Isomerization Pathways of (Acylcycloheptatriene)iron Tricarbonyl Complexes

Gregory M. Williams* and Mark J. Pino

Department of Chemistry and Biochemistry, California State University, Fullerton, California 92634

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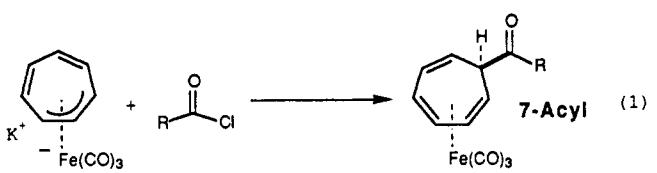
The (7-*exo*-acylcycloheptatriene)$Fe(CO)_3$ complexes (7-acyl) prepared by acylation of the mild organometallic nucleophile $(\eta^3\text{-}C_7H_7)Fe(CO)_3^-$ isomerize readily to their 5-acyl and 6-acyl isomers. The 5-acyl isomer can be prepared in high yield by deprotonation of 7-acyl or 6-acyl followed by a proton quench. Refluxing 5- or 7-acyl in methanol gives the 6-acyl isomer. Rate studies have been carried out on the sequential isomerization of 7-acyl to 5-acyl to 6-acyl. Data were obtained by ^1H NMR monitoring in methanol-d_4 at 40 °C. The results indicate that both steps of the isomerization involve an intermolecular proton-exchange mechanism. Solvent deprotonation of any of the three acyl isomers gives a common conjugate base that can be reprotonated at three sites. Kinetic protonation gives 5-acyl, and thermodynamic protonation gives 6-acyl. Mass spectral analysis shows small but significant amounts of multiple deuterium incorporation, suggesting that the common anion intermediate can also be protonated at the metal to give a transient iron hydride.

Introduction

The mild organometallic nucleophile $(\eta^3$-cycloheptatrienyl$)Fe(CO)_3^-$ has been studied in detail in recent years. Its reactions with organometallic electrophiles give a number of interesting heterobimetallic complexes linked either through the ring or by a metal–metal bond.[1-3] The anion also has potential in organic synthesis as a precursor to highly functionalized seven-membered rings. In an earlier study, we found that $K^+[(\eta^3\text{-}C_7H_7)Fe(CO)_3^-]$ reacts with acid chlorides to give (7-acylcycloheptatriene)$Fe(CO)_3$ in very good yield. Acylation occurs on the exo face of the ring, away from the $Fe(CO)_3$ fragment (eq 1).[2]



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These (7-(acyl)C_7H_7)$Fe(CO)_3$ complexes are sensitive to isomerization. In fact, in two earlier studies on the reaction of K^+ $(C_7H_7)Fe(CO)_3^-$ with alkyl chlorofomates, 7-acyls were not obtained. Instead, the isolated products had the carboalkoxy group at the 5-position (5-acyl) and/or the 6-position (6-acyl).[3]

In this paper, we describe a study of the sequential isomerization of (7-acylcycloheptatriene)$Fe(CO)_3$ complexes to their 5-acyl and 6-acyl isomers.

Results and Discussion

Preparation of 5- and (6-Acylcycloheptatriene)Fe(CO)$_3$. The (7-(acyl)C_7H_7)$Fe(CO)_3$ complexes can be converted to their 5- and 6-substituted isomers in excellent yield (Scheme I). Deprotonation of 7-acyl with KH in THF gives a deep red organoiron anion within minutes at room temperature. Addition of a stoichiometric amount of glacial acetic acid at −78 °C gives a lemon-yellow solution from which the 5-acyl isomer can be isolated (70–85%). Protonation gives only trace amounts of the 6-acyl and 7-acyl complexes (<3%). The products are purified by chromatography on Florisil; silica gel and alumina can cause extensive isomerization.

Both (7-(acyl)(C_7H_7)- and (5-(acyl)C_7H_7)$Fe(CO)_3$ can be converted to the 6-acyl isomer by refluxing in methanol for several hours. The products are isolated as yellow solids by chromatography on Florisil (80–90%). Characterization of all three isomers was discussed in a previous paper.[2a]

There was very little recovered 7-acyl in any of these reactions, and there was no evidence for isomers with the acyl group bonded to the η^4-diene fragment.

Scheme I. Conversion of (7-Acylcycloheptatriene)Fe(CO$_3$) to the 5- and 6-Acyl Isomers

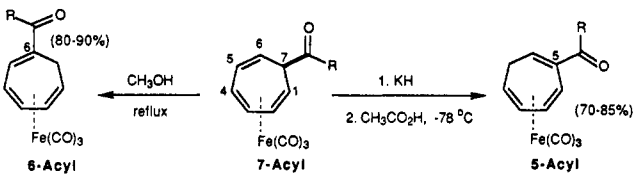

Table I. Isomerization Rate Data for the Conversion of 7-Acyl to 5-Acyl

acyl	k_{obs}, h^{-1}	$t_{1/2}$, h	rel rate
acetyl	2.0×10^{-1}	3.5	11
benzoyl	6.5×10^{-2}	11	3.5
carbomethoxy	2.4×10^{-2}	28	1.3
propionyl	1.8×10^{-2}	38	1.0
trimethylacetyl	no reacn		0

Table II. Isomerization Rate Data for the Conversion of 5-Acyl to 6-Acyl

acyl	k_{obs}, h^{-1}	$t_{1/2}$, h	rel rate
benzoyl	9.3×10^{-3}	75	8.5
carbomethoxy	5.0×10^{-3}	140	4.6
propionyl	2.3×10^{-3}	300	2.1
acetyl	1.6×10^{-3}	430	1.4
trimethylacetyl	1.1×10^{-3}	630	1.0

(1) (a) Reuvers, J. G. A.; Takats, *J. Organometallics* **1990**, *9*, 578–583. (b) Edelmann, F.; Takats, J. *J. Organomet. Chem.* **1988**, *344*, 351–356. (c) Ball, R. G.; Edelmann, F.; Kiel, G.-Y.; Takats, J. *Organometallics* **1986**, *5*, 829–839. (d) LiShingMan, L. K. K.; Reuvers, J. G. A.; Takats, J.; Deganello, G. *Organometallics* **1983**, *2*, 28–39. (e) Airoldi, M.; Deganello, G.; Dia, G.; Saccone, P.; Takats, J. *Inorg. Chim. Acta* **1980**, *41*, 171–178. (f) Bennett, M. J.; Pratt, J. L.; Simpson, K. A.; LiShingMan, L. K. K.; Takats, J. *J. Am. Chem. Soc.* **1976**, *98*, 4810–4817.

(2) (a) Williams, G. M.; Rudisill, D. E.; Barnum, B. A.; Hardcastle, K.; Heyn, R. H.; Kozak, C. J.; McMillan, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 205–215. (b) Williams, G. M.; Rudisill, D. E. *Tetrahedron Lett.* **1986**, *27*, 3465–3468.

(3) (a) Airoldi, M.; Barbera, G.; Deganello, G.; Gennaro, G. *Organometallics* **1987**, *6*, 398–403. (b) Behrens, H.; Geibel, K.; Kellner, R.; Knochel, H.; Moll, M.; Sepp, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *31B*, 1021–1022.

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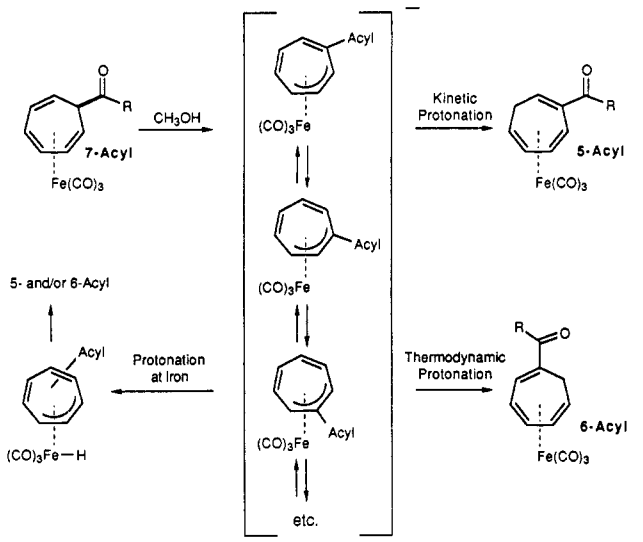
Scheme II. Mechanism of Isomerization of (Acylcycloheptatriene)Fe(CO)$_3$ Complexes



Kinetics of Isomerization. Information on the mechanism of isomerization was obtained by conducting rate studies on the conversion of 7-acyl to 5-acyl, and 5-acyl to 6-acyl. Chemical shifts of the hydrogens on the noncomplexed double bond (H-5 and H-6) are distinct for all three isomers. In each case, data were obtained by monitoring the disappearance of the signal for H-6 or H-5 (integrated relative to cyclohexane as an internal standard). Samples were sealed under vacuum in CD_3OD and maintained at a constant temperature of 40 (±1) °C. Further details are given in the Experimental Section. Results of the rate studies are summarized in Tables I and II.

Overview of the Mechanism. Previous studies on (cycloheptatriene)Fe(CO)$_3$ suggest two fundamental reactions that could account for the acyl isomerizations described herein: intermolecular proton exchange on the exo face of the ring or a reversible intramolecular ligand-to-metal hydrogen transfer.

Maltz and Kelly found that $(C_7H_8)Fe(CO)_3$ undergoes stereospecific base-catalyzed proton exchange at the 7_{exo}-position in methanol-d_4.[4] Infrared spectroscopy was used to establish the stereochemistry of the process. Brookhart, Karel, and Nance later confirmed the stereochemistry of proton exchange with a detailed ^1H NMR analysis.[5] As part of that study, (7-*exo*-DC_7H_7)Fe(CO)$_3$ was subjected to thermal isomerization in C_6D_6. Heating at 72 °C returned ^1H to the 7_{exo}-site with a half-life of about 7 h. Monitoring by ^2H NMR spectroscopy showed that the deuterium displaced from the 7_{exo}-position was incorporated in sites H-1 through H-6 about the ring. These results are consistent with a mechanism that involves reversible hydrogen transfer from the 7_{endo}-position to the metal to give the metal hydride intermediate, (η^3-C_7H_6D)$(CO)_2FeH$. Scrambling of the deuterium atom implies that rotation of the trienyl ligand in the intermediate is faster than return of the hydrogen atom to the bottom face of the ring.

In the following sections we will present evidence that the acyl-substituted cycloheptatriene complexes isomerize via exo proton exchange through a common anionic intermediate. In a minor process, protonation at the metal center gives an iron hydride that leads to small amounts of multiple deuterium incorporation in fully isomerized samples of 6-acyl. The mechanism of isomerization is presented in Scheme II.

Conversion of 7-acyl to 5-acyl. Isomerization of 7-acyl to 5-acyl occurs by a simple proton exchange. Removing the 7-endo hydrogen of 7-acyl gives the organoiron conjugate base. Formally, kinetic reprotonation at the γ-carbon of the dienolate fragment brings the acyl into conjugation with the noncomplexed double bond (Scheme II).

Data from the rate studies are consistent with the proposed mechanism. The rate of isomerization of 7-acyl to 5-acyl varies with the substituent in the following order: R = Me > Ph > OMe ≥ *n*-Pr >>> *t*-Bu (Table I).

The case for 7-endo deprotonation is best supported by the relative rates of isomerization for the three keto derivatives: acetyl, propionyl, and trimethylacetyl. At 40 °C, 7-acetyl isomerizes to 5-acetyl within 12 h, while the 7-propionyl derivative is 11 times slower. In contrast, 7-trimethylacetyl remains unchanged for weeks under identical conditions. Refluxing 7-trimethylacetyl in methanol for 60 h gives a 10% yield of 6-trimethylacetyl and 80% recovered starting material. Since the pK_a's of the these three compounds should be very similar, the difference in rates can be attributed to steric effects. Access to the 7-endo hydrogen of 7-acyl is restricted by the steric bulk of the Fe(CO)$_3$ fragment and by the acyl group in the 7_{exo} position. Even with potassium hydride, deprotonation of 7-trimethylacetyl is slow; complete conversion to the conjugate base requires 2 h at 25 °C. All other 7-acyls examined to date react with KH vigorously, giving deep red solutions of the anion within minutes at room temperature.

Electronic effects on the rate of isomerization are revealed by the data for 7-benzoyl and 7-carbomethoxy. Here, the more acidic 7-benzoyl derivative isomerizes 3.5 times faster that its 7-CO_2Me counterpart, even though the former is more hindered.

The rate data are inconsistent with an intramolecular mechanism. If isomerization occurred by abstraction of H-7_{endo} by the Fe(CO)$_3$ fragment, steric interference by the acyl group on the top side of the ring would be minimal. Instead, rates of reaction depend on both steric and electronic effects.

Evidence for exo proton exchange also comes from incorporation of deuterium in 5-acyl. The ^1H NMR spectrum of 5-acyl-d_0 shows a two-proton multiplet for the hydrogens on C-7 at δ 2.5. In CD_3OD, the resonance for H-7_{endo} of 7-acyl gradually vanishes, and a broad signal for the H-7 hydrogens of 5-acyl appears at δ 2.5. In fully isomerized samples, this signal integrates for just one hydrogen. Thus, 7-acyl to 5-acyl isomerization incorporates one deuterium atom at C-7, most likely in the exo position. An intramolecular mechanism would lead to 5-acyl-d_0.

In an attempt to promote isomerization by an iron hydride mechanism, benzene-d_6 solutions of 7-benzoyl and 7-trimethylacetyl were kept at 40 °C for 3 weeks. There was no evidence for either 5-acyl or 6-acyl. Heating for 3 days at 65 °C gave trace amounts of 6-acyl. These results do not rule out an intramolecular mechanism in *methanol*, but it is unlikely that the transition state for endo hydrogen abstraction would be sufficiently polar to cause such a solvent effect.

Conversion of 5-acyl to 6-acyl. Magnetic resonance experiments indicate that the second step of the isomerization also takes place by a proton-exchange mechanism (Scheme II). A sample of 5-benzoyl-d_0 was dissolved in

(4) Maltz, H.; Kelly, B. A. *J. Chem. Soc., Chem. Commun.* **1971**, 1390–1391.
(5) Brookhart, M.; Karel, K. K.; Nance, L. E. *J. Organomet. Chem.* **1977**, *140*, 203–210.

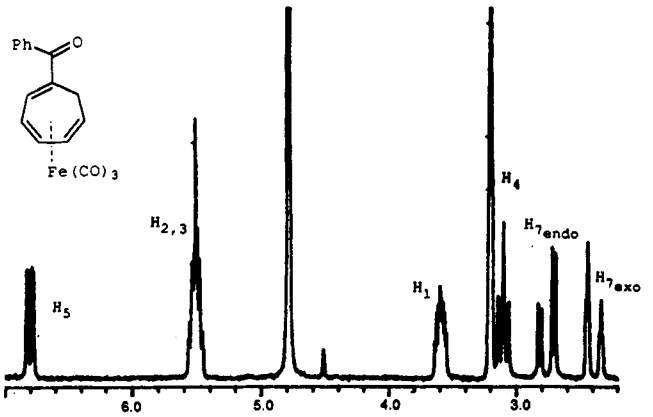


Figure 1. ^{1}H NMR spectrum of (6-benzoylcycloheptatriene)-$Fe(CO)_3$.

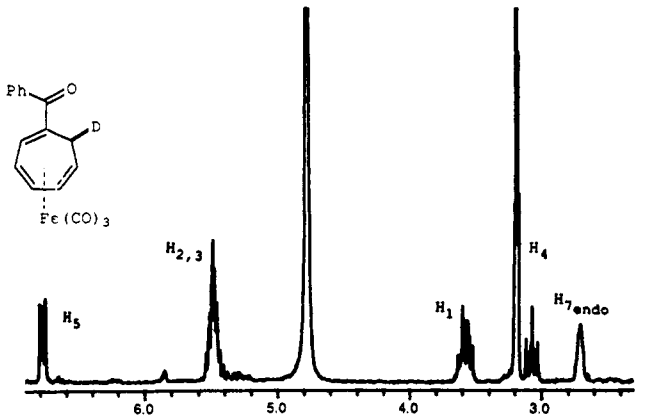


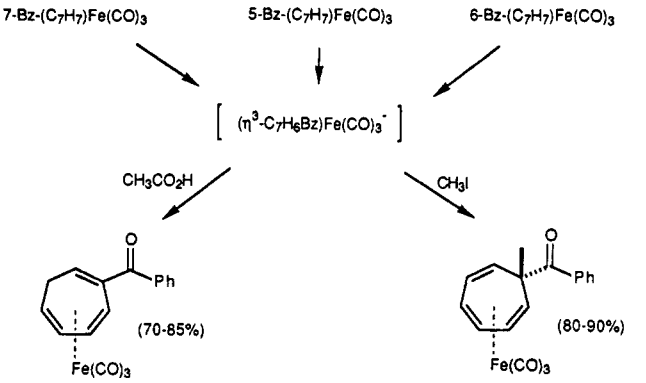
Figure 2. ^{1}H NMR spectrum of (6-benzoyl-7-*exo*-deuteriocycloheptatriene)$Fe(CO)_3$.

methanol-d_4. After 24 h at 40 °C, the integrated intensity of the H-7_{exo}/H-7_{endo} multiplet had diminished to one hydrogen. Thus, 5-benzoyl-d_0 is converted to 5-benzoyl-7_{exo}-d_1 before 6-benzoyl can be detected. Isomerization of 5-benzoyl-7_{exo}-d_1 to 6-benzoyl takes 11 days at 40 °C.

The ^{1}H NMR spectrum of 6-benzoyl-d_0 shows distinct signals for H-7_{endo} (δ 2.86; dd; J_{gem} = 22 Hz, $J_{1\text{-}7_{endo}}$ = 5.7 Hz, $J_{5\text{-}7_{endo}} \approx 0$) and H-$7_{exo}$ (δ 2.56; dt; $J_{1\text{-}7_{exo}}$ = 2.7 Hz, $J_{5\text{-}7_{exo}}$ = 2.2 Hz). The magnitudes of the coupling constants ($J_{1\text{-}7_{endo}} > J_{1\text{-}7_{exo}}$ and $J_{5\text{-}7_{exo}} > J_{5\text{-}7_{endo}}$) and the relative chemical shifts (endo downfield of exo) are in full agreement with Brookhart's very thorough analysis of the ^{1}H NMR spectrum of (cycloheptatriene)$Fe(CO)_3$.[5] Isomerized samples of 6-benzoyl show a broad one-hydrogen singlet at δ 2.87, consistent with incorporation of one deuterium atom in the 7_{exo}-position. The spectra of 6-benzoyl-7_{exo}-d_1 and 6-Benzoyl-d_0 are shown in Figures 1 and 2. Since 7-exo proton exchange is faster than the conversion of 5-acyl to 6-acyl, an intramolecular mechanism through an iron hydride intermediate would result in multiple deuterium incorporation.

Rate data are also in accord with an exo proton exchange for this step of the isomerization. Rates vary with acyl substituent in the following order: Ph > OMe > *n*-Pr > Me > *t*-Bu (Table II). As expected, the three alkyl acyls isomerize at comparable rates. Since the intermediate anion is formed by removing an exo hydrogen, steric effects of the acyl group are minimal. Isomerization of the benzoyl derivative is the fastest of the group, consistent with a lower pK_a. The carbomethoxy compound is converted to the 6-acyl isomer more rapidly than one would expect on the basis of pK_a arguments, but the rate study examines *overall* isomerization, not the rate of deprotonation. The

Scheme III. Deprotonation of All Three Acyl Isomers Giving the Same Conjugate Base



σ-withdrawing capacity of the methoxy group may accelerate this isomerization.

Rate studies show that isomerization of 5-acyl to 6-acyl is approximately 10 times slower than the conversion of 7-acyl to 5-acyl. In fully isomerized samples, the final ratio of products is 4:1 in favor of 6-acyl. The 7-acyl isomer cannot be detected in equilibrium mixtures. Heating for months at 40 °C does not change the distribution of isomers. To verify the equilibrium position, a sample of 6-benzoyl was monitored by ^{1}H NMR spectroscopy (CD_3OD, 40 °C). Integration after 160 h gave the expected 4:1 mixture.

Isomerization of 5-acyl to 6-acyl requires rotation of the seven-membered ring in the intermediate anion. The parent anion, $(C_7H_7)Fe(CO)_3^-$, is highly fluxional; the ^{1}H NMR spectrum of the PPN^+ salt shows a singlet for the seven ring hydrogens at temperatures as low as −160 °C.[1d] A variable-temperature ^{1}H NMR study of the $[(CO_2Et)C_7H_6]Fe(CO)_3^-$ anion was performed by Deganello et al.[3a] At room temperature, the spectrum of this anion shows three groups of broad signals for the ring hydrogens, consistent with η^3-binding for the trienyl ligand. As the temperature is lowered, all signals broaden and disappear into the baseline at −82 °C.

Evidence for a Common Intermediate. Both steps of the isomerization involve a common conjugate base in which the $Fe(CO)_3$ fragment disrupts the ring π-system, thereby eliminating the antiaromatic character of the acylcycloheptatrieneide anions. The common intermediate is most likely a fluxional (η^3-trienyl)$Fe(CO)_3$ anion. In addition to the NMR evidence presented above, X-ray crystallography confirms η^3-binding in $[Ph_4As^+][(\eta^3\text{-}C_7H_7)Fe(CO)_3^-]$,[6] and molecular orbital calculations suggest that the η^3-trienyl form is slightly lower in energy than the alternative formulation, an allyl anion bound to a neutral (η^4-diene)$Fe(CO)_3$ complex.[7] This also seems to be the case for the acyl derivatives. The formyl anion (η^3-CHO-C_7H_6)$Fe(CO)_3$ crystallizes in the η^3-mode with the formyl group bonded to the central carbon of the allyl fragment.[8]

Evidence for a common intermediate in the two steps of the isomerization comes from anion-quenching experiments. Stoichiometric deprotonation of any of the three benzoyl isomers with potassium hydride provides a deep red solution that reacts with methyl iodide to give the known compound [7,7′-*exo*-Me-*endo*-Bz-C_7H_6]$Fe(CO)_3$.[2] Quenching the anion with acetic acid gives 5-benzoyl (Scheme III).

(6) Sepp, E.; Purzer, A.; Thiele, G.; Behrens, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 261–264.
(7) Hofmann, P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 251–260.
(8) Takats, J. Personal communication.

Table III. Deuterium Incorporation during Isomerization of ((Benzoyl)C_7H_7)Fe(CO)$_3$

reacn	time	% d_0	% d_1	% d_2	% d_3	% (d_4 + d_5)
5 → 6	160 h	7	41	37	15	0
6 → 5	160 h	41	31	19	9	0
7 → 6	180 h	0	34	39	21	6
7 → 6	3 mo	0	24	33	28	15

Mass Spectrometric Analysis for Deuterium Incorporation. In order to verify deuterium incorporation during acyl isomerization, several samples of 6-benzoyl from our rate studies were analyzed by mass spectrometry. The parent ions of these compounds were not observed, so the mass envelope around the (M^+ - CO) peak was examined for deuterium incorporation. The results are summarized in Table III.

The data show that isomerization occurs with a small, but significant amount multiple deuterium incorporation. A sample of 6-benzoyl brought forward from the parent 7-d_0 isomer was 34% d_1, 39% d_2, 21% d_3, and 6% d_4 + d_5. However, the ^{1}H NMR spectrum of the same sample showed deuterium incorporation only at the 7$_{exo}$-position (Figure 1). In addition, the ^{13}C NMR spectrum of fully isomerized 6-benzoyl shows deuterium coupling only to C-7 (28.9 ppm, t, J_{C-D} = 20.2 Hz). These results suggest that deuterium is *always* present at the 7$_{exo}$-position, but the other deuterium atoms are scrambled through the other six sites around the ring. There is not quite enough deuterium at any one site to be detected by integration of the ^{1}H NMR spectrum, and long-term acquisition failed to improve the signal to noise ratio of the ^{13}C NMR spectrum enough to observe deuterium coupling to any ring position except C-7.

A two-step exo proton exchange process for the conversion of 7-acyl to 6-acyl incorporates only one deuterium atom in the isomerized product. Multiple deuterium incorporation suggests that the intermediate anion is occasionally protonated at the metal center, giving (η^3-(acyl)C_7H_7)Fe(CO)$_3$D. Reductive elimination introduces a deuterium atom at the 7$_{endo}$-position and pushes a hydrogen atom to the 7$_{exo}$-site. Now, exo proton exchange gives 5-acyl-d_2, or, eventually, 6-acyl-d_2. Scrambling the "extra" deuterium atoms throughout the ring suggests that rotation of the η^3-trienyl ligand is fast compared to reductive elimination of deuterium to the 7$_{endo}$-position. This was the case in Brookhart's study of (C_7H_7D)Fe(CO)$_3$, as discussed above.[5]

Conclusions

Isomerization of (7-acylcycloheptatriene)Fe(CO)$_3$ occurs in methanol by a proton-exchange mechanism through the 5-acyl intermediate to give 6-acyl as the final product. Solvent deprotonation of any of the three acyl isomers gives a common conjugate base that can be reprotonated at one of three sites. Kinetic protonation gives 5-acyl, and thermodynamic protonation gives 6-acyl. The equilibrium mixture of these two isomers is ca. 4:1. Multiple deuterium incorporation in isomerized samples points to a minor pathway in which the common anionic intermediate is protonated at the metal center to give a transient iron hydride.

Experimental Section

General Considerations. The preparation of all compounds was conducted in the absence of water and oxygen using Schlenk techniques and/or a Vacuum Atmospheres MO40-2 drybox. Tetrahydrofuran (THF) was distilled from sodium–benzophenone. Cycloheptatriene (Aldrich) and iron pentacarbonyl (Aldrich) were used as obtained to prepare (cycloheptatriene)iron tricarbonyl by a literature method.[9] Acid halides were distilled from calcium hydride and deoxygenated by freeze–pump–thaw cycles. Potassium hydride was stored and used in a drybox as a solid after the oil was removed by hexane extraction. Reaction mixtures were separated and purified by flash column chromatography using Florisil (100–200 mesh) under aerobic conditions with reagent grade anhydrous diethyl ether and 30–60 petroleum ether. All magnetic resonance spectra were recorded on a Bruker AC200 spectrometer (200 MHz ^{1}H; 50.3 MHz ^{13}C). Spectra are reported in ppm from internal tetramethylsilane. All coupling constants are reported in Hz. Infrared spectra were obtained on a Perkin-Elmer 1310 spectrometer. Mass spectra were recorded at the University of California, Riverside. Elemental analyses were performed by Galbraith Laboratories, Inc.

Preparation of (7-Acylcycloheptatriene)Fe(CO)$_3$. With the exception of the propionyl derivative, the 7-acyl species used in this study were known compounds.[2]

[1-4-η-(7-*exo*-Propionyl)cycloheptatriene]iron Tricarbonyl (7-Propionyl). A THF solution of [K^+][(C_7H_7)Fe(CO)$_3^-$] was added dropwise to an excess of propionyl chloride as described previously.[2] The resulting murky yellow-orange solution was filtered through Florisil; removal of solvent left a brown oil. Purification on Florisil (15:1 petroleum ether/Et_2O) gave a 75% yield of the desired product as an orange oil: ^{1}H NMR ($CDCl_3$) 5.96 (m, 1 H, H-5, J_{5-6} = 10.5, J_{5-7} = 1.5, J_{5-4} = 8.0), 5.40 (m, 2 H, H-2, 3), 5.16 (dd, 1 H, H-6, J_{6-7} = 4.5), 3.47 (dt, 1 H, H-7), 3.05 (br t, 2 H, H-1, 4), 2.45 (m, 2 H, H-C(O)CH_2CH$_3$), 1.00 (t, 3 H, Me); ^{13}C NMR ($CDCl_3$) 210.3 (Fe—CO), 202.1 (C=O), 131.5, 122.7 (C-5, 6), 94.6, 88.2 (C-2, 3), 58.2, 57.5, 55.2 (C-1, 4, 7), 32.6 (C(O)CH_2CH$_3$), 8.0 (C(O)CH$_2$CH_3); IR (cyclohexane) 2052, 1982, 1718 cm^{-1}; HRMS $C_{13}H_{12}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{12}H_{12}O_3Fe$ (M^+ - CO) 260.0138, found 260.0136.

Isomerization of 7-Acyl to 5-Acyl. [1-4-η-(5-Carbomethoxy)cycloheptatriene]iron Tricarbonyl (5-CO_2Me). In a general procedure, a THF solution of 7-CO_2Me (1.0 g, 3.5 mmol) was deprotonated with KH as described previously.[2] The anion was cooled to −78 °C, and 0.21 mL (3.6 mmol) of glacial acetic acid was added by syringe. The mixture was warmed slowly to room temperature to give a bright yellow solution. Filtration through Florisil and removal of the solvent left a yellow solid. Purification on Florisil (20:1 petroleum ether/Et_2O) gave 0.76 g (76%) of 5-CO_2Me as a yellow solid. Alternatively, 5-CO_2Me was synthesized starting with 6-CO_2Me. Deprotonation with KH, protonation by acetic acid, and workup by chromatography on Florisil (10:1 petroleum ether/Et_2O) gave the desired yellow solid in 83% yield. All spectroscopic data for 5-CO_2Me are in complete agreement with the literature.[3a]

[1-4-η-(5-Benzoyl)cycloheptatriene]iron Tricarbonyl (5-Benzoyl). Chromatography on Florisil with 15:1 petroleum ether/Et_2O gave a yellow solid (80%): ^{1}H NMR ($CDCl_3$) 7.63, 7.46 (m, 5 H, Ph), 5.98 (dt, 1 H, H-6, J_{6-4} = 1.3, J_{6-7} = 4.5), 5.46 (qd, 1 H, H-3, J_{3-1} = 1.5, J_{3-2} = 7.8, J_{3-4} = 6.7), 5.38 (dd, 1 H, H-2, J_{2-1} = 7.7, J_{2-3} = 7.8), 3.81 (dd, 1 H, H-4, J_{4-2} = 1.1, J_{4-3} = 6.7, J_{4-6} = 1.3), 3.31 (m, 1 H, H-1, J_{1-2} = 7.7, J_{1-3} = 1.5, J_{1-7} = 4.3), 2.57 (m, 2 H, H-7, 7′, J_{7-7} = 24); ^{13}C NMR ($CDCl_3$) 210.6 (Fe—CO), 197.0 (C=O), 140.5, 138.9, 138.0, 128.0 (phenyl, C-5, 6), 93.3, 89.2 (C-2, 3), 57.4, 53.1 (C-1, 4), 30.7 (C-7); IR ($CHCl_3$) 2051, 1985, 1645 cm^{-1}. Anal. Calcd for $C_{17}H_{12}O_4Fe$: C, 60.75; H, 3.60. Found: C, 60.68; H, 3.63.

[1-4-η-(5-Acetyl)cycloheptatriene]iron Tricarbonyl (5-Acetyl). Chromatography on Florisil with 10:1 petroleum ether/Et_2O gave an orange oil (72%): ^{1}H NMR ($CDCl_3$) 6.38 (dt, 1 H, H-6), 5.32 (m, 2 H, H-2, 3), 3.88 (dd, 1 H, H-4), 3.24 (m, 1 H, H-1), 2.49 (dt, 2 H, H-7, 7) 2.25 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$) 210.2 (Fe—CO), 198.1 (C=O), 144.4, 136.2 (C-5, 6), 94.1, 89.3 (C-2, 3), 58.7, 52.9 (C-1, 4), 29.5, 25.9 (C-7, Me). All spectra for 5-acetyl are in complete agreement with the literature.[10]

[1-4-η-(5-Trimethylacetyl)cycloheptatriene]iron Tricarbonyl (5-Trimethylacetyl). Chromatography on Florisil with 25:1 petroleum ether/Et_2O gave a yellow solid (76%): ^{1}H NMR ($CDCl_3$) 5.68 (dt, 1 H, H-6, J_{6-7} = 4.4), 5.29 (m, 2 H, H-2, 3), 3.21 (m, 2 H, H-1, 4, J_{4-6} = 0.9), 2.45 (qt, 2 H, H-7, 7, J_{7-1} = 4.1, J_{7-7}

(9) Burton, R.; Pratt, L.; Wilinson, G. *J. Chem. Soc.* **1961**, 594–602.
(10) Cunningham, D.; McArdle, P.; Sherlock, H.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1972**, 2340.

= 23), 1.18 (9H, *tert*-butyl); ^{13}C NMR ($CDCl_3$) 210.6 (Fe—CO), 210.0 (C=O), 140.6, 127.7 (C-5, 6), 92.7, 89.2 (C-2, 3), 57.7, 54.4 (C-1, 4), 44.1 (C-7), 29.9, 28.1 (*tert*-butyl); IR (cyclohexane) 2070, 1990, 1665 cm^{-1}; HRMS $C_{15}H_{16}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{14}H_{16}O_3Fe$ ($M^+ - CO$) 288.0449, found 288.0448.

[1-4-η-(5-Propionyl)cycloheptatriene]iron Tricarbonyl (5-Propionyl). Chromatography on Florisil with 15:1 petroleum ether/Et_2O gave an orange oil (84%): ^1H NMR ($CDCl_3$) 6.34 (dt, 1 H, H-6, J_{6-7} = 4.2), 5.33 (m, 2 H, H-2, 3), 3.84 (dd, 1 H, H-4), 3.22 (m, 1 H, H-1), 2.53 (m, 4 H, H-7, 7, CH_2), 1.05 (t, 3 H, Me); ^{13}C NMR ($CDCl_3$) 210.6 (Fe—CO), 200.2 (C=O), 140.4, 135.0 (C-5, 6), 93.0, 89.1 (C-2, 3), 57.1, 51.3 (C-1, 4), 30.6, 30.4, 8.8 (C-7, CH_2CH_3); IR (cyclohexane) 2059, 1988, 1684 cm^{-1}; $C_{13}H_{12}O_4Fe$ (M^+) not observed; *m/e* calcd for $C_{12}H_{12}O_3Fe$ ($M^+ - CO$) 260.0138, found 260.0136.

Preparation of [1-4-η-(6-Carbomethoxy)cycloheptatriene]iron Tricarbonyl (6-CO_2Me). In a general procedure, CH_3OH (40 mL) and 1.0 g (3.45 mmol) of 5-CO_2Me were refluxed together for 18 h. Reaction progress was monitored by thin-layer chromatography. Removal of the solvent and chromatography on silica gel (20:1 petroleum/Et_2O), left a yellow solid (89%). All spectral data for 6-CO_2Me were in complete agreement with the literature.[3a] The same product was isolated in 81% yield starting with 7-CO_2Me. When this reaction was conducted with a catalytic amount of sodium methoxide, 6-CO_2Me was isolated in 85% yield after 1 h of reflux.

[1-4-η-(6-Benzoyl)cycloheptatriene]iron Tricarbonyl (6-Benzoyl). Chromatography on silica gel (10:1 petroleum ether/Et_2O) and recrystallization gave a yellow solid (80%) whose spectra agree with literature data:[11] ^1H NMR ($CDCl_3$) 7.46 (m, 5 H, Ph), 6.85 (dt, 1 H, H-5, $J_{5-7_{exo}}$ = 2.2, $J_{5-7_{endo}} \approx 0$), 5.45 (m, 2 H, H-2, 3), 3.62 (m, 1 H, H-1, $J_{1-7_{endo}}$ = 5.2, $J_{1-7_{exo}}$ = 2.7), 3.02 (m, 1 H, H-4, J_{4-5} = 8.4), 2.86 (dd, 1 H, H-7_{endo}, $J_{7_{exo}-7_{endo}}$ = 22), 2.56 (dt, 1 H, H-7_{exo}); ^{13}C NMR (CD_3OD) 211.6 (Fe—CO), 190.0 (C=O), 151.0, 132.3 (C-5, 6), 129.7, 192.2 (Ph), 96.1, 90.6 (C-2, 3), 62.0, 55.3 (C-1, 4), 30.0 (C-7); IR (cyclohexane) 2052, 1983, 1628 cm^{-1}. Alternatively, the same product was synthesized in 88% yield starting from 7-benzoyl.

[1-4-η-(6-Acetyl)cycloheptatriene]iron Tricarbonyl (6-Acetyl). Chromatography on Florisil (12:1 petroleum ether/Et_2O) gave a yellow-orange solid (83%). Alternatively, the same product was synthesized in 81% yield starting from 7-acetyl. All spectroscopic data for 6-acetyl were in complete agreement with the literature.[11]

[1-4-η-(6-Trimethylacetyl)cycloheptatriene]iron Tricarbonyl (6-Trimethylacetyl). After refluxing 5-trimethylacetyl in methanol for 60 h, chromatography on silica (20:1 petroleum ether/Et_2O) gave a yellow-orange solid (80%): ^1H NMR ($CDCl_3$) 7.00 (dd, 1 H, H-5), 5.35 (m, 2 H, H-2, 3), 3.47 (m, 1 H, H-1, $J_{1-7_{endo}}$ = 5.3), 3.06 (m, 1 H, H-4, J_{4-3} = 6.9, J_{4-5} = 8.2), 2.61 (dd, 1 H, H-7_{endo}, $J_{7_{exo}-7_{endo}}$ = 22), 2.38 (dt, 1 H, H-7_{exo}), 1.66 (s, 9 H, *tert*-butyl); ^{13}C NMR ($CDCl_3$) 210.3 (Fe—CO), 206.3 (C=O0, 139.7, 124.9 (C-5,6), 93.8, 88.7 (C-2, 3), 60.1, 53.5 (C-1, 4), 29.7, 28.8 (C-7, *tert*-butyl); IR (cyclohexane) 2060, 1987, 1660 cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_4Fe$: C, 56.98; H, 5.10. Found: C, 56.86; H, 5.06. Refluxing 7-trimethylacetyl in methanol for 60 h gave 10% 6-trimethylacetyl and 81% recovered starting material.

[1-4-η-(6-Propionyl)cycloheptatriene]iron Tricarbonyl (6-Propionyl). Chromatography on Florisil (15:1 petroleum ether/Et_2O) and removal of solvent gave a yellow-orange solid (86%): ^1H NMR ($CDCl_3$) 7.08 (dd, 1 H, H-5, $J_{5-7_{exo}}$ = 1.7), 5.37 (m, 2 H, H-2, 3), 3.49 (m, 1 H, H-1), 3.07 (dt, 1 H, H-4, J_{4-3} = 7.2, J_{4-5} = 8.4), 2.69 (dd, 1 H, H-7_{endo}, $J_{7_{exo}-7_{endo}}$ = 22.4), 2.31 (dt, 1 H, H-7_{exo}), 2.49 (m, 2 H, CH_2), 1.03 (t, 3 H, Me); ^{13}C NMR ($CDCl_3$) 210.1 (Fe—Co), 200.3 (C=O), 142.4, 134.9 (C-5, 6), 94.1, 88.9 (C-2, 3), 60.3, 53.5, (C-1, 4), 29.7, 28.6, 8.9 (C-7, (CO)-$CH_2CH_2CH_3$); IR (cyclohexane) 2052, 1988, 1667 cm^{-1}; HRMS $C_{13}H_{12}O_4OFe$ (M^+) not observed; *m/e* calcd for $C_{12}H_{12}O_3Fe$ ($M^+ - CO$) 260.0138, found 260.0136. Anal. Calcd for $C_{13}H_{12}O_4Fe$: C, 54.20; H, 4.20. Found: C, 54.60; H, 4.24. Alternatively, the same product was synthesized in 83% yield starting from 7-propionyl.

Preparation of Samples for NMR-Monitored Rate Studies. All samples for rate studies were 0.70 M in Fe. In a general procedure, 7-CO_2Me (13.4 mg, 0.049 mmol) was dissolved in 0.70 mL of CD_3OD. Cyclohexane, 1.0 μL, was added as an integration standard. The sample was degassed by three freeze–pump–thaw cycles, and the tube was sealed under vacuum. The sample was placed in a constant-temperature bath (40.0 °C) for the duration of the experiment. All samples were monitored until equilibrium was established. Pseudo-first-order data were linear with R^2 values in excess of 0.985, except for 7-propionyl → 6-propionyl, for which R^2 = 0.979. There was little or no thermal decomposition of the organometallic complexes, even after months of heating at 40.0 °C.

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Registry No. 5-acetyl, 66615-42-7; 6-acetyl, 36594-82-8; 7-acetyl, 107407-06-7; 5-benzoyl, 107493-71-0; 6-benzoyl, 36630-33-8; 7-benzoyl, 107407-10-3; 5-CO_2Me, 106095-10-7; 6-CO_2Me, 106095-12-9; 7-CO_2Me, 107440-24-4; 5-propionyl, 137124-50-6; 6-propionyl, 137124-52-8; 7-propionyl, 137124-54-0; 5-trimethylacetyl, 137124-51-7; 6-trimethylacetyl, 137124-53-9; 7-trimethylacetyl, 107407-08-9.

(11) Johnson, B. F. G.; Lewis, J.; McArdle, P.; Randall, G. L. P. *J. chem. Soc., Dalton Trans.* **1972**, 456.