chem. Soc.* 1976, *98*, 4443.

(7) See the supplementary material for analytical data for compounds **3** and **5**.

at the coordinated ring; their combined yield is approximately 10%. The final product is the exo (acylidene)iron complex **5** (yellow oil, <10%). The assignment of structure of **5** is based on NMR data. Most telling are one-proton multiplets at δ 5.4 and 5.25, due to the internal protons of the coordinated diene. The external diene protons are also nonequivalent. These data clearly show the coordinated seven-membered ring to be unsymmetrical. The three-proton singlet at δ 2.1 and the IR band at 1722 cm^{-1} indicate the ring to be acyl substituted. The NMR signal at highest field (δ 1.15) is a quartet of doublets assigned to the exo proton on C-6, consistent with a boat conformation for the seven-membered ring.[7,8] In this geometry, the dihedral angle between the outer diene proton (H-4) and an endo proton on C-5 would be close to 90°. Accordingly, we observe only minor coupling (<1 Hz) between H-4 and H-5. An exo proton on C-5 (in the boat conformation) should exhibit a larger value (5-7 Hz) for J_{45}.[9] Complex **5** shows no tendency to isomerize to a symmetrical structure. Thus, after refluxing in THF for 12 h **5** can be recovered in 94% yield. There is no evidence for formation of **3**. Exo substituents at C-5 would have no steric interaction with the metal center. Accordingly, recent studies on the functionalization of cycloheptadienyliron cations with nucleophiles show exo C-5 substituted iron dienes to be configurationally stable.[8]

Isolation of *exo*-acyl **5** is intriguing in that it implies that anion **2** can act as an ambident nucleophile. We felt that it might be possible to control the reduction of **1** such that either the exo or endo (acylidene)iron complex could be prepared selectively. To promote electrophilic attack on the exo face of the dienyl ligand of **2** it was necessary to block reactivity at the metal. This was accomplished by treatment of anion **2** with CO to provide a new species, **6**, which we suggest is *tricarbonyl*iron anion.[10] Acylation of **6** provides **5** in 52% yield. The *endo*-acyl **3** is present in only minor amounts (<5%) (eq 2). Byproducts $(C_7H_{10})Fe(CO)_3$ and $[(C_7H_9)Fe(CO)_3]_2$ are formed in 10% combined yield.
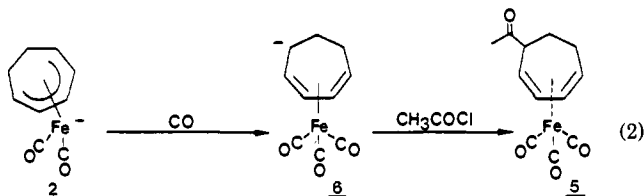
(Diene)Fe(CO)$_3$ complexes can be acylated under Friedel–Crafts conditions.[11] However, such procedures have not been well developed and appear to provide product mixtures. Our dienyliron anions should be much more versatile reagents, reacting with a wide range of organic electrophiles. Further, anions derived from **1** provide the first opportunity for selective control of stereochemistry in the functionalization of iron dienes. Extensive studies to determine the precise nature of anions **2** and **6** and their patterns of reactivity are in progress.

Supplementary Material Available: Crystallographic data, an ORTEP diagram, and tables for positional parameters and temperature factors for **3** as well as ^{1}H NMR, ^{13}C NMR, IR, and elemental analyses for **3** and **5** (9 pages). Ordering information is given on any current masthead page.

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(9) Our ^{1}H NMR analysis is in full accord with assignments of (5-*exo*- and (5-*endo*-anilinocycloheptadiene)tricarbonyliron.[7] Becker, Y.; Eisenstadt, A.; Shvo, Y. *J. Organomet. Chem.* **1978**, *166*, 63.

(10) IR (THF, cm^{-1}) 2032 s, 1972 s, 1937 s, 1852 s, 1837 s, sh. Absorptions at 2032 and 1972 are indicative of $(C_7H_{10})Fe(CO)$ and $[(C_7H_9)-Fe(CO)_3]_2$. The bands at 1937, 1852, and 1837 are consistent with the tricarbonyliron anion shown in eq 2.

(11) Johnson, B. F. G.; Lewis, J.; Parker, D. G. *J. Organomet. Chem.* **1977**, *141*, 319. Johnson, B. F. G.; Lewis, J.; Parker, D. G.; Raithby, P. R.; Sheldrick, G. M. *Ibid.* **1978**, *150*, 118. Birch, A. J.; Raverty, W. D.; Hsu, S.-Y.; Pearson, A. J. *Ibid.* **1984**, *260*, C59.

A New Fe/S Cluster with the (Fe6S6)3+ Prismatic Core and p-Methylphenolate Terminal Ligands. The Synthesis, Structure, and Properties of (Et4N)3Fe6S6(OC6H4-p-CH3)6

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In most of the non-heme iron proteins (NHIP) oligonuclear Fe/S cores, such as Fe$_2$S$_2$ or Fe$_4$S$_4$, are attached to the protein matrix by coordination to deprotonated cysteinyl S atoms and possess characteristic spectroscopic "signatures".[1] Among these proteins there exist several members that display unusual spectroscopic and magnetic characteristics and consequently do not belong to any of the generally recognized classes. These unusual characteristics have been attributed to either the coordination of common (i.e., Fe$_4$S$_4$ or Fe$_2$S$_2$) Fe/S cores by ligands other than cysteinyl thiolates or to the presence of unusual Fe/S centers. Examples of these new "unconventional" NHIP include the Rieske proteins which contain Fe$_2$S$_2$ cores attached to the protein "backbone" by less than a full complement of non-sulfur ligands[2] and Fe/S proteins that contain the Fe$_3$S$_3$[3] or Fe$_3$S$_4$[4] cores.

Recently we reported on the synthesis and structural characterization of the $(Fe_6S_6Cl_6)^{n-}$ clusters ($n = 3$,[5] 2^6). These clusters contain the Fe$_6$S$_6$ prismatic core, which is a new structural unit and belongs in the general class of the oligonuclear (FeS)$_n$ centers. The $(Fe_6S_6Cl_6)^{3-}$ cluster is characterized by a $S = 1/2$ magnetic ground state and is a metastable homologue of the $(Fe_4S_4Cl_4)^{2-}$ cluster. In hot CH$_3$CN solution, the transformation shown in eq 1 proceeds readily and quantitatively.

$$2(Fe_6S_6Cl_6)^{3-} \rightarrow 3(Fe_4S_4Cl_4)^{2-} \qquad (1)$$

At ambient (and lower) temperatures, in CH$_3$CN solution, the reaction represented by eq 1 is slow and the substitution of the terminal Cl$^-$ ligands in the $(Fe_6S_6Cl_6)^{3-}$ cluster with ligands such as RS$^-$ or RO$^-$ (R = aryl groups) can be accomplished by metathetical reactions.[5b]

In this paper we report on the properties and crystal structure of $(Et_4N)_3(Fe_6S_6(OC_6H_4-p-CH_3)_6$ (I), which is obtained in 75% yield by the reaction of $(Et_4N)_3(Fe_6S_6Cl_6)$ with the Na$^+$ salt of p-CH$_3$C$_6$H$_4$OH in CH$_3$CN at ambient temperature. The conversion of I to the corresponding cubane, by a reaction similar to the one depicted in eq 1, takes place in low yield only after prolonged heating in CH$_3$CN solution[7] and reveals exceptional stability by comparison to the halide and thiophenolate analogues. The electronic spectrum of I in CH$_3$CN solution is very similar to but broader than the spectrum of the corresponding $(Fe_4S_4(OC_6H_4-p-CH_3)_4)^{2-}$ "cubane"[8] and shows absorptions at 427 (ϵ 19 720), 272 (ϵ 42 360), and 232 nm (ϵ 62 300). This new cluster is quite sensitive to hydrolysis and represents the first example of a nonconventional (FeS)$_n$ core bound exclusively by phenolate terminal ligands.

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(6) Coucouvanis, D.; Kanatzidis, M. G.; Dunham, W. R.; Hagen, W. R. *J. Am. Chem. Soc.* **1984**, *106*, 7998.

(7) The integrity of I was monitored by ^{1}H NMR. Only after prolonged heating (ca. 2 h) in CH$_3$CN solution the characteristic isotropically shifted ^{1}H NMR spectra of the $[Fe_4S_4(OR)_4]^{2-}$ cluster begin to appear.

(8) Cleland, W. E.; Holtman, D. A.; Sabat, M.; Ibers, J. A.; DeFotis, G. C.; Averill, B. A. *J. Am. Chem. Soc.* **1983**, *105*, 6021.