Table IV. Summary of Crystal Data, Intensity Collection, and Refinements

formula	$C_{13}H_{22}N_2O_2S_3Pt \cdot 0.5CH_3OH$
formula wt	545.62
crystal system	monoclinic
space group	$P2_1/c$
a, b, c, Å	11.753 (6), 9.574 (3), 19.183 (9)
β, deg	126.78 (3)
V, Å^3	1729 (1)
Z	4
ρ_{calcd}, g cm^{-3}	2.096
cryst color	colorless
cryst dimens, mm	0.3 × 0.3 × 0.1
radiation	Cu Kα (λ = 1.54178 Å)
μ, mm^{-1}	188.3
$2\theta_{max}$, deg	130
refinement	anisotropic block-diagonal least-squares method
no. of unique reflcns	2940
no. of obsd reflcns [$\|F_o\| > 4\sigma(F_o)$]	2603
no. of reflcns used	2543
R	0.040
R_w	0.060

Kinetic Measurements. The complexation of ligands **9** and **10** with $K_2Pt^{II}Cl_4$ in CH_3OH–20% H_2O (v/v) involves two separate steps, which were confirmed by the ^1H NMR spectroscopy and TLC methods. We isolated and identified all the intermediates and products. The first step is the reaction from **9** (or **10**) to Pt^{II}-out complex **27** (or **28**). The second step goes from the Pt^{II}-out complex to Pt^{II}-in complex **17** (or **19**).

The first reaction between **9** (or **10**) (0.49–1.87 mM) and $K_2Pt^{II}Cl_4$ (0.025 mM) in CH_3OH–20% KCl (v/v)–HCl buffer (pH = 3.0) at 35.0 ± 0.1 °C and I = 0.2 (KCl) was spectrophotometrically monitored by UV absorption increase at 300 nm (or 320 nm) due to the formation of Pt^{II}-out complex **27** (or **28**). Under the employed conditions the hydrolysis of $[Pt^{II}Cl_4]^{2-}$[34] and formation of 2:1 macrocycle–Pt^{II} complex **29** (see the preceding paragraph) were negligible. The reactions were carried out under pseudo-first-order conditions with a large excess of the ligands over $K_2Pt^{II}Cl_4$, where the rate constants k_{obs} (s^{-1}) were obtained by a log plot method. A plot of k_{obs} vs ligand concentration gave a straight line ($r > 0.99$), and from the slope we determined the second-order rate constant k_1 (M^{-1} s^{-1}).

The succeeding reactions from Pt^{II}-out complexes **27** and **28** (0.10 mM) in CH_3OH–20% borate buffer (pH = 9.0) were spectrophotometrically monitored at 255 and 265 nm by measuring the increase in absorbance of the final products **17** and **19** at 35 ± 0.1 °C and I = 0.2 ($NaClO_4$). The first-order rate constants k_2 (s^{-1}) were obtained by a log plot method, because of a low steady-state concentration of the monoamide-deprotonated species.[10]

Electrochemical Measurements. Electrochemical experiments were performed with a Yanaco P-1100 system at 25.0 ± 0.1 °C and I = 0.1 (Et_4NClO_4). The working and the counter electrodes were a glassy-carbon electrode and a platinum wire, respectively. The saturated calomel reference electrode (SCE) was checked periodically against the Ni^{III}/Ni^{II} couple ($E_{1/2}$ = +0.495 V) of the Ni^{II}–cyclam complex in 0.1 $NaClO_4$ aqueous solution at 25 °C. Controlled-potential coulometry was carried out with a three-electrode system on a Yanaco VE-9 potentiostat and a Yanaco V10-CM coulometer. The working electrode was made of platinum gauze, and the working compartment was separated from the counter compartment by a sintered-glass disk.

Supplementary Material Available: Tables of anisotropic temperature factors and thermal parameters, crystallographic details, bond distances, and bond angles (6 pages); listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

(34) Grantham, L. F.; Elleman, T. S.; Martin, Jr. D. S. *J. Am. Chem. Soc.* **1955**, *77*, 2965–2971.

Friedel–Crafts Acetylation of Bis(trimethylsilyl)- and Bis(tributylstannyl)ferrocene: Implications on the Mechanisms of Acylation and Proton Exchange of Ferrocene Derivatives[1]

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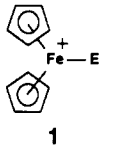
Received September 12, 1990

Abstract: The first unequivocal examples of intermolecular Friedel–Crafts reactions of ferrocene derivatives proceeding via exo attack of the electrophile are reported. Treatment of 1,1′-bis(trimethylsilyl)- (**5a**) or 1,1′-bis(tributylstannyl)ferrocene (**5b**) with acetyl chloride in the presence of $AlCl_3$ affords a mixture of three isomeric acetylferrocenes, 1′-acetyl- (**6**), 2-acetyl- (**7**), and 3-acetyl-1-(trialkylsilyl and -stannyl)ferrocene (**8**). Acetylation of 3,3′-dideutero-1,1′-bis(trimethylsilyl)ferrocene (**5a**D_2) under identical conditions generates the corresponding dideuterated products **6a**D_2–**8a**D_2. Both **6a**D_2 and **7a**D_2 contain 1.0 deuterium atom in each cyclopentadienyl ring whereas **8a**D_2 contains 0.5 deuterium atom in the substituted ring and 1.5 deuterium atoms in the "unsubstituted" ring. This demonstrates that the products are formed via exo attack of the electrophile followed by an intramolecular, interannular proton transfer. The lack of scrambling of the deuterium label also suggests that protonation of ferrocenes could also occur through the exo attack of a proton rather than direct protonation at the metal center.

Introduction

Notwithstanding the plethora of synthetic and theoretical studies of ferrocene and its derivatives over the past four decades, the mechanisms of two fundamental reactions, namely the Friedel–Crafts acylation and the proton exchange, are still subject to debate.[2] The central questions of this controversy are the following: (1) Does electrophilic substitution of ferrocenes occur via an exo or an endo attack of the cyclopentadienyl ring? (2) What role, if any, does the cationic C_{2v} ferrocenium species **1** play in such electrophilic substitution reactions?

The intermediacy of **1** in electrophilic substitution reactions of ferrocenes was first proposed by Rosenblum et al.[3] in 1963. In a study of competitive acetylation, they observed that ferrocene



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(1) Presented at the XIVth International Conference on Organometallic Chemistry, August 19–24, 1990 in Detroit, MI.

(2) (a) Wailis, N. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. N., Eds.; Pergammon: New York, 1982; Vol. 8, Chapter 59, pp 1019–1021. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 173–174.

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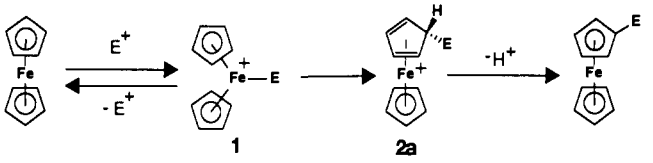
Scheme I

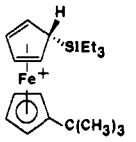


1 2a

was four orders of magnitude more reactive than acetylferrocene. As UV spectra of isomeric substituted ferrocenes provided no evidence for the existence of resonance coupling between the cyclopentadienyl rings, the mechanism of electrophilic substitution shown in Scheme I was proposed. According to this mechanism, ferrocene and **1** exist in equilibrium, the concentration of the latter being determined by the oxidation potential of the former and the electron affinity of the electrophilic species. In the case of acetylferrocene, the equilibrium concentration of **1** would be lower, thus diminishing the rate of electrophilic substitution. In a subsequent step, the electrophile migrates from the iron atom to an endo position on the cyclopentadienyl ring (endo attack) to generate the σ-complex **2a**. Loss of a proton from the exo face of the cyclopentadienyl ring affords the substituted product.

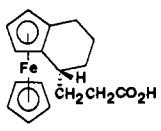
In apparent accord with such a mechanism is the observation of ferrocene protonated at the metal center **1** (E = H), rather than an isomeric σ-complex, in highly acidic medium[4] and the oxidation of ferrocenes by certain electrophiles.

The validity of this mechanism was challenged by Rinehart and co-workers,[5] who observed no steric effect in the acylation of singly and doubly trimethylene-bridged ferrocenes where the approach to the metal center is clearly hindered. Benkeser[6] later noted that the low relative rate of protonolysis of 1′-*tert*-butyl-1-(triethylsilyl)ferrocene could be explained by either a lower equilibrium concentration of a protonated ferrocene intermediate (an analogue of **1**) or steric compression in a σ-complex such as **3**.

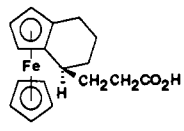


3

To examine the role of the iron atom in electrophilic substitution more closely, Rosenblum and Abbate[7] studied the intramolecular cyclizations of the epimeric acids **4a** and **4b**. They found that the exo-acid **4b** underwent cyclization faster than its endo epimer **4a**. As cis addition of the acylium ion to the cyclopentadienyl ring is the favored mode of reaction in both cases (i.e. prior attack at the metal center followed by cyclization is only possible in **4a**), the authors concluded that "the metal atom is not an essential participant in electrophilic substitution of ferrocene" and suggested that metal participation in acylation does not provide any energetic advantage.



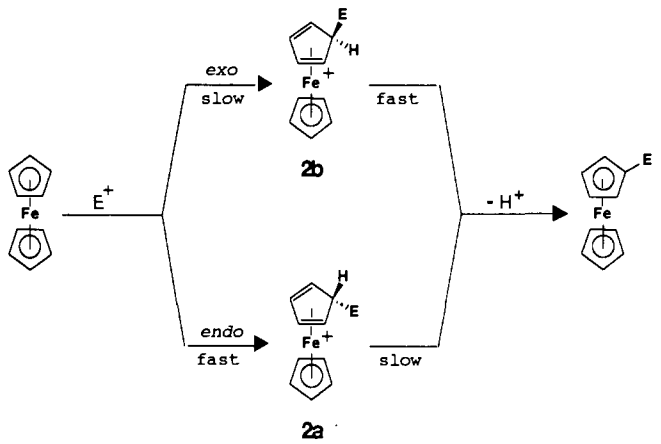
4a



4b

Traylor and co-workers questioned the existence of ferrocenium species **1**, arguing that the ^{1}H NMR evidence for ferrocene protonated at the metal center, **1** (E = H), was equally consistent with σ-complex **2a** (E = H) if rapid proton exchange between cyclopentadienyl rings occurred.[8] They proposed that electrophilic substitution of ferrocenes proceeded by direct formation of σ-complexes **2a** and **2b** without the intermediacy of **1**, the preferred mode of electrophilic attack being determined by the strength of the electrophile.[9] Weak electrophiles (e.g. $HgCl_2$) would attack ferrocene on the more electron rich endo face of the cyclopentadienyl ring to generate σ-complex **2a** (Scheme II). In the subsequent rate-determining step, loss of a proton from the exo face generates the substituted product. The rate-determining step of the electrophilic substitution of ferrocene with strong electrophiles (e.g. $CH_3COCl{\cdot}AlCl_3$) would be the initial exo attack that engenders **2b**. In this case, fast loss of the endo proton of **2b** provides the substituted ferrocene. Proton exchange of ferrocenes was presumed to occur via both pathways. This mechanistic scheme receives experimental support from the correlation of the rates of these reactions with the σ^+ parameters determined for endo and exo attack of ferrocene and the observance of isotope effects upon mercuration and proton exchange of ferrocene.

Scheme II



2a

Objections to this mechanistic interpretation were raised by Bitterwolf and Ling[10] who investigated the protonation of mono- and heteroannularly substituted dialkylferrocenes by ^{1}H NMR spectroscopy. The substituted rings of such protonated ferrocenes give rise to A_2B_2 NMR patterns which are characteristic of ring tilting and consistent with a species such as **1**. Given the proximity of the iron bound proton to the cyclopentadienyl rings in **1**, these authors surmized that proton exchange reactions, as well as other electrophilic substitution reactions of ferrocene, most likely involve this intermediate.

Conflicting results were obtained by Illuminati et al. They demonstrated that the hydrolysis of (trimethylsilyl)ferrocene occurs readily under conditions where the concentration of protonated ferrocene **1** (E = H) would be less than 10^{-10} M.[11] In a subsequent study of the behavior of metallocenes in acidic media, they propose that the proton exchange of ferrocenes occurs via the σ-complex **2a** (i.e. exo attack of H^+ followed by endo loss of H^+) and that protonation at the metal center, in fact, inhibits this process.[12]

We now report our recent work in this area which has led to the discovery of the first unequivocal examples of intermolecular Friedel–Crafts acylations of ferrocene derivatives occurring by exo attack of the electrophile. These results infer that the protonation of ferrocene, which engenders **1** (E = H), could also arise through an exo attack of a proton.

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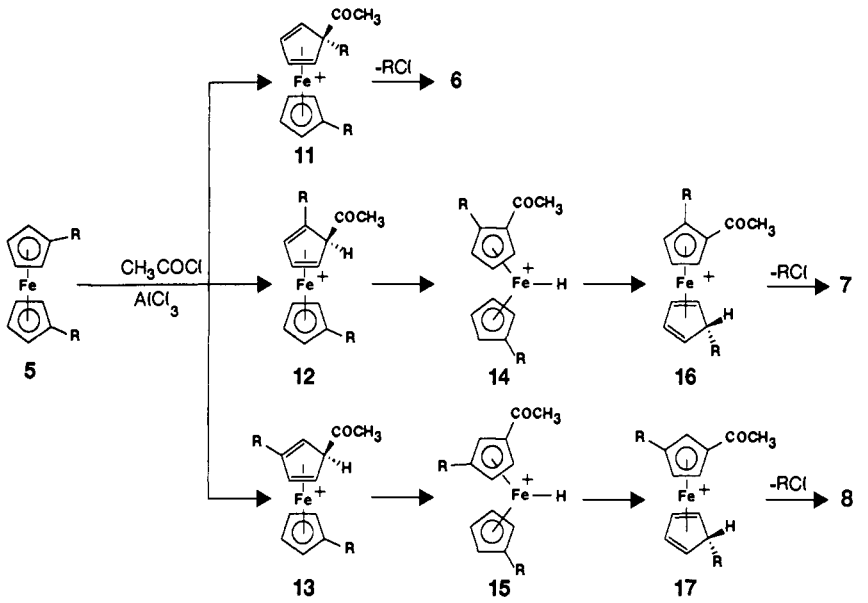
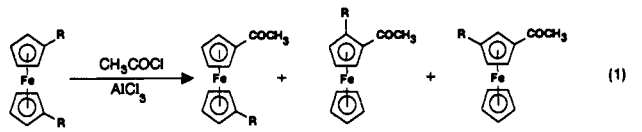
(4) Curphey, T. J.; Santer, J. O.; Rosenblum, M.; Richards, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 5249–5250.
(5) Rinehart, K. L.; Bublitz, D. E.; Gustafson, D. H. *J. Am. Chem. Soc.* **1963**, *85*, 970–982.
(6) Benkeser, R. A.; Nagai, Y.; Hooz, J. *J. Am. Chem. Soc.* **1964**, *86*, 3742–3746.
(7) Rosenblum, M.; Abbate, F. W. *J. Am. Chem. Soc.* **1966**, *88*, 4178–4184.
(8) Ware, J. C.; Traylor, T. G. *Tetrahedron Lett.* **1965**, 1295–1302.
(9) (a) Traylor, T. G.; Ware, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2304. (b) Mangravite, J. A.; Traylor, T. G. *Tetrahedron Lett.* **1967**, 4461–4466.
(10) Bitterwolf, T. E.; Ling, A. C. *J. Organomet. Chem.* **1972**, *40*, 197–203.
(11) Cerichelli, G.; Floris, B.; Illuminati, G.; Ortaggi, G. *J. Org. Chem.* **1974**, *39*, 3948–3950.
(12) Cerichelli, G.; Illuminati, G.; Ortaggi, G.; Giuliani, A. M. *J. Organomet. Chem.* **1977**, *127*, 357–370.

Scheme III



Results and Discussion

The aluminum chloride catalyzed acetylation of either 1,1′-bis(trimethylsilyl)ferrocene (**5a**)[13] or 1,1′-bis(tributylstannyl)-ferrocene (**5b**),[14] both obtained by the treatment of 1,1′-dilithioferrocene·2TMEDA[15] with the corresponding trialkylsilyl

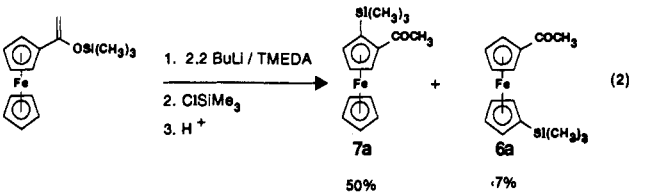


		5	6	7	8	
a R=SiMe$_3$	-70 °C		31.0%	15.5%	53.0%	(99.5%)
	RT		26.0	15.5	58.0	(99.5)
b R=SnBu$_3$	-70 °C		28.5	16.5	46.5	(91.5)
	RT		23.0	13.0	44.0	(80.0)

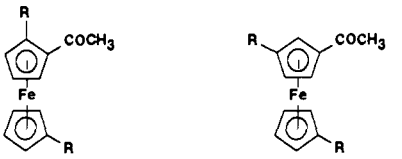
and -tin halides, affords mixtures of the isomeric monoacylated products **6–8** (eq 1). While the addition of powdered aluminum chloride to a stirred solution of **5a** and acetyl chloride in methylene chloride furnishes nearly quantative yields of **6a–8a** at both −70 °C and ambient temperature, much lower yields of **6b–8b** (−70 °C, <78%; room temperature, <63%) are obtained by employing this procedure. In addition to **6b–8b**, the acetylation of **5b** engenders acetylferrocene (−70 °C, ~8%; room temperature, ~14%) and diacetylferrocene (−70 °C, trace; room temperature, 6%). The formation of acetylferrocene can be directly linked to the sensitivity of **5b** to aluminum chloride. Treatment of a solution of **5b** in methylene chloride with aluminum chloride at −70 °C for 0.5 h (the approximate time required for acetylation of **5b** at this temperature) results in the formation of ~11% tributylstannylferrocene and ~3% ferrocene. The acetylation of (tributylstannyl)ferrocene, in turn, produces acetylferrocene exclusively and in high yield. On the other hand, the interaction of **5a** with aluminum chloride at −70 °C for 1.5 h (the approximate time required for acetylation of **5a** at this temperature) results in its near quantitative recovery; less than 1% of (trimethylsilyl)ferrocene could be detected by 300-MHz ^{1}H NMR.

To minimize the aluminum chloride catalyzed decomposition of **5b**, a solution of **5b** was added dropwise to the preformed $AlCl_3$·CH_3COCl complex in methylene chloride. This led to higher yields of the acylated products **6b–8b** and greatly suppressed the formation of acetylferrocene. The latter product was obtained in ~2% yield, regardless of the temperature. Under these conditions, diacetylation (6%) occurred only at ambient temperature.

The isomers **6–8** can be separated by column chromatography and unambiguously identified by ^{1}H NMR spectroscopy. The spectrum of **6** exhibits four triplets of equal intensity (2 H) whereas in the spectra of **7** and **8** a singlet of high intensity (5 H) indicates the presence of an unsubstituted cyclopentadienyl ring. The additional broad singlet in the spectrum of **8** is expected for a 1,3-disubstituted ferrocene. The 1,2-disubstituted ferrocene **7a** has also been prepared by an independent route (eq 2). Metalation of the trimethylsilyl enolether of acetylferrocene with 2 equiv of butyllithium[16] followed by treatment with trimethylsilyl chloride and dilute acid engenders **7a** in 50% yield accompanied by a small amount (<7%) of **6a** contaminated by an unidentified product.



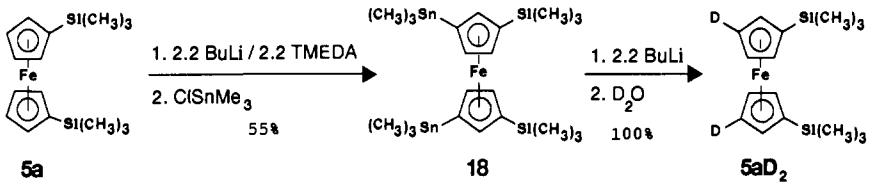
The formation of products **7** and **8** cannot result from endo attack of **3** by acylium ion followed by exo loss of a proton. This would require the intermediacy of two trisubstituted ferrocenes, **9** and **10**, which are not observed under the reaction conditions. In addition, to engender **7** and **8**, **9** and **10** would have to undergo



rapid and selective protonolyses in the presence of the starting material **5**, certainly more electrophilic than any of the acylated ferrocenes, and **6**, which does not seem very probable. The protonoylsis of **5** would result in the formation of its monosubstituted analogue and, ultimately, acetylferrocene. The fact that no trace of the latter product is observed upon acylation of **5a** argues strongly against the generation of HCl and intermolecular

(13) Rausch, M.; Vogel, M.; Rosenberg, H. *J. Org. Chem.* **1957**, *22*, 900–903.
(14) Pellegrini, J. P., Jr.; Spilners, J. J. U.S. Patent 3,350,434, October 31, 1967.
(15) Rausch, M. D.; Ciappenelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127–136.
(16) The ortho-metalation of the trimethylsilyl enolether of acetophenone has been reported: Klein, J.; Medlik-Balan, A. *J. Org. Chem.* **1976**, *41*, 3307–3312.

Scheme IV

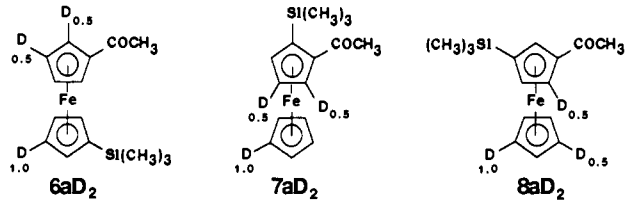


proton exchange in general. As the interaction of **5b** with aluminum chloride leads to the formation of both (tributylstannyl)ferrocene and ferrocene, the generation of HCl, in this case, cannot be rigorously excluded.

In contrast, the course of these two Friedel–Crafts reactions can be easily explained by an initial exo electrophilic attack followed by an intramolecular interannular proton migration (Scheme III). Attack of the acylium ion can take place at three different positions to afford the (cyclopentadiene)(cyclopentadienyl)iron cations **11–13**. Loss of the endo trimethylsilyl or tributylstannyl group of **11** through nucleophilic attack of chloride furnishes **6** directly. The cations **12** and **13**, where hydrogen occupies the endo position, undergo proton transfers to generate the metal protonated species **14** and **15**, respectively. Subsequent proton transfer from the metal to the more electron rich ring at the position substituted by R engenders the stabilized (cyclopentadiene)(cyclopentadienyl)iron cations **16** and **17**. Loss of the exo R groups provides the observed homoannularly disubstituted ferrocenes **7** and **8**.

To demonstrate the validity of the above mechanism, 3,3′-dideuterio-1,1′-bis(trimethylsilyl)ferrocene (**5aD$_2$**) was prepared via a two-reaction sequence (Scheme IV). 3,3′-Bis(trimethylsilyl)-1,1′-bis(trimethylstannyl)ferrocene (**18**) was obtained in 55% yield via dimetalation of **5a** followed by trapping with trimethyltin chloride. The use of trimethylsilyl chloride as electrophile affords 1,1′,3,3′-tetrakis(trimethylsilyl)ferrocene which can also be prepared by the reaction of bis(trimethylsilyl)cyclopentadienide with $FeCl_2$.[17] Transmetalation of **18** with butyllithium and subsequent quenching with D_2O provided a quantitative yield of **5aD$_2$**. Comparison of the ^1H NMR spectrum of **5aD$_2$** with that of **5a** clearly indicates the introduction of deuterium in the 3 and 3′ positions as the relative intensity of the absorptions at 4.28 and 4.05 ppm is now 1:2 and the higher field absorption appears as a doublet. This assignment is in agreement with the results of Slocum and Ernst,[18] who observed an attenuation of the high-field resonance upon deuteration of (trimethylsilyl)ferrocene at the 2 position. The mass spectrum of **5aD$_2$** displays a molecular peak at m/e 332 (d_2) of intensity 100, a M − 1 peak (d_1) of intensity 8, and a M − 2 (d_0) peak of intensity 7. The corresponding values for **5a** are 100, 2, and 6, respectively. Thus, **5aD$_2$** is at least 94% dideuterated and contains ≤1% of **5a**.

The acetylation of **5aD$_2$** was carried out at −70 °C in the same manner as that of **5a**. As expected, three isomeric monoacylated ferrocenes **6aD$_2$–8aD$_2$** were obtained in the same yield and ratio as their undeuterated analogues. Examination of the mass, ^1H NMR, and undecoupled ^{13}C NMR spectra[19] of **6aD$_2$–8aD$_2$** indeed establish that the proposed intramolecular proton migration occurs without scrambling of the deuterium label. Comparison of the



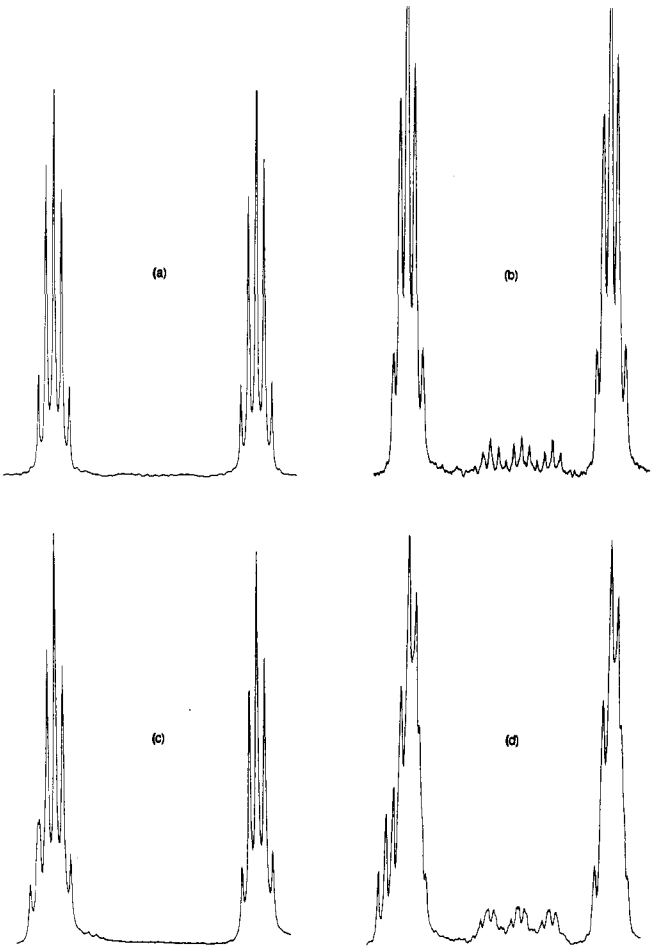


Figure 1. Undecoupled ^{13}C NMR spectrum of the "unsubstituted" cyclopentadienyl ring of **7a** (a), **7aD$_2$** (b), **8a** (c), and **8aD$_2$** (d).

mass spectra of **6aD$_2$–8aD$_2$** with those of **6a–8a** clearly shows that each product is dideuterated to the same extent as **5aD$_2$**, 94–95%, and contians ≤1–2% of the undeuterated species. Whereas only a $C_5H_4D_1Fe$ (MW = 122) fragment is present in the spectrum of **7aD$_2$**, **8aD$_2$** affords both $C_5H_4D_1Fe$ and $C_5H_3D_2Fe$ (MW = 123) fragments. This difference is also manifested in the ^{13}C NMR spectra. The unsubstituted cyclopentadienyl ring of both **7a** and **8a** gives rise to a double quintet displaying couplings of 176 and 6.7 Hz (the downfield pentet in the spectrum of **8a** overlaps with an absorption of a carbon from the substituted ring). The symmetry of these signals indicates that $^2J_{CH}$ and $^3J_{CH}$ are identical (Figure 1). The four protonated carbon atoms of the "unsubstituted" cyclopentadienyl ring of **7aD$_2$** also appear as a double quintet and the remaining deuterated carbon atom as a triple quintet. The symmetry of the former absorption results from a coincidental near equivalence of the β deuterium shift[20] with $^2J_{CH}$ and $^3J_{CH}$. The substituted ring contains 0.5 deuterium atom at both the 4 and 5 positions. In contrast, the 1,3-disubstituted ferrocene **8aD$_2$** contains deuterium uniquely in the 5 position of the substituted ring and the carbon atoms of the "unsubstituted" ring appear as broad multiplets due to the superimposition of the spectra of the mono- and dideuterated species.

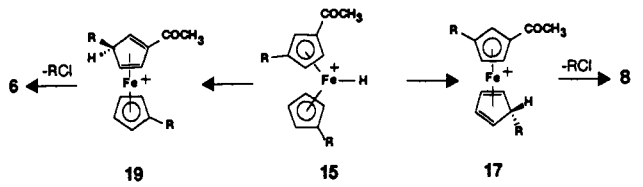
From analysis of the ^1H NMR spectrum of **6aD$_2$**, it is evident that the 1,1′-disubstituted ferrocenes **6** *do not* result from ipso

(17) (a) Tolstikov, G. A.; Miftakhov, M. S.; Monakov, Y. B. *Zh. Obshch. Khim.* **1976**, *46*, 1778–1782. (b) Okuda, J. *J. Organomet. Chem.* **1988**, *356*, C43–C46. (c) Okuda, J. *J. Organomet. Chem.* **1989**, *373*, 99–105.

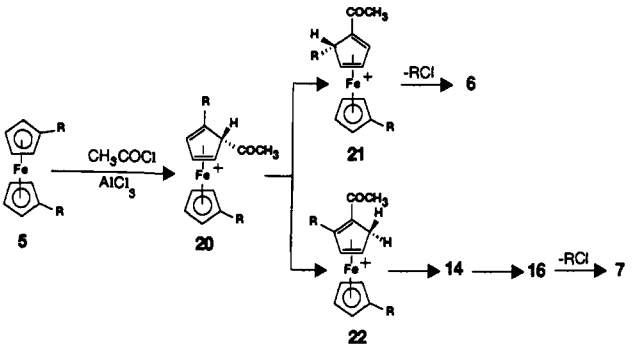
(18) Slocum, D. W.; Ernst, C. R. *J. Org. Chem.* **1973**, *38*, 1620–1621.

(19) To ensure correct assignment of the absorptions in the ^{13}C NMR spectra, C–H correlation spectra were recorded for each of the three products **6a–8a**.

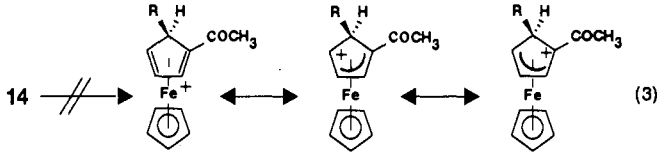
Scheme V



Scheme VI

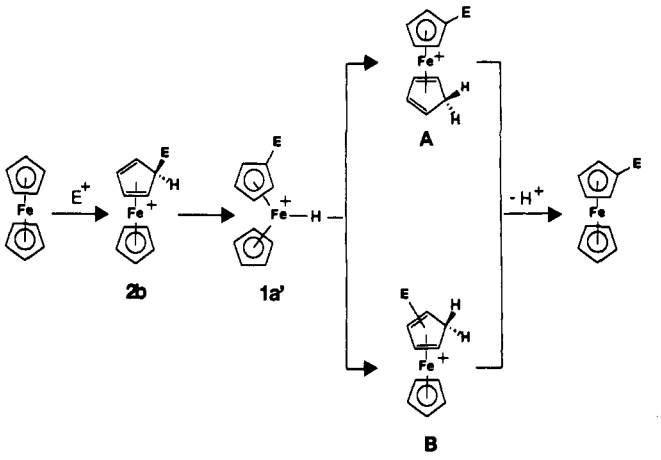


attack of **5** by the acylium ion. The direct displacement of a trimethylsilyl group would afford a product containing 1.0 deuterium atom in the 3 and 3′ positions. The product obtained, while being 100% labeled at the 3 position, is 50% labeled at both the 2′ and the 3′ positions! The fact that the yield of **7a** and the *combined* yield of **6a** and **8a** remain constant with temperature (see eq 1) indicates that **6** and **8** are derived from a common intermediate. Apparently, migration of the iron bound proton of **15** can occur either to the acylated cyclopentadienyl ring to generate **19** or to the monosubstituted cyclopentadienyl ring to afford **17** (Scheme V). Subsequent loss of trimethylsilyl chloride or tributyltin chloride from these intermediates engenders **6** and **8**, respectively. This back transfer is less favorable in the case of **14** since the carbon bearing the acetyl group would be in direct resonance with the positive charge (eq 3). Steric hindrance to ipso attack has also been observed with 1-methyl-3,4-bis(trimethylsilyl)furan which undergoes Friedel–Crafts acylation exclusively at the 2 position.[21]



This labeling experiment also serves to exclude a more complicated alternative mechanism involving endo attack of the acylium ion followed by an exo 1,5 hydrogen shift (Scheme VI, shown for α attack only).[22] Endo electrophilic attack of **5** at the α position would engender the (cyclopentadiene)(cyclopentadienyl)iron cation **20** having an exo hydrogen. It is conceivable that this species could undergo two different (or even multiple) 1,5 hydrogen shifts to generate a pair (or more) of analogous cations, **21** and **22**. Loss of RCl from **21** affords **6** whereas ring-to-metal transfer of the endo proton of **22** furnishes **14** and, ultimately, the 1,2-disubstituted ferrocenes **7** (see Scheme III). If products **6** and **7** are produced at comparable rates, **5aD$_2$** would yield **7aD$_2$** having 0.5 deuterium atom at the 4 position of the substituted ring and 1.5 deuterium atoms in the unsubstituted ring. This is clearly in contrast with the results obtained: **7aD$_2$** is 50% labeled at both the 3 and the 4 positions and contains only

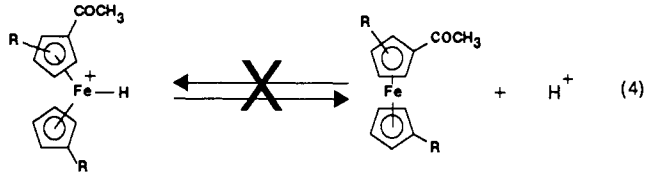
Scheme VII



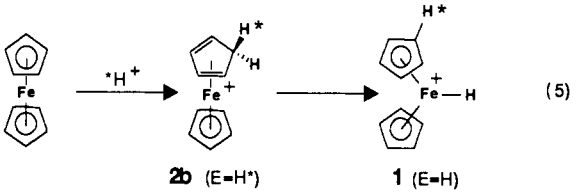
one deuterium atom in the unsubstituted ring. Similarly, the 1,3-disubstituted ferrocene **8aD$_2$** produced by this pathway would be partially labeled at the 2 and the 4 position rather than the observed 50% deuteration at the 4 position only. It is evident that multiple 1,5 hydrogen shifts and/or substantial differences in the energy requirements of these shifts would cause the unequal partitioning of the deuterium label in each of the acylated products.

As both **6** and **8** result from an initial β-attack of acylium ion, the ratio of β:α attack for **5a** is 5.7:1 while that of **5b** is ~4.5:1 (calculated from the product distribution at −70 °C). These values seem reasonable when compared with those determined by Benkeser et al.[6] for isopropyl- (4.5:1) and *tert*-butylferrocene (12.7:1). In their study, acetylation was carried out with acetic anhydride in the presence of BF_3.

The occurrence of this intramolecular interannular proton transfer proves that these Friedel–Crafts acylations indeed proceed via an exo attack of the electrophile and provides good evidence for the existence of a protonated iron intermediate. The fate of this iron bound proton of proposed intermediates **14** and **15** is particularly interesting. The lack of scrambling of the deuterium label indicates that direct deprotonation and its microscopic reverse, direct protonation, do not occur and are, therefore, energetically less favorable than metal-to-ring proton transfer (eq 4).



This implies, in turn, that protonation of ferrocenes could also arise from exo attack of H^+ to generate the σ-complex **2b** (E = H) in which the endo hydrogen, one of the original hydrogen atoms of the cyclopentadienyl ring, then migrates from the ring to the metal (eq 5).[23] The microscopic reverse of this reaction would



result in proton exchange. Such a mechanism can easily explain the retardation of proton exchange of metallocenes under highly acidic conditions, observed by Illuminati and co-workers,[12] as a

(20) 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.

(21) Ho, M. S.; Wong, H. N. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1238–1240. It is interesting to note that these authors also observe an intramolecular proton migration.

(22) This possibility was suggested by a referee.

(23) This process has been observed by T. E. Bitterwolf and co-workers in an unpublished study.

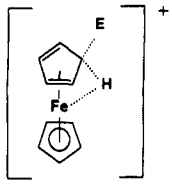


Figure 2.

simple shift of the equilibrium toward the right, i.e. the stabilization of species **1** (E = H). Calculations of the electron deformation density (EED) and the molecular electrostatic potential (MEP) reveal that the areas of highest electron density are found in the planes of the cyclopentadienyl rings whereas the electron density at the metal center is markedly lower.[24] This difference in electron density is actually enhanced upon modification of the geometry of ferrocene from D_{5h} to C_{2v}. That the ultimate site of protonation be nonetheless at the metal is supported by photoionization spectra which indicate that the SOMO of the ferricenium cation is composed of 65% Fe 3d orbital and 35% cyclopentadienyl ring orbital.[25]

Given these results, a general mechanism for the electrophilic substitution of ferrocenes can be formulated which excludes direct electrophilic attack of the iron atom (see Scheme VII). Exo electrophilic attack generates the σ-complex **2b** which undergoes a ring-to-metal proton migration to afford **1a'**. Subsequent proton transfer to the unsubstituted ring or back to the substituted ring furnishes either the σ-complex **A** and/or one or both of the isomeric σ-complexes **B**, respectively. Exo loss of a proton from these intermediates yields the substituted product. When E^+ is a strong electrophile, the α positions of the substituted ring are highly deactivated and proton migration occurs either to the β positions of this ring or to the unsubstituted ring. When E^+ is a weak electrophile, all three σ-complexes **A** and **B** could be involved. In the case of protonation (E = H), **A** and **B** are identical and proton exchange occurs.

As σ-complexes have never been observed, it is equally probable that such proton transfers proceed in a concerted fashion through a four-center transition state rather than in the stepwise manner presented above (Figure 2).

To prove the generality and validity of this mechanism, the role of the trimethylsilyl and the tributylstannyl groups in these reactions must be determined. The steric bulk of these groups could hinder the approach of the electrophile to the metal center thereby excluding an endo attack. It is also possible that the thermodynamically preferred mode of protonation is dependant upon the substitution of the ferrocene; for some derivatives the exo mode is lower in energy whereas for others the direct mode is favored. Meot-Ner[26] has recently demonstrated that protonation of ferrocene *in the gas phase* occurs directly on the metal. The process of metal-to-ring proton migration was estimated, in this study, to be endothermic by at least 5 kcal/mol.

The mercuration of ferrocenes is commonly believed to arise from an endo attack of an electrophilic mercury(II) species. Evidence of iron–mercury interaction has been obtained from Mossbauer[27] and IR spectroscopy[28] of ferrocene–$HgCl_2$ adducts and by UV spectroscopy of ferrocene in the presence of $HgCl_2$.[29] On the contrary, it has not been shown that these interactions lead to electrophilic substitution.

Conclusion

We have shown that the Friedel–Crafts acetylations of 1,1'-bis(trimethylsilyl)ferrocene (**5a**) and 1,1'-bis(tributylstannyl)-ferrocene (**5b**) proceed by an exo attack of acylium ion. Two of the three products of these reactions result from a subsequent intramolecular interannular proton migration. These results suggest that all electrophilic substition and proton exchange reactions of ferrocenes could occur via exo electrophilic attack. This premise is currently under investigation in our laboratories.

Experimental Section

General. The solvents used were dried and distilled as follows: from sodium–benzophenone ketyl, THF; from sodium, hexane; from CaH_2, TMEDA; from phosphorus pentoxide, CH_2Cl_2. Reagents were purified by standard procedures when deemed appropriate. 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 WP 100 SY (100 mHz) or a Bruker 300 AC (300 mHz) spectrometer and are reported in ppm relative to internal tetramethylsilane. ^{13}C NMR spectra were recorded on a Varian VXR-400S spectrometer at 90.56 MHz and 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. Elementary analyses were performed by the Analytic Departement, Ciba-Geigy Research Center, Fribourg.

1,1'-Bis(trimethylsilyl)ferrocene (5a). To a stirred suspension of 112 g (0.6 mol) of ferrocene in hexane (100 mL) was quickly added 825 mL of a 1.6 M solution of butyllithium in hexane (1.32 mol) followed by the dropwise addition, over a period of 30 min, of 198 mL (153 g, 1.32 mol) of TMEDA. During this time the temperature rose to 30 °C. The mixture was allowed to stir at room temperature for 16 h. After 1 h, all the ferrocene had dissolved. The precipitation of the TMEDA complex of the dianion began approximately 1 h later. The reaction mixture was cooled to 0 °C and 191 mL (164 g, 1.50 mol) of trimethylsilyl chloride was added dropwise over a 1.5-h period. The mixture was allowed to warm to room temperature, stirred for 1.5 h, and then poured into 1 L of ice water. The organic phase was separated and the aqueous phase was extracted with hexane (2 × 200 mL). The combined extracts were washed with H_2O, dried ($MgSO_4$), and concentrated to give a deep red oil. The unreacted ferrocene was removed by sublimation at room temperature at 6×10^{-2} mmHg. Subsequent distillation at 6×10^{-2} mmHg afforded 10.6 g (0.041 mol, 7%) of (trimethylsilyl)ferrocene, followed by 150 g (0.45 mol, 76%) of pure **5a**: bp 85 °C (lit.[8] 87–88°C (6×10^{-2} mmHg)); IR (neat) 3095, 2960, 2900, 1245, 1165, 1035, 830, and 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.29 (t, 4, J = 1.7 Hz), 4.07 (t, 4, J = 1.7 Hz), and 0.29 (s, 18) ppm; MS (70 eV) m/e 332 (7), 331 (30), 330 (molecular peak, 100), 329 (2), 328 (6), 243 (30), 242 (22), and 73 (78).

1,1'-Bis(tributylstannyl)ferrocene (5b). This product was prepared following the procedure for **5a**, employing 18.6 g (0.1 mol) of ferrocene. The residue was distilled to afford, after a 10.1-g forerun containing predominately (tributylstannyl)ferrocene and **5b**, 49.5 g (0.065 mol, 65%) of **5b**. The forerun can be chromatographed (hexane, SiO_2) to furnish 1.6 g (0.003 mol, 3%) of (tributylstannyl)ferrocene and an additional 3.3 g (0.004 mol, 4%) of **5b**. However, as **5b** undergoes slow conversion to (tributylstannyl)ferrocene in the presence of silica gel, only predistilled **5b** was used in the experiments described: bp 210–212 °C (4×10^{-3} mmHg); IR (neat) 3080, 2950, 2920, 2865, 2845, 1465, 1375, 1140, 1025, 820, and 500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.25 (t, 4, J = 1.6 Hz), 3.98 (t, 4, J = 1.6 Hz), 2.01–0.70 (m, 54) ppm.

Friedel–Crafts Acetylation of 5a. To a solution of 1.65 g (5.0 mmol) of **5a** and 0.39 mL (0.42 g, 5.5 mmol) of acetyl chloride in CH_2Cl_2 (20 mL) at −70 °C was added 0.73 g (5.5 mmol) of finely powdered $AlCl_3$. The reaction mixture immediately became purple. After being stirred at −70 °C for 1.5 h, the mixture was poured into ice water (100 mL). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated to give 1.58 g of a red oil. Chromatography (9:1 hexane–ethyl acetate, SiO_2) afforded 0.23 g (0.77 mmol, 15.5%) of the high R_f product **7a** and 1.26 g (4.2 mmol, 84.0%) of a 1:1.7 mixture (by ^1H NMR) of **6a** and **8a**. Acetylation at room temperature affords, after 15 min, 0.23 g (0.77 mmol, 15.5%) of **7a** and 1.26 g (4.2 mmol, 84.0%) of a 1:2.2 mixture of **6a** and **8a**. Pure **8a** is obtained by crystallization of the mixture in hexane. Pure **6a** is obtained by repeated chromatography of the mother liquor:

6a: IR (neat) 3090, 2955, 1670, 1450, 1275, 1245, 1160, 1035, and 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.80 (t, 2, J = 1.9 Hz), 4.52 (t, 2, J =

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1.9 Hz), 4.43 (t, 2, J = 1.7 Hz), 4.17 (t, 2, J = 1.7 Hz), 2.45 (s, 3), and 0.29 (s, 9) ppm; ^{13}C NMR ($CDCl_3$) δ 202.0 (CO, q, 1, J = 6.0 Hz), 79.4 (C1′, m, 1), 74.5 (C2 and C5, dq, 2, J = 174, 7.5 Hz), 74.5 (C1, m, 1), 73.1 (C3 and C4, dq, 2, J = 175, 7.0 Hz), 72.6 (C3′ and C4′, dq, 2, J = 176, 6.5 Hz), 69.7 (C2′ and C5′, dq, 2, J = 178, 6.4 Hz), 27.5 ($COCH_3$, q, 1, J = 127 Hz), and −0.3 ($Si(CH_3)_3$, quadruple septet, 3, J = 119, 2.0 Hz) ppm; MS (70 eV), m/e 302 (6), 301 (24), 300 (molecular peak, 100), 299 (2), 298 (6), 286 (6), 285 (66), 195 (12), 143 (11), 122 (2), 121 (C_5H_5Fe, 8), 75 (7), and 56 (8).

Anal. Calcd for $C_{15}H_{20}FeOSi$: C, 60.00; H, 6.71. Found: C, 59.82; H, 6.85.

7a: mp 94–96 °C; IR (KBr) 3100, 2960, 2905, 1670, 1435, 1330, 1250, 1145, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.83 (dd, 1, J = 2.4, 1.1 Hz), 4.59 (t, 1, J = 2.4 Hz), 4.45 (dd, 1, J = 2.4, 1.1 Hz), 4.20 (s, 5), 2.40 (s, 3), and 0.29 (s, 9) ppm; ^{13}C NMR ($CDCl_3$) δ 202.5 (CO, q, 1, J = 5.8 Hz), 83.8 (C2, q, 1, J = 7.1 Hz), 79.1 (C5, ddd, 1, J = 175, 9.0, 6.0 Hz), 74.7 (C4, dm, 1, J = 175 Hz), 73.9 (C1, m, 1), 73.7 (C3, dm, 1, J = 176 Hz), 69.7 (C1′–C5′, double quintet, 5, J = 176, 6.7 Hz), 27.6 ($COCH_3$, q, 1, J = 127 Hz), and 0.2 ($Si(CH_3)_3$, quadruple septet, 3, J = 119, 1.9 Hz) ppm; MS (70 eV), m/e 302 (4), 301 (13), 300 (molecular peak, 51), 299 (1), 298 (3), 285 (100), 195 (19), 143 (17), 122 (1), 121 (C_5H_5Fe, 15), 75 (13), and 56 (9).

Anal. Calcd for $C_{15}H_{20}FeOSi$: C, 60.00; H, 6.71. Found: C, 59.84; H, 6.72.

8a: mp 71–72 °C; IR (KBr) 3095, 2950, 2890, 1670, 1450, 1245, 1145, and 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.89 (dd, 1, J = 2.3, 1.3 Hz), 4.70 (br s, 1), 4.42 (dd, 1, J = 2.3, 1.3 Hz), 4.16 (s, 5), 2.41 (s, 3), and 0.25 (s, 9) ppm; ^{13}C NMR ($CDCl_3$) δ 201.9 (CO, q, 1, J = 5.6 Hz), 82.0 (C3, br q, 1, J = 5.8 Hz), 78.1 (C1, m, 1), 76.9 (C5, ddd, 1, J = 175, 8.5, 6.0 Hz), 74.6 (C4, dt, 1, J = 176, 7.1 Hz), 72.2 (C2, dt, 1, J = 178, 6.3 Hz), 70.1 (C1′–C5′, double quintet, 5, J = 176, 6.7 Hz), 27.7 ($COCH_3$, q, 1, J = 127 Hz), and −0.3 ($Si(CH_3)_3$, quadruple septet, 3, J = 119, 1.7 Hz) ppm; MS (70 eV), m/e 302 (6), 301 (23), 300 (molecular peak, 100), 299 (2), 298 (6), 285 (40), 195 (14), 143 (5), 122 (1), 121 (C_5H_5Fe, 10), 75 (4), and 56 (8).

Anal. Calcd for $C_{15}H_{20}FeOSi$: C, 60.00; H, 6.71. Found: C, 59.84; H, 6.85.

Friedel–Crafts Acetylation of 5b. To a suspension of 0.73 g (5.5 mmol) of finely powdered $AlCl_3$ in CH_2Cl_2 (15 mL) at room temperature was added 0.39 mL (0.42 g, 5.5 mmol) of acetyl chloride. Within 10–15 min, the formation of the $CH_3COCl{\cdot}AlCl_3$ complex was complete and a homogeneous solution was obtained. To this solution, cooled to −75 °C, was added, dropwise over a period of 20 min, a solution of **5b** in CH_2Cl_2 (5 mL). The speed of the addition was regulated as to maintain the temperature of the reaction at ca. −70 °C. After the addition was complete, the reaction mixture was allowed to stir at −70 °C for 10 min and then poured into ice water (100 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined extracts were dried (Na_2SO_4) and concentrated to yield 4.14 g of a red oil. Kugelrohr distillation of the oil at 80 °C (8×10^{-3} mmHg) for ~2 h resulted in the isolation of a mixture of tributyltin chloride and acetylferrocene. Removal of the bulk of the former product by chromatography (hexane followed by CH_2Cl_2, SiO_2) afforded 0.05 g of a mixture containing ~0.03 g (0.13 mmol, ~2.5%) of acetylferrocene by ^{1}H NMR. The material that did not distill was chromatographed (19:1 hexane–ethyl acetate, SiO_2) to afford 0.43 g (0.83 mmol, 16.5%) of **7b**, 0.74 g (1.43 mmol, 28.5%) of **6b**, and 1.20 g (2.32 mmol, 46.5%) of **8b**. Acetylation of **5b** at room temperature affords, after 15 min, 0.33 g (0.64 mmol, 13.0%) of **7b**, 0.60 g (1.16 mmol, 23.0%) of **6b**, 1.14 g (2.20 mmol, 44.0%) of **8b**, ~0.02 g (0.09 mmol, ~2.0%) of acetylferrocene, and 0.08 g (0.30 mmol, 6.0%) of 1,1′-diacetylferrocene. The amount of 1,1′-diacetylferrocene was determined in a separate trial by direct chromatography since it partially sublimes during the Kugelrohr separation of acetylferrocene and tributyltin chloride:

6b: IR (neat) 3080, 2955, 2920, 2870, 2850, 1675, 1455, 1375, 1275, 1110, 1025, and 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.72 (t, 2, J = 1.9 Hz), 4.41 (t, 2, J = 1.9 Hz), 4.37 (t, 2, J = 1.5 Hz), 4.04 (t, 2, J = 1.5 Hz), 2.39 (s, 3), and 1.90–0.70 (m, 27) ppm.

Anal. Calcd for $C_{24}H_{38}FeOSn$: C, 55.75; H, 7.41. Found: C, 55.89; H, 7.46.

7b: IR (neat) 3080, 2950, 2920, 2860, 2840, 1660, 1460, 1430, 1325, 1250, 1130, and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.80 (dd, 1, J = 2.5, 1.1 Hz), 4.63 (t, 1, J = 2.5 Hz), 4.41 (dd, 1, J = 2.5, 1.1 Hz), 4.14 (s, 5), 2.37 (s, 3), and 1.90–0.70 (m, 27) ppm.

Anal. Calcd for $C_{24}H_{38}FeOSn$: C, 55.75; H, 7.41. Found: C, 55.84; H, 7.46.

8b: IR (neat) 3090, 2955, 2920, 2870, 2850, 1670, 1445, 1290, 1130, and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.89 (dd, 1, J = 2.4, 1.0 Hz), 4.63 (br s, 1), 4.36 (dd, 1, J = 2.4, 1.0 Hz), 4.14 (s, 5), 2.41 (s, 3), and 1.90–0.70 (m, 27) ppm.

Anal. Calcd for $C_{24}H_{38}FeOSn$: C, 55.75; H, 7.41. Found: C, 55.71; H, 7.23.

3,3′-Bis(trimethylsilyl)-1,1′-bis(trimethylstannyl)ferrocene (18). The dimetalation of 9.90 g (0.030 mol) of **5a** was carried out according to the procedure for the preparation of **5a**. The dianion was treated with 13.15 g (0.067 mol) of trimethyltin chloride and the crude product was isolated in a similar manner. The residue was recrystallized twice from ethanol to afford 7.83 g (0.012 mol, 40%) of **18**: mp 140–141.5 °C; IR (KBr) 3070, 2940, 2890, 1420, 1245, 1180, 1065, 915, 815, 765, 750, and 525 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.28–4.10 (m, 4), 4.10–3.95 (m, 2), 0.28 (s with Sn satellites at 0.55 and 0.01 ppm, 18), and 0.26 (s, 18) ppm.

Anal. Calcd for $C_{22}H_{42}FeSi_2Sn_2$: C, 40.28; H, 6.45. Found: C, 40.37; H, 6.45.

3,3′-Dideuterio-1,1′-bis(trimethylsilyl)ferrocene (5aD$_2$). To a stirred solution of 4.59 g (7.0 mmol) of **18** in THF (35 mL) at −70 °C was added 9.8 mL of a 1.6 M solution of butyllithium in hexane (15.4 mmol). After 5 min, an orange precipitate formed. The reaction mixture was allowed to stir at −70 °C for 1.25 h. At this time, 1.4 mL (0.07 mol) of D_2O was added and the mixture was allowed to warm to room temperature. The reaction mixture was concentrated. The residue was diluted with hexane (50 mL), washed with H_2O (3 × 20 mL), dried ($MgSO_4$), and concentrated to give a red oil. The oil was chromatographed (hexane, SiO_2) to yield 2.35 g (7.0 mmol, 100%) of **5aD$_2$**: IR (neat) 3095, 3075, 2960, 2900, 2310 (weak), 1245, 1160, 1025, 835, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.28 (t, 2, J = 1.7 Hz), 4.05 (d, 4, J = 1.7Hz), and 0.22 (s, 18) ppm; ^{13}C NMR ($(CD_3)_2SO$) δ 73.02 (dt, 2, J = 174, 7.7 Hz), 72.95 (dt, 2, J = 174, 7.7 Hz), 72.0 (m, 2), 71.2 (dt, 2, J = 173, 7.1 Hz), 71.1 (tq, 2, J = 27, 7.0 Hz), and −0.4 (quadruple septet, 6, J = 119, 2.0 Hz) ppm; MS (70 eV), m/e 334 (11), 333 (28), 332 (molecular peak, 100), 331 (8), 330 (7), 245 (19), 244 (20), and 73 (50).

Friedel–Crafts Acetylation of 5aD$_2$. This reaction was carried out at −70 °C in the same manner as that of **5a**, employing 1.66 g (5.0 mmol) of **5aD$_2$**. The workup afforded 1.64 g of a red oil. The residue was chromatographed (9:1 hexane–ethyl acetate, SiO_2) to give 0.25 g (0.83 mmol, 16.5%) of **7aD$_2$** and 1.26 g (1.65 mmol, 83.0%) of a 1:1.7 (by ^{1}H NMR) mixture of **6aD$_2$** and **8aD$_2$**. Pure samples of the latter two products were obtained as before.

6aD$_2$: IR (neat) 3080, 2950, 2890, 2300 (weak), 1665, 1450, 1440, 1265, 1245, 1155, and 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.80 (br d, 1.5, J = 1.9 Hz), 4.52 (br d, 1.5, J = 1.9 Hz), 4.43 (t, 1, J = 1.7 Hz), 4.17 (d, 2, J = 1.7 Hz), 2.45 (s, 3), and 0.29 (s, 9) ppm; ^{13}C NMR ($CDCl_3$) δ 201.9 (q, 1, J = 5.7 Hz), 79.3 (m, 1), 74.46 (dt, 1, J = ~175, 6.8 Hz), 74.4 (m, 1), 74.39 (dt, 1, J = ~175, 6.3 Hz), 73.0 (dt, 1, J = 175, 7.0), 73.4–72.1 (m, 1.5, J ~ 27, 7.0 Hz), 72.54 (dt, 0.5, J = ~176, 6.3 Hz), 72.48 (dt, 1, J = ~176, 6.3 Hz), 69.70 (dt, 1, J = 178, 6.2 Hz), 69.64 (dt, 0.5, J = 178, 5.8 Hz), 69.56 (tq, 0.5, J = 27, 6.8 Hz), 27.5 (q, 1, J = 127 Hz), and −0.27 (quadruple septet, 3, J = 119, 1.1 Hz) ppm; MS (70 eV), m/e 304 (6), 303 (27), 302 (molecular peak, 100), 301 (7), 300 (8), 288 (17), 287 (81), 144 (16), 122 ($C_5H_4D_1Fe$, 8), 121 (C_5H_5Fe, 3), 75 (9), and 56 (8).

7aD$_2$: IR (KBr) 3085, 2950, 2890, 2310 (weak), 1670, 1430, 1415, 1320, 1245, 1145, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.83 (br s, 0.5), 4.59 (d, 0.5, J = 2.1 Hz), 4.45 (br d, 1, J = ~1.6 Hz), 4.20 (s, 4), 2.40 (s, 3), and 0.29 (s, 9) ppm; ^{13}C NMR ($CDCl_3$) δ 202.3 (q, 1, J = 5.7 Hz), 83.8 (br s, 1), 79.1 (2 dd, 1, J = 177, ~7 Hz), 74.7 (dd, 0.5, J = 175, 6.8 Hz), 74.3 (tt, 0.5, J = 28, 7.0 Hz), 74.0 (m, 1), 73.7 (dd, 0.5, J = 177, 6.5 Hz), 73.6 (tt, 0.5, J = 28, 7.0 Hz), 69.7 (double quintet, 4, J = 177, ~6 Hz), 69.6 (triple quintet, 1, J = 27,7.0 Hz), 27.7 (q, 1, J = 127 Hz), and 0.30 (quadruple septet, 3, J = 119, 2.0 Hz) ppm; MS (70eV), m/e 304 (3), 303 (12), 302 (molecular peak, 54), 301 (4), 300 (4), 288 (22), 287 (100), 196 (13), 144 (7), 122 ($C_5H_4D_1Fe$, 8), 121 (C_5H_5Fe, 1), 75 (6), and 56 (8).

8aD$_2$: IR (KBr) 3095, 2960, 2900, 2320 (weak), 1670, 1450, 1440, 1250, 1145, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.89 (dd, 0.5, J = 2.5, 1.1 Hz), 4.70 (br d, 1, J = 1.1 Hz), 4.42 (br dd, 1, J = 2.5, 1.1 Hz), 4.16 (s, 3.5), 2.41 (s, 3), and 0.25 (s, 9) ppm; ^{13}C NMR ($CDCl_3$) δ 202.0 (q, 1, J = 5.9 Hz), 82.0 (m, 1), 78.1 (m, 1), 76.9 (ddd, 0.5, J = 174, 9.0, 6.0 Hz), 76.8 (dd, 0.5, J = 176, 9.0 Hz), 74.7 (dt, 0.5, J = 176, 6.7 Hz), 74.6 (dd, 0.5, J = 176, 7.4 Hz), 72.2 (dt, 0.5, J = 177, 6.4 Hz), 72.0 (tt, 0.5, J = 27, 5.9 Hz), 70.0 (dm, 3.5, J = 177 Hz), 69.9 (tm, 1.5), 27.7 (q, 1, J = 127 Hz), and −0.33 (quadruple septet, 3, J = 119, 1.9 Hz) ppm; MS (70 eV), m/e 304 (7), 303 (22), 302 (molecular peak, 100), 301 (7), 300 (8), 288 (17), 287 (50), 123 ($C_5H_3D_2Fe$, 4), 122 ($C_5H_4D_1Fe$, 6), 75 (4), and 56 (6).

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