Sequential Friedel–Crafts Diacetylation of Ferrocene: Interannular Proton Transfers as a Mechanistic Probe[1]

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(Pentadeuteriocyclopentadienyl)cyclopentadienyliron(II), **4**, was prepared by the sequential addition of lithium tris(trimethylsilyl)cyclopentadienide and lithium pentadeuteriocyclopentadienide to $FeBr_2$ followed by fluoride-induced removal of the trimethylsilyl groups of the resulting ferrocene **3**. Analysis of the deuterium content of the acetylferrocene **5** and the 1,1′-diacetylferrocene **7**, obtained from the Friedel–Crafts acetylation of **4**, reveals that the former is formed by initial exo attack of $AlCl_3$–CH_3COCl, whereas precomplexation of the electrophile at the metal center (endo attack) precedes the formation of the latter.

Introduction

Since the aromatic properties of ferrocene were first revealed,[2] the mechanisms of its electrophilic substitution reactions have received considerable attention. Theoretically, the primary electrophilic attack of ferrocene can occur at two different sites: at the metal center to afford the cationic C_{2v} ferrocenium species **1** or directly at a carbon atom of a cyclopentadienyl ring to generate one of the σ-complexes **2a** or **2b** (Scheme 1). Support for initial attack at iron stems from the observation that ferrocene is protonated at the iron atom and undergoes proton exchange in highly acidic media.[3] Furthermore, the intermediacy of a species such as **1** can serve to explain why certain electrophiles, rather than undergoing substitution at carbon, effect the oxidation of ferrocene to the ferrocenium cation.[4] Direct attack of the cyclopentadienyl ring, without metal intervention, has been proposed to occur via two different modes depending upon the strength of the electrophile.[5] Strong electrophiles (e.g. RCOCl–$AlCl_3$) attack exo to furnish the σ-complex **2b** whereas weak electrophiles (e.g. $HgCl_2$) attack the more electron-rich endo face of the cyclopentadienyl ring to afford **2a**. Proton exchange, on the other hand, is assumed to proceed via both exo and endo attack. This mechanistic scheme was substantiated with kinetic evidence.

Recent studies in our laboratory have shown that the Friedel–Crafts acetylation of 1,1′-bis(trimethylsilyl)- and 1,1′-bis(tributylstannyl)ferrocene occurs by exo attack of the acylating agent with stepwise or concurrent protonation of the metal center (Scheme 2).[6] The subsequent transfer of the proton from the metal to either of the cyclopentadienyl rings results in the exo elimination of a trimethylsilyl or tributylstannyl group. The intramolecular nature of such proton transfers was unequivocally proved through isotopic labeling. An assessment of the generality of this mechanism, however, is only possible through the elucidation of the effect of the silyl and stannyl substituents on the mode of electrophilic attack and on the fate of the metal hydride. The steric bulk of these groups could hinder the approach of the electrophile to the metal center thereby excluding endo attack whereas their facile protonolysis may serve as the driving force for the intramolecular proton transfers. Through the synthesis and study of (pentadeuteriocyclopentadienyl)cyclopentadienyliron (**4**), we have now determined that whereas the acetylation of ferrocene does indeed proceed via exo attack of the acylating agent, the formation of diacetylferrocenes must result from endo attack.

Results and Discussion

The preparation of the pentadeuterated ferrocene **4** is outlined in Scheme 3. The sequential treatment of iron(II) bromide in THF at −78 °C with lithium tris(trimethylsilyl)cyclopentadienide[7] and lithium pentadeuteriocyclopentadienide,[8] according to the procedure of Okuda and Herdtweck,[9] followed by warming to room temperature afforded the silylated ferrocene **3** in 68% yield. This represents a great improvement over the published synthesis (30%) in which the less soluble iron(II) halide–1.5THF adducts were employed.[10] Treatment of **3** with tetrabutylammonium fluoride in HMPA at 70 °C for 16 h afforded **4** in over 90% yield. The mass spectrum of **4** exhibits a molecular peak at *m/e* 191 and peaks corresponding to the $C_5H_5Fe^+$ and $C_5D_5Fe^+$ fragments at *m/e* 121 and 126, respectively. Comparison of its mass spectrum with that of ferrocene-d_0 reveals that the former contains ~4.98 deuterium atoms and is composed of ~98% 4-d_5 and 2% 4-d_4. In the undecoupled ^{13}C NMR spectrum of **4**, the deuterated cyclopentadienyl ring appears as a broad triplet at 67.43 ppm (J = 26 Hz) whereas its protonated counterpart is a double pentet centered at 67.75 ppm (J = 176 and 7 Hz).

The acetylation of **4** was achieved by adding powdered $AlCl_3$ to a solution of **4** and acetyl chloride in CH_2Cl_2 at

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(1) Presented at the Seventh IUPAC Symposium on Organo-metallic Chemistry Directed Towards Organic Synthesis, Kobe, Japan, September 19–23, 1993.

(2) Woodward, R. B.; Rosenblum, M.; Whiting, M. C. *J. Amer. Chem. Soc.* **1952**, *74*, 3458–3459.

(3) (A) Curphey, T. J.; Santer, J. O.; Rosenblum, M.; Richards, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 5249–5250. (b) Bitterwolf, T. E.; Ling, A. C. *J. Organomet. Chem.* **1972**, *40*, 197–203.

(4) Rosenblum, M.; Santer, J. O.; Howells, W. G. *J. Am. Chem. Soc.* **1963**, *85*, 1450–1458.

(5) Mangravite, J. A.; Traylor, T. G. *Tetrahedron Lett.* **1967**, 4461–4466.

(6) Cunningham, A. F., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 4864–4870.

(7) Jutzi, P.; Sauer, R. *J. Organomet. Chem.* **1973**, *50*, C29–C30.

(8) (a) Zagorski, M. G.; Salomon, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 3498–3503. (b) Gallinella, E.; Mirone, P. *J. Labelled Comp.* **1971**, *7*, 183–4.

(9) Okuda, J.; Herdtweck, E. *Chem. Ber.* **1988**, *121*, 1899–1905.

(10) The quality of the $FeBr_2$ is determinant: commercial samples which are dark brown rather than light yellow in color afford inferior yields. $FeBr_2$·1.5THF precipitates from a solution of $FeBr_2$ in THF upon standing at room temperature for several hours.

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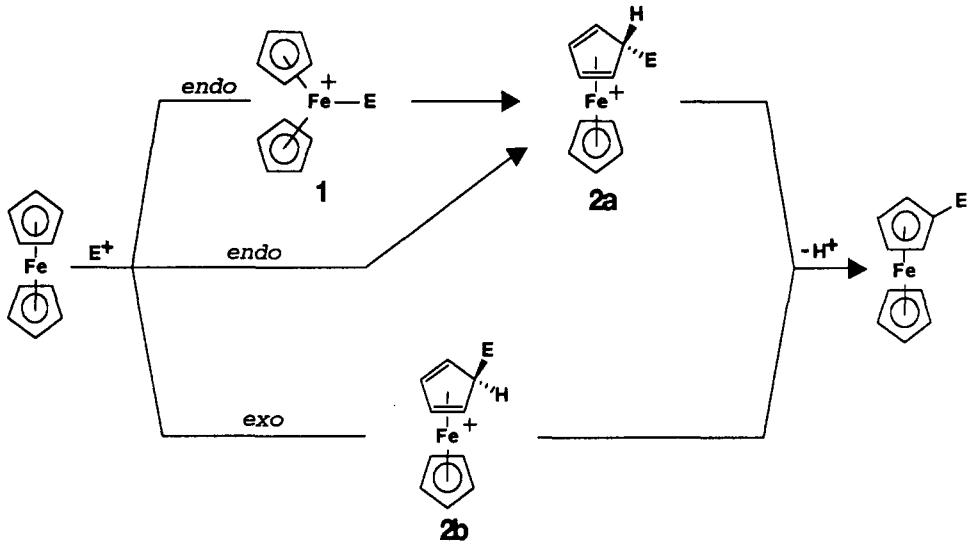
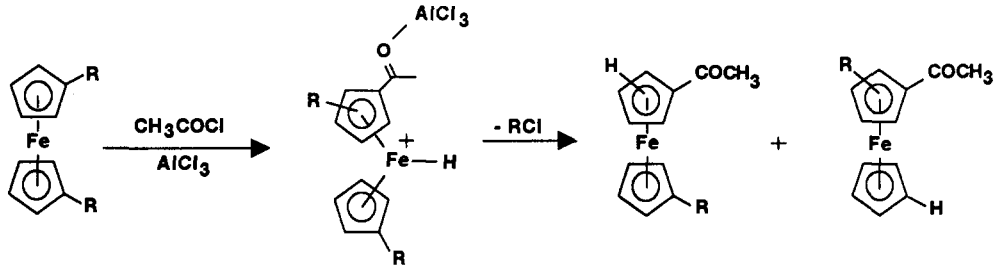
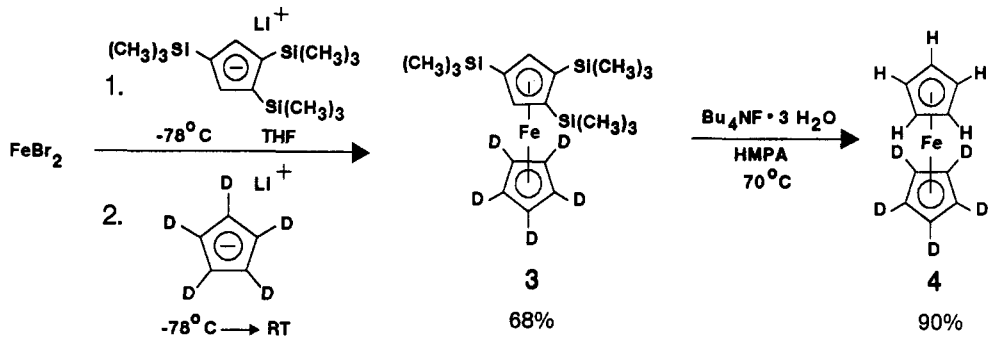
Scheme 1



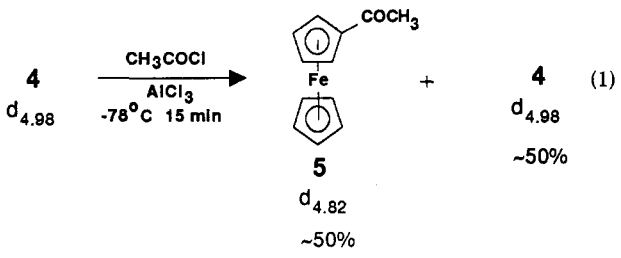
Scheme 2



Scheme 3



−78 °C (eq 1). A color change from orange to deep purple

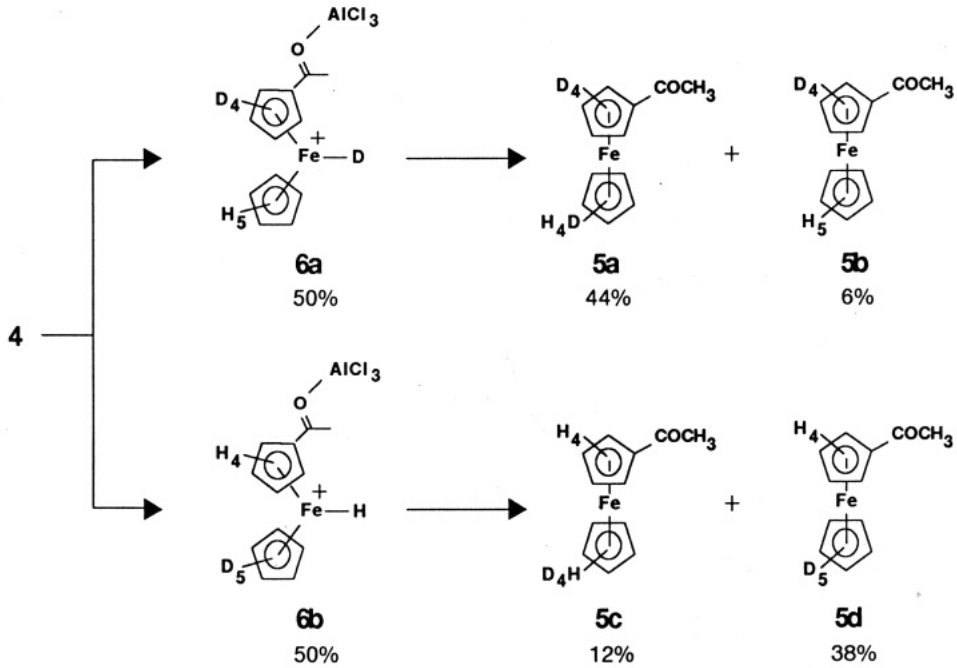


(1)

indicates the formation of the aluminum trichloride complex of acetylferrocene **5** which is obtained in ~50% yield within 15 min. Longer reaction times (2.5 h) do not lead to higher conversion as the remaining **4** is protonated and inert to electrophilic substitution.[4] The relative intensities of the molecular peaks of the mass spectrum of **5** (*m/e* 234 (d_5 + 1), 14%; 233 (d_5), 100%; 232 (d_4), 18%) show that the product contains 4.82 deuterium atoms and is composed of 82% **5**-d_5 and 18% **5**-d_4. The predominance of **5**-d_5 is not a result of the preferential attack of the C_5H_5 ring by the acylating agent as the ratio of the 500-MHz ^{1}H NMR integral of the cyclopentadienyl protons of the substituted ring to that of the methyl group is exactly half of that observed in acetylferrocene. This is in accord with the work of Mangravite and Traylor,[5] who found no isotope effet upon acetylation of ferrocene and perdeuterioferrocene. The recovered **4** is virtually unchanged.

The high deuterium content of **5** is very easily explained, however, by invoking a mechanism based on the exo attack of the electrophile which would provide equal amounts of the cationic metal deuteride **6a** and the corresponding metal hydride **6b** (Scheme 4). Deuterium transfer from the metal to the unacylated ring in **6a** resulting in the exo loss of a proton and the formation of **5a** is clearly thermodynamically favored over the corresponding proton transfer of **6b**, in which a C–H bond is created at the expense of a C–D bond. Comparison of the $C_5H_{5-x}D_xFe$ fragments (*m/e* 121–126) of the mass spectra of **5** with those of acetylferrocene-d_0 and acetylferrocene-d_9 (Figure

Scheme 4



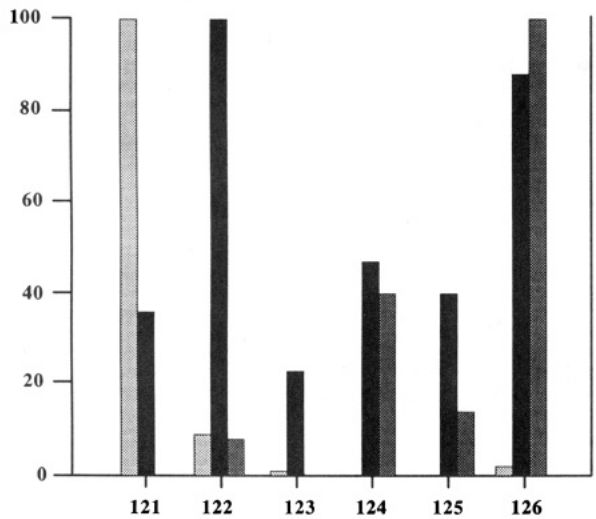


Figure 1. Comparison of the mass spectra of **5** (solid bar), acetylferrocene-d_0 (dotted bar), and acetylferrocene-d_9 (cross-hatched bar) in the m/e 121–126 region (normalized to 100%).

1) allows identification of **5** as a mixture of 44% **5a**, 6% **5b**, 12% **5c**, and 38% **5d**. This is also in accord with the ^{1}H NMR of **5** in which the integral of the singlet for the unsubstituted cyclopentadienyl ring corresponds to exactly 2.18 protons. Thus, the ratio of deuterium transfer to the unsubstituted ring versus transfer to the acylated ring is ~7:1. The corresponding ratio of proton transfers is ~1:3. The monodeuteriocyclopentadienyl ring of **5a** is easily identified in the undecoupled ^{13}C NMR spectrum (Figure 2). Whereas the deuterated carbon appears as a triple pentet at 69.50 ppm (J = 27 and 7 Hz), slightly deshielded relative to the perdeuterated cyclopentadienyl ring of **5d** (69.42 ppm, triplet, J = 26 Hz), the broad double pentet for the protonated carbons is located 0.05 ppm upfield[11] from that of the unacylated ring of **5b** (69.70 ppm, J = 176 and ~7 Hz vs 69.75 ppm, J = 177 and 7.5 Hz; this latter signal is superimposable with that of undeuterated acetylferrocene). Due to their low intensity and position, the signals for the tetradeuteriocyclopentadienyl ring of **5c** cannot be unequivocally assigned.

Whereas interannular proton transfers (**6a** → **5a**, **6b** → **5c**) are readily identified by isotopic labeling, the loss of a proton via the acylated ring (**6a** → **5b**, **6b** → **5d**) cannot be distinguished from direct deprotonation of the metal center. Nonetheless, since the acetylation of acetylferrocene provides, in addition to the major product, 1,1′-diacetylferrocene, a small amount of 1,2-diacetylferrocene,[12] it is reasonable to assume that homoannular transfer of a proton to the α position, which would engender much less steric repulsion, also occurs. In fact, the α carbon appears to possess the highest electron density of all the ring positions of acetylferrocene by ^{13}C NMR analysis (α C, 69.6; β C, 72.2; unsubstituted ring, 69.8 ppm).[13,14] Disregarding other factors which influence deprotonation, this would imply that the activation energies for interannular and α-homoannular proton transfers are similar. Indeed, this is reflected in the product ratio: the preference for the formation or retention of carbon–deuterium bonds determines to an overwhelming extent the course of the proton transfer.

It should be emphasized that the observed preference for deprotonation of **4** via the cyclopentadienyl rings, as well as the analogous protodesilylation (protodestannylation) of the substituted ferrocenes (Scheme 2),[6] not only serve to identify the exo attack of an electrophile but also provide further insight into the mechanism of proton exchange of ferrocene derivatives. If the deprotonation of species of the general structure **1** (E = H) occurs exclusively via metal to ring transfer of H^+ followed by

(11) For examples of β deuterium isotope shifts in benzene derivatives see: Bell, R. A.; Chan, C. L.; Sayer, B. G. *J. Chem. Soc., Chem. Commun.* **1972**, 67–68. The double pentet for the protonated carbons of **5a** is a result of the near equivalence of the β deuterium shift, $^2J_{CH}$, and $^3J_{CH}$.

(12) Under standard conditions, 1,1′- and 1,2-diacetylferrocene are formed in a ~60:1 ratio. No 1,3-diacetylferrocene is detected: Rosenblum, M.; Woodward, R. B. *J. Am. Chem. Soc.* **1958**, *80*, 5443–5449.

(13) Braun, S.; Abram, T. S.; Watts, W. E. *J. Organomet. Chem.* **1975**, *97*, 429–441.

(14) Proton transfer to the acylated ring has been observed upon acetylation of 1,1′-bis(trimethylsilyl)- and 1,1′-bis(tributylstannyl)ferrocene (see ref 6). In this case, however, the transfer occurs to the β carbon and is driven by the loss of R_3MCl.

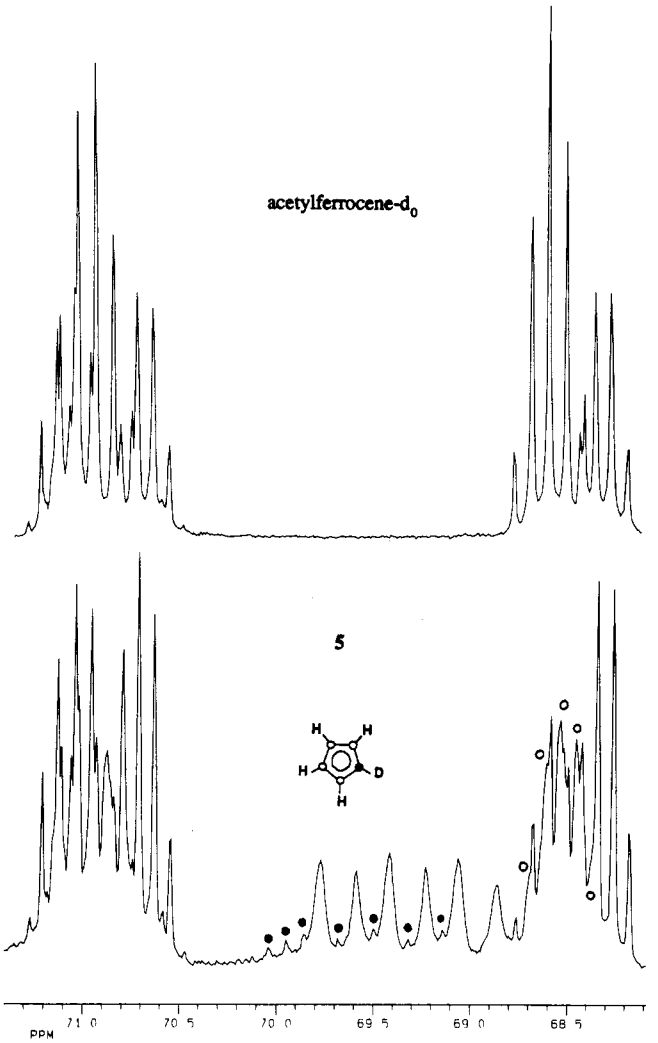
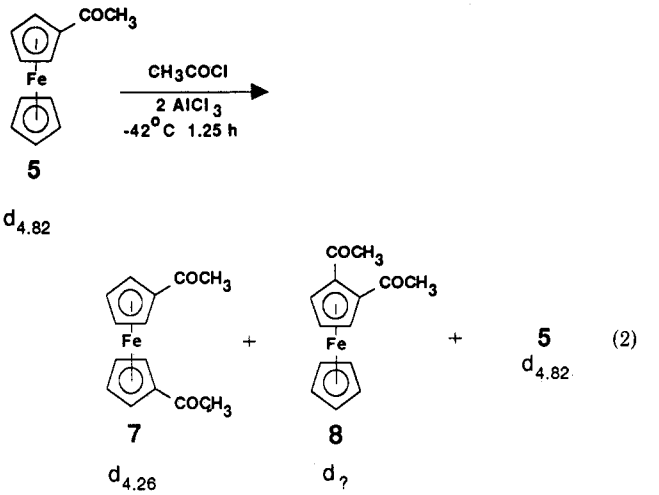


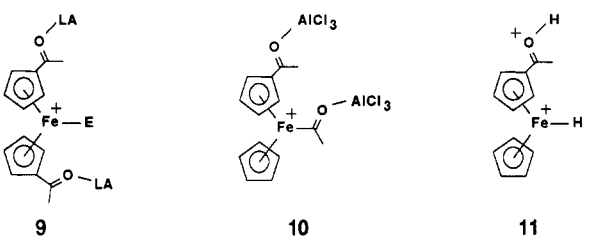
Figure 2. Comparison of the undecoupled ^{13}C NMR spectra of **5** and acetylferrocene-d_0 in the 68.1–71.4 ppm region. (For clarity, only the upfield signals of the C–H absorption are identified.)

loss of the exo proton from the resulting σ-complex **2a** (such a process may also be concerted), then the formation of **1** (E = H) must also arise from an exo attack of H^+ and not from direct protonation at iron. According to a recent computational study,[15] initial ring protonation may occur more readily since it requires less charge transfer from the site of protonation and, therefore, less reorganization of molecular structure. Protonation at the iron atom is, nonetheless, thermodynamically favored by 42 kcal/mol.

The acetylation of **5** proceeds slowly at −42 °C in the presence of 2 equiv of $AlCl_3$ and 4 equiv of acetyl chloride to provide <5% of 1,1′-diacetylferrocene **7** and a trace of 1,2-diacetylferrocene **8** after 1.25 h (eq 2).[16] The acetylferrocene **5** is recovered unchanged ($d_{4.82}$) in 88% yield. GC/MS analysis of the mixture of **7** and **8** reveals that the former contains approximately 4.26 atoms of deuterium and is composed of 32% **7**-d_5, 62% **7**-d_4, and 7% **7**-d_3. The deuterium content of **8** could not be accurately determined due to its low concentration and the presence of impurities with similar retention times. Thus, the diacetylation engenders the loss of slightly more deuterium than hydrogen. This result is difficult to reconcile with the



mechanism proposed for the formation of **5** since the conversion of the corresponding metal hydride (deuteride) **9a** to the diacetylferrocenes **7** and **8** would also be expected to proceed with preferential loss of H^+. Apparently, the acetylation of acetylferrocene involves the precomplexation of the electrophile to the metal center to provide **10** followed by concurrent or stepwise endo transfer of the electrophile to the cyclopentadienyl ring and exo loss of a proton.[17] In fact, if it is assumed that the transformation of **5a–d** to **7** does not exhibit an isotope effect, which is most likely the case, given the loss of 0.56 deuterium atom and only 0.44 hydrogen atom, such a mechanism predicts that **7** should contain exactly 4.26 deuterium atoms, as is observed. The deuterium content of **8** should be slightly higher (4.32), but the experimental value lacks the necessary precision to allow a reasonable comparison.



a LA = $AlCl_3$, E = H (D)
b LA = $AlCl_3$, E = $COCH_3 \cdot AlCl_3$
c LA = H^+, E = H

The change in the mode of electrophilic attack from exo to endo upon diacetylation of ferrocene can be directly

(15) McKee, M. L. *J. Am. Chem. Soc.* **1993**, *115*, 2818–2824.
(16) It is important to stop the reaction at very low conversion to avoid cyclopentadienyl proton (deuterium) exchange of **5** and acetyl proton exchange of **7** with the acid liberated upon acetylation.

(17) The experimental results for diacetylation are also in accord with a mechanism based on the exo attack of the acylating agent, to afford a σ-complex related to **2b**, followed by endo proton loss without metal intervention. Such a mechanism conflicts, however, with the results obtained for monoacetylation whereby exo attack is accompanied by metal protonation. Furthermore, recent calculations of the charge distribution in ring-protonated **2b** (E = H) and metal-protonated ferrocene **1** (E = H) (see ref 15) show that the majority of the positive charge of the former resides in the η^4-cyclopentadienyl ring: depending upon the basis set used, the charge varies from +0.52 to +0.85. Assuming that the same partition of charge is valid for related substituted σ-complexes, this alternative mechanism predicts that the substituents of the cyclopentadienyl ring not undergoing electrophilic attack should exert only a weak influence on the reactivity of the complex. Thus, since the acetylation of ferrocene occurs readily and that of acetylferrocene affords a small amount of 1,2-diacetylferrocene, one would also expect to obtain triacetylferrocenes from both 1,2- and 1,1′-diacetylferrocene under similar conditions. The fact that neither of these reactions occurs (see text and ref 18) also speaks against a mechanism involving endo proton loss without metal intervention. A similar argument can be advanced to invalidate another potential pathway involving endo electrophilic attack without precomplexation.

attributed to the high energy of complexes such as **9a** in which an electrophile is bonded to an electron-deficient metal center. Likewise, neither the aluminum trichloride promoted acetylation of diacetylferrocene[18] nor the exchange of its cyclopentadienyl protons,[19] which could be envisaged to proceed via the related species **9b** and **9c**, respectively, has been observed. In contrast, the proposed intermediate for the acetylation of acetylferrocene, **10**, is closely related to **6**, postulated for the acetylation of ferrocene, and diprotonated acetylferrocene **11**, which has been observed in superacid medium.[20]

Preferred exo monoacetylation of ferrocene, on the other hand, may arise from a number of factors. Exo attack allows the metal to serve as an internal base and assist in proton removal. This could lower the activation of exo acylation relative to endo acylation in which the proton must be removed by an external base (unreacted ferrocene or Cl^-, for example) in a bimolecular process. Second, the exo approach of the electrophile is relatively unhindered whereas precomplexation (i.e. the formation of **1**) engenders steric interactions not only between the electrophilic species and the cyclopentadienyl rings but also between the cyclopentadienyl rings themselves. Such interactions are manifested in restricted ring rotation, well documented for substituted ferrocenes protonated at iron.[3b] Finally, it should be noted that the endo acylation of an electron-rich ferrocene has been reported. In this case, however, the tethered acylium ion could not achieve the geometry required for exo attack.[21]

Summary

In conclusion, we have shown that the monoacylation of ferrocene is accomplished through an exo attack of the acylating agent to furnish an iron hydride intermediate. Subsequent metal to ring proton transfer with exo loss of a cyclopentadienyl proton engenders the product. This mode of reactivity may be general for ferrocenes having electron-donating or slightly electron-withdrawing substituents. Acetylferrocene and other related derivatives undergo acylation via precomplexation of the electrophile to the metal center (endo attack) since exo attack would lead to a highly electron-deficient iron hydride. Further studies with related metallocenes of differing oxidation potentials as well as the effect of the electrophile on the mode of reactivity with **4** will be reported in due course.

Experimental Section

General Methods. The solvents used were dried and distilled as follows: from sodium–benzophenone ketyl, THF; from CaH_2, CH_2Cl_2. Anhydrous $FeBr_2$ was purchased from Alfa Inorganics. Samples that were yellow in color gave greatly superior results than those which were brown. Hexadeuteriocyclopentadiene[8] and tris(trimethylsilyl)cyclopentadiene[7] were prepared as reported in the literature. Routine monitoring of reactions was carried out with glass-backed TLC plates of Merck 60 F_{254} silica gel. Flash column chromatography was performed on Merck 60H F_{254} silica gel. ^1H NMR spectra were recorded on a Bruker 300 AC spectrometer (300 MHz) or a Varian U 500K (500 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker 300 AC spectrometer (75.468 MHz). Chemical shifts are reported in ppm relative to internal tetramethylsilane. Mass spectra were recorded on a Finigan MAT 212-SS300 spectrometer at 70 eV. IR spectra were recorded on a Nicolet 20SX spectrometer. Melting points were recorded on a Büchi 535 apparatus and are not corrected.

(Pentadeuteriocyclopentadienyl)[1,2,4-tris(trimethylsilyl)cyclopentadienyl]iron(II) (3). A solution of lithium tris(trimethylsilyl)cyclopentadienide was prepared by the addition of 17.2 mL of a 1.6 M solution of butyllithium in hexane (0.0275 mol), over a 10-min period, to a solution of 7.63 g (0.0250 mol) of tris(trimethylsilyl)cyclopentadiene in 12 mL of THF under a nitrogen atmosphere at 0 °C. A solution of lithium pentadeuteriocyclopentadienide was prepared in the same manner from 1.80 g (0.0250 mol) of hexadeuteriocyclopentadiene in 25 mL of THF. To 5.39 g (0.025 mol) of finely powdered $FeBr_2$ under a nitrogen atmosphere at room temperature was added 10 mL of THF. The exothermic solvation (35 °C) of the iron salt led to the formation of chucks of solid which were broken up with a glass rod. The resulting fine yellow-orange suspension was stirred for ~10 min at room temperature and then cooled to −78 °C. The solution of lithium tris(trimethylsilyl)cyclopentadiene was then added dropwise, over a period of 30 min, to the suspension of $FeBr_2$. The brown suspension was allowed to stir at −78 °C for 1 h. At this time, the lithium pentadeuteriocyclopentadienide solution was added in the same manner and the reaction mixture was allowed to warm slowly to room temperature and stir for 20 h. The reaction mixture was poured into water (200 mL) containing a small amount of NaCl and extracted with hexane (2 × 100 mL). The combined organic extracts were washed with saturated aqueous NaCl solution, dried ($MgSO_4$), and concentrated to give a red oil. The oil was chromatographed (SiO_2, hexane) to give, after a first fraction containing five products including hexakis(trimethylsilyl)ferrocene, 6.93 g (0.017 mol, 68%) of **3** as a red oil followed by 0.80 g (0.004 mol, 16%) of perdeuterioferrocene. **3**: IR (neat) 3063, 2957, 2894, 2322 (C–D), 1416, 1400, 1247, 1090, 988, 929, and 831 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.16 (s, 2), 0.27 (s, 18), and 0.23 (s, 9) ppm; MS (70 eV) *m/e* 409 (16%), 408 (41%), 407 (molecular peak, 100%), 406 (5%), 405 (6%), 304 (29%), 126 (21%), and 73 (99%). **3-d_0**: MS (70 eV) *m/e* 404 (16%), 403 (36%), 402 (molecular peak, 100%), 401 (1%), 400 (6%), 299 (31%), 121 (14%), and 73 (77%). **3** is, therefore, ~96% d_5 and 4% d_4 ($d_{4.96}$).

(Pentadeuteriocyclopentadienyl)cyclopentadienyliron-(II) (4). A solution of 6.91 g (0.017 mol) of **3** and 10.70 g (0.034 mol) of tetrabutylammonium fluoride–$3H_2O$ in 35 mL of HMPA was heated at 70 °C for 24 h. The reaction mixture was poured into water (300 mL) and extracted with hexane (2 × 100 mL). The combined organic extracts were passed through a bed of ~20 g of SiO_2, eluting with hexane, and then concentrated to give 3.05 g of crude **4**. Sublimation (70 °C, 5 × 10^{-2} mbar) gave 2.93 g (0.015 mol, 90%) of **4** as an orange solid: mp 175–176 °C; IR (KBr) 3094, 2329 (C–D), 2321 (C–D), 2275 (C–D), 2251 (C–D), 1408, 1106, 1043, 996, and 816 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.15 (s, 5) ppm; undecoupled ^{13}C NMR ($CDCl_3$) δ 67.75 (dp, C–H, J = 176 and 7 Hz), and 67.43 (t, C–D, J = 26 Hz) ppm; MS (70 eV) *m/e* 193 (1%), 192 (13%), 191 (molecular peak, 100%), 190 (3%), 189 (7%), 126 (17%), 125 (2%), 124 (2%), 123 (1%), 122 (3%), 121 (17%), and 56 (24%). **4-d_0**: MS (70 eV) *m/e* 188 (1%), 187 (12%), 186 (molecular peak, 100%), 185 (1%), 184 (9%), 122 (3%), 121 (40%), and 56 (19%). **4** is, therefore, ~98% d_5 and 2% d_4 ($d_{4.98}$).

(18) The reaction of ferrocene with either (a) 10 equiv of CH_3COCl–$AlCl_3$ in CH_2Cl_2 at room temperature or (b) 3 equiv of CH_3COCl–$AlCl_3$ in CH_2Cl_2 at reflux affords only diacetylferrocenes: (a) Nesmeyanov, A. N., Leonova, E. V.; Kochetkova, N. S.; Malkova, A. I. *J. Organomet. Chem.* **1975**, *96*, 271–274. (b) Rausch, M. D.; Fischer, E. O.; Grubert, H. *J. Am. Chem. Soc.* **1960**, *82*, 76–82. 1,2-Diacetylferrocene does not undergo further acetylation upon treatment with a large excess of CH_3COCl–$AlCl_3$ in CH_2Cl_2 at room temperature or reflux (see ref 12). However, the preparation of tetraacetylferrocene, by refluxing a mixture of ferrocene and trifluoroacetic acid in acetic anhydride for 5 h, is claimed in US Patent 2,852,542 (Sweeney, W. M., February 29, 1956). Evidence for the triacetylation of the more electron rich 1,1′-dimethylferrocene has been reported: Nesmeyanov, A. N.; Perevalova, E. G.; Beinoravichute, Z. A.; Malygina, I. L. *Dokl. Akad. Nauk. SSSR* **1958**, *120*, 1263–6.

(19) No exchange of the cyclopentadienyl protons of 1,1′-diacetylferrocene occurs in triflic acid whereas exchange is observed with acetylferrocene: Roberts, R. M. G.; Silver, J.; Wells, A. S. *Inorg. Chim. Acta* **1986**, *119*, 171–176.

(20) (a) Rimmelin, P.; Sommer, J.; Sandström, J.; Seita, J. *J. Organomet. Chem.* **1976**, *114*, 175–177. (b) Olah, G. A.; Mo, Y. K. *J. Organomet. Chem.* **1973**, *60*, 311–321.

(21) Rosenblum, M.; Abbate, F. W. *J. Am. Chem. Soc.* **1966**, *88*, 4178–4184.

Acetylferrocene-$d_{4.82}$ (5). To a stirred solution of 0.21 g (1.08 mmol) of **4** and 0.09 mL (0.10 g, 1.30 mmol) of acetyl chloride in 20 mL of CH_2Cl_2 under a nitrogen atmosphere at −78 °C was added 0.29 g (2.16 mmol) of powdered $AlCl_3$. The reaction mixture became almost immediately purple and was allowed to stir at −78 °C for 15 min. At this time, the mixture was poured into ice water (50 mL). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 until the extracts were colorless. The combined extracts were dried (Na_2SO_4) and concentrated to give a deep red solid. No diacetylferrocene was present by TLC analysis (6:1 hexane:ethyl acetate). The solid was chromatographed (SiO_2; hexane and then 6:1 hexane:ethyl acetate) to afford 0.09 g (0.46 mmol, 43%) of **4** and 0.13 g (0.56 mmol, 52%) of **5**. Recovered **4**: MS (70 eV) *m/e* 193 (1%), 192 (11%), 191 (molecular peak, 100%), 190 (3%), 189 (8%), 188 (2%), 126 (20%), 125 (4%), 124 (3%), 123 (1%), 122 (4%), 121 (23%), and 56 (19%). Recovered **4** is, therefore, identical to **4** and is ~98% d_5 and 2% d_4 ($d_{4.98}$). **5**: mp 85–86 °C; IR (KBr) 3114, 3098, 3090, 3075, 3067, 2329 (C-D), 2320 (C-D), 2298 (C-D), 2275 (C-D), 1663, 1655, 1455, 1421, 1373, 1357, 1280, 1227, and 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.86 (t, 1, *J* = 1.9 Hz), 4.47 (t, 1, *J* = 1.9 Hz), 4.26 (s, 2.18), and 2.17 (s, 3) ppm (the number of protons was determined through comparison of the spectrum of **5** with that of **5**-d_0); undecoupled ^{13}C NMR ($CDCl_3$) δ 201.95 (q, 1, *J* = 5.5 Hz), 79.14 (m, 1), 72.25 (dm, 1, *J* = 179 Hz), 71.92 (t, 1, *J* = 27 Hz), ~69.72 (dm, ~2.18 (estimated from MS and ^1H NMR), *J* = ~176 Hz), 69.50 (tp, ~0.44, *J* = 27 and 7 Hz), 69.42 (t, ~2.38, *J* = 26 Hz), 69.49 (dq, 1, *J* = 178 and 6.2 Hz), 69.23 (t, 1, *J* = 27 Hz), and 27.36 (q, 1, *J* = 127 Hz) ppm; MS (70 eV) *m/e* 235 (1%), 234 (14%), 233 (d_5, 100%), 232 (d_4, 22%), 231 (8%), 190 (68%), 134 (52%), 126 (10%), 125 (5%), 124 (6%), 123 (3%), 122 (12%), 121 (4%), and 56 (26%). (Acetyltetradeuteriocyclopentadienyl)(pentadeuteriocyclopentadienyl)iron: MS (70 eV) *m/e* 239 (1%), 238 (13%), 237 (molecular peak, d_9, 100%), 235 (7%), 194 (57%), 138 (37%), 126 (16%), 125 (3%), 124 (7%), 123 (0%), 122 (1%), 121 (≪1%), and 56 (20%). **5**-d_0: MS (70 eV) *m/e* 230 (2%), 229 (16%), 228 (molecular peak, 100%), 226 (6%), 185 (59%), 129 (40%), 126 (≪1%), 125 (0%), 124 (0%), 123 (≪1%), 122 (2%), 121 (23%), and 56 (66%). **5** is, therefore, ~82% d_5 and 18% d_4 ($d_{4.82}$).

Acetylation of 5. To a solution of 0.08 g (0.36 mmol) of **5** and 0.09 mL (0.10 g, 1.27 mmol) of acetyl chloride in 7 mL of CH_2Cl_2 at −42 °C (dry ice/acetonitrile) under a nitrogen atmosphere was added 0.10 g (0.72 mmol) of powdered $AlCl_3$. The reaction mixture became gradually purple and was allowed to stir at −42 °C until, after 75 min, a trace of 1,1-diacetylferrocene **7** was visible by TLC analysis (6:1 hexane:ethyl acetate). The mixture was poured into ice water (25 mL). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 until the extracts were colorless. The combined extracts were dried (Na_2SO_4) and concentrated to give a deep red solid. The solid was chromatographed (SiO_2, 6:1 hexane:ethyl acetate and then 1:1 hexane:ethyl acetate) to afford 0.07 g (~88% recovery) of **5** and ~0.005 g (<5%) of a mixture containing **7** and **8**. Recovered **5**: MS (70 eV) *m/e* 235 (2%), 234 (15%), 233 (d_5, 100%), 232 (d_4, 22%), and 231 (7%), 190 (50%), 134 (29%), 126 (5%), 125 (3%), 124 (2%), 123 (2%), 122 (7%), 121 (2%), and 56 (17%). Recovered **5** is, therefore, identical to **5** and is ~82% d_5 and 18% d_4 ($d_{4.82}$). GC/MS of the mixture of **7** and **8** only allowed the accurate determination of the mass spectrum for **7**: MS (70 eV) *m/e* 277 (1%), 276 (11%), 275 (d_5, 68%), 274 (d_4, 100%), 273 (d_3, 15%), 272 (6%), 204 (20%), 203 (30%), 202 (5%), 71 (13%), and 56 (13%). **7**-d_0: MS (70 eV) *m/e* 272 (2%), 271 (18%), 270 (molecular peak, 100%), 269 (1%), 268 (6%), 200 (7%), 199 (44%), 198 (2%), 71 (23%), and 56 (34%). **7** is, therefore, 32% d_5, 62% d_4, and 7% d_3 ($d_{4.26}$).

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